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FLUORINATED POLYMERS AND FLUIDS

E. R. Lynch, S. A. Evans and K. N. Ayad
Monsanto Chemicals, Limited

A. K. Barbour, M. W. Buxton, J. Tilney-Bassett,
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R. D. Chambers and W. K. R. Musgrave
University of Durham

TECHNICAL REPORT AFML-TR-65-13, Part III

April 1967

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Air Force Materials Laboratory
Research and Technology Division
Air Force Systems Command
Wright-Patterson Air Force Base, Ohio

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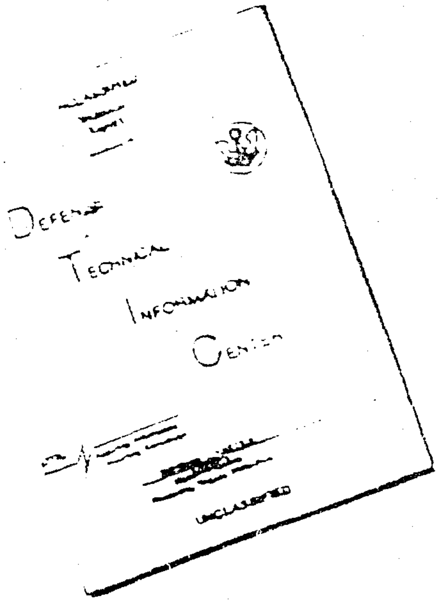
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FOREWORD

This report "Fluorinated Polymers and Fluids" for the period st December 1965 to 30th November, 1966, covers work carried out nder Contract AF33(615)-1344. This contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." The work was performed under subcontract from Monsanto Research Corporation by Monsanto Chemicals Limited, Imperial Smelting Corporation (N.S.C.) Ltd., the University of Birmingham, and the University of Durham. It is a continuation of work described in Technical Report AFML-TR-65-13, Part II.

The work is administered by Research and Technology Division, Air Force Materials Laboratory, Nonmetallic Materials Division, Wright-Patterson Air Force Base, Ohio. Lt. R. De Pasquale, MANP, is the project engineer. For Monsanto Research Corporation, Dr. J. M. Butler serves as the contract coordinator. For Monsanto Chemicals Limited, Mr. E. R. Lynch serves as project leader, assisted by Mrs. S. A. Evans and Dr. K. N. Ayad; Mr. R. A. Lidgett and Mrs. J. Ellis are responsible for infra-red and gas chromatographic investigations. For Imperial Smelting Corporation, Dr. A. K. Barbour serves as project leader, assisted by Dr. M. W. Buxton, Dr. J. Tilney-Bassett, Dr. R. H. Mobbs and Dr. D. E. M. Wotton. At the University of Birmingham, the research is carried out by Mr. D. Oldfield supervised by Professor J. C. Tatlow, and Dr. P. L. Coe. At the University of Durham, the research is carried out by Mr. F. G. Eastwood and Mr. C. A. Heaton, supervised by Dr. R. D. Chambers and Professor W. K. R. Musgrave.

Manuscript released by the authors December 1966 for publication as an RTD Technical Report.

This technical report has been reviewed and is approved.

William E. Gibbs
WILLIAM E. GIBBS
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ABSTRACT

Preparations and synthetic studies have been carried out on difluoropyromellitic dianhydride, 2,2',5,5',6,6'-hexafluoro-3,3'-dihydroxybenzidine, 2,4,5-trifluororesorcinol, perfluoro-4-hydroxyphenyldimethylcarbinol and tetrafluorobenzene-1,3-dithiol. These and other compounds were employed in the synthesis of fluorinated aromatic model compounds and polymers. The hydrogenic analogues of the latter were prepared for comparison of thermo-oxidative stability by thermo-gravimetry in air. A low molecular weight perfluoro polycarbonate had slightly higher thermo-oxidative stability than its hydrogenic analogue, poly(m-phenylene carbonate). A low molecular weight co-polycarbonate from tetrafluoro-m-phenylene bischloroformate had slightly higher thermo-oxidative stability than the analogous copolymer from m-phenylene bischloroformate and Bisphenol A. A complex of pyromellitic dianhydride and tetrafluoro-m-phenylene diamine yielded polyimide of higher thermo-oxidative stability than poly(m-phenylene-pyromellitimide). Other fluorinated polymers: polycarbonates, polyimides, and a poly(1,3,4-oxadiazole) had lower thermo-oxidative stabilities than their hydrogenic analogues. A perfluoro poly-(bibenzoxazole) could not be prepared. The reaction between pentafluorobenzene sulphonyl chloride and perfluoro-aromatics suggests new routes to perfluorinated polyphenylenes, related polymers and fluids. Synthetic routes to perfluoro aralkyl compounds, with potential as thermo-oxidatively stable fluids are being investigated. These compounds are: perfluoro-1,6-diphenylhexane, perfluoro-3,3'-di(n-butyl)biphenyl, 1,2-di(pentafluorophenylthio)tetrafluoroethane, and compounds derived from the reaction of perfluoro o- and p-xylene and decafluorocyclohexene with aryl lithium compounds. Further fluorination with cobaltic fluoride has yielded perfluoro alicyclic compounds of moderately high thermal stability. Similar types of structure are also under synthetic study. Perfluorinated heterocyclics synthesised or still under study include: 2,5-di(tetrafluoro-4-pyridyl)-1,3,4-oxadiazole, 2,5-di(tetrafluoro-4-pyridyl)-1,3,4-thiadiazole, N-(tetrafluoro-4-pyridyl) pentafluorobenzamide, di(tetrafluoro-4-pyridyl)amine, perfluoro(4-pyridylisopropyl)ketone, perfluoro(phenyl isopropyl)ketone, perfluoro(4-isopropylphenyl isopropyl)ketone, hydrazides, esters and ethers based on perfluoropyridine, perfluoroquinoline and perfluoroisoquinoline. The thermal decomposition points of two heterocyclic ethers and an ester are reported.

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PART I

PERFLUOROAROMATIC INTERMEDIATES

M.W. Buxton, R.H. Mobbs, J.F. Tilney-Bassett
and D.E.M. Wotton

Imperial Smelting Corporation (N.S.C.) Limited

INTRODUCTION

This part of the Report is concerned with the synthesis of perfluoroaromatic intermediates required by Monsanto Chemicals Limited for the preparation of model condensates and polymers which are used for thermal stability tests.

The work described was carried out in the period 1st December, 1965, to 30th November, 1966, and is a continuation of that reported in Technical Report AFML-TR-65-13, Part II.

SUMMARY

Bromination of difluorodurene to 1,2,4,5-tetra(bromomethyl)-3,6-difluorobenzene and oxidation of this tetrabromo- compound is a more satisfactory route for preparing laboratory quantities of difluoropyromellitic acid than the oxidation of difluorodurene, reported previously. Difluoropyromellitic dianhydride is produced by heating the acid in boiling thionyl chloride.

Satisfactory procedures were established for preparing hexafluoro-3,3'-dihydroxybenzidine, 2,4,5-trifluororesorcinol, tetrafluoro-4-hydroxyphenylbis(trifluoromethyl)carbinol, and tetrafluorobenzene-1,3-dithiol. Other intermediates were prepared by methods already available.

The following compounds were supplied to Monsanto Chemicals Limited, Ruabon, for synthesis of model condensates and polymers:-

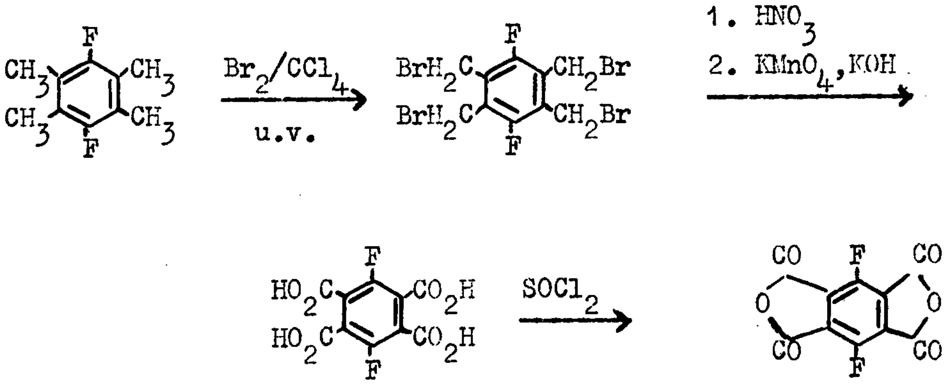
	g.
Pentafluorobenzene	100
Decafluorobiphenyl	450
Octafluoronaphthalene	200
Pentafluorobenzenesulphonyl chloride	200
Pentafluoroiodobenzene	100
Pentafluorobenzoic acid	250
Tetrafluoroterephthalonitrile	25
Tetrafluoroterephthalic acid	100
Tetrafluororesorcinol	150
Tetrafluoro-σ-phenylenediamine	25

	g.
Tetrafluoro-m-phenylenediamine	200
(Chlorodifluoromethyl)benzene	11
Pentafluorobenzonitrile	30
Octafluoro-4,4'-dihydroxybiphenyl	50
2,4,5-Trifluororesorcinol	3
Hexafluoro-3,3'-dihydroxybenzidine	30
Nonafluoro-4-hydroxybiphenyl	25
Perfluoro-p-xylene	50
Tetrafluoroisophthalic acid	100
Difluoropyromellitic acid	10
Difluoropyromellitic dianhydride	20
1,3-Dibromotetrafluorobenzene	50
Tetrafluoro-4-hydroxyphenylbis(trifluoromethyl)carbinol	25

DISCUSSION

1. DIFLUOROPYROMELLITIC DIANHYDRIDE (I)

This intermediate is required by Monsanto Chemicals Ltd. for reaction with tetrafluoro-m-phenylenediamine to give a perfluoro-(polyimide) for comparison of its thermal stability with that of the hydrogenic polymer. A satisfactory preparative route to the dianhydride I has now been worked out. It involves the following sequence of reactions:-



The preparation of difluorodurene from durene, reported previously (ref. 1), has been repeated to provide a large quantity of this starting material. No changes were made in the procedures for the first three stages and similar yields were obtained:- 3,6-dinitrodurene (79%), 2-nitro-6-aminodurene (93%) and 3-fluoro-6-nitrodurene (78%). The fourth stage, the reduction of 3-fluoro-6-nitrodurene to 3-amino-6-fluorodurene, has previously been found difficult to control but an improved procedure has now been used giving an 88% yield. A more reliable process enables aminofluorodurene to be converted to 3-fluorodurene-6-diazonium borofluoride in 90% yield. It is now found that the decomposition of the diazonium borofluoride can be performed satisfactorily on a larger scale than hitherto used to give difluorodurene in 89% yield.

Difluorodurene reacts with bromine in boiling carbon tetrachloride, under irradiation with ultra violet light, to give 1,2,4,5-tetra-(bromomethyl)-3,6-difluorodurene in 84% yield.

A satisfactory method of oxidising the tetra(bromomethyl)-compound to difluoropyromellitic acid was worked out. This involves a careful oxidation with concentrated nitric acid and treatment of the product with an alkaline solution of potassium permanganate. The resulting solution of potassium difluoropyromellitate was converted to the free acid (86.5% yield) by ion exchange.

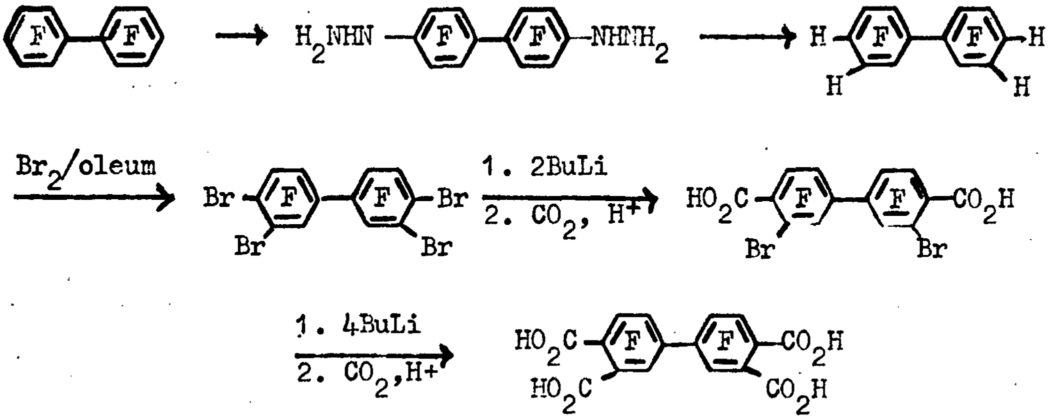
Conversion of difluoropyromellitic acid to the dianhydride was achieved by heating the acid with boiling thionyl chloride. The dianhydride, m.p. 279.5 - 280.5° (decomp.), was identified by elemental analysis and infrared spectroscopy. It was handled in a dry box to avoid the possibility of hydration.

2. TETRAFLUOROISOPHTHALIC ACID (II)

Compound II has again been prepared from 1,2,3,5-tetrafluorobenzene using the procedure supplied to us (ref. 2).

3. HEXAFLUOROBIPHENYL-3,3',4,4'-TETRACARBOXYLIC ACID (III)

Another tetracarboxylic acid of interest for use in the synthesis of fluorinated polyimides is compound III which is being prepared by the published method (ref. 3).



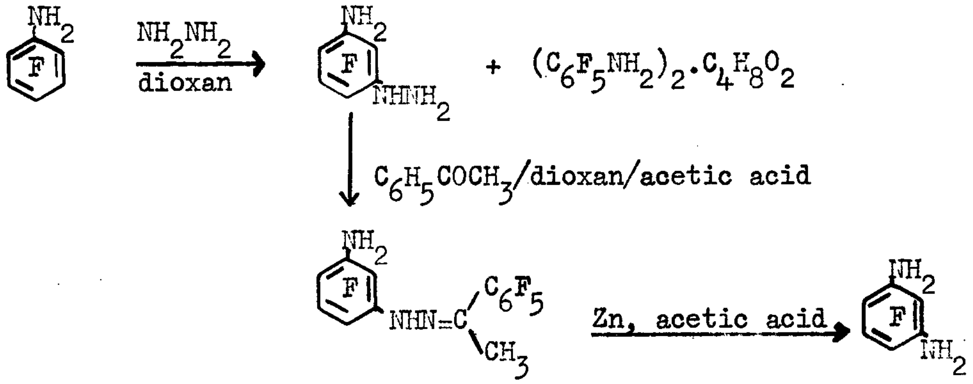
Following the published method we obtained a 58% yield of 2,2',3,3',6,6'-hexafluorobiphenyl from octafluoro-4,4'-dihydrazinobiphenyl, but by mixing the reactants in the inverse order, i.e. adding sodium ethoxide to octafluoro-4,4'-dihydrazinobiphenyl, the hexafluorobiphenyl was obtained in 84% yield. Bromination of the hexafluorobiphenyl gave 3,3',4,4'-tetrabromohexafluorobiphenyl. In two experiments, the yields were 16% and 35%. Metalation of this tetrabromo-compound (2 moles of butyl lithium/mole of the tetrabromo-compound) and carbonation of the dilithio derivative gave 3,3'-dibromohexafluorobiphenyl-4,4'-dicarboxylic acid in 60% yield. Metalation and carbonation of the dibromo-acid gave impure compound III, m.p. 216-218°, in 91% yield. The product could not be purified by thin layer chromatography and further work is required to obtain compound III in a pure state.

4. TETRAFLUORO-o-PHENYLENEDIAMINE (IV)

Compound IV was prepared in 10% yield from 2,3,4,5-tetrafluoroaniline as described previously (ref. 4).

5. TETRAFLUORO-m-PHENYLENEDIAMINE (V)

Further amounts of this diamine have been prepared by two procedures. The diamine V was obtained from pentafluoroaniline in 31% yield by the following published reactions (ref. 5a, b):



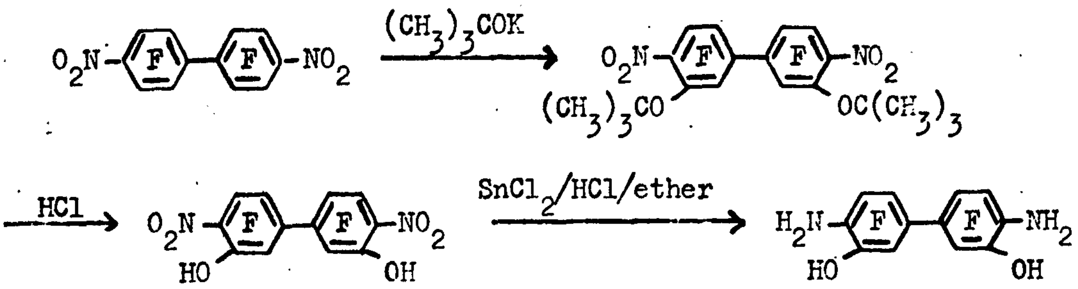
The by-product obtained from the reaction of pentafluoroaniline with hydrazine in dioxan appears to be a complex of pentafluoroaniline with dioxan of formula $(C_6F_5NH_2)_2C_4H_8O_2$. On heating above its melting point the complex decomposes into pentafluoroaniline and dioxan and the infrared spectrum is consistent with the compound being a complex of pentafluoroaniline and dioxan. It has the same melting point as a compound obtained by Holland et al., (ref. 5a) which they report as pentafluoroanilinoethanol.

In the second method, the diamine V was obtained in 24% yield by the reaction of pentafluoroaniline with ammonia and purification of the crude tetrafluoro-m-phenylenediamine so produced, via the bis(phthalimido)- derivative (ref. 4).

6. HEXAFLUORO-3,3'-DIHYDROXYBENZIDINE (VI)

We first prepared compound VI by treatment of octafluoro-4,4'-dinitrobiphenyl with sodium hydroxide or potassium hydroxide in tertiary butanol, followed by reduction of the resultant hexafluoro-3,3'-dihydroxy-4,4'-dinitrobiphenyl. Subsequently, the benzidine was examined by thin layer chromatography which revealed the presence of an impurity. The only way of removing the impurity seemed to be by preparative layer chromatography. To avoid this rather tedious process, an alternative preparation of compound VI was investigated and found to give the product in pure form.

This process, outlined below, was used to prepare the benzidine required by Monsanto for the synthesis of fluorinated benzoxazoles.



Treatment of octafluoro-4,4'-dinitrobiphenyl with potassium tertiary butoxide in boiling tertiary butanol gave hexafluoro-3,3'-di(tertiary butoxy)-4,4'-dinitrobiphenyl which was obtained pure by recrystallisation. Debutylation of this compound with hydrogen chloride in benzene gave pure hexafluoro-3,3'-dihydroxy-4,4'-dinitrobiphenyl which was reduced to compound VI in 63% yield by the method described before (ref. 4).

7. TETRAFLUORORESORCINOL (VII)

Previous preparations of compound VII by heating pentafluorophenol with aqueous potassium hydroxide have given ca. 25% yield and about 50% conversion of pentafluorophenol. Longer reaction times did not appear to improve the yield while higher reaction temperatures caused loss of material by charring, the reaction temperature being quite critical. In an improved preparation, the molar ratio of potassium hydroxide to pentafluorophenol was increased from 3:1 to 6:1, and other quantities and conditions remained the same. A 98% conversion of pentafluorophenol was achieved and compound VII obtained in 58% yield.

8. 2,4,5-TRIFLUORORESORCINOL (VIII)

A trifluorodihydroxybenzene was required by Monsanto for mass spectrometric examination. Initially it was planned to prepare 2,3,5-trifluorohydroquinone by treating 1H-heptafluorocyclohexa-1,4-diene with oleum and reducing the benzoquinone so formed (ref. 6). It was found impossible to prepare sufficiently pure 1H-heptafluorocyclohexa-1,4-diene for this route to be followed.

The preparation of 2,4,5-trifluororesorcinol by treatment of 2,3,5,6-tetrafluorophenol with potassium hydroxide solution (cf. the preparation of tetrafluororesorcinol) has the disadvantage that 2,3,5,6-tetrafluorophenol, prepared by reaction of pentafluorophenol with potassium hydroxide in tertiary butanol, may not be isomerically pure. Furthermore, conditions have not yet been found to effect a chromatographic separation of the most likely impurity, 2,3,4,5-tetrafluorophenol, from 2,3,5,6-tetrafluorophenol, so its presence or absence in the latter cannot be established. The infrared spectrum of 2,3,4,5-tetrafluorophenol has an absorption at 955 cm. which is not present in the spectrum of 2,3,5,6-tetrafluorophenol. However, because of neighbouring absorptions, the limit of detection of the former in the latter is probably ca. 5%. A proton magnetic resonance spectrum of a sample of 2,3,5,6-tetrafluorophenol showed that very little of the o-isomer was present. Thus it seemed likely that the amount of 2,3,4,5-tetrafluorophenol present in 2,3,5,6-tetrafluorophenol prepared by the action of potassium hydroxide in tertiary butanol was at most 5%. Therefore reactions of 2,3,5,6-tetrafluorophenol with potassium hydroxide solution were carried out in the hope that the small amount of isomeric impurities which could arise would be removed in the purification procedure.

At 150°, 29% of the tetrafluorophenol was converted giving crude V in 9% yield. At 180°, the conversion was 47% and the yield of V was 12%. Purification of V by sublimation and recrystallisation gave material with a poor elemental analysis. Part of the crude trifluororesorcinol was converted to the diacetate in high yield. The diacetate was purified by recrystallisation and then hydrolysed giving the trifluororesorcinol in 60% yield.

Subsequently an improved yield (20%) of the trifluororesorcinol was obtained when 2,3,5,6-tetrafluorophenol was reacted with a 100% excess of potassium hydroxide solution.

9. FLUOROHYDROXYBIPHENYLS

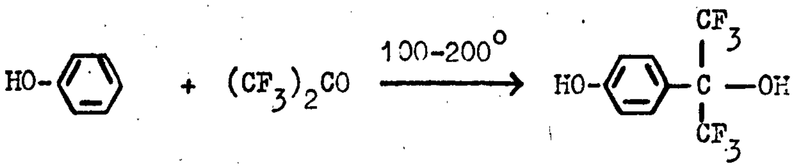
Nonafluoro-4-hydroxybiphenyl IX is required by Monsanto Chemicals Limited for work on the mode of decomposition of fluorinated polycarbonates.

It was prepared by the reaction of potassium hydroxide with decafluorobiphenyl in tertiary butanol at room temperature according to a described method (ref. 7). A mixture of compound IX and 4,4'-dihydroxyoctafluorobiphenyl was obtained from which the former (25% yield) was isolated, in fair purity, by recrystallisation. Further purification by ether extraction of the soluble sodium salt of compound IX from the insoluble disodium salt of the dihydroxy-compound (ref. 7) was not successful in our hands. However, 99% pure material was obtained fairly easily by preparative layer chromatography.

The preparation of octafluoro-4,4'-dihydroxybiphenyl X has been carried out by an improved procedure (based on a literature method ref. 7). The yield was 67%, which is a considerable improvement on earlier preparations.

10. TETRAFLUORO-4-HYDROXYPHENYLBIS(TRIFLUOROMETHYL)CARBINOL (XI)

Several reports (refs 8,9) describe the preparation of 4'-hydroxyphenylbis(trifluoromethyl)carbinol by reaction of phenol with hexafluoroacetone.



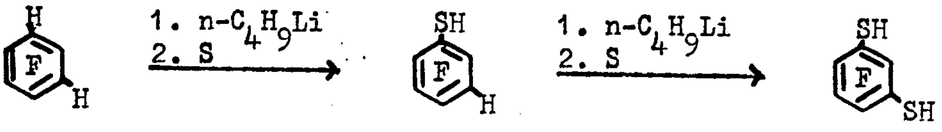
An attempt to carry out a similar reaction using 2,3,5,6-tetrafluorophenol failed and the tetrafluorophenol was recovered in good yield.

The carbinol XI is prepared successfully by the following procedure. Treatment of 2,3,5,6-tetrafluorophenol with two equivalents of butyl lithium and then with hexafluoroacetone gave compound XI contaminated with an impurity, believed to be a hydrate of hexafluoroacetone, which proved impossible to remove by distillation. The impurity was removed by distilling the crude product from phosphoric oxide and the pure carbinol was then obtained.

A larger-scale experiment gave compound XI in 58% yield.

11. TETRAFLUOROBENZENE-1,3-DITHIOL (XII)

Compound XII, required by Monsanto Chemicals Limited for the syntheses of perfluoropolyphenylene sulphide structures, was prepared by the following route:-



Treatment of 1,2,3,5-tetrafluorobenzene in tetrahydrofuran with one equivalent of n-butyl lithium in hexane followed by addition of elemental sulphur gave 2,3,4,6-tetrafluorothiophenol in 67% yield.

Treatment of 2,3,4,6-tetrafluorothiophenol in tetrahydrofuran with 2 equivalents of n-butyl lithium in hexane, followed by addition of sulphur to the dilithio-compound, gave compound XII in 54% yield. An attempt to prepare the dithiol in a single-stage reaction by treating 1,2,3,5-tetrafluorobenzene with two moles of butyl lithium and subsequent addition of sulphur gave only

2,3,4,6-tetrafluorothiophenol in 20% yield and higher-boiling liquid and solid materials which contained no dithiol and were not identified.

12. 2,4,5-TRIFLUORO-3,6-BIS(TRIFLUOROMETHYL)THIOPHENOL (XIII)

A synthesis of compound XIII by the action of sodium hydrogen sulphide on perfluoro-p-xylene in dimethylformamide solution is described in the literature (ref. 10). We have repeated this reaction, using predominantly ethanediol as solvent in place of dimethylformamide and obtained the thiol XIII in an improved yield of 69%.

13. 2,5-DIFLUORO-3,6-BIS(TRIFLUOROMETHYL)BENZENE-1,4-DITHIOL (XIV)

Compound XIV has been previously produced as a by-product in a reaction used to prepare compound XIII (ref. 10). An attempt to improve the yield of compound XIV by using a larger excess of sodium hydrogen sulphide and carrying out the reaction at a higher temperature was unsuccessful and only a poor yield (9%) of the dithiol was obtained.

EXPERIMENTAL

Difluoropyromellitic dianhydride

1. 3,6-Dinitrodurene

Nitration of durene (500 g., 3.73 moles) using 95% nitric acid (2,500 ml.) gave 3,6-dinitrodurene (660 g., 79% yield), m.p. 210-211° (from acetone).

Recrystallisation of lower melting solids (126 g.) obtained from the mother liquors of 3,6-dinitrodurene crystallisations gave an impure compound, m.p. 126-127° (from methylated spirits), which may be α,3,6-trinitrodurene (I.R. No. 4268A).

Anal.	Calc. for $C_{10}H_{11}N_3O_6$:	C, 44.7;	H, 4.1%
	Found:	C, 45.9;	H, 4.5

2. 3-Amino-6-nitrodurene

Reduction of 3,6-dinitrodurene (660 g., 2.95 moles) in ethanol (7.375 l.) using a solution of sulphur (288 g., 9 g. atoms), sodium sulphide nonahydrate (2,235 g., 9.3 moles) in water (2,750 ml.) gave 3-amino-6-nitrodurene (535 g., 93% yield), m.p. 162-164°.

3. 3-Fluoro-6-nitrodurene

Diazotisation of 3-amino-6-nitrodurene (535 g., 2.76 moles) in anhydrous hydrofluoric acid (1,900 ml.) with solid sodium nitrite (192 g., 2.76 moles) gave 3-fluoro-6-nitrodurene (422 g., 78% yield), 97.8% purity, and less pure material (74 g., 56-73% purity).

4. Alternative procedures for the reduction of 3-fluoro-6-nitrodurene

(a) With iron powder and aqueous ammonium chloride

3-Fluoro-6-nitrodurene (19.7 g., 0.1 mole), iron powder (18 g.), ammonium chloride (10.7 g.), and water (25 ml.) were heated at reflux and stirred for 1½ hr. Steam distillation of the mixture yielded organic material (18 g.), m.p. 71-73°, shown by infrared analysis to contain both the starting material and the desired amine.

(b) With iron filings and alcoholic hydrochloric acid

3-Fluoro-6-nitrodurene (19.7 g., 0.1 mole), fine iron filings (17 g.), and methylated spirits (50 ml.) were heated to reflux.

Concentrated hydrochloric acid (1 ml.) was added and the mixture boiled under reflux for 2 hr. On working up, only starting material (19 g.) was recovered.

(c) 3-Amino-6-fluorodurene (improved preparation)

3-Fluoro-6-nitrodurene (421 g., 2.14 moles) was stirred with glacial acetic acid (2,535 ml.) and granulated tin (844 g., 7.1 g. atoms) in a 20 l. flask fitted with an internal cooling coil. The mixture was heated to 50° and a portion of 12N hydrofluoric acid (250 ml.) was added. A vigorous reaction occurred, the internal temperature rose to 110° and was controlled by the internal cooling coil. The rest of the hydrochloric acid to be reacted (total 2,535 ml.) was added during 10 min. to the mixture at 95-105°. The mixture was boiled rapidly for 1 hour, then cooled, and neutralised with 50% NaOH (3,170 g. NaOH) to pH 11. The product was isolated by steam distillation, dissolved in ether (3 l.) and the ether solution dried (molecular sieve). Removal of the ether gave 3-amino-6-fluorodurene (315 g., 88% yield).

5. 3-Fluorodurene-6-diazonium borofluoride

Powdered 3-amino-6-fluorodurene (473 g., 2.83 moles) was added to stirred 12N hydrochloric acid (591 ml., 7.1 moles) in a 5 l. flask fitted with internal cooling coil. The amine hydrochloride was formed. Water (300 ml.) was added and the amine was diazotised at 0° by adding a solution of 99% sodium nitrite (207 g., 2.83 moles) in water (287 ml.). The mixture was filtered and to the filtrate, kept at 0°, was added with stirring during 20 minutes a filtered solution of sodium borofluoride (468 g., 4.25 moles) in water (709 ml.). The mixture was stirred for 2 hr. at 0° and then filtered. The solid collected was washed with 10% sodium borofluoride at 0° (4 x 60 ml.), and with ice cold water (50 and 170 ml.). The solid was dried at 35°/1 mm. Yield 671 g. A second crop (11.5 g.) was obtained by salting out from the filtrate. Total yield 682.5 g., 90.5% yield, m.p. 87-88° (decomp.).

6. 3,6-Difluorodurene

Dry 3-fluorodurene-6-diazonium borofluoride (680 g., 2.56 moles) was added in small portions during 3 hr. to a 5 l. flask containing a stirred suspension of sodium fluoride (109 g., 2.52 moles) in water (1 l.), heated in an oil bath at 110°. Each portion of diazonium borofluoride was allowed to decompose completely before the next portion was added. When cool, the solid product was collected and distilled. The distillate was redistilled through a 6 in. packed column to give 3,6-difluorodurene (386 g., 89%), b.p. 116-119.5°/42 mm., m.p. 60.5 - 62°.

7. 1,2,4,5-Tetra(bromomethyl)-3,6-difluorobenzene

A solution of 3,6-difluorodurene (380 g., 2.23 moles) in carbon tetrachloride (6 l.) was dried by azeotroping the water in a Dean-Stark apparatus. The solution was then heated to gentle reflux in a 20 l. flask fitted with an internal cooling coil. A solution of bromine (1,428 g., 8.95 moles) in carbon tetrachloride (500 ml.) was added over $\frac{1}{2}$ hr. and the stirred reaction mixture was irradiated with ultra violet light and boiled for 14 hr. until the bromine had been consumed. During this period the evolved hydrogen bromide was passed through a trap at -50° to trap out bromine which was then returned periodically to the reaction vessel.

The bulk of the carbon tetrachloride (6.2 l.) was distilled off and after cooling the residual solution the solid which crystallised out was filtered off and washed with carbon tetrachloride. Yield: 909.7 g. (84%), m.p. 177-179.5°. Evaporation of the filtrate yielded a further 149.8 g. with a wide melting range.

8. Difluoropyromellitic acid

1,2,4,5-Tetra(bromomethyl)-3,6-difluorobenzene (800 g., 1.65 moles) was added with stirring during 1 hr. to 95% nitric acid (3 litres s.g. 1.5) maintained at 25-35°. The mixture was stirred at 35° for 20 minutes and was then slowly distilled until the internal pot temperature rose to 110°. A mixture (1504 g.) of dinitrogen tetroxide, bromine, and nitric acid distilled off. The cooled mixture was diluted with water (1 litre) and concentrated to 2.25 litres. More water (2 litres) was added and the mixture was concentrated to dryness.

The solid residue was stirred with water (2 l.) and a solution of potassium permanganate (350 g., 2.2 moles) and potassium hydroxide (280 g., 4.25 moles) in water (2 litres) at 65°, was added over 1 hr. The temperature rose to 95°. More potassium hydroxide (55 g.) was added during the reaction to ensure alkalinity. The mixture was boiled for 20 minutes, then potassium permanganate (50 g., in total 400 g., 2.53 moles) was added and the mixture was stirred at 90° for 1 hr. Excess permanganate was destroyed by the addition of ethanol (15 ml.) and manganese dioxide was filtered off and water washed, the washings being added to the filtrate. The resultant solution was concentrated to 1 litre and run onto a 3' x 4" column containing amberlite I.R. 120 (3,400 g.) which had been previously eluted during $3\frac{1}{2}$ hr. with 3N hydrochloric acid (16 litres) followed by water (8 litres). The alkaline potassium difluoropyromellitate solution was eluted with water (6 litres) and the eluant evaporated to yield impure difluoropyromellitic acid (410 g., 86.5% yield). Recrystallisation from hot water gave material with m.p. 258° (decomp.).

9. Difluoropyromellitic Dianhydride

Difluoropyromellitic acid (2 g., 0.069 mole) was heated in boiling thionyl chloride (5.5 ml.) for 4 hr. The thionyl chloride was distilled off, finally at 100°/0.2 mm. An infrared spectrum (No. 4975) of the solid showed anhydride carbonyl absorptions at 1700, 1790 and 1830 cm.$^{-1}$ but no acidic -OH or carbonyl bands, evidence that the anhydride had been formed.

Anal. Calc. for $C_{10}F_2O_6$: C, 47.3; H, 0.0; F, 15.0%
Found: C, 46.7; H, 0.4; F, 14.7

In a second, larger scale, preparation difluoropyromellitic acid (24 g., 0.083 mole) was heated in boiling thionyl chloride (60 ml.) for 4 hr. The thionyl chloride was removed at reduced pressure to yield difluoropyromellitic dianhydride (20 g., 94% yield), m.p. 279.5 - 280.5° (decomp.).

Tetrafluoroisophthalic acid

Using the method described by Holland (ref. 2), tetrafluoroisophthalic acid (233 g.) was prepared in 49% overall yield from 1,2,3,5-tetrafluorobenzene (300 g.) in a two-stage reaction. This is an improvement on the 20% yield obtained in an earlier preparation (ref. 4).

Hexafluorobiphenyl-3,3',4,4'-tetracarboxylic acid

1. Octafluoro-4,4'-dihydrazinobiphenyl

Decafluorobiphenyl (300 g., 0.90 moles) was stirred with hydrazine hydrate (200 g., 4.0 mole) in boiling dioxan for 4½ hr. The solution was concentrated to 1 litre and the residue was poured into water (1.5 l.). The solid thrown down was collected, water washed and thoroughly dried. Yield: 312.8 g. (97.3%), m.p. 206 - 208.5°. This solid was stirred for 1½ hr. with a boiling 1:1 v/v mixture of ethanol and benzene (2.4 l.). After cooling to 0°, the solid was collected, washed with ethanol/benzene mixture (2 x 50 ml.) and dried, yielding pure octafluoro-4,4'-dihydrazinobiphenyl (289 g., 90% yield), m.p. 210-212°. Infrared spectrum No. 4687B.

2. 2,2',3,3',6,6'- Hexafluorobiphenyl

(a) Literature preparation

Sodium metal (37.3 g., 1.62 g. atom) was reacted during 2 hr. with absolute ethanol (2.5 litres) under nitrogen. To the cooled solution was added octafluoro-4,4'-dihydrazinobiphenyl

(290 g., 0.81 mole). The mixture was stirred at reflux for 5 hr. in which time 90% of the theoretical nitrogen evolution had occurred. The bulk of the solvent was removed and the residue was poured into water (5 l.). The solid was collected and the solution was ether extracted (2 x 500 ml.). The solid was dissolved in the ether extract which was dried and evaporated to give crude product (187 g.). This was recrystallised from 85% v/v aqueous ethanol to give 121.5 g. (57.5% yield), m.p. $54-55^{\circ}$, 95% pure by gas chromatography.

(b) Improved preparation

Sodium ethoxide solution [prepared by dissolving sodium (57.5 g., 2.5 moles) in ethanol (4.5 l.)] was added dropwise under nitrogen to a suspension of octafluoro-4,4'-dihydrazinobiphenyl (448 g., 1.25 moles) in boiling ethanol (1 l.) over 4 hours. Nitrogen was evolved. The mixture was boiled for a further 4 hours, during which time the evolution of nitrogen ceased. Ethanol (3 l.) was distilled out, and water (100 ml.) was added, followed by aqueous hydrochloric acid (6N, 100 ml.). The acidic mixture was evaporated to low bulk at reduced pressure, chloroform (1 l.) was added, and the insoluble sodium fluoride was filtered off. The filtrate was distilled at reduced pressure, giving 275.5 g. (84% yield) of the title compound (containing up to 10% of the heptafluorobiphenyl) and 29 g. of residual tar.

The crude distillate (236 g.) was fractionally distilled up a 2 ft. packed column to give two fractions:- (i) b.p. 125°/20 mm., 100 g., 96.0% $C_{12}F_6H_4$ and 4.0% $C_{12}F_7H_3$; (ii) b.p. 113°/11 mm., 46 g., 99+% $C_{12}F_6H_4$ and 0.5% $C_{12}F_7H_3$.

3. 3,3',4,4'-Tetrabromohexafluorobiphenyl

The title compound was prepared twice in 34.5% and 16.4% yields from 2,2',33,',6,6'-hexafluorobiphenyl by a literature method (ref. 3).

4. 3,3'-Dibromohexafluorobiphenyl-4,4'-dicarboxylic acid

The title compound (58.2 g.) was prepared in 60% yield from 3,3',4,4'-tetrabromohexafluorobiphenyl (110.7 g.) as previously described (ref. 3). The product, m.p. $297-299^{\circ}$, appeared to contain ca. 8% of an impurity when analysed by thin layer chromatography.

5. Hexafluorobiphenyl-3,3',4,4'-tetracarboxylic acid

The title compound (45.5 g.), m.p. $216-218^{\circ}$, was prepared in 91% yield from 3,3'-dibromohexafluorobiphenyl-4,4'-dicarboxylic acid

(58.2 g.) as previously described (ref. 3). An attempt to purify the compound by preparative layer chromatography gave a very poor recovery, probably because of decomposition on the plate.

Tetrafluoro-σ-phenylenediamine

This compound was prepared from 2,3,4,5-tetrafluoroaniline (250 g., 1.51 mole) by the acetylation, nitration, hydrolysis and reduction sequence previously described (ref. 4). There was obtained tetrafluoro-σ-phenylenediamine (26.5 g., 10%), m.p. 131-132°, 99+% pure by gas chromatography (polypropylene glycol at 175°). It gave only a single spot on thin layer chromatography, and had the expected infrared spectrum.

Tetrafluoro-m-phenylenediamine

(a) From pentafluoroaniline via 2,4,5,6-tetrafluoro-3-hydrazinoaniline

1. 2,4,5,6-Tetrafluoro-3-hydrazinoaniline

Pentafluoroaniline (183 g., 1.0 moles) was heated with anhydrous hydrazine (67.5 g., 2.1 moles) in boiling dry dioxan (100 ml.) under nitrogen for 26 hr. The mixture was then poured into water (750 ml.). The solid was collected, washed with water and dried at 40-60°/0.5 mm. A sublimate of bis(pentafluoroanilino)dioxan (25.4 g., 11.2% yield), m.p. 51 - 52.5°, was obtained. Recrystallisation of this material from petroleum ether (b.r. 40-60°) gave material melting at 54-55°. An infrared spectrum (No. 4563) shows all the bands present in the spectra of pentafluoroaniline and dioxan.

<u>Anal</u>. Calc. for $C_{16}H_{12}F_{10}N_2O_2$: C, 42.3; H, 2.7; F, 41.8%
Found: C, 43.5; H, 2.9; F, 40.7

The 2,4,5,6-tetrafluoro-3-hydrazinoaniline (110 g.), m.p. 101.5-108°, did not sublime and was purified by recrystallisation from petroleum ether, b.r. 100 - 120°, (2 l.). Yield: 68.0 g., (35%), m.p. 107-108.5°.

<u>Anal</u>. Calc. for $C_6H_5F_4N_3$: C, 36.9; H, 2.6; F, 39.0%
Found: C, 37.4; H, 2.4; F, 38.8

Exhaustive methylene chloride extraction of the aqueous solution (6 hr.) gave 31.0 g. of organic material. Distillation of this material yielded a first fraction (7.2 g.), b.r. 47°/103 mm. - 110°/25 mm., and higher-boiling material (7.2 g.). Two recrystallisations of the latter from water gave tetrafluoro-m-phenylenediamine (2.02 g.), m.p. 127.5 - 128.5°.

2. Acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone

2,4,5,6-Tetrafluoro-3-hydrazinoaniline (62.1 g., 0.318 moles), acetophenone (47.9 g., 46.5 ml., 0.39 moles), 95% ethanol (800 ml.) and acetic acid (20 ml.) were stirred at reflux for 40 minutes. The solution was cooled to 0° and filtered. The solid product was washed with a little ethanol and dried giving 67.5 g., m.p. 123 - 124.5°. The filtrate was diluted with water (3 l.) giving more solid (25.0 g.), m.p. 120-123°. This material was recrystallised from 50% ethanol (200 ml.) giving 24.5 g., m.p. 122-123°, and again from 80% ethanol (120 ml.) giving 21.0 g., m.p. 123-124°. The total yield of acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone was 88.5 g., 93.5% yield, m.p. 123 - 124.5°.

3. Tetrafluoro-m-phenylenediamine

Acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone (81.7 g., 0.278 mole), zinc powder (179 g., 2.74 g. atom) and glacial acetic acid (1154 ml.) were stirred at reflux for 4½ hr. The mixture was then cooled to room temperature and filtered. The filtrate was diluted to 6 litres with water. Ether extraction (3 x 500 ml.) of this solution gave crude material (49.3 g.) which was heated for 1½ hr. with 0.29N sodium hydroxide solution (1 l.). After cooling and filtering, the filtrate was extracted with ether and the extracts were evaporated giving tetrafluoro-m-phenylenediamine, 46.8 g. (95%).

(b) By the reaction of pentafluoroaniline with ammonia and purification of the impure tetrafluoro-m-phenylenediamine via the bis(phthalimido)-derivative

1. Pentafluoroaniline and ammonia

Pentafluoroaniline (1,510 g., 8.25 moles) and concentrated ammonia solution (1,460 ml., s.g. 0.880, 24.2 moles) were shaken and heated together for 53 hours at 190-200° in a stainless steel autoclave. The product was steam distilled to yield material (1,311 g.) containing isomeric tetrafluorophenylenediamines (918 g., 62% yield) and pentafluoroaniline (300 g.). Most of the pentafluoroaniline was removed by distillation at reduced pressure and the residue was slurried in petrol-ether (b.r. 80-100°) to give pentafluoroaniline-free material (853 g.) containing approximately 75% of tetrafluoro-m-phenylenediamine, 20% of the para isomer and 1-2% of the ortho isomer.

2. Tetrafluoro-1,3-bis(phthalimido)benzene

Part of the tetrafluorophenylenediamine mixture (329 g., 1.75 moles) was stirred with phthalic anhydride (541 g., 3.66 moles) in refluxing glacial acetic acid (4.5 l.) for $3\frac{1}{4}$ hr. and allowed to stand overnight. The crude product (470 g.), m.p. 309-312°, was filtered off and stirred in refluxing glacial acetic acid (8 l.) for $1\frac{1}{2}$ hr. The residue, (305 g.), m.p. 315-316°, was filtered off from the hot solution. This material was slurried in boiling 2-ethoxyethanol (7 l.) for 3 hr. and the cooled solution was filtered to yield white, crystalline 2,4,5,6-tetrafluoro-1,3-bis(phthalimido)benzene (255 g., 33%), m.p. 316-317°. A true recrystallisation of a small sample, using an excess of solvent, did not appreciably raise this melting point and the bulk material showed only a single spot when analysed by thin layer chromatography.

In similar preparations the pure product was obtained in yields of 30-40%.

3. Tetrafluoro-1,3-phenylenediamine

To 2,4,5,6-tetrafluoro-1,3-bis(phthalimido)benzene (230 g., 0.52 mole) in boiling ethanol (5.2 l.) was added hydrazine hydrate (64 ml., 1.27 moles) during 10 minutes. The mixture was stirred at reflux for 50 minutes. After cooling, the solution was filtered, and the solids were washed with cold ethanol. The filtrate was evaporated to dryness and the solid residue was stirred with 7.5% aqueous sodium hydroxide solution (2.8 l.). The creamy suspension was then ether extracted (4 x 500 ml.) and the extracts water washed until neutral. Ether was removed from the dried, combined extracts leaving a residue (90.3 g.) which was sublimed at 78°/0.1 mm. yielding tetrafluoro-1,3-phenylenediamine (89 g., 95% yield), m.p. 130.5 - 131.5°, 99+% pure by gas chromatography and containing no o- and p- isomers.

In similar preparations the pure diamine was obtained in yields of 93-95%.

Hexafluoro-3,3'-dihydroxybenzidine

1. 3,3'-Di(tertiary butoxy)hexafluoro-4,4'-dinitrobiphenyl

(a) Small-scale reaction

A solution of octafluoro-4,4'-dinitrobiphenyl (3.88 g., 0.01 mole) in tertiary butanol (25 ml.) at 50° was added rapidly to a nitrogen protected solution of potassium tertiary butoxide, prepared by reacting potassium (0.80 g., 0.02 g. atom) with boiling tertiary butanol (25 ml.), then cooling the mixture to 20°. The red solution was stirred for $\frac{1}{2}$ hr., then water (20 ml.) was added and the mixture was steam distilled to remove tertiary butanol. When cool, the solid was filtered off, the solution was ether extracted and the extracts evaporated to give more solid. The combined solids (3.15 g.), i.e. 63.5% yield, were recrystallised once from petrol ether (b.p. 60 - 80°) and twice from methanol giving 3,3'-di(tertiary butoxy)hexafluoro-4,4'-dinitrobiphenyl (0.74 g., 1.49% yield), m.p. 142 - 142.5°, I.R. No. 4283A.

<u>Anal</u>. Calc. for $C_{20}H_{18}F_6N_2O_6$: C, 48.4; H, 3.6; F, 23.0%
Found: C, 49.0, 49.1; H, 3.8, 3.7; F, 23.5, 23.2

The aqueous steam distillation residue was acidified with concentrated hydrochloric acid (2 ml.) and the precipitated organic material ether extracted. Evaporation of the extracts gave a residue (0.97 g.), which was recrystallised three times from petrol ether (b.p. 80-100°), yielding yellow crystals of hexafluoro-3,3'-dihydroxy-4,4'-dinitrobiphenyl, m.p. 147-147.3°, pure by thin layer chromatographic analysis.

<u>Anal</u>. Calc. for $C_{12}H_2F_6N_2O_6$: C, 37.5; H, 0.5; F, 29.7%
Found: C, 38.0, 38.2; H, 0.3, 0.3; F, 29.9, 30.1.

(b) <u>Improved large-scale procedure</u>

Octafluoro-4,4'-dinitrobiphenyl (156 g., 0.412 mole) in tertiary butanol at 50° was added rapidly to a stirred suspension of potassium tertiary butoxide prepared by reacting potassium (32.0 g., 0.82 g. atom) with boiling tertiary butanol (1 l.) and then cooling the mixture to ambient temperature. The mixture was stirred at 60°, then kept at ambient temperature for 65 hr. The tertiary butanol was removed in a rotary evaporator leaving a solid residue which was extracted in a Soxhlet apparatus for 12½ hr. with petrol ether (b.p. 60-80°). Crude product (87.7 g.) crystallised from the extract on cooling. This was filtered off and more material was obtained on concentrating the filtrate, giving a total yield of 141.7 g. Recrystallisation of the less pure fractions from methanol and the pure fraction from petrol ether gave 3,3'-di(tertiary butoxy)-hexafluoro-4,4'-dinitrobiphenyl (99.9 g., 49.6% yield), m.p. 144-145°, with an infrared spectrum comparable to that of an authentic sample.

Exhaustive extraction of the Soxhlet thimble residue with ether (1 l.) for 40 hr. gave, on evaporation of the extracts, a red solid (38 g.). This was dissolved in water, the solution was acidified and the precipitated product recrystallised yielding crude hexafluoro-3,3'-dihydroxy-4,4'-dinitrobiphenyl (18.03 g.), m.p. 100-105°.

2. Hydrolysis of 3,3'-di(t-butoxy)hexafluoro-4,4'-dinitrobiphenyl

Dry hydrogen chloride was passed during 4 hr. through a solution of 3,3'-di(t-butoxy)hexafluoro-4,4'-dinitrobiphenyl (83.0 g., 0.167 mole) in dry benzene (850 ml.) at 20°. The solvent was removed at 100°/20 mm. to yield a residue of hexafluoro-3,3'-dihydroxy-4,4'-dinitrobiphenyl (65.5 g., 100%), m.p. 145-146°. Thin layer chromatographic analysis showed the presence of two impurities in this material. Recrystallisation from petrol ether (2.5 l., b.r. 100-120°) gave the pure compound (55.8 g., 87%), m.p. 146-147°. This material gave only a single spot when analysed by thin layer chromatography.

3. Hexafluoro-3,3'-dihydroxybenzidine

Reduction of hexafluoro-3,3'-dihydroxy-4,4'-dinitrobiphenyl as described previously (ref. 4) gave hexafluoro-3,3'-dihydroxybenzidine in 63% yield.

Tetrafluororesorcinol

Pentafluorophenol (185 g., 1 mole) was shaken and heated with a solution of 85% potassium hydroxide (402 g., 6.06 moles) in water (500 ml.) at 150° for 5 hr. in an 800 ml. capacity stainless steel autoclave. The cold contents were poured into 9N hydrochloric acid (1.33 l.) and the solution was extracted with methylene chloride (6 x 200 ml.). Evaporation of the dried extracts gave pentafluorophenol (5.5 g.), 87% pure by gas chromatography. The aqueous acidic solution remaining after the methylene chloride extraction was ether extracted (3 x 500, 3 x 300 ml.) and the dried extracts were distilled yielding crude tetrafluororesorcinol (146.3 g.). Fractional distillation of this material gave tetrafluororesorcinol (109.7 g., 58% yield), b.p. 110-124°/15 mm., 95% pure by gas chromatography. This material was added to the products from similar reactions and the bulked material was purified to 99+% by recrystallisation from benzene.

2,4,5-Trifluororesorcinol

(1) The reaction between aqueous potassium hydroxide and 2,3,5,6-tetrafluorophenol

(a) at 150°

2,3,5,6-Tetrafluorophenol (166 g., 1.0 mole) and a solution of potassium hydroxide (200 g., 85% purity, 3.0 mole) in water (500 ml.) were shaken and heated at 150° for 5½ hr. in an 800 ml. capacity stainless steel autoclave. Hydrochloric acid (6N, 1 litre) was added and the mixture extracted with methylene chloride (5 x 200 ml.). Aspiration of the solvent and distillation of the residue yielded 2,3,5,6-tetrafluorophenol

(117.7 g., 0.71 mole). The aqueous solution remaining after the methylene chloride extraction was ether extracted (5 x 200 ml.). The ether was distilled from the extract and the residue of crude trifluororesorcinol (4.48 g., 9% yield), m.p. 80.5 - 84°, was sublimed at 50-60°/0.1 mm., then the sublimate was recrystallised twice from dry benzene to give 1.96 g., m.p. 79-81°. Thin layer chromatographic analysis showed that this product was pure.

Anal. Calc. for $C_6H_3F_3O_2$: C, 43.9; H, 1.8; F, 34.7%
Found: C, 41.4; H, 1.8; F, 35.9.

An infrared spectrum (No. 4199) was consistent with the proposed structure but the aromatic C-H was not detected due to the overlap of bonded -OH in the solid spectra. It was impossible to find a suitable solvent to give a strong enough liquid phase spectrum to detect aromatic -CH.

(b) at 180°

2,3,5,6-Tetrafluorophenol (119 g., 0.72 mole) and a solution of potassium hydroxide (144 g., 2.15 moles) in water (360 ml.) were heated and shaken at 180° for 5 hr. then worked up as in (a) above. 2,3,5,6-Tetrafluorophenol (56.6 g., 0.34 mole) was recovered and crude 2,4,5-trifluororesorcinol (7.24 g., 12% yield), m.p. 75-80°, obtained.

(2) 2,4,5-Trifluororesorcinyl diacetate

Crude 2,4,5-trifluororesorcinol (4.1 g., 0.025 mole) from experiment (1) (b) above was heated and stirred on a steam bath for 5 hr. with acetic anhydride (31 g.) containing freshly fused sodium acetate (1.65 g.). The reaction product was poured into water (100 ml.) and the buff precipitate filtered off, washed with 2½% sodium bicarbonate solution (20 ml.) and dried in vacuo over phosphoric oxide. Yield: 5.4 g., 87%, m.p. 65.5 - 67.5°. Two recrystallisations from 50% v/v aqueous ethanol gave the diacetate (3.5 g.), m.p. 67 - 67.5°, showing a single spot by thin layer chromatography. The infrared spectrum (No. 4255) was consistent with the proposed structure.

Anal. Calc. for $C_{10}H_7F_3O_4$: C, 48.3; H, 2.8; F, 23.0%
Found: C, 48.3; H, 2.8; F, 23.0.

(3) Hydrolysis of 2,4,5-trifluororesorcinyl diacetate

The purified diacetate (3.17 g., 0.013 mole) was heated at reflux with 5N sulphuric acid (60 ml.) for 3 hr. The clear solution was ether extracted (6 x 50 ml.) and the extracts water washed (2 x 10 ml.).

Removal of the ether yielded crude 2,4,5-trifluororesorcinol (2.20 g., 100%). Recrystallisation of this material from benzene gave 2,4,5-trifluororesorcinol (1.32 g.), m.p. 83-86°. The infrared spectrum (No. 4398A) showed that it was purer than the sample prepared in (1) (a) above.

<u>Anal.</u> Calc. for $C_6H_3F_3O_2$: C, 43.9; H, 1.8; F, 34.7%
Found: C, 43.2; H, 2.2; F, 35.2.

Thin layer chromatographic analysis showed only a single spot.

(4) <u>Improved complete preparation of 2,4,5-trifluororesorcinol</u>

2,3,5,6-Tetrafluorophenol (166 g., 1.0 mole) was shaken and heated with a solution of 85% potassium hydroxide (402 g., 6.06 moles) in water (500 ml.) at 150° for 5 hr. in an 800 ml. capacity stainless steel autoclave. After the usual working up, there was obtained crude 2,4,5-trifluororesorcinol (36 g., 22% yield) and 2,3,5,6-tetrafluorophenol (81 g., 0.49 mole).

Sublimation of the crude 2,4,5-trifluororesorcinol at 60-80°/0.04 mm. yielded product (31.8 g.), m.p. 80-82° (sealed tube), which was acetylated as described previously above, to give 2,4,5-trifluororesorcinyl diacetate (33.1 g., 69% yield), m.p. 69 - 69.5°. Hydrolysis of this material (30 g.) as described previously, yielded 2,4,5-trifluororesorcinol (13.0 g., 66% yield), m.p. 82-84°, pure by thin layer chromatographic analysis and having the correct infrared spectrum. The orientation of the substituents was confirmed by nuclear magnetic resonance spectroscopy.

<u>Nonafluoro-4-hydroxybiphenyl</u>

To a stirred solution of decafluorobiphenyl (75 g., 0.225 mole) in tertiary butanol (360 ml.) at 40-50° was added powdered 85% potassium hydroxide (33.5 g., 0.5 mole) in portions over $\frac{3}{4}$ hr. The solution was stirred at room temperature for 5 hr. during which time a white solid precipitated. Water (500 ml.) was added and the mixture allowed to stand overnight. Tertiary butanol was distilled off at reduced pressure and the residue was acidified with 12<u>N</u> hydrochloric acid (90 ml.) and ether extracted. The dried extracts were evaporated to leave a solid residue (75 g.) which was shown by thin layer chromatographic analysis to contain roughly equal amounts of nonafluoro-4-hydroxybiphenyl and octafluoro-4,4'-dihydroxybiphenyl.

A range of solvents was tried in attempts to purify the product by recrystallisations. Only petrol ether (b.r. 60-80°) gave crystals enriched in the monohydroxy-compound. Three recrystallisations of the crude mixture (70.5 g.) from this solvent gave 4-hydroxynonafluorobiphenyl (19.8 g., 25% yield), m.p. 120.5 - 123°, containing a little of the dihydroxy-compound, as indicated by thin layer chromatographic analysis.

A second preparation gave crude nonafluoro-4-hydroxybiphenyl (75.4 g.) containing approx. 70% of the monohydroxy-compound and 30% of the dihydroxy-compound (by T.L.C. analysis). This mixture (73 g.) was separated by preparative layer chromatography in 15 runs, (5 g. per 20 x 100 cm. plate, coated with a 1 mm. layer of GF 254 silica gel, and eluted with a 9:1 v/v mixture of chloroform and glacial acetic acid) to yield 39.6 g. of buff solid. Recrystallisation of this material from petrol-ether (b.r. 60-80°) gave pure nonafluoro-4-hydroxybiphenyl (31.1 g., 40% yield from decafluorobiphenyl), m.p. 119-120°, showing only a single spot when analysed by thin layer chromatography.

Octafluoro-4,4'-dihydroxybiphenyl

Decafluorobiphenyl (150 g., 0.45 mole) was stirred in refluxing tertiary butanol (720 ml.) while powdered 85% potassium hydroxide (135 g., 2 moles) was added over 1 hr. The stirred suspension was held at reflux for a further hour then water (1 litre) was added and the mixture allowed to stand overnight. Tertiary butanol was distilled off under reduced pressure and concentrated hydrochloric acid (350 ml.) was added to the residue. The resulting solution was ether extracted and the extracts were dried and evaporated to yield crude product (152 g.), m.p. 202.5 - 205.5°. Two recrystallisations from toluene gave octafluoro-4,4'-dihydroxybiphenyl (98.4 g., 67%), m.p. 210.5 - 212.5°, with the correct infrared spectrum. Only a single spot was observed when this material was analysed by thin layer chromatography.

Tetrafluoro-4-hydroxyphenylbis(trifluoromethyl)carbinol

(a) By reaction of hexafluoroacetone with 2,3,5,6-tetrafluorophenol

Dry redistilled 2,3,5,6-tetrafluorophenol (17.7 g., 0.106 mole) and hexafluoroacetone (20.5 g., 0.123 mole) were sealed in vacuo in a 75 ml. capacity "Pyrex" ampoule which was shaken and heated at 100° for 48 hr. The gaseous products were vented into a vacuum system yielding hexafluoroacetone (13.5 g.) and leaving a white residue. This slowly degassed on standing to leave only 2,3,5,6-tetrafluorophenol (18.2 g., 100% recovery).

(b) From the dilithio-derivative of 2,3,5,6-tetrafluorophenol and hexafluoroacetone

To a stirred solution of 2,3,5,6-tetrafluorophenol (33.2 g., 0.2 mole) in tetrahydrofuran (250 ml.) at -75° under nitrogen was added a solution of 2.24 N butyl lithium in hexane (180 ml., 0.4 mole) over ½ hr. The mixture was then stirred at -65° for a further 3½ hr. Dry hexafluoroacetone (34.9 g., 0.21 mole) was condensed into the mixture via a dip-tube over ½ hr. at -65°, causing a vigorously exothermic reaction. The resultant greenish suspension was stirred at -75° for ½ hr., allowed to warm slowly to -10° and then acidified with 6N hydrochloric acid (150 ml.). The aqueous phase was separated off, ether extracted (4 x 100 ml.), and the combined extracts added to the organic phase. Evaporation of the solvent from this mixture gave a liquid residue which was fractionally distilled twice at reduced pressure to give fractions as follows, (i) b.r. 50-52°/0.1 mm., 13.67 g., 86% pure, (ii) b.r. 52-53°/ 0.15 mm., 9.79 g., 92% pure, and (iii) b.p. 53°/0.15 mm., 18.71 g., 96.5% pure.

Material (13 g.) from fraction (i) was heated with phosphoric oxide (1.7 g.) at gentle reflux (70-80°/0.1 mm.) for 1¾ hr., then distilled to give white, crystalline tetrafluoro-4-hydroxyphenylbis-(trifluoromethyl)carbinol (7.3 g.), b.p. 58-62°/0.1 mm., 99+% pure by gas chromatographic analysis.

Anal. Calc. for $C_9H_2F_{10}O_2$: C, 32.5; H, 0.6; F, 57.2%
Found: C, 32.4; H, 0.9; F, 57.0.

The infrared spectrum (No. 4982) of this material was consistent with the proposed structure and confirmed that the material was of higher purity than the carbinol before treatment with phosphoric oxide.

A second preparation from 2,3,5,6-tetrafluorophenol (66.4 g., 0.4 mole) and hexafluoroacetone (76.4 g., 0.46 mole), exactly as above, gave 103.7 g. of 91% pure material. This product was heated at reflux for 1 hr. at 0.1 mm. with phosphoric oxide (10 g.), then distilled to give the title compound (76.9 g., 58% yield), b.p. 56-57°/0.05 mm., of greater than 98% purity (by gas chromatographic analysis).

2,3,4,6-Tetrafluorothiophenol

A solution of n-butyl lithium in hexane (2.18N, 140 ml., 0.30 mole) was added in 1 hr. to a solution of 1,2,3,5-tetrafluorobenzene (45.1 g., 0.30 mole) in dry tetrahydrofuran (250 ml.) under nitrogen at -60 to -70°. The mixture was stirred for a further ½ hr. Dried sulphur (10 g., 0.31 g. atom) was added in portions over ½ hr. to give a deep orange brown solution which was stirred at -60 to -70° for a further 2 hr. and then allowed to warm to ca. 10° in ½ hr. 6N Hydrochloric acid (450 ml.) was added, causing a pale brown organic layer to form. The organic layer was separated, water washed (2 x 100 ml.) and dried. After distillation of the solvent there remained a residue (63.5 g.) which was fractionally distilled yielding 2,3,4,6-tetrafluorothiophenol (36.5 g., 67%), b.p. 148-150°/756 mm. This material was 98.3% pure by gas chromatography. A part (5 g.) was redistilled to yield an analytical sample, 98.9% pure by gas chromatography.

Anal. Calc. for $C_6H_2F_4S$: C, 39.6; H, 1.1; F, 41.7%
Found: C, 39.5; H, 0.9; F, 41.3.

An infrared spectrum (No. 4389) showed the presence of aromatic C-H, -SH and a highly fluorinated aromatic ring.

Tetrafluorobenzene-1,3-dithiol

(a) From 2,3,4,6-tetrafluorothiophenol

To a stirred solution of 2,3,4,6-tetrafluorothiophenol (28.1 g., 0.154 mole) in tetrahydrofuran (175 ml.) at -70° was added over 2 hr. a 2.24 N solution of n-butyl lithium in hexane (140 ml., 0.31 mole). The greenish-white suspension obtained was stirred a further 2 hr. The Gilman Colour Test IIA was then negative. Dry sulphur (5.52 g., 0.172 g. atom) was added over ¼ hr. and the mixture was stirred at -65° for 1¼ hr., and at -50° for ½ hr. 6N hydrochloric acid (450 ml.) was added to the solution at -10°. The organic layer was separated and the aqueous layer was ether extracted (3 x 200 ml.). The dried combined organic layers were distilled to yield, after removal of the solvent, tetrafluorobenzene-1,3-dithiol (17.66 g., 54% yield), b.p. 97-98°/15 mm., 99+% pure by gas chromatographic analysis. The infrared spectrum (No. 4813) was consistent with the proposed structure.

Anal. Calc. for $C_6H_2F_4S_2$: C, 33.6; H, 0.94; F, 35.5%
Found: C, 33.8; H, 1.0; F, 35.3.

Treatment of the dithiol (2 g.) in ether solution at 0° with an excess of diazomethane gave 1,3-dimethylthiotetrafluorobenzene (2.29 g., 100%) which crystallised from aqueous ethanol as white plates, m.p. 69.5 - 71°, with an infrared spectrum consistent with the proposed structure.

Anal. Calc. for $C_8H_6F_4S_2$: C, 39.7; H, 2.5; F, 32.3%
Found: C, 39.2; H, 2.4; F, 31.7.

(b) Attempted preparation from 1,2,3,5-tetrafluorobenzene

To a stirred solution of 2.24 N butyl lithium in hexane (134 ml., 0.30 mole) and tetrahydrofuran (450 ml.) at -70°, was added over ½ hr. a solution of 1,2,3,5-tetrafluorobenzene (22.5 g., 0.15 mole) in tetrahydrofuran (50 ml.). The resultant solution was stirred a further ½ hr. at -75° and then gave a negative Gilman Colour Test IIA. Dry sulphur (9.62 g., 0.30 g. atom) was added over ½ hr. and the resultant solution was stirred at -75° for 1½ hr. and at -50°

for $1\frac{1}{2}$ hr. becoming a deep orange colour. Acidification with 6*N* hydrochloric acid (500 ml.) gave a two phase system which was worked up as in (a) above to give 2,3,4,6-tetrafluorothiophenol (5.5 g., 20% yield), high-boiling material, b.r. 110-114°/0.4 mm. containing no 1,3-dithiol, and a tarry residue (13.2 g.).

2,4,5-Trifluoro-3,6-bis(trifluoromethyl)thiophenol

A solution of perfluoro-p-xylene (28.6 g., 0.1 mole) in dimethylformamide (50 ml.) was added, over 1 hr., to a stirred solution of sodium hydrogen sulphide (44.8 g., 0.8 mole) in ethanediol (100 ml.) at 25°. The mixture was stirred for a further $\frac{1}{2}$ hr. at this temperature and was then acidified with a solution of anhydrous calcium chloride (15.5 g., 0.14 mole) in concentrated hydrochloric acid (100 ml.). The solution was steam distilled and the distillate was ether extracted (4 x 100 ml.). The dried extracts were distilled to yield 2,4,5-trifluoro-3,6-bis(trifluoromethyl)thiophenol (20. 6 g., 69% yield), b.p. 65-66°/15 mm., 99+% pure by gas chromatographic analysis.

2,5-Difluoro-3,6-bis(trifluoromethyl)benzene-1,4-dithiol

Perfluoro-p-xylene (28.6 g., 0.1 mole) in dimethylformamide (40 ml.) was added over $\frac{3}{4}$ hr. to a stirred suspension of sodium hydrogen sulphide (56 g., 1 mole) in dimethylformamide (175 ml.) at 100°. The red-brown solution was stirred as it cooled and was then poured rapidly into a solution of anhydrous calcium chloride (20 g.) in 12*N* hydrochloric acid (125 ml.). The solution was steam distilled and the distillate was ether extracted. The dried extracts were evaporated under nitrogen to give a residue (9 g.) which was distilled to yield the monothiol (0.77 g.), b.p. 68-70°/16 mm., and crude 2,5-difluoro-3,6-bis(trifluoromethyl)benzene-1,4-dithiol (2.85 g., 9% yield), b.p. 115-116°/16 mm. After two recrystallisations of this material from petrol ether (b.r. 40-60°) the pure product (0.94 g.) was obtained, m.p. 66 - 66.5°.

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PART II

MODEL COMPOUNDS AND POLYMERS

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INTRODUCTION

The aim of this part of the programme is to determine if fully fluorinated (or almost fully fluorinated) aromatic polymers offer any improvement in thermo-oxidative stability over their hydrogenic analogues. Preliminary work has provided fully and partly fluorinated aromatic model compounds and their hydrogenic analogues, for comparison of thermal decomposition temperatures in nitrogen. Where the thermal stability of model compounds justifies it the fluorinated structures are being incorporated into polymers for comparison of thermo-oxidative stability with the analogous hydrogenic polymers.

The preparation of polymers and their evaluation for thermo-oxidative stability has absorbed the greatest effort in the work covered by this report, with only a limited effort directed towards model compounds and new reactions.

SUMMARY

1. Further synthetic work has been directed towards fully fluorinated or partly fluorinated model compounds: benzoxazoles, benzimidazoles, and an imide. There was limited success in the synthesis of perfluoro-2,2'-diphenyl-6,6'-bibenzoxazole; a corresponding bibenzimidazole or its isomers could not be obtained. Compounds of unknown structure were obtained in attempts to prepare perfluoro-2-phenylbenzimidazole. The tetramethyl ester of difluoropyromellitic acid did not condense with pentafluoroaniline.

2. The thermal stability of a perfluoro cycloaliphatic compound was found to be reasonably high, but the thermal decomposition point could not be obtained because the boiling point was too low for the apparatus. This compound, from the University of Birmingham, was derived by saturating with fluorine an aralkyl compound derived from decafluoro-o-xylene.

3. Complexes have been made from pyromellitic dianhydride and perfluoro aromatic diamines, which yield polyimides on heating.

4. A polyimide made by heating a complex containing pyromellitic dianhydride and tetrafluoro-m-phenylene diamine has higher thermo-oxidative stability than the hydrogenic polyimide obtained via a polyamic acid. Other methods of preparation and other fluorinated diamines gave lower thermo-oxidative stability.

5. Attempts have been made to prepare laminates from glass cloth impregnated with a resin containing pyromellitic dianhydride and tetrafluoro-m-phenylene diamine.

6. Difluoropyromellitic acid and its tetramethyl ester did not give stable polyimides when heated with tetrafluoro-m-phenylene diamine.

7. A number of polycarbonates have been prepared and examined for thermo-oxidative stability: hydrogenic against perfluorinated, or partly fluorinated structures. It was found that perfluoro poly (m-phenylene carbonate) has increased thermo-oxidative stability over its hydrogenic analogue only when these polymers are made by a chloroformate melt condensation. This is the most satisfactory of the four methods examined for preparing perfluoropolycarbonates. Even so, the p-isomeric structure has a slightly lower thermo-oxidative stability than the hydrogenic p-isomer structure. A co-polymer containing the 2,2'-diphenylpropylidene and the tetrafluoro-m-phenylene moieties, had greater thermo-oxidative stability than a similar co-polymer from Bisphenol A and m-phenylene bischloroformate.

8. A model reaction for a new route to perfluoro polyarylenes has been investigated, from pentafluorobenzene sulphonyl chloride and decafluorobiphenyl. Probably there are three olefinic products of this reaction, one of which is probably 6-chloro-1,5-di(pentafluorophenyl)-2,3,4,5,6-pentafluorocyclohexa-1,3-diene. The latter was dehalogenated to yield perfluoro-m-terphenyl. The reaction scheme represents a new route to a mixture of the perfluoro terphenyl isomers. A similar reaction was carried out but with the decafluorobiphenyl replaced by octafluoronaphthalene.

9. Perfluoro poly (1,3,4-oxadiazole) from tetrafluoroterephthalic acid and hydrazine in oleum gave low molecular weight polymer of low thermo-oxidative stability.

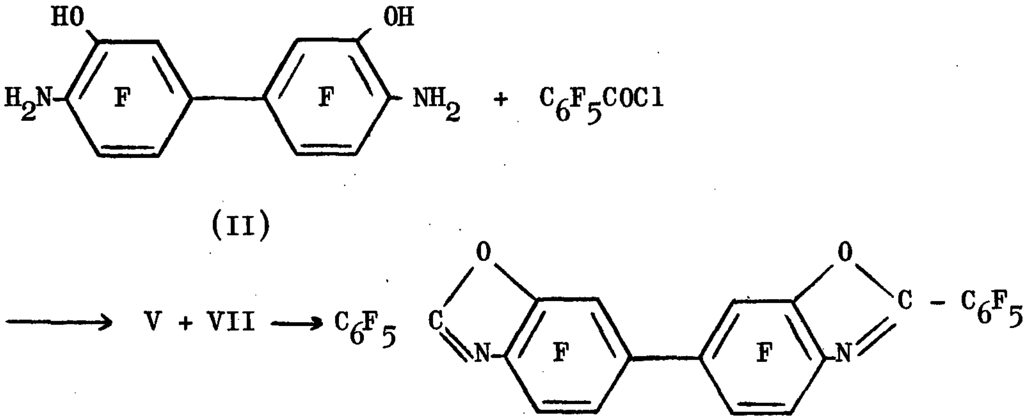
10. Perfluoro polybenzoxazole was not obtained by the condensation of tetrafluoro-isophthaloyl chloride with 3,3'-dihydroxy-2,2',5,5',6,6'-hexafluorobenzidine.

DISCUSSION

SYNTHESES OF MODEL COMPOUNDS

Benzoxazoles

(a) It has been reported (Ref. 1) that hexafluoro 3,3'-dihydroxybenzidine (II) and pentafluorobenzoyl chloride yield perfluoro bibenzoxazole (I) via intermediates (V) and (VII): Reaction (i). The numbering of these formulae are, as far as possible, consistent with the numbers in Ref. 1 (Annual Report for 1965, this Contract). Thus compounds (V) and (VII) have the same numbers in Ref. 1.



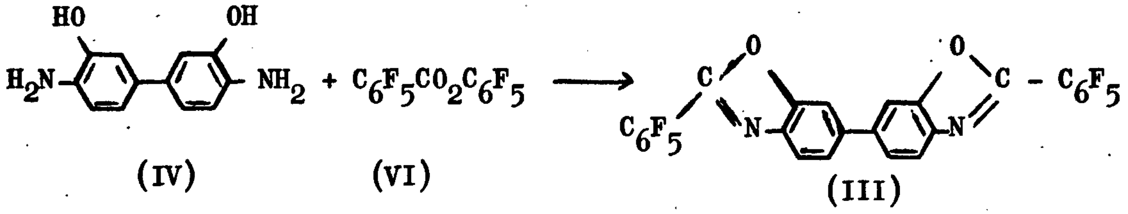
(II)

(I) ......Reaction (i)

In order to obtain more information about the formation of the intermediate compounds (V) and (VII), useful for subsequent investigation of polymer formation, pentafluorobenzoyl chloride was condensed with (II) dissolved in aqueous sodium hydroxide. A solution of 3,3'-dihydroxyhexafluorobenzidine in sodium hydroxide solution was treated with 2 molar proportions of pentafluorobenzoyl chloride. After $1\frac{1}{2}$ hours the neutralised mixture gave a precipitate which proved to be identical with the pentafluorobenzoyl derivative, compound (V), m.p. 274-275.5°. A reaction time of 17 hours gave a product which was identical with compound (VII), m.p. 329 - 330°.

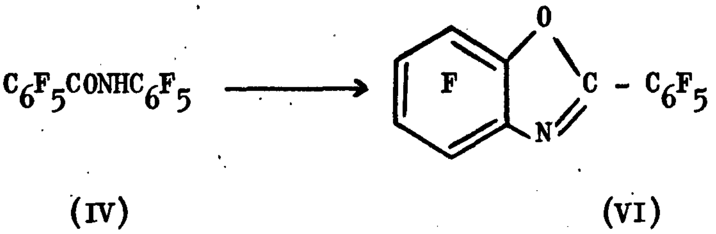
These results are not inconsistent with those reported (Ref. 1) for the conversion of (V) to (VII) by alkali.

(b) The partly fluorinated bibenzoxazole (III) can be obtained from 3,3'-dihydroxybenzidine (IV) and pentafluorobenzoyl chloride via a pentafluorobenzoyl derivative (Ref. 1). It was hoped for a better yield by condensing (IV) with perfluoro phenyl benzoate (VI): Reaction (ii)



......Reaction (ii)

This type of reaction would then be more suitable for formation of a poly (bibenzoxazole). Such a reaction is well known for the hydrogenic analogue of (I) and (III) and for the hydrogenic poly (bibenzoxazole). However, reaction (ii) did not yield any of the desired compound (III).



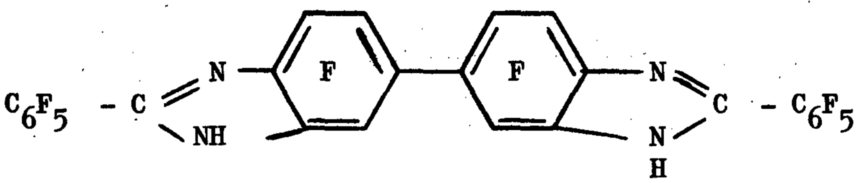
.... Reaction (iii)

In a continuation of efforts (ref. 1) to cyclise decafluorobenzanilide (IV) to perfluorobenzoxazole (VI), Reaction (iii), the anilide was boiled under reflux in 2N sodium hydroxide for 65 hours, and treated with sodium hydroxide at 300-350°. Acidification yielded products of m.p. above 400° in each case, and there was no evidence for the formation of sodium fluoride.

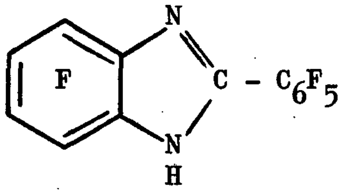
The potassium salt of decafluorobenzanilide in refluxing nitrobenzene gave a product with an indefinite melting point. In refluxing toluene, the products were unreacted potassium salt and decafluorobenzanilide. After heating the potassium salt at 350°, there was no apparent elimination of KF and the product had a m.p.$\gg$400°.

Benzimidazoles

Earlier attempted syntheses of (VIII) have been reported (ref. 4). The latest attempt was the condensation of 3,3',4,4'-tetra-amino-2,2',5,5',6,6'-hexafluoro-biphenyl with perfluoro (phenyl benzoate) at 300-340° under nitrogen. This gave a material, m.p. 235-255°, which could not be purified by recrystallisation. Similarly, a material, m.p. 225-235°, was obtained from 3,3'-bis(pentafluorobenzamido)hexafluorobenzidine at 300-350° under nitrogen.



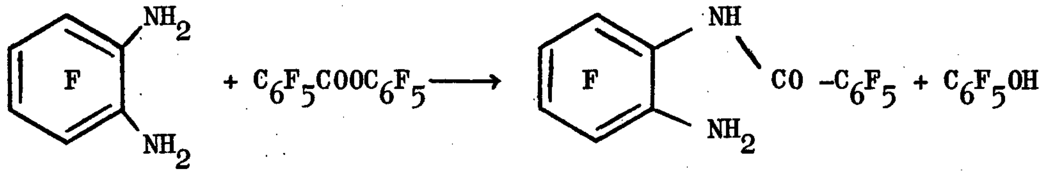
(VIII)



(IX)

As difficulty has been experienced in the preparation of the bibenzimidazole (VIII), later work has been concentrated on the preparation of 2-(pentafluorophenyl)-tetrafluorobenzimidazole (IX) as a simpler compound to synthesise.

Tetrafluoro-o-phenylene diamine was allowed to react with pentafluorobenzonitrile, and the dihydrochloride of the diamine with perfluorobenzoic acid. Different products, m.p. 180-2° (with sublimation), and m.p. 94° respectively, were obtained and these have yet to be identified. A third product, m.p. 182-182.5°, was obtained in low yield by the reaction of o-phenylene diamine and perfluoro (phenyl benzoate) in refluxing toluene solution: Reaction (iv). The infra-red spectrum and elemental analysis suggest that this is the amide (X)

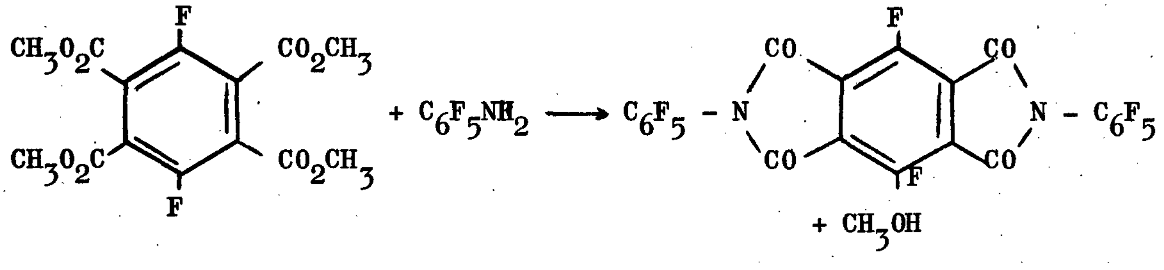


(X)

........Reaction (iv)

Imides

Tetramethyl difluoropyromellitate did not react with pentafluoroaniline as required: Reaction (v)



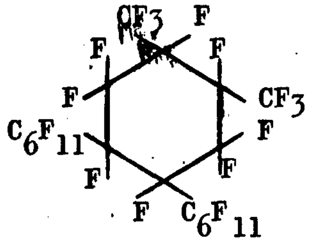
......Reaction (v)

The conditions under which this was attempted were (a) in refluxing ethanolic solution, (b) in an excess of refluxing pentafluoroaniline at 160-165°. In both cases the starting ester was recovered.

THERMAL STABILITY OF MODEL COMPOUNDS

An attempt was made to determine the T_D of the compound (A) but the boiling point was too low for the apparatus available (ref. 10)

The isoteniscope was pressurised in the case of (A) so that a rate of pressure increase was obtained at 308° of ca. 7 mm Hg. in 60 minutes. This compares with a rate of increase of 0.84 mm Hg per minute which defines the T_D. Therefore this compound appears to have reasonably high thermal stability.



(A)

See Table 7, Appendix IIA for the thermal stability of heterocyclics.

POLYMERS

1. Polyimides

(a) Investigation of Preparative Methods and Thermo-Oxidative Stability

It has been stated in the literature (Ref. 9) that when comparing solvents for polyimide preparation, the polymer with the highest inherent viscosity was obtained with dimethyl sulphoxide. However, reaction of tetra-fluoro-m-phenylene diamine with pyromellitic dianhydride in dimethyl sulphoxide gave a polyamic acid with an inherent viscosity of 0.055 dl/g. This compared with a maximum figure of 0.2 dl/g. for the product of the same reaction in dimethyl acetamide.

High thermo-oxidative stability has been demonstrated for a polyimide PI(2) derived from PMDA (pyromellitic dianhydride) and m-F(tetrafluoro-m-phenylene diamine (ref. 1, page 53). It has been shown by TGA in air that this stability is of the same order as that of the corresponding hydrogenic polyimide PI(1) derived from PMDA and m-H (m-phenylene diamine). These polyimides were prepared by identical methods, i.e. from PMDA and the diamine in dry DMAC (dimethylacetamide) via a polyamic acid intermediate. However, the inherent viscosity of PI(1) was considerably higher at 1.4 dl/g than that of PI(2) at 0.1 dl/g and this must reflect a wide difference in average molecular weight. A higher molecular weight in PI(2) would have provided polymers for a fairer comparison of thermo-oxidative stability with PI(1), and would have enabled films to be cast. However, variations in the conditions of preparing the fluorinated polyamic acid did not give a higher inherent viscosity than 0.2 dl/g. Similarly, polyamic acids of low inherent viscosity (below 0.1 dl/g) were obtained from PMDA with p-F (tetrafluoro-p-phenylene diamine) or OFB (octafluorobenzidine). In the case of these two polyamic acids the inherent viscosities are given correctly on page 53 of ref. 1; page 85 of ref. 1 contains misprints.

Complexes C1, C2 and C3 have now been obtained from m-F, p-F and OFB in THF. The solvent was not anhydrous (and contained 0.1% hydroquinone as stabiliser) so that the complexes, obtained by evaporation of the THF, contained carboxylic groups as indicated by the I.R. spectra (Spectrum No.2003 for C1), TGA in air, with the temperature rising at 1°/min. showed that these complexes lost weight up to ca. 300°, and above this the TGA curve suggested that stable polyimide had been formed. By interrupting the programmed TGA at 300° in the case of C1 it was shown by I.R. (Spectrum No.2004) that a polyimide had been formed. The TGA curves are given in Figures 1 and 2. Figure 1 also includes a TGA curve at a higher rate of heating (6°/minute) for C1.

As stable polyimide appeared to be formed at both rates of heating, the 6°/minute rate was employed to heat the complexes C1 and C2 to 400°. Polyimides PI(11) and PI(12) made in this way were maintained at 400° for 48 hours. The weight loss of PI(11) was 8% and that of PI(12) was 22.5%. These losses compare with a 15% loss for PI(1) treated similarly: see Table 1, and Figure 3.

Included in Figure 1 is a TGA curve for a substance believed to be half-ester salt (S1) showing its conversion presumably to polyimide. The substance S1 was obtained by dissolving PMDA in methanol, followed by the addition of tetrafluoro-m-phenylene diamine, and evaporation to dryness. It would appear from Figure 1 that S1 gives rise to material of reasonably high thermo-oxidative stability. The substance S1 was heated to 400° at 6°/minute, to yield PI(13) which was kept at 400° for 24 hours. The result of this test is shown in Figure 3 and in Table 1: PI(13) suffered a weight loss of 25%. In case this result was due to the initial rate of heating being too high, a similar material PI(14) was made by heating S1 to 400° at 1°/minute, and PI(14) was maintained at 400°: the weight loss at 400° over 48 hours was 49%, Figure 4. The use of methanol is therefore deleterious to thermo-oxidative stability when preparing such fluorinated polyimides in the above manner.

Polyimide also appears to be obtained by heating C4 which was obtained by the evaporation of a solution of PMDA and m-F in NMP (N-methyl pyrrolidone), as shown by the shape of the TGA curve in Figure 1. When C4 was heated to 400° to form PI(15) and this was kept at 400° for 24 hours the weight loss was 19%: see Table 1 and Figures 1 and 3. This complex has no sharp melting point. It softens at 140°, partially melts at 150°, shows signs of gas evolution with resolidification at 170°, and is a dark brown solid at 200°, becoming black at 250°. However, C4 does not seem to be a complex in the sense of C1 as shown by the spectra (Nos.2137 and 2003) and C4 has similarities to the polyimide made by heating C1 to 300° (cf. spectra Nos. 2137 and 2004). The PMDA used in the formation of C4 was unpurified, ex Ruhroel Chemiewerk, Bottrop, West Germany, and the NMP was not anhydrous. In the other preparations of complexes etc., highly purified PMDA was employed. It is proposed to repeat the preparation of C4 using pure PMDA and pure NMP.

The dianhydride of difluoropyromellitic acid has hitherto not been available. In its absence the acid and the tetramethyl ester have been employed in the preparation of a salt, and complexes, with m-F. The salt S2 was obtained by evaporating an ethanolic solution of the acid and m-F, and this heated to 300° on the thermobalance gave material which had greatly reduced I.R. absorption due to carboxyl, and now had I.R. absorption attributed to an imide. When S2 was heated in vacuo in order to dry it more completely there was sublimation of m-F. The TGA curves for S2 before and after this extra drying are given in Figure 5. The thermo-oxidative stability is not as high as that of S1, the half ester salt obtained from PMDA and m-F in methanol. The salt S3, obtained by evaporation of a solution of difluoropyromellitic acid and m-F in NMP was similarly heated under programmed TGA at 1°/minute, and had similar thermo-oxidative stability to S2 (Figure 5). For comparison the TGA curve of difluoropyromellitic acid is given in Figure 5. Even the acid shows somewhat greater thermo-oxidative stability than does C5, obtained by the evaporation of a THF solution of m-F and the tetramethyl ester of difluoropyromellitic acid. Although designated C5 for convenience, it is doubtful if this material should be regarded as a complex, from the evidence of the TGA analysis.

(b) Polyimide Laminates from PMDA and tetrafluoro-m-phenylene diamine

It is possible that molecular weights of the above fluorinated polyimides may be sufficiently high for the preparation of laminates, even though the formation of films is impracticable.

As a combination of PMDA and tetrafluoro-m-phenylene diamine appears to yield the most thermo-oxidatively stable system, and as the diamine is readily available, this system was chosen for attempts to prepare laminates. The PMDA was that referred to above from Ruhroel Chemiewerk.

A methanolic solution of PMDA and m-F was not stable above ca. 20% concentration (% based on g. of solid to ml. methanol). Even at this concentration there was some deposition of solid on standing, and this solution had far too low a viscosity for application to glass cloth. The solution (at 17%) was, however, applied to an asbestos (chrysotile) felt, which was dried to yield a "prepreg." From this a six ply laminate (3" x 2") was obtained by curing at 315°/500 p.s.i. for 25 minutes. There was no flash, i.e. extrusion of resin from the edges of the laminate. When cut into strips (3" x ½") the flexural strength was found to be of the order of 3000 p.s.i.

A 20% (g per ml. solvent) solution of PMDA/m-F in a 1:1 mixture of methanol: NMP was not sufficiently viscous, but was applied by brushing to 181E glass cloth (A1100 finish) and the prepreg was dried in warm air. No lamination was achieved at 321°/500 p.s.i. for 30 minutes, and material which was extruded from the edges of the glass cloth was powdery. For the preparation of laminates from glass cloth it appeared to be necessary to use a more powerful solvent than methanol, in order to obtain a concentrated, viscous solution.

A 33% solution (% weight of solid per weight of solution) in NMP was applied by brushing to heat cleaned Marglass 116T glass cloth, to yield a prepreg containing approximately 50% resin (the resin here is defined as solids plus residual NMP). A twelve ply 2" x 2" laminate was obtained at 321°/500 p.s.i. over 30 minutes, which contained 13% of cured polymer, but which was easily delaminated by pulling apart with the fingers. Polymer which had been extruded from the prepreg in the hot press was partly fused.

The above results suggested that a partial curing prior to hot pressing would be desirable. Therefore prepreg (approx. 39% resin on Marglass 116T) prepared from a 34% w/w solution of PMDA/m-F in NMP, was treated under various conditions of temperature and pressure prior to final curing of 6 ply at 315°/250 p.s.i. for 30 minutes. In no case was a true laminate obtained. When there was some degree of adhesion of the layers of glass cloth they could be easily separated. Only in one case was there some degree of fusion of the polymer in the glass cloth, as shown by microscopic examination.

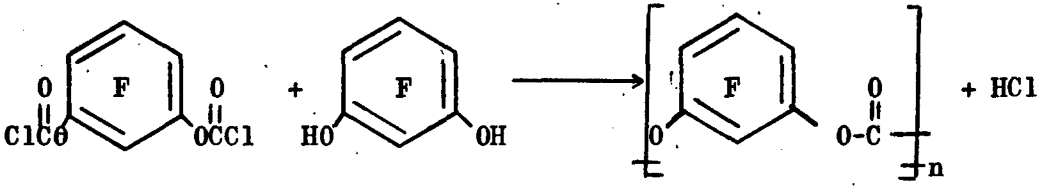
In further work a 51% w/w solution of PMDA/m-F in NMP yielded prepregs (50-52% resin on Marglass 116T) and these were "B-staged" at 120° for 30 minutes to yield prepregs containing 42-47% resin: see Table 2. Six ply laminates were obtained from each prepreg by heating in a press at 170°/10 p.s.i. for 2 minutes, followed by increase of pressure to 250 p.s.i. for 30 minutes and then an increase of temperature to 315° over 45 minutes. The laminates were allowed to cool in the press. There was a small degree of adhesion between the layers of glass cloth, but again the layers could be easily separated. Although there was no flash, there was fusion of the resin as shown by microscopic examination of the separated layers. When a laminate was similarly prepared, but without the above B-stage at 120°, there was no fusion but there was some flash.

2. Polycarbonates - Preparative Methods

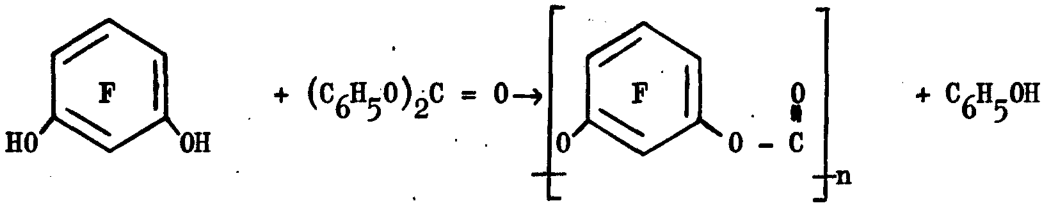
Earlier work (Ref. 4) showed that perfluoro-m-phenylene bis-carbonate had a higher T_D than its hydrogenic analogue. It was not possible to obtain other comparisons of the thermal stability of perfluoro and hydrogenic carbonate stuctures by means of model compounds, so that it was decided to obtain comparisons of thermo-oxidative stability from polycarbonates. This has now been done.

Polycarbonates have been prepared by four main methods :
(a) Bischloroformate Melt Polymerisation (a melt of bischloroformate and a dihydric phenol, e.g. Reaction vi); (b) Interfacial Polycondensation (a bischloroformate and a dihydric phenol in a solvent/aqueous alkali system);

(c) Transesterification (again a melt method employing phenyl carbonate and a dihydric phenol: Reaction vii); (d) Solution Polymerisation (a bischloroformate and a dihydric phenol). The results of (a), (b) and (c) are summarised in Tables 3, 4 and 5, where inherent viscosities were determined in dimethyl acetamide solution(0.5% at 30°). The elemental analyses were generally unsatisfactory.



...... Reaction (vi)



......Reaction (vii)

(a) In the chloroformate melt method preliminary results showed that a more thermo-oxidatively stable polycarbonate could be obtained by operating first at 200° and then at 300° rather than continuously at 200°, during the condensation of resorcinol with m-phenylene bischloroformate. It was also found that tetrafluororesorcinol and tetrafluoro-m-phenylene bis-chloroformate reacted more completely at 300° (after 6 hr. at 200° there was still bischloroformate present). A series of polycarbonates has therefore been prepared at 200°-300°. All of the polycarbonates obtained by the chloroformate melt method are given in Table 3. The inherent viscosities were obtained in dimethylacetamide solution. Where the polymers were soluble the inherent viscosities were low, particularly in the case of the perfluoro polycarbonates. In an attempt to increase the chain length of PC 5 by reaction with magnesium oxide, a fraction, PC 6 was obtained, of higher inherent viscosity (0.11 dl/g).

Nonafluorobiphenyl-4-chloroformate was required in order to determine its mode of decomposition at elevated temperature. This would throw light on the structure of polycarbonates made by melt condensation of a bischloroformate and a dihydric phenol. Phosgene and 4-hydroxynonafluorobiphenyl in ethereal $C_6H_5NEt_2$ yielded a material which was distilled to yield a solid, probably perfluoro di(biphenylyl) carbonate.

(b) In the interfacial polycondensation method a solution of the dihydroxy compound in a suspension of aqueous sodium bicarbonate was vigorously stirred with a solution of the bischloroformate in tetrachloroethane. The mixture was poured into acetone and the polymer collected by filtration. The polymers are listed in Table 4.

The inherent viscosities of the perfluoropolymers are lower than those of the hydrogenic polymers. PC 8 was obtained as a fraction from the reaction of PC 7 with magnesium oxide in an attempt to increase the molecular weight.

(c) The polycarbonates were prepared by transesterification with diphenyl carbonate at 300° as described in the literature (Ref. 2). By this method the end groups would be -OH or $-O-CO-OC_6H_5$. Elemental analyses for the perfluoro polycarbonates were not consistent with the required structures, perhaps because some charring may have occurred during the preparations. When some of the preparations were carried out at 250° lower polymers were obtained, for which elemental analyses are not available. The use of disodium tetrafluororesorcinate as catalyst (cf. Ref. 3) gave no solid product. The preparations are listed in Table 5. The inherent viscosities were measured in dimethyl acetamide solution.

(d) A single poly (tetrafluoro-m-phenylene carbonate) with an inherent viscosity 0.06 dl./g. has been prepared by treating the disodium salt of tetrafluororesorcinol with tetrafluorophenylene-1,3-bischloroformate in dimethylacetamide solution. This solvent was chosen because of the limited solubility of the disodium salt in other solvents. It was known from earlier work that the bischloroformate reacts with dimethylacetamide, but it was hoped that the primary reaction would be between the bischloroformate and the disodium salt.

An attempt to prepare poly(tetrafluoro-m-phenylene carbonate) from the perfluoro dihydric phenol and its bischloroformate in refluxing nitrobenzene gave only a trace of sticky black solid when the nitrobenzene was removed by steam distillation.

Polycarbonates - Thermo-oxidative Stability

The polycarbonates listed in Tables 3-5 have been examined by TGA in air on the Stanton HTD Thermobalance. The curve of the rate of heating is given in Appendix IIB Figure 14, and Figures 7-12 give the TGA curves for the polymers. It would seem that the method for the preparation of polycarbonates of the highest thermo-oxidative stability is the chloroformate melt method. This applies both to hydrogenic and perfluoro polycarbonates, with the exception of PC 12.

The polymers (200 mg.) were heated in a platinum crucible, in a furnace open to the air, at ca. 0.6°C min.^{-1} up to 190° and at 1°C min.^{-1} above 190°C.

(a) Chloroformate Melt Preparations

The polymers prepared by the chloroformate melt method are given in Figures 7 and 8. Poly (m-phenylene carbonate) had a lower thermo-oxidative stability when prepared at 200° (PC11) than when prepared at 200°, rising to 300° (PC10).

It has been found that perfluoro poly(m-phenylene carbonate) (PC5) has a higher thermo-oxidative stability than the hydrogenic analogue (PC11), even though the inherent viscosity of the perfluoro polymer was only 0.07 dl./g. It is probable that the molecular weight of PC11 is much higher than that of PC5. The treatment of PC5 with magnesium oxide in o-dichlorobenzene gave a polycarbonate (PC6) of higher inherent viscosity but which had lower thermo-oxidative stability. However, PC6 was contaminated with inorganics. The infra red spectrum of PC5 is given as No. 2317.

Perfluoro poly (p-phenylene carbonate) (PC14) did not have as high a thermo-oxidative stability as its hydrogenic analogue (PC17) or PC5. PC17 had the highest thermo-oxidative stability of any polycarbonate mentioned in this report, but it was not greatly above that of PC5.

(b) Interfacial Condensation Preparations

The polycarbonates prepared by the interfacial condensation of a bischloroformate with a dihydric phenol are generally not as thermo-oxidatively stable as the polycarbonates of similar structure prepared by the chloroformate melt method (a), the order of thermo-oxidative stability is different: see Figure 9 (PC11 and PC12 are exceptions to the general observation on relative thermo-oxidative stability when methods (a) and (b) are compared).

Figure 10 shows the TGA curves of polymers derived by the interfacial condensation of Bisphenol A with m-phenylene bischloroformate and tetrafluoro-m-phenylene bischloroformate. The co-polymer containing fluorine has the greater thermo-oxidative stability, but does not approach PC5 or PC17 in thermo-oxidative stability.

(c) Melt Transesterification Preparations

The TGA curves for the polycarbonates prepared by melt transesterification are shown in Figure 11. It will be seen that these polymers had a different order of thermo-oxidative stability from those as prepared under (a) and (b). The perfluorinated polycarbonates had relatively poor thermo-oxidative stability, less than the thermo-oxidative stability of their hydrogenic analogues.

3. Perfluoroarylenes

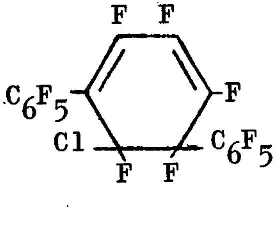
It has been reported (Ref. 5) that hexafluorobenzene is arylated by means of aroyl peroxides. The reaction leads to pentafluorobiphenyl derivatives: for example benzoyl peroxide and hexafluorobenzene yield 2,3,4,5,6-pentafluorobiphenyl. It is also known (Ref. 6) that biphenyl and other high boiling materials can be arylated by means of aryl sulphonyl chlorides, e.g. pentafluorobenzene sulphonyl chloride and 1,3,5-trichlorobenzene yield 2',4',6'-trichloro-2,3,4,5,6-pentafluorobiphenyl with the concomitant formation of sulphur dioxide and hydrogen chloride. All of these reactions are believed to be homolytic substitutions. In the case of the substitution of hexafluorobenzene by the phenyl radical, the fate of the displaced fluorine atom is unknown.

These reactions suggest that decafluorobiphenyl could be substituted by the pentafluorophenyl radical generated by the homolysis of pentafluorobenzene sulphonyl chloride. If successful, analogous reagents for the reaction will be investigated to produce perfluorinated materials suitable for the preparation of polymers and fluids.

In a typical experiment the acid chloride and a trace of cuprous chloride were refluxed with decafluorobiphenyl, this substrate being present in a ninefold exeess. Gases evolved were continuously swept by nitrogen into dilute aqueous sodium hydroxide. No fluoride was detected in such traps but chloride was usually detected but at lower than 10% of that theoretically possible. Sulphur dioxide was detected in much larger quantities, but the evolution of this gas proceeds at a reasonable rate only when there is cuprous chloride present, together with some unknown impurity in the original decafluorobiphenyl. When the excess of decafluorobiphenyl has been recovered it is not so reactive in a subsequent reaction even though cuprous chloride is added. See Table 6 for a summary of these reactions.

If decafluorobiphenyl is replaced by octafluoronaphthalene there is a similar reaction, but this has not been investigated in as much detail. However, gas chromatography in both cases indicates that higher molecular materials have been produced. In the case of octafluoronaphthalene there were two products of higher retention time, present in approximately a 3:1 ratio. There were three products in the case of decafluorobiphenyl, two of which appeared to be perfluoro m- and p-terphenyl, but the peaks were very broad compared with the peaks in an authentic mixture of the pure compounds (samples of these were provided by J. Thrower of the Royal Aircraft Establishment).

The excess of decafluorobiphenyl was distilled off to give a residue which was fractionally recrystallised to give a compound (XI) $C_{18}ClF_{15}$, m.p. 158-9°, one of several possible isomers, e.g. (XIa).



(XIa)

The infra-red spectrum of (XI) is not inconsistent with the structure (XIa), and the molecular weight of (XI) is correct for (XIa) as determined by mass spectrometry (by Dr. R.I. Reed of Glasgow University). Therefore substitution into the substrate does not seem to occur, and the main reaction may be formulated as in Reaction .... (viii)

$$C_6F_5SO_2Cl + C_{12}F_{10} \longrightarrow \underset{(XI)}{C_{18}ClF_{15}} + SO_2$$

..........Reaction (viii).

The indication of perfluoro-m and -p-terphenyl in the reaction mixture by gas chromatography could have been due to dehalogenation in the chromatography column, but we have no prof of this.

Attempts to dehalogenate a sample of (XI), m.p. ca. 154°, at 200° or 250° by means of a mixture of nickel and iron, failed. However, impure perfluoro-m-terphenyl was obtained when this sample was treated with zinc dust in refluxing ethanol. The m.p. 122-4° was low (lit. m.p. 125-6°), and the infra-red spectrum suggests that the product of dehalogenation is perfluoro-m-terphenyl containing about 15% of the p-isomer. Mass spectrometry confirms the molecular weight, but suggests that there is a small amount of hydrogenic impurity.

4. Polyoxadiazoles

As reported previously (Ref. 1), perfluoro polyoxadiazoles are not formed by heating perfluoropolyhydrazides at 256°. This is probably the highest temperature at which perfluoro polyhydrazides may be heated without an undue amount of decomposition.

Alternative approaches to the preparation of perfluoro polyoxadiazoles are (i) the condensation of hydrazine with dibasic acids in oleum, (ii) the cyclisation of polyhydrazides at relatively low temperatures by means of an acid anhydride or acid chloride, (iii) the condensation of a diacid chloride with a bistetrazole.

Method (i) has now been attempted. Whilst this method works satisfactorily for hydrogenic polyoxadiazoles (e.g., an inherent viscosity 0.7 dl/g. was obtained from terephthalic acid and hydrazine in 27% oleum), tetrafluoroterephthalic acid has yielded polymer of inherent viscosity 0.05 dl/g., in low yield, with low thermo-oxidative stability: See Figure 13.

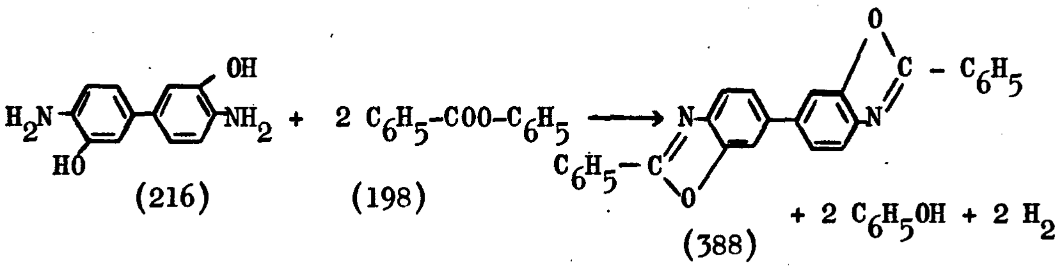
5. Polybenzoxazoles

A perfluoro polybenzoxazole could not be obtained using a method reported for the hydrogenic analogue (ref. 8) by condensing tetrafluoroisophthalyl chloride with 3,3'-dihydroxy-2,2',5,5',6,6'-hexafluorobenzidine in a mixture of dimethylacetamide, pyridine and cyclohexanone. There was obtained a polymer with inherent viscosity 0.04 dl/g. This should be a polyamide, or the isomeric polyester, but the elemental analysis did not indicate such a formulation. Heating this product at 300°/20 mm in an attempt to obtain the polybenzoxazole yielded a black powder which gave an elemental analysis inconsistent with any reasonable structure. This, heated on the thermobalance at 1°/minute and at 6°/minute showed rapid decomposition at ca. 300° and at ca. 350°, respectively: see Figure 6.

EXPERIMENTAL

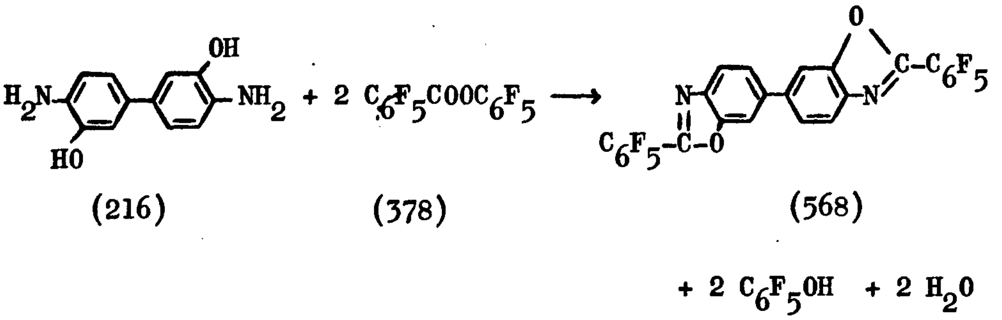
1. BENZOXAZOLES

2,2'-Diphenyl-6,6'-bibenzoxazole (cf. ref. 12)



3,3'-Dihydroxybenzidine (2.16 g. : 0.01 mole) and phenyl benzoate (4.5 g. : 0.0227 mole) were stirred together at 300° under nitrogen for 2 hours. The cold residue was ground up and washed with water and a little cold benzene to give a green powder (3.3g.), m.p. 258-310°. This was recrystallised from chlorobenzene, some insoluble material (0.9g.), m.p. 330°, being filtered off to give yellowish crystals of 2,2'-diphenyl-6,6'-bibenzoxazole (1.62g.) m.p. and mixed (ref.1) m.p. 255-257°. The benzene insoluble material appears to be a polybenzoyl derivative of dihydroxy benzidine and this was not isolated when the reaction was repeated at 350°. At the higher temperature, the 2,2'-diphenyl-6,6'-bibenzoxazole was obtained in higher yield (4.3g.), m.p. 255-257°.

2,2'-Di(pentafluorophenyl-6,6'-bibenzoxazole



Pentafluorobenzoyl chloride (3.1g : 0.0134 mole), pentafluorophenol (2.46 g.: 0.0134 mole) and N,N-diethylaniline (3.2 ml.) in dry benzene (20 ml.) were refluxed for 2 hours. Filtration and then distillation of the benzene from the filtrate, gave a white residue, m.p. 27-30°. Recrystallisation from petrol ether (b.p. 40-60°) gave perfluoro (phenyl benzoate) as white needles (2.9 g.), m.p. 36.5-37.5°.

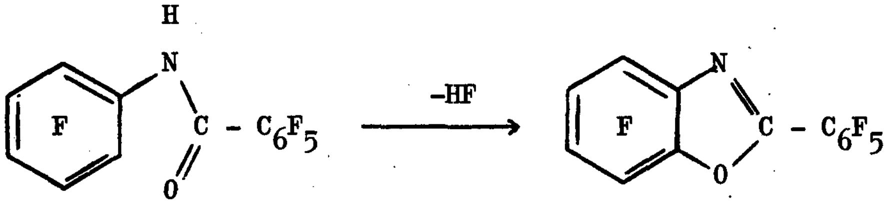
3,3'-Dihydroxy benzidine (0.54 g.: 0.025 mole) and perfluoro-(phenyl benzoate) (2.0 g.: 0.053 mole) were stirred together under nitrogen at 300° for 1 hour and then 350° for 1 hour. The residue was ground up and boiled with benzene (200 ml.), the insoluble material (1.5 g.), m.p. > 400°, being separated by filtration, and petrol ether (b.p. 60-80°) added to the filtrate. A small amount (0.02 g.) of crude 2,2'-di(pentafluorophenyl)- 6,6'-bibenzoxazole, m.p. 210-235°, was precipitated.

Precursors of 2,2'-di(pentafluorophenyl)-hexafluoro-6,6'-bibenzoxazole

Pentafluorobenzoyl chloride (3.25 g.: 0.014 mole) was added to a stirred solution of 3,3'-dihydroxyhexafluorobenzidine (2.26 g.: 0.007 mole) in 2N sodium hydroxide solution (25 ml.: 0.05 mole). After 1 hour, when the oily chloride had disappeared and a brown precipitate had formed, the mixture was just acidified with 2N HCl. A white solid (3.5 g.) m.p. ca. 267°, was collected by filtration and part of this was recrystallised three times from aqueous ethanol to give a poly (pentafluorobenzoyl) derivative of 3,3'-dihydroxyhexafluorobenzidine, m.p. 271-274° (mixed m.p. with compound V, Ref. 1, 272-275°).

The above reaction was repeated on a 5% scale and allowed to continue for 17 hours. A black solid (0.02 g.), m.p. 291-325°, was collected by filtration of the acidified reaction mixture. Recrystallisation from ethanol gave an off-white solid, mp. 320-325° (mixed m.p. with compound VII, Ref.1, 320-327°).

Attempted Cyclisation of Decafluorobenzanilide

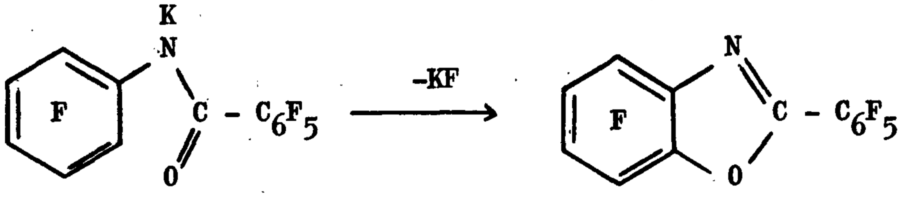


(377) (357)

(a) Decafluorobenzanilide (1 g.) in 2N sodium hydroxide (50 ml.) was heated on the steam bath for 65 hours. On cooling the dark red solution, an off-white precipitate (0.1 g.), m.p. > 400°, was formed and was collected by filtration. Acidification of the filtrate with dilute HCl gave another precipitate (1.3 g.), m.p. > 400°. Both solids were almost insoluble in water. Their infra-red spectra are similar but resemble those of inorganic compounds.

(b) Decafluorobenzanilide (0.5 g.) and sodium hydroxide (0.2 g.) were heated at 300° (bath) for 30 minutes and then at 350° for 1 hour. The excess of sodium hydroxide was removed by washing with water to leave a black solid, m.p. 400° (sinters 165°). The water wash gave a negative test for fluoride.

Attempted cyclisation of the potassium salt of Decafluorobenzanilide



(415) (357)

The potassium salt was prepared by distilling to dryness a solution of equimolecular quantities of decafluorobenzanilide and potassium hydroxide in ethanol.

(a) A solution of the potassium salt (0.5 g.) in redistilled nitrobenzene (10 ml.) was refluxed for 4 hours. An off-white solid (0.04 g.), m.p. $>$ 400°, soluble in warm dilute HCl, was collected by filtration of the cold reaction mixture. The nitrobenzene was steam distilled from the filtrate to leave a brown resinous material (0.3 g.) from which the water was decanted. Recrystallisation from benzene gave an off-white solid (0.04 g.), m.p. 270-280° (to a gel), which was insoluble in warm dilute HCl.

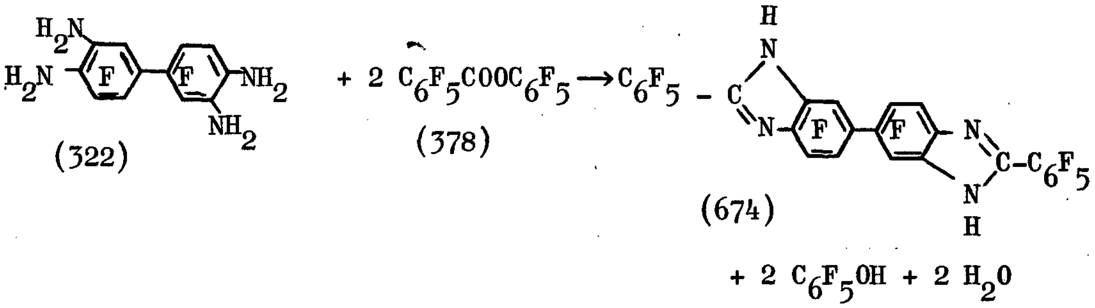
(b) A suspension of the potassium salt (0.5 g.) in dry toluene (25 ml.) was heated on the steam bath for 18 hours. A white solid (0.27 g.) m.p. $>$ 400°, was collected by filtration, and the filtrate was distilled to dryness. The residue consisted of white crystals (0.12 g.), m.p. 173-180° (mixed m.p. with decafluorobenzalilide 173-183°)

(c) The potassium salt (0.5 g.) was heated at 300° (bath) for one hour when it became a semi-solid. The temperature was raised to 350° for a further hour, and the solid product was cooled and washed with water. The water wash gave a negative test for fluoride. The residue was a black solid (0.4 g.), m.p. $>$ 400° (sinters 165°).

2. BENZIMIDAZOLES

2,2'-Di(pentafluorophenyl)hexafluoro-6,6'-bibenzimidazole - Attempted Preparations

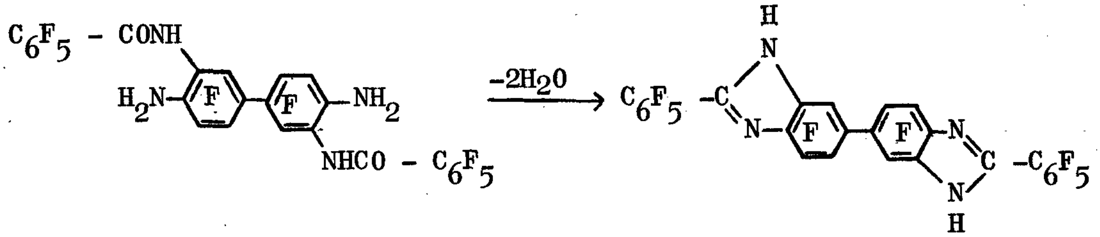
(a) from 3,3',4,4'-tetra-aminohexafluorobiphenyl



(322) (378) (674)

3,3',4,4'-Tetra-aminohexafluorobiphenyl (0.28 g. : 0.0087 mole) and perfluoro (phenyl benzoate) (0.8 g. : 0.025 mole) were stirred together at 300° (bath) for 1 hour and then at 340° for 1 hour. The cold residue was washed with benzene and then recrystallised from chlorobenzene to give a white powder (0.07 g.), m.p. 235-255°.

(b) from 3,3'-bis(pentafluorobenzamido)hexafluorobenzidine (ex I.S.C.)

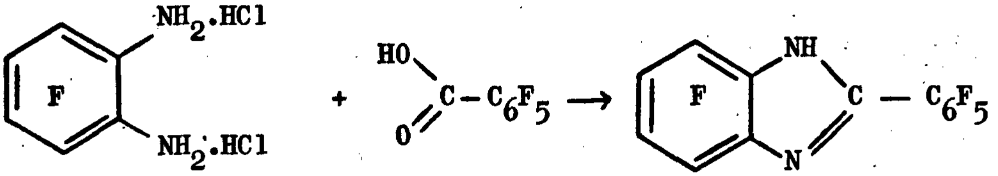


(638) (674)

3,3'-Bis(pentafluorobenzamido)hexafluorobenzidine (1 g.) was heated under nitrogen at 300° for 1 hour and then at 350° for 1 hour. The cold solid was washed with benzene and then recrystallised from chlorobenzene to give off-white crystals (0.4 g.), m.p. 225-245°. A second recrystallisation gave crystals, m.p. 225-235°.

2-(Pentafluorophenyl)-tetrafluorobenzimidazole - Attempted Preparations

(a) From tetrafluoro-o-phenylene diamine dihydrochloride and pentafluorobenzoic acid.



(253) (212) (235)

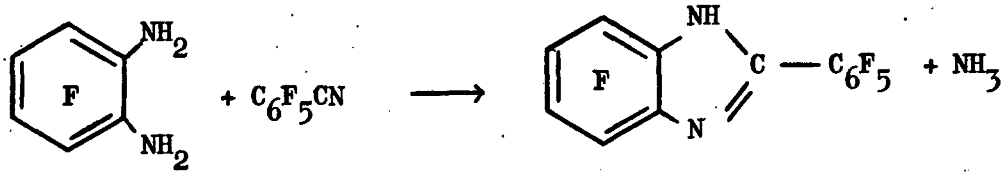
$+ 2H_2O + 2HCl$

Dry HCl gas was passed into a solution of tetrafluoro-o-phenylene diamine (5 g.) in ether (50 ml.) until precipitation was complete. The dihydrochloride (5.7 g.) was collected by filtration, washed with ether and dried.

The dihydrochloride (5.06 g.: 0.02 mole) was added to a solution of pentafluorobenzoic acid (6.4 g.: 0.03 mole) in toluene (50 ml.). The suspension was stirred and refluxed for 5 hours. Solution was then complete and a trace of water had collected in a Dean and Stark trap. The toluene was distilled off and the residue was recrystallised twice from water and then sublimed to give white needles (1.5 g.), 93.5-94°.

		C	H	F	N	M.W.
Calc. for $C_{13}HF_9N_2$		C, 43.8;	H, 0.3;	F, 48.0;	N, 7.9;	M.W., 356
Found	(1)	C, 39.4,	H, 1.7;		N, 8.8;	M.W., 198
	(2)	C, 40.1;	H, 1.7;	F, 40.3;	N, 9.8	

(b) From tetrafluoro-o-phenylene diamine and pentafluorobenzonitrile



(180) (193) (356)

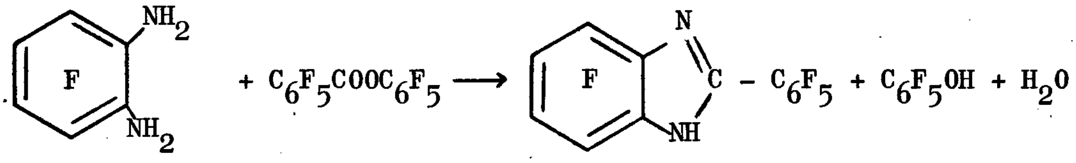
The temperature of a mixture of tetrafluoro-o-phenylene diamine (1.8 g.: 0.01 mole) and pentafluorobenzonitrile (1.93 g.: 0.01 mole) was raised slowly, testing for ammonia evolution. At 296°, no ammonia had been detected and the pressure was reduced to 0.4 mm. when a white sublimate collected in the condenser. The residue in the flask was a charred black solid insoluble in organic solvents.

The sublimate was recrystallised from aqueous ethanol to give a white solid (0.2 g.), m.p. 180-182°C. (Mixed m.p. with product of (c) was depressed).

Calc. for $C_{13}HF_9N_2$: C, 43.8; H, 0.3; F, 48.0; N, 7.9

Found (1) : C, 28.3; H, 2.0; F, 48.05; N,10.8

(c) From tetrafluoro-o-phenylene diamine and perfluoro (phenyl benzoate)



(180) (378) (356)

A solution of tetrafluoro-o-phenylene diamine (1.57 g. : 0.0087 mole) and perfluoro (phenyl benzoate) (3.5 g.: 0.0093 mole) in toluene (50 ml.) was refluxed with stirring for 6 hrs. A Dean and Stark trap was used but no water was collected. The toluene was distilled off and the residue was recrystallised from aqueous ethanol (twice) and then from benzene to give white needles (0.4 g.) m.p. 182-182.5°. (Mixed m.p. with product of (b) was depressed). Infra-red analysis suggests that this is the uncyclised amide X, not the benzimidazole.

Calc. for $C_{13}HF_9N_2$: C, 43.8; H, 0.3; F, 48.0; N, 7.9; M.W. 356

Calc. for $C_{13}H_3F_9N_2O$: C, 41.7; H, 0.8; F, 45.8; N, 7.5; M.W. 374

Found (1) : C, 41.3, H, 0.8; F, 44.2; N, 7.3; M.W. 353
(2) : C, 40.9; H, 1.0; N, 7.3;

3. IMIDES

The attempted preparation of 3,6-Difluoro-N,N'-di(pentafluorophenyl) pyromellitimide.

(a) Pentafluoroaniline (0.3 g.; 1.63 millimole) in ethanol (5 ml.) was added to a warm solution of tetramethyl difluoropyromellitate (0.25 g.; 0.72 millimole) in ethanol (5 ml.), and the mixture was refluxed for 7½ hr. The ester (0.21 g.), m.p. 121.5-122°, was recovered on cooling the solution.

(b) Tetramethyl difluoropyromellitate (0.5 g.; 1.44 millimole) was heated with pentafluoroaniline (3.0 g.; 16.3 millimole) at 160-165° (bath) for 16 hr. The reaction mixture yielded crystals of the ester (0.39 g.), m.p. 120-121°, from ethanol.

4. POLYIMIDES AND INTERMEDIATES

The preparation of Complexes between PMDA and Diamines

C1. PMDA/m-F

PMDA (1.09 g: 0.005 mole; pure, recryst. Ac_2O, and sublimed) was dissolved in warm THF (16 ml; ex B.D.H. not anhydrous, and containing 0.1% hydroquinone). A solution of m-F (0.9g: 0.005 mole; 99+ % pure ex I.S.C.) in THF (5 ml.) was added to the PMDA solution, a further quantity (4 ml) of THF being used to transfer the diamine solution. The colour of the PMDA solution was pale orange, which changed to intense ruby red during the mixing. This colour remained for several hours, but next day the colour of the solution was pale yellow.

The THF was removed by evaporation from a bath at 18°, at water pump pressure, to yield an orange solid (2.9 g). The above product (1g) was kept at 50-55°/0.1 mm. for 4 hrs. to remove residual THF. The I.R. spectrum of this complex C1 is given as No.2003, from which it appears to be mainly a mixture of pyromellitic acid and tetrafluoro-m-phenylene diamine.

The spectrum and TGA curve are very similar to those of a material obtained by removing residual THF at 0.1 mm. from a bath rising from 50° to 90° over 4 hours. Therefore, a moderately elevated temperature in drying the complex does not seem to affect the complex. The TGA curve of C1 is given in Figure 1.

C2. PMDA/p-F

This was prepared as for C1, but employing tetrafluoro-p-phenylene diamine in place of the m- isomer, and similar colour changes were observed.

The I.R. spectrum is No.2240 and the TGA curve is No.2 in Figure 2.

C3. PMDA/OFB

The preparation was carried out as for C1 but octafluorobenzidine (1.64g; 0.005 mol) was employed in place of tetrafluoro-m-phenylene diamine. There was no colour change on mixing the PMDA and diamine solutions. The I.R. spectrum of C3 is given as No.2241 and the TGA curve is No.3 in Figure 2. PI(16) obtained by heating C3 to 400°: Table 1 and TGA curve 6 of Fig. 3.

C4. PMDA/m-F

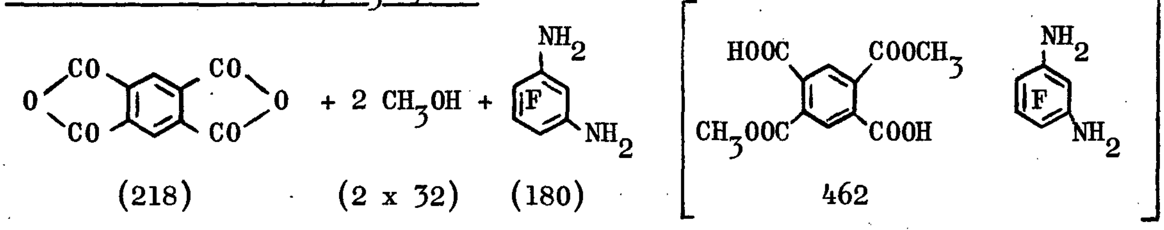
The PMDA was as received from Ruhroel Chemiewerk, Bottrop, West Germany. The diamine was as used for C1. The NMP was not anhydrous.

The PMDA (2.18g: 0.01 mol) was dissolved in warm NMP (42 ml), and to this deep red solution there was added the solid diamine (1.8g: 0.01 mol), with NMP (8 ml) employed to transfer the diamine. The deep red colour remained after the diamine had been added. After 1 hr. at room temperature the NMP was distilled off, first at 0.4 mm from a bath at 35-45° for 20 hrs. to yield a viscous brown oil, and then at 0.3 mm from a bath at 90° to yield a yellow solid (5.3 g.). This was finally dried at 100°/1 mm for 4 hrs. The product, C4, was soluble in NMP and in acetone. It had no definite m.p. (see Discussion). The I.R. spectrum is No.2137 and the TGA curve is No.5 of Figure 1.

C5. Tetramethyldifluoropyromellitate/tetrafluoro-m-phenylene diamine complex.

Solutions of tetramethyl difluoropyromellitate (1.153 g : 0.0033 mole) in tetrahydrofuran (20 ml) and tetrafluoro-m-phenylene diamine (twice sublimed, 0.6 g : 0.0033 mole) in tetrahydrofuran (20 ml) were mixed, and after standing for 30 mins., the solvent was distilled off at reduced pressure on the steam bath. The residual complex (1.56 g) was dried at 56°/15 mm. see TGA curve No.2 in Figure 5.

S1. Half-ester salt PMDA/CH_3OH/m-F



A solution of sublimed tetrafluoro-m-phenylenediamine (1.8 g : 0.01 mole) in dry methanol (10 ml) was added to a solution of pyromellitic dianhydride (2.18 g : 0.01 mole) in methanol (5 ml). The solution was distilled to dryness at reduced pressure on the steam bath. The residual brown solid was dried at 70°/24 mm. to give the complex (4.24 g).

The TGA curve is No.6 of Figure 1.

S2. A solution of tetrafluoro-m-phenylene diamine (1.80 g : 0.01 mole) in ethanol (25 ml) was added during 10 mins. to a solution of difluoropyromellitic acid (2.90 g : 0.01 mole) in ethanol (25 ml). The ethanol was then distilled off at reduced pressure to leave brown crystals (3.4 g), mp>300°.) After drying for 10 mins. at 100°/15 mm. a sample was removed for thermogravimetric analysis (Curve No.4 of Figure 5). The bulk of the product was heated at 100°/15 mm. for a further 3 hours, when tetrafluoro-m-phenylene diamine (0.5 g) m.p. and mixed m.p. 129-134°, sublimed in the cool part of the drier. Part of the residue after the longer drying time was heated to 300° on the Stanton Thermobalance and the infra-red spectrum of the materials before and after heating on the Thermobalance compared. In the heat-treated material, the absorption due to the carboxyl group was greatly reduced and absorption due to the imide group had appeared.

S3. This was carried out as in S2 but replacing ethanol with N-methylpyrrolidone. The last traces of solvent were removed at 90°/0.4 mm pressure during 2 days. The thermogravimetric analysis curve is No.3 in figure 5.

Poly (tetrafluoro-m-phenylene)pyromellitimide (Ref. 9)

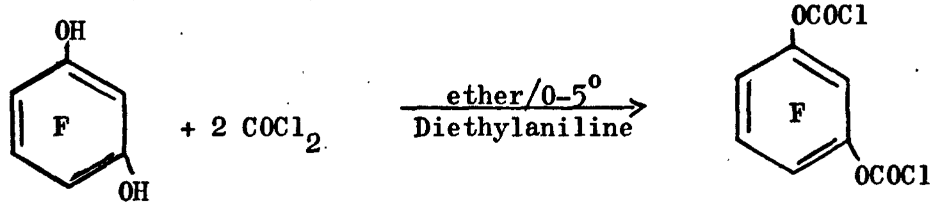
Pure pyromellitic dianhydride (2.180 g. : 0.01 mole) in dimethyl sulphoxide (25 ml.) was added quickly to tetrafluoro-m-phenylene diamine (1.8010 g. : 0.01 mole, sublimed 99.2% pure) in dimethyl sulphoxide (25 ml.). After 10 minutes stirring, the deep red colour of the solution had faded to pale yellow. At intervals, 1 ml. of the solution was removed, diluted to 10 ml. with dimethyl sulphoxide and the inherent viscosity measured at 30°. The maximum value of 0.055 dl/g. compared with 0.2 dl/g. for the same reaction in dimethyl acetamide.

Time (hours)	Inherent Viscosity
6	0.05
23	0.05
30	0.055
96	0.054

Because of the low inherent viscosity, no attempt was made to cyclise the polyamic acid to the polyimide.

5. POLYCARBONATES

Tetrafluorophenylene-1,3-bis chloroformate



(182) (2 x 99) (307)

Tetrafluororesorcinol, m.p. 96-98°, was azeotropically dried in benzene and then recrystallised from the cooled solution. Phosgene was passed into anhydrous ether (150 ml.) at 0-5° until 61 g. had been absorbed. The dry recrystallised tetrafluororesorcinol (33.6 g.) was added quickly, followed by addition over 30 minutes of N,N-diethylaniline (52.3 ml.) in anhydrous ether (120 ml.). After stirring for 3 hours and then standing for 18 hours, the diethylaniline hydrochloride was separated by filtration, and the ether was distilled from the filtrate. The residue gave tetrafluorophenylene-1,3-bis-chloroformate, b.p. 73-74°/3.5 mm. (cf. ref.1, P.74).

Calc. for $C_8F_4Cl_2O_4$: C,31.3 ; H,0.0 ; Cl, 23.1 ; F,24.8

Found : C,31.6 ; H,0.0 ; Cl, 22.5 ; F,25.2

Tetrafluorophenylene -1,4-bischloroformate

This was prepared as for the 1,3-bischloroformate but on half the scale. After distilling off the ether, the white residue was twice recrystallised from petrol (b.p. 40-60°), some insoluble being filtered off, to give white needles (9 g), m.p. 78.5 - 79°.

Calc. for $C_8F_4Cl_2O_4$: C, 31.3; H, 0.0; F, 24.8; Cl, 23.1
Found : C, 31.5; H, 0.2; F, 24.6; Cl, 23.0

Poly(tetrafluoro-m-phenylene carbonate)

PCl. From the disodium salt of tetrafluororesorcinol in DMAC.

Ethanolic sodium hydroxide (0.8 g NaOH in 30 ml ethanol) containing tetrafluororesorcinol (2.2 g) was refluxed for 1 hr. The ethanol was distilled off under nitrogen and the residue extracted with hot benzene to remove the excess tetrafluororesorcinol (0.14 g.). The disodium salt (2.67 g.; 98% yield) was dried in a vacuum desiccator. It was insoluble in most organic solvents with the exception of DMF and DMAC.

Calc. for $C_6F_4O_2Na_2$: C, 31.9; H, 0.0; F, 33.6

Found : C, 34.1; H, 1.6; F, 30.1

The disodium salt (1.63 g.; 0.005 mole) was added during 30 min. to a stirred solution of tetrafluorophenylene-1,3-bischloroformate (1.54 g.: 0.005 mole) in DMAC (50 ml.). After 16 hours the solution was poured into water and the brown precipitate collected by filtration, washed with water and dried. The inherent viscosity from a 0.5% solution in DMAC at 30° was 0.06 dl./g. and no softening point below 320°.

Calc. for $C_7F_4O_3$: C, 40.4; H, 0.0; F, 36.5

Found : C, 40.0; H, 0.6; F, 31.7

PC2. Transesterification at 250°

A mixture of diphenyl carbonate (3.96 g.) and tetrafluororesorcinol (3.37 g.) was heated at 250° first at atmospheric pressure for 3 hours and then at 20 mm. for 2 hours. A white sublimate of diphenyl carbonate and tetrafluororesorcinol collected in the receiver and condenser. The residue was extracted with 50% aqueous acetone and dried at 100°/0.4 mm., when it melted. The cold polymer was a dark solid (2 g.) with an inherent viscosity of 0.025 dl./g. from a

0.5% solution in DMAC at 30°, and a softening range of 58-75°.

PC3. Transesterification at 250° with sodium salt catalyst.

A mixture of diphenyl carbonate (4.28 g.), tetrafluororesorcinol (3.63 g.) and its disodium salt (0.01 g.) was heated at 250° at atmospheric pressure for 3 hours and then at 20 mm. pressure for two hours. The molten residue solidified on cooling but was completely soluble in 50% aqueous acetone. Addition of more water to the solution caused the separation of a small amount of oil.

PC4. Transesterification at 300°

A mixture of tetrafluororesorcinol (5.1 g.: 0.028 mole) and diphenyl carbonate (5.99 g.: 0.028 mole) was held at 300°/25 mm. pressure for 3 hours, some of the reactants distilling out. The residue was extracted with acetone and dried to give a black brittle solid (3.7 g.) insoluble in DMAC and concentrated sulphuric acid, with no softening point below 320°.

Calc. for $C_7F_4O_3$: C, 40.4; H, 0.0; Cl, 0.0; F, 36.5

Found : C, 55.4; H, 1.4; Cl, 0.03; F, 23.3

PC5 and PC6, Chloroformate melt polymerisation

Tetrafluororesorcinol (7.28 g. : 0.04 mole) and tetrafluorophenylene-1,3-bis chloroformate (12.3 g. : 0.04 mole) were heated together at 200° for 6 hours to give a semi-solid, smelling of chloroformate. This gave a dark brittle glass, after 15 minutes at 300°, which was ground and the volatiles removed at 100°/1 mm. to leave a light brown powder (9 g.). The inherent viscosity from a 0.5% solution in DMAC at 30° was 0.07 dl/g. and the softening point 127 - 133° (PC5).

Calc. for $C_7F_4O_3$: C, 40.4; F, 36.5; H, 0.0; Cl, 0.0

Found : C, 40.7; F, 32.3; H, 0.05; Cl, 0.5

An attempt was made to fractionate, by stirring the polycarbonate (3 g.) with methylene chloride (30 ml.) at 25° for 5 hours and then filtering the mixture. The filtrate was evaporated to leave a brown solid (0.03 g.). The methylene chloride-insoluble material was dried at 100°/0.4 mm. to yield the polycarbonate (2.7 g.). The inherent viscosity from a 0.5% solution in DMAC at 30° was 0.04 dl/g.

Calc. for $C_7F_4O_3$: C, 40.4; F, 36.5; H, 0.0; Cl, 0.0

Found : C, 40.4; F, 31.9; H, 0.1; Cl, 0.4

In a second attempt to fractionate, the polycarbonate (2.7 g.) was treated with magnesium oxide in o-dichlorobenzene at 190° as in (a) to give a methylene chloride-soluble brown gum (1.31 g.) and an insoluble fraction. The latter after freeing from magnesium oxide was a brown powder (0.79 g.) with an inherent viscosity from a 0.5% solution in DMAC at 30° of 0.11 dl /g, and with a partial softening point of 163 - 170° (PC 6).

Calc. for $C_7F_4O_3$: C, 40.4; F, 36.5; H, 0.0; Cl, 0.0

Found : C, 37.2; F, 31.9; H, 0.5; Cl, 0.0

0.291 mg. residue from combustion of 4.346 mg.

PC 7 and PC8 Interfacial polycondensation

This was prepared as PC2 but on four times the scale. The polycarbonate was obtained from the interfacial reaction as a light brown product (6.2 g.). The inherent viscosity from a 0.5% solution in DMAC at 30° was 0.04 dl/g, and the partial softening point 207 - 240° (PC7).

Calc. for $C_7F_4O_3$: C, 40.4; F, 36.5; H, 0.0; Cl, 0.0

Found : C, 39.1; F, 31.7; H, 0.4; Cl, 0.5

0.089 mg. residue from combustion of 4.208 mg.

In an attempted fractionation, the polycarbonate (3 g.) was stirred with methylene chloride (30 ml.) at 25° for 5 hours before filtering the mixture. The filtrate was distilled to dryness to leave a brown gum (0.26 g.). The methylene-chloride-insoluble material was dried at 100°/0.4 mm. to give the polycarbonate (2.43 g.) which had an inherent viscosity in a 0.5% solution in DMAC at 30° of 0.05 dl/g, and a partial softening point of 200-300°.

Calc. for $C_7F_4O_3$: C, 40.4; F, 36.5; H, 0.0; Cl, 0.0

Found : C, 39.1; F, 31.6; H, 0.3; Cl, 0.35

0.120 mg. residue from combustion of 4.218 mg.

Treatment of the polycarbonate (3 g.) with magnesium oxide and o-dichlorobenzene at 190° followed by methylene chloride at 25° gave a methylene chloride-soluble fraction (1.6 g.) and a methylene chloride-insoluble fraction (0.27 g.). The inherent viscosity of the latter from a 0.5% solution in DMAC at 30° was 0.165 dl/g. (PC 8).

Calc. for $C_7F_4O_3$: C, 40.4; F, 36.5; H, 0.0

Found : C, 42.3; F, 24.95; H, 1.7

0.105 mg residue from combustion of 4.169 mg.

Poly (m-phenylene carbonate)

PC 10 and PC 11 Chloroformate melt polymerisation.

Phenylene -1,3-bischloroformate (0.979 g.: 0.0042 mole) and resorcinol (0.379 g.: 0.0042 mole) were heated together at 200° for 6 hours and then at 300° for 15 minutes. The cold residue was ground up and volatiles removed at 100°/0.4 mm. The product, PC 10, (0.6 g.) was a brown powder insoluble in DMAC.

Calc. for $C_7H_4O_3$: C, 61.8; H, 2.9; 0, 35.3

Found : C, 64.4; H, 3.25; 0, 32.15

This is a repeat of a polymerisation at 200°, described in Ref.1 (page 75,a). That polycarbonate is now referred to as PC 11 and has inherent viscosity 0.18 dl/g., and a softening point of 190-220°.

PC 12 Interfacial Polymerisation

This is described in Ref. 1 p.76 (c). The softening point is 202-210°.

PC 13 Transesterification (Ref.2)

Resorcinol (5.5 g: 0.05 mole) and diphenyl carbonate (10.7 g.: 0.05 mole) were heated together at 300° for 1 hour. The pressure was reduced to 20 mm and phenol, unreacted resorcinol, and diphenyl carbonate were distilled off during 3 hours. The residue was extracted with boiling acetone to leave a brown powder (3.75 g.) which recrystallised from diethyl oxalate to give a white powder (3.24 g.), m.p. 212.5°. The inherent viscosity from a 0.5% solution in DMAC at 30° was 0.18 dl./g.

Calc. for $C_7H_4O_3$: C, 61.8; H, 2.9; 0, 35.3

Found : C, 63.0; H, 3.2; 0, 32.1

Poly (tetrafluoro-p-phenylene carbonate)

PC 14 Chloroformate melt polymerisation

A mixture of tetrafluorophenylene-1,4-bischloroformate (3.07 g.: 0.01 mole) and tetrafluorohydroquinone (1.82 g.: 0.01 mole) was heated at 200° for 6 hours and then at 300° for 15 min. The polymer was ground up and the volatiles removed at 100°/0.4 mm. to give a buff-coloured powder (2.79 g.) insoluble in organic solvents, and with a softening point above 320°.

Calc. for $C_7F_4O_3$: C, 40.4; H, 0.0; F, 36.5; Cl, 0.0

Found : C, 39.3; H, 0.0; F, 35.0; Cl, 0.1

PC 15 Interfacial polymerisation

A solution of tetrafluorophenylene-1,4-bischloroformate (3.07 g.: 0.01 mole) in sym-tetrachloroethane (60 ml.) was added to a solution of tetrafluorohydroquinone (1.82 g.: 0.01 mole) in water (60 ml.) containing sodium hydrogen carbonate (10 g.). After stirring for 6 hours and standing overnight, the suspension was poured into acetone (300 ml.). There was no precipitate even on dilution with water. The solution was distilled to dryness and the residue partly dissolved in ether. The insoluble sodium hydrogen carbonate was dissolved in dilute hydrochloric acid, and the ether solution washed with water and then dried before distilling off the ether. The dark brown residue (2.79 g.) was dried at 100°/0.3 mm. The inherent viscosity of this low molecular weight polymer in DMAC at 30° was 0.03 dl./g, and the softening point 132 - 136°.

Calc. for $C_7F_4O_3$: C, 40.4; H, 0.0; F, 36.5

Found : C, 44.6; H, 1.3

PC 16 Transesterification at 300°

Tetrafluorohydroquinone (2.8 g.: 0.0154 mole) and diphenyl carbonate (3.2 g.: 0.015 mole) were heated together at 200° for ½ hour. The temperature was then raised to 300° and the pressure reduced to 30 mm. During 2½ hours an orange liquid distilled. The residue was extracted with boiling aqueous acetone, and then dried at 100°/0.4 mm. The polymer (0.5 g.) was a black brittle solid insoluble in DMAC and concentrated sulphuric acid and with no softening point below 320°.

Calc. for $C_7F_4O_3$: C, 40.4; H, 0.0; F, 36.5

Found : C, 50.4; H, 1.1; F, 39.8

Poly (p-phenylene carbonate)

PC 17 Chloroformate melt polymerisation

Hydroquinone (1.1 g.: 0.01 mole) and phenylene-1,4-bischloroformate (2.35 g.: 0.01 mole) were heated together at 200° for 6 hours and then at 200° for 15 mins. The cold residue was ground up and heated at 100°/0.4 mm. to remove volatiles. The polymer was a white powder (2.33 g.) insoluble in DMAC, not softening below 320°.

Calc. for $C_7H_4O_3$: C, 61.8; H, 2.9; O, 35.3

Found : C, 60.8; H, 3.1; O, 31.5

PC 18 Interfacial polymerisation

The preparation of this polymer is described in Ref. 1, P.77. A softening point was not observed up to 320°.

PC 19 Transesterification

This preparation was as for PC 13 with hydroquinone in place of resorcinol. The product was a brown powder (5.74 g.), m.p.> 400°, insoluble in diethyl oxalate, DMAC and concentrated sulphuric acid.

Calc. for $C_7H_4O_3$: C, 61.8; H, 2.9; 0, 35.3

Found : C, 63.0; H, 3.2; 0, 32.1

Poly (octafluoro-4,4'-biphenylylene carbonate)

PC 20 Transesterification

A mixture of 4,4'-dihydroxyoctafluorobiphenyl (4.95 g.: 0.015 mole) and diphenyl carbonate (3.2 g.: 0.015 mole) was heated at 200° at atmospheric pressure for ½ hour, and then at 300°/20 mm. when all of the mixture distilled at a vapour temperature of 198°. The experiment was repeated, but the mixture was kept at 300° for 6 hours before applying vacuum. Part distilled at 208°/30 mm. during 2 hours. The cold residue was extracted with hot 50% aqueous acetone and dried at 100°/0.4 mm. The polycarbonate (0.6 g.) had an inherent viscosity in DMAC at 30° of 0.04 dl./g. and softened at 75-82°.

Calc. for $C_{13}F_8O_3$: C, 47.0; H, 0.0; F, 38.5

Found : C, 53.7; H, 1.7; F, 29.0

Poly (4.4'-biphenylylene carbonate)

PC 21 Transesterification

A mixture of diphenyl carbonate (3.2 g.: 0.015 mole) and 4,4'-dihydroxybiphenyl (2.79 g.: 0.015 mole) was heated at 300° for 5 hours. Reduction of pressure to 20 mm. for 2 hours gave a small amount of distillate. The residue was extracted with hot 50% aqueous acetone and dried at 100°/0.4 mm. to give a pale brown powder (2.9 g.) insoluble in DMAC and concentrated sulphuric acid, not softening below 320°.

Calc. for $C_{13}H_8O_3$: C, 73.6; H, 3.8

Found : C, 74.3; H, 4.2

(Tetrafluoro-m/p-phenylene carbonate) copolymer

PC 22 Chloroformate melt polymerisation

A mixture of tetrafluorohydroquinone (1.82 g.: 0.01 mole) and tetrafluorophenylene-1,3-bischloroformate (3.07 g.: 0.01 mole) was heated at 200° for 5 hours and then at 300° for 15 minutes. The residue was ground up, and heated at 100°/0.3 mm. for 2 hours to give a brown powder (2.57 g.). The inherent viscosity from a 0.5% solution in DMAC at 30° was 0.04 dl./g, and the softening point 200-240°.

Calc. for $C_7F_4O_3$: C, 40.4; H, 0.0; F, 36.5; Cl, 0.0

Found : C, 39.0; H, 0.0; F, 34.0; Cl, 1.5

(Octafluoro-4,4'-biphenylylene/tetrafluoro-m-phenylene carbonate) copolymer

PC 23 Chloroformate melt polymerisation

This was prepared by melt polymerisation of a mixture of 4,4'-dihydroxyoctafluorobiphenyl (3.3 g.: 0.01 mole) and tetrafluorophenylene-1,3-bischloroformate (3.07 g.: 0.01 mole) for 5 hours at 200° and then 15 minutes at 300°. The polycarbonate (4.37 g.) had an inherent viscosity from a 0.5% solution in DMAC at 30° of 0.05 dl./g. and a softening point of 136 - 144°.

Calc. for $C_{20}F_{12}O_6$: C, 42.7; H, 0.0; Cl, 0.0; F, 40.4

Found (1) : C, 42.0; H, 0.4; Cl, 0.4; F, 39.7

Copolymer from Bisphenol A/tetrafluorophenylene-1,3-bischloroformate

PC 24 and PC 25 Interfacial polymerisation

A solution of tetrafluorphenylene-1,3-bischloroformate (6.14 g.; 0.02 mole) in tetracloroethane (40 ml.) was added to a mixture of Bisphenol A (4.56 g.: 0.02 mole), sodium hydrogen carbonate (5 g.) and water (40 ml.). After stirring for 6 hours and then standing for 3 days, the mixture was poured into acetone (350 ml.) and filtered.

The acetone insoluble fraction was washed with dilute HCl, water, petrol (b.p. 40-60°), and dried at 100°/0.3 mm.

The polymer, PC 24 (1.46 g), softening range 165-185°, had inherent viscosity 0.046 dl/g in DMAC (0.5% at 30°). The solvent was distilled from the filtrate and the residue was reprecipitated from ethereal solution by the addition of petrol, to yield PC 25 as brown powder (0.6 g), inherent viscosity 0.1 dl/g, softening range 149-169°.

Calc. for $C_{23}H_{14}F_{4}O_{6}$: C, 59.7; H, 3.1; F, 16.5

Found (PC24): C, 54.2; H, 3.5; F, 18.6
Found (PC25): C, 62.1; H, 3.8

Copolymer from Bisphenol A/phenylene-1,3-bischloroformate

PC 26 Interfacial polycondensation

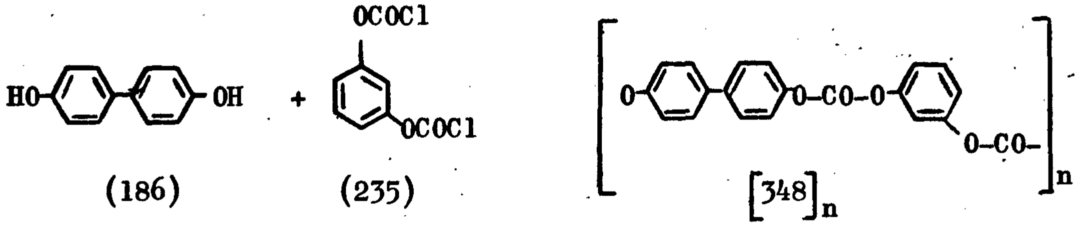
A solution of phenylene-1,3-bischloroformate (8 g.: 0.035 mole) in tetrachloroethane (70 ml.) was added to a stirred mixture of Bisphenol A (6.84 g.: 0.03 mole) sodium hydrogen carbonate (10 g.) and water (70 ml.). After stirring for 6 hours and standing overnight, the suspension was poured into acetone (700 ml.). Only sodium hydrogen carbonate remained insoluble. The acetone solution was distilled to dryness and the residue washed with dilute HCl, water and petrol, and then dried at reduced pressure. The polymer (7.18 g.) melted below 50°.

The inherent viscosity from a 0.5% solution in DMAC at 30° was 0.06 dl./g.

Calc. for $C_{23}H_{19}O_{6}$: C, 70.7; H, 4.65; O, 24.6

Found : C, 68.3; H, 5.4; O, 21.2

PC 27 4,4'-Biphenylylene/m-phenylene carbonate copolymer



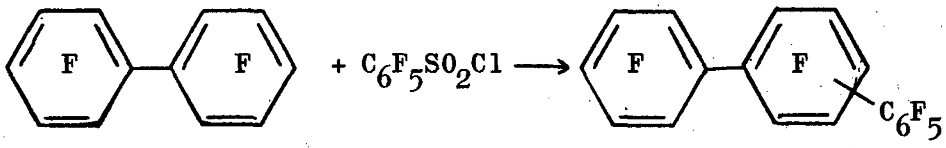
4,4'-Dihydroxybiphenyl (2.79 g : 0.015 mole) and phenylene - 1,3-bis chloroformate (3.525 g : 0.015 mole) were heated together at 200° for 5 hours and then at 300° for 15 mins. The polymer was cooled, ground and the volatiles removed at 100°/0.4 mm. to give a pale brown powder (4.14 g). The inherent viscosity from a 0.5% solution in N,N-dimethylacetamide at 30° was 0.155 dl/g and the softening temperature 224-230°.

Calc. for $C_{20}H_{12}O_{6}$: C, 68.9 ; H, 3.5 : Cl, 0.0

Found : C, 67.5 ; H, 3.5 : Cl, 1.4

6. POLYARYLENES

(a) Reaction of $C_6F_5SO_2Cl$ with decafluorobiphenyl



(via XI)

The following is a typical experiment. See Table 6 (Appendix IIA) for other experiments.

A mixture of decafluorobiphenyl (ex I.S.C., 200 g : 0.6 mole), pentafluorobenzene sulphonyl chloride (16 g : 0.06 mole) and cuprous chloride (0.16 g) was refluxed under nitrogen, off gases being passed through a trap containing 2N sodium hydroxide solution. At intervals the trap solution was changed and analysed for SO_2 and chloride. After 5 hours, 99.7% of the theoretical SO_2 and 6% of the theoretical chloride had been measured.

Decafluorobiphenyl (177.5 g) was distilled off at 100°/25 mm and the residue was dissolved in ether (500 ml). The ether solution was boiled with charcoal and the charcoal and cuprous chloride removed by filtration. The filtrate was washed twice with 2N sodium hydroxide, four times with water, and dried. The ether was distilled off to leave a reddish solid, which recrystallised from petrol (b.p. 60-80°) to give white needles, m.p. 151-153°.

The experimental details of this and other preparations are summarised in Table 6, Appendix, IIA, where substrates of various purities were used with and without cuprous chloride catalyst. In one preparation (3) which was identical with the one described above, but using a different sample of decafluorobiphenyl from I.S.C., the rates of SO_2 and chloride evolution were not quite so fast, and the product was further purified by sublimation to give white needles, m.p. 158-159°. The I.R. spectrum of this compound is No.1974 (Appendix IIC).

Calc. for $C_{18}F_{14}$:	C, 44.8 ;	H, 0.0 ;	F, 55.2 ;	Cl, 0.0;	M.W.482
Calc. for $C_{18}F_{15}Cl$:	C, 40.3 ;	H, 0.0 ;	F, 53.1 ;	Cl, 6.6;	M.W.536.5
Found :	C, 40.0 ;	H, 1.0 ;	F, 52.9 ;	Cl, 6.3;	M.W. 511 and 540

The total yields of products were not determined. Table 6 gives the m.p. of the product obtained by fractionation of the reaction mixture. The results of gas chromatography are referred to in the Discussion. Mass spectrometry (Dr. R.I. Reed) showed that the the product had a molecular weight in agreement with $C_{18}F_{15}Cl$ (found 536 and 538)

Attempted dehalogenations of $C_{14}F_{15}Cl$ (Compound XI)

For these experiments the purest sample of (XI), as prepared under 3 Table 6 was not used.

With nickel and iron at 250°

Part of the product of (6) (0.5 g), m.p. 153-154°, nickel powder (0.1 g) and iron powder (0.1 g) were heated together at 250° for 30 min. No halogen was detected in a water trap through which the off-gases were passed. White crystals (0.38 g), m.p. 149 - 153° sublimed out.

With nickel and iron at 200°

The sublimate (0.38 g) from the previous experiment was made up to 0.5 g with more of the starting material, m.p. 153-154°, and heated with nickel (0.1 g) and iron powder (0.1 g) at 200° for 7 hours. White crystals sublimed out but were remelted and allowed to run back into the flask. The contents of the flask were boiled with petrol and the metals were removed by filtration. The filtrate was cooled and white crystals (0.2 g) of the starting material, m.p. 155-156° were precipitated.

With zinc and ethanol (cf. Ref. 6)

A suspension of part of the product of (7) (0.5 g, m.p. 147-151°) in ethanol (10 ml) was added during 1 hour to a refluxing suspension of zinc powder (0.234 g) in ethanol (10 ml). After refluxing for 24 hours, dilute HCl was added and the suspension filtered hot. The filtrate, on cooling, deposited white crystals (0.3 g), m.p. 122-124°, completely soluble in ether. Evaporation of the mother liquor gave only an oil (0.2 g).

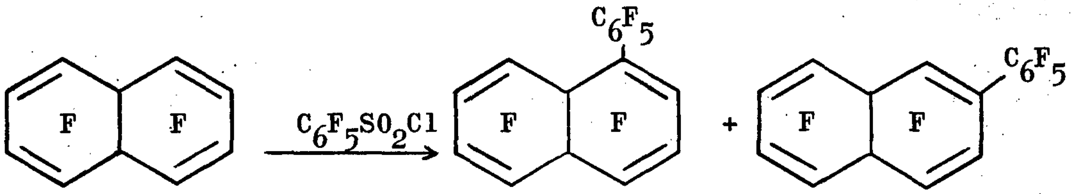
Calc. for $C_{18}F_{15}Cl$: C, 40.3 ; F, 53.1 ; Cl, 6.6 ; H, 0.0

Calc. for $C_{18}F_{14}$: C, 44.8 ; F, 55.2 ; Cl, 0.0 ; H, 0.0

Found : C, 44.6 ; F, 52.3 ; Cl, 0.0 ; H, 1.8

The infra-red spectrum of this material was not inconsistent with it being perfluoro- m-terphenyl containing about 15% of the p-isomer. There was no alkyl absorbtion as might have been expected from the H content. It is therefore likely that the latter was an artefact of the procedure used for analysis. The dehalogenation of a pure sample of (XI) will be carried out in order to obtain a more conclusive result. (Note added in proof: Mass spectrometry confirms the product as perfluoro terphenyl by determination of the M.W. as 482. There is evidence for hydrogenic impurity, but not more than 1%).

(b) Perfluoro (phenyl naphthalenes) - Attempted Preparation



(272) (266.5)

(1) Octafluoronaphthalene (ex I.S.C. : 81.6 g : 0.3 mole) pentafluorobenzene sulphonyl chloride (8 g : 0.03 mole) and cuprous chloride (0.08 g.) were refluxed together (210°), with a nitrogen stream to carry off-gases through a small trap in a solid CO_2/acetone bath and then through a trap containing 10 ml of 2N NaOH. At intervals the latter was changed and the caustic solution analysed for SO_2, Cl^- and F^-. No fluoride ion was detected, but after 131 hours, 64% of the theoretical SO_2 and 7% of the theoretical chloride had been evolved.

Octafluoronaphthalene (67.8 g) was distilled off at 97-102°/17 mm, and the residue (15.1 g) was dissolved in ether. The ethereal solution was boiled with charcoal, the charcoal and cuprous chloride were filtered off, and the filtrate was washed with sodium hydroxide solution and with water, and dried. The semi-solid (13.1 g), obtained by distilling off the ether, was fractionally distilled at reduced pressure. The first fraction (7.2 g), boiling range 95 - 122°/18 mm was mainly octafluoronaphthalene. The second fraction (5.3 g), boiling range 155-162°/18 mm was a yellow liquid. This was shown by vapour phase chromatography to contain a small amount of octafluoronaphthalene but to consist mainly of a 3/1 ratio of low and higher retention time components. Attempts to separate these two components by distillation and chromatography have so far failed.

(2) A repeat experiment was carried out using octafluoronaphthalene (44 g : 0.162 mole) recovered from (1), pentafluorobenzene sulphonyl chloride (4.31 g : 0.0162 mole) and cuprous chloride (0.04 g). After 101 hours at reflux, 75% of the theoretical SO_2 and 18% of the theoretical chloride had been evolved. The excess octafluoronaphthalene was distilled off at 120°/68 mm and the residue was dissolved in ether. The ethereal solution was washed with dilute sodium hydroxide solution, water, and dried. The orange solid obtained by distilling off the ether was distilled at reduced pressure. The fore fraction (6.9 g) boiling at 94-130°/17 mm consisted mainly of octafluoronaphthalene. The second fraction (1.5 g), boiling at 146-160°/17 mm was a mixture of liquid and solid.

The products of experiments (b), (1) and (2) are probably analogues of compound (XI)

7. POLYOXADIAZOLES (Ref. 7)

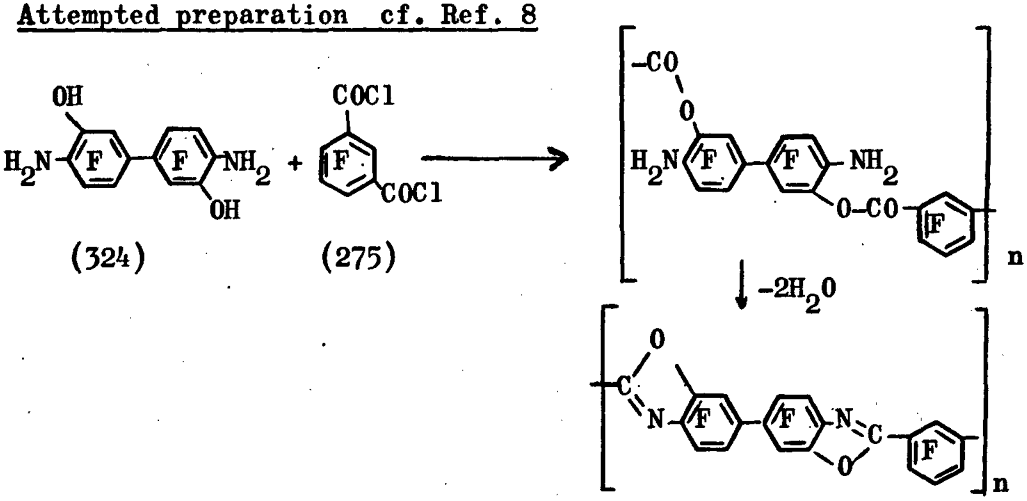
Terephthalic acid and hydrazine sulphate in equivalent proportions in 27% oleum yielded a poly (1,3,4-oxadiazole) having an inherent viscosity 0.7 dl/g. in 0.5% solution in 98% sulphuric acid at 30°. Possibly some degradation of the polymer occurred, when the mixture of polymer and sulphuric acid was warmed during the preparation of the polymer solution for viscosity determination.

An analogous preparation but using tetrafluoroterephthalic acid yielded perfluoro polymer of inherent viscosity 0.05 dl/g. determined at 0.25% concentration in 98% sulphuric acid. See Fig.13 for TGA.

8. POLYBENZOXAZOLES

Poly 2,2'-di(tetrafluoro-m-phenylene)-hexafluoro-6,6'-bibenzoxazole

Attempted preparation cf. Ref. 8



(324) (275)

A solution of 3,3'-dihydroxyhexafluorobenzidine (3.24 g : 0.01 mole) in DMAC (20 ml) and pyridine (3 ml) was cooled to 0° and a solution of tetrafluoro-isophthaloyl chloride (2.75 g : 0.01 mole) in redistilled cyclohexanone (12 ml) was added during 25 mins. The deep red solution was stirred at 0° for 3 hours and then allowed to warm to room temperature overnight. The suspension was poured into water (500 ml) and the water was decanted to leave a reddish gum. After 3 hours at 60-70°/15 mm, the gum gave a brittle solid which was ground up. This polyester (or polyamide) had an inherent viscosity of 0.04 dl/g measured from a 0.5% solution in DMAC at 30°

Calc. for $C_{20}H_4F_{10}N_2O_4$: C, 45.6 ; H, 0.8 ; F, 36.1 ; N, 5.3

Found : C, 52.7 ; H, 3.5 ; F, 21.4 ; N, 5.6

This intermediate was heated on an aluminium tray at 300°/20 mm for 36 hr. to give a dark brown powder, which did not give an analysis corresponding to the required polybenzoxazole.

Calc. for $C_{20}F_{10}N_2O_2$: C, 49.0 ; H, 0.0 ; Cl, 0.0 ; F, 38.75 ; N, 5.7

Found : C, 57.7 ; H, 1.8 ; Cl, 0.0 ; F, 21.5 : N, 6.8

9. THE PREPARATION OF POLYIMIDE LAMINATES

1. Resin

In a typical procedure the m-F (35·63 g) in NMP (80 ml) was added to a solution of PMDA (43.1 g) in NMP (300 ml). The excess of NMP was distilled off at 50°/0.25 mm over two days (two eight hour periods) to give a viscous solution of 42% concentration. This solution is referred to as "resin" for the purpose of impregnating glass cloth.

2. Prepreg

The glass cloth employed was Marglass 116T, a closely woven cloth of weight 0.187 g per square inch, heat cleaned by the manufacturers. A known weight of resin was brushed onto a known weight of glass cloth and this prepreg was allowed to dry in air over three to four days at room temperature. Further treatment, "B-Staging", is exemplified in Table 2.

3. Lamination

This was carried out in a hydraulic press with electrically heated plattens. The greatest degree of fusion of the resin was obtained when the conditions of temperature and pressure were as described in Table 2, for 3 inch by 4 inch, 6 ply laminates. Even with these conditions the layers could be readily separated. Variations in the pressing conditions will be necessary to determine the optimum degree of lamination.

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PART III FLUIDS

Section 1

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INTRODUCTION

Fully fluorinated aromatic structures containing one or more perfluoroalkyl substituents of suitable chain length may possess good high temperature stability and may therefore be suitable for use as fluids operating over a wide temperature range. Similar properties may be expected of perfluoro-α,ω-bis(phenyl)alkanes and in similar structures incorporating sulphide linkages.

PART III SECTION 1

SUMMARY

Treatment of perfluoro-1,4-dibenzoylbutane and perfluoro-3,3'-di(n-butyryl)biphenyl with an excess of sulphur tetrafluoride under vigorous conditions has given perfluoro-1,6-diphenylhexane and perfluoro-3,3'-di(n-butyl)biphenyl, respectively.

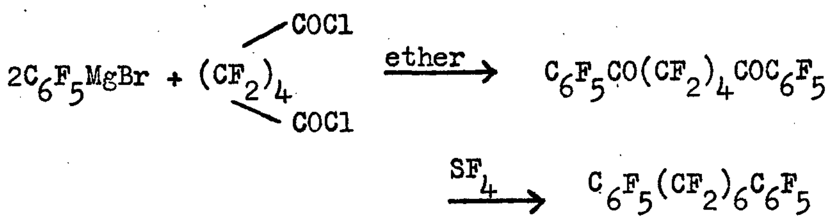
In order to prepare less symmetrical structures the intermediates 3-hydro-3'-(1-hydroxyhexafluoroisopropyl)octafluorobiphenyl and 3,4'-dihydro-octafluorodiphenyl sulphide were prepared.

2,3,4,5,6-Pentafluorobenzal fluoride was prepared by the reaction of pentafluorobenzaldehyde with sulphur tetrafluoride. Preliminary attempts to halogenate the hydrogen atom in this compound are reported.

DISCUSSION

1. PERFLUORO-1,6-DIPHENYLHEXANE (I)

One type of compound required for evaluation as a stable fluid is a perfluoro-α,ω-diphenylalkane. Compound I was selected for synthesis because the intermediates required are readily accessible. The reaction sequence used is:-



$$2C_6F_5MgBr + (CF_2)_4\begin{smallmatrix}\nearrow COCl\\ \searrow COCl\end{smallmatrix} \xrightarrow{ether} C_6F_5CO(CF_2)_4COC_6F_5$$

$$\xrightarrow{SF_4} C_6F_5(CF_2)_6C_6F_5$$

The reaction of pentafluorophenylmagnesium bromide with octafluoroadipoyl chloride gave variable results. The first reaction gave perfluoro-1,4-dibenzoylbutane in 70% yield (ref. 1) but a larger scale preparation gave only a 46% yield of the dibenzoylbutane and a higher-boiling product, believed to be mainly perfluoro-1,1',6,6'-tetraphenylhexan-1,6-diol, in 21% yield. Attempts to improve the yield of perfluoro-1,4-dibenzoylbutane by adding the Grignard reagent to the acid chloride were not successful; in several experiments the yield was 40-50%. In one of these reactions two acidic products were isolated in small yield. The higher melting one proved to be octafluoroadipic acid. The second compound, m.p. 40-44°, was a deliquescent solid which gave an anilinium salt, m.p. 207-210°. The identity of this compound was not established.

When perfluoro-1,4-dibenzoylbutane was heated with a large excess of sulphur tetrafluoride in the presence of anhydrous aluminium fluoride at 175° for 70 hours, white crystalline perfluoro-1,6-diphenylhexane, m.p. 59-60°, b.p. 284-286°/755 mm., was obtained in 49% yield. The identity of this material was confirmed by elemental analysis, infrared and N.M.R. spectroscopy. A sample was sent to Monsanto Chemicals Ltd. for measurement of its thermal decomposition temperature. In a second reaction, using larger quantities of reactants, it was found necessary to heat the reaction mixture for a much longer period to effect full fluorination. The product was dispatched to Dr. C. Tamborski, Wright-Patterson Air Force Base, for oxidative stability measurements, but it appears to be too low boiling for test by the procedure in use.

Because of the low boiling point of the compound, the thermal decomposition temperature could not be determined. At the maximum temperature (343°C) at which pressure readings were taken there was only a small amount of decomposition (ref. 2).

2. PERFLUORO-5-BENZOYLPENTANOIC ACID (II)

This acid may be the unidentified product isolated from the reaction of C_6F_5MgBr with octafluoroadipoyl chloride (see above). It could be a useful intermediate for the synthesis of candidate fluids. For example, it could be converted, by means of the Hunsdiecker reaction, to $C_6F_5CO(CF_2)_4I$ and this iodide could be used to prepare perfluoro-1-iodo-5-phenylpentane, a useful intermediate for telomerisation with tetrafluoroethylene, and perfluoro-1,10-diphenyldecane. The reactions leading to these compounds are illustrated below

$$\begin{tikzcd}
 & C_6F_5CO(CF_2)_8COC_6F_5 \arrow[r, "SF_4"] & C_6F_5(CF_2)_{10}C_6F_5 \\
C_6F_5CO(CF_2)_4CO_2Ag \arrow[r, "I_2"] & C_6F_5CO(CF_2)_4I \arrow[u, "Cu"'] \arrow[r, "SF_4"] & C_6F_5(CF_2)_5I
\end{tikzcd}$$

Therefore the preparation of compound II by the reaction of C_6F_5MgBr with an equimolar quantity of octafluoroadipoyl chloride was investigated. Surprisingly, in ether solution the reaction appeared to be very slow since after 9½ hours under reflux and 32 hours at ambient temperature Grignard reagent remained. Trace amounts of perfluoro-1,4-dibenzoylbutane were formed and pentafluorobenzene was recovered in an amount which showed that at least 55% of the Grignard reagent had not reacted. Octafluoroadipic acid was isolated to an extent which showed that at least 66% of the acid chloride had not reacted. A second acid was isolated which was purified by recrystallisation and sublimation until it had a constant melting point of 155-157°. This acid was hygroscopic and the elemental analysis obtained was in poor agreement with the figures calculated for compound II. The S- benzylisothiouronium derivative had a satisfactory carbon and hydrogen analysis but a high fluorine figure. On balance it appeared likely that the acid isolated was compound II but since a second preparation did not improve the low yield (11%) it seemed that it would not be a readily accessible intermediate and no further work was done on this topic.

3. HEPTAFLUORO-m-TOLYLMAGNESIUM CHLORIDE (III)

As perfluoro-1,6-diphenylhexane had proved to be a solid at room temperature, it was thought that a less symmetrical compound such as perfluoro-1,6-di(m-tolyl)hexane might have a lower melting point and hence be of more value as a fluid. This compound might be prepared from octafluoroadipoyl chloride and heptafluoro-m-tolylmagnesium chloride. It was known, from other work in this laboratory, that the Grignard reagent III was unstable in tetrahydrofuran, giving rise to polymeric material. Wall has reported similar results with 4-chloroheptafluorotoluene (ref. 3). This compound will form a stable Grignard reagent in ether solution however. Grignard formation from 3-chloroheptafluorotoluene in ether solution has proved to be very slow since after $5\frac{1}{2}$ hours at reflux, only 61% of the 3-chloro-compound had reacted giving, after hydrolysis, 3H-heptafluorotoluene in 35% yield. Since the reaction between pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride usually gives only about a 40-50% yield of the required diketone, the reaction of compound III, in its present state of preparation, with octafluoroadipoyl chloride did not seem very profitable and no further work was carried out.

4. 2,3,4,5,6-PENTAFLUOROBENZAL FLUORIDE (IV)

Telomerisation reactions between pentafluoroiodobenzene and tetrafluoroethylene were envisaged in the "Technical Proposal" for this Contract to provide intermediate iodides for coupling reactions and for reactions with the cuprous salts of fluorinated thiols. However, work by Monsanto Chemicals Ltd. shows that C_6F_5I does not undergo telomerisation reactions with tetrafluoroethylene. It is expected that $C_6F_5CF_2I$ will be a better radical source than C_6F_5I and hence more reactive with tetrafluoroethylene. The preparation of $C_6F_5CF_2I$ was therefore investigated.

This iodide might be prepared by iodination of compound IV, which it was found could be prepared (51% yield) by reaction of pentafluorobenzaldehyde with sulphur tetrafluoride at elevated temperature.

$$C_6F_5CHO \xrightarrow{SF_4} \underset{(51\%)}{C_6F_5CHF_2} \longrightarrow C_6F_5CF_2I$$

Later a somewhat more convenient synthesis of compound IV became available (ref. 4) in which pentafluorobenzal chloride is fluorinated with potassium fluoride in sulpholane. Pentafluorobenzal chloride can be prepared from pentafluorobenzaldehyde and phosphorus pentachloride (ref. 5). Compound IV was obtained from the aldehyde in 65-66% overall yield.

The bromination of compound IV was attempted in preference to iodination since methods for brominating similar structures have been reported (ref. 6), and the product, perfluorobenzyl bromide, should, like the iodo-compound, be a good radical source in telomerisation reactions. Three methods of bromination were tried:-

(a) N-bromosuccinimide and ultra-violet irradiation, (b) bromine in carbon tetrachloride with ultra-violet irradiation, and (c) bromine and aluminium, but they all failed to yield perfluorobenzyl bromide. We now propose to lithiate compound IV with methyl lithium (ref. 4) and to treat the product with iodine or bromine to make the corresponding perfluorobenzyl halide.

5. PERFLUORO-3,3'-DI(n-BUTYL)BIPHENYL (V)

Compound V is an example of another type of structure, a perfluoro(dialkylbiphenyl), which is of interest for evaluation as a stable fluid.

The synthesis of perfluoro-3,3'-di(n-butyl)biphenyl, an intermediate in the preparation of V, has been described (ref.1). Treatment of this diketone with sulphur tetrafluoride in the presence of aluminium fluoride at 175-180° for 124 hours gave V in 27% yield. The product is solid at ambient temperature, melting at 48.5 - 49.5°. Purification was hampered by a marked tendency of the product to supercool and recrystallisation proved difficult for this reason.

Although the material was a solid at room temperature, it was of interest to measure its thermal decomposition temperature in order to provide a guide to the behaviour of further models of this type which will be designed to have a lower melting point than compound V. Again, because of the low boiling point of the compound, the T_D could not be measured, but at the maximum temperature (308°C) at which pressure readings were made there was only a small amount of decomposition (ref. 2).

6. 3-HYDRO-3'-(1-HYDROXYHEXAFLUOROISOPROPYL)OCTAFLUOROBIPHENYL (VI)

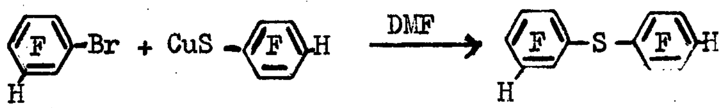
The symmetrical perfluoro-3,3'-di(n-butyl)biphenyl (see above) had a melting point of 48.5 - 49.5°. A perfluoro(dialkylbiphenyl) with a lower melting point might result if the molecule is made less symmetrical by having different alkyl substituents at the 3- and 3'- positions.

As a first step in the synthesis of such a compound the mono-lithio derivative of 3,3'-dihydro-octafluorobiphenyl has been treated with hexafluoroacetone at low temperature in tetrahydrofuran-hexane solution. The reaction product was found to be a mixture of three components. The first of these was 3,3'-dihydro-octafluorobiphenyl (24% yield) and the second (isolated in pure form in 17% yield by preparative gas chromatography) was compound VI. The third component could not be isolated in pure form, but from infrared spectroscopic and gas chromatographic evidence it appeared most probably to be 3,3'-bis(1-hydroxyhexafluoroisopropyl)octafluorobiphenyl. This experiment illustrates the difficulty of obtaining a high yield of the mono-lithio-compound by treatment of 3,3'-dihydro-octafluorobiphenyl with one equivalent of n-butyl lithium.

7. 3,4'-DIHYDRO-OCTAFLUOROBIPHENYL SULPHIDE (VII)

One approach to the problem of introducing asymmetry into fluorinated biphenyl structures has been described above.

A second method would be to attach the same perfluoroalkyl groups to different positions in each ring. The preparation of the required unsymmetrical octafluorobiphenyl starting materials presents difficulties but similar unsymmetrically substituted octafluorodiphenyl sulphides could be readily prepared by known reactions (ref. 7), e.g.



By using other combinations of bromotetrafluorobenzene and cuprous tetrafluorothiophenates a number of isomeric unsymmetrical dihydro-compounds could be prepared.

The dihydro-sulphide VII has now been prepared in 67% yield by reaction of cuprous 2,3,5,6-tetrafluorothiophenate with 2,3,4,6-tetrafluorobromobenzene in boiling dimethylformamide. Conversion of this compound into its dilithio- derivative and reaction with perfluorobutyraldehyde followed by oxidation and treatment of the product diketone with sulphur tetrafluoride should then give a disubstituted compound of the type sought.

EXPERIMENTAL

Perfluoro-1,4-dibenzoylbutane

(a) Reaction between octafluoroadipoyl chloride and pentafluorophenylmagnesium bromide

Octafluoroadipoyl chloride (20.5 g., 0.063 mole) in ether (40 ml.) was added in $\frac{1}{2}$ hr. to a stirred, cooled (0 - 5°) solution of pentafluorophenylmagnesium bromide prepared from bromopentafluorobenzene (31.4 g., 0.127 mole) and magnesium (3.34 g., 0.137 g. atom) in ether (80 ml.). After the addition, the mixture was stirred and allowed to reach room temperature in $\frac{1}{2}$ hr. It was left unstirred overnight (15 hr.), stirred a further $5\frac{1}{2}$ hr., then poured into 2.5 N sulphuric acid (40 ml.). The ether layer was separated and the aqueous layer ether extracted (3 x 50 ml.). The combined ether solutions were water washed (3 x 100 ml.) and dried (Hi-Drite). After distillation of the ether, the residue (37.2 g.) which remained was fractionally distilled at reduced pressure to give perfluoro-1,4-dibenzoylbutane, b.p. 94 - 110°/0.15 mm., (17.04 g., 46%), and a fraction (12.04 g., 21%), b.p. 110 - 162°/0.15 mm., believed to be impure perfluoro-1,1',6,6'-tetraphenylhexan-1,6-diol. The latter compound proved to be too involatile for analysis by gas chromatography (no peak emerged at 200° on a silicone grease column). An infrared spectrum (No. 4422) showed the presence of some C=O, -OH, $-(CF_2)-_n$ and highly fluorinated aromatic rings.

On keeping, the liquid perfluoro-1,4-dibenzoylbutane solidified to an off-white solid, m.p. 30 - 32.5°.

(b) Reaction between octafluoroadipoyl chloride and pentafluorophenylmagnesium bromide in refluxing ether using inverse addition

To a stirred solution of octafluoroadipoyl chloride (39 g., 0.12 mole) in ether (75 ml.) under nitrogen was added, during $1\frac{3}{4}$ hr., a filtered Grignard solution prepared from bromopentafluorobenzene (60 g., 0.24 mole) and magnesium (6.4 g., 0.27 g. atom) in ether (150 ml.). A white solid commenced to precipitate during the addition and increased in amount during the subsequent period of stirring at reflux (1 hr.). The mixture was stirred for 6 hr. at ambient temperature, then hydrolysed with ice-cold water (75 ml.). The ether layer was separated, extracted with 2.5% sodium hydroxide solution (2 x 50 ml.) and water washed, the washings being added to the alkali extracts. Removal of the ether left a residue (52 g.) which was fractionally distilled to give perfluoro-1,4-dibenzoylbutane (29.8 g., 43% yield), b.p. 110-115°/0.3 mm., and an impure compound believed to be perfluoro-1,1'-6,6'-tetraphenylhexan-1,6-diol (6.5 g., 6% yield), b.p. 155-168°/0.3 mm.

The aqueous alkali extracts were acidified with concentrated hydrochloric acid (10 ml.) and ether extracted (4 x 50 ml.). The dried extracts were evaporated to give a solid residue (12.6 g.). Sublimation of this residue at 70°/0.03 mm., gave a deliquescent white solid (5.0 g.), and on further sublimation at 150°/0.05 mm. a second compound (7.3 g.) was isolated.

The white solid (5.0 g.) was resublimed at 65°/0.03 mm. yielding 3.9 g., m.p. 40-44° (sealed tube). This solid was a strong acid, liberating carbon dioxide from sodium bicarbonate solution. Peaks present in the infrared spectrum (No. 4586A and 4586B) were consistent with the presence of a highly fluorinated aromatic ring and a $(CF_2)_n$ chain. Treatment of the acid (3.02 g.) in ether (15 ml.) with aniline (0.76 g.) in ether (5 ml.) gave a crystalline product (3.61 g.) which was recrystallised twice from acetone/petrol ether (b.r. 40-60°) to yield a white solid (0.31 g.), m.p. 207-210°.

Anal. Found: C, 44.5; H, 3.5; F, 32.4; N, 5.0%, equiv. 254.

The buff sublimate (7.3 g.) obtained at the higher temperature was recrystallised twice from toluene/benzene to give octafluoroadipic acid (2.4 g.), m.p. 132-133° (sealed tube). Its identity was confirmed by an infrared spectrum and mixed melting point.

(c) Purification of crude perfluoro-1,4-dibenzoylbutane

The perfluoro-1,4-dibenzoylbutane from (b) above was combined with similar material from other reactions to give 62.3 g. of 94% purity. This was distilled through a 6" Vigreux column giving perfluoro-1,4-dibenzoylbutane (53.3 g.), b.p. 105-110°/0.20 mm., 98% pure by gas chromatography. The analytical sample was a mid-cut, b.p. 110°/0.2 mm., m.p. 34.5°, 99+% pure by gas chromatography.

Anal. Calc. for $C_{18}F_{18}O_2$: C, 36.6; H, 0.0; F, 57.9%
Found: C, 36.2; H, 0.0; F, 58.0

Perfluoro-1,6-diphenylhexane

(a) Perfluoro-1,4-dibenzoylbutane (24.8 g., 0.042 mole) and dry aluminium fluoride (2 g.) were sealed in an 800 ml. capacity stainless steel autoclave. Sulphur tetrafluoride (56 g., 0.52 mole) was added by vacuum transfer, then the vessel was heated and shaken at 175° for 70 hr. The cold autoclave was vented through 3N sodium hydroxide solution and the brown solid product remaining in the autoclave was dissolved in ether (150 ml.). The ether solution was washed with 2.5% sodium bicarbonate solution (1 x 100 ml., 2 x 50 ml.), then with water (2 x 50 ml.), and dried.

Distillation of the ether yielded a brown, crystalline solid (19.2 g.), m.p. 45 - 56°, which was recrystallised twice from absolute ethanol yielding white crystals of perfluoro-1,6-diphenylhexane (13.1 g., 49%), m.p. 59 - 60°, b.p. 284-286°/755 mm.

Anal. Calc. for $C_{18}F_{22}$: C, 34.2; F, 65.7%
Found: C, 34.1; F, 65.9

An infrared spectrum (No. 4285) was consistent with the proposed structure which was confirmed absolutely by N.M.R. analysis.

(b) Perfluoro-1,4-dibenzoylbutane (50 g., 0.085 mole), anhydrous aluminium fluoride (4 g.) and sulphur tetrafluoride (85 g., 0.78 mole) were heated for 124 hr. at 175°. The crude product (36.3 g.) was recrystallised twice from ethanol to give pure perfluoro-1,6-diphenylhexane (28 g., 52% yield), m.p. 59.5 - 60°.

Perfluoro-5-benzoylpentanoic acid

(a) Reaction between equimolar quantities of pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride

To a vigorously stirred solution of octafluoroadipoyl chloride (32.6 g., 0.1 mole) in ether (50 ml.) at reflux under nitrogen was added during 1½ hr. a Grignard solution prepared from bromopentafluorobenzene (24.64 g., 0.1 mole) and magnesium (2.69 g., 0.11 g. atom) in ether (40 ml.). The solution was stirred at reflux a further hour. No precipitate was observed then but a thick precipitate had formed after the mixture had been kept overnight. The mixture was stirred at reflux a further 7 hr. then left overnight. A positive Gilman Colour test was still obtained showing the presence of unreacted Grignard reagent. The mixture was hydrolysed by the addition of ice-cold water (60 ml.). The ether layer was separated, the aqueous layer was exhaustively ether extracted and the extracts and ether layer were combined, washed with 2½% sodium hydroxide solution (2 x 175 ml.) and with water. Distillation of the dried ether solution through a 12" column filled with glass helices gave a fraction (11.2 g.), b.p. 50-100°, containing 82% pentafluorobenzene, and a residue (1.08 g.) which was not examined further. Thus at least 55% of the Grignard reagent had not reacted with the acid chloride.

The aqueous alkali wash liquors were acidified with 12N hydrochloric acid (30 ml.) and the solution was exhaustively ether extracted. The dried extracts were distilled to leave a solid brown residue (32.5 g.) which was slurried in boiling benzene (150 ml.). The solid (18.95 g.), m.p. 134-137° (sealed tube), which did not dissolve was filtered off. It was almost pure octafluoroadipic acid, identified by its infrared spectrum. A second batch (2.67 g.), m.p. 133-137° (sealed tube), crystallised out from the filtrate. The mother liquors were evaporated down to yield an acid (5.01 g.), m.p. 155-159° (sealed tube). The infrared spectrum of this material (No. 4720) showed the highly fluorinated aromatic ring absorption. Recrystallisation of this acid from carbon tetrachloride (35 ml.) and sublimation of the crystals at 120°/0.05 mm. gave a hygroscopic white solid (1.06 g.), m.p. 155-157° (sealed tube). Elemental analysis figures were in poor agreement with those for the suspected perfluoro-5-benzoylpentanoic acid.

Anal. Calc. for $C_{12}HF_{13}O_3$: C, 32.7; H, 0.23; F, 56.1%, equiv. 440.2

Found: C, 35.1; H, 0.5; F, 53.8%, equiv. 445

Part of the acid (0.5 g.) was dissolved in water (10 ml.) and neutralised with 5% sodium hydroxide solution. The solution was added to a solution of S-benzylisothiouronium chloride in water (10 ml.) yielding a precipitate, m.p. 212° (after two crystallisations from aqueous ethanol).

Anal. Calc. for $C_{20}H_{11}F_{13}O_3N_2S$: C, 39.6; H, 1.8; F, 40.7%

Found: C, 39.8; H, 1.7; F, 43.3.

A second preparation of the acid on the same scale gave the product in very similar low yield.

Heptafluoro-m-tolylmagnesium chloride

(a) Preparation with short period of reflux followed by carbonation

To a stirred suspension of magnesium turnings (0.66 g., 0.027 g. atom) in ether (15 ml.), activated with a few drops of 1,2-dibromoethane, was added at ambient temperature 3-chloroheptafluorotoluene (6.30 g., 0.025 mole) in ether (5 ml.). The brisk initial reaction subsided when about one quarter of the toluene solution had been added so the solution was reactivated and brought to reflux. The remaining toluene solution was added during 45 min. and the solution was heated and stirred at reflux for a further 2¼ hr. becoming almost black. Carbon dioxide gas was bubbled through at ambient temperature for 2 hr. The product was poured onto a mixture of ice (50 g.) and concentrated hydrochloric acid (20 ml.). The ether layer was separated and the aqueous layer was ether extracted (3 x 50 ml.). Distillation of the dried combined ether solutions gave fractions containing 3H-heptafluorotoluene (1.12 g., 20% yield) and 3-chloroheptafluorotoluene (3.57 g., 57% recovery). Further work-up of the distillation residue yielded heptafluoro-m-toluic acid (0.17 g., 3% yield), m.p. 57-60°, undepressed in admixture with authentic material and having an identical infrared spectrum (ref. 1). Thus the amount of 3-chloroheptafluorotoluene consumed was 43% which is in agreement with the amount of magnesium consumed (0.29 g., 44% conversion).

(b) Preparation using longer reflux period without carbonation

Reagent quantities were exactly as in (a). The reaction again subsided after about one half of the 3-chloroheptafluorotoluene solution had been added, but was reactivated by the addition of a small amount of a reacting mixture of magnesium and 1,2-dibromoethane in ether. Total time of addition of the toluene solution was 15 min. The solution was heated at reflux for 5½ hr., when only a little magnesium remained, then cooled and acidified with 6N hydrochloric acid (40 ml.). Carbonation was not carried out but the mixture was otherwise worked up as in (a). 3-Chloroheptafluorotoluene (2.46 g., 39% recovery) and 3H-heptafluorotoluene (2.03 g., 35% yield) were obtained.

2,3,4,5,6-Pentafluorobenzal fluoride

(a) By reaction between pentafluorobenzaldehyde and sulphur tetrafluoride

Pentafluorobenzaldehyde (80 g., 0.41 mole) and sulphur tetrafluoride (93 g., 0.88 mole) were shaken in an 800 ml. capacity stainless steel autoclave at 140-150° for 8 hr. and at 160-170° for 3 hr. The liquid product was poured into a stirred suspension of sodium fluoride (5 g.) in dry pentane (100 ml.). A solid was filtered off and the pentane evaporated, leaving a liquid residue (74.5 g.). Distillation of this residue through a 6" column packed with glass helices gave a fraction (45.5 g., 51% yield), b.p. 124-127°, 98.6% pure by gas chromatography. A mid-cut, b.p. 124-125°, was 99+% pure 2,3,4,5,6-pentafluorobenzal fluoride.

Anal. Calc. for C_7HF_7: C, 38.6; H, 0.5; F, 61.0%
Found: C, 38.6; H, 0.6; F, 60.9.

The infrared spectrum (No. 4708) was consistent with the proposed structure. The high-boiling residue (21.5 g.) from the distillation was distilled at reduced pressure and gave solid materials of wide boiling ranges which liberated hydrogen fluoride on standing. These were not further investigated.

(b) By reaction of pentafluorobenzal fluoride with potassium fluoride

(i) Pentafluorobenzal chloride

Pentafluorobenzaldehyde (98.1 g., 0.5 mole) and phosphorus pentachloride (150 g., 0.72 mole) were heated and stirred at

100° for 1 hr. and the product poured onto ice (500 g.). Ether (250 ml.) was added and the mixture was stirred vigorously. The ether layer was separated, washed with 10% sodium metabisulphite solution (100 ml.), with 10% sodium carbonate solution (100 ml.), and finally with water (200 ml.). The dried ether solution was distilled to give pentafluorobenzal chloride (102.7 g., 81% yield), b.p. 82-84°/30 mm., 98.7% pure by g.l.c. analysis.

(ii) Pentafluorobenzal fluoride

To the pentafluorobenzal chloride (101.6 g., 0.405 mole) from (b) above, in pure sulpholane (450 ml.), was added anhydrous potassium fluoride (198 g.). The mixture was stirred at 150-160° for 7 hr. The dark brown product was poured into water (1¼ litres) and steam distilled to yield pentafluorobenzal fluoride (70 g., 79% yield), b.p. 124-125°, 99+% pure by g.l.c. analysis.

A second preparation from pentafluorobenzaldehyde (196.1 g., 1.0 mole), exactly as above, gave pentafluorobenzal fluoride (144.7 g., 66% yield), b.p. 122-124°, 99+% pure by g.l.c. analysis.

Perfluorobenzyl bromide (attempted preparations)

(a) With N-bromosuccinimide and u.v. light

Freshly prepared N-bromosuccinimide (19.58 g., 0.11 mole) and pentafluorobenzal fluoride (21.8 g., 0.1 mole) were stirred and heated in refluxing carbon tetrachloride (250 ml.) under ultraviolet irradiation. After 4 hr. no conversion of starting material had occurred (by g.l.c. analysis). Benzoyl peroxide (1 g.) was added and the mixture was further heated and irradiated for 5 hr. Again, analysis of a sample showed that no reaction had occurred. Pentafluorobenzal fluoride and N-bromosuccinimide were recovered.

(b) With bromine in carbon tetrachloride and u.v. light

Pentafluorobenzal fluoride (21.8 g., 0.1 mole) and bromine (16.8 g., 0.11 mole) were heated in refluxing carbon tetrachloride (25 ml.) and irradiated with u.v. light for 10 hr. No conversion of starting material occurred and only pentafluorobenzal fluoride was recovered.

(c) With bromine and aluminium

Bromine (16 g.) and aluminium clippings (0.1 g.) were stirred together until reaction ceased. Pentafluorobenzal fluoride (10.9 g) was added over 5 mins. to the mixture at room temperature, some heat being evolved. The mixture was refluxed for 3½ hr. and poured onto crushed ice (50 g.). The heavy organic layer was washed with 10% sodium metabisulphite solution (150 ml.), with 10% sodium carbonate solution (50 ml.) and with water (50 ml.). The dried product (6.5 g.) contained 97% starting material and traces of several other products.

Perfluoro-3,3'-di(n-butyl)biphenyl

Perfluoro-3,3'-di(n-butyryl)biphenyl (13.85 g., 0.022 mole since 94% purity) and anhydrous aluminium fluoride (0.82 g.) were heated and shaken with sulphur tetrafluoride (35.5 g., 0.33 mole) at 175° for 53 hr. in an 800 ml. capacity stainless steel autoclave. The cold autoclave was vented through 3N sodium hydroxide solution (2 l.) and the viscous liquid contents dissolved in ether (100 ml.). The ether solution was washed with 2.5% sodium bicarbonate solution (2x50 ml.), with water (2 x 25 ml.), and dried (magnesium sulphate). Distillation of the ether yielded a residue (13.30 g.) which was shown by infrared analysis to contain ca 50% of starting material. This residue (12.92 g.) was again treated with sulphur tetrafluoride (31 g., 0.29 mole) in the presence of anhydrous aluminium fluoride (1.77 g.) for 71.5 hr. at 175-180°. Working up as before gave a solid residue (12.40 g.), m.p. 39-50°, which contained only a trace of starting material. Two recrystallisations of 11.8 g. of the product from methylated spirit gave buff crystals (5.75 g.), m.p. 47.5 - 49°. The product was distilled at ca 0.1 mm. from a bath at 130-140° to give a colourless, viscous liquid which slowly solidified to white crystals of perfluoro-3,3'-di(n-butyl)biphenyl (4.73 g., 27% yield), m.p. 48.5 - 49.5°.

Anal.	Calc. for $C_{20}F_{26}$:	C, 32.7;	F, 67.3%
	Found:	C, 32.6;	F, 67.3.

The infrared spectrum (No. 4403A) of this material showed the complete absence of carbonyl absorption and was consistent with the proposed structure which was confirmed by N.M.R. analysis.

3-Hydro-3'-(1-hydroxyhexafluoroisopropyl)octafluorobiphenyl

To a stirred solution of 3,3'-dihydro-octafluorobiphenyl (33.6 g., 0.12 mole) in dry tetrahydrofuran (250 ml.) at -78° was added a 2.22N solution of n-butyl lithium in hexane (50 ml., 0.11 mole) during 30 min. The mixture was stirred at -76° for 2½ hr., then hexafluoroacetone (23.5 g., 0.14 mole) was added over ½ hr. No temperature rise was observed. After the addition, the mixture was stirred at -70° for 30 min. and at -50° for 20 min. The mixture was allowed to warm to -10° and was acidified with 6N hydrochloric acid (150 ml.). The pale yellow hexane layer was separated and the aqueous layer was ether extracted (4 x 100 ml.). The combined organic phases were dried and distilled to yield a viscous residue (51.3 g., 102% yield).

Distillation of this product through a 6" Vigreux column at reduced pressure gave a white sublimate (7.96 g.), shown by g.l.c. analysis and infrared spectroscopy to be 3,3'-dihydro-octafluorobiphenyl, and the following liquid fractions; fn. (1) b.r. 85-87°/0.1 mm. (16.9 g.), fn. (2) b.r. 87-90°/0.1 mm., (7.14 g.), fn. (3) b.r. 106-108°/0.04 mm. (8.88 g.) and a residue (1.2 g.). Fractions (1) to (3) consisted mainly of two components 'A' and 'B' in the following proportions - fn. (1) 83%, 16%; fn. (2) 63%, 36%; fn. (3) 14%, 81%.

Fraction (1) was separated by preparative gas chromatography (20' x $\frac{3}{8}$" silicone gum rubber on celite column at 270°, 35 p.s.i. He carrier gas) to yield 3-hydro-3'-(1-hydroxyhexafluoroisopropyl)octafluorobiphenyl (9.5 g.), b.p. 95-97°/0.08 mm., 99+% pure by g.l.c. analysis and having an infrared spectrum (No. 4929) consistent with the proposed structure.

Anal. Calc. for $C_{15}H_2F_{14}O$: C, 38.8; H, 0.43; F, 57.3%
Found: C, 38.5; H, 0.6; F, 57.7

The infrared spectrum of fraction (3) (No. 4827) suggested that it consisted largely of the disubstituted product, but an attempted purification by preparative gas chromatography (20' x $\frac{3}{8}$" silicone gum rubber on celite at 350°, 35 p.s.i. He carrier gas) was unsuccessful, trouble being experienced with sample vaporisation at the column inlet and condensation at the detector outlet.

3,4'-Dihydro-octafluorodiphenyl sulphide

2,3,4,6-Tetrafluorobromobenzene (75.7 g., 0.33 mole) and cuprous 2,3,5,6-tetrafluorothiophenate (94 g., 0.38 mole) were stirred in refluxing dimethylformamide (500 ml.) for 6 hours. The dark brown solution was filtered hot and the filtrate was poured into water (2.5 l.). The cream suspension produced was ether extracted (5 x 500 ml.) and the combined dried extracts were distilled through a 6" glass helices packed column to give 3,4'-dihydro-octafluorodiphenyl sulphide (73.2 g., 67% yield), b.p. 69°/0.06 mm., of 99+% purity, by gas chromatography.

Anal. Calc. for $C_{12}H_2F_8S$: C, 43.6; H, 0.6; F, 46.0%
Found: C, 43.8; H, 0.5; F, 46.2.

An infrared spectrum (No. 5021) was consistent with the proposed structure.

REFERENCES TO PART III (SECTION I)

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PART III, SECTION 2

SUMMARY

Iodopentafluorobenzene under U.V. irradiation in benzene yields 2,3,4,5,6-pentafluorobiphenyl, but does not telomerise with tetrafluoroethylene under U.V. irradiation or in the presence of azodi-isobutyronitrile. Neither iodobenzene nor benzyl iodide undergoes the above telomerisation under the same conditions, but the telomerisation of heptafluoroiodopropane has been confirmed, as reported in the literature. Pentafluorothiophenol under U.V. irradiation does not react with benzene.

1,2-Di-iodotetrafluoroethane, obtained from iodine and tetrafluoroethylene as described in the literature, reacted with cuprous pentafluorothiophenate in dimethylformamide to yield an impure sulphur compound, which may be the required 1,2-di(pentafluorophenylthio)tetrafluoroethane.

DISCUSSION

General

Perfluoroalkyl iodides of the types (I) and (II) are potential intermediates in syntheses of perfluoroalkyl sulphides. The iodides could conceivably be obtained in telomerisations : Reactions (i) and (ii).

$$C_6F_5I + C_2F_4 \longrightarrow C_6F_5(CF_2CF_2)_n\ I \qquad \text{.......Reaction (i)}$$

$$C_6F_5CF_2I + C_2F_4 \longrightarrow C_6F_5CF_2(CF_2CF_2)_n\ I \qquad \text{...... Reaction (ii)}$$

It is known that iodobenzene when photolysed in benzene gives biphenyl (ref. 1), and that perfluoroalkyl iodides telomerise with tetrafluoroethylene, ethylene and chlorotrifluoroethylene (refs. 2 & 3). Telomerisations with the last two olefins could ultimately lead to syntheses of carboxylic acids of type (III), cf. Ref. 2, of interest in such syntheses as described in Section 1.

$$Ar_F(CF_2)_n\ CO_2H \qquad \text{(III)}$$

Similarly useful intermediates would arise if pentafluorothiophenol telomerised with tetrafluoroethylene: Reaction (iii). The precedents for this reaction are the known reactions between trifluoromethyl mercaptan and halogeno-olefins and the addition of phenyl and ethyl mercaptan to tetrafluoroethylene (refs. 4,5 and 6)

$$C_6F_5SH + C_2F_4 \longrightarrow \underset{\text{(IV)}}{C_6F_5S(CF_2CF_2)H} \qquad \text{...... Reaction (iii)}$$

Iodides

It was first established that the reaction of iodopentafluorobenzene (V) in benzene, initiated by light does yield pentafluorobiphenyl: Reaction (iv). The yield was ca. 6%.

$$C_6F_5I + C_6H_6 \xrightarrow[\substack{2540\mathring{A} \\ \text{or} \\ 3660\mathring{A}}]{hv} \underset{(V)}{C_6F_5{\cdot}C_6H_5} \qquad \text{.....Reaction (iv)}$$

However, (V) was not isolated when iodopentafluorobenzene was refluxed in benzene with benzoyl peroxide.

Iodopentafluorobenzene, in a quartz container, was shaken in an atmosphere of tetrafluoroethylene slightly above atmospheric pressure, while exposed to light of wavelength 2540A. No reduction in the volume of the tetrafluoroethylene was detected, and the iodo compound was recovered unchanged. No reaction took place between iodopentafluorobenzene and tetrafluoroethylene, in a sealed tube, using light of the same wavelength.

It is not very likely that the failure of the above reaction is due to the purity of the tetrafluoroethylene (about 20% only present in the gas used) since the known telomerisation of heptafluoroiodopropane (Ref. 3) was successfully repeated using the same tetrafluoroethylene. It seems that aromatic iodides do not telomerise readily with tetrafluoroethylene. This view is supported by the failure of iodobenzene to telomerise in a sealed tube under the influence of light.

Perfluorobenzyl iodide (for Reaction (ii)) is not readily available. An examination of the chances of success of this reaction could be obtained from a study of the reaction of (iododifluoromethyl)benzene (VI) or benzyl iodide with tetrafluoroethylene, as shown in Reactions (v) and (vi).

$$C_6H_5CF_2I + C_2F_4 \xrightarrow{hv} C_6H_5CF_2CF_2CF_2I \qquad \text{.......Reaction (v)}$$

$$C_6H_5CH_2I + C_2F_4 \xrightarrow{hv} C_6H_5CH_2CF_2CF_2I \qquad \text{...... Reaction (vi)}$$

A possible starting material for (VI) is the available (chlorodifluoromethyl) benzene. The preparation from the latter compound by means of sodium iodide in acetone was examined without success. The method used was similar to that applied to the conversion of benzyl chloride to benzyl iodide (Ref. 7). The telomerisation of benzyl iodide with tetrafluoroethylene under the influence of light of wavelengths 3660 and 2540 A failed. It thus appears that the chances of success with reaction (ii) are not high.

In view of the lack of success in the above telomerisations 1,2-di-iodotetrafluoroethane was prepared from tetrafluoroethylene and iodine in sealed tubes at 165° as described in the literature (ref. 8). This compound was obtained but three further attempts to repeat the reaction resulted in shattered tubes.

Thiols

Pentafluorothiophenol in benzene irradiated by light as for the iodides, yielded only perfluoro diphenyl disulphide. Reaction (vii) did not occur, and it is possible that the disulphide may have originated from an oxidation reaction, arising from air in the mixture

$$C_6F_5SH + C_6H_6 \xrightarrow{hv} C_6F_5C_6H_5 \qquad \text{......Reaction (vii)}$$

Sulphides

$$C_6F_5SM + ICF_2CF_2I \longrightarrow C_6F_5SCF_2CF_2SC_6F_5 \qquad \text{...Reaction (viii)}$$

(where M is Na or Cu) (VII)

Sodium pentafluorothiophenate and 1,2-di-iodotetrafluoroethane in refluxing acetone yielded largely insoluble material. A soluble fraction, m.p. 198-216°, containing sulphur and the C_6F_5 group (I.R. spectrum) was not obtained in a pure state.

Cuprous pentafluorothiophenate in N,N-dimethylformamide at 70-90° yielded a mixture, one fraction of which was possibly (VII). This, b.p. 78-80°/0.1 mm analysed for $C_{14}F_{13}S_{1.6}$. The infra-red spectrum showed the presence of the C_6F_5 group. When this reaction was repeated at 140° the product, b.p. 140-148°, contained hydrogen.

EXPERIMENTAL

Materials used :

1. The fluoro compounds were supplied by I.S.C. except heptafluoroiodopropane which was purchased from K. and K. Laboratories and C_2F_4 which was supplied by I.C.I. The liquids were freshly redistilled before use. The unsuccessful telomerisation reaction was examined twice. In the second experiment, the iodofluoro compound was also dried over molecular sieve type 3A (B.D.H.) prior to use.

2. Benzene was dried by heating over the molecular sieve and distilled through a 9" Fehske column.

3. Light was supplied from a Desaga Mini Uvis lamp (Chemlab, Cambridge). The distance between the lamp and the tubes was $2\frac{1}{2}$ to 3 inches.

4. The dimensions of the tubes (ampoules) were about 2.2 x 22 cm.

Reactions of iodopentafluorobenzene in benzene

1. Photolysis in a Pyrex tube

A solution of iodopentafluorobenzene (1.5 g. : 0.005 mole) in anhydrous benzene (100 cc.) was placed in a Pyrex tube and frozen in a CO_2/acetone mixture. The tube was sealed at 0.2 mm. pressure and the liquid was exposed to light of wavelength 3660A for 22 hours. Iodine released in the reaction was ca. 1% the theoretical (estimated spectroscopically). The reaction mixture was washed with a 5% solution of sodium bisulphite, water, and dried ($MgSO_4$). Unchanged reactants were recovered using a 6" Vigreux column at atmospheric pressure. The residue was dried at 0.1 mm. pressure. It gave crude 2,3,4,5,6-pentafluorobiphenyl, 0.05 g. (4.1%), m.p. 80-90° (Lit. m.p. 111-112°, Ref. 9).

2. Photolysis in a quartz tube

In a quartz tube, sealed at atmospheric pressure (air trapped) a solution of iodopentafluorobenzene (2.9 g. : 0.1 mole) and anhydrous benzene (70 cc.) was exposed to light of wavelength 2540A for 22 hours. Iodine released was 12.6% of the theoretical. The reaction product was separated as described above. The yield of 2,3,4,5,6-pentafluorobiphenyl was 6.6%. It melted, after repeated recrystallisations from petroleum ether (b.p. 40-60°) at 113° and the m.p. was not depressed when mixed with the product of the previous experiment.

Calc : C 58.2 ; F, 38.1 ; I, 0.0

Found : C, 59.1; F, 38.6 ; I, 0.0

Molecular weight, Found 250. Calculated for $C_{12}H_5F_5$ 244

The I.R. spectrum was not inconsistent with that of pentafluorobiphenyl.

3. With benzoyl peroxide

A mixture of iodopentafluorobenzene (5.9g.; 0.02 mole), anhydrous benzene (100 ml.) and freshly recrystallised and dried benzoyl peroxide (0.1g.) was heated under reflux in a dry nitrogen atmosphere. After 7½ hours the reaction mixture was cooled to room temperature, washed three times with 5% sodium sulphite solution (200 ml.) and with water, and dried over Mg SO_4. The liquid, b.p. 93°/80 mm, isolated by distillation using a 2" Fenske column, proved to be iodopentafluorobenzene (I.R. spectrum).

A small amount of a waxy solid (0.02g.) was noticed in the top of the fractionating column. It melted alone at 85-90° and when mixed with 2,3,4,5,6-pentafluorobiphenyl at 90-95° (the latter melts alone at 113° Ref. 3). When an attempt was made to purify this solid by sublimation, a few drops of oil were obtained. This behaviour is different from that of 2,3,4,5,6-pentafluorobiphenyl which sublimes (Ref. 9).

Attempted reaction of iodopentafluorobenzene with tetrafluoroethylene

(a) Under slight pressure

The apparatus used is shown in Fig. 1.

Iodopentafluorobenzene (29.4 g., 0.1 mole) was placed in the reaction tube 9 which was immersed in an acetone/CO_2 bath. When the liquid solidified, the apparatus was evacuated to a pressure of 20 mm (via 3) and was filled with dry nitrogen (via 4). The process was repeated 3 times. The apparatus was finally evacuated and tetrafluoroethylene (1 litre) was allowed into the burette 2. The gas was then allowed into the apparatus at a slow rate and the cooling mixture surrounding the reaction tube 9 was removed. Finally the water level in 11 was raised to about 5 inches higher than in 2, light of wavelength 2540A was switched on, and the reaction tube 9 was shaken mechanically.

After 24 hours there was no change in the level of the water in 2. All the liquid in 9 distilled at 166° through a small Fenske column.

A similar result was obtained when a small amount of azodi-isobutyronitrile was used as a radical reaction initiator for 45 hours, there being anhydrous calcium chloride in the drying tubes 6.

It was later found that only about 20% of tetrafluoroethylene was present in the gas used.

(b) Under pressure

The apparatus used in the previous experiment was modified as shown in Fig. 1B.

Iodopentafluorobenzene (29.4 g., 0.1 mole) was placed in flask 13 and the latter and flask 12 were cooled in liquid nitrogen. The apparatus up to flask 13 was evacuated to a pressure of 20 mm., via 3. Flask 12 was isolated from 13 (while keeping the latter under reduced pressure) using tap 14. Tetrafluoroethylene was transferred from 2 into 12 by increasing the level of water in the former slowly. The tetrafluoroethylene (now solid) in 12 was transferred to 13 by connecting the two flasks with one another while isolating them from the rest of the apparatus and by allowing 12 to warm to room temperature. (No residue was detected in 12 after the distillation of tetrafluoroethylene). The increase in weight of 13 was recorded. The process was repeated until the required weight (2.0 g., 0.02 mole) was obtained. The contents of 13 were cooled once more for 15-20 minutes before it was connected to the pump via 15. When the pressure reached about 0.01 mm., 13 was sealed off. The weight of the ampoule with its contents was checked in order to test any possible loss of weight in the last stage. A maximum decrease in weight of about 0.2 g. was detected.

The ampoule, in an upright position, was attached to a shaker and the liquid was exposed to light of wavelength 2540A for about 20 hours (the gas in the ampoule was protected from light with tin foil). The ampoule was then opened at room temperature, and the weight of the residue corresponded to that of the original iodo compound. The liquid was distilled using a 3" Vigreux column. It boiled completely at 166°.

A similar observation was made when the reaction was carried out using a catalytic amount of azodi-isobutyronitrile.

Attempted reaction of iodobenzene with tetrafluoroethylene

The conditions were essentially as described in the previous experiments, and the iodobenzene was recovered unchanged.

Telomerisation of heptafluoroiodopropane with tetrafluoroethylene (Ref.2)

The reaction was carried out essentially as in the previous two experiments, using heptafluoroiodopropane (29.6 g., 0.1 mole) and tetrafluoroethylene (2.5 g., 0.025 mole).

After the reaction, the liquid in the ampoule showed an increase in weight of about 2.5 g. Excess heptafluoroiodopropane was recovered and the residue was distilled through a short Fenske column. The following fractions were collected :

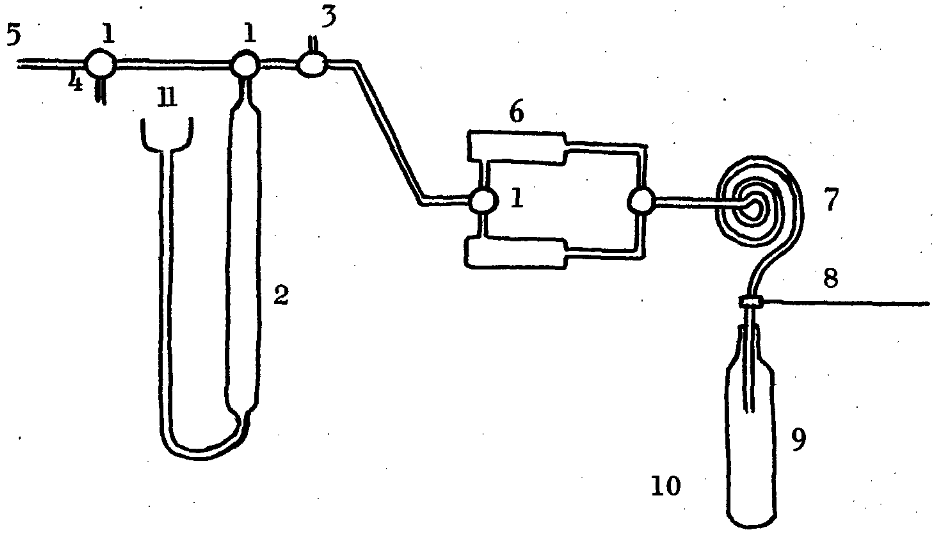
1. b.p. 82-96° (2.2 g.), mainly $C_5H_{11}I$ (by gas chromatography)

2. b.p. 140-150° (1.9 g.), about 20% $C_5H_{11}I$ (by gas chromatography)

3. Waxy residue. (1.0 g.)

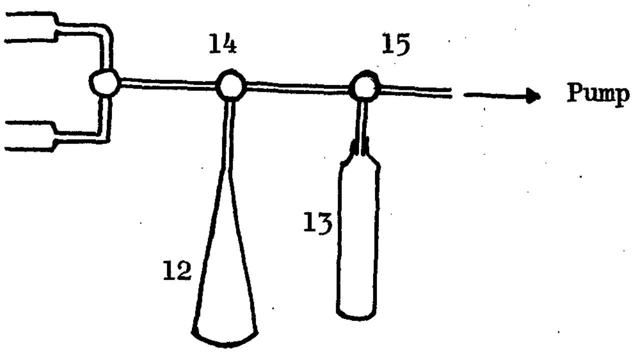
Gas chromatography showed the presence of at least 6 components spread over the three fractions.

FIG. 1A



1. 3 way tap
2. Graduated burette (2 litres)
3. Connection to vacuum pump
4. Connection to dry nitrogen source
5. Connection to C_2F_4 source
6. Drying tubes (about 180 cc each, containing granulated anhydrous calcium chloride)
7. Glass coil
8. Shaker arm
9. Quartz reaction tube, the upper part covered with aquadag and tin foil, exposing most of the liquid
10. Light source
11. Water reservoir

FIG. 1B



12. Pear shaped flask
13. Quartz reaction tube
14. Connection to oil and mercury diffusion pump

Photolysis of benzyl iodide with tetrafluoroethylene

Freshly prepared benzyl iodide (20g., 0.09 mole, Ref. 1) and tetrafluoroethylene (2.0g., 0.02 mole) were placed in a quartz ampoule which was sealed at 0.05 mm. An electric heater was placed under the ampoule in order to keep the benzyl iodide in the molten state. The air temperature around the lower half of the ampoule was 35-40°. The liquid part of the mixture was then exposed simultaneously to light of wavelengths 2540 and 3660 A for 17½ hrs. The vapour in the ampoule was protected from the light with tin foil.

The reaction mixture, distilled through a short column, boiled at 134-136°/58-61 mm. and had an I.R. spectrum identical with that of benzyl iodide.

1,2-Di-iodotetrafluoroethane

A mixture of iodine (12.7g., 0.1 mole) and tetrafluoroethylene (4g., 0.04 mole) was sealed in a Pyrex tube at a pressure of 0.025 mm, and heated at 165° for 7 hours. The product was washed with a 10% solution of sodium sulphite and with water. The aqueous solution was extracted with ether (200 cc) twice, and the combined extracts and oil were dried over Mg SO_4. The product (7.5g.), b.p. 47-48°/80 mm was isolated using a 2" Fenske column. The yield was 7.5g. (Lit. b.p. 65°/150 mm., Ref. 8).

Photolysis of pentafluorothiophenol with tetrafluoroethylene

Pentafluorothiophenol (34.0g.; 0.17 mole) and tetrafluoroethylene (1.3g.; 0.013 mole) were sealed in a quartz ampoule at 0.01 mm. The liquid part of the mixture was exposed simultaneously to light of wavelengths 2540 and 3660 A during 17 hrs. with the vapour in the ampoule protected with tin foil. The crude product had an I.R. spectrum similar to that of pentafluorothiophenol. The reaction product when distilled gave pentafluorothiophenol (identified by b.p. and I.R. spectrum). There was a small amount of residue which had an I.R. spectrum very similar to that of decafluorodiphenyl disulphide. No $-CF_2-CF_2H$ group could be identified in the I.R. spectrum.

Photolysis of pentafluorothiophenol in benzene

A solution of pentafluorothiophenol (2.0 g. : 0.01 mole) in anhydrous benzene (70 cc.) was placed in a quartz tube which was sealed at atmospheric pressure (air trapped). The liquid was exposed to light of wavelength 2540A for 22 hours. The bulk of the unchanged reactants were recovered by distillation at atmospheric pressure and the last few cubic centimetres by warming on a steam bath at 21 mm. The residue, 0.15 g., solidified on cooling, m.p. 51° (recryst. alcohol). It had the same m.p. when mixed with decafluorobiphenyl disulphide (m.p. 51°) prepared essentially as described in Ref.10. The identity of the product was further confirmed by comparing the spectrum of the two compounds.

Reactions with 1,2-di-iodotetrafluorethane

(a) With sodium pentafluorothiophenate

Sodium pentafluorothiophenate was prepared as follows :

A mixture of pentafluorothiophenol (5.3g., 0.026 mole), sodium hydroxide (1g., 0.025 mole) and water (35 ml.) was heated under reflux in a nitrogen atmosphere for 60 minutes. The mixture was cooled to room temperature and filtered (about 0.05g. of solid was obtained). The filtrate was extracted with ether. Water was removed from the filtrate by heating at 100° first at 17 mm. and finally at 0.1 mm. to yield the sodium salt (5.5g.).

A mixture of 1,2-di-iodotetrafluoroethane (2.5g.; 0.07 mole), sodium pentafluorothiophenate (3.14g.; 0.14 mole) and acetone (25 ml.) was heated under reflux for 5¾ hours. The mixture was then poured into water (ca. 250 ml.) and the solid (0.5 g.), m.p. 130-195° was filtered off, washed with water and dried. The product was incompletely soluble in most organic solvents. Part of this was extracted with hot xylene, petrol (60°-80°) was added, and the solution was cooled in solid carbon dioxide/ acetone. The crystals obtained, m.p. 198° - 216° and the crude products had the same elemental content.

Calc. for $C_{14}F_{14}S_2$: C, 33.7; H, 0.0; F, 53.4; S, 12.9%

Found (crude) : C, 39.0; H, 0.0; F, 49.81; S, 11.6

Found (recrystallised): C, 39.2; H, 0.0; F, 49.4; S, 11.9

The I.R. spectrum indicated the presence of the pentafluorophenyl group in these substances.

(b) Reaction of cuprous pentafluorothiophenate with 1,2-di-iodotetrafluoroethane

Cuprous pentafluorothiophenate was prepared as follows :

A mixture of cuprous oxide (29g.; 0.05 mole), pentafluorothiophenol (10g., 0.05 mole) and ethanol (63ml.) was refluxed in a nitrogen atmosphere for 21 hours. The solid (8.5g.) was collected by filtration, washed with ethanol and dried.

A stirred mixture of cuprous pentafluorothiophenate (3.7g., 0.14 mole) 1,2-di-iodotetrafluoroethane (2.5g., 0.07 mole) and dimethylformamide (50ml.) was heated at 70-90° for 5 hours, and poured into an excess of water. The greenish brown solid was collected by filtration and the filtrate was extracted with chloroform. The solvent was distilled from the dried extracts to give a brown oil (4.3g.). This was distilled to yield fractions as follows:

1. (2g.) b.p. 90-92°/100 mm., colourless oil, n_D^{25} 1.4350

2. (1g.) b.p. 92°/100 mm., colourless oil, n_D^{25} 1.4375

3. (0.5g.) b.p. 76-78/0.1 mm., brown-red semi solid

Fraction (2) had an I.R. spectrum inconsistent with that of bis(pentafluorophenylthio)tetrafluoroethane. The I.R. spectrum of fraction (3) suggested the presence of the pentafluorophenyl group. This solid was different from the solids of the previous experiment. The three fractions had the following elemental analyses.

Calc. for $C_{14}F_{14}S_2$: C, 33.7; H, 0.0: F, 53.4; S, 12.86%.

Found (Fraction 1) : C, 41.3; H, 8.7; F, 2.95; S, 0.0.

Found (Fraction 2) : C, 40.5; H, 8.7; F, 3.57; S, 1.76

Found (Fraction 3) : C, 36.25; H, 0.0; F, 53.1; S, 11.16

(c) The experiment as in (b) was repeated but the reaction mixture was stirred at 140° for 21 hours. It was then stirred into excess water. The solid was filtered off and the filtrate was extracted with chloroform. The dried extracts ($MgSO_4$) were distilled to yield dimethylformamide.

The solid obtained after the reaction mixture was diluted with water, was extracted with boiling chloroform, carbon tetrachloride and benzene. The dried extracts ($MgSO_4$) were distilled. After removing the solvents, a fraction b.p. 140-148°/0.1 mm. of a yellow semi-solid (0.5g.) was obtained. The I.R. spectrum showed the presence of the pentafluorophenyl group.

Calc. for $C_{14}F_{14}S_2$: C, 33.7; H, 0.0; F, 53.4; S, 12.86%

Found : C, 40.4; H, 2.2; F, 46.2.

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PART IV

FLUOROCARBON FLUIDS

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INTRODUCTION

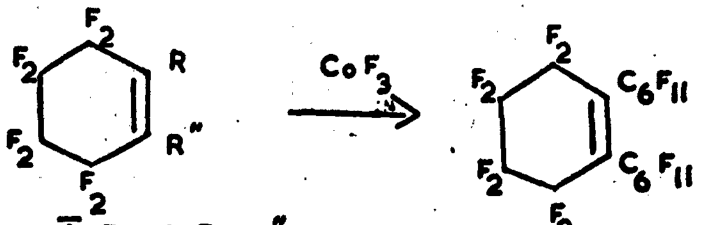
This work has been directed towards the preparation of polyfluoro-polyalicyclic compounds, with various perfluoroalkyl substituents, in several orientations. These compounds are useful model compounds as well as having potential use as fluids in their own right. Thermal and oxidative stability tests on these compounds should give an insight into the types of structure which may be useful in building larger molecules.

SUMMARY

Compounds derived from the reaction of o- and p-perfluoroxylene and decafluorocyclohexene with aryl lithium reagents(1) have been fluorinated with cobaltic fluoride to give the corresponding alicyclic compounds. The two samples so far submitted to Monsanto Chemicals Ltd. are high boiling liquids, but do not have sufficiently high boiling points. Present work is aimed at higher molecular weight compounds with the hope of increasing boiling points but still maintaining low melting points. Attempts have been made to prepare penta- and heptafluorobenzyl lithium derivatives from penta- and heptafluorotoluenes, and to use these reagents to prepare compounds with $CH_2\leq$ and CF_2 groups between rings.

DISCUSSION

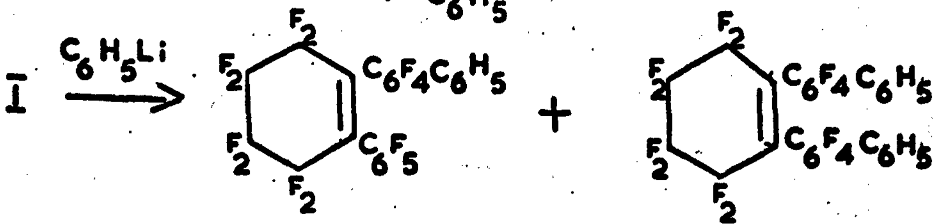
Fluorination of hydrocarbons by cobaltic fluoride is well known, but only recently has fluorination of fluoroolefins and fluoroaromatic compounds been studied(2). In the current work not only was the difficulty of fluorination of the available multi-cyclic aromatic compounds (see previous report) an unknown factor, there was a technical problem of introduction of high melting point, high boiling point compounds into a cobalt trifluoride reactor. The solution to the first problem was indicated by previous work(2) and it was found by using a sufficiently high



I R = C_6F_5 = R''

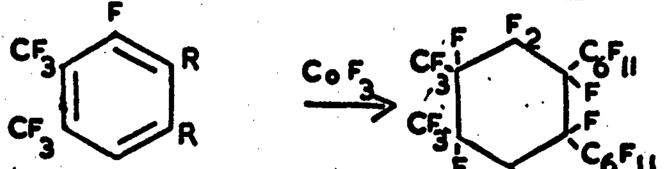
II R = R'' = C_6H_5

III



XII

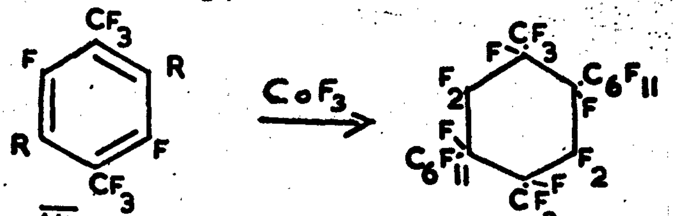
XIII



IV R = C_6F_5

V R = C_6H_5.

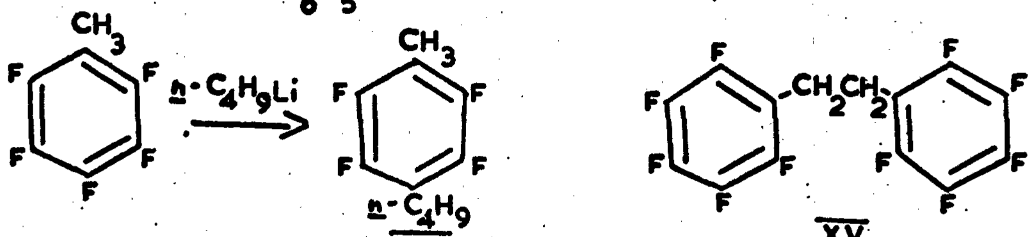
VI



VII R=C_6F_5

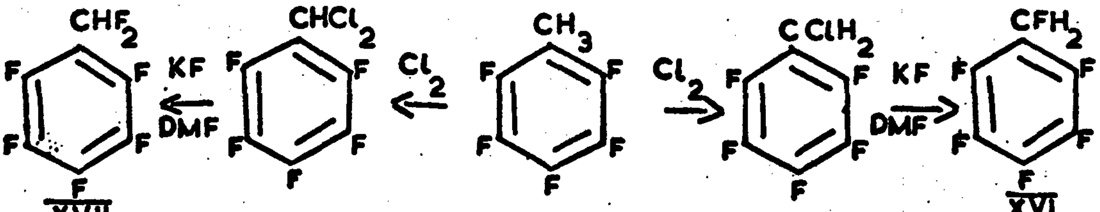
VIII R=C_6H_5

IX



XIV

XV



XVII

XVI

temperature, complete fluorination without great decomposition could be achieved. Several methods of addition to the reactors were investigated and it was found that addition of the sample as a fine powder gave the best results.

Using the conditions mentioned above, fluorination of 1,2-bis(pentafluorophenyl)-octafluorocyclohexane (I) and of 1,2-bis(phenyl)-octafluorocyclohexene (II) gave two components, one comprising >95% of the mixture; the latter was indicated by physical methods and analysis to be 1,2-bis(undecafluorocyclohexyl)-octafluorocyclohexene (III). This compound, a viscous high boiling liquid, was shown to be resistant to attack by a variety of oxidising agents and to sulphuric and fuming sulphuric acids.

Fluorination of 3,4-bis(trifluoromethyl)-dodecafluoro-o-terphenyl (IV) and of 3,4-bis(trifluoromethyl)-difluoro-o-terphenyl (V) gave essentially one component. Purification by chromatography on alumina gave a compound which appeared as a single component both on GLC and TLC analysis, and which was shown by mass spectrometry and analysis to be 1,2-bis(perfluorocyclohexyl)-4,5-bis(trifluoromethyl)-octafluorocyclohexane (VI), a viscous high boiling liquid, shown by isoteniscope measurements to be stable at its boiling point(3). Fluorination of the corresponding derivatives of perfluoro-p-xylene (VII and VIII) gave the corresponding 1,4-bis(perfluorocyclohexyl)-3,6-bis(trifluoromethyl)-octafluorocyclohexane (IX) as a semisolid at room temperature which did not decompose at its boiling point.

Since the compounds mentioned above have boiling points of ca 290° which are too low for isoteniscopic decomposition rates to be measured, work has commenced on the synthesis of aromatic precursors which should lead to higher boiling materials. Thus, perfluoro-p-xylene was treated with 4-lithio-nonafluorobiphenyl to give 2,5-bis(2',2",3',3",4',5',5",6',6"-nonafluorobiphenylyl)-1,4-bis(trifluoromethyl)-difluorobenzene (or eicosafluoro-2",5"-bis(trifluoromethyl)-p-quinquephenyl) (X). Hydrolysis of the trifluoromethyl groups in this compound gave the corresponding dicarboxylic acid (XI). Similarly (I) was reacted further with phenyl lithium to give two products which were shown to be 1-pentafluorophenyl-2-(2',3',5',6'-tetrafluorobiphenylyl)-octafluorocyclohexene (XII) and 1,2-bis(2',3',5',6'-tetrafluorobiphenylyl)-octafluorocyclohexene (XIII). These latter compounds are being prepared in large quantities for fluorination studies.

It is of interest to find the effect of interposition of methylene and difluoromethylene groups between the alicyclic rings in the series of compounds described above. An obvious way to introduce these groups seemed to be via penta- and heptafluorobenzyl lithium reagents, and work has been carried out to prepare these reagents.

Attempts have been made to metallate 2,3,4,5,6-pentafluorotoluene alone and in the presence of triethylene diamine, a known catalyst for metallation of toluene$^{(4)}$, using n-butyl lithium as the metallating agent. In each case the product obtained was 1-methyl-4-n-butyltetrafluorobenzene (XIV). When bromomethylpentafluorobenzene was treated with n-butyl lithium only decafluorobibenzyl (XV) could be isolated. No reactions have so far been attempted with fluorinated substrates since it seems that nucleophilic attack by the butyl anion will always be the predominating reaction. There seemed to be two possible methods of preparation of heptafluorotoluene, a precursor of heptafluorobenzyl lithium, (a) reaction of pentafluorobenzaldehyde with sulphur tetrafluoride, and (b) chlorination and subsequent fluorination of 2,3,4,5,6-pentafluorotoluene. Since the latter method afforded the benzyl and benzylidene compounds, and is more suitable to larger scale work, this was used. By standard chlorination techniques the known 2,3,4,5,6-pentafluorobenzyl chloride and 2,3,4,5,6-pentafluorobenzylidene dichloride were prepared and were surprisingly easily fluorinated by a potassium fluoride exchange method to 2,3,4,5,6-pentafluorobenzyl fluoride (XVI) and

2,3,4,5,6-pentafluorobenzylidene difluoride (XVII) respectively. Preliminary attempts have been made to metallate these compounds with methyl lithium and it seems that methane is evolved. With n-butyl lithium nucleophilic attack at the para position of the ring occurred.

EXPERIMENTAL

General Fluorination Procedure

The compound, ground to a fine powder, was passed, in small portions, in a stream of nitrogen (2 ℓ./hr.), into a small stirred reactor containing cobaltic fluoride and maintained at 250-350°. When addition was complete, the reactor was purged with nitrogen (2 ℓ./hr.) for 2 hr. The product was collected in glass traps cooled in liquid air, and was worked up as described below.

Two reactors were used: initially an older reactor (A) of the general type described before (see Advances in Fluorine Chemistry, Volume 1, p. 166) constructed from a nickel tube (46 cm. x 4.4 cm. i/d.). It was heated electrically along its length and contained 180 g. of cobalt difluoride which was agitated by a rotating stirrer (4 revs./min.). Subsequently a newer reactor (B) was used. It was of similar design but had more refined controls and better stirring. It contained 150 g. of cobalt difluoride.

Fluorination of Aromatic Fluorocarbons

(a) 1,2-Bis(pentafluorophenyl)-octafluorocyclohexene (2 g.) (I) gave a compound (1.8 g.) b.p. >260°.

Calc. for $C_{18}F_{30}$: C, 27.5; H, 0%
Found: C, 27.3; H, 0.07%

The infrared spectrum showed a small double bond stretching frequency. The results are consistent with the product being 1,2-bis-(undecafluorocyclohexyl)-octafluorocyclohexene (III).

Fluorination of 1,2-bis(phenyl)-octafluorocyclohexene (2 g.) (II) gave an identical product (1.9 g.).

(b) 2',5'-Bis(trifluoromethyl)-dodecafluoro-p-terphenyl (2 g.) (VII) and 2',5'-bis(trifluoromethyl)-3',6'-difluoro-p-terphenyl (VIII) (2 g.) gave a compound (1.9 and 2.7 g. respectively) b.p. >>270° with an infrared spectrum consistent with a saturated fluorocarbon structure (IX).

Calc. for $C_{20}F_{36}$: C, 26.0; H, 0%
Found: C, 26.4; H, 0.3%

Calc. for $C_{20}F_{36}$ 924
M.W. (Mass spectrometry) 924.

This compound, on purification, gave a solid, m.p. ca. 10° which may be a mixture of conformational isomers (IX).

(c) 3',4'-Bis(trifluoromethyl)-dodecafluoro-o-terphenyl (2.0 g.) and 3',4'-bis(trifluoromethyl)-2',5'-difluoro-o-terphenyl (1.4 g.) (V) gave a saturated fluorocarbon (VI) (2.1 and 1.2 g. respectively) b.p. ca. 300° which does not solidify.

Calc. for $C_{20}F_{36}$: C, 26.0; H, 0%
Found: C, 26.0; H, 0%

Reaction of Decafluoro-p-xylene and 4-Lithiononafluorobiphenyl

A solution of n-butyl lithium in n-hexane (6.3 c.c., 0.16 g., BuLi/ml.) was rapidly added at -76° to a stirred solution of 4H-nonafluorobiphenyl (5.3 g.) in dry ether (100 c.c.). After 30 min., decafluoro-p-xylene (2.3 g.) in dry ether (50 c.c.) was added. The solution was warmed to -40° and stored at this temperature for 10 days. Water was then added and the solution allowed to attain room temperature, when dilute sulphuric acid (150 c.c.) was added. The ether layer and the combined extracts of the aqueous layer were dried ($MgSO_4$) and the ether distilled off to leave a white solid (1.0 g.) (X) m.p. 196° from EtOH.

Calc. for $C_{32}F_{26}$: C, 43.7; H, 0%
Found: C, 43.7; H, 0.0%

Reaction of Eicosafluoro-2",5"-bis(trifluoromethyl)-p-quinquephenyl with Oleum

Eicosafluoro-2",5"-bis(trifluoromethyl)-p-quinquephenyl (X) (0.5 g.) and fuming sulphuric acid (3.0 ml., 65% SO_3) were heated together in a sealed glass tube at 200° for 24 hr. The dark brown liquid produced was poured onto ice to give a buff precipitate (0.3 g.) which gave, on crystallisation from ethanol, white plates of eicosafluoro-2",5"-dicarboxy-p-quinquephenyl (XI) (0.1 g.), m.p. 219-220°.

Calc. for $C_{32}H_2F_{20}O_4$: C, 46.2; H, 0.2%
Found: C, 46.1; H, 0.2%

The infrared spectrum of the compound was consistent with its proposed structure.

Reaction of Phenyl Lithium with 1,2-Bis(pentafluorophenyl)-octafluorocyclohexene

Phenyl lithium (1.6 g., 0.019 mole) in dry ether (50 ml.) was added to 1,2-bis(pentafluorophenyl)-octafluorocyclohexene (I) (5.0 g., 0.009 mole) in dry ether (80 ml.), stirred under nitrogen at 15°. The solution was stirred under reflux for 4 hr., then the reaction flask was stoppered and kept at 15° for 7 days. The reaction mixture was then washed with 4N sulphuric acid (100 ml.), the washings were extracted with ether (2 x 100 ml.) and the ether distilled as before to leave a brown oil (5.6 g.). Chromatography of a portion of the oil (2.4 g.) on silica gel and elution with petroleum ether (b.p. 60-80°) gave (i) 1,2-bis(pentafluorophenyl)-octafluorocyclohexene (0.06 g.); (ii) a white solid crystallisation from ethanol gave colourless prisms of 1-pentafluorophenyl-2-(2',3',5',6'-tetrafluorobiphenylyl)-octafluorocyclohexene (XII) (0.08 g.), m.p. 80.5-81°.

Calc. for $C_{24}H_5F_{17}$: C, 46.7; H, 0.9%
Found: C, 46.7; H, 0.6%

The infrared, ultraviolet and ^1H and ^{19}F magnetic resonance spectra of the compound were consistent with the proposed structure.

(iii) A solid, which gave on crystallisation from ethanol colourless crystals of 1,2-bis(2',3',5',6'-tetrafluorobiphenylyl)-octafluorocyclohexene (XIII) (0.17 g.), m.p. 104-105°.

Calc. for $C_{30}H_{10}F_{16}$: C, 53.4; H, 1.5%
Found: C, 53.4; H, 1.5%

The spectral characteristics of the compound supported its structure.

Reaction of 2,3,4,5,6-Pentafluorotoluene with n-Butyl Lithium

(a) In tetrahydrofuran. A solution of n-butyl lithium in n-heptane (20 ml., 0.16 g., BuLi/ml.) was added as rapidly as possible to 2,3,4,5,6-pentafluorotoluene (9 g.) in dry tetrahydrofuran (THF) (100 ml.) at -78°. The deep orange solution was stirred at -78° for 5 min. and then carbon dioxide was bubbled through for 4 hr. Water (200 ml.) and dilute sulphuric acid (100 ml.) were added, followed by addition of ether (200 ml.). The organic layer was separated and washed with sodium bicarbonate solution (100 ml.). The latter was reacidified (sulphuric acid) and extracted with ether (2 x 100 ml.), the ether dried ($MgSO_4$) and distilled to leave an unidentified brown oil (0.4 g.). The original ether layer was dried ($MgSO_4$) and the solvents distilled off to yield a brown oil, fractional distillation of which gave 1-methyl-4-n-butyltetrafluorobenzene (XIV) (7.7 g.), b.p. 203°.

Calc. for $C_{11}H_{12}F_4$: C, 60.0; H, 5.4%
Found: C, 60.4; H, 5.3%

(b) In a similar experiment, but using ether as solvent, the same compound (7.5 g.) was obtained.

(c) In similar experiments, but using triethylene diamine (TED) to activate the toluene, the same product was obtained in similar yields.

Reaction of Bromomethylpentafluorobenzene with n-Butyl Lithium

A solution of n-butyl lithium in n-heptane (4.9 ml., 0.16 g., BuLi/ml.) was added to bromomethylpentafluorobenzene (3.2 g.) in THF (50 ml.) at -78°. A transitory yellow colour was observed followed by a white precipitate; after 1 hr. water (50 ml.) was added and the solution warmed to 15°. Ether (100 ml.) was added and the organic layer separated and dried ($MgSO_4$). Distillation of the solvent afforded a white crystalline solid (0.7 g.) believed from infrared and ^1H n.m.r. spectroscopy to be 1,2-bis(pentafluorophenyl)ethane (XV), m.p. 79-80°.

Preparation of Fluoromethylpentafluorobenzene (XVI)

Chloromethylpentafluorobenzene(2) (12 g.) was added with stirring to a suspension of dried potassium fluoride (10 g.) in dry dimethylformamide (DMF) (25 ml.). The mixture was stirred at 140° for 6 hr., cooled and the whole distilled in steam to yield a light green organic layer (8.0 g.) shown by g.l.c. to contain two components in the ratio 95:5. Further treatment of this layer with fresh potassium fluoride and DMF gave fluoromethylpentafluorobenzene (XVI) (4.5 g.), b.p. 134°.

Calc. for $C_7H_2F_6$: C, 42.0; H, 1.0%
Found: C, 42.3; H, 1.2%

Preparation of Difluoromethylpentafluorobenzene (XVII)

Dichloromethylpentafluorobenzene(2) (10.5 g.) was added to dried potassium fluoride (15 g.) in dimethylformamide (45 ml.). The mixture was stirred at 145° for 6.5 hr., then steam distilled to yield a dense liquid, distillation of which, from phosphorus pentoxide, afforded difluoromethylpentafluorobenzene (XVII) (7.8 g.), b.p. 125°.

Calc. for C_7F_7H: C, 38.5; H, 0.4%
Found: C, 38.5; H, 0.2%

The ^1H, ^{19}F n.m.r. spectra were consistent with the proposed structure.

Reaction of n-Butyl Lithium with Fluoromethylpentafluorobenzene

Addition of a solution of n-butyl lithium (0.8 g., 0.012 mole) in n-hexane (5 ml.) to fluoromethylpentafluorobenzene (2.0 g., 0.01 mole) in dry THF (80 ml.) under nitrogen at -78° produced a deep orange solution. Acetaldehyde (2.0 g., 0.08 mole) was added after 3/4 hr., and the solution was warmed to 15°. Water (50 ml.) and ether (150 ml.) were added to the solution, which was now colourless, and the ether layer was washed with 4N sulphuric acid (2 x 100 ml) and the washings extracted with ether (2 x 100 ml.). The ether layer and extracts were combined, dried ($MgSO_4$) and the ether distilled through a 6" column packed with glass helices to leave a brown liquid (4.7 g.). Separation by preparative g.l.c. (silicone gum, 150°, 15 ℓ. N_2/hr.) gave (i) ether; (ii) fluoromethylpentafluorobenzene; and (iii) 1-n-butyl-4-fluoromethyltetrafluorobenzene (0.3 g.).

Calc. for $C_{11}H_{11}F_5$: C, 55.5; H, 4.6%
Found: C, 55.7; H, 4.6%

The compound had infrared, ^1H and ^{19}F magnetic resonance spectra which were consistent with its structure.

Reaction of n-Butyl Lithium with Difluoromethylpentafluorobenzene

(a) A solution of n-butyl lithium (1.6 g., 0.055 mole) in n-hexane (10 ml.) was added to difluoromethylpentafluorobenzene (2.0 g., 0.0009 mole) in dry THF (80 ml.), stirred under nitrogen at -78°, producing a deep orange solution. The solution was warmed to 15° after 1/2 hr., and 4N sulphuric acid (50 ml.) was added after 2.5 hr. Ether (150 ml.) was added and the ether layer was then treated as above to give an orange liquid (6.0 g.). Analytical g.l.c. of the liquid (silicone gum, 150°) showed the presence of (i) n-hexane (30%), and (ii) an unknown with longer retention time (70%). This was separated by distillation and identified as 1-n-butyl-4-difluoromethyltetrafluorobenzene, b.p. 198-200°.

Calc. for $C_{11}H_{10}F_6$: C, 51.6; H, 3.9%
Found: C, 51.6; H, 3.6%

The ^1H and ^{19}F magnetic resonance spectra of the compound were consistent with its structure.

(b) Addition of a solution of n-butyl lithium (0.64 g., 0.01 mole) in n-hexane (4 ml.) to difluoromethylpentafluorobenzene (2.0 g., 0.009 mole) in dry THF (60 ml.) at -78° produced a deep orange solution as before. After 1/2 hr. a Gilman IIA colour test(1) on the solution for the presence of butyl lithium was negative and a stream of dry carbon dioxide was then passed into the solution for 1.5 hr. The solution was then warmed to 15° and water (50 ml.) and ether (150 ml.) were added. The ether layer was washed with 4N sulphuric acid (2 x 100 ml.) and sodium bicarbonate solution (2 x 100 ml.). The ether layer was dried ($MgSO_4$) and the ether distilled as before to give a brown liquid (2.0 g.) which was shown by analytical g.l.c. (silicone gum, 140°) to contain (i) n-hexane (31%); (ii) difluoromethylpentafluorobenzene (42%); and (iii) 1-n-butyl-4-difluoromethyltetrafluorobenzene (27%).

The alkaline extract was reacidified, extracted with ether (2 x 100 ml.) and the ether extract dried and the ether distilled to leave no residue.

Chromatography of the liquid on silica gel, eluted with petroleum ether (b.p. 60-80°) followed by dichloromethane gave no new material.

Reaction of Methyl Lithium with Difluoromethylpentafluorobenzene

Difluoromethylpentafluorobenzene (1.2 g., 0.0055 mole) in dry ether (100 ml.), freshly distilled from lithium aluminum hydride, was stirred under nitrogen in a three-necked flask at -78°. The flask was fitted with a nitrogen inlet tube, a dropping funnel and an outlet connected, through a silica gel drying tube, to a water-filled inverted burette to measure the volume of gas evolved in the flask. An ethereal solution of methyl lithium (4 ml., 1.5N) was added until evolution of gas suddenly ceased (120 ml., 0.0053 mole). A light blue colour developed in the solution and decafluoro-p-xylene (2.0 g., 0.0069 mole) was added after 2 hr. The flask was then stoppered and kept at -40° for 40 hr., then warmed to 15° and water (20 ml.) was added. The ether layer was then worked up in the usual way to give an orange liquid (2.7 g.).

Analytical g.l.c. (silicone gum, 80°) of the liquid showed the presence of (i) ether; (ii) decafluoro-p-xylene; (iii) difluoromethylpentafluorobenzene; and (iv) a small amount of an unknown component. Chromatography of the liquid on silica gel eluted with petroleum ether (b.p. 60-80°) gave no new material.

In a similar experiment iodine was added instead of decafluoro-p-xylene and the product found contained only ether, difluoromethylpentafluorobenzene and a small amount of the same unknown component.

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4. J. F. Eastham, C. G. Screttas. J.A.C.S. 1965, 87, 3276.
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PART V

FLUORINATED HETEROCYCLIC COMPOUNDS

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Introduction.

The object of this work is to make model compounds based on perfluoropyridine and in particular on acids and ethers derived from this source to see whether they, and consequently any polymers derived from them, are thermally and oxadatively stable.

Summary.

Tetrafluoroisonicotinic acid (I) has been dehydrated with trifluoroacetic anhydride to give tetrafluoroisonicotinic anhydride (II). The anhydride is unstable in air, being rapidly and exothermically hydrolysed.

Tetrafluoroisonicotinyl chloride (III) has now been prepared in much improved yield ($>60\%$) than previously.[1] It reacted with anhydrous methanol to give methyl tetrafluoroisonicotinate (IV).

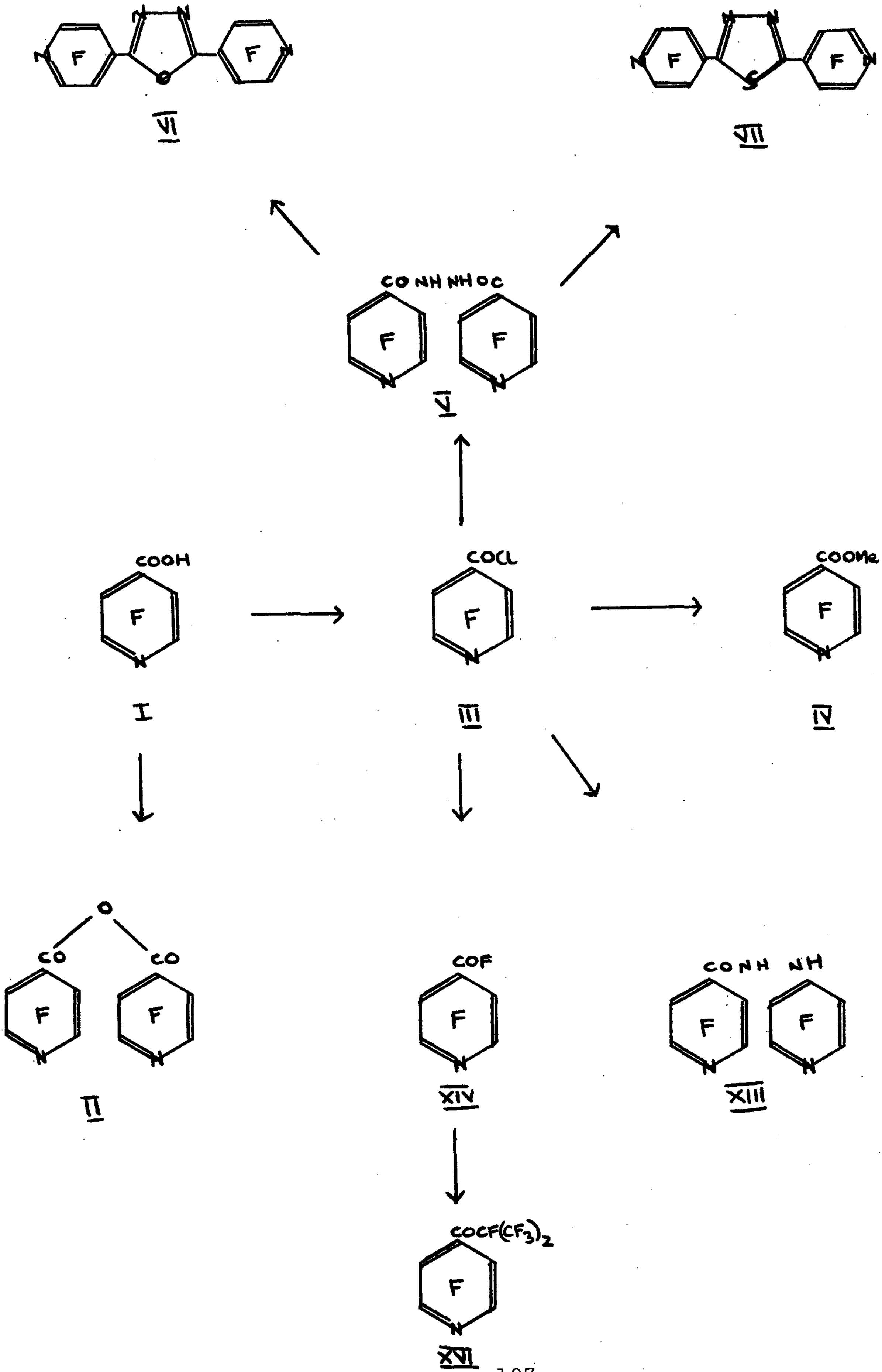
N,N'-bis(tetrafluoroisonicotinyl)hydrazine (V) has been prepared by the reaction between tetrafluoroisonicotinyl chloride and hydrazine hydrate in dilute sodium hydroxide solution. It has been converted into 2,5-bis-(tetrafluoro-4-pyridyl) -1,3,4-oxadiazole (VI) and 2,5-bis(tetrafluoro-4--pyridyl)-1,3,4-thiadiazole (VII) by reaction with phosphorus pentoxide and phosphorus pentasulphide respectively at elevated temperatures.

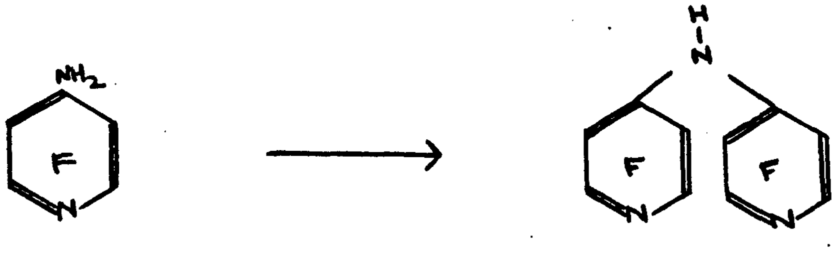
A number of amides and hydrazides have been prepared from pentafluorobenzoyl and tetrafluoroisonicotinyl chlorides. The amides are N-(tetrafluoro-4-pyridyl)pentafluorobenzamide (VIII) and N-(pentafluorophenyl)-pentafluorobenzamide (IX). Bis(tetrafluoro-4-pyridyl)amine (X) has been prepared by the reaction between the sodio derivative of 4-aminotetrafluoropyridine and pentafluoropyridine. It is required for use in the synthesis of tertiary amides.

The hydrazides are N'-(tetrafluoro-4-pyridyl)pentafluorobenzohydrazide (XI), N'-(pentafluorophenyl)pentafluorobenzohydrazide (XII) and N'-(tetrafluoro-4-pyridyl)tetrafluoroisonicotinohydrazide (XIII).

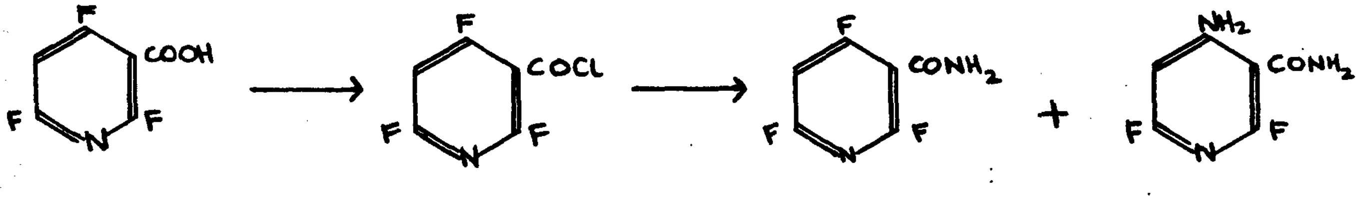
Tetrafluoroisonicotinyl and pentafluorobenzoyl chlorides have been reacted with freshly roasted potassium fluoride at elevated temperature to give tetrafluoroisonicotinyl (XIV) and pentafluorobenzoyl fluorides (XV) respectively. Other possible methods of preparation of these acid fluorides have been investigated. Perfluoro(4-pyridyl isopropyl)ketone (XVI) has been prepared by the fluoride ion catalysed reaction between tetrafluoroisonicotinyl fluoride and hexafluoropropene in acetonitrile at elevated temperature. A similar reaction using pentafluorobenzoyl fluoride yielded a mixture of perfluoro-(phenyl isopropyl) (XVII) and perfluoro-(4-isopropylphenyl isopropyl)ketones (XVIII). Under the same conditions the corresponding acid chlorides did not react with hexafluoropropene.

2,4,6-Trifluoronicotinyl chloride (XIX) has been prepared and has been reacted with anhydrous ammonia in benzene to yield a mixture of 2,4,6-trifluoronicotinamide (XX) and 4-amino-2,6-difluoronicotinamide (XXI).

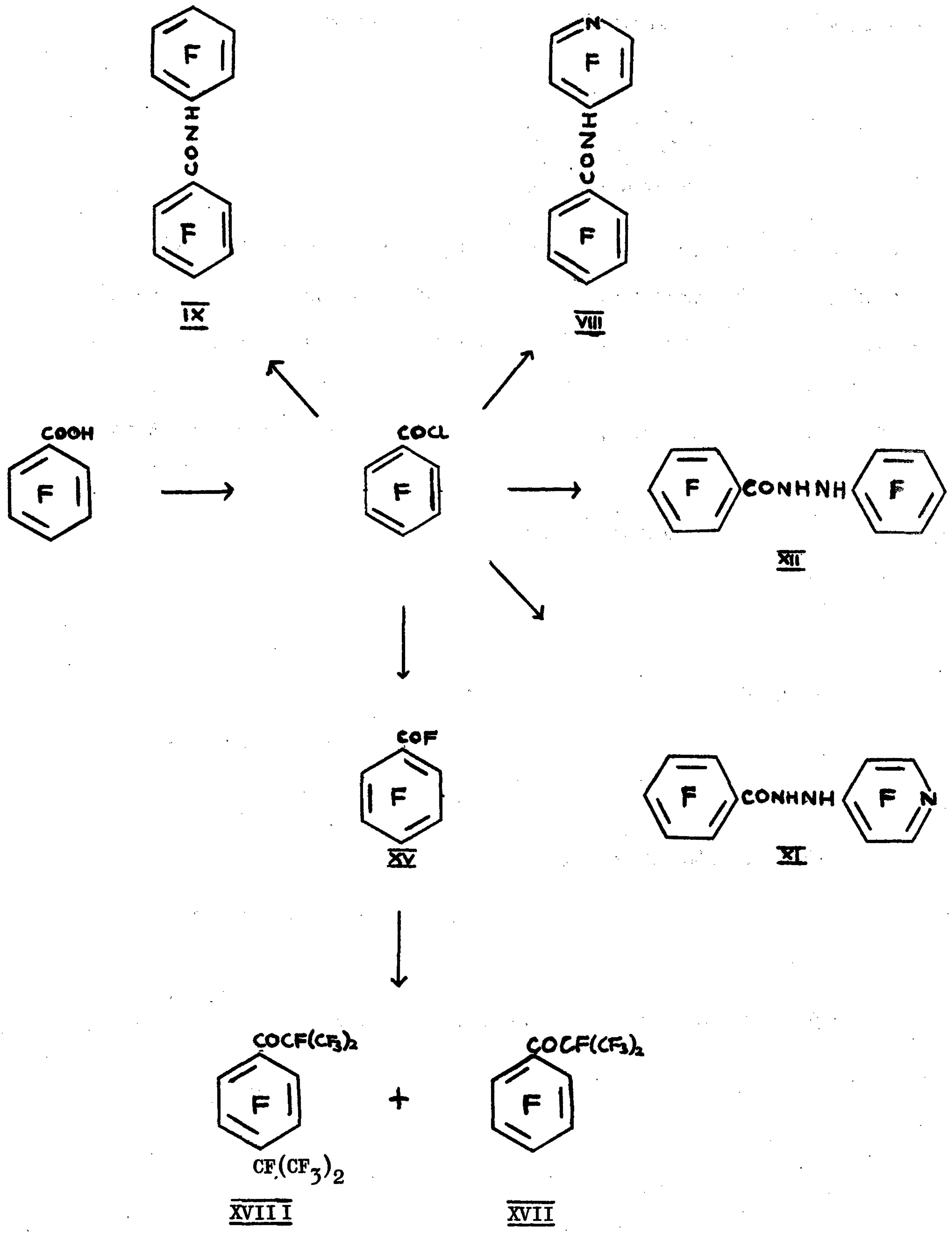

VI
VII
CONHNHOC
V
COOH
I
COCl
III
COOMe
IV
CO
O
CO
II
COF
XIV
CONH NH
XIII
COCF(CF3)2
XVI
F
N
S



X

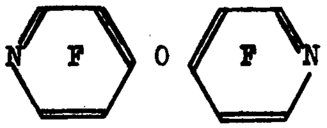


XIX XX XXI


CONH
IX
CONH
VIII
COOH
COCl
CONHNH
XII
COF
XV
CONHNH
XI
COCF(CF3)2
CF(CF3)2
XVIII
+
COCF(CF3)2
XVII

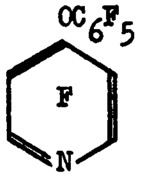
A slightly impure sample of octafluoro-4,4'-dipyridyl

XXII

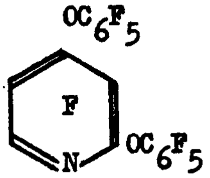


ether has been prepared by heating pentafluoropyridine and the potassium salt of tetrafluoro-4-hydroxypyridine in dry tetrahydrofuran as solvent in a sealed tube for 2 days. The following ethers have been prepared by refluxing potassium pentafluorophenate with either pentafluoropyridine, heptafluoroisoquinoline, 4-bromotetrafluoropyridine or octafluoro-4,4'-bipyridyl in dry tetrahydrofuran as solvent.

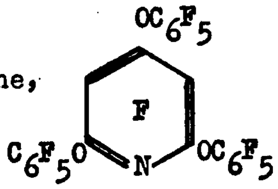
XXIII. 4-Pentafluorophenoxy-tetrafluoropyridine,



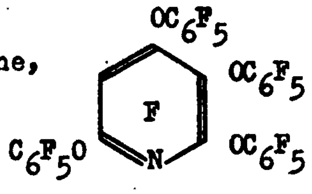
XXIV. 2,4-Di(pentafluorophenoxy)trifluoropyridine,



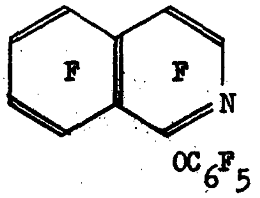
XXV. 2,4,6-Tri(pentafluorophenoxy)difluoropyridine,



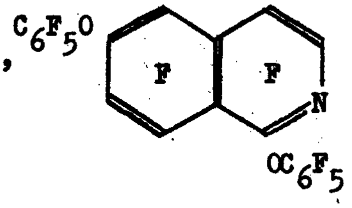
XXVI. 2,3,4,6-Tetra-(pentafluorophenoxy)-fluoropyridine,



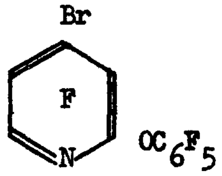
XXVII. Pentafluorophenoxy-hexafluoroisoquinoline,



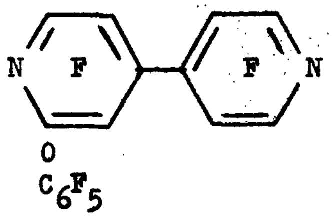
XXVIII. Dipentafluorophenoxy-pentafluoroisoquinoline,



XXIX. 4-Bromo-2-pentafluorophenoxytrifluoropyridine,

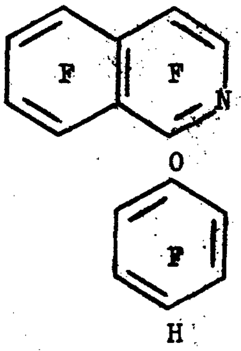


XXX. 2-Pentafluorophenoxy-heptafluoro-4,4'-bipyridyl,



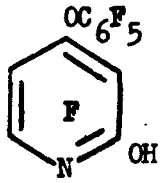
Reaction of heptafluoroisoquinoline and potassium 2,3,5,6-tetrafluorophenate dihydrate in refluxing tetrahydrofuran yielded:-

XXXI. 2',3',5',6'-Tetrafluorophenoxy-hexafluoroisoquinoline,

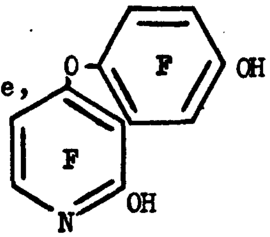


Two hydroxy-derivatives of 4-pentafluorophenoxytetrafluoropyridine have been prepared by refluxing this ether with twofold and fourfold molar amounts of potassium hydroxide in t-butanol:-

XXXII. 2-Hydroxy-4-pentafluorophenoxy-trifluoropyridine,

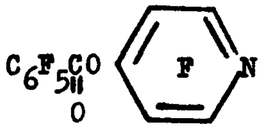


XXXIII. 2,4'-Dihydroxy-4-tetrafluorophenoxy-trifluoropyridine,

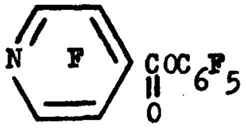


The following esters have been prepared by refluxing the corresponding phenol and acid chloride in dry benzene with N,N-diethylaniline.

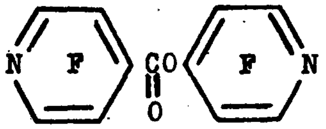
XXXIV. 4-Pentafluorophenoxy-tetrafluoropyridine,



XXXV. Tetrafluoroisonicotinyloxy-pentafluorobenzene,



XXXVI. Tetrafluoroisonicotinyloxy-tetrafluoropyridine,



The structures of some of these compounds are tentative and rest on the assumption that the reactions expected of the fluorinated heterocyclic compounds have occurred.

Compounds XXV, XXVI and XXXIV have been sent for thermal stability tests and the results appear in Appendix IIA, Table 7.

Compounds VI and XXXV will be sent for testing in the near future.

Discussion.

Derivatives of Fluorinated Acids.

Considerable difficulty was encountered in the attempted preparation of tetrafluoroisonicotinyl chloride from tetrafluoroisonicotinic acid using thionyl chloride. Indeed strong evidence was later obtained to show that the product from this reaction was tetrafluoroisonicotinic anhydride (impure).[2] It was therefore decided to prepare tetrafluoroisonicotinic anhydride and use this in place of the acid chloride in the synthesis of hydrazides. The anhydride was readily obtained in reasonable yield (40%) by heating tetrafluoroisonicotinic acid and trifluoroacetic anhydride together under reflux for 5 hrs. Unfortunately it is rapidly and exothermically hydrolysed back to tetrafluoroisonicotinic acid which precluded its use in the synthesis of hydrazides.

On gently warming a stirred mixture of tetrafluoroisonicotinic acid and phosphorus pentachloride a vigorous reaction occurred with rapid evolution of hydrogen chloride. When this initial reaction had subsided the resulting liquid was heated under reflux for 1 hour. Tetrafluoroisonicotinyl chloride was then obtained in 60% yield by distillation under reduced pressure through a Vigreux column. This acid chloride was readily converted into methyl tetrafluoroisonicotinate by heating with anhydrous methanol for a short time.

N,N'-bis(tetrafluoroisonicotinyl)hydrazine has been prepared by the reaction between tetrafluoroisonicotinyl chloride and hydrazine hydrate in dilute sodium hydroxide solution, a method which was used for the preparation of N,N'-bis(pentafluorobenzoyl)hydrazine.[3] The yield was almost 60%. This hydrazine underwent a cyclodehydration reaction on heating to 210° for 5 hrs. with phosphoric oxide, yielding 2,5-bis(tetrafluoro-4-pyridyl)-1,3,4-oxadiazole. The yield of crude product was almost quantitative but purification by recrystallisation from methylated spirits considerably reduced the yield of pure material. The hydrazine and phosphorus pentasulphide on heating together under reflux in xylene for 41 hrs. gave 2,5-bis-(tetrafluoro-4-pyridyl)-1,3,4-thiadiazole. The yield of pure material was again poor (16%).

N-(Tetrafluoro-4-pyridyl)pentafluorobenzamide and N-(pentafluorophenyl)-pentafluorobenzamide have been prepared by the reaction of pentafluorobenzoyl chloride with 4-aminotetrafluoropyridine and pentafluoroaniline respectively. The yields were 80·7% and 72·2%. 4-Aminotetrafluoropyridine has been shown to react readily with sodium hydride in tetrahydrofuran to give a sodio derivative which reacts with pentafluoropyridine to give bis-(tetrafluoro-4-pyridyl)amine, the overall yield being 52·7%. This amine is required for the synthesis of tertiary amides.

Pentafluorobenzoyl chloride reacted exothermically with 4-hydrazinotetrafluoropyridine in benzene at room temperature. The reaction was completed by heating under reflux for 1 hr. On cooling the solution went solid. It was stirred with N-hydrochloric acid for 30 mins. and then the solid filtered off, washed with water, dried, and recrystallised from aqueous methylated spirits to give white crystals of N'-(tetrafluoro-4-pyridyl)pentafluorobenzohydrazide in 61·5% yield. A similar reaction between pentafluorobenzoyl chloride and pentafluoroaniline gave N'-(pentafluorophenyl)pentafluorobenzohydrazide in excellent yield (90·7%). When, however, tetrafluoroisonicotinyl chloride and 4-hydrazinotetrafluoropyridine were reacted together and the reaction mixture stirred with N-hydrochloric acid, no precipitate was obtained. The mixture was therefore extracted with ether, the extracts dried ($MgSO_4$) and the ether distilled off leaving a white solid which, after purification by sublimation under high vacuum, was shown to be N'-(tetrafluoro-4-pyridyl)tetrafluoroisonicotinohydrazide. The yield was poor - 23·3%.

Considerable difficulty has been experienced in repeating experiments for the preparation of tetrafluoroisonicotinyl fluoride from tetrafluoroisonicotinyl chloride. Points which had to be borne in mind were (a) it would be advantageous to use the acid chloride as soon as it was made so as to reduce the danger of hydrolysis. Since the only convenient method of assessing the purity of the acid chloride was elemental analysis, which could take up to a few days, this meant that acid chloride of unknown purity would be used. Also it appears (from elemental analysis) that a very narrow boiling range is no indication of purity, (b) the danger of the acid chloride decomposing would be minimised by keeping the temperature as low as possible. Since this would almost certainly lead to a reduction in reaction rate, a compromise would have to be reached.

In the first experiment carried out tetrafluoroisonicotinyl chloride and freshly roasted potassium fluoride (ratio by weight 1:2) were placed in a Carius tube which was evacuated, sealed, and then heated to 210° for 40 hrs. Pure tetrafluoroisonicotinyl fluoride was obtained in 65% yield. However in further attempts to prepare the acid fluoride incomplete reaction occurred, approximately equal amounts of starting material and product being obtained. In an attempt to overcome this the reaction was carried out in a stainless steel autoclave at 190° for 15 hrs., then at 225° for 7 hrs., a greater ratio of potassium fluoride to acid chloride (5:1) being used. 2,3,5,6-Tetrafluoropyridine was the rather unexpected product which was obtained from this reaction. It was obtained in 66% yield and was presumably formed by decarboxylation of either tetrafluoroisonicotinic acid or its potassium salt which would be formed by hydrolysis of the acid chloride. This was confirmed by heating together tetrafluoroisonicotinic acid and potassium fluoride in a sealed tube at 190° for 15 hrs. and then at 210° for 5 hrs., 2,3,5,6-tetrafluoropyridine being obtained in 85% yield. It was then decided to try and push the fluorination reaction to completion by carrying it out at a higher temperature, although this would increase the possibility of decomposition. The reaction was carried out in an evacuated, sealed Carius tube at 260° for 40 hrs. Acid fluoride, which contained no detectable amount of acid chloride (by infra-red spectrum), was obtained in 72% yield. Repetition of this experiment using a lower ratio of potassium fluoride to acid chloride (3:1 instead of 8:1) gave pure acid fluoride in 50% yield. A further preparation using the above conditions but on a larger scale gave only 50% conversion. However the acid chloride used in this reaction had a 4° boiling range and was analytically quite impure whereas that used in the previous two reactions had a narrower boiling range -2°.

From the above results it appears that this fluorination reaction can be affected quite profoundly by impurities (e.g.,phosphorous oxychloride and phosphorus pentachloride) in the acid chloride. It seems however that if only analytically pure acid chloride is used, then the reaction will go to completion.

Pentafluorobenzoic acid is available commercially and was used to prepare pentafluorobenzoyl chloride which was reacted with anhydrous potassium fluoride at elevated temperature to give pentafluorobenzoyl fluoride in high yield. The corresponding tetrafluoroisonicotinyl halides are only prepared from the commercially available pentachloropyridine by a multi-stage synthesis.[4,5] Since it is reasonable to assume that the corresponding chlorides and fluorides will behave similarly, it was decided to use the more readily available pentafluorobenzoyl halides in order to establish experimental conditions for reactions which have been proposed in this present programme. The corresponding tetrafluoroisonicotinyl halide can then be used under the established experimental conditions. In this way a considerable saving in time and effort can be achieved.

Pentafluorobenzoyl fluoride was prepared by reacting pentafluorobenzoyl chloride and anhydrous potassium fluoride (large excess) together in an evacuated, sealed glass tube at 250° for 48 hrs. The product was isolated by vacuum transfer followed by distillation under reduced pressure. Yields were high, the best being 88·6%. When the process was scaled up however, yields were poor because it became very difficult to free the product from the large amount of potassium fluoride present during the vacuum transfer operation.

It was therefore decided to investigate other possible methods of preparation of the acid fluoride. α-Fluoroamines have been used to convert carboxylic acids to acid fluorides in good yields,[6] and so 1-chloro-1,2,2-trifluorotriethylamine was prepared in order to try the method. In the first reaction the α-fluoroamine was added to the acid at room temperature. Little reaction occurred, so the reactants were heated to 85° for 2 hrs. Distillation under reduced pressure of the liquid obtained yielded only a small amount of pentafluorobenzoyl fluoride. Repetition of the reaction at 100° for 4 hrs. gave no acid fluoride.

Potassium fluoride in sulpholane has been widely used to replace chlorine by fluorine and it was thought that it might be successful in this case. Pentafluorobenzoyl chloride was heated with potassium fluoride (100% excess) in sulpholane to 160° for 24 hrs. Removal of the solid by filtration gave a liquid which, after distillation under reduced pressure, was shown by infrared spectroscopy to be an approximately 50/50 mixture of pentafluorobenzoyl chloride and fluoride. If the reaction is repeated at a higher temperature with a longer reaction time a successful conversion may be achieved.

A convenient synthesis of perfluoroisopropyl ketones, $(CF_3)_2CFCOR_f$, by the fluoride ion catalysed addition of a fluoroacyl fluoride to hexafluoropropene using acetonitrile as solvent has been described.[7] The group R_f was a perfluoroalkyl group. This reaction has now been extended to cases where R_f is a perfluoroaryl group. Thus pentafluorobenzoyl fluoride and hexafluoropropene (50% excess) when heated together and <u>shaken</u> in acetonitrile, in the presence of a catalytic amount of potassium fluoride, at 135° for 36 hrs. yield a mixture of perfluoro(phenyl isopropyl)ketone (35%) and perfluoro-(4-isopropylphenyl isopropyl)ketone (65%). The reaction is thought to proceed via a fluorocarbanion intermediate which is formed by the reversible addition of a fluoride ion to the fluoro-olefin. Reaction between this anion and the acyl fluoride at its highly electrophilic carbonyl group, either by direct displacement or addition-elimination, would yield the fluoro ketone and fluoride ion

$$F^- + CF_3CF{=}CF_2 \longrightarrow (CF_3)_2CF^-$$

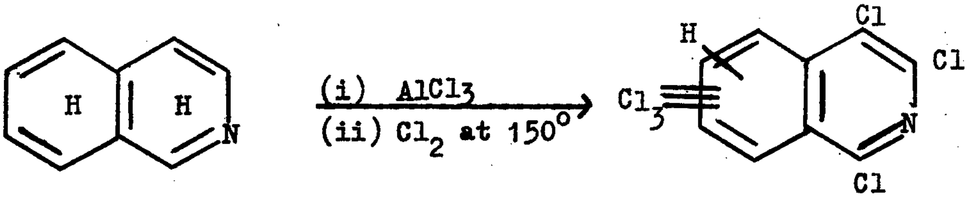
$$(CF_3)_2CF^- + R_fCOF \longrightarrow (CF_3)_2CFCOR_f + F^-$$

This mechanism explains the formation of two products in the above reaction. Perfluoro(phenyl isopropyl)ketone is formed first. The para fluorine atom in this compound is more susceptible, than the one in pentafluorobenzoyl fluoride, to nucleophilic substitution since the $-COCF(CF_3)_2$ group is more powerfully electron attracting than the $-COF$ group, and is readily replaced by the heptafluoroisopropyl anion giving perfluoro-(4-isopropylphenyl isopropyl)ketone. The above theory is supported by the fact that, under the same conditions pentafluorobenzoyl chloride does not react with hexafluoropropene. Under similar conditions tetrafluoroisonicotinyl fluoride gave a single product, perfluoro-(4-pyridyl isopropyl)ketone. When tetrafluoroisonicotinyl chloride was used as the reactant it was recovered unchanged. The extension of the above reaction to the preparation of fluoroaromatic isopropyl diketones from fluoroaromatic di-acyl fluorides will be investigated.

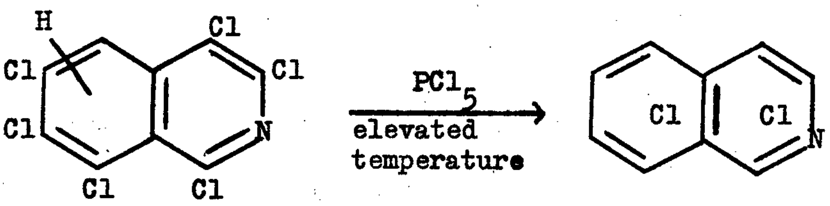
2,4,6-Trifluoronicotinic acid[8] reacted readily with phosphorus pentachloride to yield 2,4,6-trifluoronicotinyl chloride. The acid chloride was not analytically pure. Reaction with anhydrous ammonia in benzene gave a mixture of 2,4,6-trifluoronicotinamide and 4-amino-2,6-difluoronicotinamide. The mixture was not separated but elemental analysis indicated a mixture of the two compounds and mass spectral analysis confirmed this. This result contrasts with the product obtained previously when 2,4,6-trifluoronicotinic acid was reacted with thionyl chloride and the resulting product treated with anhydrous ammonia in benzene to give only 4-amino-2,6-difluoronicotinamide.[9] We have shown that tetrafluoroisonicotinic acid reacts with thionyl chloride to give what is almost certainly tetrafluoroisonicotinic anhydride,[2] and it is equally likely that thionyl chloride and 2,4,6-trifluoronicotinic acid react similarly to give 2,4,6-trifluoronicotinic anhydride. If this is so then the different results obtained above can be rationalised as follows: In 2,4,6-trifluoronicotinic anhydride there is presumably little difference in reactivity, towards the nucleophile ammonia, between the labile 4-fluorine atom and the acyl carbon atom and substitution occurs equally at both places giving only one product i.e. 4-amino-2,6-difluoronicotinamide. However in 2,4,6-trifluoronicotinyl chloride the acyl carbon atom is slightly more reactive than the 4-fluorine atom and substitution takes place there preferably, resulting in a mixture of products being obtained.

Fluorinated Ethers.

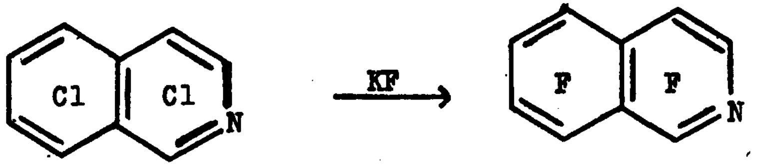
Heptafluoroisoquinoline has been prepared by the following method[10]:- hexachloroisoquinoline was prepared, in yields as high as 87% by the chlorination, with a vast excess of chlorine, at 150° of the complex formed between isoquinoline (1·23 moles) and aluminium chloride (3·75 moles).



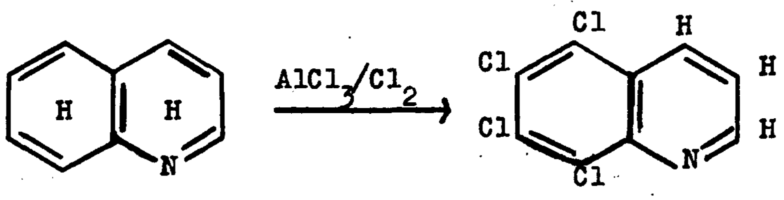
Its structure has not yet been determined. Further chlorination of this product with phosphorus pentachloride in an autoclave at elevated temperatures gave good yields (up to 68%) of heptachloroisoquinoline.

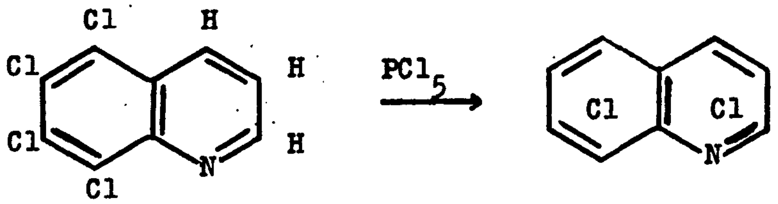


Heptafluoroisoquinoline and 4-chlorohexafluoroisoquinoline were prepared from heptachloroisoquinoline by the action of anhydrous potassium fluoride on heptachloroisoquinoline in an autoclave at elevated temperature.



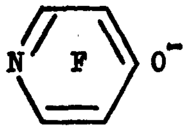
Heptafluoroquinoline is being prepared by a method similar to that used for the preparation of heptafluoroisoquinoline.[11] The complex formed between quinoline and aluminium chloride was chlorinated with a large excess of chlorine at 140-160°. Good yields (up to 81%) of a mixture which was essentially tetrachloroquinoline together with a little pentachloroquinoline were obtained. Further chlorination of this mixture with phosphorus pentachloride in an autoclave at elevated temperatures gave good yields (up to 78%) of heptachloroquinoline.





Heptafluoroquinoline and two other highly fluorinated quinolines, one of which has been shown to be a monochlorohexafluoroquinoline, will be prepared by the action of anhydrous potassium fluoride on the heptachloroquinoline.

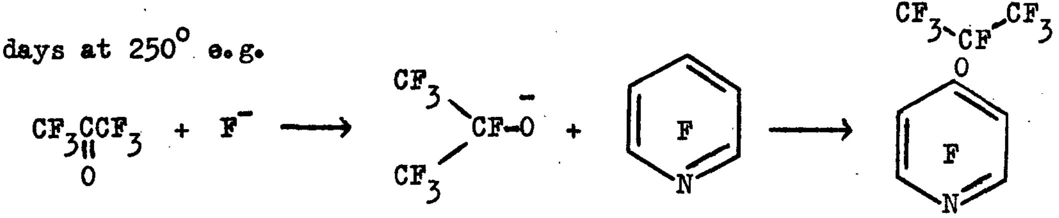
The general method of making ethers of the type shown in the summary is to reflux pentafluoropyridine or heptafluoroisoquinoline with the potassium salt of the phenol in the required molar proportions until no more potassium fluoride is precipitated. Enough tetrahydrofuran is used to dissolve completely the potassium salt of the phenol. At the end of the reflux period the reaction mixture is poured into an excess of water. If the product is a solid it is filtered off, dried, and purified by vacuum sublimation and recrystallisation from a suitable solvent. If the product is an oil it is extracted into ether, the ethereal layer separated and dried ($MgSO_4$) and then the ether is removed by evaporation to leave the product. The product is purified either by distillation or by preparative scale gas-liquid chromatography.

In this way and using pentafluorophenol from which to prepare the potassium salt, 4-pentafluorophenoxy-tetrafluoropyridine, 2,4-dipentafluorophenoxy-trifluoropyridine, 2,4,6-tripentafluorophenoxy-difluoropyridine and 2,3,4,6-tetrapentafluorophenoxyfluoropyridine have been prepared from pentafluoropyridine by reacting it with one, two, three, and approximately four molar proportions of the potassium pentafluorophenate. 1-Pentafluorophenoxy-hexafluoroisoquinoline and 1,6-dipentafluorophenoxy-pentafluoroisoquinoline have been prepared from heptafluoroisoquinoline by reacting it with one and two molar proportions of potassium pentafluorophenate. Using 4-hydroxytetrafluorobenzene from which to prepare the potassium salt 2',3',5',6'-tetrafluorophenoxy-1-hexafluoroisoquinoline has been prepared. 2-Pentafluorophenoxyheptafluoro-4,4'-bipyridyl and 4-bromo-2-pentafluorophenoxy-trifluoropyridine have been prepared by reacting octafluoro-4,4'-bipyridyl and 4-bromotetrafluoropyridine with an equimolar amount of potassium pentafluorophenate. Attempts to prepare octafluoro-4,4'-dipyridyl ether and undecafluoro(pyridyl-isoquinolyl)ether using the above general method with either the anhydrous or hydrated potassium salt of tetrafluoro-4-hydroxypyridine and either pentafluoropyridine or heptafluoroisoquinoline were not successful. Only product in very low yield or unchanged starting material was obtained. The nitrogen atom para to the oxygen in the potassium salt of tetrafluoro-4-hydroxypyridine must remove more negative charge from the oxygen into the ring than would a para fluorine atom in the $C_6F_5O^-$ anion thus making the  a less effective nucleophile. An attempt to prepare undecafluoro(pyridyl-isoquinolyl) ether by refluxing heptafluoroisoquinoline and the potassium salt of tetrafluoro-4-hydroxypyridine in dimethylformamide was unsuccessful. The reaction product was an intractable tar. Dimethylformamide, unless specially purified, slowly decomposes to give dimethyl amine and at its boiling point serves as a source of this compound;[12] the failure of this reaction could be due to the reaction of dimethylamine with heptafluoroisoquinoline.

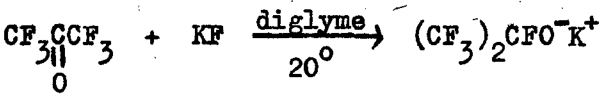
It has now been found possible to prepare octafluoro-4,4'-dipyridyl ether in fair yield by heating equi-molar amounts of pentafluoropyridine and the potassium salt of tetrafluoro-4-hydroxypyridine in a sealed tube with dry tetrahydrofuran at 150° for 48 hours. The preparation differs from previous attempts in that a higher temperature was made possible by carrying it out in a sealed tube. The analysis of the isolated reaction product was not perfect but, when more of this product can be prepared, redistillation should yield a really pure sample.

An unsuccessful attempt has been made to prepare 2-pentafluorophenoxy-tetrafluoropyridine by heating 4-bromo-2-pentafluorophenoxy-trifluoropyridine with potassium fluoride in sulpholan at 200° for 4 hours. The reaction will be repeated using caesium fluoride instead of potassium fluoride with a higher reaction temperature.

Attempts to prepare fluorinated ethers, using a method recently discovered here,[13] were not successful. Unreacted starting materials were recovered after either pentafluoropyridine, 3,5-dichlorotrifluoropyridine, or octafluorotoluene, a slight excess of hexafluoroacetone, caesium or potassium fluoride and sulpholan were heated together in a Carius tube, for up to 6 days at 250° e.g.



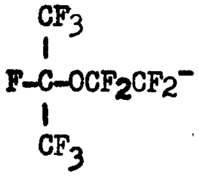
Perhaps a wrong choice of solvent has been made. Sulpholan was found to be the best solvent for the reaction of polyfluoro aromatic compounds in the presence of fluoride ion, but is not necessarily a suitable solvent when an oxy-anion rather than a carbanion is the attacking nucleophile. Hexafluoroacetone will form a soluble adduct with potassium fluoride or caesium fluoride in diglyme at 20°.[14,15]



$$CF_3\underset{O}{\overset{\|}{C}}CF_3 + KF \xrightarrow[20^\circ]{\text{diglyme}} (CF_3)_2CFO^-K^+$$

Possibly pentafluoropyridine would react with this adduct in diglyme solution at an elevated temperature in a sealed tube and such an experiment is planned for the future. When the reactions, described above, were carried out using sulpholan as solvent and potassium or caesium fluoride as source of fluoride ion, solution of the metal fluoride did not occur; this probably indicates that little or none of the perfluoroisopropoxide ion had been formed.

It has recently been found that tetrafluoroethylene, in the presence of a suitable metal fluoride-polar solvent combination, will condense with certain perfluoroketones to yield the corresponding perfluoro tertiary alcohols.[15] For example, hexafluoroacetone was added to a slurry of caesium fluoride in diglyme. The ketone and caesium fluoride form a soluble complex.

Subsequent addition of tetrafluoroethylene produced the perfluoro-t-pentyl alcohol. No evidence of formation of the anion  $F-C(CF_3)_2-OCF_2CF_2^-$ was found.

The reaction producing the alcohol involves attack by the anion $CF_3CF_2^-$, derived from tetrafluoroethylene and caesium fluoride, upon the equilibrium concentration of the ketone. Thus it would seem that the $(CF_3)_2CFO^-$ anion is a much weaker nucleophile than the $(CF_3)_2CF^-$ anion towards pentafluoropyridine. Reaction occurred between pentafluoropyridine and hexafluoropropene in sulpholan after 14 hours at 120°.[13] Reaction conditions using the $(CF_3)_2CFO^-$ will have to be more forcing than these and potassium or caesium fluoride in diglyme as solvent will have to be used with a longer period of heating at a higher temperature. Using a compound more activated towards nucleophilic substitution than pentafluoropyridine, e.g., heptafluoroisoquinoline or heptafluoroquinoline would promote reaction.

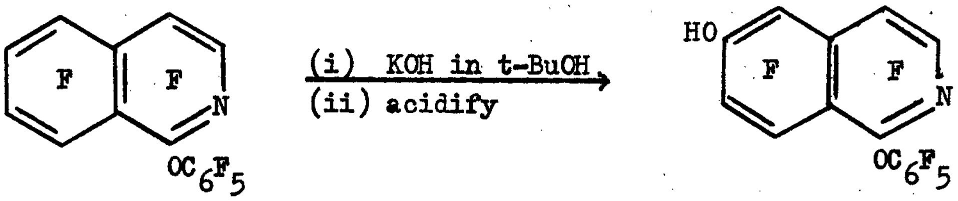
Fluorinated Hydroxyethers.

Hydroxy-derivatives derived from two monoethers have been prepared for the following reasons:-

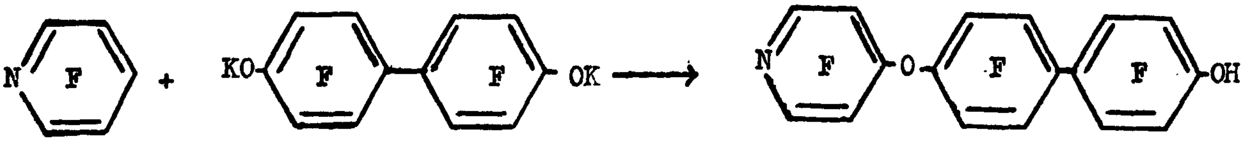
1. A good analysis has not been obtained for 4-pentafluorophenoxytetrafluoropyridine and so preparation of a pure derivative was required.
2. Mixed ethers of higher molecular weight could be prepared from the potassium salts of the hydroxy ethers.
3. As the ethers become more complicated in structure the interpretation of the nuclear magnetic resonance spectra becomes more difficult. It is easier, for example, to deduce where a hydroxyl group is substituted in 4-pentafluorophenoxytetrafluoropyridine than a pentafluorophenoxy-group. Assuming that both nucleophiles enter the same position, this technique could be helpful in interpreting the spectra of more complicated examples.

Mono- and dihydroxy derivatives of 4-pentafluorophenoxytetrafluoropyridine have been prepared by reacting this compound with a two- or four-fold molar amount of potassium hydroxide in refluxing t-butanol. Acidification yielded the hydroxy derivatives in good yield.

1-Pentafluorophenoxy-hexafluoroisoquinoline has been reacted with a two-fold molar quantity of potassium hydroxide in refluxing t-butanol. A solid product has been obtained on acidification, which, as yet, has resisted purification. The reaction could be:-



Pentafluoropyridine has been reacted with an equimolar amount of the dipotassium salt of octafluoro-4,4'-dihydroxybiphenyl in refluxing tetrahydrofuran. A solid was precipitated on acidification which, although it has been purified by recrystallisation, did not give the analytical results required for the reaction:



FLUORINATED ESTERS.

Preparation of Starting Materials.

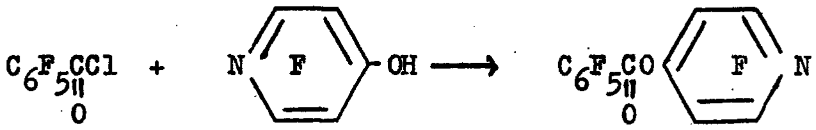
Pentafluorobenzoyl chloride[16] and tetrafluoroisonicotinyl chloride (page 130 of this report) have been prepared by heating the acids with phosphorus pentachloride.

4-Hydroxytetrafluoropyridine has been prepared by refluxing pentafluoropyridine with aqueous sodium hydroxide solution. 1-Hydroxyhexafluoroisoquinoline[17] and 4,4'-dihydroxyoctafluorobiphenyl[18] have been prepared by reacting heptafluoroisoquinoline and decafluorobiphenyl respectively with potassium hydroxide in t-butanol.

Esters

The preparation of a fully fluorinated ester by the reaction between the acid and the phenol in the presence of trifluoroacetic anhydride[19] has not been successful. Tetrafluoroisonicotinic acid and pentafluorophenol in equimolar amounts were heated with an excess of trifluoroacetic anhydride at 60°. The work up of the reaction mixture yielded a 90% recovery of tetrafluoroisonicotinic acid and 0·1 g. of an oil. Gas-liquid chromatography showed that the oil was a mixture of four components. Purification was not attempted.

Fully fluorinated esters have been prepared by reacting a hydroxy-derivative with an acid chloride in benzene containing N,N-diethylaniline,[20] for example:-



Reasonably pure specimens of the following esters have been prepared:-

(a) 4-Pentafluorobenzoyloxy-tetrafluoropyridine from tetrafluoro-4-hydroxypyridine and pentafluorobenzoyl chloride.

(b) Tetrafluoroisonicotinyloxy-pentafluorobenzene from pentafluorophenol and tetrafluoroisonicotinyl chloride.

(c) 4-Tetrafluoroisonicotinyloxy-tetrafluoropyridine from tetrafluoro-4-hydroxypyridine and tetrafluoroisonicotinyl chloride.

Impure specimens of the following esters have been prepared:-

(d) 1-Pentafluorobenzoyloxy-hexafluoroisoquinoline from hexafluoro-1-hydroxyisoquinoline and pentafluorobenzoyl chloride.

(e) 1-Tetrafluoroisonicotinyloxy-hexafluoroisoquinoline from hexafluoro-1-hydroxyisoquinoline and tetrafluoroisonicotinyl chloride.

(f) 4,4'-Ditetrafluoroisonicotinyloxy-octafluorobiphenyl from 4,4'-dihydroxyoctafluorobiphenyl and tetrafluoroisonicotinyl chloride.

It has not been possible to purify the solid esters (d), (e) and (f). No solvent has been found suitable for the recrystallisation of these esters as they are as insoluble in the hot as the cold for a large range of solvents and sublimation is ineffective as a means of purification. They are reasonably soluble in benzene and it is hoped that this will permit purification by chromatography on an alumina column.

Experimental

Tetrafluoroisonicotinic anhydride, II

Tetrafluoroisonicotinic acid (1·7 g.) and trifluoroacetic anhydride (4 ml.) were heated together under reflux for 5 hrs. Distillation under reduced pressure (0·05 mm.) gave, after removal of excess trifluoroacetic acid and anhydride, a clear liquid (0·65 g., 40·1%). This was redistilled to give TETRAFLUOROISONICOTINIC ANHYDRIDE, b.p. 110–110·5° at 0·05 mm.

Calc. for $C_{12}F_8N_2O_3$	C: 38·7;	F: 40·9
Found:	C: 38·8;	F: 40·3

The mass spectrum was consistent with the proposed structure.

Tetrafluoroisonicotinyl chloride, III

Tetrafluoroisonicotinic acid (10 g.) and phosphorus pentachloride (12·2 g.; 10% excess) were stirred together. On slight warming a vigorous reaction occurred with rapid evolution of hydrogen chloride. When the reaction had moderated the solution was heated under reflux for 1 hr. On cooling and standing at room temperature for 1 hr., the excess phosphorus pentachloride crystallised out. The liquid product (19·65 g.) was decanted off and distilled under reduced pressure (13 mins.) through a Vigreux column to yield two fractions

(1) b.p. 16–42°.

(2) b.p. 42–43°, 6·70 g.

The yield of acid chloride (based on wt. of fraction (2)) was 61·2%. However the infra-red spectrum of fraction (1) showed the presence in it of acid chloride

Calc. for C_6F_4ClNO	C: 33·7;	F: 35·6;	Cl: 16·6
Found:	C: 33·4;	F: 35·8;	Cl: 16·7

Methyl tetrafluoroisonicotinate, IV

Tetrafluoroisonicotinyl chloride (3·8 g.) and anhydrous methanol (12 ml.) were heated under reflux for 30 mins. Excess methanol was distilled off leaving a slightly cloudy liquid (3·0 g.). Distillation gave a clear liquid (2·75 g., 80·6%). This was redistilled to yield METHYL TETRAFLUOROISONICOTINATE b.p. 182-182·5°, identified by analysis and its proton N.M.R., mass and infra-red spectra.

Calc. for $C_7H_3F_4NO_2$ C: 40·3; H: 1·44; F: 36·4

Found: C: 40·2; H: 1·45; F: 36·0

N,N'-Bis(tetrafluoroisonicotinyl)hydrazine, V

Tetrafluoroisonicotinyl chloride (5 g.) was added to a stirred solution of N sodium hydroxide (25 ml.) and followed immediately by the dropwise addition of hydrazine hydrate (1·15 ml.) in water (2 ml.). A vigorous exothermic reaction occurred and a white solid appeared. After a further 30 mins. stirring at room temperature the reaction mixture went almost completely solid. Water (10 ml.) was added and the mixture stirred for a further 15 mins. The white solid was filtered off and washed with water. Acidification of the filtrate gave no precipitate. The white solid was dried at 110° for 1 hr. (2·67 g., 59·6%). Recrystallisation twice from aqueous methanol (once in the presence of charcoal) yielded white needles of N,N'-BIS(TETRAFLUOROISONICOTINYL)HYDRAZINE, decomp. 250-262°, identified by elemental analysis and its mass, infrared and proton and fluorine N.M.R. spectra.

Calc. for $C_{12}H_2F_8N_4O_2$ C: 37·3; H: 0·50; F: 39·4

Found: C: 37·2; H: 0·64; F: 39·4

2,5-Bis(tetrafluoro-4-pyridyl)-1,3,4-oxadiazole, VI

An intimate mixture of N,N'-bis(tetrafluoroisonicotinyl)hydrazine (0·20 g.) and phosphoric oxide (0·25 g.) was placed in a Carius tube which was then evacuated, sealed and heated for 4 hrs., during which the temperature rose to 210°, and then five hours at this temperature. On cooling some white and some brown solid were obtained. The tube was opened, water added and the mixed solid filtered off and washed with water. It was dried at 110° for 15 mins. (0·197 g.; 100%). Two recrystallisations from methylated spirits (once in the presence of charcoal) yielded 2,5-BIS(TETRAFLUORO-4-PYRIDYL) 1,3,4-OXADIAZOLE, m.p. 144-145·5° as a white solid (0·041 g.; 21·6%).

Calc. for $C_{12}F_8N_4O$ C: 39·1; F: 41·3
Found: C: 39·0; F: 40·1

The mass and infra-red spectra were consistent with the proposed structure.

2,5-Bis(tetrafluoro-4-pyridyl)-1,3,4-thiadiazole, VII

N,N'-bis(tetrafluoroisonicotinyl)hydrazine (0·53 g.) and phosphorus pentasulphide (0·60 g.) were heated together in anhydrous xylene under reflux for 41 hrs. The solution darkened considerably on extensive heating. On completion of the reaction the hot solution was filtered leaving some brown solid. Removal of the solvent (by distillation) from the filtrate yielded a brown green solid which was extracted into boiling methylated spirits (some brown solid did not dissolve). Charcoal was added and the hot solution filtered. On cooling white needles (0·070 g.; 16%) crystallised out. A further recrystallisation from methylated spirits yielded white needles of 2,5-BIS(TETRAFLUO-4-pyridyl)-1,3,4-THIADIAZOLE, m.p. 140-1°.

Calc. for $C_{12}F_8N_4S$ C: 37·5; F: 39·6
Found: C: 37·6; F: 39·4

The mass spectrum was consistent with the proposed structure.

N-(Tetrafluoro-4-pyridyl)pentafluorobenzamide, VIII

4-Aminotetrafluoropyridine (1 g.) and diethylaniline (0·94 g.) were stirred in xylene (5 mls.) at room temperature. Pentafluorobenzoyl chloride (1·39 g.) in xylene (5 mls.) was added and the solution heated under reflux for 18 hrs. giving a green solution. The solution was cooled and then stirred at room temperature for 30 mins. with N hydrochloric acid (15 ml.). The green solid which precipitated was filtered off, washed with water and dried (1·75 g.; 80·7%). Sublimation (at 115°) under reduced pressure (0·01 mms.) gave a white solid which was recrystallised from aqueous methylated spirits yielding N-(TETRAFLUORO-4-PYRIDYL)PENTAFLUOROBENZAMIDE m.p. 170·5 - 1·5°.

Calc. for $C_{12}HF_9N_2O$ C: 40·0; H: 0·29; F: 47·5
Found: C: 39·9; H: 0·44; F: 47·0

N-(Pentafluorophenyl)pentafluorobenzamide, IX

Using the method used in the previous experiment (but with benzene as solvent in place of xylene):- pentafluorobenzoyl chloride (1·1 g.) and pentafluoroaniline (0·86 g.) gave N-(PENTAFLUOROPHENYL)PENTAFLUOROBENZAMIDE (1·18 g.; 72·2%) m.p. 178·5 - 179·5° from benzene/ethanol.

Calc. for $C_{13}HF_{10}NO$ C: 41·4; H: 0·27; F: 50·4
Found: C: 41·6; H: 0·55; F: 49·9

Bis(tetrafluoro-4-pyridyl)amine, X

To a stirred solution of 4-aminotetrafluoropyridine (1 g.) in T.H.F. (8 ml.) was added sodium hydride (0·316 g.; 50% dispersion in oil). After the vigorous reaction had subsided the mixture was heated under reflux for 45 mins. Pentafluoropyridine (1·02 g.) was added and the solution heated under reflux for 12 hrs. After cooling, the yellow solution obtained was poured into a mixture of water (40 ml.) and concentrated hydrochloric acid (4 ml.) yielding a yellow oil which was extracted into ether, the extracts dried ($MgSO_4$), and the solvent distilled off. Sublimation under reduced pressure (·001 mm.) at 70° gave a white solid (1·0 g.; 52·7%). This was purified by recrystallisation from benzene/pet. ether (80-100) followed by sublimation at 70° (0·01 mm.) yielding BIS(TETRAFLUORO-4-PYRIDYL)AMINE m.p. 147·5-149°.

Calc. for $C_{10}HF_8N_3$	C: 38·1;	H: 0·32;	F: 38·25
Found:	C: 37·9;	H: 0·59;	F: 38·2

N'-(Tetrafluoro-4-pyridyl)pentafluorobenzohydrazide, XI

4-Hydrazinotetrafluoropyridine (0·78 g.) and N,N-diethylaniline (0·66 g.) in benzene (5 ml.) were stirred at room temperature. Pentafluorobenzoyl chloride (1 g.) was added and an exothermic reaction occurred. The reactants were then heated under reflux for 1 hr. and on cooling the solution went solid. N hydrochloric acid (5 ml.) was then added and the mixture stirred for 15 mins. The solid was then filtered off, washed with water and dried over phosphoric oxide in vacuo. Two recrystallisations from aqueous methylated spirits (once in the presence of charcoal) yielded white crystals of N'-(TETRAFLUORO-4-PYRIDYL)PENTAFLUOROBENZOHYDRAZIDE (1·0 g.; 61·5%) m.p. 184-185·5° (decomp.)

Calc. for $C_{12}H_2F_9N_3O$	C: 38·4;	H: 0·53;	F: 45·6
Found:	C: 38·4;	H: 0·65;	F: 44·9

N'-(Pentafluorophenyl)pentafluorobenzohydrazide, XII

Method as in previous experiment using:- pentafluorophenylhydrazine (0·5 g.) and pentafluorobenzoyl chloride (0·58 g.) gave N'-(PENTAFLUOROPHENYL)-PENTAFLUOROBENZOHYDRAZIDE (0·90 g.; 90·7%) m.p. 194-195·5° (from aqueous methylated spirits).

Calc. for $C_{13}H_2F_{10}N_2O$	C: 39·8; H: 0·51; F: 48·5
Found:	C: 40·1; H: 0·61; F: 48·0

N'-(Tetrafluoro-4-pyridyl)tetrafluoroisonicotinohydrazide, XIII

Tetrafluoroisonicotinyl chloride (1·17 g.) was added to 4-hydrazinotetrafluoropyridine (1 g.) and N,N-diethylaniline (1·17 g.) in benzene (3 ml.). A strongly exothermic reaction occurred giving a yellow solution which was heated under reflux for 1½ hrs. After cooling it was stirred for 30 mins. with N hydrochloric acid. No precipitate was obtained. The mixture was extracted with ether, the extracts dried ($MgSO_4$) and the solution concentrated to give a white solid which was filtered off (0·46 g.; 23·3%). It was sublimed at 120° under high vacuum (·001 mm.) giving N'-(TETRAFLUORO-4-PYRIDYL)-TETRAFLUOROISONICOTINOHYDRAZIDE m.p. 173-4°.

Calc. for $C_{11}H_2F_8N_4O$	C: 36·9; H: 0·56; F: 42·45
Found:	C: 37·0; H: 0·86; F: 42·0

Tetrafluoroisonicotinyl fluoride, XIV

(a) Tetrafluoroisonicotinyl chloride (3·0 g., b.p. 60-66° at 36 mms.) and freshly roasted potassium fluoride (6·0 g.) were placed in a Carius tube which was then evacuated, sealed and heated to 210° for 40 hrs. The tube was allowed to cool, then opened and the product distilled out under vacuum (1·81 g., 65·3%). It was then distilled under reduced pressure (30 mms.) yielding TETRAFLUOROISONICOTINYL FLUORIDE b.p. 55-56°.

Calc. for C_6F_5NO	C: 36·5; F: 48·2
Found:	C: 36·4; F: 48·2

(b) Tetrafluoroisonicotinyl chloride (6·95 g., b.p. 58–65° at 25 mm.) and freshly roasted potassium fluoride (12 g.) were reacted as above. The product was shown (infra-red spectrum) to be a mixture of starting material and product, the relative amounts (estimated by the intensity of the carbonyl group absorption) being 1·5:1. On heating the product with fresh potassium fluoride (12 g.) to 130° for 40 hrs. further fluorination occurred, the ratio changing to 0·6:1.

(c) Freshly roasted potassium fluoride (15 g.) and tetrafluoroisonicotinyl chloride (3·21 g., b.p. 54–64 at 23 mms.) were placed in a stainless steel autoclave (120 ml.) which was then sealed and evacuated to a pressure of 10 mms. The autoclave was heated to 190° for 15 hrs., then 225° for 7 hrs. The product, which was distilled out under vacuum (1·5 g.; 66·1%), was 2,3,5,6-tetrafluoropyridine.

(d) Tetrafluoroisonicotinic acid (0·5 g.) and freshly roasted potassium fluoride (2·5 g.) were placed in a Carius tube which was then evacuated, sealed and heated to 190° for 5 hrs. and then 210° for 5 hrs. The tube was cooled, opened and the product (0·3 g., 84·8%) distilled out under vacuum and shown to be 2,3,5,6-tetrafluoropyridine.

(e) Freshly roasted potassium fluoride (15 g.) was placed in a Carius tube which was then attached to a vacuum line and evacuated to a pressure of 0·01 mms. at which it was maintained for 4 hrs. Tetrafluoroisonicotinyl chloride (1·83 g., b.p. 50–52° at 11 mms.) was then distilled into the tube under vacuum, the tube sealed and then heated to 260° for 40 hrs. The tube was cooled, opened and the product distilled out under vacuum (1·22 g., 72·3%). Its infra-red spectrum showed it to be pure tetrafluoroisonicotinyl fluoride.

(f) Repetition of experiment (e) using tetrafluoroisonicotinyl chloride (1·64 g., b.p. 50-52° at 11 mm.) and potassium fluoride (5 g.) gave pure tetrafluoroisonicotinyl fluoride (0·75 g., 49·6%).

(g) Repetition of experiment (e) using acid chloride (6·68 g., b.p. 53-57° at 17 mms.) and potassium fluoride (25 g.) gave a product which consisted of acid chloride and acid fluoride in approx. equal amounts.

Pentafluorobenzoyl fluoride, XV

(a) Pentafluorobenzoyl chloride (0·85 g.) was distilled under vacuum into a Carius tube containing freshly roasted potassium fluoride (5 g.). The tube was sealed under vacuum and then heated to 250° for 48 hrs. After cooling, the tube was opened and the product distilled out under vacuum (0·70 g.; 88·6%). The liquid product was then distilled under reduced pressure (21 mms.) to yield PENTAFLUOROBENZOYL FLUORIDE b.p. 55-56°.

Calc. for C_7F_6O	C: 39·25;	F: 53·3
Found:	C: 38·9;	F: 53·3

(b) The above experiment was repeated using pentafluorobenzoyl chloride (16·0 g.) and freshly roasted potassium fluoride (50 g.). The weight of acid fluoride obtained was only 4·3 g.

(c) Pentafluorobenzoic acid (2·0 g.) was stirred and then 1-chloro-1,2,2-trifluorotriethylamine (1·78 g.) was added dropwise. Little reaction occurred so the mixture was heated to 85° for 2 hrs. After cooling the yellow liquid obtained was distilled under reduced pressure (14 mms.) giving three fractions:

(1) 45-60°, 0·14 g.

(2) 96-122, o·68 g.

(3) 122-124°, 0·80 g.

Fraction (1) was shown by infra-red spectroscopy to be pentafluorobenzoyl fluoride. Some unreacted pentafluorobenzoic acid crystallised from fraction (3).

(d) The above reaction was repeated using a reaction temperature of 100° and a reaction time of 4 hrs. No acid fluoride was obtained.

(e) Pentafluorobenzoyl chloride (8·66 g.), anhydrous potassium fluoride (7·0 g.; 100% excess) and sulpholane (15 ml.) were heated together to 160° for 24 hrs. with stirring. After cooling the solid was filtered off and the filtrate distilled under reduced pressure (19·5 mms.)

(1)	57-57·5°	1·45 g.
(2)	57·5-59°	4·05 g.

The infra-red spectra showed both fractions to be an approximately 50/50 mixture of pentafluorobenzoyl chloride and fluoride.

Perfluoro(phenyl isopropyl)ketone XVII and perfluoro(4-isopropylphenyl isopropyl)ketone XVIII.

Pentafluorobenzoyl fluoride (4·35 g.), hexafluoropropene (5 g.), acetonitrile (5 ml.) and anhydrous potassium fluoride (0·4 g.) were placed in a Carius tube which was evacuated and sealed. It was shaken at 135° for 36 hrs. yielding a dark red liquid which separated into two layers on cooling. The tube was opened and the lower layer separated off (9·0 g.). It was distilled under reduced pressure (16 mms.) yielding some acetonitrile and two other fractions

(1)	62-80°	2·75 g.
(2)	80-86°	2·80 g.

The two fractions were analysed by vapour phase chromatography (on silicone elastomer at 100°) and both contained the same two products but the relative amounts of each were different.

	Fraction (1)	Fraction (2)	Average
Component of shorter retention time	62·5	9·0	35·75
Component of longer retention time	37·5	91·0	64·25

The two fractions were combined and the two products separated by prep. scale V.P.C. (on silicone elastomer at 120°). The component of shorter retention time was shown by infra-red, mass and ^{19}F N.M.R. spectra to be PERFLUORO(PHENYL ISOPROPYL)KETONE b.p. 155° (Siwoloboff).

Calc. for $C_{10}F_{12}O$ C: 33·0; F: 62·6
Found: C: 33·1; F: 62·2

Similarly the compound of longer retention time was shown to be PERFLUORO(4-ISOPROPYLPHENYL ISOPROPYL)KETONE b.p. 191° (Siwoloboff).

Calc. for $C_{13}F_{18}O$ C: 30·35; F: 66·5
Found: C: 30·3; F: 66·4

The approximate yields were 27% and 34% respectively.

The above experiment was repeated using pentafluorobenzoyl chloride in place of pentafluorobenzoyl fluoride at 135° for 24 hrs. It was shown by infra-red spectroscopy that no reaction had occurred.

Perfluoro-(4-pyridyl isopropyl)ketone, XVI

Tetrafluoroisonicotinyl fluoride (3·8 g.), hexafluoropropene (3·0 g.), acetonitrile (5 ml.) and anhydrous potassium fluoride (0·5 g.) were placed in a Carius tube which was then evacuated and sealed. The tube was shaken at 135° for 24 hrs. On cooling the liquid was still homogeneous. The tube was cooled, opened and the liquid obtained distilled under reduced pressure (19 mms.)

$$\left.\begin{array}{l}(1)\ \ 36\text{–}46^{\circ}\\ (2)\ \ 46\text{–}60^{\circ}\end{array}\right\}\ 2{\cdot}88\ \text{g.}$$

The infra-red spectra of the two fractions were identical. Analysis by V.P.C. (on silicone elastomer at 100°) showed essentially one peak with a very small peak ($<1\%$) of much shorter retention time (unreacted acid fluoride). An analytical sample was obtained by prep. scale V.P.C. (on silicone elastomer at 120°). The product was identified by infra-red, mass and ^{19}F N.M.R. spectra as PERFLUORO-(4-PYRIDYL ISOPROPYL)KETONE b.p. 151° (Siwoloboff).

Calc. for $C_9F_{11}NO$ C: 31·1; F: 60·2
Found: C: 31·3; F: 60·2

This experiment was repeated using tetrafluoroisonicotinyl chloride but only starting material was recovered.

2,4,6-Trifluoronicotinyl chloride, XIX

2,4,6-Trifluoronicotinic acid (0·88 g.) and phosphorus pentachloride (1·055 g., 1% excess) were stirred together. On slight warming a vigorous reaction occurred with rapid evolution of hydrogen chloride. When the vigorous reaction had subsided the resulting liquid was heated to 85° for one hour. Distillation, under reduced pressure (15 mms.) of the liquid obtained gave some low boiling material (phosphorus oxychloride) and a main fraction b.p. 73·5 - 74° which was almost certainly 2,4,6-trifluoronicotinyl chloride (0·57 g., 56·7%).

Calc. for C_6HClF_3NO C: 36·8; H: 0·51
Found: C: 35·9; H: 0·74

Reaction of 2,4,6-Trifluoronicotinyl chloride with anhydrous ammonia.

Anhydrous ammonia was bubbled through a solution of 2,4,6-trifluoronicotinyl chloride (0·42 g.) in benzene (15 ml.) for 15 mins. The benzene was then heated on a water bath and the insoluble white solid filtered off from the benzene solution and washed with ether (15 ml.). The combined organic solutions were then distilled in order to remove the solvent, leaving behind a white solid which was sublimed at 90° and 0·01 mms. pressure (0·215 g.). The solid was twice recrystallised from benzene to give a white solid, some of which melted at approx. 140° and the remainder at 168°.

Calc. for $C_6H_5F_2N_3O$ C: 41·6; H: 2·89; F: 22·0

Calc. for $C_6H_3F_3N_2O$ C: 40·9; H: 1·70; F: 32·4

Found: C: 41·3; H: 2·60; F: 26·2

The product thus appeared to be a mixture of 2,4,6-trifluoronicotinamide XX and 4-amino-2,6-difluoronicotinamide XXI. Mass spectral analysis confirmed this.

Fluorinated Ethers

PREPARATION OF STARTING MATERIALS.

A. Phenols.

Tetrafluoro-4-hydroxypyridine.

Pentafluoropyridine (14·5 g.), sodium hydroxide (7·2 g.) and water (120 ml.) were heated under reflux for 16½ hours. The homogeneous product was acidified with concentrated hydrochloric acid (30 ml.) and extracted with ether (3 x 250 ml.). The ethereal extract was dried ($MgSO_4$) and then evaporated to give a white solid that was sublimed at 60°/1 mm. to yield tetrafluoro-4-hydroxypyridine (11·0 g., 81% yield; m.pt. 95-97°C).

Hexafluoro-1-hydroxy-isoquinoline.

Heptafluoroisoquinoline (1·46 g.), potassium hydroxide (0·66 g.) and t-butanol (35 ml.) were heated under reflux with stirring for 2 hours. The reaction mixture was cooled, water (45 ml.) added and the t-butanol distilled off. The cooled aqueous solution was acidified with dilute hydrochloric acid. A white precipitate was formed. The precipitate was filtered on to a sintered funnel and dried overnight over phosphorus pentoxide. The crude yield was 1·43 g. It was recrystallised from hot benzene (17 ml.) to give 1·2 g. of hexafluoro-1-hydroxyisoquinoline (m.pt. 176-182°C).

4,4'-Dihydroxyoctafluorobiphenyl.

Decafluorobiphenyl (41·5 g.) in t-butanol (200 ml.) was stirred while powdered 85% KOH (43 g.) was added. The mixture was refluxed for 50 minutes. 300 ml. of water was then added and the t-butanol distilled off. The aqueous solution was acidified with hydrochloric acid and extracted with ether. The extracts were dried ($MgSO_4$) and evaporated to leave a semi-solid which crystallised on being triturated with water (100 ml.). The solid was dried in vacuo to give almost pure 4,4'-dihydroxy-octafluorobiphenyl (36·1 g.) m.pt. 190-199°. After purification by sublimation at 120-130°/0·01 mm. Hg it had m.pt. 212°.

B. The Potassium Salts of the Phenols.

These were prepared by dissolving the phenols in a large excess of hot 6N aqueous potassium hydroxide and cooling the solution in ice. The precipitated potassium salts were filtered off and recrystallised from a small volume of water. The anhydrous salts could be prepared by boiling the hydrated salts with benzene for six hours.

C. Acid Chlorides.

Pentafluorobenzoyl Chloride.

Pentafluorobenzoic acid (4·2 g.) and phosphorus pentachloride (4·7 g.) were stirred together. On warming slightly a vigorous reaction occurred with rapid evolution of hydrogen chloride. When the reaction had moderated the solution was heated at 100° for one hour. On cooling and standing at room temperature for one hour, the excess phosphorus pentachloride crystallised out. The liquid product was decanted off and distilled under reduced pressure (18 mms.) yielding two fractions.

(1) Phosphorus oxychloride, b.p. 23-40°.

(2) Pentafluorobenzoyl chloride, b.p. 60-61°,

The yield of acid chloride (based on the weight of fraction (2)) was 83·9%.

Tetrafluoroisonicotinyl Chloride.

This was prepared by the method described on pg. 130.

D. Octafluoro-4,4'-bipyridyl.

A four-necked flask fitted with stirrer, dropping funnel, and condenser, and containing magnesium (0·2 g.) and dry tetrahydrofuran (45 ml.) was purged with dry nitrogen and cooled to -20°. A solution of 4-bromotetrafluoropyridine (1·0 g.) in dry tetrahydrofuran (0·5 ml.) was added and after a few minutes reaction commenced. The mixture was allowed to warm to -10° to 0° and maintained at this temperature for 1 hour. To the Grignard reagent was added pentafluoropyridine (0·75 g.) at -35 to 40°. The mixture was then hydrolysed with dilute sulphuric acid and extracted with ether, and solvent was distilled from the dried extracts to leave a brown crystalline material. Sublimation under reduced pressure yielded octafluoro-4,4'-bipyridyl (0·91 g., 68%), m.p. 81-82°, identified by its infra-red spectrum.

E. The Potassium Salt of Tetrafluoro-4-hydroxypyridine.

Pentafluoropyridine (14•5 g.), potassium hydroxide (11 g.) and water (120 ml.) were heated under reflux for 17 hours. Potassium hydroxide (35 g.) was added carefully to the homogeneous solution with stirring. After the potassium hydroxide had dissolved the solution was cooled well in ice. The crystallised potassium salt was filtered on a sintered funnel, pressed dry, and washed with a little acetone, and kept in a desiccator overnight, 17•5 g. (76% yield) of the dihydrate, as indicated by analysis, were obtained.

PREPARATION OF ETHERS

Octafluoro-4,4'-dipyridyl ether, XXII

The potassium salt of tetrafluoro-4-hydroxypyridine (4•82 g.), pentafluoropyridine (3•38 g.), and dry tetrahydrofuran (60 ml.) were heated to 150° for 2 days. The potassium salt dissolved in the tetrahydrofuran and a brown precipitate was deposited. The contents of the tube were dried with magnesium sulphate and the tetrahydrofuran evaporated to leave a dark brown solid and a yellow oil. Ether was added to the mixture and the oil was pipetted off. The solid (3•1 g.) was insoluble in ether and an infra-red spectrum indicated that it was unreacted potassium salt.

Distillation of the ethereal solution of the oil under reduced pressure (14 mm.) yielded:-

(i) Octafluoro-4,4'-bipyridyl ether, b.pt. 113° - 120°, 0•6 g., boiling mainly at 119°.

$C_{10}F_8N_2O$ requires	C, 38•0;	F, 48•1
Found:	C, 38•7;	F, 45•7

(ii) A high boiling fraction, 121-192°, 0•2 g., which possibly contains products derived from the reaction of pentafluoropyridine with two or three moles of the potassium salt of tetrafluoro-4-hydroxypyridine.

The n.m.r. spectrum of fraction (i) confirms its structure although its analysis indicates that it is slightly impure.

4-Pentafluorophenoxy-tetrafluoropyridine XXIII and 2,4-Dipentafluorophenoxy-trifluoropyridine XXIV.

Anhydrous potassium pentafluorophenate (2·76 g., 12·4 m.moles), pentafluoropyridine (1·0 g., 5·9 m.moles) and dry tetrahydrofuran (10 ml.) were refluxed together for 8 hours. The potassium salt dissolved in the tetrahydrofuran and a brown precipitate was formed. The product was poured into water and extracted with ether. The ethereal extract was dried ($MgSO_4$) and evaporated to leave a dark brown oil. This oil was shown by analytical gas-liquid chromatography (silicone grease at 200°) to contain:-

(a) pentafluoropyridine (a trace),
(b) pentafluorophenol (a trace),
(c) 4-pentafluorophenoxy-tetrafluoropyridine,
(d) a new product.

Distillation under reduced pressure (15 mm.) yielded:-

(i) 4-Pentafluorophenoxy-tetrafluoropyridine, b.pt. 102°, 0·643 g.,
(ii) 2,4-Dipentafluorophenoxy-trifluoropyridine, b.pt. 165-167°, 0·301 g., a light yellow solid that solidified on standing.

$C_{17}F_{13}NO_2$ requires:	C, 40·6;	F, 49·7%
Found:	C, 41·0;	F, 49·7%

A previous experiment identical except for using an equimolar proportion of potassium pentafluorophenate (1·38 g.) yielded 4-pentafluorophenoxy-tetrafluoropyridine on distillation under reduced pressure (15 mm.). A small shoulder on the single product peak of the gas-liquid chromatograph indicated the presence of a small amount of impurity. An attempt to separate a pure sample of the ether (0·26 g.) by preparative scale gas-liquid chromatography was not successful.

$C_{11}F_9NO$ requires:	C, 39·6; F, 51·3%
Found:	C, 38·9; F, 50·6%

F^{19} n.m.r. spectroscopy indicated that the compound was the 4-isomer.

Pentafluorophenoxy-hexafluoroisoquinoline, XXVII

Anhydrous potassium pentafluorophenate (0·666 g., 3 m.mole) and heptafluoroisoquinoline (0·765 g., 3 m.mole) and tetrahydrofuran (10 ml.) were refluxed together for 1½ hours. The reaction mixture quickly darkened to give a green coloured solution and a black solid. The mixture was poured into 100 ml. of water and a light brown oil was precipitated. On rubbing this gave a brown solid (m.pt. 116-120°) which was purified by vacuum sublimation (0·05 mm.) at room temperature, to remove a trace of heptafluoroisoquinoline, at 40° to remove a little pentafluorophenol and at 80° to sublime the product. The white solid was recrystallised from methanol to give a solid which melted sharply at 124°C.

$C_{15}F_{11}NO$ requires:	C, 42·9%; F, 49·9%
Found:	C, 42·6%; F, 49·6%
Yield:	0·756 g., (62%).

2',3',5',6'-Tetrafluorophenoxy-hexafluoroisoquinoline, XXXI

Potassium 2,3,5,6-tetrafluorophenate dihydrate (0·480 g., 2 m.mole), heptafluoroisoquinoline (0·510 g., 2 m.mole), and dry tetrahydrofuran (10 ml.) were refluxed together for 1½ hours. The mixture was poured into water and a brown solid was precipitated (yield 0·93 g., m.pt. 101-105°). This solid was purified by vacuum sublimation at 0·05 mm. to give:-

(a) at room temperature - heptafluoroisoquinoline (a trace)

(b) at 80° - 2',3',5',6'-tetrafluorophenoxy-hexafluoroisoquinoline - a white solid, m.pt. 104-108°. This was recrystallised from methanol to give a white solid which melted sharply at 110·5°.

$C_{15}F_{10}ONH$ requires:	C, 44·9;	F, 47·4;	H, 0·25%
Found:	C, 44·8;	F, 47·6;	H, 0·39%

Dipentafluorophenoxy-pentafluoroisoquinoline, XXVIII

Anhydrous potassium pentafluorophenate (1·332 g., 6 m.moles), heptafluoroisoquinoline (0·765 g., 3 m.moles), and dry tetrahydrofuran (10 ml.) were refluxed for 5 hours. The mixture was poured into 100 ml. of water and a yellow solid (m.pt. 105-125°) was precipitated. This was purified by vacuum sublimation to give:-

(a) at room temperature - heptafluoroisoquinoline (a trace),

(b) at 40° - pentafluorophenol (a trace),

(c) at 80° - pentafluorophenoxy-hexafluoroisoquinoline (0·075 g.), identified by its infra-red spectrum,

(d) at 110° - dipentafluorophenoxy-pentafluoroisoquinoline (0·075 g.), m.pt. 129-131° - a yellow solid which retained its colour on repeated sublimation.

$C_{21}F_{15}NO_2$ requires:	C, 43·2%;	F, 48·9%
Found:	C, 43·0%;	F, 48·9%

2-Pentafluorophenoxy-heptafluoro-4,4'-bipyridyl, XXX

Potassium pentafluorophenate dihydrate (0·516 g.), octafluoro-4,4'-bipyridyl (0·60 g.), and tetrahydrofuran (10 ml.) were heated under reflux with stirring for 5 hours. The potassium salt dissolved in the tetrahydrofuran and a brown precipitate was formed. The mixture was poured into water and extracted with ether (3 x 50 ml.). The ethereal extract was dried ($MgSO_4$) and evaporated to leave a dark brown liquid. Distillation of this liquid under reduced pressure (17 mm.) yielded 2-pentafluorophenoxy-heptafluoro-4,4'-bipyridyl, b.pt. 175-176°, (0·186 g.) a colourless oil.

$C_{16}F_{12}N_2O$ requires:	C, 41·4;	F, 49·1%
Found:	C, 41·2;	F, 48·5%

4-Bromo-2-pentafluorophenoxytrifluoropyridine, XXIX

Potassium pentafluorophenate dihydrate (2·46 g.), 4-bromotetrafluoropyridine (2·3 g.) and tetrahydrofuran (20 ml.) were heated under reflux with stirring for 8½ hours. The mixture was poured into water and extracted with ether (3 x 50 ml.). The ethereal extract was dried ($MgSO_4$) and evaporated to leave a dark brown liquid. Distillation of this liquid under reduced pressure (16 mm.) yielded:-

(i) 4-Bromotetrafluoropyridine, b.pt. 40°, 0·3 g.

(ii) 4-Bromo-2-pentafluorophenoxytrifluoropyridine, b.pt. 144°, 1·04 g., a colourless oil.

$C_{11}F_8BrNO$ requires:	C, 33·5;	F, 38·6;	Br, 20·3
Found:	C, 33·5;	F, 39·3;	Br, 19·9

2,4,6-Tripentafluorophenoxydifluoropyridine, XXV

Pentafluoropyridine (0·52 g.), anhydrous potassium pentafluorophenate (3·17 g.) and tetrahydrofuran (20 ml.) were heated under reflux with stirring for 24 hours. The mixture was then poured into 100 ml. of water. A colourless oil was precipitated which quickly reverted to a white solid. The solid (0·54 g.) was filtered off and dried overnight in vacuo. It had m.pt. 46–65°. Because of the low melting-point of the solid it was not possible to find a solvent for recrystallisation. After subliming a portion of the product three times it was found to have melting point 65–67°.

$C_{23}F_{17}O_3N$ requires: C: 41·7; F: 48·9
Found: C, 40·4; F: 49·1

It was found that this compound was difficult to combust. This could explain the low carbon analysis.

PREPARATION OF HYDROXY ETHERS.

2-Hydroxy-4-pentafluorophenoxy-trifluoropyridine, XXXII

4-Pentafluorophenoxy-tetrafluoropyridine (1·16 g., 3·5 m.mole), potassium hydroxide (0·46 g., 7 m.mole) and t-butanol (11 ml.) were heated under reflux with stirring for 5 hours, 10 ml. of water was added, the t-butanol distilled off and the solution allowed to cool. The solution was acidified with 5 ml. of concentrated hydrochloric acid. A white solid was precipitated. This was filtered and dried over phosphorus pentoxide in vacuo (0·87 g., 75·5% yield, m.pt. 165–168°). The product was recrystallised twice from ethanol and then had melting point 169–70°.

$C_{11}F_8NO_2H$ requires: C, 39·6; F, 45·0; H, 0·50%
39·7
Found: C, 39·9; F, 45·9; H, 0·30%

2,4'-Dihydroxy-4-tetrafluorophenoxytrifluoropyridine, XXXIII

4-Pentafluorophenoxy-tetrafluoropyridine (1·16 g., 3·5 m.mole), potassium hydroxide (0·95 g., 14 m.mole) and t-butanol (11 ml.) were heated under reflux for 5 hours. A white solid was precipitated after 4 hours. This was presumably a potassium salt of the dihydroxy-derivative. 10 ml. of water were added to the mixture, the t-butanol distilled off and the solution allowed to cool. The solution was acidified with 9 ml. of concentrated hydrochloric acid. A white solid was precipitated. This was filtered and dried over phosphorus pentoxide in vacuo (1·128 g., 87·2% yield, m.pt. 152-60°). The product was crystallised twice from water and then had melting point 161-2°.

$C_{11}F_7NO_3H_2$ requires: C, 40·1; F, 40·4; H, 0·61%
Found: C, 39·8; F, 39·7; H, 0·70%

PREPARATION OF ESTERS

4-Pentafluorobenzoyloxy-tetrafluoropyridine, XXXIV

N,N'-Diethylaniline (1·56 g.) in dry benzene (5 ml.) was slowly added to a solution of tetrafluoro-4-hydroxypyridine (1·47 g.) and pentafluorobenzoyl chloride (2·30 g.) in dry benzene (15 ml.) boiling under reflux. The reaction mixture became light yellow in colour and slowly darkened. Refluxing was continued for 6 hours. At the end of the reflux period the reaction mixture was allowed to cool and then diluted with benzene (20 ml.). The mixture contained precipitated N,N'-diethylaniline hydrochloride. To remove this and any diethylaniline the mixture was washed four times with 25 ml. portions of 1N hydrochloric acid and once with water. The benzene solution was dried ($MgSO_4$) and most of the benzene removed by distillation under atmospheric pressure. The residue was purified by distillation under reduced pressure (18 mm.) to give two fractions.

(1) benzene, 23-34°

(2) 4-pentafluorobenzoyloxy-tetrafluoropyridine, 152-53°.

After the traces of benzene had been removed the temperature rose steadily up to 152°. The first few drops of the second fraction were discarded. The weight of fraction (2) was 1·92 g. Gas-liquid chromatography (silicone grease at 200°) showed that fraction (2) contained a single component that was a new compound.

Calculated for $C_{12}F_9O_2N$: C, 39·9; F, 47·4

Found: C, 40·1; F, 47·5

Tetrafluoroisonicotinyloxy-pentafluorobenzene, XXXV

N,N-Diethylaniline (1·56 g.) was added slowly to a solution of pentafluorophenol (1·84 g.) and tetrafluoroisonicotinyl chloride (2·14 g.) in dry benzene (10 ml.) boiling under reflux. The solution became light yellow in colour. Refluxing was continued for 4 hours. At the end of the reflux period the solution was diluted with benzene (20 ml.) and when cool extracted four times with 25 ml. portions of 1N hydrochloric acid and once with water. The benzene solution was dried ($MgSO_4$) and most of the benzene removed by distillation under atmospheric pressure. The residue was distilled under reduced pressure (18 mm.) to give 3 fractions

(1) benzene, 23-35°

(2) pentafluorophenol, 35-138°

(3) tetrafluoroisonicotinyloxypentafluorobenzene.

The weight of fraction (3) - the ester fraction - was 1·75 g. Examination of this fraction by gas-liquid chromatography (silicone grease at 200°) showed that this fraction contained mainly ester but was contaminated with a small amount of pentafluorophenol. Redistillation under reduced pressure (19 mm.)

yielded two fractions

(4) pentafluorophenol, 35-121°

(5) tetrafluoroisonicotinyloxy-pentafluorobenzene, 1·2 g., 140-142°.

Examination of fraction (5) by gas-liquid chromatography (silicone-grease at 200°) showed that it contained only ester.

Calculated for $C_{12}F_9O_2N$: C, 39·9; F, 47·4

Found: C, 41·0; H, 0·67

4-Tetrafluoroisonicotinyloxy-tetrafluoropyridine, XXXVI

N,N-Diethylaniline (1·56 g.) was slowly added to a solution of tetrafluoro-4-hydroxypyridine (1·47 g.) and tetrafluoroisonicotinyl chloride (2·14 g.) in dry benzene (10 ml.) boiling under reflux. The solution became light yellow in colour. Refluxing was continued for 4 hours. At the end of the reflux period the solution was diluted with benzene (20 ml.) and when cool extracted four times with 25 ml. portions of 1N hydrochloric acid and once with water. The benzene solution was dried ($MgSO_4$) and most of the benzene removed by distillation under atmospheric pressure.

The residue was distilled under reduced pressure (14 mm.) to give two fractions:-

(1) benzene, 22-34°

(2) 4-tetrafluoroisonicotinyloxy-tetrafluoropyridine, b.pt. 152-153°.

The weight of fraction (2) - the ester fraction - was 1·52 g.

Calculated for $C_{11}F_8N_2O_2$: C, 38·4;

Found: C, 37·8;

2,4,6-Tripentafluorophenoxydifluoropyridine XXV and 2,3,4,6-Tetra-(pentafluorophenoxy)-fluoropyridine XXVI.

Pentafluoropyridine (3·12 g.), anhydrous potassium pentafluorophenate (15·52 g.), 4·2 g. of a mixture of 4-pentafluorophenoxytetrafluoropyridine and 2,4-dipentafluorophenoxytrifluoropyridine and tetrahydrofuran (110 ml.) were heated under reflux with stirring for 24 hours. Most of the tetrahydrofuran was evaporated from the reaction mixture at atmospheric pressure. Distillation of the residue under reduced pressure (0·05 mm.) yielded three fractions.

(1) 22-146°, a mixture of 4-pentafluorophenoxytetrafluoropyridine and 2,4-dipentafluorophenoxytrifluoropyridine (2·0 g.).

(2) 146-156°, boiling mainly over 147-149°, 2,4,6-tripentafluorophenoxydifluoropyridine (4·710 g.).

(3) 156-160°, m.pt. 83-85° with slight softening at 57°, a new compound, probably 2,3,4,6-tetra(pentafluorophenoxy)-fluoropyridine (2·414 g.).

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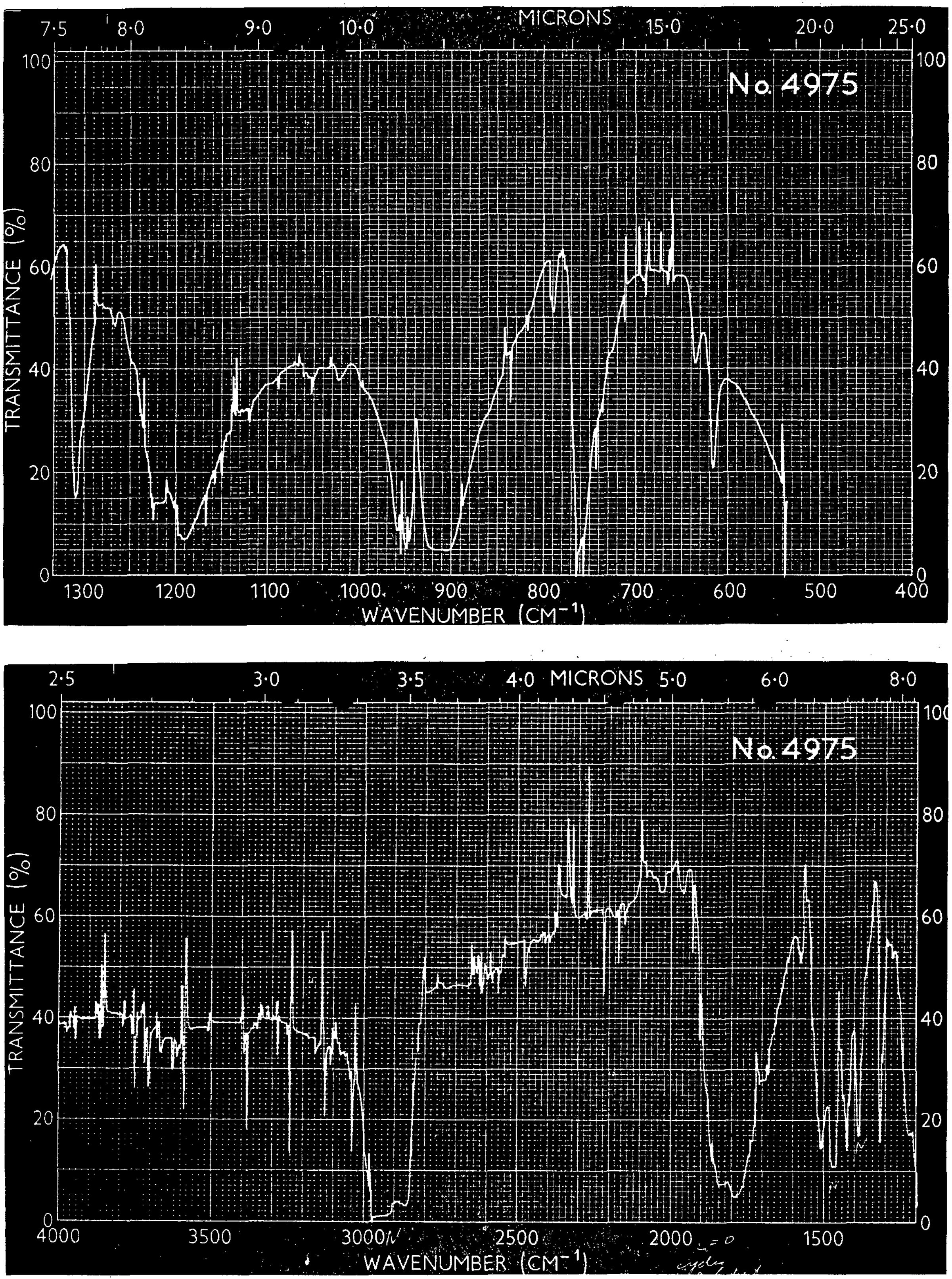
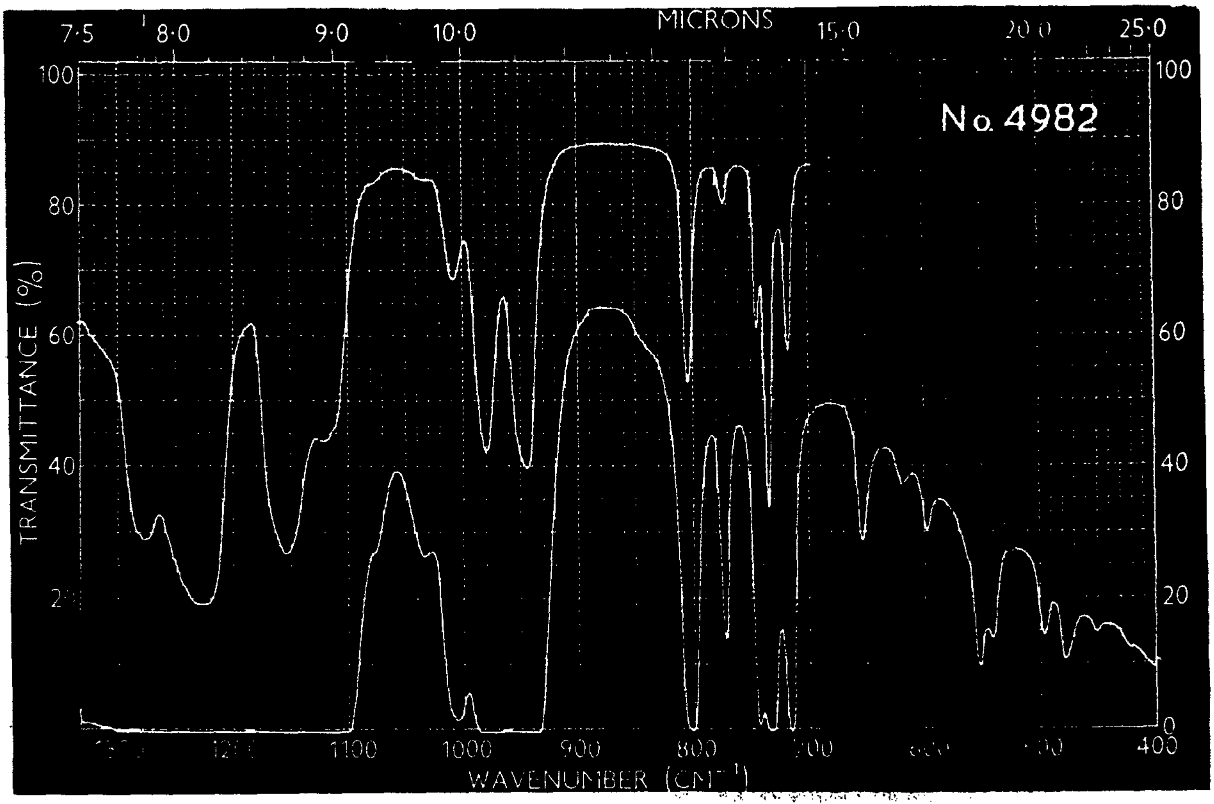
APPENDIX I

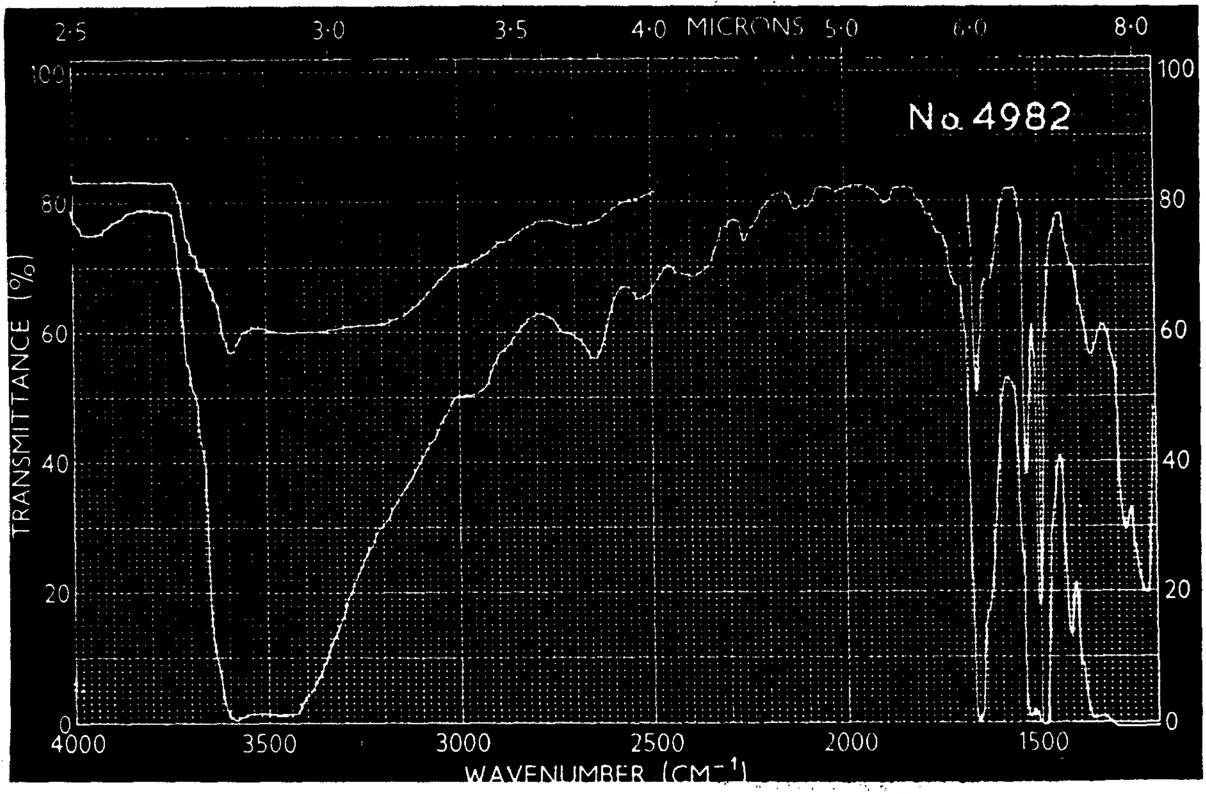
Infra-red Spectra Referred to in Part I

NUMBER	
4975	Difluoropyromellitic dianhydride (Nujol)
4982	Tetrafluoro-4-hydroxyphenylbis(trifluoromethyl)carbinol (film)
4199	
4398A	2,4,5-Trifluororesorcinol (KBr discs)
4687B	Octafluoro-4,4'-dihydrazinobiphenyl (KBr disc)
4563	Bis(pentafluoroanilino)dioxan (in CCl_4)
4268A	α,3,6-Trinitrodurene (KBr disc)
4283A	3,3'-Di(tertiarybutoxy)hexafluoro-4,4'-dinitrobiphenyl (in CCl_4)
4255	2,4,5-Trifluororesorcinyl diacetate (in CCl_4)
4389	2,3,4,6-Tetrafluorothiophenol (film)
4813	Tetrafluorobenzene-1,3-dithiol (film)

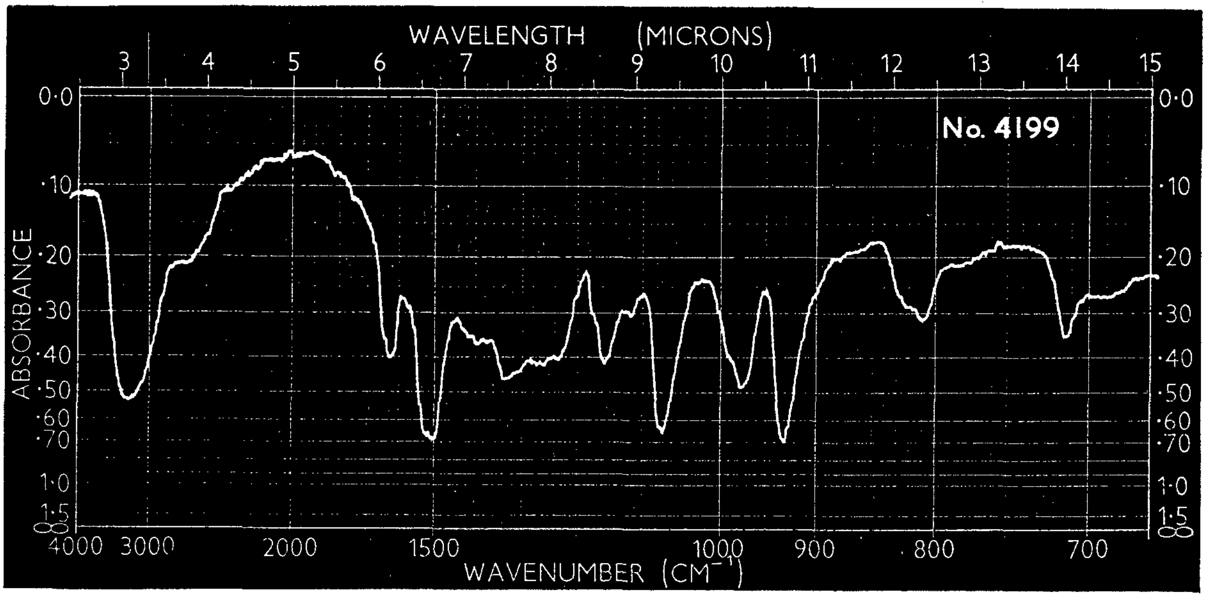


Spectrum No. 4975 Difluoropyromellitic dianhydride (Nujol)

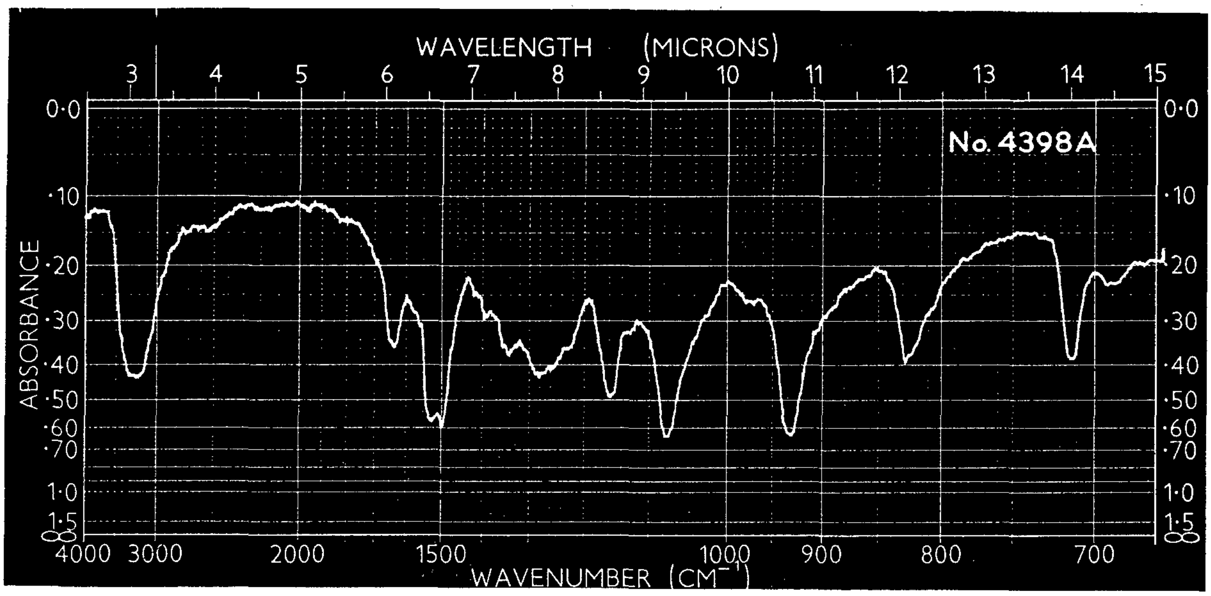




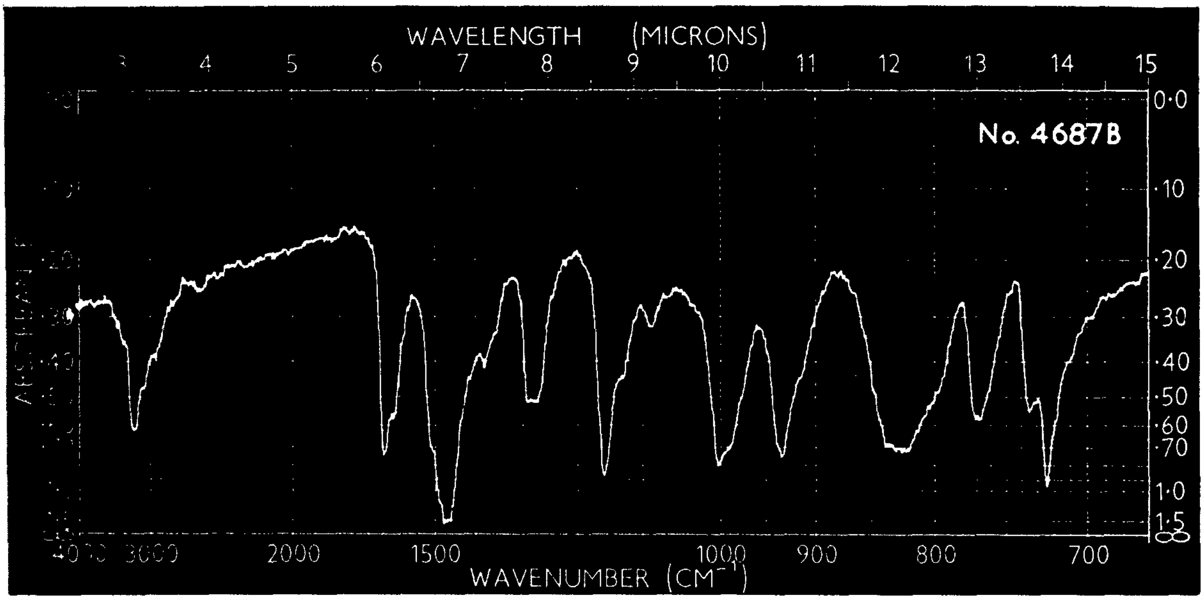
Spectrum No. 4982 Tetrafluoro-4-hydroxyphenylbis(trifluoromethyl)-carbinol (film)



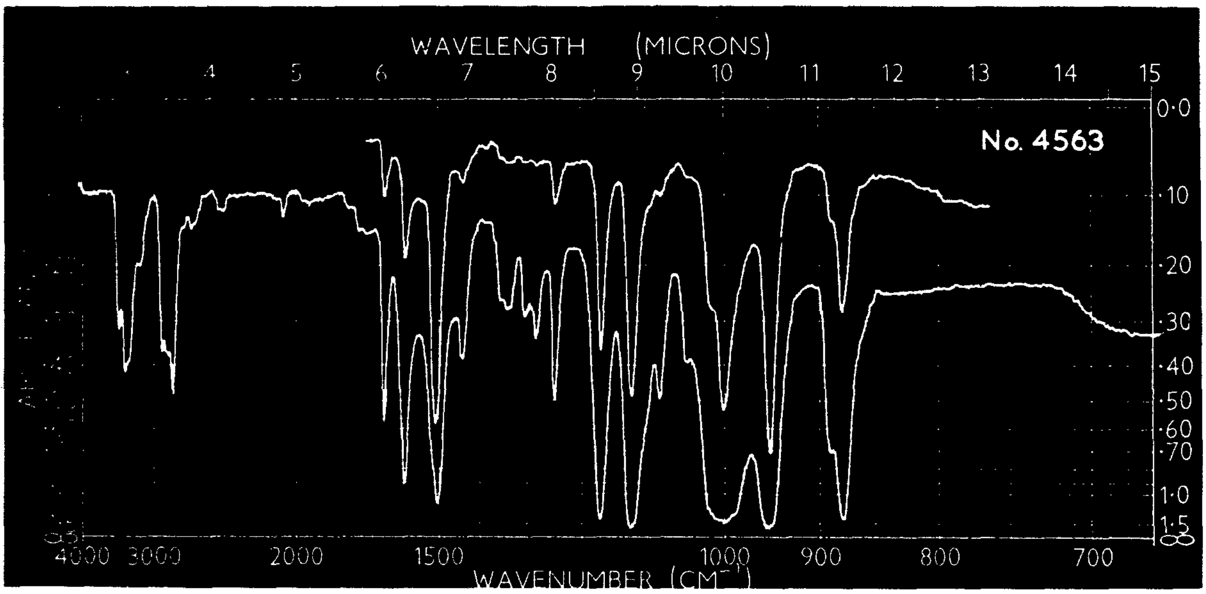
Spectrum No. 4199 2,4,5-Trifluororesorcinol (KBr discs)



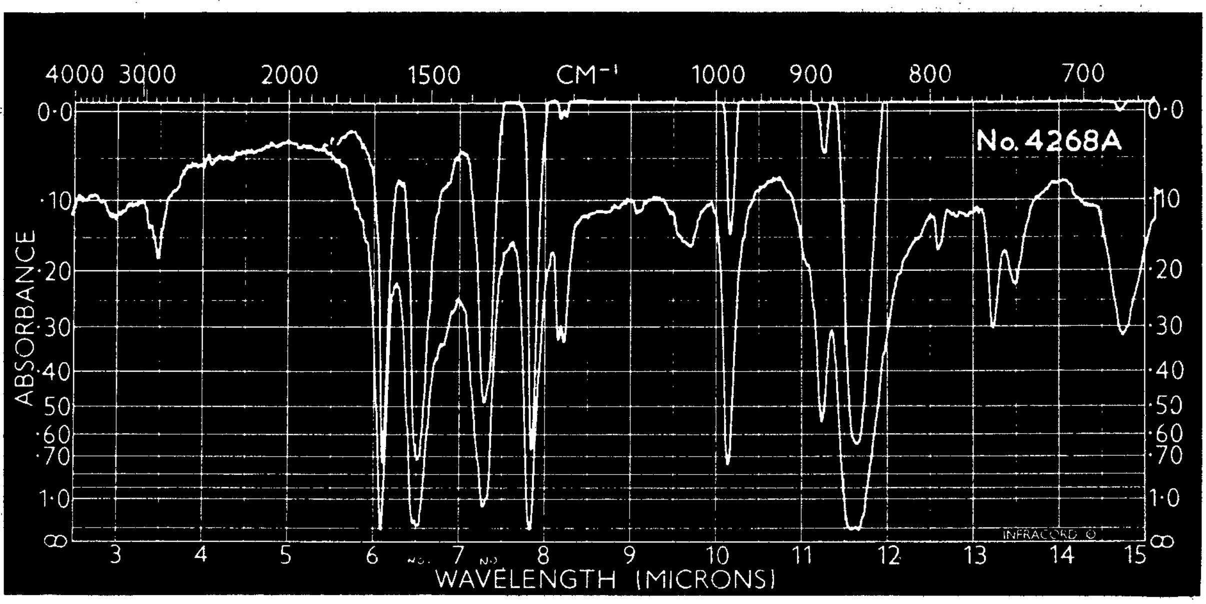
Spectrum No. 4398A 2,4,5-Trifluororesorcinol (KBr discs)



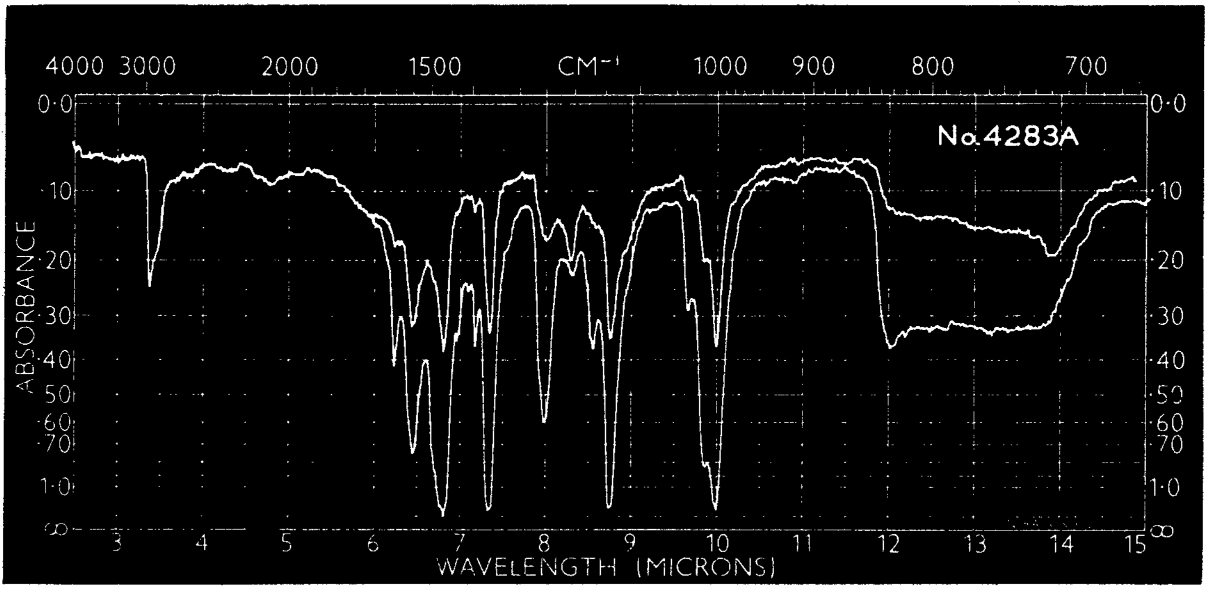
Spectrum No. 4687B Octafluoro-4,4'-dihydrazinobiphenyl (KBr disc)



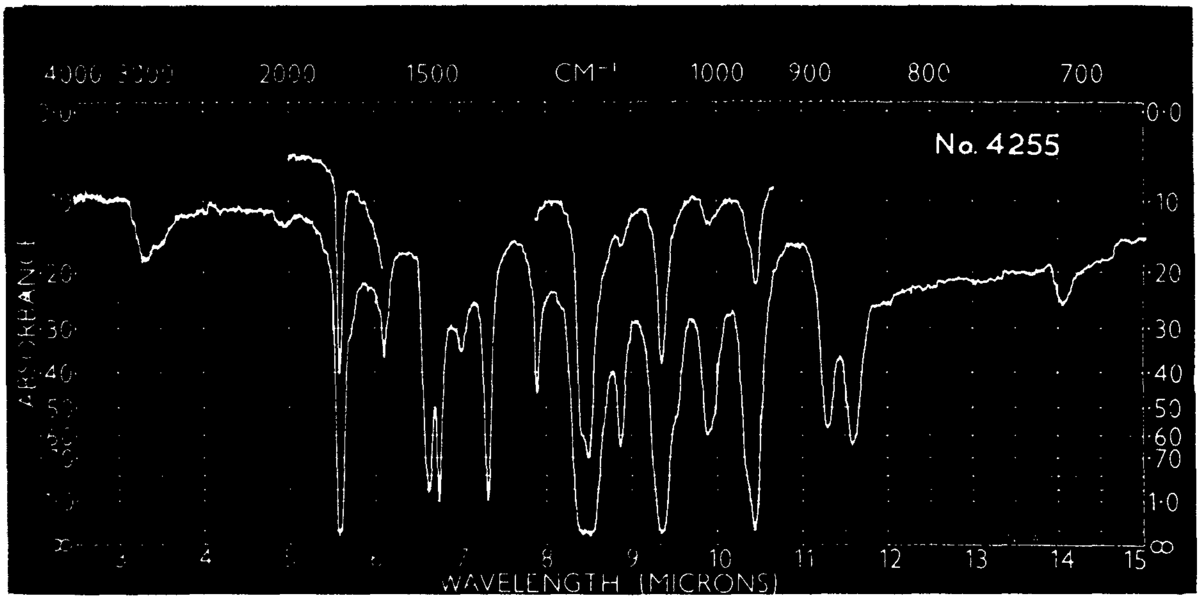
Spectrum No. 4563 Bis(pentafluoroanilino)dioxan (in CCl_4)



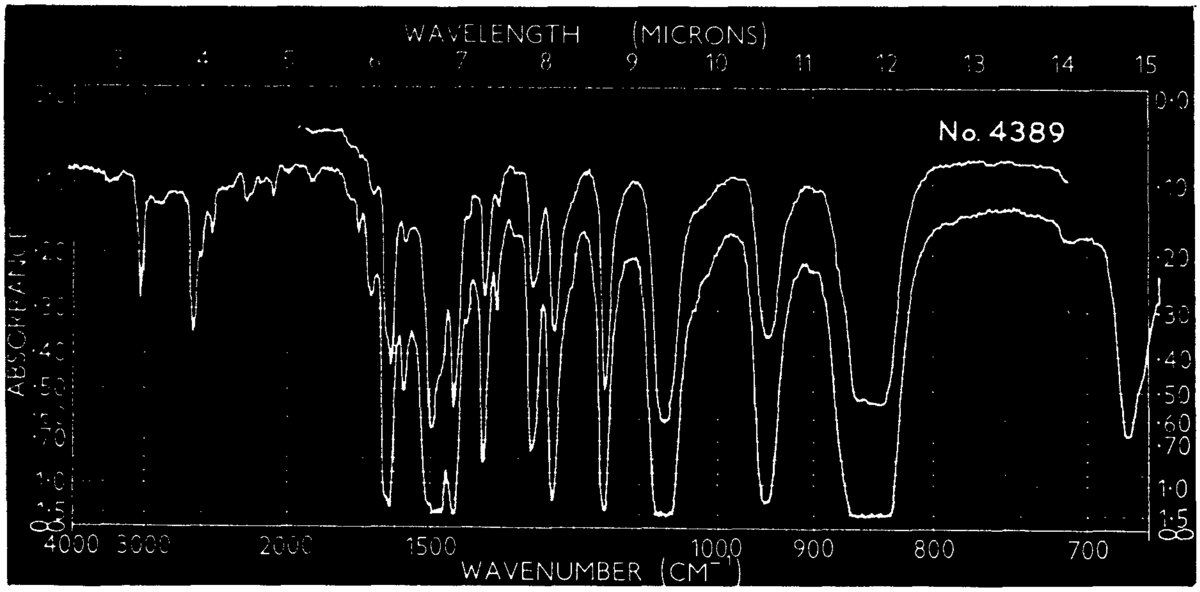
Spectrum No. 4268A α,3,6-Trinitrodurene (KBr disc)



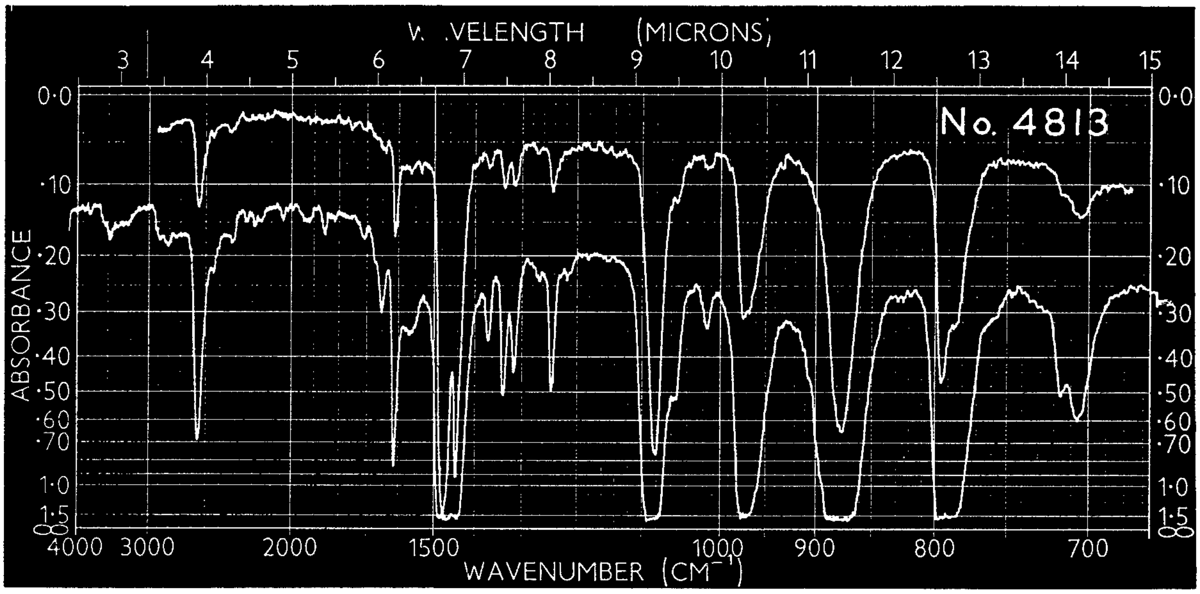
Spectrum No. 4283A 3,3'-Di(tertiarybutoxy)hexafluoro-4,4'-dinitrobiphenyl (in CCl_4)



Spectrum No. 4255 2,4,5-Trifluororesorcinyl diacetate (in CCl_4)



Spectrum No. 4389 2,3,4,6-Tetrafluorothiophenol (film)



Spectrum 4813 Tetrafluorobenzene-1,3-dithiol (film)

APPENDIX IIA

TABLE 1 TGA of Polyimides in Air

Initial Substance (Complex, salt or polyimide)	Dianhydride	Diamine	Solvent	Effect of Heat in Air on Substance			Effect of Heat on Polyimide		
				Conditions	% Wt. Loss	Polyimide obtained	Conditions	% Wt.Loss	Figure (TGA Curves in Appendix)
C 1	PMDA (pure)	m - F	THF	6°/min to 300°	26%				1
				6°/min to 400°	27%	PI(11)	400°,48 hr.	8%	1,3
C 2	PMDA (pure)	p - F	THF	6°/min to 300°	27%				
				6°/min to 400°	28%	PI(12)	400°,48 hr.	22.5%	2,3
C 3	PMDA (pure)	OFB	THF	6°/min to 300°	21%				2
				6°/min to 400°	23%	PI(16)	400°,24 hr.	38%	2,3
C 4	PMDA (Not purified: see Discussion)	m - F	NMP	6°/min to 300°	20%				
				6°/min to 400°	23%	PI(15)	400°,24 hr.	19%	3
PI(1)	PMDA (Pure)	m - H	DMAC	6°/min to 400°		PI(1)	400°,48 hr.	15%	3
S 1	PMDA (Pure)	m - F	CH_3OH	6°/min to 300°	24%				
				6°/min to 400°	30% (26%)	PI(13)	400°,24 hr.	25%	3
				1°/min to 300°	30%				
				1°/min to 400°	34%	PI(14)	400°,48 hr.	49%	4

TABLE 2

Polyimide Laminates (% are wt/total weight)

Resin: 51% PMDA/m-F in NMP					6 ply Laminates
Prepreg : from resin on Marglass 116 T*					Cured at (1) 170°/10 psi/2 min. (2) 170°/250 psi/30 min. (3) 170 - 315°/250 psi/45 min.
(a) Dried, but before the B-Stage.			(b) After the B-Stage at 120° for 30 min.		% Cured resin
% Resin	% Solids	% NMP	% wt. loss	% Resin	
46	32	14	(No B-Stage)		25
51	43	8	15	42	34
52			11	47	40
52			9	47	40

* Heat cleaned woven glasscloth, weight 0.187 g/square inch.

TABLE 3. **Polycarbonates by chloroformate melt polymerisation**

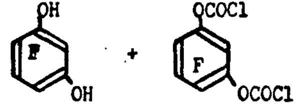
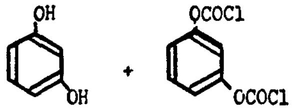
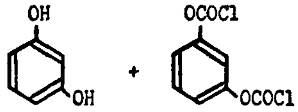
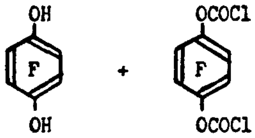
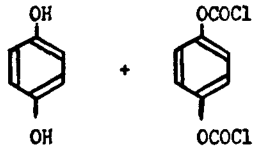
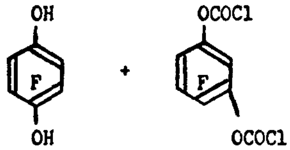
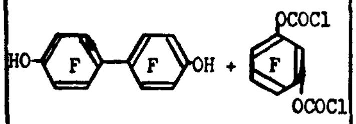
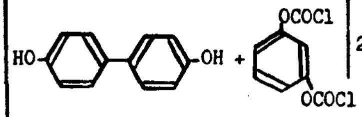
No.	Reactants	Reaction Conditions	Inherent Viscosity dl./g	Softening Point (°C)
PC(5) and (6)		200°/6 hr., then 300°/½ hr.	0.07 (before treatment) (PC(5)) 0.11 (after treatment) (PC(6))	127 - 133 163 - 170 (not complete)
PC(11)		200°/6 hr.	0.18	190 - 220
PC(10)		200°/6 hr., then 300°/10 mins.	Insoluble	
PC(14)		200°/6 hr. then 300°/10 mins.	Insoluble	Not below 320
PC(17)		200°/6 hr., then 300°/½ hr.	Insoluble	Not below 320
PC(22)		200°/5 hr., then 300°/½ hr.	0.04	200 - 240
PC(23)		200°/5 hr., then 300°/½ hr.	0.05	136 - 144
PC(27)		200°/5 hr., then 300°/½ hr.	0.155	224 - 230

TABLE 4 Polycarbonates by Interfacial Polycondensation

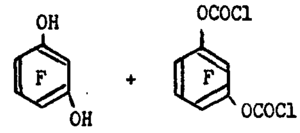
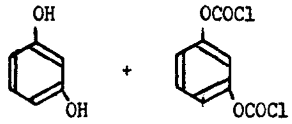
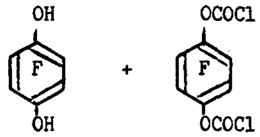
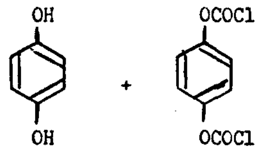
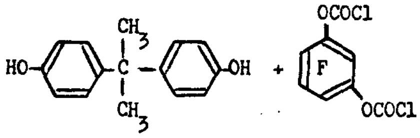
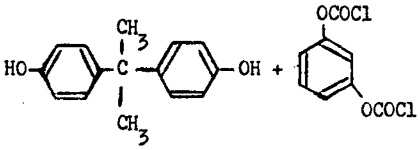
No.	Reactants	Inherent Viscosity dl./g	Softening Point $(^{\circ}C)$
PC(7) and PC(8)		0.04 (Untreated) (PC(7)) 0.165 (Treated) (PC(8))	207 - 240 (not complete) 200 - 300 (not complete)
PC(12)		0.23	202 - 210
PC(15)		0.03	132 - 136
PC(18)		0.05 (conc. H_2SO_4)	not below 320
PC(24), (25)		Acetone-insoluble 0.046 (PC(24)) Acetone-soluble 0.1 (PC(25))	165 - 185 149 - 169
PC(26)		Acetone-soluble 0.06	< 50

TABLE 5 Polycarbonates by Melt Transesterification

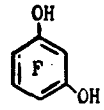
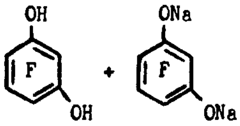
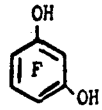
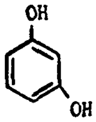
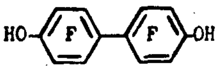
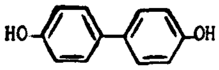
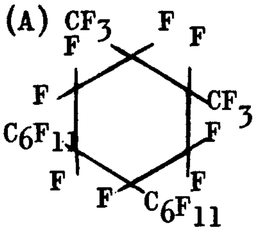
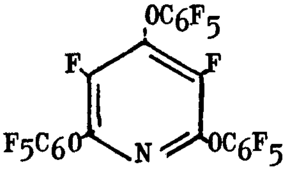
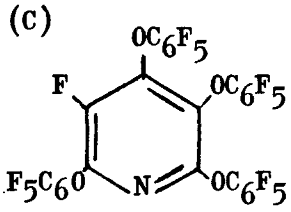
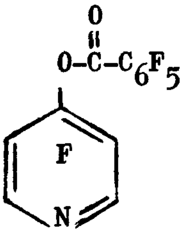
No.	Dihydric phenol reacted with $(C_6H_5O)_2$ CO	Reaction Conditions	Inherent Viscosity dl./g.	Softening Point (°C)
PC(2)		250°/Atmospheric pressure/ 3 hrs. then 250°/20 mm./2 hr.	0.025	58 - 75
PC(3)	 (Trace)	250°/Atmospheric pressure/ 3 hrs. then 250°/20 mm./2 hr.	No solid product	
PC(4)		300°/25 mm./3 hr.	Insoluble	Not below 320
PC(13)		300°/Atmospheric pressure/ 1 hr. then 300°/20 mm./3 hr.	0.18	212.5 Recrystallised
PC(16)		200°/Atmospheric pressure/ ½ hr. then 300°/30 mm./2½ hr.	Insoluble	Not below 320
PC(19)		200°/Atmospheric pressure/ ½ hr. then 300°/30 mm./2½ hr.	Insoluble	Not below 320
PC(20)		300°/Atmospheric pressure/ 6 hr. then 300°/30 mm./2 hr.	0.04	75 - 82
PC(21)		300°/Atmospheric pressure/ 5 hr. then 300°/20 mm./2 hr.	Insoluble	Not below 320

TABLE 6 **Reaction of $C_6F_5SO_2Cl$ with Decafluorobiphenyl**

No.	$C_{12}F_{10}$		$C_6F_5SO_2Cl$ moles	CuCl (g)	Refluxing Time (hr.)	% Evolution		Work-Up	Product Calc. for $C_{18}F_{15}Cl$: C,40 .3; F,53.1; Cl 6.6; M.W.536.5
	Source	Moles				SO_2	Cl^-		
1	As ex I.S.C.	0.2	0.02	-	76	47.5	-	(1) Distillation of $C_{12}F_{10}$ (2) Recrystallisation (petrol)	m.p. 138 - 140° Found: C,40.3; F,49.5; Cl, 6.4.
2	Recovered from 1	0.168	0.0168	- 0.1	11½ + 8½	- 2	- 1	(1) Distillation of $C_{12}F_{10}$ (2) Recrystallisation (petrol)	$C_{12}F_{10}$, m.p. 65 - 70°
3	As ex I.S.C.	0.2	0.02	0.05	20	81	17½	(1) Distillation of $C_{12}F_{10}$ (2) Recrystallisation (petrol) (3) Sublimation	m.p. 158 - 159° Found: C,40.0; F,52.9; Cl,6.3; M.W. 513 and 540
4	Recovered from 3 Redistilled and recrystallised	0.08	0.008	0.02	260	71	28	Distillation of $C_{12}F_{10}$	Sticky solid.
5	As ex I.S.C.	0.6	0.06	0.16	5	99.7	6	(1) Distillation of $C_{12}F_{10}$ (2) Recrystallisation (petrol)	m.p. 151-153°
6	Recovered from 5	0.525	0.0525	0.14	94	52	6	(1) Distillation of $C_{12}F_{10}$ (2) Recrystallisation (petrol) (3) Chromatography (alumina/ petrol)	(2) m.p. 153 - 154° (3) m.p. 157 - 158°
7	Recovered from 6	0.476	0.0476	0.12	102	28	5	(1) Distillation of $C_{12}F_{10}$ (2) Recrystallisation (petrol) (3) Chromatography (alumina/ acetone)	(2) m.p. 147 - 151° (3) m.p. 152 - 153° Found: C,40.4; F,52.5; Cl,7.0
8	Recovered from 7, and 1% of 2,2',3,3',5,5',6,6'-octafluoro-biphenyl added.	0.47	0.06	0.15	150	49	8	(1) Distillation of $C_{12}F_{10}$ (2) Recrystallisation (petrol)	$C_{12}F_{10}$, m.p. 56 - 58°

TABLE 7 Thermal Stability of Model Compounds

Compound	Rate of Vapour Pressure increase	T_D
(A) 	0.12 mm per minute at 308°	Not determined because of low boiling point.
(B) 	0.84 mm per minute at 329°	329°
(C) 	0.84 mm per minute at 335°	335°
(D) 	0.84 mm per minute at 266°	266°

The T_D of compound (A) is referred to in the Discussion of Part II. The thermal stability results on (B), (C), and (D) were obtained after the Discussion had been written. (A) is compound (VI) described in Part IV. (B), (C) & (D) are the compounds XXV , XXVI , and XXXIV of Part V .

APPENDIX IIB

TGA in air of polymers

Procedure : The sample (weights given below) was heated in a platinum crucible in the furnace of a Stanton HTD thermobalance. The rate of heating was approximately 0.6^{0}/minute to 190^{0} and 1^{0}/minute above 190^{0}, except where stated.

Figure 1

Curve No.			Sample Wt.
1	PI (1)	Poly (m-phenylene pyromellitimide)	200 mg.
2	PI (2)	Poly (tetrafluoro-m-phenylene pyromellitimide)	89 mg.
3	C 1	Complex PMDA/m-F, ex THF (6^{0}/minute from 60^{0})	157 mg.
4	C 1	Complex PMDA/m-F, ex THF	200 mg.
5	C 4	Complex PMDA/m-F, ex NMP	200 mg.
6	S 1	Half-ester salt PMDA/CH_3OH/m-F, ex CH_3OH	200 mg.

Figure 2

1	C 1	Complex PMDA/m-F, ex THF	200 mg.
2	C 2	Complex PMDA/p-F, ex THF	200 mg.
3	C 3	Complex PMDA/OFB, ex THF	200 mg.

Figure 3

Isothermal TGA at 400^{0}: the samples were heated to 400^{0} at 6^{0}/min.

1	PI (11)	Poly (tetrafluoro-m-phenylene pyromellitimide) ex C 1	147 mg.
2	PI (1)	Poly (m-phenylene pyromellitimide) ex polyamic acid	91 mg.
3	PI (12)	Poly (tetrafluoro-p-phenylene pyromellitimide) ex C 2	144 mg.
4	PI (15)	Poly (tetrafluoro-m-phenylene pyromellitimide) ex C 4	170 mg.
5	PI (13)	Poly (tetrafluoro-m-phenylene pyromellitimide) ex S 1	152 mg.
6	PI (16)	Poly(octafluoro-biphenylyl pyromellitimide) ex C 3	156 mg.

Figure 4

Isothermal TGA at 400°: the sample was heated to 400° at 6°/min.

Curve No.			Sample Wt.
1	PI (14)	Poly (tetrafluoro-m-phenylene pyromellitimide) ex S 1.	132 mg

Figure 5

1	S 1	Half-ester salt PMDA/CH_3OH/m-F ex CH_3OH	200 mg
2	C 5	Complex tetramethyl difluoro pyromellitate/m-F ex THF	200 mg.
3	S 3	Salt Difluoro pyromellitic acid/m-F ex NMP	200 mg.
4	S 2	Salt as S3 but ex C_2H_5OH	200 mg.
5	S 2	Salt as S2 after sublimation of m-F	200 mg.
6		Difluoropyromellitic acid	200 mg.

Figure 6

1	ex attempted preparation of poly (2,2'-di (tetrafluoro-m-phenylene) hexafluoro-6,6'-bibenzoxazole), heated at 1°/minute	200 mg.
2	ex attempted preparation of poly (2,2'-di (tetrafluoro-m-phenylene) hexafluoro-6,6'-bibenzoxazole), heated at 6°/minute.	200 mg.

Figure 7

Polycarbonates by Chloroformate Melt Polymerisation.	200 mg.

Figure 8

Co-polycarbonates by Chloroformate Melt Polymerisation.	200 mg.

Figure 9

Polycarbonates by Interfacial Polycondensation.	200 mg.

Figure 10

Polycarbonates from Bisphenol A.	200 mg.

Figure 11

Polycarbonates by Melt Transesterification.	200 mg.

Figure 12

	Sample Wt.
Comparison of polycarbonates of highest thermo-oxidative stability.	200 mg.

Figure 13

1.	Poly(p-phenylene-1,3,4-oxadiazole)	202 mg.
2.	Poly(tetrafluoro-p-phenylene-1,3,4-oxadiazole)	202 mg.

Figure 14

Heating Rate for Stanton Thermobalance (Model HTD) (approx. 1°/minute from 190°).

FIGURE I

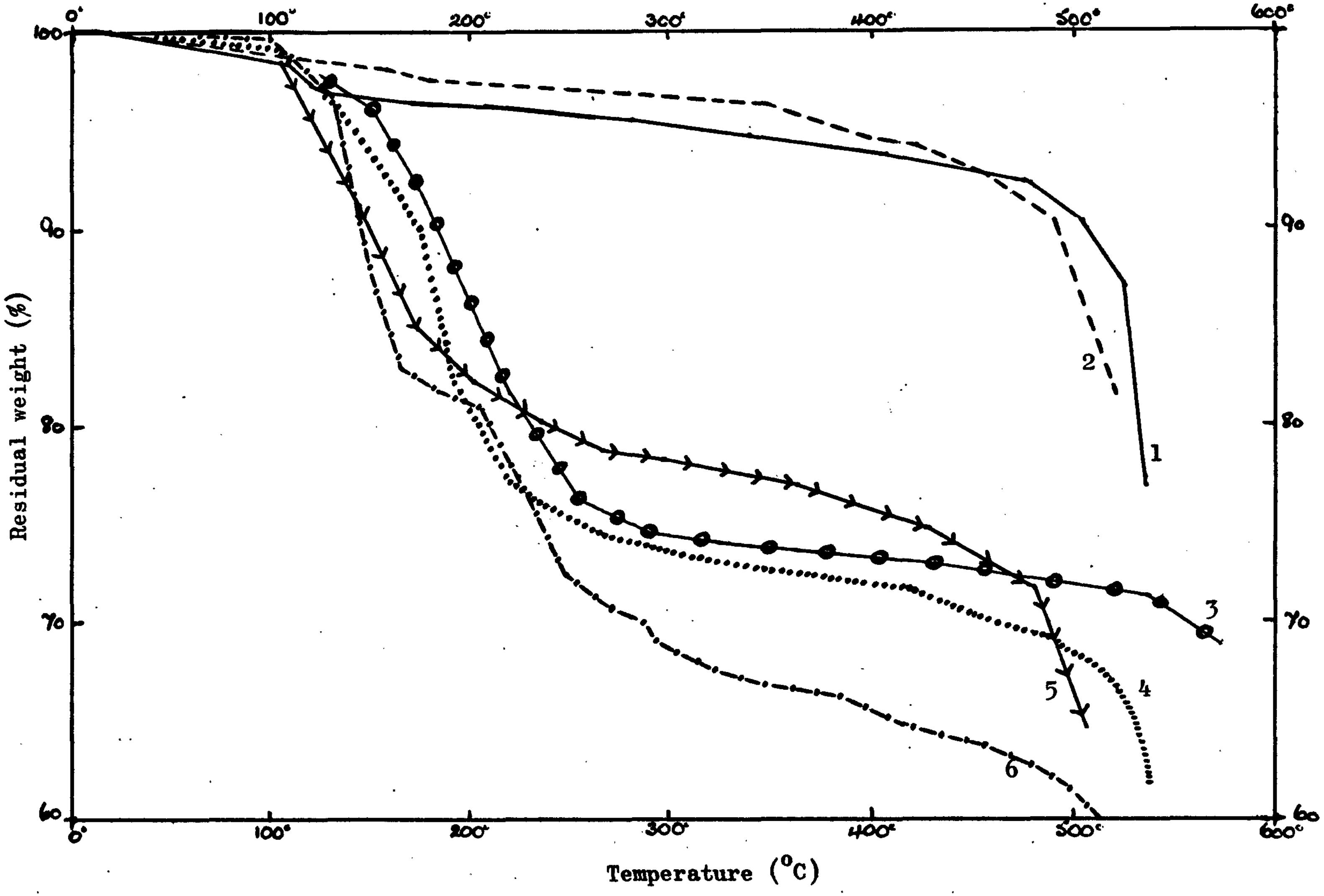

Residual weight (%)
Temperature (°C)
0°
100°
200°
300°
400°
500°
600°
100
90
80
70
60
1
2
3
4
5
6

FIGURE 2

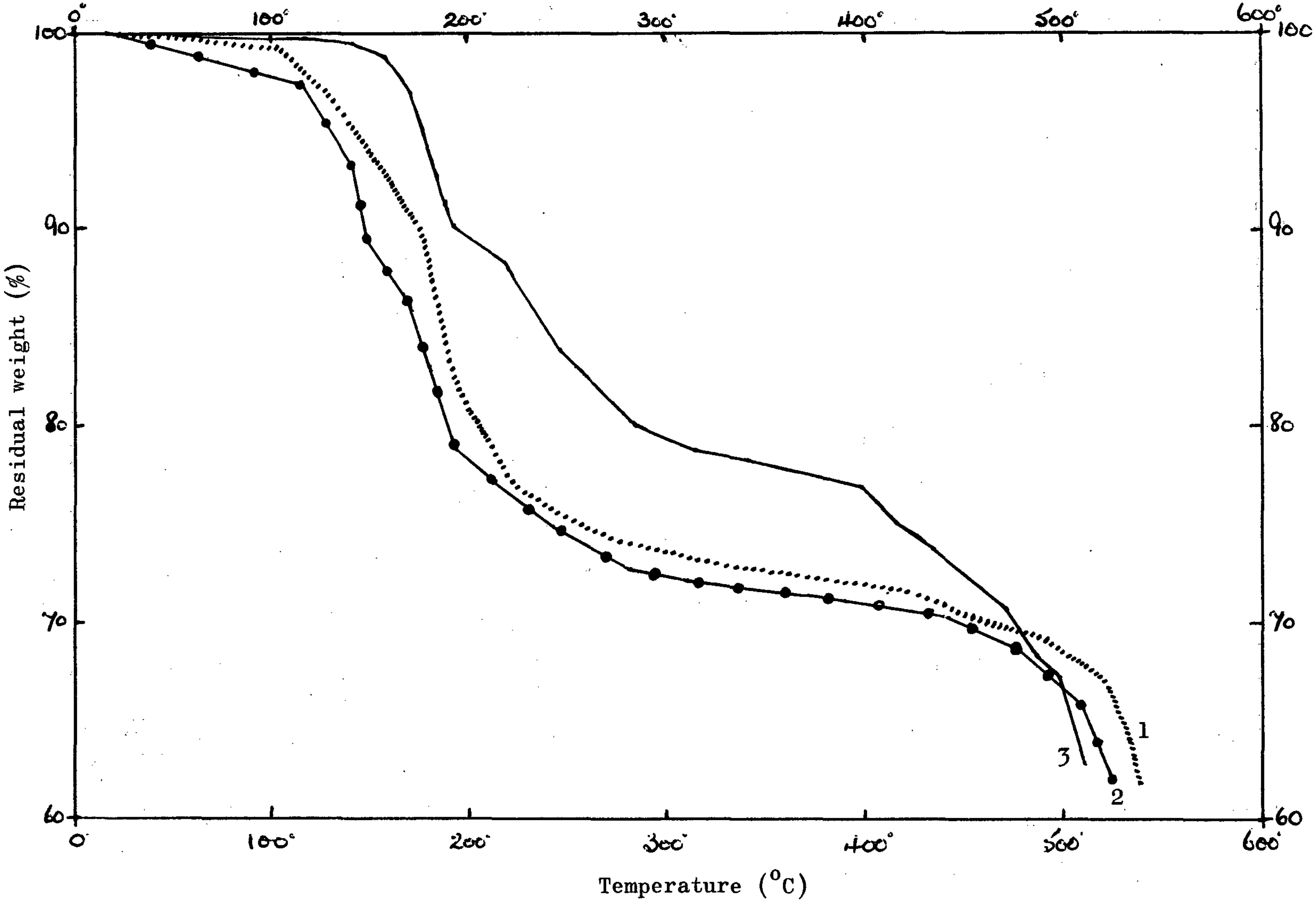

0°
100°
200°
300°
400°
500°
600°
100
90
80
70
60
1
2
3
Residual weight (%)
Temperature (°C)

FIGURE 3

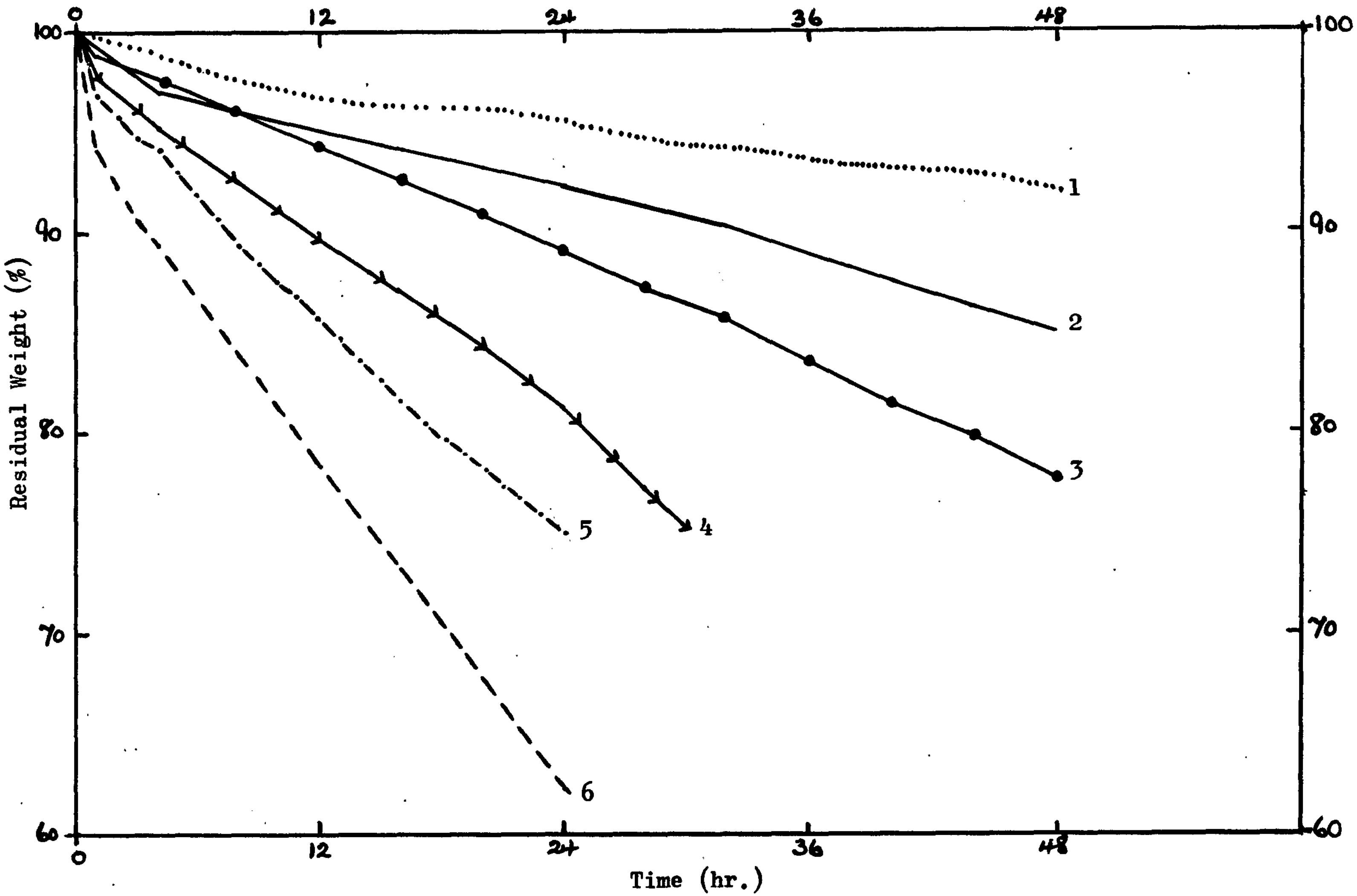


FIGURE 4

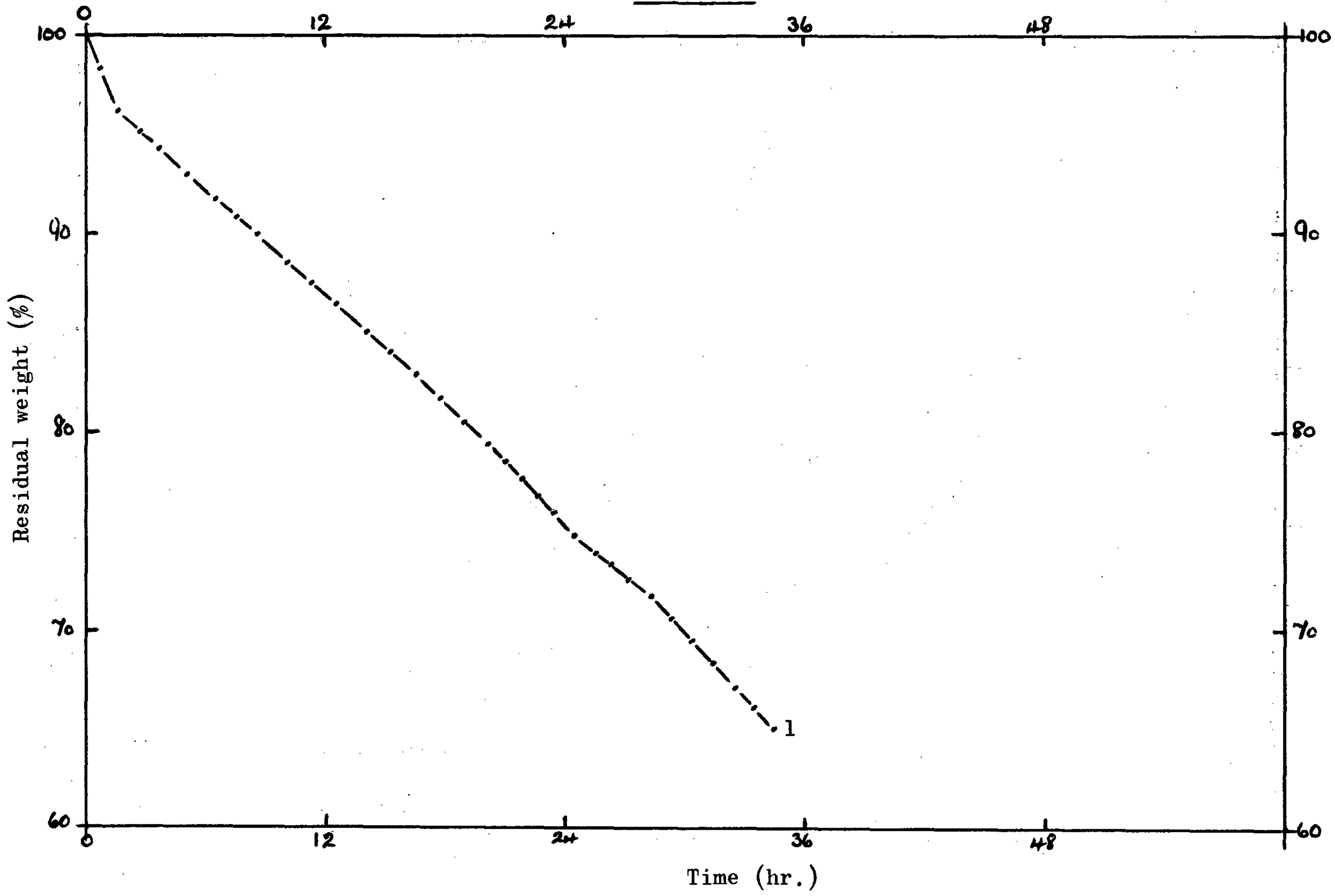


FIGURE 5 - POLYIMIDES & INTERMEDIATES

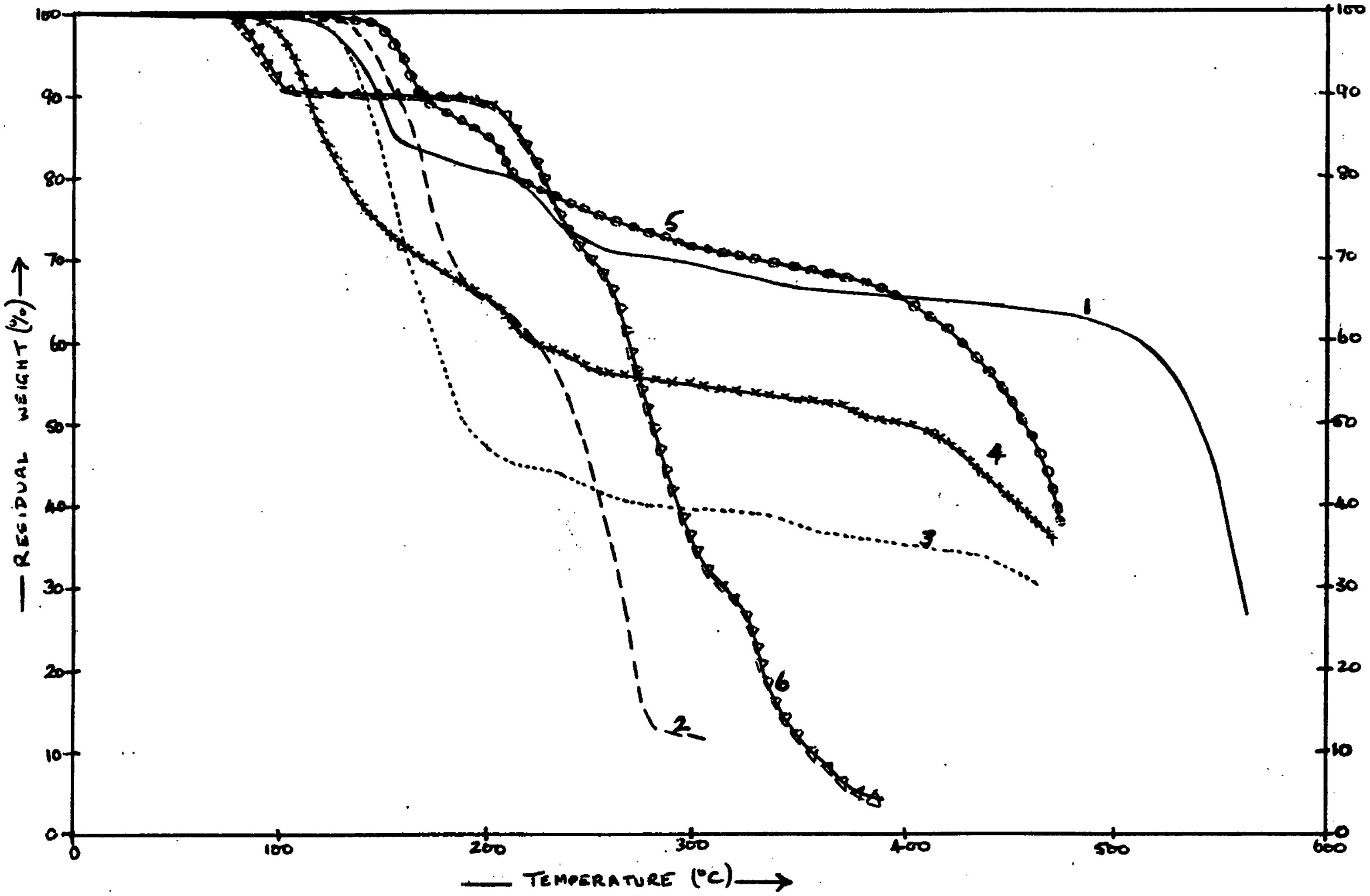


FIGURE 6 - POLYBENZOXAZOLES

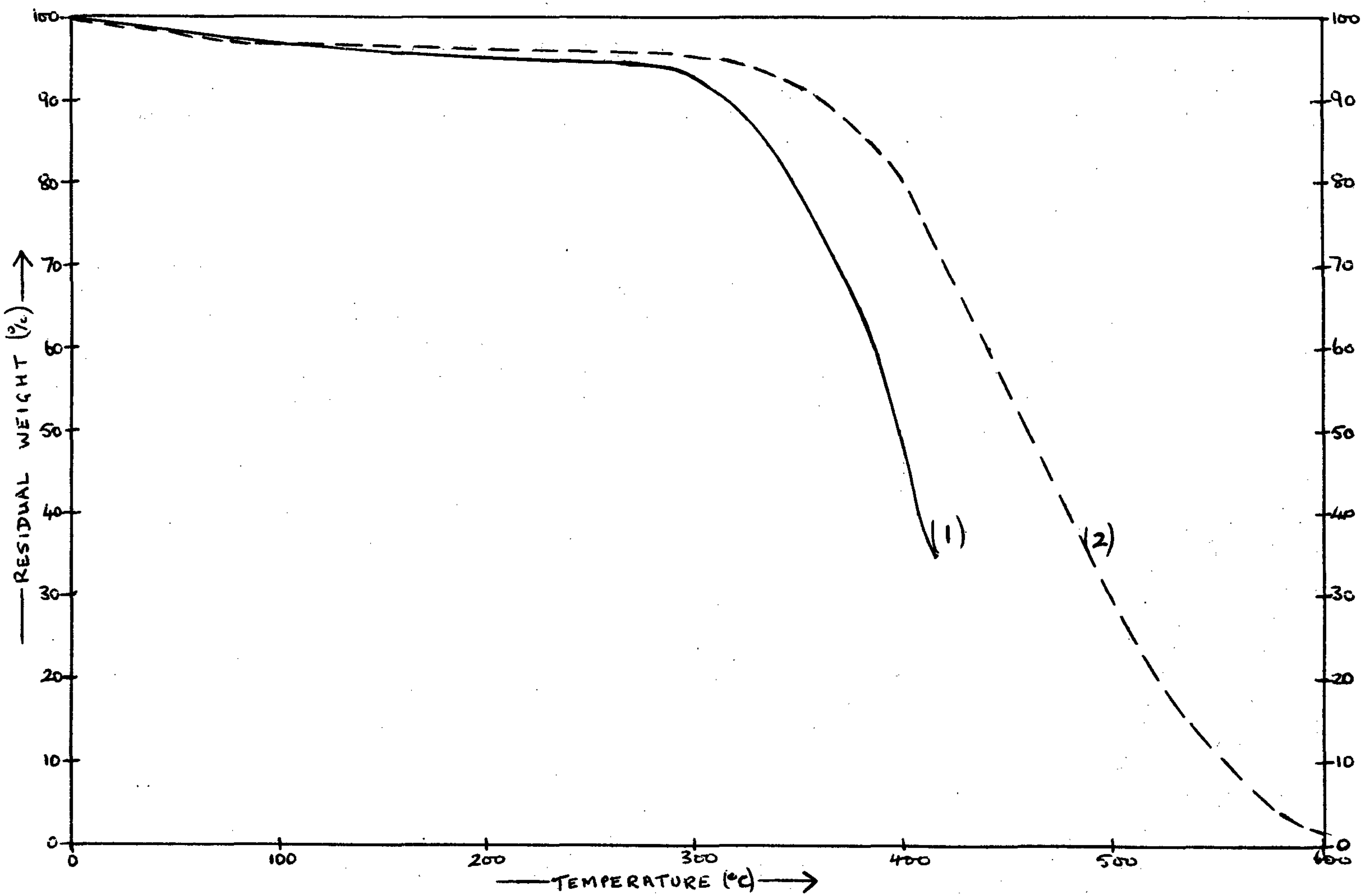


FIGURE 7 Polycarbonates by Chloroformate Melt Polymerisation

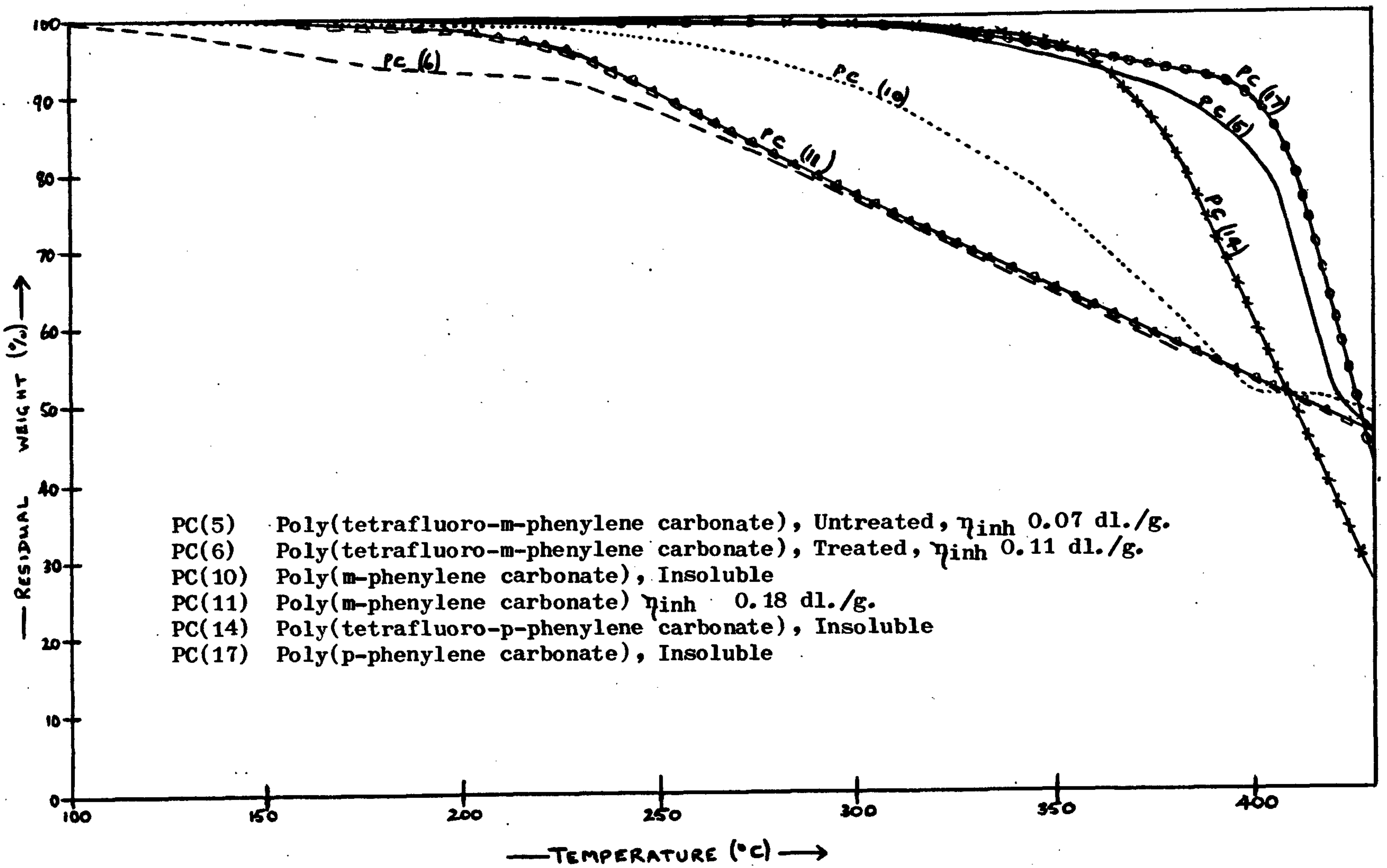


FIGURE 8 Copolycarbonates by Chloroformate Melt Polymerisation

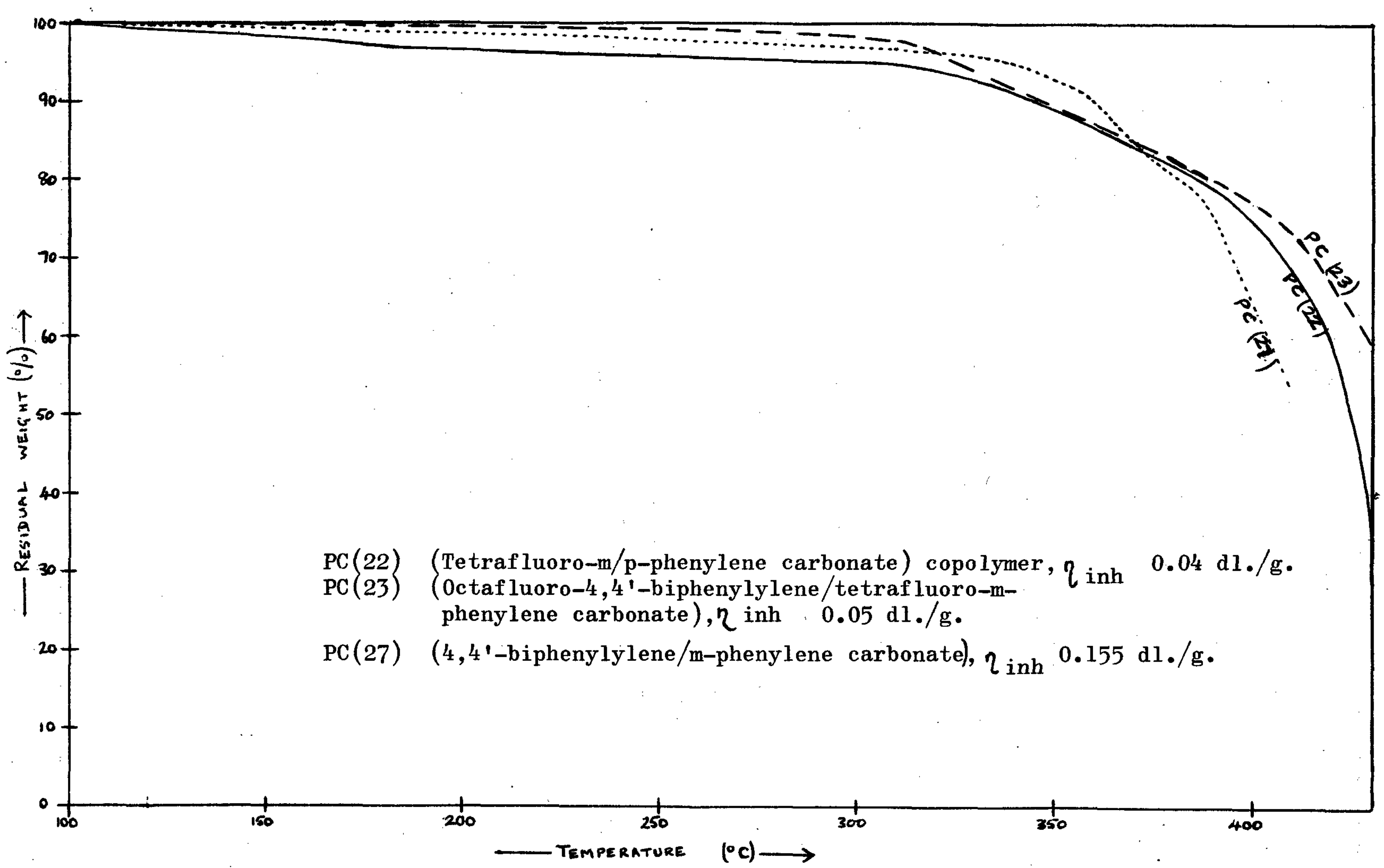


FIGURE 9. Polycarbonates by Interfacial Polycondensation

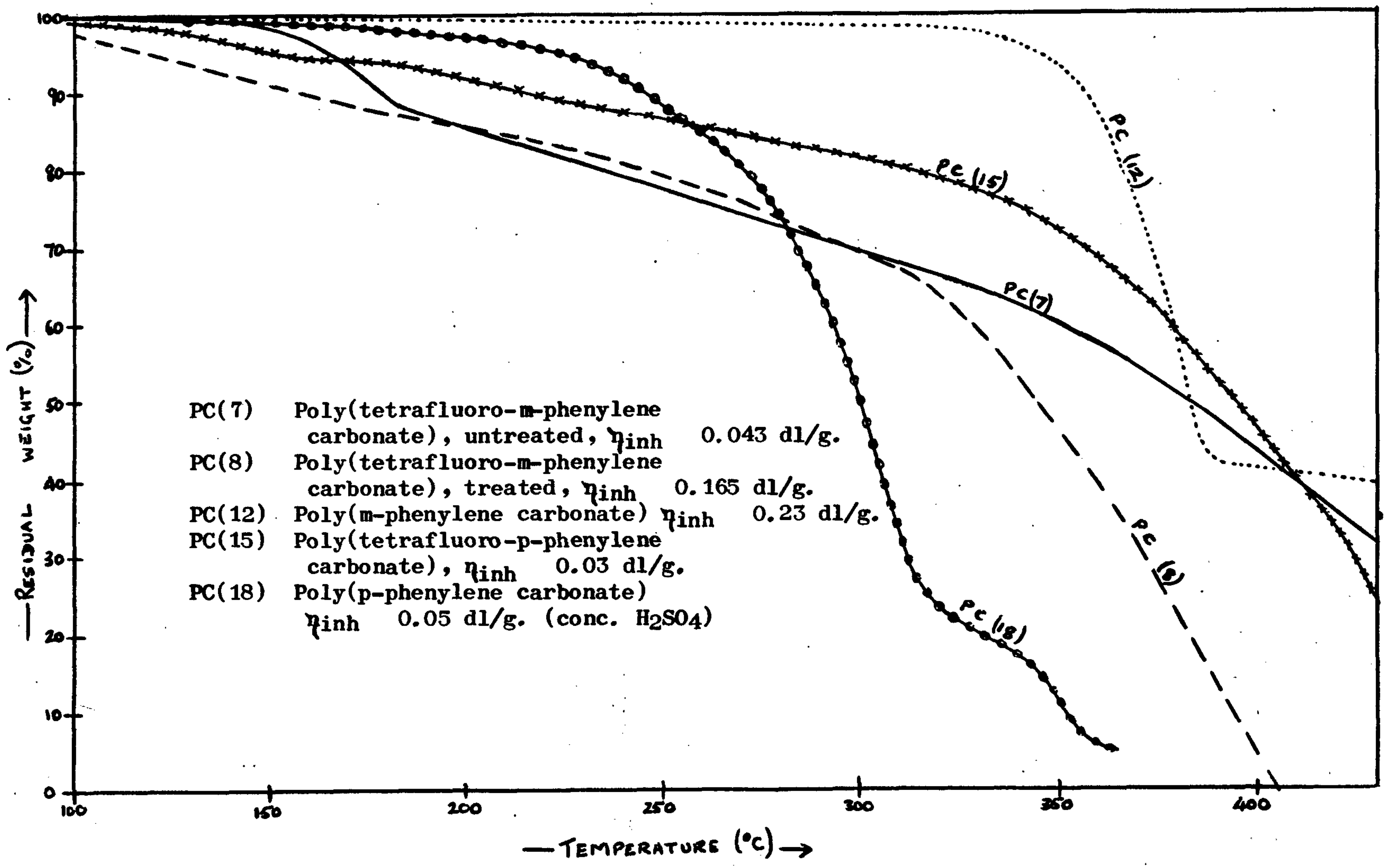
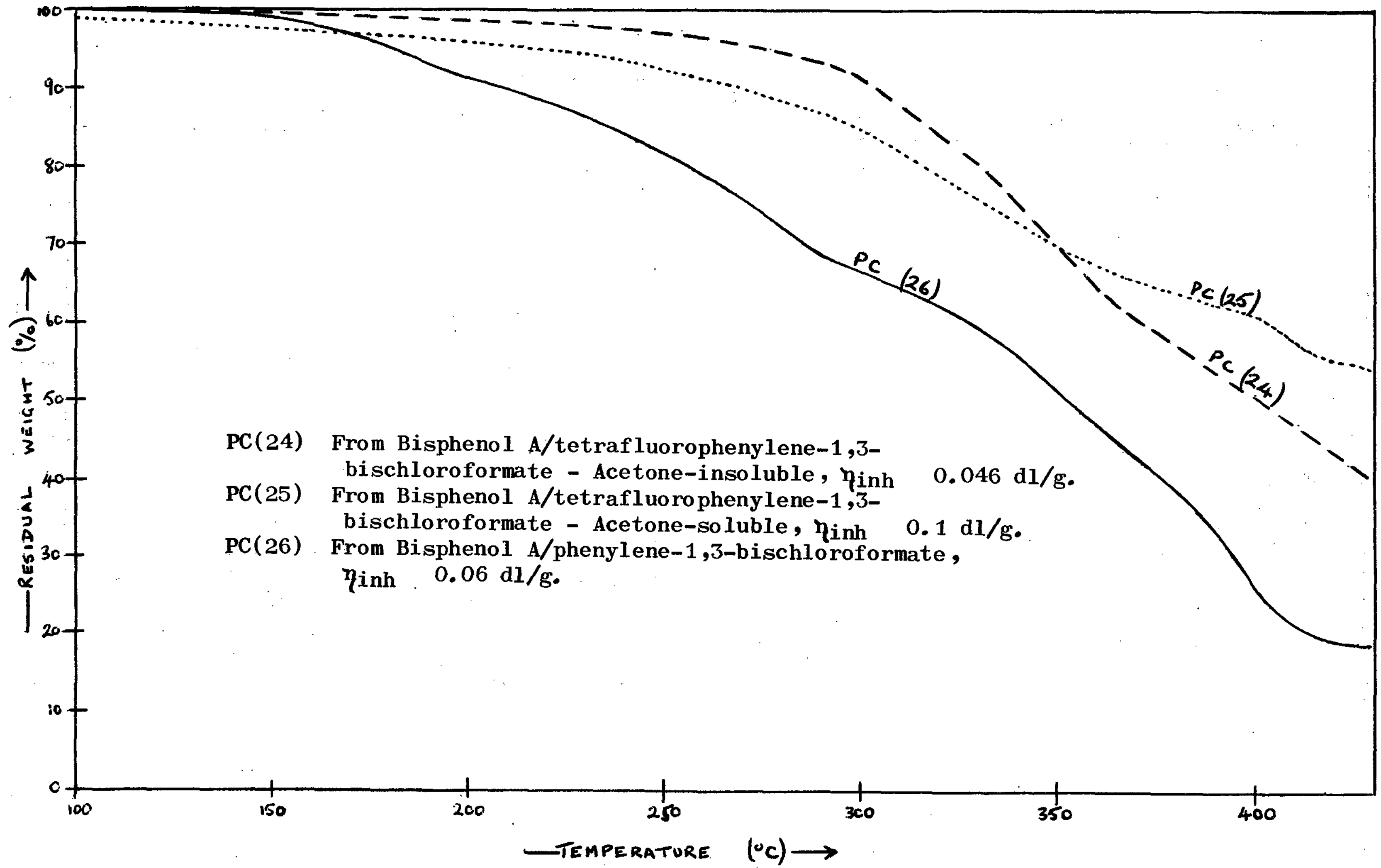


FIGURE 10. Polycarbonates from Bisphenol A



PC(24) From Bisphenol A/tetrafluorophenylene-1,3-bischloroformate - Acetone-insoluble, η_{inh} 0.046 dl/g.

PC(25) From Bisphenol A/tetrafluorophenylene-1,3-bischloroformate - Acetone-soluble, η_{inh} 0.1 dl/g.

PC(26) From Bisphenol A/phenylene-1,3-bischloroformate, η_{inh} 0.06 dl/g.

FIGURE 11. Polycarbonates by Melt Transesterification

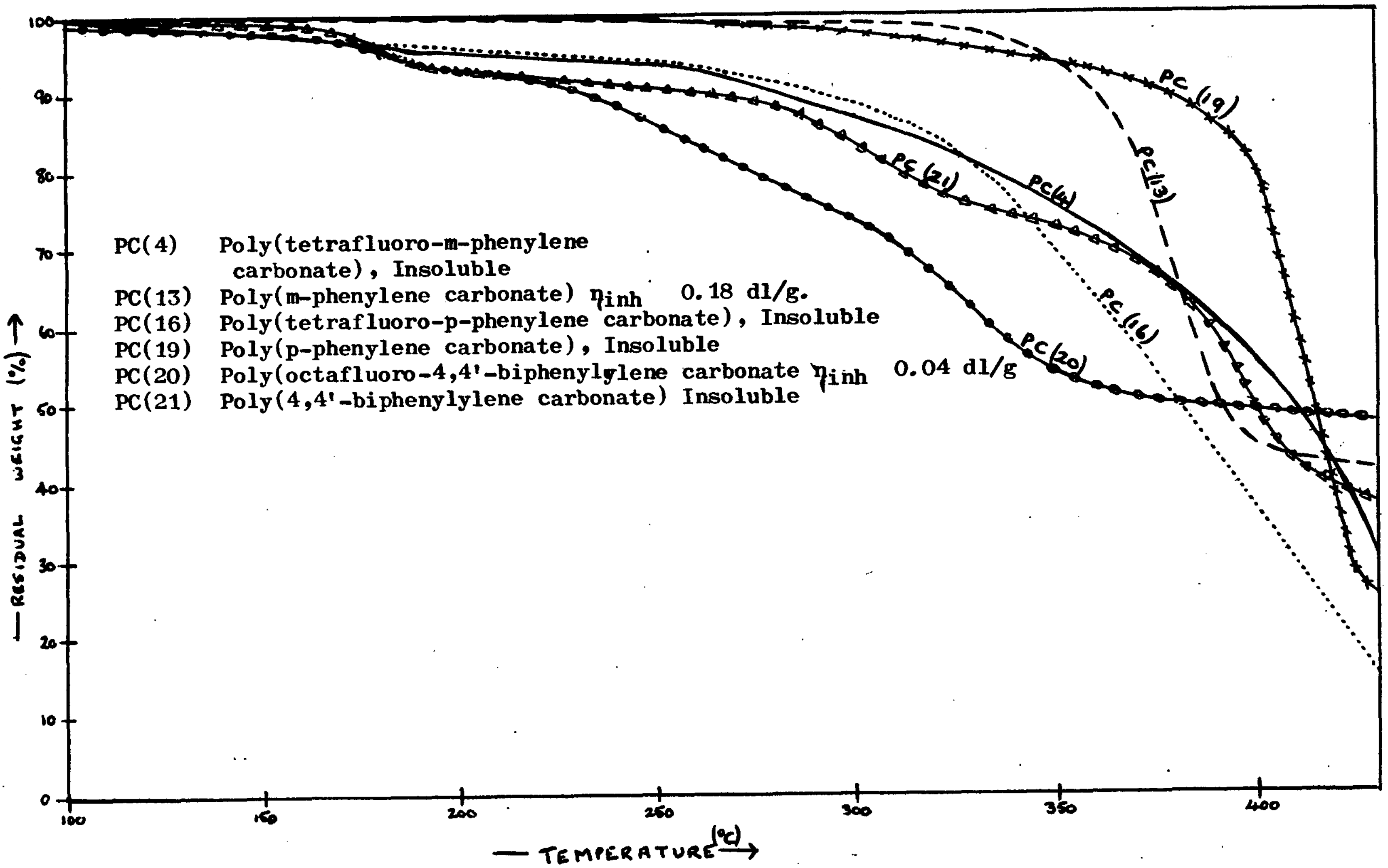
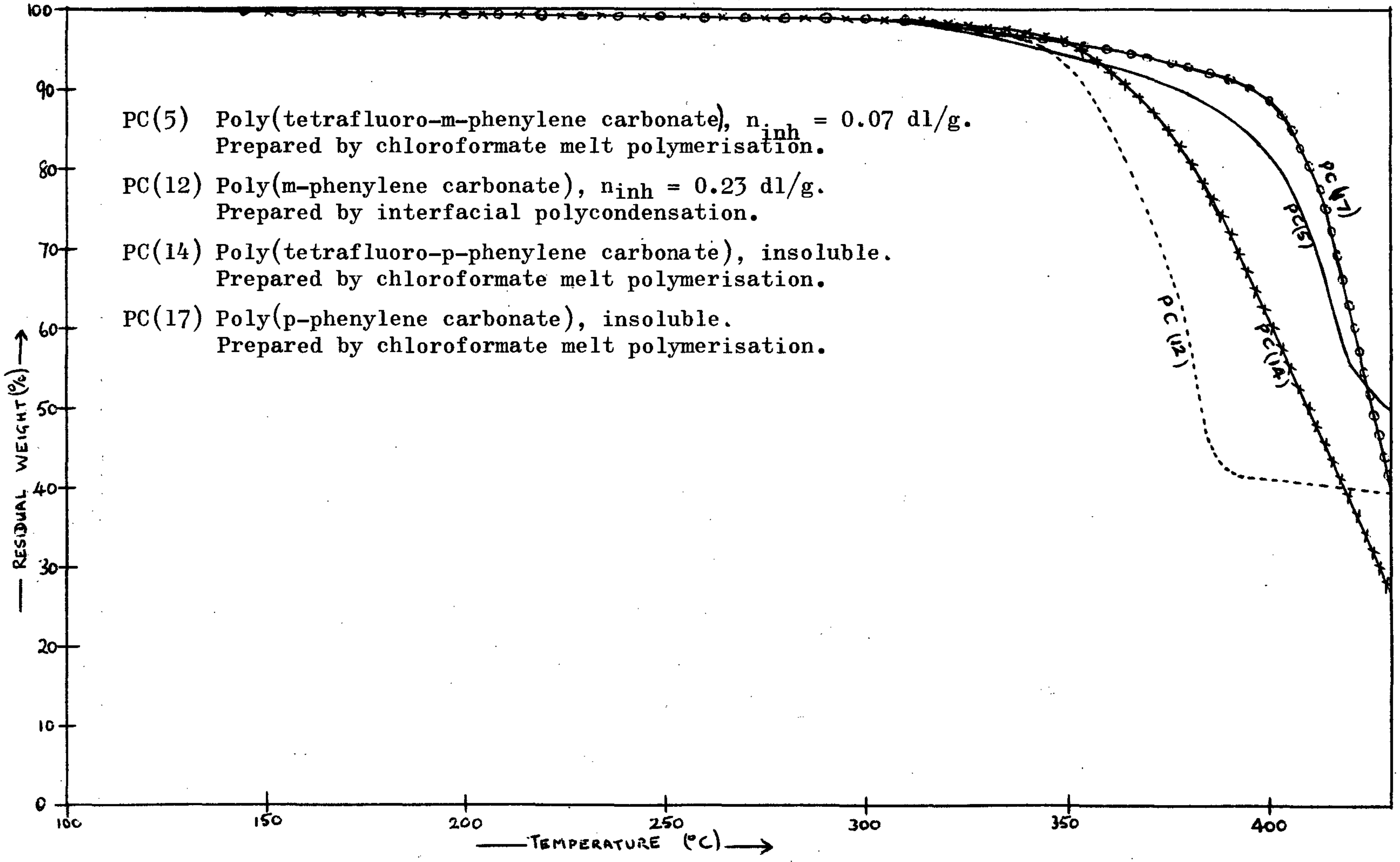


FIGURE 12. Most thermo-oxidatively stable hydrogenic and perfluoro poly(m- and p- phenylene carbonates)



PC(5) Poly(tetrafluoro-m-phenylene carbonate), n_{inh} = 0.07 dl/g. Prepared by chloroformate melt polymerisation.

PC(12) Poly(m-phenylene carbonate), n_{inh} = 0.23 dl/g. Prepared by interfacial polycondensation.

PC(14) Poly(tetrafluoro-p-phenylene carbonate), insoluble. Prepared by chloroformate melt polymerisation.

PC(17) Poly(p-phenylene carbonate), insoluble. Prepared by chloroformate melt polymerisation.

FIGURE 13. POLYOXADIAZOLES

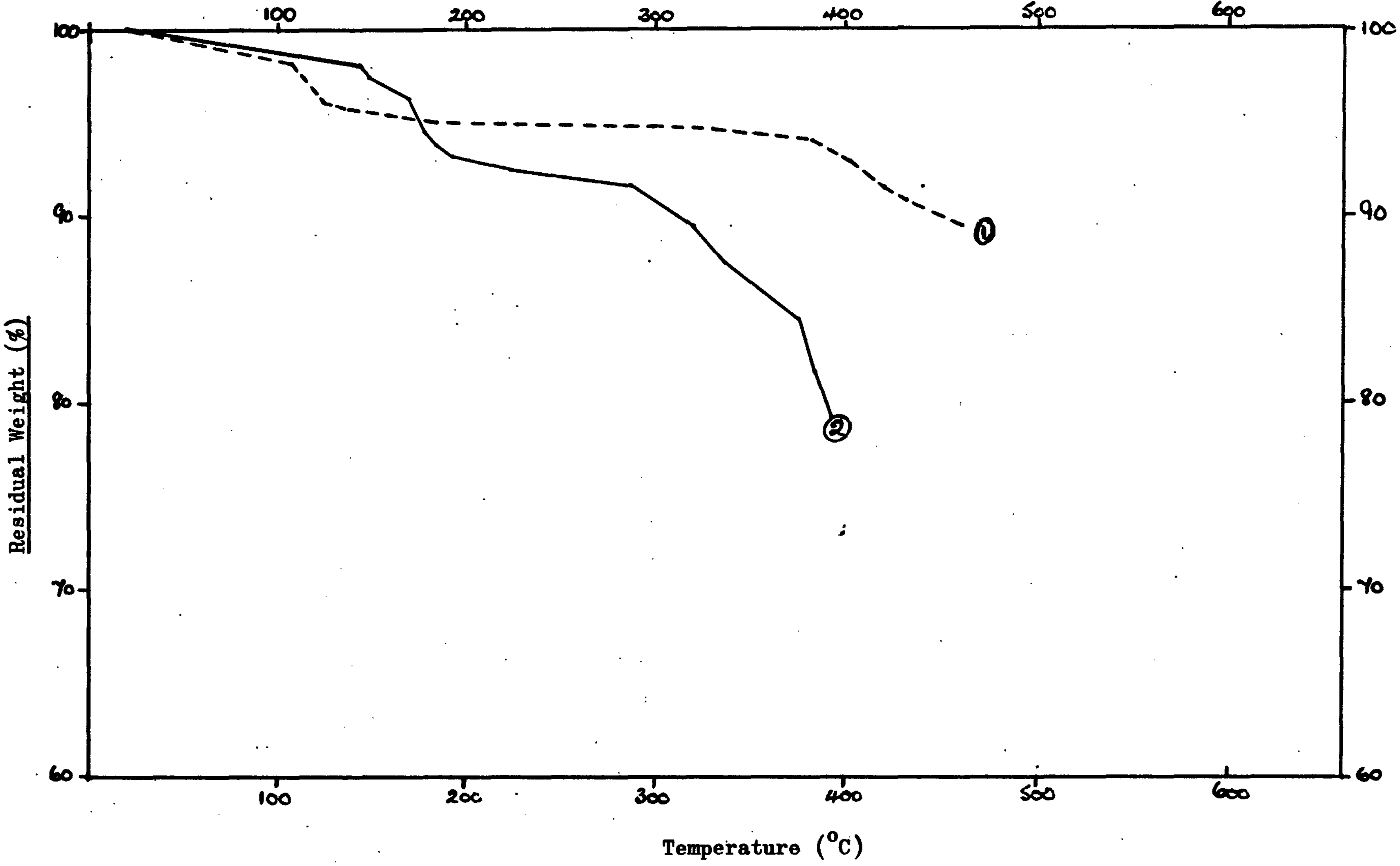
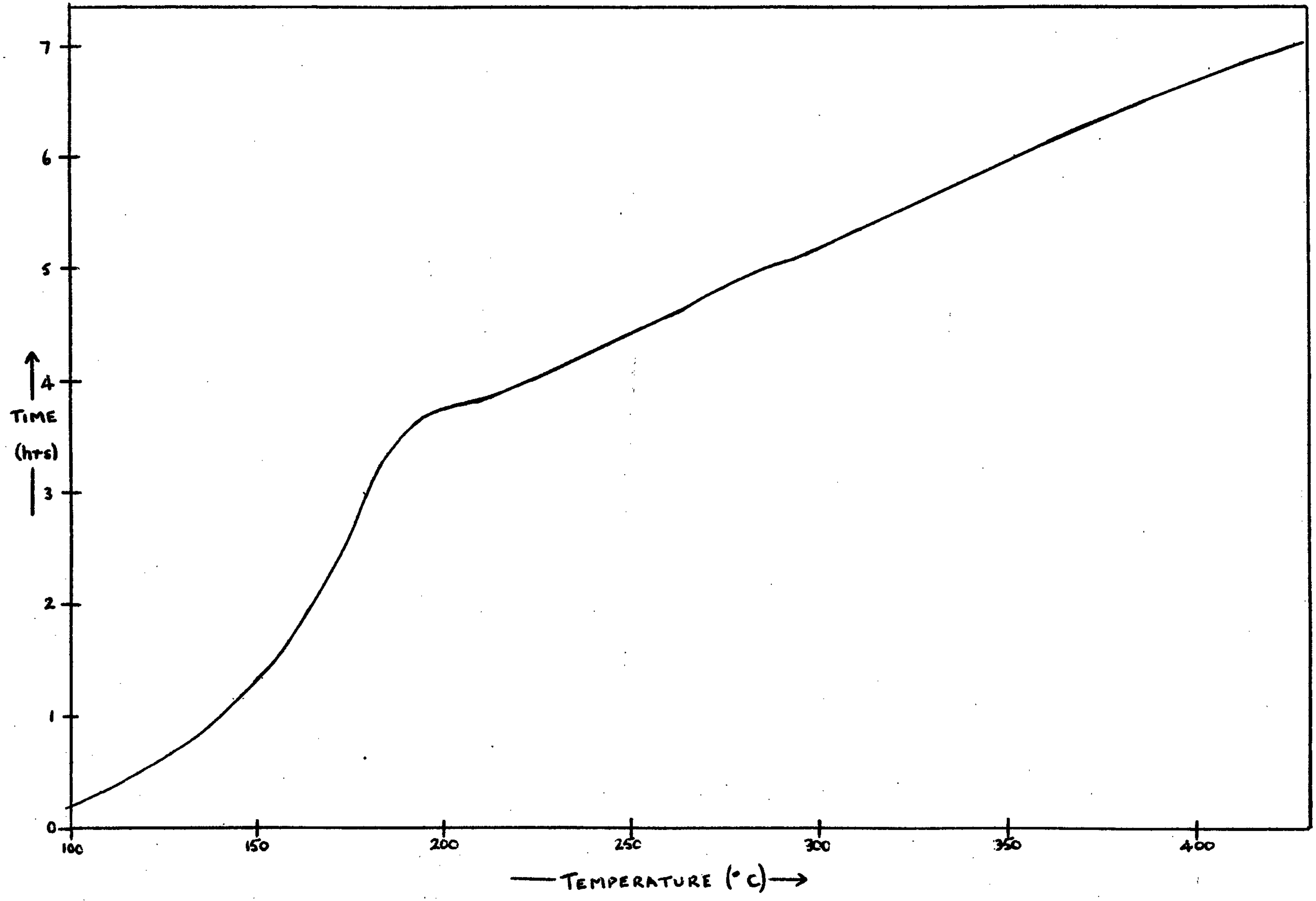


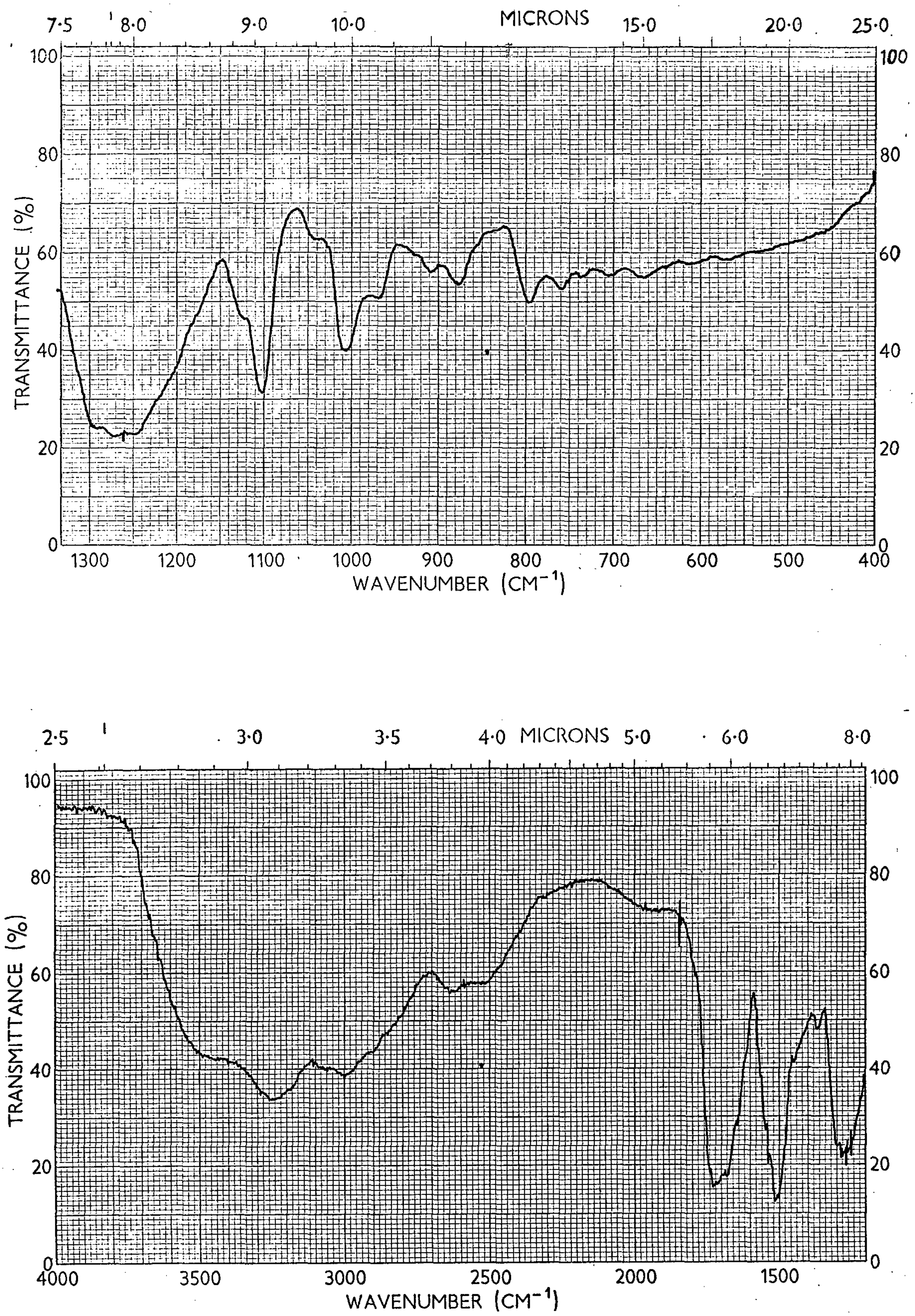
FIGURE 14. Heating Rate for Stanton Thermobalance (Model HTD)



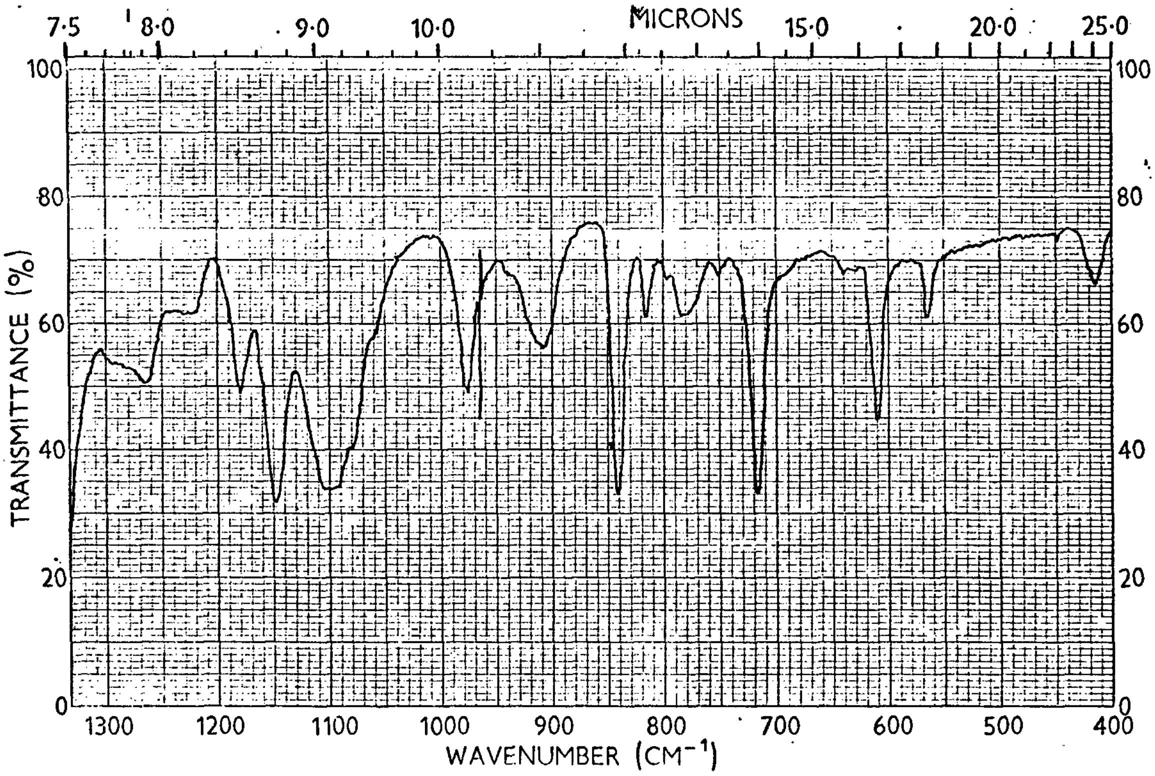
APPENDIX II C

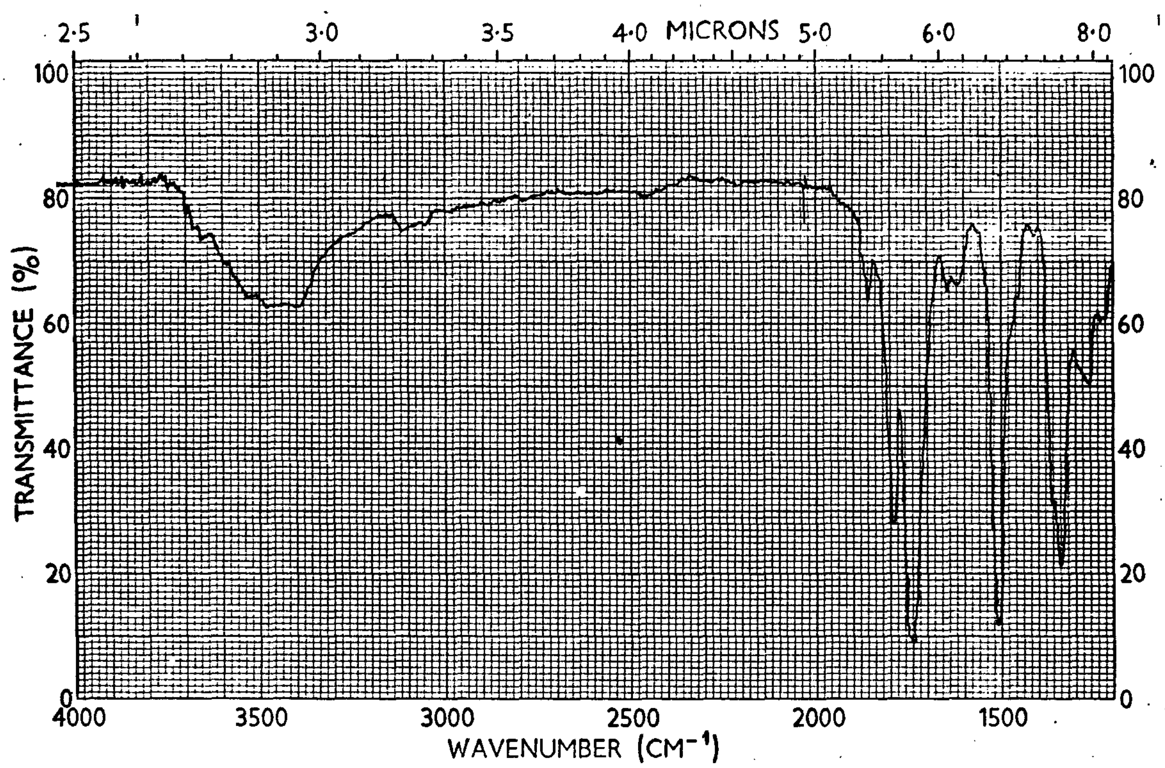
Infra-red Spectra referred to in PART II

No.	
2003	CI. PMDA/tetrafluoro-m-phenylene diamine complex. KBr disc.
2004	Product of heating CI at 1°/min. to 300° on the Stanton Thermobalance. KBr disc.
2137	C4. PMDA/tetrafluoro-m-phenylene diamine complex ex N.M.P. KBr disc.
2138	Product of heating C4 at 6°/min. to 300° on the Stanton Thermobalance. KBr disc.
2240	C2. PMDA/tetrafluoro-p-phenylene diamine complex. KBr disc.
2241	C3. PMDA/octafluorobenzidine complex. KBr disc.
2317	PC5. Poly(tetrafluoro-m-phenylene carbonate) KBr disc.
1974	Compound (XI) $C_6F_5 \cdot C_6ClF_5 \cdot C_6F_5$, m.p. 158-9°, which is probably 6-chloro-1,5-di(pentafluorophenyl)-2,3,4,5,6-pentafluorocyclohexa-1,3-diene. KBr disc.

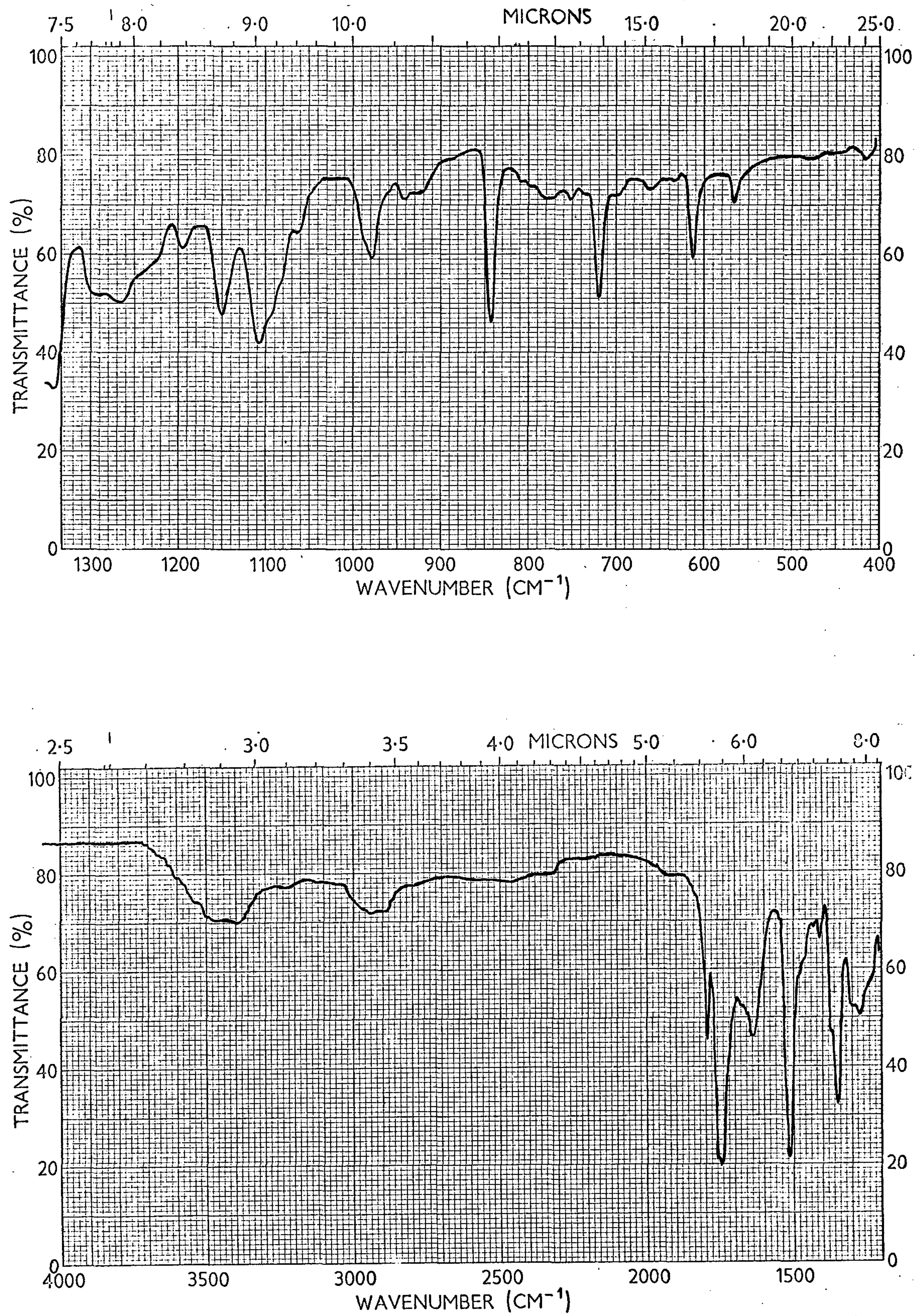


Spectrum No. 2003 CI. PMDA/tetrafluoro-m-phenylene diamine complex. KBr disc

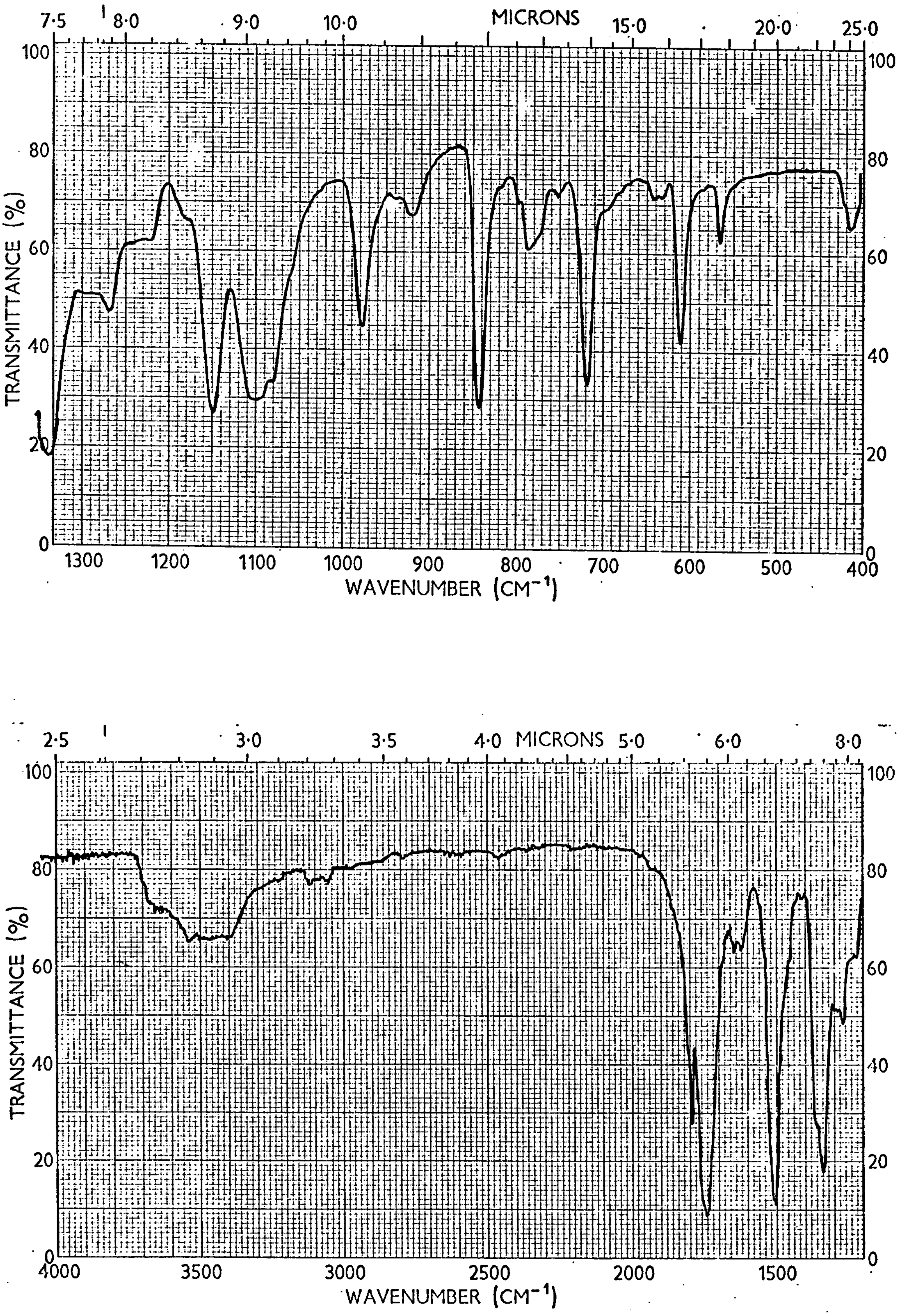




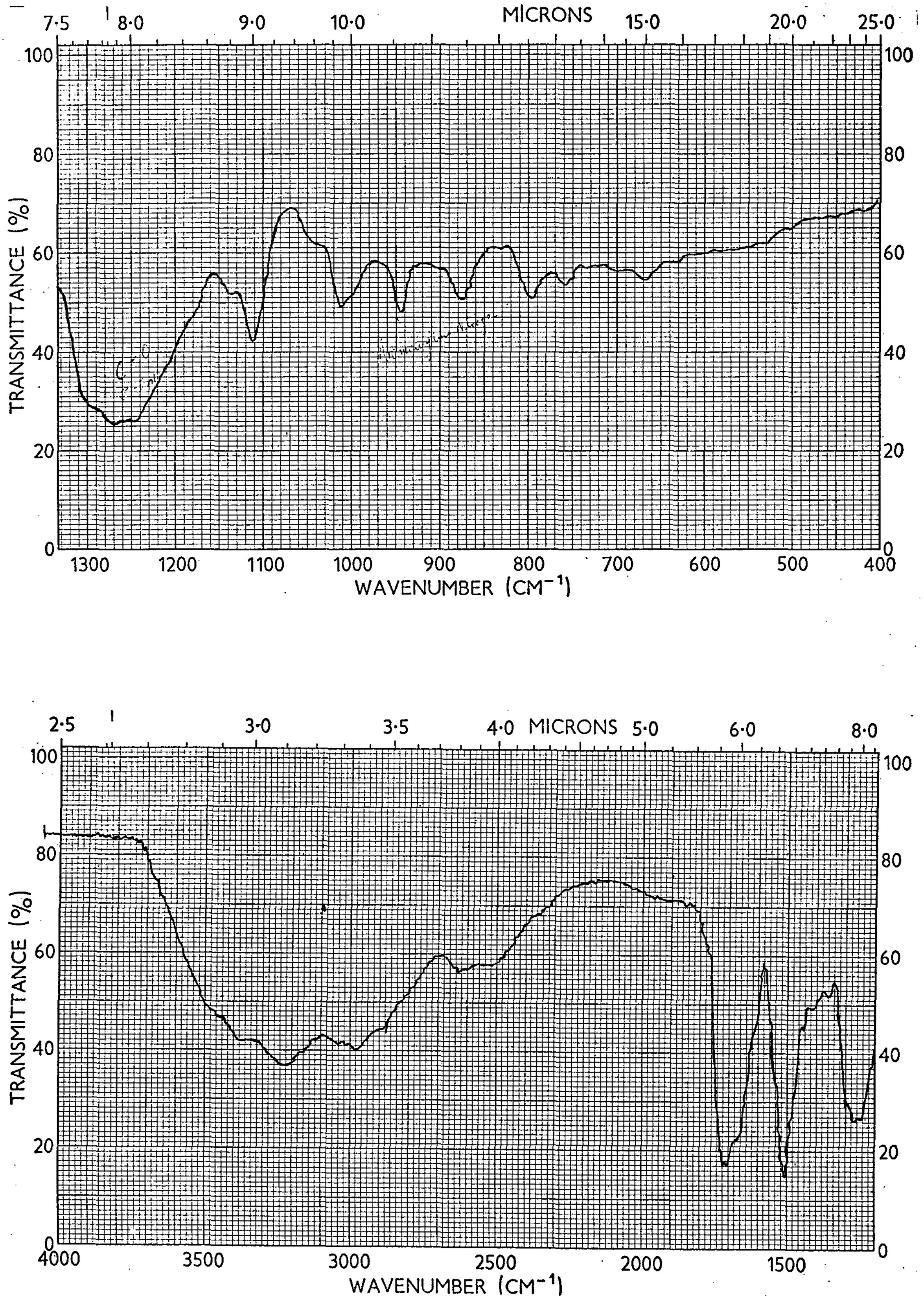
Spectrum No. 2004 Product of heating CI at 1°/min. to 300° on the Stanton Thermobalance. KBr disc



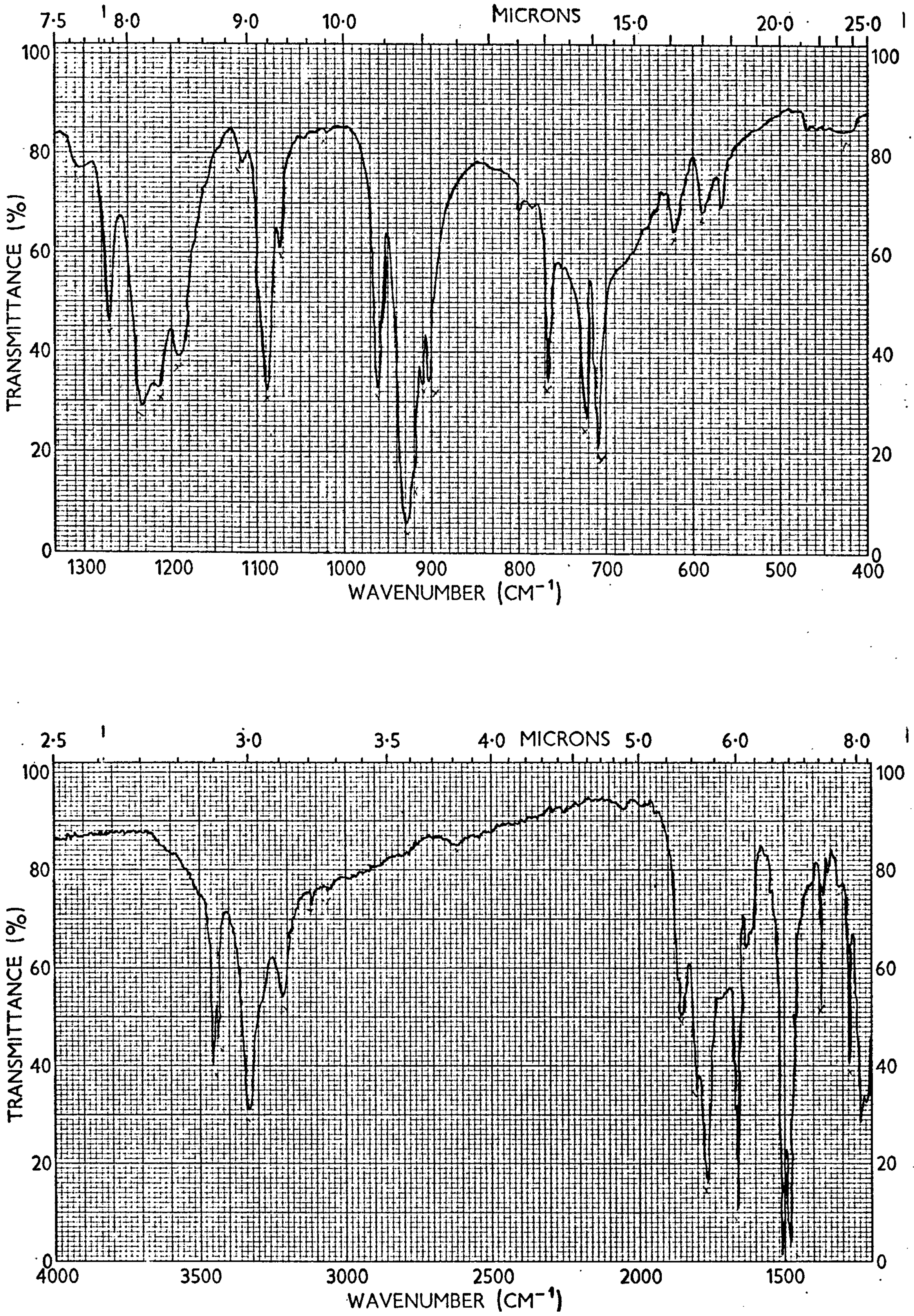
Spectrum No. 2137 C4. PMDA/tetrafluoro-m-phenylene diamine complex ex N.M.P. Kbr disc



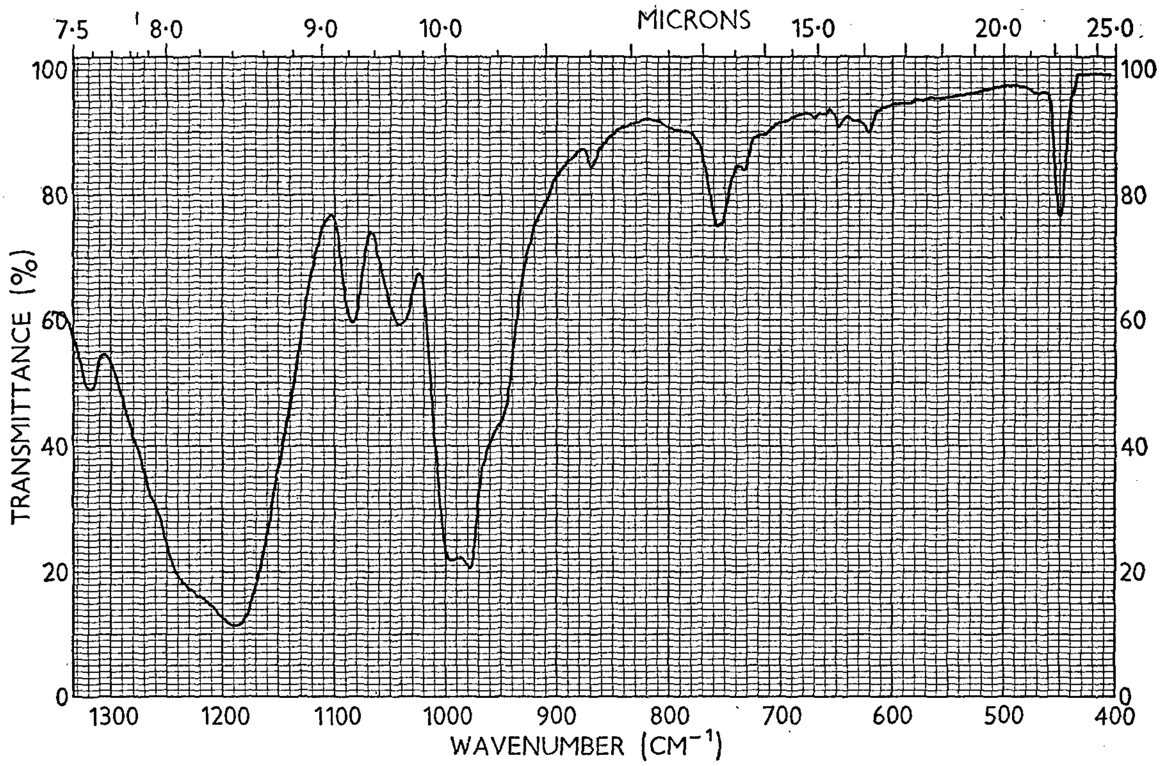
Spectrum No. 2138 Product of heating C4 at 6°/min. to 300° on the Stanton KBr disc Thermobalance

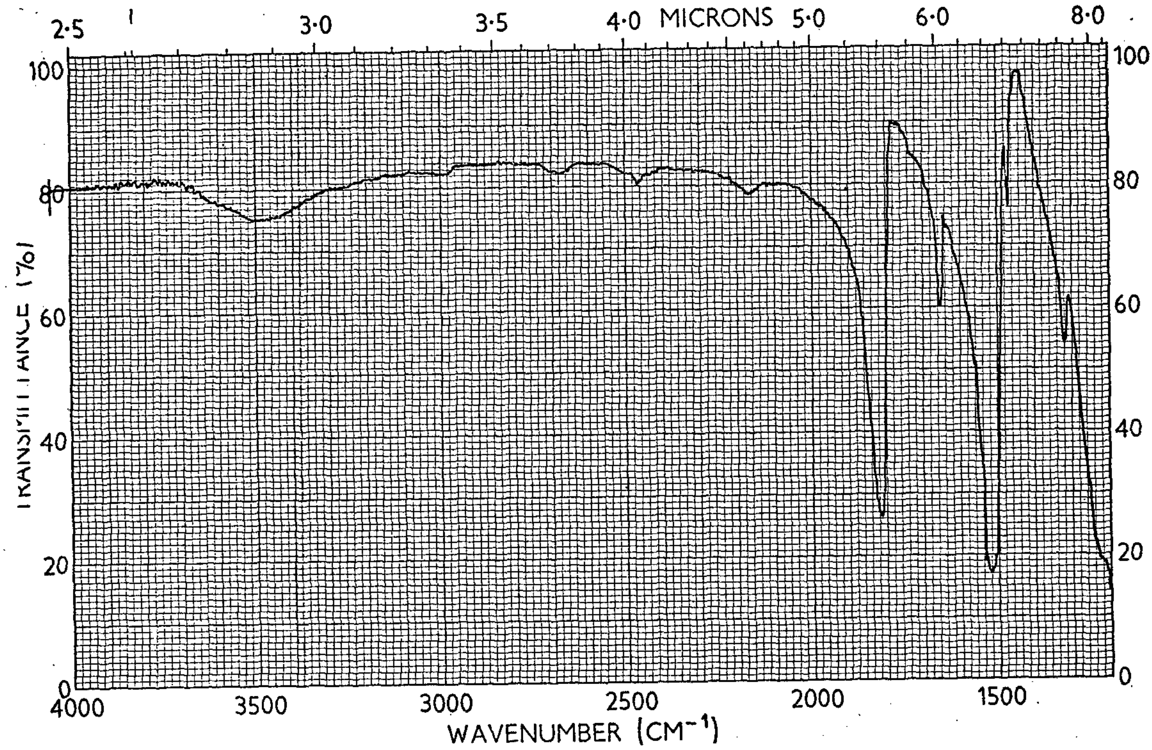


Spectrum No. 2240 C2. PMDA/tetrafluoro-p-phenylene diamine complex. KBr disc

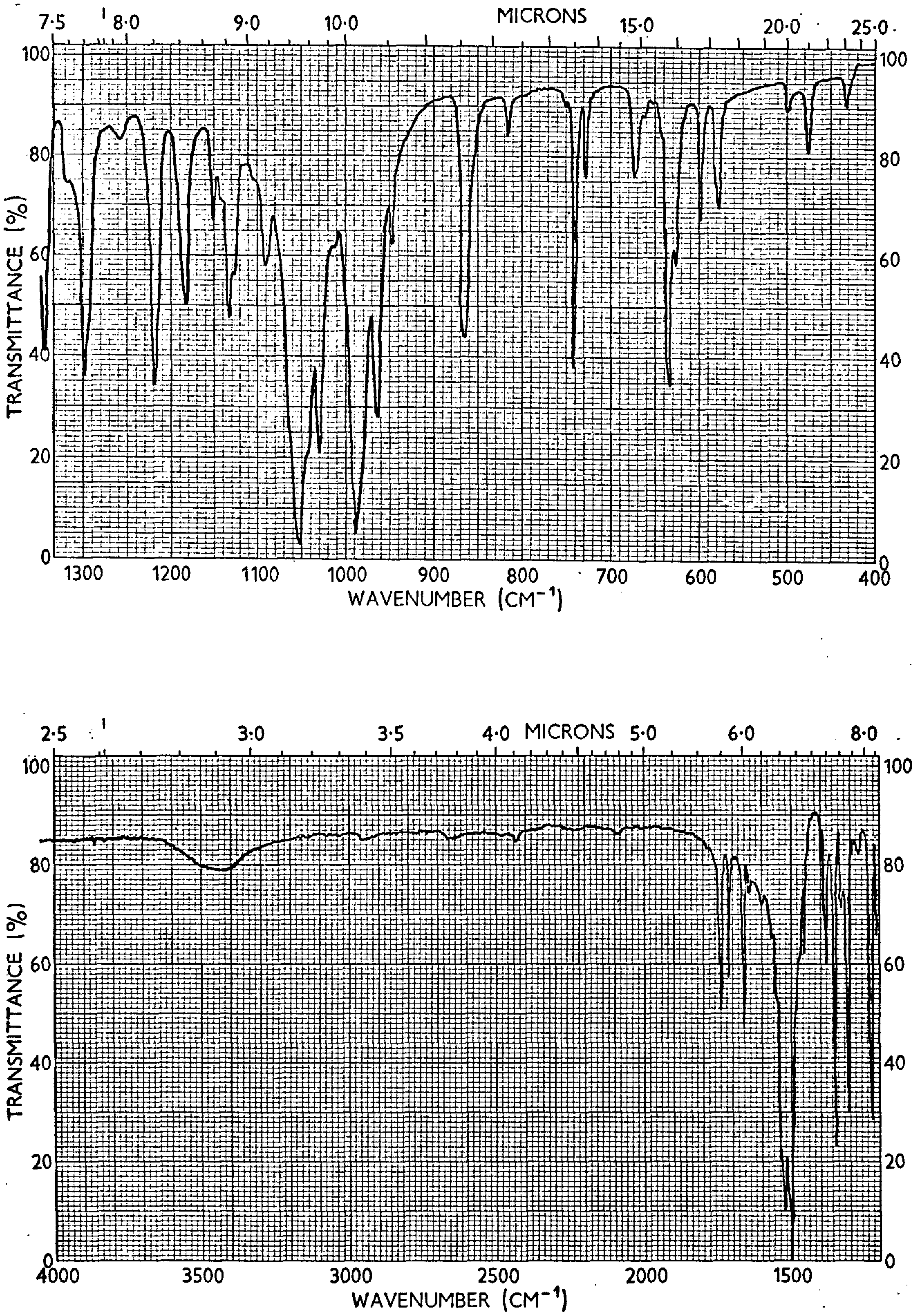


Spectrum No. 2241 C3. PMDA/octafluorobenzidine complex
KBr disc





Spectrum No. 2317 PC5. Poly(tetrafluoro-m-phenylene carbonate) KBr disc

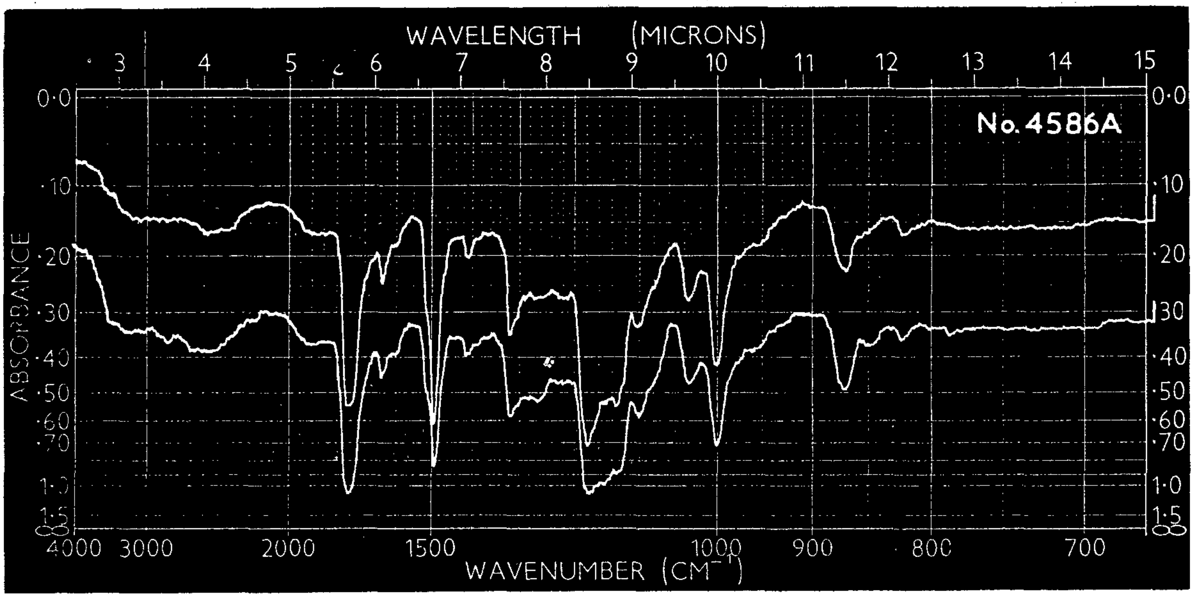


Spectrum No. 1974 Compound (XI) $C_6F_5 \cdot C_6ClF_5 \cdot C_6F_5$, m.p. 158-9°, which is probably 6-chloro-1,5-di(pentafluorophenyl)-2,3,4,5,6-pentafluorocyclohexa-1,3-diene. KBr disc

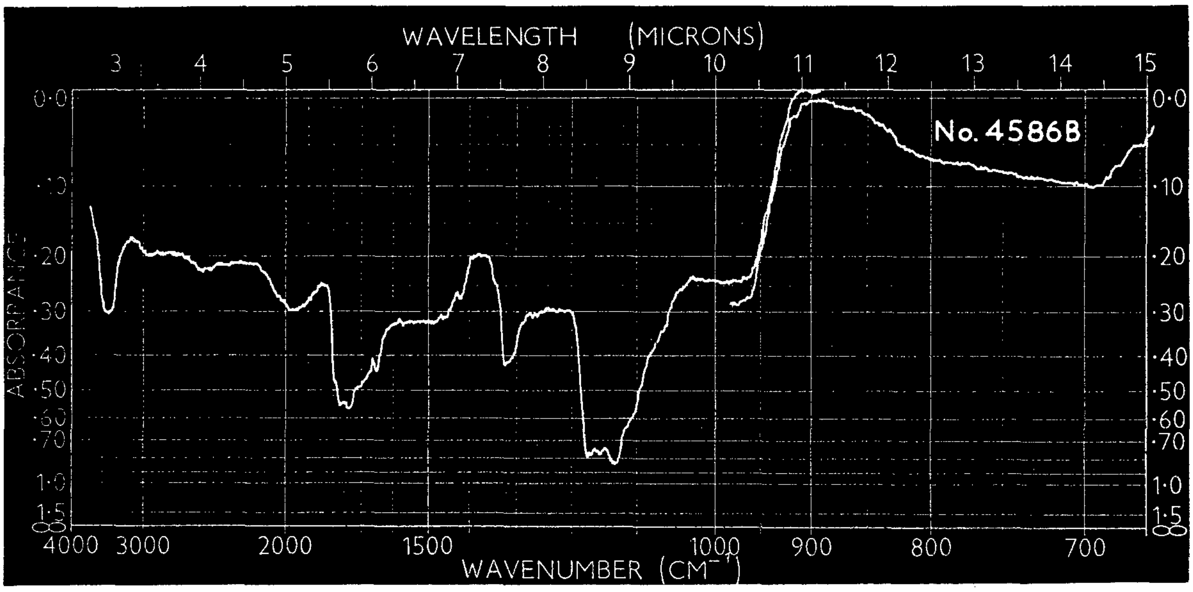
APPENDIX III

Infrared Spectra Referred to in Part III (Section I)

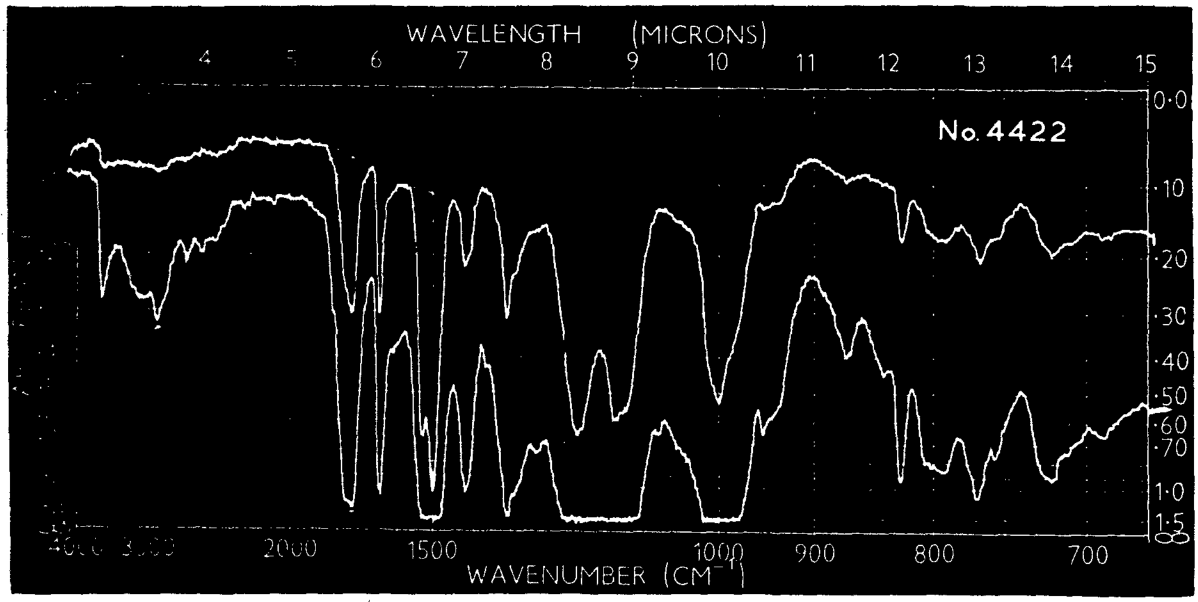
No.	
4586A) 4586B)	Unknown acid, m.p. 40-44°, from reaction of pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride (in $CHCl_3$,CCl_4)
4422	Compound believed to be impure perfluoro-1,1',6,6'-tetrafluorophenylhexan-1,6-diol (film)
4285	Perfluoro-1,6-diphenylhexane (in CCl_4)
4720	Suspected perfluoro-5-benzoylpentanoic acid (in CCl_3CN)
4708	2,3,4,5,6-Pentafluorobenzal fluoride (film)
4929	3-Hydro-3'-(1-hydroxyhexafluoroisopropyl)octafluorobiphenyl (film)
4827	Impure suspected 3,3'-bis(1-hydroxyhexafluoroisopropyl)-octafluorobiphenyl (film)
4403A	Perfluoro-3,3'-di(n-butyl)biphenyl (in CCl_4)
5021	3,4'-Dihydro-octafluorodiphenyl sulphide (in $CHCl_3$)



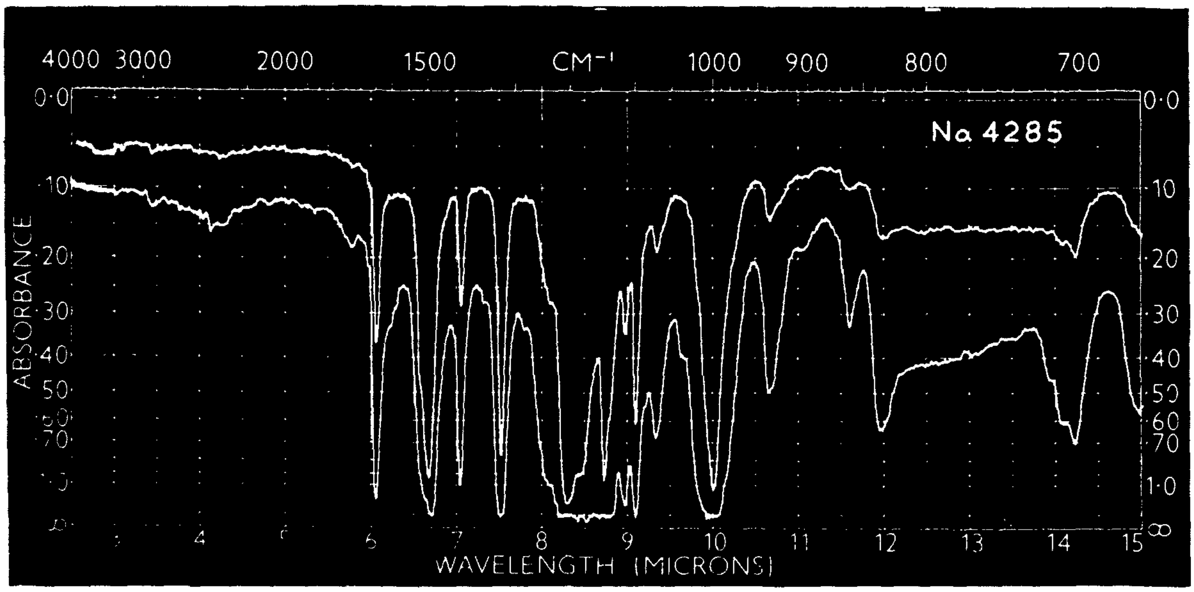
Spectrum No. 4586A Unknown acid, m.p. 40-44°, from reaction of pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride (in $CHCl_3$, CCl_4)



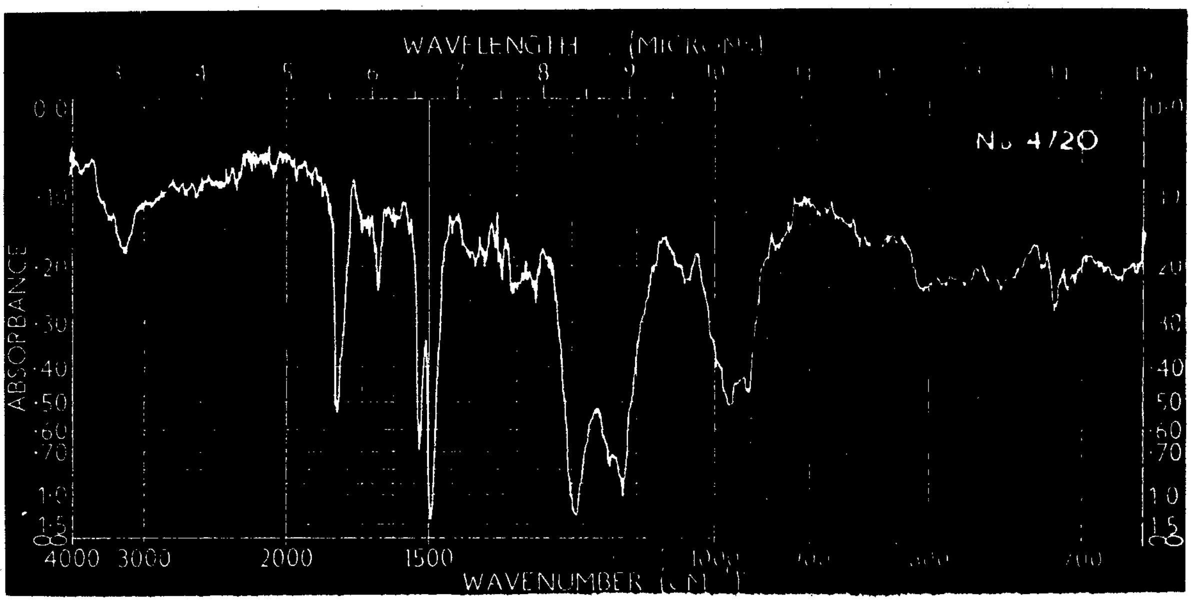
Spectrum No. 4586B Unknown acid, m.p. 40-44°, from reaction of pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride (in $CHCl_3$, CCl_4)



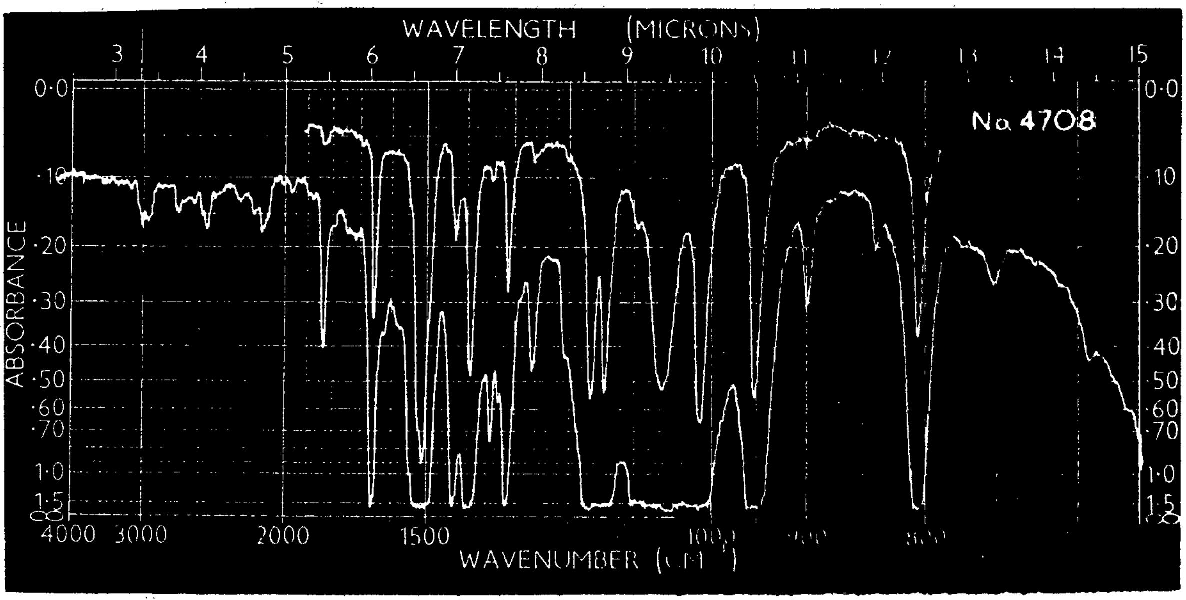
Spectrum No. 4422 Compound believed to be impure perfluoro-1,1',6,6'-tetrafluorophenylhexan-1,6-diol (film)



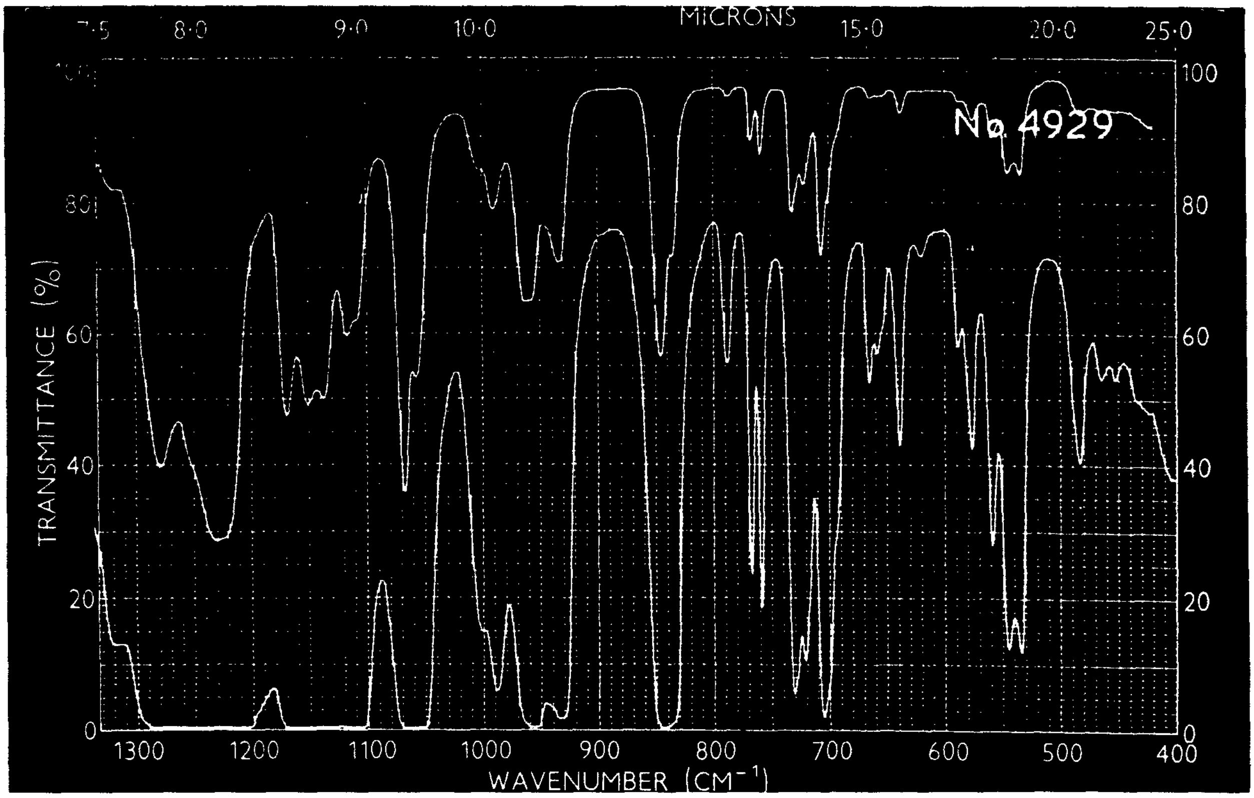
Spectrum No. 4285 Perfluoro-1,6-diphenylhexane (in CCl_4)

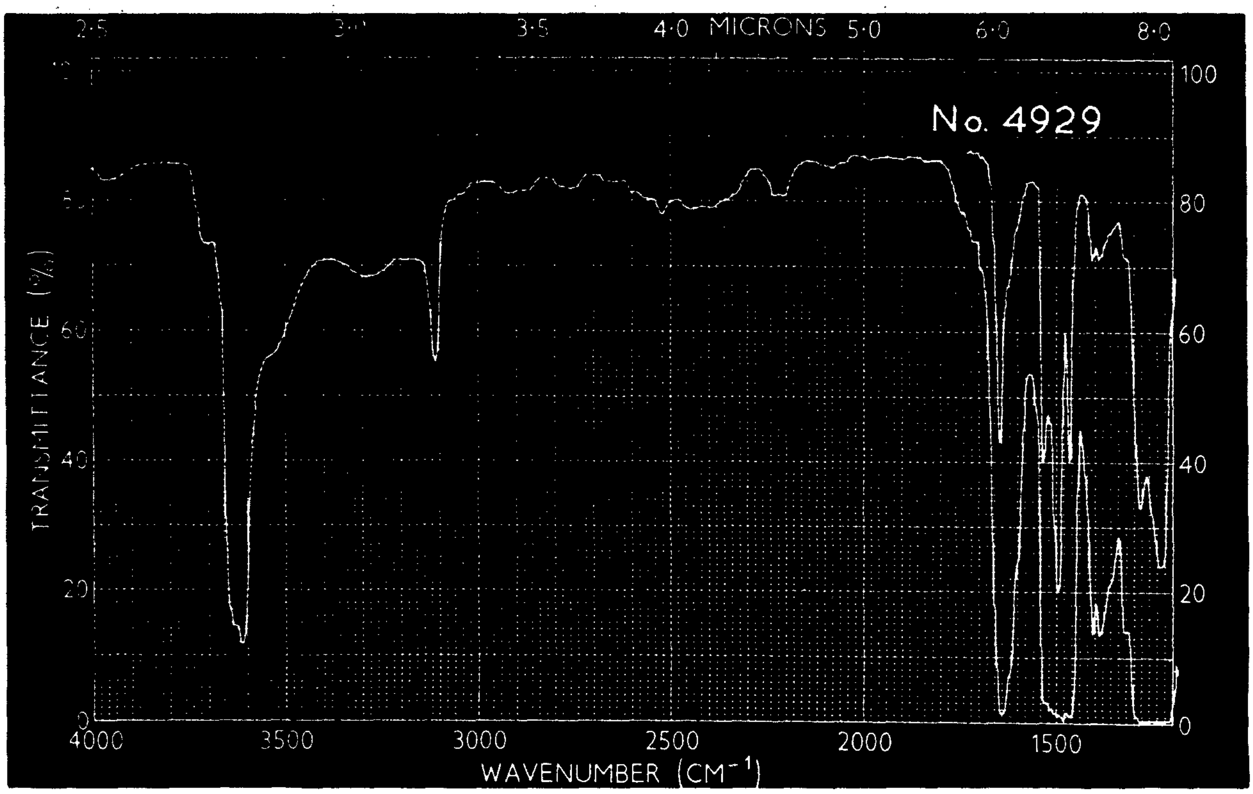


Spectrum No. 4720 Suspected perfluoro-5-benzoylpentanoic acid (in CCl_3CN)

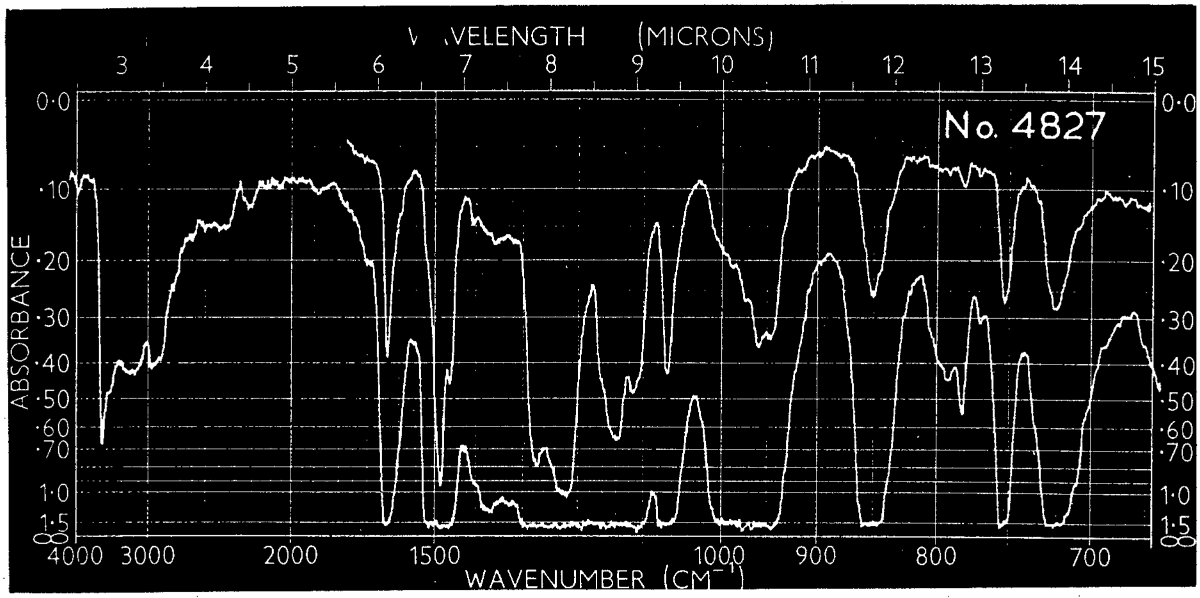


Spectrum No. 4708 2,3,4,5,6-Pentafluorobenzal fluoride (film)

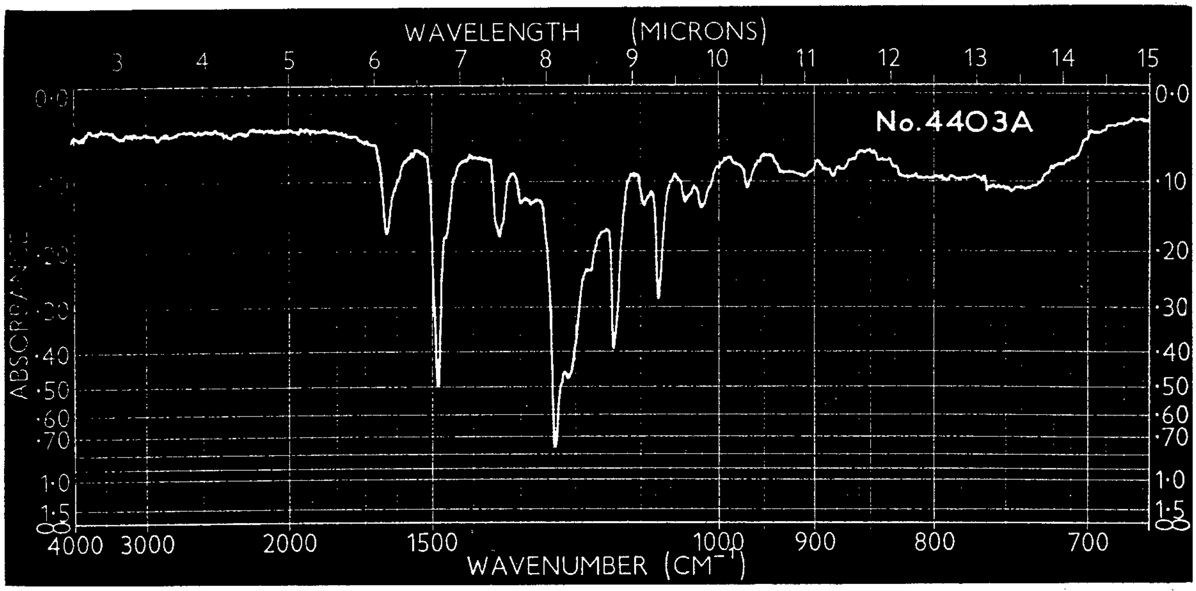




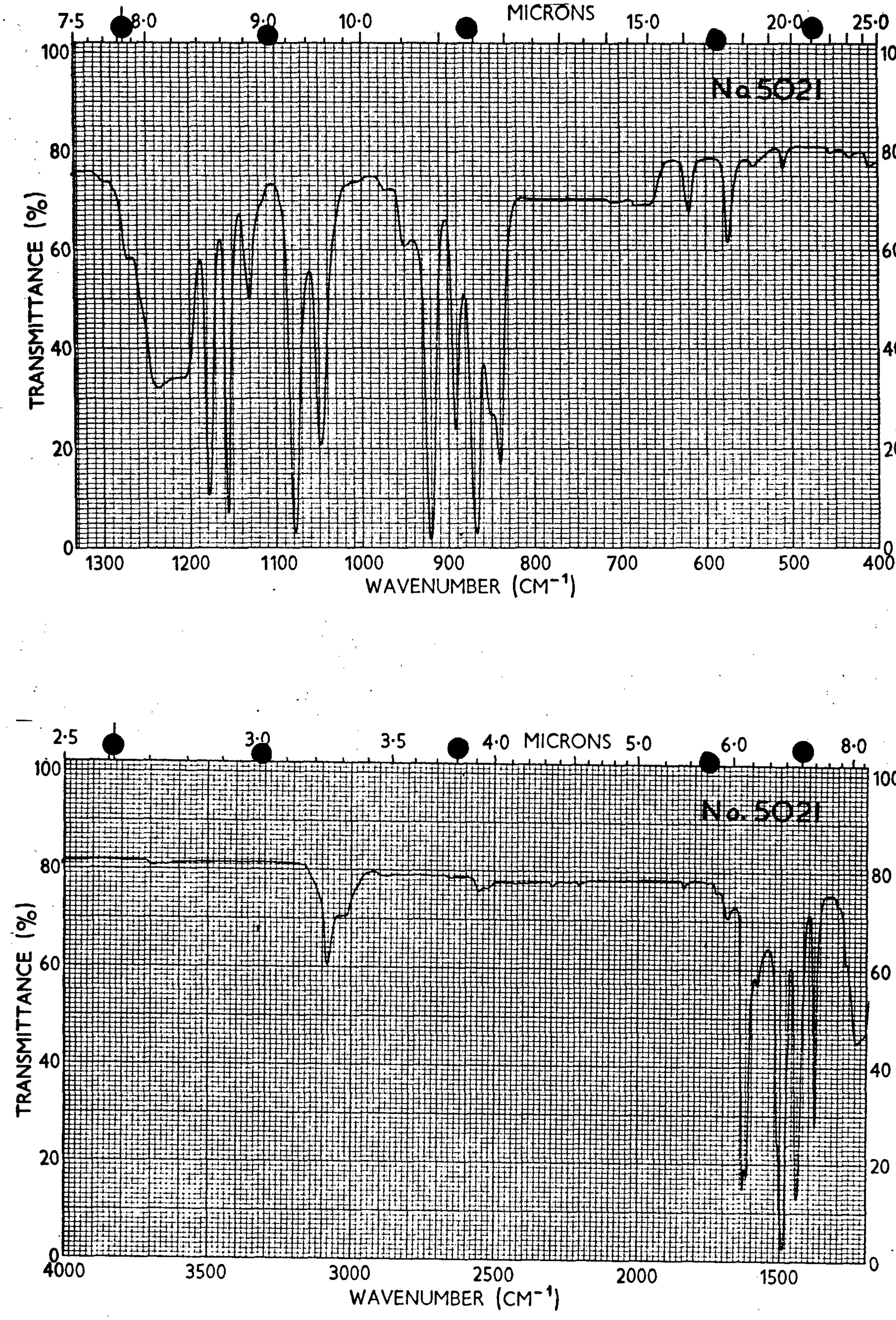
Spectrum No. 4929 3-Hydro-3'-(1-hydroxyhexafluoroisopropyl)octafluorobiphenyl (film)



Spectrum No. 4827 Impure suspected 3,3'-bis(1-hydroxyhexafluoroisopropyl)octafluorobiphenyl (film)



Spectrum No. 4403A Perfluoro-3,3'-di(n-butyl)biphenyl (in CCl_4)

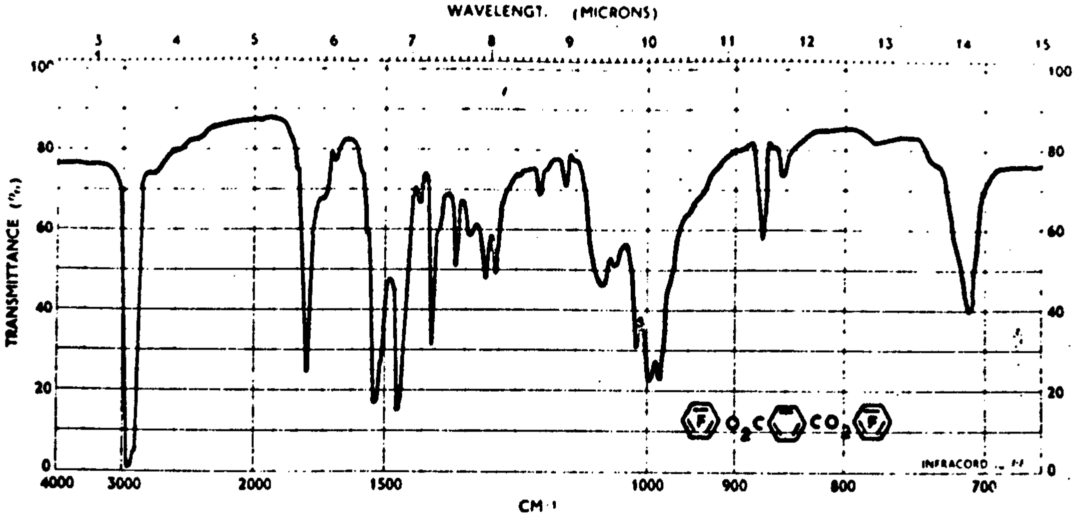


Spectrum No. 5021 3,4'-Dihydro-octafluorodiphenyl sulphide (in $CHCl_3$)

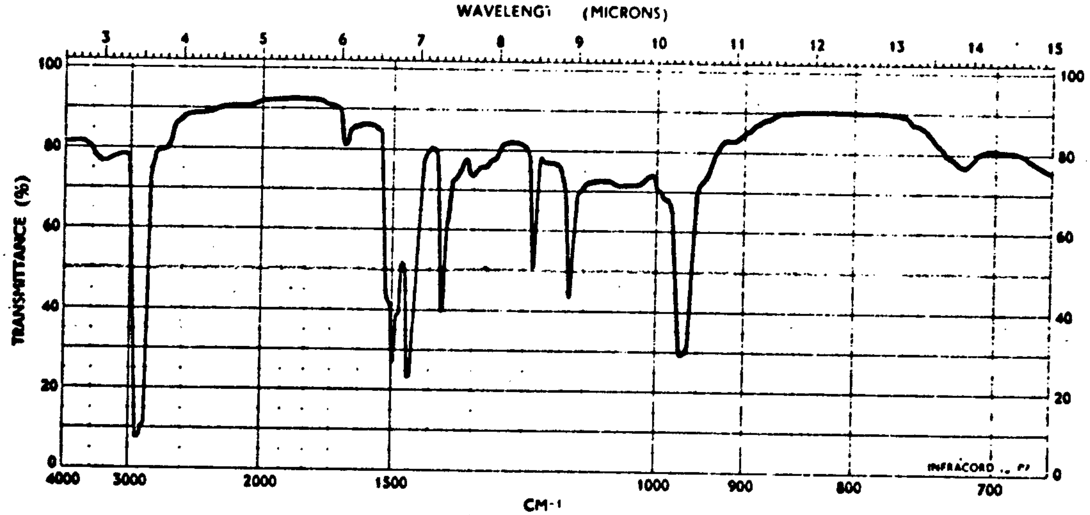
APPENDIX IV

Infra-red spectra referred to in Part IV

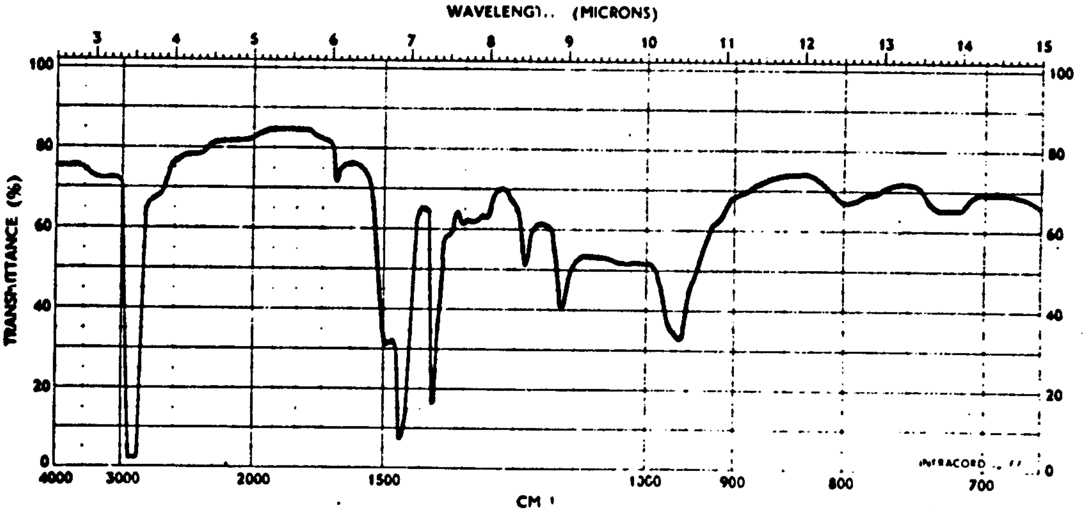
Bis (pentafluorophenyl) terephthalate
Product from bromomethylpentafluorobenzene
Product from chloromethylpentafluorobenzene
Tetrafluoroterephthaloyl chloride
1-Pentafluorophenyl-2-phenyloctafluorocyclohexene
1,2-Diphenyloctafluorocyclohexene
Dodecafluoro-4',5'-dicarboxy-*o*-terphenyl.
Dodecafluoro -2',5'-bis(trifluoromethyl)-*p*-terphenyl
Eicosafluoro -2",5"-bis(trifluoromethyl)-*p*-quinquephenyl
Suspected 1,1,2,2,3,3,4,4,5,6-decafluorodec-5-ene.
Fluoromethylpentafluorobenzene
Difluoromethylpentafluorobenzene
Dodecafluoro-2',5'-bis(carboxymethyl)-*p*-terphenyl
Dodecafluoro-2',5'-dicarboxy-*p*-terphenyl
Eicosafluoro-2",5"-dicarboxy-*p*-quinquephenyl
1-Pentafluorophenyl-2-(2,3,5,6-tetrafluorobiphenylyl)octafluorocyclohexene
1,2-Bis(2,3,5,6-tetrafluorobiphenylyl)octafluorocyclohexene
Unknown (iii) from 1,6-dihydrododecafluorohexene
1-*n*-Butyl-4-methyltetrafluorobenzene
1-*n*-Butyl-4-fluoromethyltetrafluorobenzene
1-n-Butyl-4-difluoromethyltetrafluorobenzene
2,3,6-Trifluoro-4,5-bis(trifluoromethyl)biphenyl
3',6'-Difluoro-4',5'-bis(trifluoromethyl)-*o*-terphenyl.
2,3,3',4,5,6,6'-Heptafluoro-4',5'-bis(trifluoromethyl)-*o*-terphenyl
1,2-Bis(undecafluorocyclohexyl)octafluorocyclohexene
Perfluoro(2,'5'-dimethyl - 1,1' : 4',1"-tercyclohexane)
Perfluoro(4',5'-dimethyl-1,1' : 2',1"-tercyclohexane).



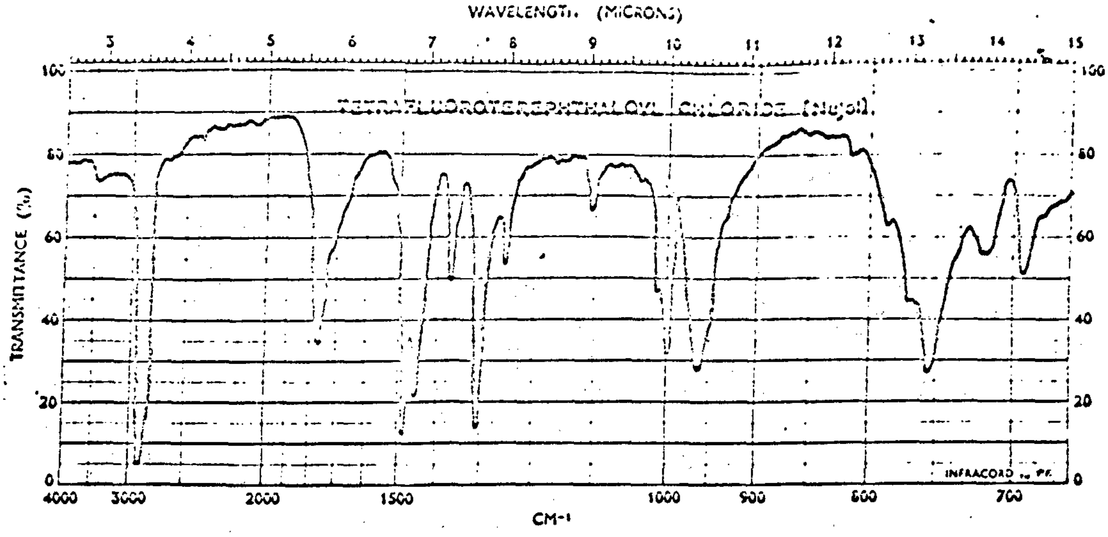
BIS(PENTAFLUOROPHENYL)TEREPHTHALATE (N)

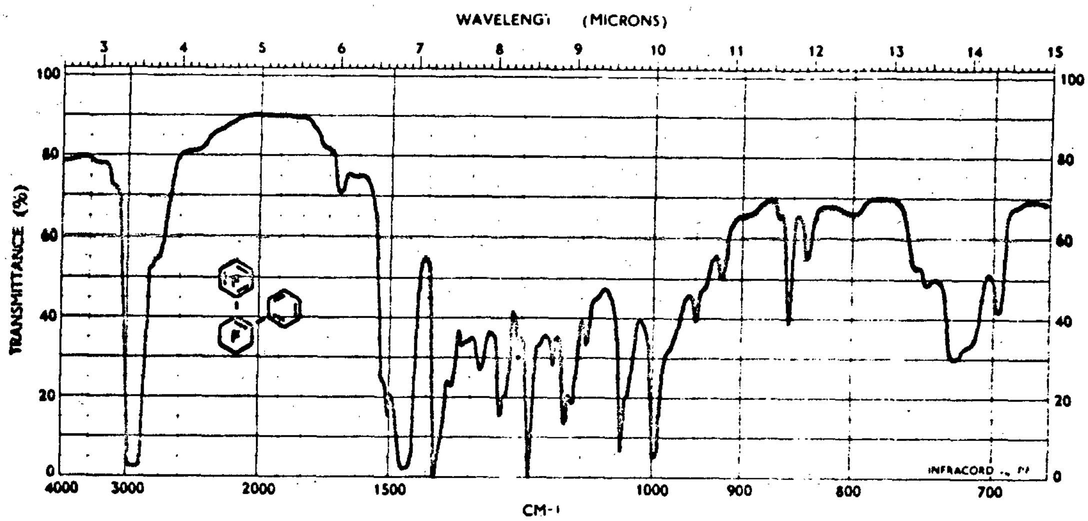


PRODUCT FROM BROMOMETHYLPENTAFLUOROBENZENE (N)

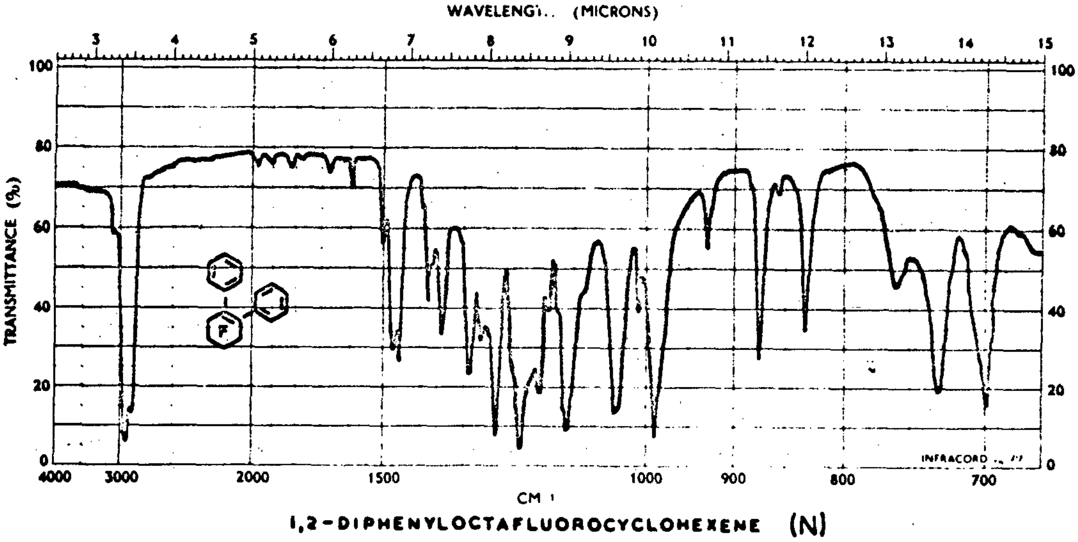


PRODUCT FROM CHLOROMETHYLPENTAFLUOROBENZENE (N)

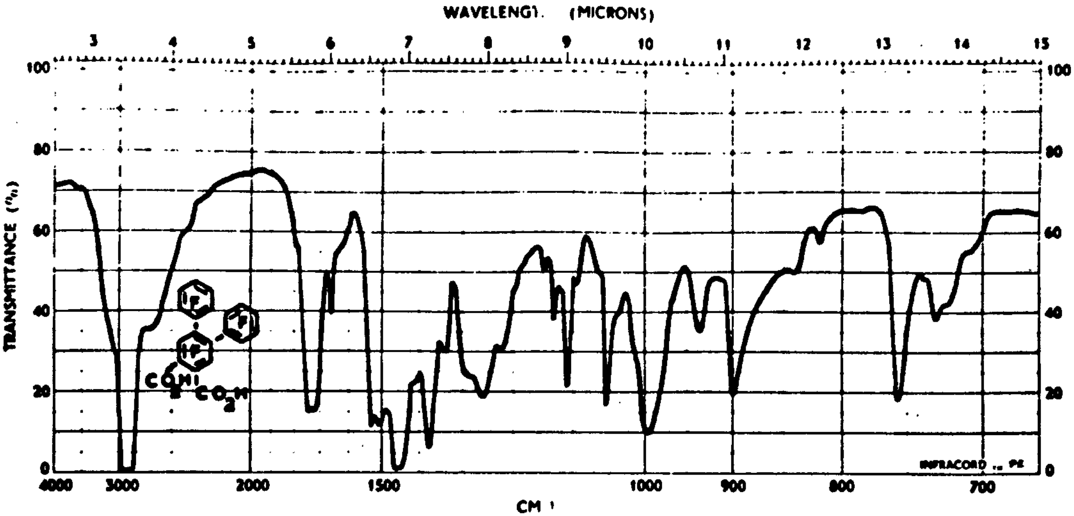




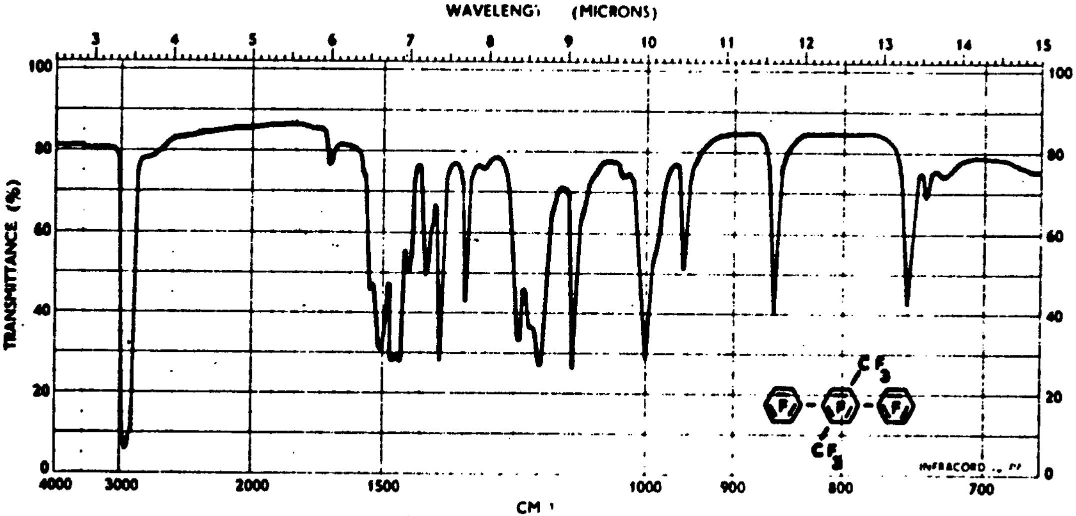
1-PENTAFLUOROPHENYL-2-PHENYLOCTAFLUOROCYCLOHEXENE (N)



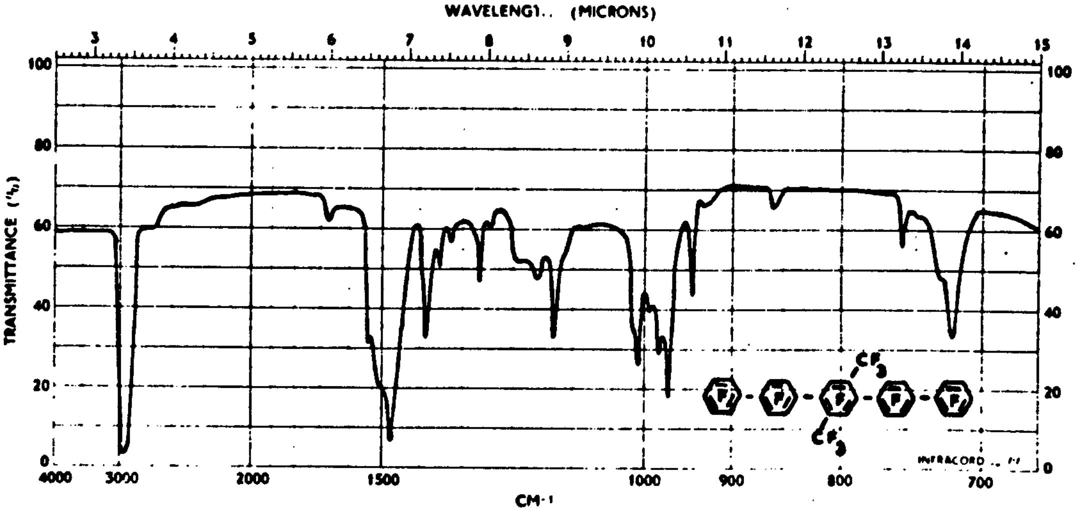
1,2-DIPHENYLOCTAFLUOROCYCLOHEXENE (N)



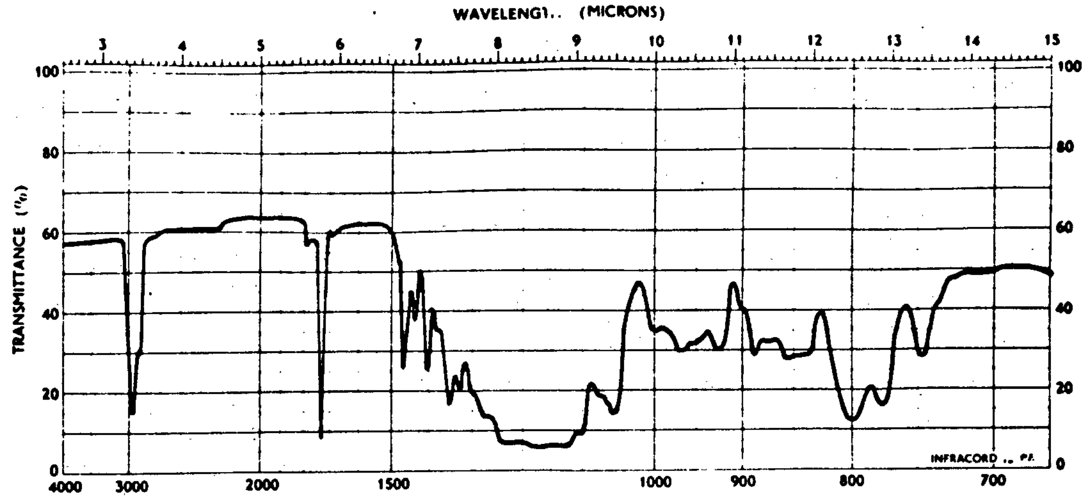
DODECAFLUORO-4',5'-DICARBOXY-o-TERPHENYL (N)



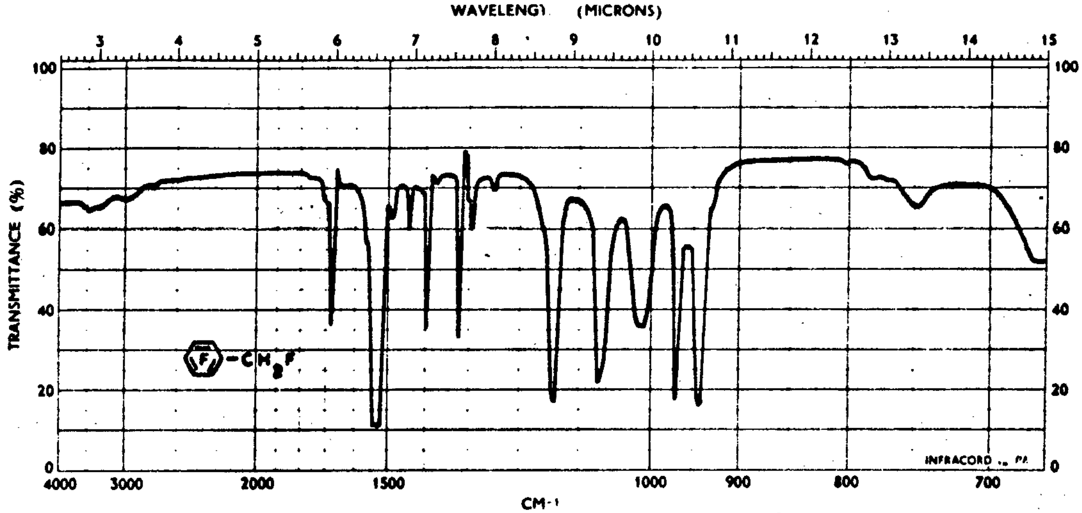
DODECAFLUORO-2',5'-BIS(TRIFLUOROMETHYL)-p-TERPHENYL (N)



EICOSAFLUORO-2",5"-BIS(TRIFLUOROMETHYL)-p-QUINQUEPHENYL (N)



SUSPECTED 1,1,2,2,3,3,4,4,5,6-DECAFLUORODEC-5-ENE (L)



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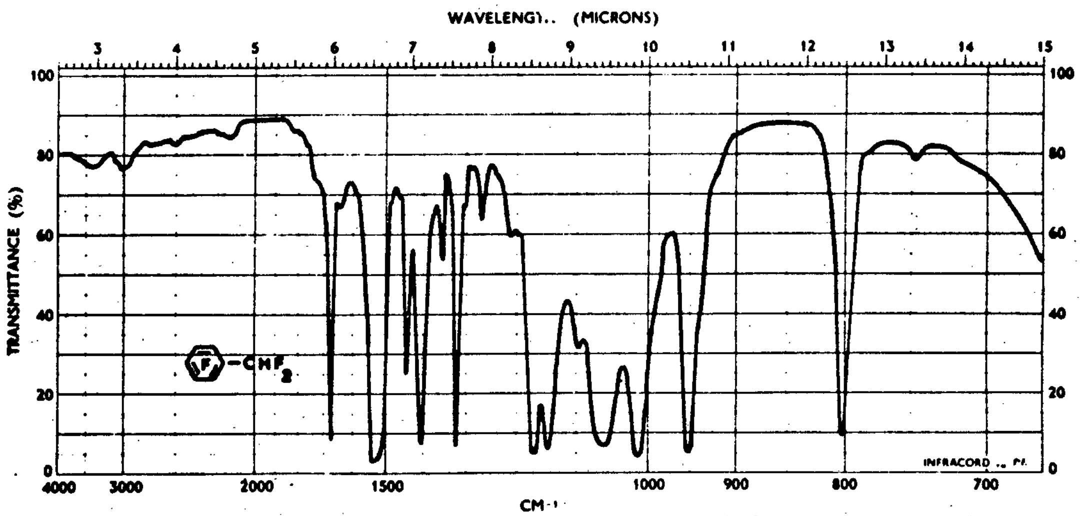

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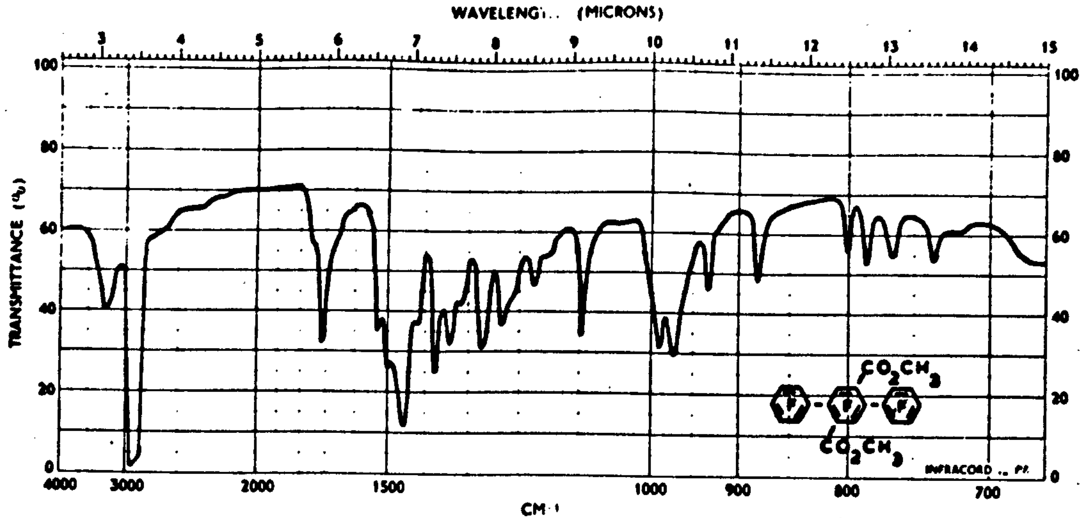
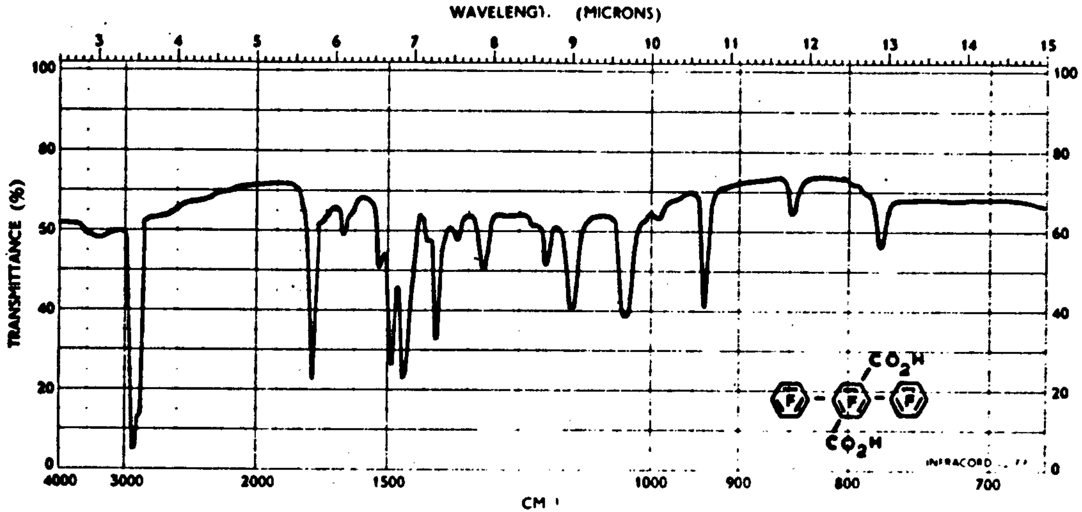


DODECAFLUORO-2',5'-BIS(CARBOXYMETHYL)-p-TERPHENYL (N)



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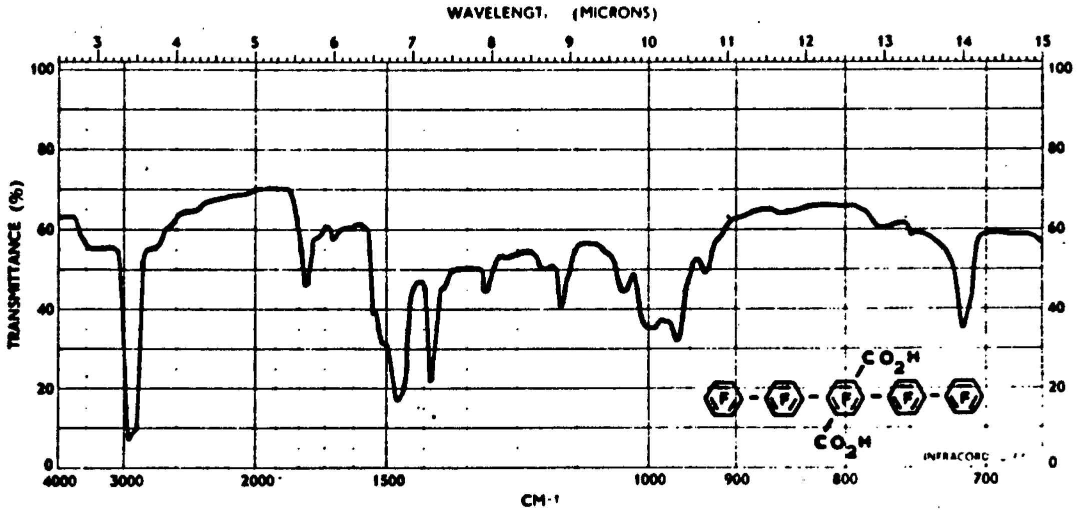

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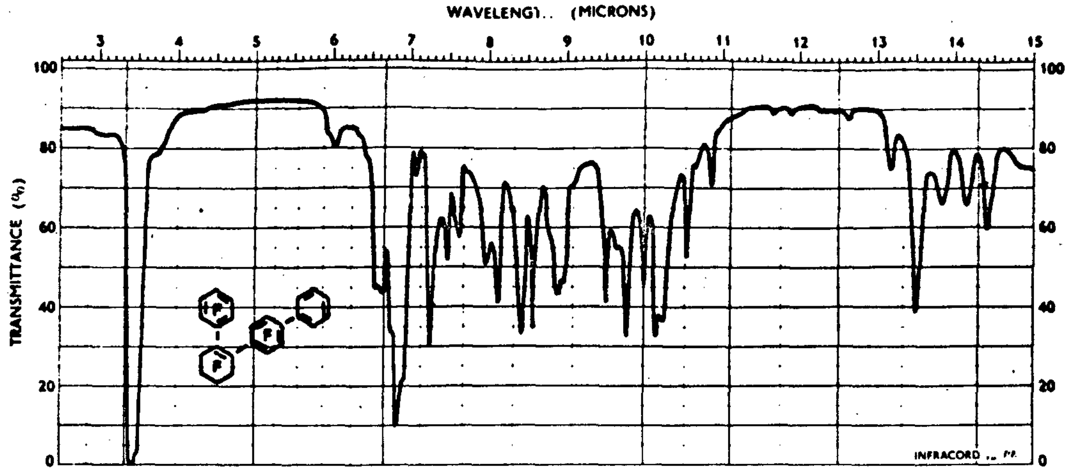
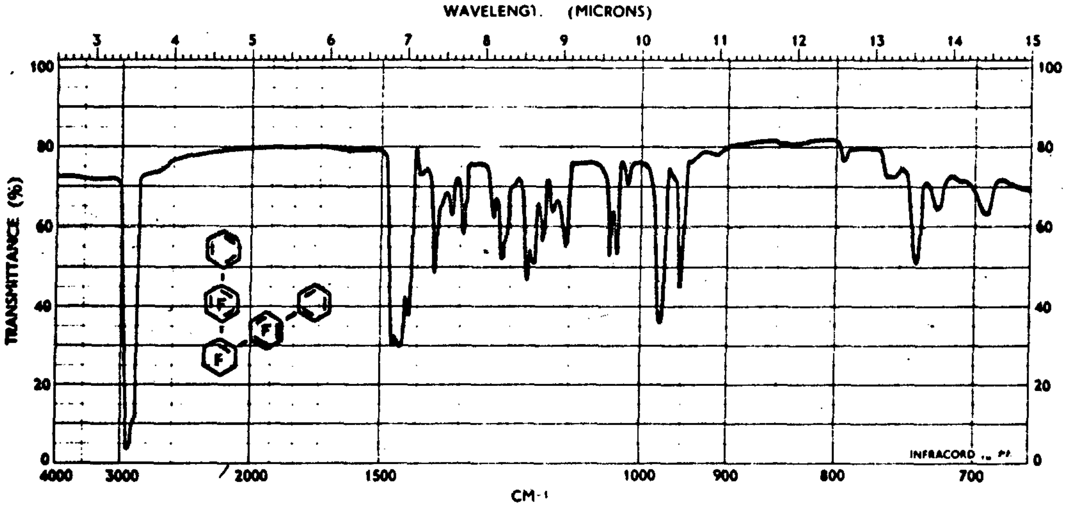
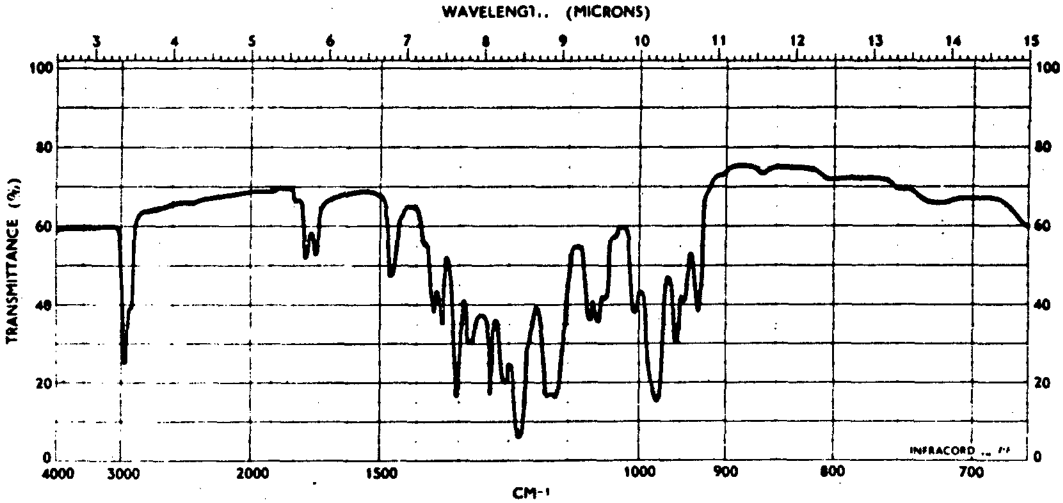


(N)

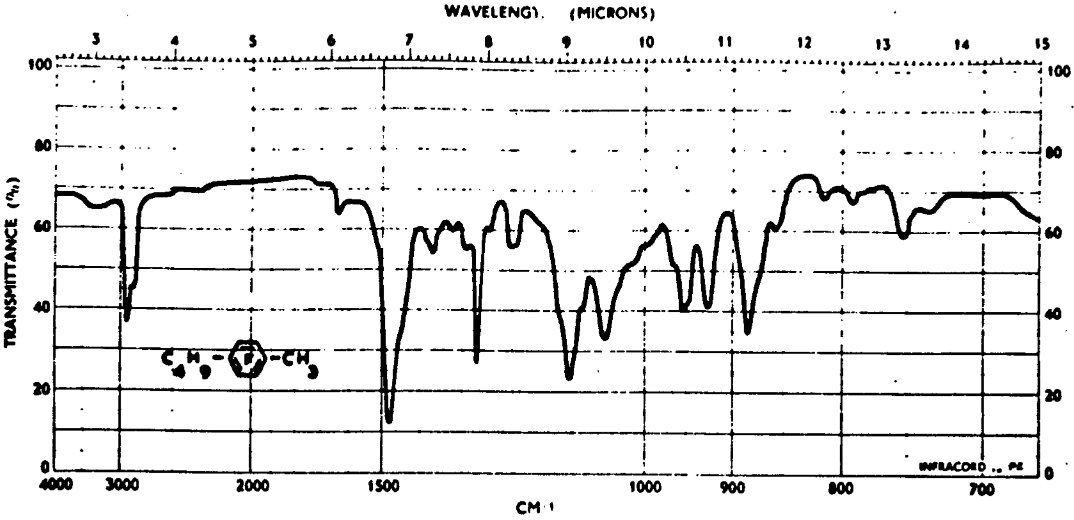
1-PENTAFLUOROPHENYL-2-(2,3,5,6-TETRAFLUOROBIPHENYLYL)OCTAFLUOROCYCLOHEXENE



1,2-BIS(2,3,5,6-TETRAFLUOROBIPHENYLYL)OCTAFLUOROCYCLOHEXENE (N)



UNKNOWN (iii) FROM 1,6-DIHYDRODODECAFLUOROHEXENE (L)



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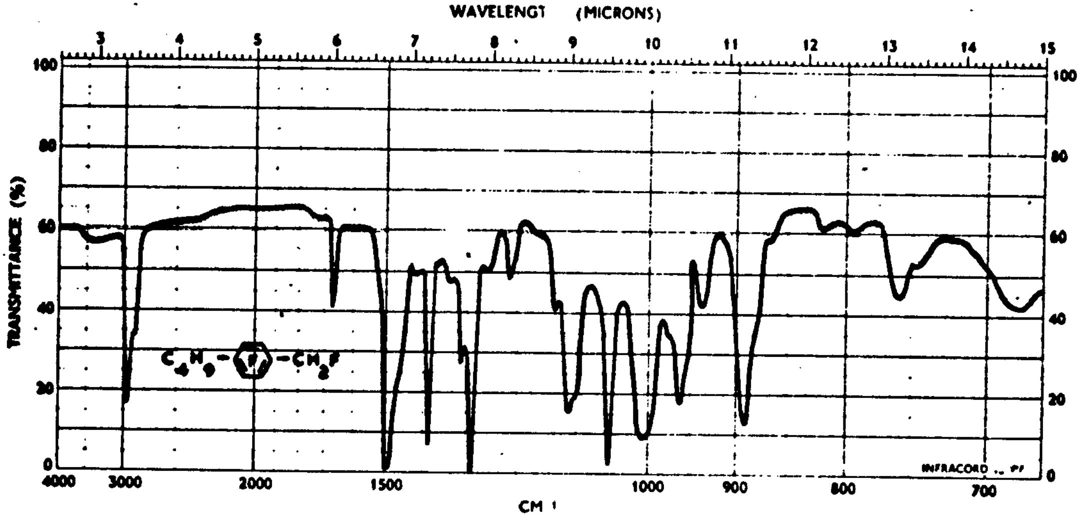

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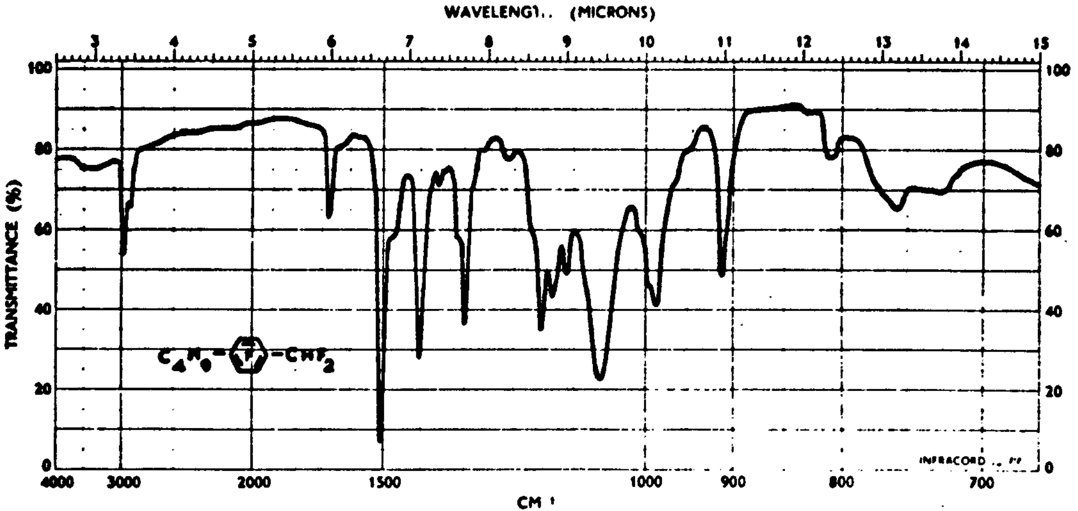

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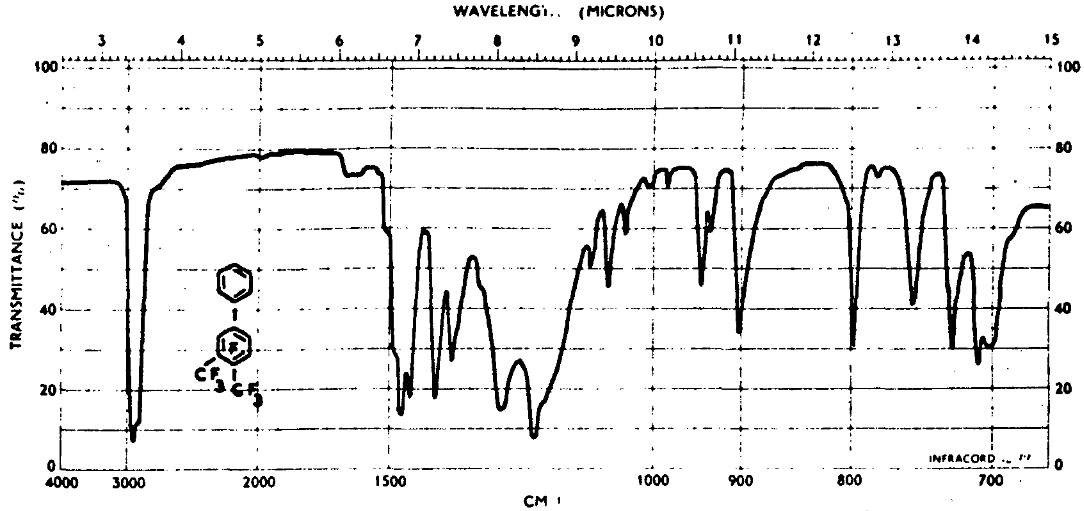
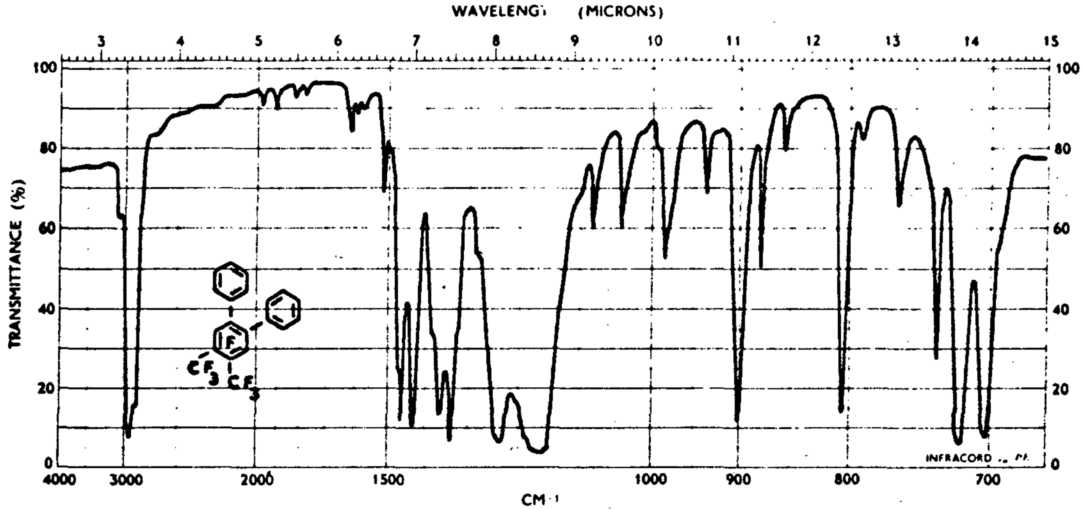
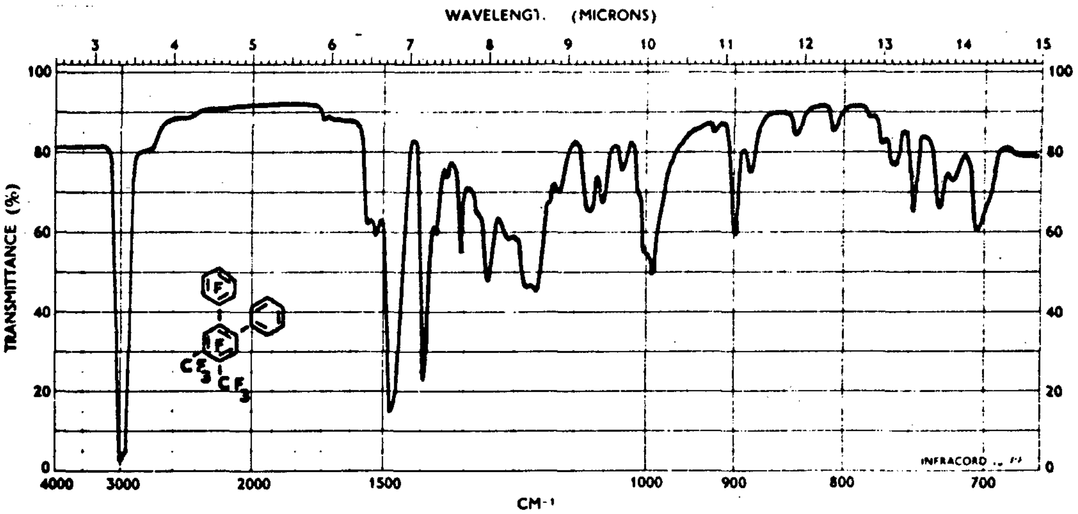


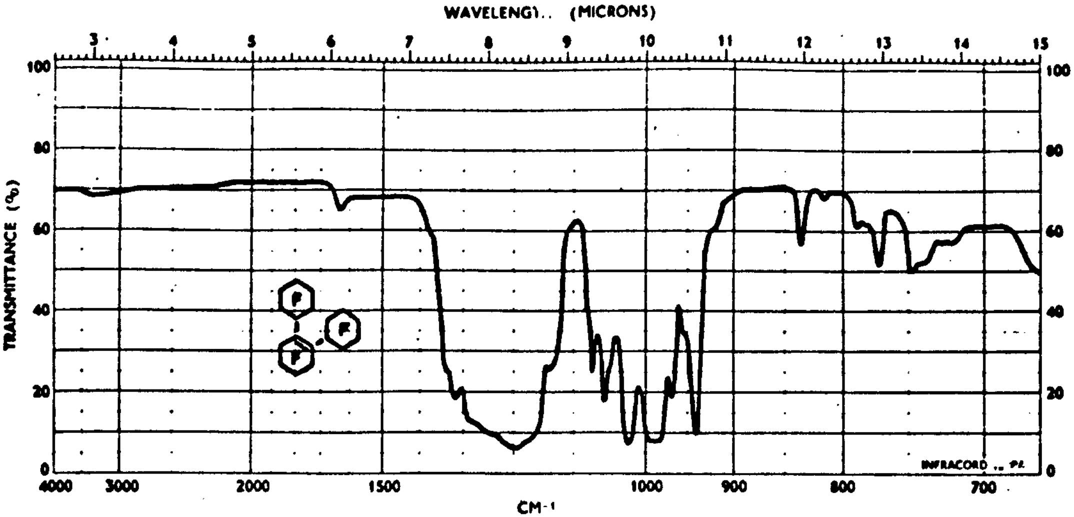
2,3,6-TRIFLUORO-4,5-BIS(TRIFLUOROMETHYL)BIPHENYL (N)



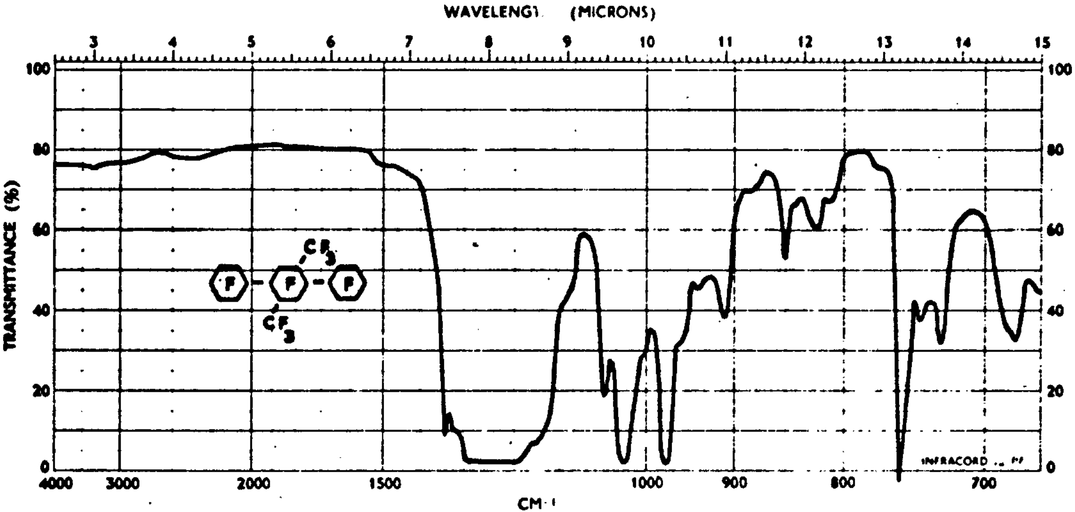
3',6'-DIFLUORO-4',5'-BIS(TRIFLUOROMETHYL)-*o*-TERPHENYL (N)



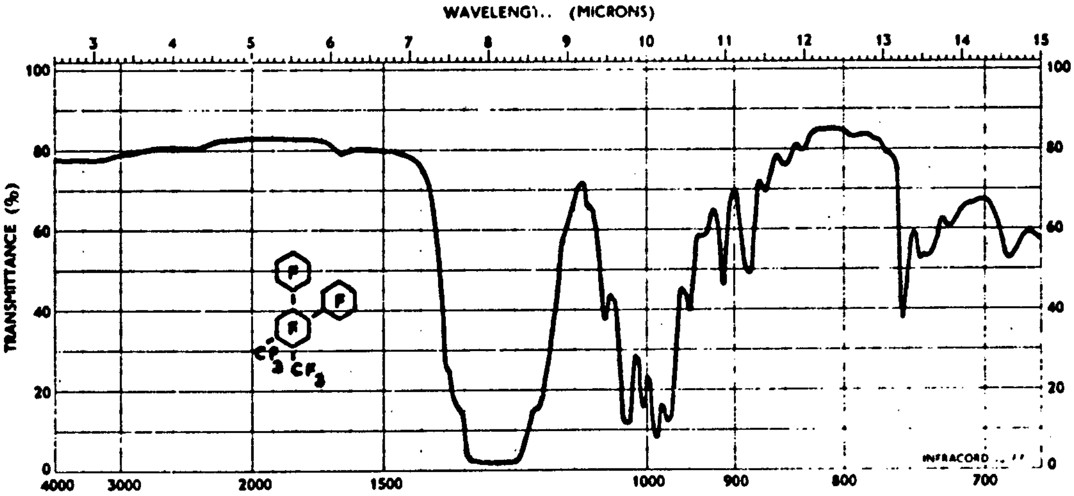
2,3,3',4,5,6,6'-HEPTAFLUORO-4',5'-BIS(TRIFLUOROMETHYL)-*o*-TERPHENYL (N)



1,2-BIS(UNDECAFLUOROCYCLOHEXYL)OCTAFLUOROCYCLOHEXENE (L)



PERFLUORO(2',5'-DIMETHYL-1,1':4',1''-TERCYCLOHEXANE) (L)



PERFLUORO(4',5'-DIMETHYL-1,1':2',1''-TERCYCLOHEXANE) (L)

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12. SPONSORING MILITARY ACTIVITY Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Div., Air Force Systems Command, Wright-Patterson Air Force Base, Ohio

13. ABSTRACT The synthesis of difluoropyromellitic dianhydride, 2,2',5,5',6,6'-hexafluoro-3,3'-dihydroxybenzidine, 2,4,5-trifluororesorcinol, perfluoro-4-hydroxyphenyldimethylcarbinol and tetrafluorobenzene-1,3-dithiol has been investigated. These and other compounds were employed in the synthesis of fluorinated aromatic model compounds and polymers. A low molecular weight perfluoro polycarbonate, a low molecular weight fluorine-containing co-polycarbonate and a fluorine-containing aromatic polyimide had higher thermo-oxidative stability than the corresponding hydrogenic polymers. Other fluorinated polycarbonates, polyimides, and a poly(1,3,4-oxadiazole) had lower thermo-oxidative stabilities. A perfluoro poly(bibenzoxazole) could not be prepared. The reaction between pentafluorobenzene sulphonyl chloride and perfluoro-aromatics suggests new routes to fluorine-containing polymers. Synthesis routes to perfluoro aralkyl compounds, with potential as thermo-oxidatively stable fluids are being investigated. Perfluoro alicyclic compounds of moderately high thermal stability have been prepared. Perfluorinated heterocyclics have been synthesised. The thermal decomposition points of two heterocyclic ethers and an ester are also reported.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Organofluorine Chemistry Aromatic Fluorine Compounds Perfluoroaromatic Polymers						

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