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AFML-TR-65-13, PART II
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PERFLUORINATED AROMATIC COMPOUNDS

M. W. Buxton, R. H. Mobbs, and J. Tilney-Bassett
Imperial Smelting Corporation, Limited

S. A. Evans and E. R. Lynch
Monsanto Chemicals Limited

J. C. Tatlow and D. Oldfield
University of Birmingham

W. K. R. Musgrave and C. A. Heaton
University of Durham

TECHNICAL REPORT AFML-TR-65-13, PART II

APRIL 1966

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

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NOTICES

AFML-TR-65-13, Part II

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FOREWORD

This report "Perfluorinated Aromatic Compounds" for the period 1 January 1965 to 30 November 1965 covers work under Contract No. AF 33(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, Ruabon, Great Britain, Imperial Smelting Corporation (N.S.C.) Limited, Avonmouth, Great Britain, The University of Birmingham, Great Britain, and The University of Durham, Great Britain.

Part I of the report describes work done by Imperial Smelting Corporation on fluoromatic intermediates. Part II describes work done by Monsanto Chemicals Limited on model compounds and polymers. Part III describes work done by Imperial Smelting Corporation on perfluoro fluids. Part IV describes the work done at the University of Birmingham on perfluoro fluids. Part V describes work done by the University of Durham on perfluoro heterocyclic compounds.

The work is administered by the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio. Mr. G. Baum is project engineer. For Monsanto Research Corporation, Dr. J. M. Butler serves as contract co-ordinator. For Monsanto Chemicals Limited, Dr. F. Long serves as project leader, assisted by Mrs. S. A. Evans and Mr. E. R. Lynch; Mrs. J. E. Ellis and Mr. R. A. Lidgett provide infra-red and gas chromatographic support. For Imperial Smelting Corporation Limited, Dr. A. K. Barbour serves as project leader, assisted by Dr. M. W. Buxton, Dr. J. Tilney-Bassett, and Dr. R. Mobbs. 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, Mr. C. A. Heaton, supervised by Professor W. K. R. Musgrave and Dr. R. D. Chambers.

Manuscript released by the authors January 1966.

This technical report has been reviewed and approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
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ABSTRACT

I. Preparations and synthetic studies have been carried out on difluoropyromellitic acid, tetrafluoroisophthalic acid, tetrafluorophenylene diamines, 3,3',4,4'-tetra-substituted-hexafluorobiphenyls, tetrafluororesorcinol, sulphides, dithiols, and 2,3,5,6-tetrafluorobenzoic acid.

II. The above, with other perfluorinated aromatic compounds, are the intermediates employed in the synthesis of perfluorinated aromatic model compounds and polymers. In addition to the perfluoro compounds and polymers the hydrogenic analogues were prepared for comparison of thermal and thermo-oxidative stabilities in the two series. Model compound structures include bibenzoxazoles, oxadiazoles, sulphonic esters, dithiocarbonates, amides, and imides, for which thermal decomposition temperatures are reported. Polymer structures include carbonates, hydrazides, and imides. Thermogravimetric examination in air is reported for polyhydrazides and polyimides.

III. Synthetic routes to perfluoro aralkyl compounds are being investigated, with the object of producing thermo-oxidatively stable fluids. Starting materials are tetrafluorobenzene, octafluorobiphenyl, and perfluoroaliphatic aldehydes.

IV. Synthetic routes to perfluoro cyclohexyls are being investigated, with the object of producing thermo-oxidatively stable fluids. The reactions of phenyl and pentafluorophenyl lithium with decafluorocyclohexene, o- and p- perfluoroxylene, have been studied. Fluorination of these products with cobaltic fluoride has commenced.

continued

V. Studies have been made of the routes to pentachloropyridine, for the exchange reaction with potassium fluoride to yield pentafluoropyridine. The latter gave tetrafluoroisonicotinic acid by a sequence of steps, which was converted to amide and hydrazide derivatives. Attempts were made to prepare 2,4,6-trifluoronicotinamide starting from 2,4,6-trifluoropyridine. The reaction of pentafluoropyridine or heptafluoroisoquinoline with potassium pentafluorophenate or the potassium salt of 4-hydroxytetrafluoropyridine appears to have yielded the appropriate heterocyclic ethers.

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PART I

PERFLUOROAROMATIC INTERMEDIATES

M.W. Buxton, R.H. Mobbs and J. Tilney-Bassett

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

A. INTRODUCTION

This part of this Report is concerned with the synthesis of perfluoroaromatic intermediates required by Monsanto Chemicals Ltd. for the preparation of model condensates and polymers which are used for thermal stability tests. The presence of hydrogen-containing impurities, which are likely to have an adverse effect on the thermal stability, was kept to a minimum by preparing the intermediates from specially purified hexa- and penta-fluorobenzene, in some cases.

The work described was carried out during the period 1st January, 1965 to 30th November, 1965 and is a continuation of work described in Technical Report AFML-TR-65-13.

B. SUMMARY

The oxidation of difluorodurene provides a synthesis of difluoropyromellitic acid suitable for preparing laboratory quantities. Satisfactory preparative procedures were established for tetrafluororesorcinol, tetrafluorobenzene-1,4-dithiol, 3,3'-bis(pentafluorobenzamido)-4,4'-diaminohexafluorobiphenyl, 4,4'-bis(2,3,5,6-tetrafluorophenylthio)octafluorobiphenyl, and 2,3,5,6-tetrafluorobenzoic acid. An alternative method for the reduction of 3,3'-dihydroxy-4,4'-dinitrohexafluorobiphenyl has been examined. Using methods provided by personnel at Wright-Patterson Air Force Base or described in the literature, preparations of tetrafluoroisophthalic acid and of tetrafluorometa- and para-phenylenediamine were carried out.

The following compounds were supplied to Monsanto Chemicals Ltd., Ruabon:-

	g.
Tetrafluoroisophthalic acid	30
Pentafluorobenzoic acid	300
Tetrafluoroterephthalic acid	50
2,3,5,6-Tetrafluorobenzoic acid	25
Tetramethyl difluoropyromellitate	5
Pentafluorophenol	100
Tetrafluorohydroquinone	50
Tetrafluororesorcinol	100
Pentafluorothiophenol	75
Pentafluorobenzenesulphonyl chloride	50
Pentafluoroaniline	75
2,3,4,6-Tetrafluoroaniline	10
Tetrafluoro-p-phenylenediamine	25
Tetrafluoro-o-phenylenediamine	5
Tetrafluoro-m-phenylenediamine	25
1,4-Bis(pentafluoroanilino)-2,3,5,6-tetrafluorobenzene	15
Decafluorocyclohexene	250
Pentafluoroiodobenzene	100
Pentafluorobenzene	100

	g.
4,4'-Dihydroxyoctafluorobiphenyl	25
4,4'-Diamino-octafluorobiphenyl	23.8
4,4'-Bis(pentafluorophenylthio)octafluorobiphenyl	5
3,3'-Dihydroxy-4,4'-diaminohexafluorobiphenyl	25
3,3'-Bis(pentafluorobenzamido)-4,4'-diaminohexafluorobiphenyl	20

C. DISCUSSION

1. 2,3,5,6-TETRAFLUOROBENZOIC ACID (I)

2,3,5,6-Tetrafluorobenzoic acid, required for the synthesis of model condensates containing some hydrogen atoms, was prepared by acidic hydrolysis of 2,3,5,6-tetrafluorobenzonitrile. This nitrile was prepared in 58% yield by the cyanation of 2,3,5,6-tetrafluorobromobenzene with cuprous cyanide in boiling dimethylformamide. A by-product from this reaction was shown to be tetrafluoroterephthalonitrile.

2. TETRAFLUOROISOPHTHALIC ACID (II)

At the start of the current Contract, work was in progress on a synthesis which involved cyanation of 3-bromoheptafluorotoluene to give perfluoro-3-methylbenzonitrile and hydrolysis of the trifluoromethyl and nitrile groups in this compound to give II.

Fluorination of pentabromobenzotrifluoride with potassium fluoride gave 3-bromoheptafluorotoluene contaminated with a hydrogen-containing impurity (ref. 1). Sulphonation of the product removed most of the hydrogen-containing impurity, presumably as a water-soluble sulphonic acid, and afforded 3-bromoheptafluorotoluene of about 96% purity.

Reaction of the bromo-toluene with cuprous cyanide in dimethylformamide yielded a complex product which was not investigated further. An infra-red spectrum of the material contained a band attributable to $-C \equiv N$.

Since the nitrile route did not appear promising, the bromo-toluene was converted to a Grignard reagent, which, upon carbonation in tetrahydrofuran, yielded heptafluoro-m-toluic acid (53%). The planned acid hydrolysis of this acid to II was not carried out because at this stage details of a more attractive route to II via 1,2,3,5-tetrafluorobenzene were received (ref. 2).

By this method 2,3,4,6-tetrafluorophenyl-lithium, prepared from n-butyl-lithium and 1,2,3,5-tetrafluorobenzene in an ether/hexane mixture at -65°, was carbonated to give 2,3,4,6-tetrafluorobenzoic acid in 36% yield. Treatment of this compound with two moles of n-butyl-lithium, followed by carbonation in tetrahydrofuran, gave II in 56.5% yield.

3. DIFLUOROPYROMELLITIC ACID (III)

Previous work (ref. 1) showed that III could be prepared by the oxidation of difluorodurene but further work was required to optimise the conditions for this reaction.

Difluorodurene was prepared from durene by the Balz-Schiemann synthesis as described previously (ref. 1). The last two stages are described in the Experimental Section as these involved the formation and thermal decomposition of 3-fluorodurene-6-diazonium borofluoride on a somewhat larger scale than that used hitherto.

The preliminary experiments with the oxidation of difluorodurene with nitric acid established that, if the temperature of the mixture was increased too rapidly, sudden uncontrollable reactions occurred causing temperature surges to as high as 250°, and partial decarboxylation of the product resulted. Conditions were found which avoided this run-away reaction but a mixture of acids was formed using these more moderate oxidation temperatures. This mixture was esterified by treatment with diazomethane. By fractional distillation of the mixed esters three of them were isolated in pure form and identified on the basis of their elemental analyses and infra-red spectra. These three esters were tetramethyl difluoropyromellitate, difluoro-bis(methoxycarbonyl)xylene, and 2,5-difluoro-3,4,6-tris(methoxycarbonyl)toluene. Hydrolysis of these esters by treatment with boiling 48% hydrobromic acid gave difluoropyromellitic acid, difluoroxylene dicarboxylic acid, and 2,5-difluorotoluene-3,4,6-tricarboxylic acid, respectively.

An alternative route from difluorodurene to difluoropyromellitic acid was examined. Bromination of difluorodurene gave 1,2,4,5-tetra-(bromomethyl)-3,6-difluorobenzene and oxidation of this tetrabromo-compound by boiling nitric acid in the presence of silver vanadate gave difluoropyromellitic acid. This route appears to offer advantages in that the oxidation is easier to control and the product is difluoropyromellitic acid uncontaminated with incompletely oxidised products.

4. TETRAFLUORO-O-PHENYLENEDIAMINE (IV)

Tetrafluoro-m-phenylenediamine, prepared by the reaction of pentafluoroaniline with ammonium hydroxide and purified by sublimation and recrystallisation, contains about 5% of the ortho isomer (ref. 3). Use of the impure m-diamine for the synthesis of model compounds by Monsanto gave products believed to contain impurities derived from the o-diamine, and to help in identifying these impurities a small quantity of IV was required.

IV was prepared as described previously (ref. 1) from 2,3,4,5-tetrafluoroaniline. Acidic hydrolysis of 2-nitro-3,4,5,6-tetrafluoroacetanilide for one hour (cf. 2 hours used previously) gave an improved yield (85%; cf. 40% obtained previously) of 2-nitro-3,4,5,6-tetrafluoroaniline. The overall yield of IV from 2,3,4,5-tetrafluoroaniline was 17%.

5. TETRAFLUORO-M-PHENYLENEDIAMINE (V)

Since ammination of pentafluoroaniline yields impure tetrafluoro-m-phenylenediamine (see above), efforts to prepare the pure isomer by other methods were continued.

Attempts to nitrate 2,3,4,6-tetrafluoroacetanilide using a mixture of concentrated nitric and sulphuric acids failed (ref. 1); with a mixture of fuming nitric acid and concentrated sulphuric acid a violent reaction ensued but no nitro-compound was isolated. Treatment of the anilide with nitronium tetrafluoroborate also failed to effect nitration.

In view of these failures, it was decided to prepare V by the method supplied by personnel at Wright-Patterson Air Force Base (ref. 4a, b).

This method involves the conversion of pentafluoroaniline to 3-hydrazinotetrafluoroaniline, formation of acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone and subsequent reduction of this compound. In our hands the overall yield was 11%. Although the method requires the use of hazardous 95% hydrazine it has the advantage that it yields V in isomerically pure form.

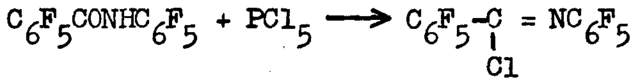
6. TETRAFLUORO-P-PHENYLENEDIAMINE (VI)

The preparation of (VI) by a Schmidt reaction on tetrafluoroterephthalic acid has recently been described by Russian workers (ref. 5). Following their procedure, but, using larger quantities, we obtained a very similar yield (78%) of the crude diamine. The method seems to be suitable for the preparation of further batches of VI as required.

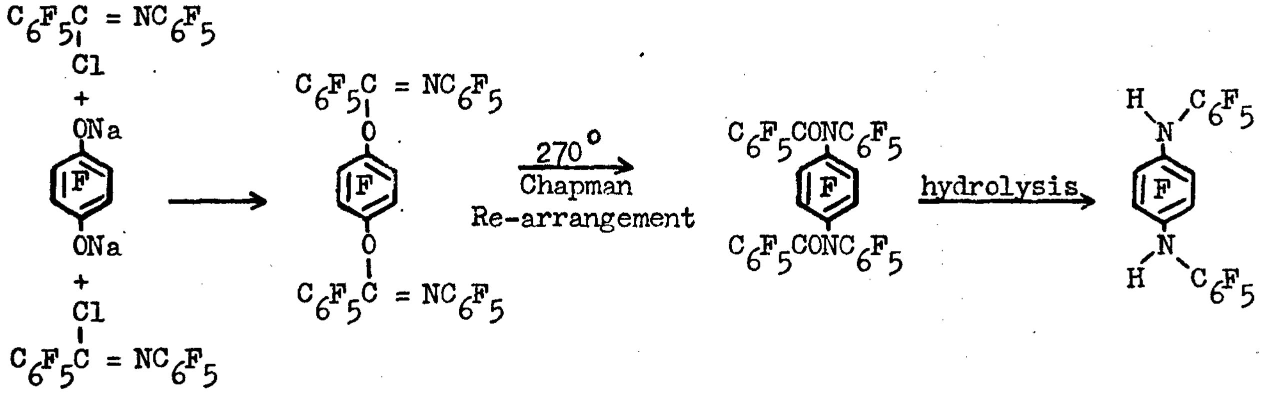
7. 1,4-BIS(PENTAFLUOROANILINO)TETRAFLUOROBENZENE (VII)

Early attempts to prepare (VII) by reaction of decafluorodiphenylamine with the sodio-derivative of pentafluoroaniline (ref. 1) gave only a small yield of VII even when forcing conditions were employed.

A second route, involving the following reactions, was next investigated:-



$$C_6F_5CONHC_6F_5 + PCl_5 \longrightarrow C_6F_5\text{-}\underset{\substack{|\\ Cl}}{C} = NC_6F_5$$



N-(pentafluorophenyl)pentafluorobenzimidoyl chloride was formed in 87% yield by reaction of decafluorobenzanilide with phosphorus pentachloride but could not be made to condense with the disodium salt of tetrafluorohydroquinone.

When tetrafluoro-p-phenylenediamine became readily available as described above it was found that reaction of its disodium derivative with hexafluorobenzene in dioxan solution gave VII in 26% yield. This method is satisfactory for preparing laboratory quantities.

A by-product, 4-aminononafluorodiphenylamine was isolated in 20% yield from this reaction.

8. 4,4'-DIAMINO-OCTAFLUOROBIPHENYL (VIII)

Monsanto have emphasised the need for high purity of intermediates used for model condensate and polymer preparations. A batch of VIII was therefore carefully purified, first by several recrystallisations from toluene which raised the purity to a maximum value of 98.1%, and secondly, by zone refining the recrystallised compound. In this way VIII of 99.4% purity was obtained.

9. 2,3,4,6-TETRAFLUOROANILINE (IX)

This amine was prepared in 85% yield and 99+% purity by reduction of 2,3,4,6-tetrafluoronitrobenzene with iron filings and ammonium chloride solution (ref. 6). It was required by Monsanto for the synthesis of model condensates containing residual hydrogen atoms.

10. 3,3'-DIHYDROXY-4,4'-DIAMINOHEXAFLUOROBIPHENYL (X)

Catalytic reduction of 3,3'-dihydroxy-4,4'-dinitrohexafluorobiphenyl, the precursor of X, was found to be unsatisfactory. Incomplete reduction occurred, possibly caused by catalyst poisoning by intermediates formed during the reduction, e.g. hydroxyazo-compounds.

Therefore, two other routes for the reduction of the nitro groups in this compound were tried, summarised below:-

1. Sodium dithionite in water at 70-80° gave a 51% yield of the diamine X.

2. Tin and hydrochloric acid in glacial acetic acid gave a 53% yield of X.

A combination of the two gave the best result. Thus, reduction of the dinitro-compound on a larger scale (0.154 molar) with sodium dithionite gave a 68.5% yield but the product was shown by thin layer chromatography to contain a number of incompletely reduced products. The impurities were removed and a pure, white product obtained by treatment of an ether solution of the crude diamine with stannous chloride in hydrochloric acid.

11. 3,3'-BIS(PENTAFLUOROBENZAMIDO)-4,4'-DIAMINOHEXAFLUOROBIPHENYL (XI)

3,3'-Bis(pentafluorobenzamido)-4,4'-dinitrohexafluorobiphenyl was prepared in yields of 54% and 60% by the interaction of 3,3'-diamino-4,4'-dinitrohexafluorobiphenyl and pentafluorobenzoyl chloride in the presence of dimethylaniline.

This dinitro compound was then reduced to XI by two methods, catalytically with hydrogen and Raney nickel, or more conveniently with a hydrochloric acid solution of stannous chloride in ether.

12. HEXAFLUOROBENZENE (XII)

Commercial hexafluorobenzene contains up to 3% of impurities which are principally pentafluorobenzene and tetrafluorobenzenes. Hence when it is treated with a nucleophile to prepare a pentafluorophenyl compound there will be hydrogen-containing tetrafluorophenyl- and trifluorophenyl-compounds in the product which are not easily removed. In many cases the detection of small amounts of these impurities may be difficult. Such impurities are undesirable when the product is required for the synthesis of model compounds for T_D determinations because the models will contain hydrogen atoms which might be eliminated as hydrogen fluoride thereby lowering the T_D.

Hexafluorobenzene required for the preparation of pure pentafluorophenyl derivatives was purified by treatment with 65% oleum at 80° for 6 hours. This treatment converts hydrofluoroaromatic compounds present into water-soluble sulphonic acids which are removed by washing the organic phase with water. Hexafluorobenzene of 99.7% purity is obtained.

13. PENTAFLUOROBENZENE (XIII)

Since commercial pentafluorobenzene contains small amounts of other polyfluorobenzenes, tetrafluorophenyl-derivatives prepared therefrom by nucleophilic attack may well contain impurities, principally pentafluorophenyl-compounds, which are difficult to detect and remove.

Accordingly, pure pentafluorobenzene was prepared by reduction of pure bromopentafluorobenzene (containing no impurities detectable by gas chromatography) using zinc powder and acetic acid (ref. 7). The product contained no impurities detectable by gas chromatography.

14. PENTAFLUOROPHENOL (XIV)

Treatment of 99.7% purity hexafluorobenzene with potassium hydroxide in t-butanol yielded 99.7% pure XIV.

15. TETRAFLUORORESORCINOL (XV)

Preparation of XV by the action of aqueous potassium hydroxide on pentafluorophenol (ref. 1) gave material which apparently contained about 6% of an impurity, detected by gas chromatography using an apiezon grease/celite column at 200°. However, analysis on a silicone oil/celite column at 150° indicated a purity of 99+% so it is possible that the impurity detected at the higher temperature is a decomposition product. In support of this supposition, thin layer chromatography yielded only a single spot.

Since it was important to be certain that the material was very pure, efforts were made to identify the impurity by the preparation of likely impurities for comparative purposes.

Tetrafluorocatechol (XVI) was prepared by the method described in the literature (ref. 8). However, it was found not to be the impurity present in XV because (a) it did not give a peak when analysed by gas chromatography under the same conditions that were used for XV, (b) on thin layer chromatography it had an R_f value different to that of XV and (c) a band at 1280 $cm.^{-1}$ present in the infra-red spectrum of tetrafluorocatechol does not appear in the infra-red spectrum of XV.

Tetrafluorohydroquinone was not the impurity since, when analysed by thin layer chromatography, it gave a spot with an R_f value different to that of XV. Infra-red spectroscopy was not very useful for detecting the presence of tetrafluorohydroquinone in XV.

The possibility that the impurity was a trifluororesorcinol was considered next. To eliminate this possibility, a quantity of XV was prepared from pentafluorophenol containing, at most, 0.3% of hydrogen-containing impurities. Surprisingly, this batch of XV again contained about 11% of the impurity according to gas chromatography using an apiezon grease/celite column at 200°. The exact quantity of impurity was difficult to estimate since the peak was incompletely resolved from the main one. This material, after recrystallisation from benzene (with little alteration in apparent purity) had a sharp melting point, an acceptable elemental analysis and gave only a single spot by thin layer chromatography. A diacetate derivative was obtained in 90% yield and after recrystallisation (m.p. not raised) had an excellent elemental analysis. Acid hydrolysis of this diacetate yielded XV with a sharp melting point and an infra-red spectrum which showed it to be only marginally more pure than XV prepared directly from 99.7% pure pentafluorophenol.

We conclude that the "impurity" is formed by partial decomposition of XV under the conditions used for gas chromatography and pure XV is in fact isolated from the reaction product of aqueous potassium hydroxide and pentafluorophenol.

17. 4,4'-DIHYDROXYOCTAFLUOROBIPHENYL (XVII)

Treatment of decafluorobiphenyl with potassium hydroxide in t-butanol (ref. 9) gave XVII in 14% yield.

18. 4,4'-BIS(2,3,5,6-TETRAFLUOROPHENYLTHIO)OCTAFLUOROBIPHENYL (XVIII)

Mass spectrometry is a useful technique for detecting small quantities of hydrogen-containing impurities in perfluoro-compounds. In order to establish the limits of detection Monsanto required a quantity of XVIII for admixture with the corresponding perfluoro-sulphide which had been prepared previously (ref. 1).

Reaction of cuprous 2,3,5,6-tetrafluorothiophenate with 4,4'-dibromo-octafluorobiphenyl in dimethylformamide yielded the crude dihydro-sulphide in 94% yield, but it proved difficult to purify the compound to a constant narrow-range melting point by recrystallisation. Similar difficulties were encountered with the perfluoro-compound and it had a 2.5 degree melting range. Since, in the case of XVIII, only a single spot was observed by thin layer chromatographic analysis and an excellent elemental analysis was obtained the material was assumed to be pure and was despatched to Monsanto.

19. PENTAFLUOROTHIOPHENOL (XIX)

Treatment of 99.7% purity hexafluorobenzene with sodium hydrogen sulphide in ethylene glycol/dimethylformamide solution gave a 60% yield of 99+% pure XIX.

20. 2,3,5,6-TETRAFLUOROTHIOPHENOL (XX)

Treatment of 99+% pentafluorobenzene with sodium hydrogen sulphide in ethylene glycol/dimethylformamide solution gave a 72% yield of 99+% pure XX.

21. TETRAFLUOROBENZENE-1,4-DITHIOL (XXI)

Initial attempts to prepare XXI involved demethylation of 1,4-bis(methylthio)tetrafluorobenzene (ref. 1) and were unsuccessful. Further attempts using sodium hydroxide solution, anhydrous aluminium chloride and hydrazine hydrate also failed to yield XXI and this approach was abandoned.

A satisfactory synthesis of XXI was achieved by treatment of the dilithio-derivative of 1,2,4,5-tetrafluorobenzene with elemental sulphur. The yield was 24%, (ref. 10).

This reaction should be capable of extension to other isomers as required.

In an initial attempt, poor-quality commercial n-butyl-lithium was used and dilithiation was apparently incomplete, 2,3,5,6-tetrafluorothiophenol being obtained in 65% yield.

Another synthesis of XXI was briefly investigated. Sodium thiolacetate, prepared by the action of thiolacetic acid on sodium methoxide, was reacted with hexafluorobenzene. Spontaneous hydrolysis of the intermediate thiolacetate yielded pentafluorothiophenol (22%) but none of compound XXI. It is not intended to pursue this reaction further.

D. EXPERIMENTAL

1. 2,3,5,6-TETRAFLUOROBENZOIC ACID

(1) 2,3,5,6-Tetrafluorobenzonitrile

2,3,5,6-Tetrafluorobromobenzene (100g., 0.401 mole), cuprous cyanide (39.5g., 0.442 mole), and dry dimethylformamide (75 ml.) were heated under reflux and stirred for 5½ hours. The mixture was then poured into a solution containing anhydrous ferric chloride (70g., 0.425 mole), 10N hydrochloric acid (50 ml., 0.55 mole) and water (200 ml.) at 90°. This mixture was heated at 90° for 15 minutes and was then steam distilled. The organic steam distillate was dried and distilled to give:-

(i) 2,3,5,6-tetrafluorobenzonitrile (47.9g.), b.p. 84-86°/40 mm., n_D^{25} 1.4950, 93.4% purity. The nitrile crystallised on keeping at 15°. It was recrystallised from petroleum ether (b.p. 40-60°) at 0° giving crystals of the nitrile (38.1g., 58.5%), m.p. 31.5-33°, 99% purity. I.R. No. 3784.

<u>Anal</u>. Calc. for C_7HF_4N: C, 48.7; H, 0.6; F, 43.2%

Found: C, 48.4; H, 0.7; F, 43.2

(ii) a solid residue (6.8g.), which on recrystallisation from ethanol and then from ethyl acetate gave a material which had an infra-red spectrum No. 3785a identical to that of authentic tetrafluoroterephthalodinitrile.

<u>Anal</u>. Calc. for $C_8F_4N_2$: C, 48.0; H, 0.0; F, 38.0%

Found: C, 47.9; H, 0.0; F, 39.1

Hydrolysis of this material with sulphuric acid gave an acid with m.p. 280-281° (from water) and an infra-red spectrum No. 3845 identical to that of authentic tetrafluoroterephthalic acid.

(2) 2,3,5,6-Tetrafluorobenzoic acid

2,3,5,6-Tetrafluorobenzonitrile (34.0g., 0.194 mole) and sulphuric acid (s.g. 1.84, 34.0 ml., 0.63 mole) were heated to 80° when an exothermic reaction set in. When this was over the mixture was heated at 125-135° for 15 minutes, then cooled to 90°. Water (42.5 ml.) was added, diluting the acid to 60% w/w. The mixture was boiled for 6 hours. Water (42.5 ml.) was then added and the mixture cooled to 20° with stirring. The solid which formed was filtered off, washed with water and dried. It weighed 34.9g. Extraction of the aqueous solution with ether (2 x 50 ml.) gave a further 1.0g. Total yield: 35.9g., 95%, m.p. 147-149°. Harper et al. (ref. 11) cite 150.5-152°, Alsop et al. (ref. 12) cite 154°.

Purification by sublimation at 110°/0.1 mm. and by recrystallisation from water (150 ml.) and from petroleum ether (b.p. 100-120°) did not raise the m.p. Infra-red spectrum No. 3805.

Anal. Calc. for $C_7H_2F_4O_2$: C, 43.3; H, 1.0; F, 39.2%

Found: C, 43.3; H, 1.0; F, 39.1

2. TETRAFLUOROISOPHTHALIC ACID

a. From 3-bromoheptafluorotoluene

(1) Purification of 3-bromoheptafluorotoluene

3-Bromoheptafluorotoluene (54.0g.), containing 23% of a hydrogenic impurity was shaken at room temperature with 65% oleum (12.1g.) for $5\frac{1}{4}$ hours then poured onto crushed ice (200g.). The organic layer was water washed (2 x 20 ml.), dried ($MgSO_4$), and filtered, giving 46.1g. of material 93% pure by gas chromatography. I.R. 3434.

A part (42.04g.) of this product was treated again with 65% oleum (2.7g.) at room temperature for 6 hours, giving, after a similar work-up, 37.23g. of material 96% pure by gas chromatography.

An N.M.R. analysis of this material showed it to be at least 95% the meta isomer, but hydrogenic impurities were present.

(2) Reaction of 3-bromoheptafluorotoluene with cuprous cyanide

3-Bromoheptafluorotoluene (17.72g., 96% purity, 0.057 mole), cuprous cyanide (6.02g., 0.067 mole), and dry dimethyl formamide (150 ml.) were stirred and heated together at reflux temperature for 11 hours. The mixture progressively darkened to a deep green. A solution of ferric chloride (20g.) in concentrated hydrochloric acid (15 ml.) was added, followed by water (50 ml.). The resultant dark brown solution was steam distilled yielding a yellow oil (6.93g.) having the following composition by gas chromatography:-

3H-heptafluorotoluene (37%)

3-bromoheptafluorotoluene (7%)

3,3'-bis(trifluoromethyl)octafluorobiphenyl (5%)

two unidentified materials with very similar retention times just shorter than that of the starting material (24% and 10%)

other unidentified materials (small amounts)

In infra-red spectrum (No. 3428) of the crude product showed strong absorptions for aromatic -C-H and -C≡N.

(3) Carbonation of the Grignard reagent prepared from 3-bromoheptafluorotoluene

Magnesium turnings (3.71g., 0.15g. atom) in dry tetrahydrofuran (90 ml.) were activated by the addition of ethylene dibromide (0.5 ml.). When reaction began the solution was cooled to 0° and 3-bromoheptafluorotoluene (15.5g., 95.9% purity on 0.05 mole) in 10 ml. tetrahydrofuran was run in over 30 minutes. An exothermic reaction occurred. The dark solution was cooled to -20°, stirred for a further 30 minutes, then carbonated at -20° by passing in carbon dioxide for 105 minutes and while the solution was warming to 15° (30 minutes). The solution was poured onto a mixture of crushed ice (150g.) and 11.5N hydrochloric acid (50 ml.). The upper tetrahydrofuran layer was separated off, water washed (3 x 20 ml.) and dried ($MgSO_4$); the washings were added to the aqueous layer. The aqueous layer was exhaustively ether extracted for 30 hours and the dried extracts distilled yielding a brown residue (1.56g.) which was added to the tetrahydrofuran solution. Distillation of the tetrahydrofuran at reduced pressure gave an involatile residue (11.08g.) which solidified. When recrystallised twice from benzene there was obtained heptafluoro-m-toluic acid (7.0g., 53.5%), m.p. 56.5-58.5°. The infra-red spectrum (No. 3630) showed -C=0 and -OH absorptions and the material dissolved in water giving an acid solution which liberated carbon dioxide from sodium bicarbonate.

Anal. Calc. for $C_8HF_7O_2$: C, 36.7; H, 0.38; F, 50.8%; equiv. 262.1

Found: C, 37.0; H, 0.4; F, 50.7%; equiv. 265

b. From 1,2,3,5-tetrafluorobenzene

(1) 2,3,4,6-tetrafluorobenzoic acid

1,2,3,5-Tetrafluorobenzene (150g., 1.0 mole) in dry ether (900 ml.) was added over 2 hours to a solution of butyl-lithium (68g., 1.0 mole) in hexane (676 ml.), cooled at -65°, under nitrogen. The mixture was then stirred at -65° for 30 minutes. Dry carbon dioxide (45g.) was then bubbled through the solution while it warmed to room temperature. The solution was then acidified with 6N hydrochloric acid (900 ml.). The aqueous layer was extracted with ether (3 x 150 ml.). The ether was removed from the dried extract leaving a solid (86g.). Recrystallisation of this product from petroleum ether (1 l., b.p. 60-80°) followed by sublimation gave white crystals of 2,3,4,6-tetrafluorobenzoic acid (70g., 36% yield), 99% purity, m.p. 101-102°.

(2) 2,3,4,6-tetrafluoroisophthalic acid

Butyl-lithium (46.2g., 0.722 mole) in hexane (344 ml.) was added over 3 hours to a solution of 2,3,4,6-tetrafluorobenzoic acid (70g., 0.361 mole) in tetrahydrofuran (1400 ml.) maintained at -65° under a nitrogen atmosphere. The mixture was stirred at -65° for 30 minutes, then carbonated at -65° using a stream of carbon dioxide. The mixture was allowed to warm to 15° whilst carbon dioxide was still being passed in. Hydrochloric acid (1400 ml., 6N) was added. The organic layer was separated and the aqueous phase was extracted with ether (3 x 250 ml.). Evaporation of the combined dried extracts left crude tetrafluoroisophthalic acid which was purified by Soxhlet extraction with petroleum ether (b.p. 60-80°), followed by recrystallisation from nitrobenzene (57g. in 400 ml.). Yield: 49g., (56.5%), m.p. 210-211.5°.

3. DIFLUOROPYROMELLITIC ACID

(1) 3-Fluorodurene-6-diazonium borofluoride

3-Amino-6-fluorodurene (116g., 0.695 mole) was added to concentrated sulphuric acid (56.5 ml.) in water (348 ml.) and heated to 100° to ensure complete formation of the sulphate. The solution was cooled to 0° and diazotised by the addition of sodium nitrite (47.6g., 0.695 mole) in water (140 ml.).

To the filtered diazotised solution was added sodium tetrafluoroborate (111g., 1.01 mole) in water (207 ml.) and after 30 minutes at 0° the precipitated borofluoride was filtered off, washed with 5% sodium tetrafluoroborate solution (200 ml.), with water (100 ml.) and dried.

The filtrate was heated at 100° until no more nitrogen was evolved, then cooled and filtered. The precipitated solid was filtered off and recrystallised twice from petrol-ether (b.p. 80-100°) giving 3-fluoro-6-hydroxydurene, m.p. 126.5-127.5°. I.R. No. 3487.

Anal. Calc. for $C_{10}H_{13}FO$: C, 71.5; H, 7.7; F, 11.3%

Found: C, 71.4; H, 7.8; F, 11.7

From two preparations there was obtained:

(i) 3-fluorodurene-6-diazonium borofluoride (186.5g., 100%)

(ii) 3-fluorodurene-6-diazonium borofluoride (143.7g., 78.6%) and 3-fluoro-6-hydroxydurene (19g., 16.8%)

(2) Difluorodurene

Equal weights (40-60g.) of dry sand and 3-fluorodurene-6-diazonium borofluoride were mixed in a flask and decomposed by intermittent heating. The reaction was completed by warming the flask in boiling water until the organic phase was completely liquid. Difluorodurene was distilled from the mixture. In this way, decomposition of 3-fluorodurene-6-diazonium borofluoride (206.5g., 0.78 mole) gave difluorodurene (109g., 83%).

Recrystallisation of the product from methanol gave material of 99.4% purity, m.p. 60-62°.

(3) Oxidation of difluorodurene

Difluorodurene (172g., 1.01 mole) was oxidised using 25% nitric acid in an autoclave yielding 202g. of mixed acids. A typical experiment is described below:

Difluorodurene (20g.) and 25% w/w nitric acid (450 ml.) were heated during 1½ hours to 155-160° in a 1 litre glass-lined autoclave, then maintained at 150-160° for 1½-3½ hours. The autoclave was cooled, the contents evaporated to dryness and the residue was taken up in dilute hydrochloric acid, diluted to 2 litres and exhaustively ether extracted. The ether was removed leaving a solid residue. This was analysed by thin layer chromatography on alumina using 3:1 ethanol:ammonia as eluent and U.V. light to detect the spots. A typical analysis was:-

0/15	2/15	4/15	7/15	8/15	11.5/15
dense	dense	weak	weak-very weak	weak-medium	very weak

The fraction at 0/15 was identified by comparison with an authentic sample as due to difluoropyromellitic acid.

(4) Isolation of acids from the oxidation of difluorodurene

To an ice cooled slurry of difluorodurene oxidation products (185g.) in ether (500 ml.) was slowly added a solution of diazomethane, prepared from N-nitrosomethylurea (430g.), 50% w/w potassium hydroxide solution (1250 ml.) and ether (4675 ml.) until an excess was present. The mixture was allowed to stand overnight then the ether was evaporated leaving mixed esters (215g.). Analysis of this product at 200° on a 2'9" column, packed with silicone oil on celite gave the following result:-

Retention time	1'0"	1'0"	1'20"-2'0"	2'35"	3'0"-4'0"	4'48"	5'40"
% of mixture	1.4	13.8	7.9	51.3	3.2	21.7	0.5

The mixed esters were distilled through a 1 ft. column packed with glass helices to give (a) a fraction, b.p. 127-130°/2 mm., which was recrystallised from light petroleum (b.p. 40-60°), then from 80% methanol to give difluoro-bis(methoxycarbonyl)xylene (13g.), m.p. 68.5-69.5°, 97.8% purity by gas chromatography, I.R. No. 4055.

<u>Anal</u>. Calc. for $C_{12}H_{12}F_2O_4$: C, 55.9; H, 4.65; F, 14.7%

Found: C, 56.1; H, 4.9; F, 14.7

(b) an unidentified product (9.0g.), b.p. 134-157°/2 mm., purity 58%

(c) a fraction, b.p. 167.5-168°/ 2 mm., which, after recrystallisation from light petroleum (b.p. 40-60°) and then from 80% methanol, gave 2,5-difluoro-3,4,6-tris(methoxycarbonyl)toluene (66.5g.), m.p. 54-56°, 98% purity by gas chromatography, I.R. No. 4014.

Anal. Calc. for $C_{13}H_{12}F_2O_6$: C, 51.6; H, 4.0; F, 12.6%

Found: C, 51.6; H, 3.9; F, 12.6

(d) a residue which was recrystallised from ethanol to give tetramethyl difluoropyromellitate (22g.), m.p. 119-120°, b.p. 185-187°/2 mm., 369-370°/771 mm., 98.4% purity by gas chromatography, with an identical infra-red spectrum to that of an authentic sample (ref. 1).

Hydrolysis of these esters in boiling 60-80% sulphuric acid did not proceed to completion. A more satisfactory method of hydrolysis was by heating the ester in boiling 48% hydrobromic acid. The general procedure was to heat the ester (1g.) in boiling 48% hydrobromic acid (10 ml.) for 5-6 hours. The organic acid was isolated either by allowing it to crystallise or by evaporation of the hydrobromic acid. High yields of products were obtained.

Difluoroxylene dicarboxylic acid had m.p. 265-270° after recrystallisation from water, then from a small volume of acetic acid. I.R. No. 4091.

Anal. Calc. for $C_{10}H_8F_2O_4$: C, 52.2; H, 3.5; F, 16.5%

Found: C, 52.0; H, 3.1; F, 16.4

2,5-Difluorotoluene-3,4,6-tricarboxylic acid had m.p. 214-215° after recrystallisation from 48% hydrobromic acid. I.R. No. 4095.

Anal. Calc. for $C_{10}H_6F_2O_6$: F, 14.6%

Found: F, 14.7

Tetramethyl 3,6-difluoropyromellitate (5.0g.) was stirred in boiling 48% hydrobromic acid (25 ml.) for 5 hours, then the mixture was evaporated to dryness leaving difluoropyromellitic acid (4.3g.), m.p. 252-257°. The acid was dissolved in water (10 ml.). Addition of 48% hydrobromic acid caused difluoropyromellitic acid to crystallise. The crystals were collected, washed with hydrobromic acid and dried in vacuo over potassium hydroxide pellets. The yield was 3.9g., 94%, m.p. 258-260° (decomp.). I.R. No. 4127.

Treatment of a solution of difluoropyromellitic acid (0.032g.) in water (0.5 ml.) with a filtered solution of barium oxide (0.043g.) in water (0.5 ml.) gave barium difluoropyromellitate (0.056g.). I.R. No. 4134. Analysis is awaited.

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

A solution of bromine (11.0g., 0.069 mole) in dry carbon tetrachloride (10 ml.) was added dropwise during 45 minutes to a boiling solution of difluorodurene (2.9g., 0.017 mole) in carbon tetrachloride (50 ml.). The mixture was irradiated with ultra violet light until the bromine colour faded (90 minutes). The solution was concentrated and cooled, when crystals formed. The crystals were washed with methanol and dried. Wt. = 7.02g., m.p. 179-182°. Evaporation of the solvent from the filtrate gave a further amount (0.52g.) of product. Recrystallisation of the combined solids from petroleum (b.p. 100-120°) gave 1,2,4,5-tetra(bromomethyl)-3,6-difluorobenzene (6.93g., 84% yield), m.p. 181-182°, I.R. No. 4083.

<u>Anal</u>. Calc. for $C_{10}H_8Br_4F_2$: C, 24.7; H, 1.65; Br, 65.9; F, 7.8

Found: C, 24.3; H, 1.5; Br, 65.6; F, 8.2

(6) Oxidation of 1,2,4,5-tetra(bromomethyl)-3,6-difluorobenzene

(a) With nitric acid

1,2,4,5-Tetra(bromomethyl)-3,6-difluorobenzene (2.0g.) was stirred in 95% nitric acid (15 ml.) for 15 minutes. The acid went into solution then crystals formed. The mixture was kept at room temperature overnight then the crystals were collected, washed with nitric acid, and dried over potassium hydroxide. Wt: 1.49g., m.p. 147-150° (decomp.). Evaporation of the filtrate gave more solid (0.09g.), m.p. 205-215° (decomp.).

A second experiment was performed using the same quantities but the reaction mixture was boiled for 15 minutes. On cooling the solution a crystalline product (0.99g.), m.p. 147-150°, was obtained. Evaporation of the mother liquor gave another solid product (0.40g.), m.p. 205-215° (decomp.).

The products melting at 147-150° were combined and recrystallised twice from acetic acid to give a solid (2.07g.), m.p. 150.5-152°, I.R. No. 4090.

<u>Anal</u>. Found: C, 28.8; H, 3.0; Br, 0; F, 9.4%

(b) With nitric acid in the presence of silver vanadate

1,2,4,5-Tetra(bromomethyl)-3,6-difluorobenzene (4.0g., 0.008 mole), and silver vanadate (0.40g., 0.002 mole) were heated in boiling 95% nitric acid (25 ml.) for 1½ hours. The mixture was concentrated by distilling off 17 ml. of water. 95% nitric acid (50 ml.) was added and the mixture was boiled for 14 hours then evaporated to dryness. The residue was again heated in boiling nitric acid (25 ml.) for 5 hours. The mixture was evaporated to dryness. The residue was boiled with water, filtered, and the filtrate was evaporated to give 2.62g., m.p. 255-265°. This treatment with water was repeated four times. The acid obtained was dissolved in water (10 ml.), the solution filtered, 48% hydrobromic acid was added to the filtrate, and the filtrate was kept at 0° until crystallisation was complete. The crystals were collected, washed with 48% hydrobromic acid and dried to give difluoropyromellitic acid (1.26g.), m.p. 258-260° (decomp.). Thin layer chromatography showed the presence of two trace impurities.

(7) Thermal stability of tetramethyl 3,6-difluoropyromellitate

Two 0.10g. samples of this ester were sealed in glass ampoules and kept at 300-304° for 3 hours. Some decomposition seemed to have occurred since the melting point was lowered from 119-120° to 113.5-116° and the purity was lowered from 98.4 to 93.1%.

4. TETRAFLUORO-O-PHENYLENEDIAMINE

(1) 2,3,4,5-Tetrafluoroacetanilide

2,3,4,5-Tetrafluoroaniline (200g., 1.21 mole) was treated with acetic anhydride (500 ml.) containing concentrated sulphuric acid (6 drops) at room temperature for 64 hours. The product was isolated as white crystals by pouring the mixture into water (3.75 litres). Recrystallisation gave 2,3,4,5-tetrafluoroacetanilide (177g., 71%), m.p. 103-105.5°.

(2) 2-Nitro-3,4,5,6-tetrafluoroacetanilide

To 2,3,4,5-tetrafluoroacetanilide (85g., 0.41 mole) in concentrated sulphuric acid (255 ml.) at 0° was added concentrated nitric acid (240 ml.) over 65 minutes, the temperature being kept at 10-15°. The mixture was stirred at 10-15° for a further 2 hours and then poured onto ice (1.75 kg.). The precipitate was washed with water, 5% sodium bicarbonate solution (300 ml.) and then with water again to yield 2-nitro-3,4,5,6-tetrafluoroacetanilide (69g., 67%), m.p. 146-149.5.

Repetition of this preparation on the same scale gave the nitro-compound in 76% yield, and the combined products (147g.) were recrystallised from 50% aqueous ethanol to yield buff crystals of the anilide (126g., 61.8%), m.p. 150-151.5°.

(3) 2-Nitro-3,4,5,6-tetrafluoroaniline

2-Nitro-3,4,5,6-tetrafluoroacetanilide (50.4g., 0.20 mole) and 50% sulphuric acid (109 ml. 98% sulphuric + 200 ml. water) were stirred and heated at reflux for 1 hour to give a deep red solution containing brown solid. The solid was filtered off, the filtrate ether extracted (3 x 200 ml.) and the solid dissolved in the extracts which were then water washed (2 x 30 ml.) and dried. Evaporation of the solvent gave a brown paste of crude 2-nitro-3,4,5,6-tetrafluoroaniline (42.5g., 100%), m.p. 41-43°. Sublimation of 38.9g. at 50-60°/0.1 mm. gave pure nitro-amine (33g., 85%), m.p. 40-41.5°.

(4) Tetrafluoro-o-phenylenediamine

2-Nitro-3,4,5,6-tetrafluoroaniline (21g., 0.1 mole) in ethanol (200 ml.) containing about 1g. of W4 Raney nickel was hydrogenated at atmospheric pressure and room temperature. The theoretical amount of hydrogen (7.2 litres) was taken up in 155 minutes. After filtering off the nickel, the solution was concentrated in vacuo (60 ml.) and the residue poured into water (250 ml.) to yield a mauve precipitate (13.8g.), m.p. 128-129.5°. Sublimation of this at 100°/0.1-0.2 mm. and two recrystallisations of the sublimate from benzene gave tetrafluoro-o-phenylenediamine (8.0g., 45%), m.p. 131.5-132.5°, of 99+% purity by gas chromatography and having the correct infra-red spectrum.

5. TETRAFLUORO-M-PHENYLENEDIAMINE

a. Attempted preparations from 2,3,4,6-tetrafluoroacetanilide

(1) Attempted nitration of 2,3,4,6-tetrafluoroacetanilide

(a) With fuming nitric acid/concentrated sulphuric acid

To a mixture of stirred concentrated sulphuric acid (10 ml.) and fuming nitric acid (8 ml., s.g. 1.5) at room temperature was added 2,3,4,6-tetrafluoroacetanilide (6.17g., 0.29 mole) over 10 minutes. During the addition only a small temperature rise occurred but this was followed by a violent reaction with expulsion of the flask contents. Some material remaining was diluted with water but no solid product was obtained.

(b) With nitronium tetrafluoroborate

To 2,3,4,6-tetrafluoroacetanilide (10.35g., 0.05 mole) in dry tetramethylene sulphone (50 ml.) was added a solution of nitronium tetrafluoroborate (8.30g., 0.063 mole) in tetramethylenesulphone (120 ml.), under nitrogen.

After approximately 20 ml. of solution had been added at room temperature with no apparent rise in temperature the acetanilide solution was heated to 50° while the remainder of the tetrafluoroborate solution was added (1 hour). The red-brown mixture was stirred for a further 2½ hours at 50-60° under nitrogen then poured into water (250 ml.). The solution was cooled in ice but no precipitate formed. Neutralisation of the solution yielded only 0.92g. of a carbonaceous material.

b. Preparation from 3-hydrazino-2,4,5,6-tetrafluoroaniline

(1) 3-Hydrazino-2,4,5,6-tetrafluoroaniline (typical experiment)

Pentafluoroaniline (1.83g., 1 mole), 95% anhydrous hydrazine (67.5g., 2.0 mole), and dioxan (100 ml.) were refluxed for 24 hours. The mixture was poured into cold water (750 ml.). The precipitated solid was filtered off, washed and dried (167g.). Sublimation of the product at 60°/0.1 mm. yielded pentafluoroanilinoethanol (41g., 18%), m.p. 48-51°. The residue (113g.) was recrystallised from petrol ether (b.p. 80-100°) to give 3-hydrazino-2,4,5,6-tetrafluoroaniline (81g., 42%), m.p. 105.5-106.5°. I.R. No. 3483.

(2) Acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone

3-Hydrazinotetrafluoroaniline (30g., 0.154 mole), acetophenone (23g., 0.192 mole), ethanol (150 ml.) and acetic acid (10 ml.) were refluxed for 40 minutes. After cooling, the product was filtered off (40g.) and recrystallised from 75% ethanol to give acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone (35g., 77%), m.p. 121.5-123°. I.R. No. 3642.

Other preparations gave yields of 74% and 62%.

(3) Tetrafluoro-m-phenylenediamine

Acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone (49g., 0.165 mole), zinc dust (66.5g., 0.92g. atom ca. 90% pure), and acetic acid (306 ml.) were stirred at reflux for 3 hours. The solution was filtered from zinc, the filtrate diluted with water (1 litre) and extracted with benzene (2 x 100 ml.) then with ether (3 x 100 ml.). Evaporation of the extracts gave a solid which, when sublimed, yielded a mixture containing (by gas chromatographic analysis) 85% tetrafluoro-m-phenylenediamine and 15% 5-amino-2,3,4,6-tetrafluoroacetanilide. Treatment of the mixture with 0.5% sodium hydroxide solution (150 ml.) at reflux for 90 minutes and filtration of the cooled mixture yielded tetrafluoro-m-phenylenediamine (10.5g., 35%), m.p. 129-130°, of 99% purity by gas chromatography. I.R. No. 3641.

6. TETRAFLUORO-P-PHENYLENEDIAMINE

Sodium azide (32.0g., 0.493 mole) was added in small portions over 2 hours to a stirred mixture of tetrafluoroterephthalic acid (50g., 0.21 mole), chloroform (312 ml.), and 20% oleum (208 ml.) at 40-45°. The mixture was maintained at this temperature a further 4 hours, then poured onto ice (500g.). The precipitated amine was filtered off and added to the separated sulphuric acid layer of the filtrate. This was neutralised with 40% sodium hydroxide solution (900 ml.) and the precipitated amine filtered off from the hot solution. A further small quantity of the amine was obtained by ether extracting the cooled filtrate. Yield of crude tetrafluoro-p-phenylenediamine 29.7g., 78.5%. The product was sublimed to give pure p-diamine (25.8g., 62.8%), m.p. 144-146°. I.R. No. 3543;

7. 1,4-BIS(PENTAFLUOROANILINO)TETRAFLUOROBENZENE

a. Attempted preparation via perfluoro(hydroquinone 1,4-bis-(N-phenylbenzimidoate))

(1) Decafluorobenzanilide

Pentafluorobenzoyl chloride (100g., 0.434 mole), pentafluoroaniline (80g., 0.437 mole), dimethylaniline (53g., 0.485 mole), and benzene (300 ml.) were stirred together for 2 hours at ambient temperature and refluxed for a further 2 hours. The solid was filtered off and recrystallised from aqueous ethanol (675 ml.) yielding crystalline decafluorobenzanilide (134.8g., 82.5%), m.p. 183-185°, I.R. No. 3424.

Anal. Calc. for $C_{13}HF_{10}NO$: C, 41.4; H, 0.3; F, 50.4%

Found: C, 41.2; H, 0.4; F, 50.6

(2) N-(pentafluorophenyl)pentafluorobenzimidoyl chloride

Decafluorobenzanilide (120g., 0.304 mole), phosphorus pentachloride (67g., 0.321 mole), and toluene (150 ml.) were heated at 100° for 3 hours.

After removal of toluene and phosphorus oxychloride the residue was distilled giving crude decafluorobenzimidoyl chloride (115g.) which was dissolved in petrol ether (100 ml., b.p. 40-60°). Undissolved decafluorobenzanilide (1.0g.) was filtered off. Evaporation of the solvent from the filtrate and distillation of the residue gave N-(pentafluorophenyl) pentafluorobenzimidoyl chloride (112g., 87.5%), b.p. 82-84°/ 0.4 mm., m.p. 29-30°. I.R. No. 3449.

Anal. Calc. for $C_{13}ClF_{10}N$: C, 39.5; H, 0.0; Cl, 9.0; F, 48.1%

Found: C, 39.3; H, 0.2; Cl, 9.3; F, 48.1

(3) Attempted preparation of perfluoro(hydroquinone 1,4-bis(N-phenylbenzimidoate))

(a) Tetrafluorohydroquinone (24.2g., 0.133 mole) in ethanol (50 ml.) was added to a solution of sodium (6.12g., 0.266 g. atom) in ethanol (100 ml.). A solution of N-(pentafluorophenyl)-pentafluorobenzimidoyl chloride (109g., 0.266 mole) in ether (80 ml.) was added and the resultant mixture was shaken for 35 hours. After working up, only tetrafluorohydroquinone (1.8g., 7.5%) and decafluorobenzimidoyl chloride (86.7g., 82.5%) were recovered.

(b) Potassium metal (8.38g., 0.21g. atom) and methanol (14.0g.) in toluene (100 ml.) yielded potassium methoxide which was separated from the toluene by decantation. Methanol (50 ml.), then a solution of tetrafluorohydroquinone (19.55g., 0.107 mole) in methanol (50 ml.), and toluene (100 ml.) were added. The mixture was distilled to remove methanol, N-(pentafluorophenyl)-pentafluorobenzimidoyl chloride (85g., 0.215 mole) was added, and the mixture stirred at 100-115° for 14 hours. After working up, only unchanged N-(pentafluorophenyl)pentafluorobenzimidoyl chloride was obtained (79.4g., 93% recovery).

b. Preparation from disodium salt of 2,3,5,6-tetrafluoro-p-phenylenediamine and hexafluorobenzene

2,3,5,6-Tetrafluoro-p-phenylenediamine (21g., 0.116 mole), hexafluorobenzene (43.5g., 0.234 mole), sodium hydride (50% in oil 22.4g., 0.467 mole) and freshly purified dioxan (400 ml.) were refluxed under nitrogen for 22 hours. Water (400 ml.), then 10N hydrochloric acid (50 ml., 0.55 mole) were added carefully. The solvent was removed by steam distillation until the vapour temperature reached 100° (900 ml. distillate). After cooling the mixture, the product, a grey powder (45.9g.), was collected. It was recrystallised from petroleum ether (600 ml., b.p. 80-100°) giving 1,4-bis(pentafluoroanilino)-2,3,5,6-tetrafluorobenzene

(14.4g.), m.p. 173-175.5°. Sublimation of insoluble crystallisation residues gave a further quantity (3.7g.). Total yield: 18.1g., 30%. The combined products were purified by sublimation at 138°/0.2 mm. followed by crystallisation from petroleum ether (250 ml., b.p. 100-120°) giving the amine (15.4g., 25.6%), m.p. 177-178.5°. I.R. No. 3735.

Sublimation of the evaporated crystallisation residues at 100°/0.303 mm. gave 4-aminononafluorodiphenylamine (8.3g., 20.5%), m.p. 102-103. I.R. No. 3710.

<u>Anal</u>. Calc. for $C_{12}H_3F_9N_2$: C, 41.0; H, 0.9; F, 49.5%

Found: C, 41.0; H, 0.9; F, 49.5

8. 4,4'-DIAMINO-OCTAFLUOROBIPHENYL (PURIFICATION)

4,4'-Diamino-octafluorobiphenyl prepared by the reaction of aqueous ammonia with decafluorobiphenyl had a purity of 93.6% when analysed by gas chromatography and showed three impurity spots when analysed by thin layer chromatography. This material (100g.) was recrystallised four times from xylene yielding a product (52g.), 98.1% pure by gas chromatography (silicone oil on celite at 200°). Two minor impurities were detected by thin layer chromatography. No further purification was effected by recrystallisation, but the purity was improved by zone melting.

In three equal batches a total of 43.8g. were purified by 18-23 passes of a molten zone, travelling at 1"/hr., through a 0.9 x 15 cm. tube of the solid material.

By cutting off the upper part of the column containing the purified material there was obtained white crystals (25.12g.), m.p. 178-180° with a purity of 99.4%, as determined by gas chromatography. Thin layer chromatographic analysis showed the presence of one minor impurity.

9. 2,3,4,6-TETRAFLUOROANILINE

A stirred suspension of iron filings (70g., 1.25g. atom) in a solution of ammonium chloride (4.02g.) in water (90 ml.) was heated to ca. 50°. Drop-wise addition of 2,3,4,6-tetrafluoronitrobenzene (72g., 0.37 mole) was begun and continued at a rate to sustain steady reflux. When addition was complete (45 minutes) the product was steam distilled to give 2,3,4,6-tetrafluoroaniline (51.6g., 85%), 99+% by gas chromatography. Distillation of 35.5g. yielded a mid-cut (29.8g.), b.p. 61°/20 mm., 99+% pure by gas chromatography. I.R. No. 3382.

10. 3,3'-DIHYDROXY-4,4'-DIAMINOHEXAFLUOROBIPHENYL

(a) Using sodium dithionite

3,3'-Dihydroxy-4,4'-dinitrohexafluorobiphenyl (9.6g., 0.025 mole) and sodium dithionite (47.5g., 85% purity, 0.15 mole) dissolved in water (200 ml.) were heated at 70-80° for 1 hour. The reaction mixture was neutralised to pH 7 by addition of sodium hydroxide and heated again at 70° for 1 hour. After cooling, the mixture was treated with 12N hydrochloric acid (50 ml.) and sodium acetate (70g.), diluted and continuously extracted with ether for 7½ hours. Evaporation of the dried extract gave a solid which, on crystallisation from water (70 ml.), gave 3,3'-dihydroxy-4,4'-diaminohexafluorobiphenyl (41g., 51%), m.p. 183-186° (decomp.).

(b) Using tin and hydrochloric acid in acetic acid

3,3'-Dihydroxy-4,4'-dinitrohexafluorobiphenyl (8.1g., 0.0211 mole), granulated tin (19.0g., 0.1264g. atom), hydrochloric acid (35-37%, 45 ml. ca. 0.45-0.55 mole), and acetic acid (45 ml.) were heated gently to 80° until all the tin had reacted. The mixture was cooled to room temperature, diluted with water (150 ml.) and neutralised by addition of 12N sodium hydroxide. The tin oxides were filtered off, washed with water, dried, and extracted in a Soxhlet apparatus with ether. The aqueous solution was continuously extracted with ether and the combined extracts were evaporated yielding 3,3'-dihydroxy-4,4'-diaminohexafluorobiphenyl (4.9g., 72%), which on crystallisation from water gave 3.6g., 53%, m.p. 182-184° (decomp.).

(c) Reduction of 3,3'-dihydroxy-4,4'-dinitrohexafluorobiphenyl on a larger scale (59.1g., 0.154 mole) using the sodium dithionite procedure gave a product (34.2g., 68.5%), m.p. 183-185° (from water). This was shown by thin layer chromatography to contain a number of impurities, in contrast to the product obtained by the tin and hydrochloric acid reduction.

The impure product (34g.) was dissolved in ether (200 ml.) and reduced by stirring with a solution of stannous chloride (12g.) in hydrochloric acid (10 ml.) for 30 minutes. After neutralisation with sodium bicarbonate (22g.), the product was isolated by evaporation of the ether solution. The product (24.8g.), m.p. 181-185° (decomp.), was shown by thin layer chromatography to contain only 3,3'-dihydroxy-4,4'-diaminohexafluorobiphenyl.

11. 3,3'-BIS(PENTAFLUOROBENZAMIDO)-4,4'-DIAMINOHEXAFLUOROBIPHENYL

(1) 3,3'-Bis(pentafluorobenzamido)-4,4'-dinitrohexafluorobiphenyl

3,3'-Diamino-4,4'-dinitrohexafluorobiphenyl (9.6g., 0.025 mole), pentafluorobenzoyl chloride (11.5g., 0.059 mole), dimethylaniline (6.1g., 0.050 mole), and benzene (40 ml.) were refluxed for 4 hours. When cool, the syrupy liquid was treated with 1N hydrochloric acid (100 ml.) and the yellow solid which separated was filtered off, washed, and dried. It weighed 11.2g., 60%, m.p. 245-147°. Recrystallisation from benzene gave 3,3'-bis(pentafluorobenzamido)-4,4'-dinitrohexafluorobiphenyl, m.p. 245-248°. I.R. No. 3422.

Anal. Calc. for $C_{26}H_2F_{10}N_4O_6$: C, 41.6; H, 0.3; F, 40.5%

Found: C, 40.5; H, 0.4; F, 39.8

In a similar preparation the product, m.p. 249-250°, was obtained in 54% yield.

(2) 3,3'-Bis(pentafluorobenzamido)-4,4'-diaminohexafluorobiphenyl

(a) By catalytic reduction

3,3'-Bis(pentafluorobenzamido)-4,4'-dinitrohexafluorobiphenyl (23.1g., 0.03 mole) in ethanol (100 ml.) was hydrogenated for 5 hours at 20°/760 mm. using Raney nickel (15g., W2 grade) as catalyst. Evaporation of the filtered solution gave a solid which was continuously extracted with benzene. Evaporation of the benzene gave a solid, m.p. 276-278°, infra-red spectrum No. 3849a.

Anal. Calc. for $C_{26}H_6F_{16}N_4O_2$: C, 43.9; H, 0.85; F, 42.8%

Found: C, 43.7; H, 1.0; F, 43.6

(b) By reduction with stannous chloride

A solution of stannous chloride dihydrate (75.4g., 0.33 mole) dissolved in 10N hydrochloric acid (183 ml.) was added in 30 minutes to a stirred suspension of 3,3'-bis(pentafluorobenzamido)-4,4'-dinitrohexafluorobiphenyl (28.5g., 0.0371 mole) in ether (580 ml.) causing a gentle reflux. Stirring was continued for 3 hours. The mixture was carefully treated with a slurry of sodium bicarbonate (310g.) in water. The tin hydroxides were filtered off, washed, dried, and continuously extracted with ether for 16 hours. The extract was combined with the ether filtrate and evaporated. Yield 16.8g., 63.5%, of solid, m.p. 268-9°, (cf. m.p. 276-278° for a sample of 3,3'-bis(pentafluorobenzamido-4,4'-diaminohexafluorobiphenyl prepared by catalytic reduction of the dinitro-precursor). The material (16.8g.) was extracted with benzene in a Soxhlet apparatus to yield 14.5g., m.p. 272-75°, showing a single spot when analysed by thin layer chromatography.

12. HEXAFLUOROBENZENE

Hexafluorobenzene (2 kg.) of 98.6% purity (the impurities being mainly hydrogen-containing compounds) was stirred with 65% oleum at reflux for 6 hours. Gas chromatographic analysis of a sample showed a purity of 99.7% and further treatment with oleum for 4 hours did not improve this. The hexafluorobenzene was separated, washed, dried and distilled yielding material (1643g., 82% recovery), b.p. 80°, of 99.7% purity.

13. PENTAFLUOROBENZENE

To a stirred mixture of zinc powder (235g., 3.6g. atom) in glacial acetic acid (2 litres) at 120° was added over 7 hours bromopentafluorobenzene (741g., 3 mole) of 99+% purity. The pentafluorobenzene formed, together with some acetic acid, was distilled from the reaction vessel through a 1 ft. helices-packed column at a vapour temperature of approx. 115°. Mid-way through the reaction more glacial acetic acid (500 ml.) was added to the mixture to maintain the volume. The distillate (approx. 1500 ml.) was diluted with water ($3\frac{1}{2}$ litres), the organic layer was separated, water washed (4 x 250 ml.) and dried ($CaCl_2$), yielding crude pentafluorobenzene (469g.). Distillation of this product through a 1 ft. helices-packed column gave pentafluorobenzene (419.1g., 83%), b.p. 85-86°, 99+% pure by gas chromatography.

14. PENTAFLUOROPHENOL

t-Butanol (1300 ml.) and 99.7% pure hexafluorobenzene (930g., 5.0 moles) were stirred and heated to reflux. Heating was discontinued while flake potassium hydroxide (644g., 11.3 mole) was added in portions over 2 hours at a rate sufficient to maintain reflux. The solution was then stirred without heating for a further $1\frac{1}{2}$ hours. Water (1500 ml.) was added and the mixture distilled to remove the t-butanol. Steam distillation of the residual liquid gave an organic distillate (233g.), containing t-butoxypentafluorobenzene (70%) and hexafluorobenzene (25%), which was treated with gaseous hydrogen chloride. The liberated pentafluorophenol was combined with the residue from the steam distillation and acidified with a solution of anhydrous calcium chloride (280g., 2.5 mole) in 6N hydrochloric acid (1200 ml.). Exhaustive steam distillation of the mixture yielded pentafluorophenol. It was extracted with methylene chloride (4 x 100 ml.), the extract dried and the solvent distilled off. The residue was finally dried by azeotropic distillation of the water with benzene. Fractionation of the residue gave a main cut (521.5g., 57%), b.p. 145-146°, 99.7% pure pentafluorophenol by gas chromatography.

15. TETRAFLUORORESORCINOL

a. Preparation from commercial pentafluorophenol

Pentafluorophenol (185g., 1.0 mole) was heated with potassium hydroxide (200g., 3.04 mole) in water (500 ml.) at 150° for 5 hours in an autoclave. The contents were poured into water (250 ml.) then acidified with 5.75N hydrochloric acid (1 litre). Extraction with methylene chloride (5 x 200 ml.) and distillation of the dried extracts gave, from the three runs, pentafluorophenol (274.0g.) of 99+% purity. The aqueous solution remaining was continuously ether extracted (12 hours). The combined extracts from this and two identical experiments were distilled yielding, after removal of the ether, (i) b.p. 114°/15 mm., (34.5g.) containing by gas chromatographic analysis 38.6% pentafluorophenol and 55.9% tetrafluororesorcinol, and (ii) b.p. 114°/15 mm., (116g.) containing 97.2% tetrafluororesorcinol. The second fraction was refluxed with dry benzene (450 ml.) and 50 ml. benzene were distilled off. Tetrafluororesorcinol (103g.) was filtered from the cooled solution in a nitrogen atmosphere.

However, gas chromatographic analysis of the product using a newly-available apiezon on celite column revealed the presence of 6-7% of an unidentified material with a retention time slightly shorter than tetrafluororesorcinol.

b. Preparation from very pure pentafluorophenol

(a) Pentafluorophenol (185g., 1.0 mole, purity 99.7%), and a solution of potassium hydroxide (201g., 3.0 mole) in water (500 ml.) were heated at 150° for 5 hours in a rocking 1 litre autoclave. The mixture was acidified with 6N hydrochloric acid (1 litre), extracted with methylene chloride (5 x 200 ml.) to remove unreacted pentafluorophenol (86.15g.), and the residual aqueous solution was ether extracted (4 x 200 ml.). The ether extracts were dried ($CaCl_2$) and fractionated after removal of the ether to give: (i) (19.5g.), b.p. 30-113°/15 mm., (ii) (35.0g.), b.p. 113-114°/15 mm., (iii) and residue (6.0g.). Gas chromatography on an apiezon grease column at 200° showed (ii) contained tetrafluororesorcinol (85.3%) and an impurity (11.0%) with a retention time just less than that of tetrafluororesorcinol itself. Under these same conditions tetrafluorohydroquinone does not separate from tetrafluororesorcinol and tetrafluorocatechol is not eluted, apparently decomposing on the column. Two recrystallisations of the second fraction from benzene yielded a solid (28.5g.), m.p. 96.5-98.5° (sealed tube), which, by gas chromatography, now apparently contained 13.2% of the impurity. Infra-red spectra of this material (I.R. Nos. 3823, 3837) showed the absence of tetrafluorocatechol and the absence of an absorption attributable to an aromatic C-H group, although some hydrogen-containing material had been detected in tetrafluororesorcinol previously prepared from less pure pentafluorophenol. Thin layer chromatography on silica gel using a 9:1 chloroform-acetic acid solvent (capable of separating a mixture of the three dihydroxytetrafluorobenzenes) confirmed that both tetrafluorocatechol and tetrafluorohydroquinone were absent, a single spot only being obtained.

Anal. Calc. for $C_6H_2F_4O_2$: C, 39.6; H, 1.1; F, 41.7%

Found: C, 39.6; H, 1.4; F, 41.2

Treatment of this tetrafluororesorcinol (4.46g.) with acetic anhydride (37g.) and freshly fused sodium acetate (2g.) at 100° for 3½ hours yielded, on pouring into water (100 ml.), the diacetate (5.87g., 90%), m.p. 47-48°, showing only a single spot by thin layer chromatography. Recrystallisation of 4.0g. from aqueous ethanol yielded an analytical sample (3.02g.), m.p. 47-48°.

Anal. Calc. for $C_{10}H_6F_4O_4$: C, 45.1; H, 2.3; F, 28.6%

Found: C, 45.1; H, 2.3; F, 28.6

Acid hydrolysis of the purified diacetate (2.99g.) yielded, after working up, tetrafluororesorcinol (1.18g.), m.p. 94-96°, having an infra-red spectrum (No. 3921) which showed it to be only marginally more pure than tetrafluororesorcinol made from 99.7% pure pentafluorophenol.

(b) In two identical experiments a total of 370g. (2 moles) of 99+% pure pentafluorophenol was heated with potassium hydroxide (402g., 6.06 mole) in water (1 litre) at 150° for 5 hours as described above. After the usual work-up there was obtained unreacted pentafluorophenol (182.2g.) and tetrafluororesorcinol (61g., 35%), m.p. 94.5-96.5°, having the correct infra-red spectra.

16. TETRAFLUOROCATECHOL

Tetrafluoro-2,3-dihydrobenzo-1,4-dioxin (30.0g., 0.14 mole) was treated with aluminium chloride (120g.) in refluxing benzene for 6 hours to yield crude tetrafluorocatechol (21.5g.), m.p. 52-57°. Sublimation at 50-80°/1 mm. yielded 16.8g., (66%) m.p. 57-62° (sealed tube), I.R. Spectrum No. 3670a. Burdon et al. cited m.p. 67.5-69° (ref. 7). The material gave a single spot on thin layer chromatography using a silica gel support and 9:1 chloroform-acetic acid solvent, but it did not give a gas chromatographic peak on apiezon grease at 200°. At 150°, using a short silicone oil column, a peak was obtained but 'tailing' was excessive. The material gave a blue-green colour with ferric chloride solution.

17. 4,4'-DIHYDROXYOCTAFLUOROBIPHENYL

Decafluorobiphenyl (226g., 0.67 mole) was added to potassium hydroxide (200g., 3.0 mole) in t-butanol (2 l.) at 50° and the mixture stirred at reflux for 3.5 hours. Addition of water (2.5 litres), removal of the t-butanol under reduced pressure, and acidification with concentrated hydrochloric acid (200 ml.) gave a white solid which was filtered off and dried (258g.). This material was stirred with ether (3 x 60 ml.) leaving an insoluble polymeric material (29g.). The ether solution was evaporated to give a viscous paste. Filtration under suction gave a white solid (118.2g.) and a viscous, yellow filtrate which later solidified (84g.). The white solid was recrystallised from benzene and toluene giving 4,4'-dihydroxyoctafluorobiphenyl (31.2g. 14%), m.p. 212-214°.

18. 4,4'-BIS(2,3,5,6-TETRAFLUOROPHENYLTHIO)OCTAFLUOROBIPHENYL

(1) Cuprous 2,3,5,6-tetrafluorothiophenate

Cuprous oxide (16.5g., 0.115 mole) in boiling absolute ethanol (450 ml.) was stirred with 99+% purity 2,3,5,6-tetrafluorothiophenol (42g., 0.23 mole) for 4 hours. The precipitated cuprous salt was filtered off. Yield 52.2g. (93%).

(2) Reaction of cuprous 2,3,5,6-tetrafluorothiophenate with 4,4'-dibromo-octafluorobiphenyl

4,4'-Dibromo-octafluorobiphenyl (44.2g., 0.097 mole), cuprous 2,3,5,6-tetrafluorothiophenate (55.2g., 0.226 mole) and dimethylformamide (250 ml.) were stirred and heated at reflux under nitrogen for 6 hours. The brownish precipitate was filtered off and the green filtrate was poured into water (1.5 litres). The precipitated product was filtered off, dried in vacuo over phosphoric oxide and then exhaustively ether extracted. Evaporation of the dried extracts yielded an off-white solid (60g., 94%), m.p. 83-93°, which was recrystallised from ethanol to give

47.3g., m.p. 90-96°. A further recrystallisation from ethanol yielded 13.5g., m.p. 92-105°+. Evaporation of the mother liquors yielded 28.5g., m.p. 89-96°. This latter material was not purified further by recrystallisation from ethanol but a sample (4.8g.), when recrystallised twice from n-butanol, yielded 1.83g., m.p. 84.5-88.5°. I.R. No. 4022. The material gave a single spot when analysed by thin layer chromatography.

Anal. Calc. for $C_{24}H_2F_{16}S_2$: C, 43.8; H, 0.31; F, 46.2%

Found: C, 43.8; H, 0.35; F, 46.3

19. PENTAFLUOROTHIOPHENOL

Sodium hydrogen sulphide was prepared by passing hydrogen sulphide into a stirred mixture of sodium hydroxide (160g., 4.0 mole) in ethylene glycol at 90-100° for 2 hours.

To this solution at 85° was added hexafluorobenzene (224g., 1.2 mole) in dimethylformamide (240 ml.) over 1 hour. When addition was complete the mixture was refluxed for a further 30 minutes, cooled and acidified with a solution of anhydrous calcium chloride (70g., 0.64 mole) in concentrated hydrochloric acid (450 ml., 5.4 mole). Steam distillation of this mixture yielded the crude product which was water washed (2 x 200 ml.), dried ($MgSO_4$), and distilled to give a main fraction (142.5g., 60%), b.p. 146°, of 99+% pure pentafluorothiophenol.

20. 2,3,5,6-TETRAFLUOROTHIOPHENOL

Hydrogen sulphide was passed for 1¼ hours into a stirred mixture of sodium hydroxide (66.6g., 1.66 mole) and ethylene glycol (210 ml.) at 90-110°. The clear green solution obtained was stirred at 85° while a solution of 99+% pentafluorobenzene (84.0g., 0.5 mole) in dimethylformamide (100 ml.) was added over 50 minutes. The mixture was refluxed for a further 1 hour then allowed to cool. A solution of anhydrous calcium chloride (40g., 0.36 mole) in concentrated hydrochloric acid (167 ml., 2.0 mole) was added carefully to the stirred mixture, the temperature being kept between 10° and 20°. Steam distillation of the mixture yielded organic material which was separated, water washed (2 x 50 ml.) and dried ($MgSO_4$). Distillation of this material (69g.) yielded 2,3,5,6-tetrafluorothiophenol (64.7g., 72%), b.p. 152-154°, 99+% pure by gas chromatography.

21. TETRAFLUOROBENZENE-1,4-DITHIOL

a. By attempted demethylation of 1,4-bis(methylthio)-tetrafluorobenzene

(1) With sodium hydroxide

After treatment of the dithioether (5.27g.) with 15 ml. 0.089N sodium hydroxide at reflux for 30.5 hours only starting material (5.05g.) was recovered.

(2) With anhydrous aluminium chloride

Treatment of the dithioether (12.11g.) with aluminium chloride at 120-130° for 2 hours yielded a product (6.21g.), insoluble in alkali, which showed no significant -SH absorption in its infra-red spectrum.

(3) With hydrazine hydrate

Treatment of the dithioether (6.05g.) in ethanol at reflux with hydrazine hydrate for 5 hours yielded 1.3g. of alkali-soluble product which was shown to be a complex mixture by gas chromatography.

b. By reaction of sodium thiolacetate with hexafluorobenzene

(1) Sodium thiolacetate

Dry methanol (55 ml.) was added over $1\frac{1}{4}$ hours to sodium (5.75g., 0.25 mole) under nitrogen. The solution was boiled under reflux for 45 minutes and allowed to cool. Thiolacetic acid (23.6g., 0.31 mole) was then added over 20 minutes, an exothermic reaction occurring to give a light brown solution.

(2) Sodium thiolacetate and hexafluorobenzene

Hexafluorobenzene (18.6g., 0.1 mole) was added to the sodium thiolacetate solution prepared in (i) but no heat was evolved. The solution was then refluxed for 20 hours, an appreciable amount of sodium fluoride being precipitated, and then poured into water (400 ml.). A small amount (0.5g.) of precipitate was thrown down and this was filtered off. The solution was made alkaline with 10% sodium hydroxide solution and then ether extracted (1 x 150, 3 x 100 ml.). Evaporation of the dried extracts yielded only a small residue (0.5g.). Acidification of the alkaline solution with 8N hydrochloric acid (60 ml.) yielded a black oil which was extracted with ether (4 x 75 ml.).

Evaporation of the dried extracts yielded a liquid residue (6.42g.), and a yellow solid (0.4g.). The liquid residue had a strong thiol smell and was shown by gas chromatography to be 69% pentafluorothiophenol. No tetrafluorobenzene-1,4-dithiol was present. An infra-red spectrum confirmed the presence of pentafluorothiophenol and also showed that C = 0 and possibly -OH groups were present, presumably from unhydrolysed thiolacetate or acetic acid.

c. By reaction of 1,4-dilithiotetrafluorobenzene with sulphur

(1) 2,3,5,6-Tetrafluorothiophenol

To a stirred solution of commercial n-butyl lithium (10.5g., 0.16 mole) in dry pentane (300 ml.) and tetrahydrofuran (500 ml.) at -64° to -60° was added over 10 minutes a solution of 1,2,4,5-tetrafluorobenzene (12.75g., 0.085 mole) in tetrahydrofuran (20 ml.). The solution was then stirred at approximately -60° for a further 25 minutes and cooled to -70° while sublimed sulphur (5.55g., 0.19g. atom) was added portion-wise over 15 minutes. The deep yellow solution was allowed to warm to room temperature in 1.5 hours, becoming dark brown. It was acidified with 6N hydrochloric acid (300 ml.). After removal of the acid layer under nitrogen the remaining organic layer was water washed (3 x 100 ml.) and extracted with 5% sodium hydroxide solution (280 ml.). Acidification of the deep brown extracts with 6N hydrochloric acid gave a black oil which was separated and dried. Yield: 21.0g. Gas chromatographic and infra-red analysis showed that the product consisted of an unidentified low-boiling material (50.5%) and 2,3,5,6-tetrafluorothiophenol (49.3%).

(2) Tetrafluorobenzene-1,4-dithiol

To a stirred solution of freshly prepared n-butyl lithium (28.2g., 0.44 mole) in pentane (180 ml.) and tetrahydrofuran (400 ml.) at -70° was added over 30 minutes 1,2,4,5-tetrafluorobenzene (24.8g., 0.17 mole) in tetrahydrofuran (40 ml.). After the addition was complete the solution was stirred for 1 hour at -60° to -55° to ensure complete metalation and was kept at -70° while sublimed sulphur (11.0g., 0.34g. atom) was added portion-wise over 45 minutes. The deep yellow solution was stirred a further 30 minutes at -70°, allowed to warm to room temperature and acidified with 6N hydrochloric acid (500 ml.). After removal of the acid layer under nitrogen, the remaining organic layer was water washed (2 x 50 ml.) and extracted with 5% sodium hydroxide solution (2 x 225 ml.). Acidification of the deep brown extracts with 6N hydrochloric acid (120 ml.) yielded an oily emulsion which was ether extracted (3 x 100 ml.).

Removal of the ether gave a brown residue (31.43g.). Sublimation of this at 80-110°/0.5 mm. gave yellow crystals (12.40g.) and deeper yellow material (3.39g.) at a higher bath temperature, 100-140°/0.2-0.3 mm. A black residue remained (8.80g.). Recrystallisation of the first sublimate from aqueous ethanol gave pale yellow crystals (10.25g.), m.p. 64-70° which by further sublimation at 50-55°/0.2 mm. yielded very pale yellow crystals of tetrafluorobenzene-1,4-dithiol (8.90g., 24%), m.p. 70-72°, 99+% pure by gas chromatography.

<u>Anal</u>. Calc. for $C_6H_2F_4S_2$: C, 33.6; H, 0.9; F, 35.5%

Found: C, 33.7; H, 0.9; F, 35.4

An infra-red spectrum (No. 3472) showed the presence of a strong -SH absorption at 2590 cm^{-1}.

Treatment of the dithiol (2.0g.) in ether (10 ml.) at 0° with diazomethane (1.0g.) in ether (45 ml.) yielded, after evaporation of the solvent, white crystals of bis-1,4-methylthiotetrafluorobenzene (2.3g., 100%), m.p. 90-91.5°, undepressed in admixture with the same thioether prepared by the action of cuprous thiomethylate on 1,4-dibromotetrafluorobenzene (ref. 1) and having an identical infra-red spectrum.

6/MWB/SAC
4.1.66

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PART II

MODEL COMPOUNDS AND POLYMERS

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A. INTRODUCTION

Large organic molecules generally undergo thermal breakdown because some facile mode of decomposition is possible, as for example "unzipping" or β-elimination. Where no such ready pathway exists, the thermal or oxidative stability of the weakest bond in the molecule determines the upper operating temperature of the material. Previous work has shown that this point of weakness is often the C-H bond, whether this be aliphatic or aromatic, and that its replacement by a C-F bond may lead to some improvement in stability. The knowledge in this field is being extended by the preparation of aromatic polymeric materials in which all C-H bonds are replaced by C-F bonds. Very few perfluorinated aromatic polymers have been prepared.

The aim of this part of the programme is to determine if fully fluorinated aromatic polymers offer any improvement in thermal or oxidative stability over their hydrogenic analogues. Preliminary work requires the preparation of fully fluorinated aromatic model compounds and their hydrogenic analogues, for comparison of the thermal decomposition temperatures in the two series of compounds. Where the thermal stability justifies it the perfluorinated structures will be incorporated into polymers. Comparisons of thermal and oxidative stability will be made with the analogous hydrogenic polymers.

B. SUMMARY AND CONCLUSIONS

Model Compounds

1. Fully and partly fluorinated bibenzoxazoles have thermal decomposition temperatures lower than the hydrogenic analogue, but sufficiently high for fluoro-polybenzoxazoles to be investigated.

2. Studies in the dehydrofluorination of perfluoro secondary amides to benzoxazoles are in progress.

3. The thermal decomposition temperatures of perfluoro sulphonates were lower than those of the hydrogenic analogues, which were themselves low.

4. The thermal decomposition temperature of a perfluorodithiocarbonate was marginally higher than that of its hydrogenic analogue.

5. Replacement of NH by NC_6F_5 in a secondary amide, therefore giving a tertiary amide, very greatly improves the thermal stability.

6. Aromatic CH in polyfluoro compounds does not greatly lower the thermal decomposition temperature relative to the perfluoro compound, in the examples examined.

7. Very low levels of hydrogenic impurity are present in the perfluoro models that have been examined by mass spectrometry.

Polymers

1. A polyimide from pyromellitic dianhydride and tetrafluoro-m-phenylene diamine had thermo-oxidative stability slightly lower than the analogous hydrogenic polyimide of much higher molecular weight (as measured by TGA).

2. It is difficult to prepare polyamic acids of high molecular weight, probably because of the weakly nucleophilic character of perfluoro diamines.

3. Perfluoro polybenzoxazoles are not obtained from a perfluoro di-acid and a 3,3'-dihydroxy-hexafluorobenzidine in polyphosphoric acid but should be preparable by other routes.

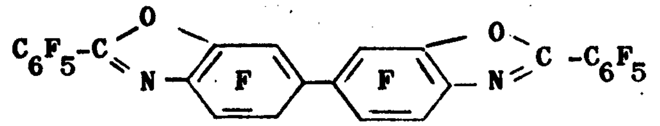
4. Polyhydrazides of the perfluoro series do not appear to yield perfluoro polyoxadiazoles by thermal cyclodehydration. Instead there is thermal decomposition. Hence it is necessary to re-examine the preparation of perfluoro polyoxadiazoles.

5. The preparation of higher molecular weight perfluoro polycarbonate from tetrafluororesorcinol is under investigation, prior to evaluation for thermo-oxidative stability.

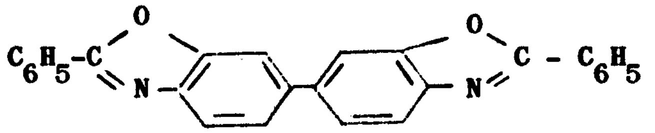
C. DISCUSSION

1. THE SYNTHESES OF MODEL COMPOUNDS AND INTERMEDIATES FOR POLYMERS.

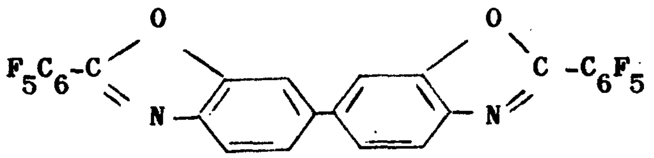
Benzoxazoles

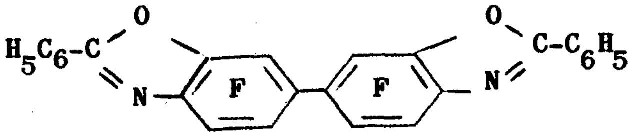


(I)



(II)


(III)


(IV)

It was required to synthesise 2,2'-di(pentafluorophenyl)-4,4'-5,5',7,7'-hexafluoro-6,6'-bibenzoxazole (I) so that it could be compared with the hydrogenic analogue (II) for thermal stability. Whilst the latter compound was readily prepared by described methods (a) from 3,3'-dihydroxybenzidine and benzoyl chloride at 250° (ref.1), and (b) by the condensation of 3,3'-dihydroxybenzidine with benzoic acid and in polyphosphoric acid (ref.2), neither of these methods gave the perfluoro bibenzoxazole (I). By the first method several compounds were obtained from experiments under slightly different conditions, and it has been shown that two of these compounds are intermediates from which (I) may be obtained. The second method, i.e. the reaction of 3,3'-dihydroxy-2,2',5,5',6,6'-hexafluorobenzidine with pentafluorobenzoic acid in polyphosphoric acid, failed to yield any condensation products.

The two samples of 3,3'-dihydroxy-2,2',5,5',6,6'-hexafluorobenzidine, received from Imperial Smelting Corporation, (i) m.p. 191-2° (ref.3), and (ii) m.p. 181-5°(decomp.) were treated with pentafluorobenzoyl chloride. Sample (i) treated with the acid chloride at 230° for nine hours afforded a compound (V), m.p. 274-275.5°, but at 230° for five hours afforded a compound (VI), m.p. 99 - 102°. Neither of these compounds could be characterised by the usual techniques of elemental analysis, molecular weight determination (osmometer) infra-red, or N.M.R. (proton) examination. The infra-red spectrum indicated the presence of carbonyl but not NH. The latter group was not indicated by N.M.R. spectroscopy. Sample (ii) treated with the acid chloride at 230° for five hours followed by 250° for five hours yielded (V) and another compound (VII), m.p. 329 - 330° (decomp.). Although the analysis for fluorine was unsatisfactory, the elemental analysis suggests that (VII) is an N- or O-bispentafluorophenyl derivative. Due to the low solubility of (VII) the molecular weight could not be determined, and the N.M.R. spectrum could not be obtained. There was no absorbtion due to NH in a mull or a disc of this compound.

Sample (i) was treated with pentafluorobenzoyl chloride in ethereal N,N-diethylaniline to yield (VIII)m.p. 298 - 300° which is probably a dipentafluorobenzoyl derivative of perfluoro 3,3'-dihydroxybenzidine.

Sample (ii) was treated with pentafluorobenzoyl chloride in ethereal N,N-diethylaniline to yield (VII) and a compound (IX), m.p.224 - 5° (decomp.).

It was found that (VII) dissolved readily in cold dilute sodium hydroxide, whilst (V) also dissolved, but slowly and on standing. When the latter solution was acidified (VII) was precipitated. The two compounds (V) and (VII) yielded the perfluoro bibenzoxazole (I) when they were heated at 350° for a few minutes. In this manner (V) afforded (I) in 30% yield [on the assumption that (V) is a bispentafluorobenzoyl derivative of the dihydroxyhexafluorobenzidine], but the yield from (VII) was very small. However, it was not possible to cyclodehydrate (VII) by means of polyphosphoric acid, even though a dibenzoyl derivative of 3,3'-dihydroxybenzidine yields (II) under the same experimental conditions.

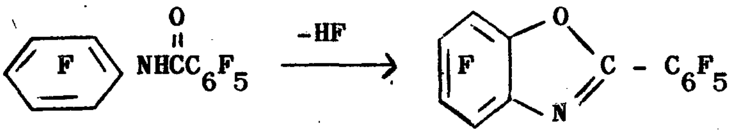
Before it was discovered that (I) could be obtained by the pyrolysis of (V) or (VII) an attempt was made to synthesise the bibenzoxazole (III). 3,3'-Dihydroxybenzidine and pentafluorobenzoic acid were heated in polyphosphoric acid at 120° during ten hours, but no reaction product could be isolated. By heating 3,3'-dihydroxybenzidine with pentafluorobenzoyl chloride there was obtained a compound (X), m.p. 289 - 291°, in high yield, having carbonyl and NH absorbtion in the infra-red. The elemental analysis suggests a formula approximating to a trispentafluorobenzoyl compound. Under milder conditions, in ethereal N,N-diethylaniline, the same reagents yielded another compound (XI), m.p. 305° (decomp.).

The compound (X) was treated under conditions that have been shown to cyclodehydrate the dibenzoyl derivative of 3,3'-dihydroxybenzidine to the bibenzoxazole (II): that is to say (X) was treated with polyphosphoric acid, and with thionyl chloride. Concentrated sulphuric acid, and phosphorus pentoxide were also employed in other experiments. However, little or no reaction occurred with each of these dehydrating agents except concentrated sulphuric acid. With this reagent a product of m.p. >400° was obtained in very low yield, and with the other reagents (X) was recovered unchanged. The higher melting compound (XI) was treated with polyphosphoric acid at 200° during fifteen hours, but no reaction was observed. However, when (X) was heated alone at 340 - 360° for three minutes water and a sublimate was evolved, and a compound of m.p. 230 - 2° was obtained in 30% yield by recrystallisation of the product from benzene. A less pure sample of the same compound was obtained in low yield by heating (XI), but with the accompaniment of charring. The infra-red spectrum and the elemental analysis are not inconsistent with this being the required bibenzoxazole (III).

An attempt to prepare 2,2'-diphenyl-4,4',5,5',7,7'-hexafluoro-6,6'-bibenzoxazole (IV) from perfluoro 3,3'-dihydroxybenzidine and benzoyl chloride at 200° gave a product from which only a trace of pure compound could be isolated. The elemental analysis approximated to that for the required compound.

To summarise the above observations it may be said that bibenzoxazoles are not readily prepared from perfluoro intermediates. Whilst the condensation of reagents gives 2,2'-diphenyl-6,6'-bibenzoxazole (II) readily, it is necessary to isolate and pyrolyse a suitable intermediate condensate in order to obtain (I) or (III). A number of intermediate condensates were obtained, which are poly(pentafluorobenzoyl) derivatives of 3,3'-dihydroxybenzidine, or of its perfluoro analogue. The characterisation of all of these intermediates was complicated by low solubilities and by unreproducible elemental analyses. However, a similarly insoluble benzoyl derivative of 3,3'-dihydroxybenzidine has also been shown to yield (II). The evidence for the structures (I) and (III) rest on this analogy, satisfactory elemental analyses, and infra-red spectra that are not inconsistent with structures (I) and (III). The molecular weights of the compounds will be determined to confirm the structures.

Another approach to a fully fluorinated benzoxazole has been examined. This was the attempted dehydrofluorination of decafluorobenzanilide to 2-pentafluorophenyl-4,5,6,7-tetrafluorobenzoxazole (XII) by heat or by means of basic reagents. Heating decafluorobenzanilide alone or in polyphosphoric acid yielded no pure compound, apart from unchanged starting material. From reactions at 100° with an excess of pyridine, or N,N-diethylaniline, impure starting material was recovered. A similar reaction with hexamethylphophoramide gave a product of lower melting point than the starting material. This lower melting product could not be purified by recrystallisation or by adsorption chromatography.



(XII)

Sulphonates

1,3-Di(phenylsulphonyloxy)benzene, 1,4-di(phenylsulphonyloxy)benzene, 4,4'-di(phenylsulphonyloxy)bipehnyl, and their perfluorinated analogues have been prepared.

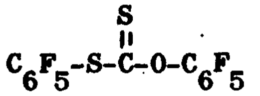
The hydrogenic sulphonates were obtained by reaction of the dihydric phenol with benzene sulphonyl chloride in aqueous sodium hydroxide, at room temperature. The perfluorinated analogues were prepared from the perfluorinated dihydric phenol and pentafluorobenzene sulphonyl chloride in benzene containing N,N-diethylaniline, at room temperature. Whilst elemental analyses were in some cases not satisfactory for sulphur or fluorine, the molecular weights were in agreement with the calculated values.

Esters of Dithiocarbonic acid

It has been found that m-phenylene biscarbonate has a lower T_D than the perfluorinated analogue, but no further comparisons could be obtained in the carbonate series using readily available intermediates (ref.4). Therefore it was proposed to examine the preparation of a number of di- and tri- thiocarbonates.

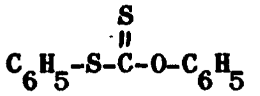
Potassium pentafluorophenyl xanthate (C_6F_5OCSSK) was required as an intermediate in the preparation of (XIII); but from the reaction of pentafluorophenol, carbon disulphide, and potassium hydroxide in ethanol no pure compound was isolated. The orange product was apparently contaminated with a large amount of potassium hydroxide, and it did not yield the expected p-nitrobenzyl ester when characterisation was attempted through a reaction with p-nitrobenzyl bromide in ethanol.

For an alternative approach to (XIII) pentafluorophenyl dithiochloroformate (C_6F_5SCSCl) was prepared by the reaction of thiophosgene with the potassium salt of pentafluorothiophenol. Phenyl dithiochloroformate was obtained in a similar way. The two dithiochloroformates were treated with the potassium salt of the appropriate mono- or di-hydric phenol to yield the following compounds.



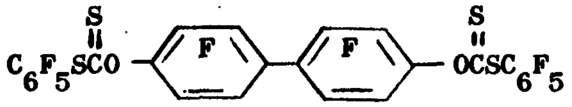
$C_6F_5\text{-S-}\overset{\overset{S}{\|}}{C}\text{-O-}C_6F_5$

(XIII)

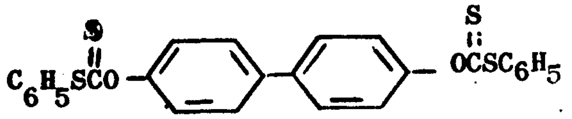


$C_6H_5\text{-S-}\overset{\overset{S}{\|}}{C}\text{-O-}C_6H_5$

(XIV)



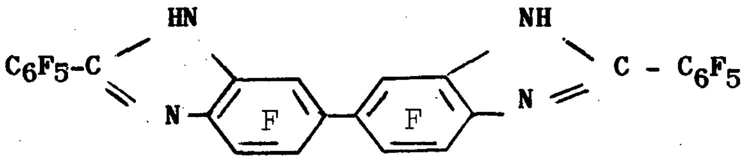
(XV)



(XVI)

Compounds (XIII) and (XIV) were prepared to show the feasibility of the reactions but were too low boiling for T_D determinations. The dithiocarbonates (XV) and (XVI) had very low thermal decomposition temperatures, and therefore it is not proposed to carry out further work in this series.

Benzimidazoles



(XVII)

Earlier attempts (ref.8) have been made to prepare the bibenzimidazole (XVII) by the reaction of 3,3'-diamino-2,2',5,5',6,6'-hexafluorobenzidine with pentafluorobenzoic acid in polyphosphoric acid, with phenyl pentafluorobenzoate, or via an uncharacterised pentafluorobenzoyl derivative.

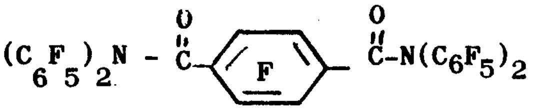
3,3'-Di(pentafluorobenzamid)-2,2',5,5',6,6'-hexafluorobenzidine has now been received from I.S.C., but attempts to cyclohydrate this intermediate by means of thionyl chloride, phosphorus pentoxide, polyphosphoric acid, concentrated sulphuric acid, or by pyrolysis, have been unsuccessful.

m-(Tetrafluorophenylene) bischloroformate

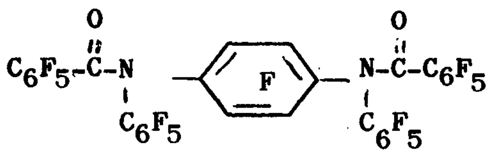
Tetrafluororesorcinol (99 + % purity) was treated with an excess of phosgene in anhydrous ether containing N,N-diethylaniline. Removal of the base hydrochloride and the volatiles yielded an oil, which on distillation under reduced pressure gave a mixture of the required bischloroformate and tetrafluororesorcinol.

Bis(tertiary amides)

The N-lithio derivative of decafluorodiphenylamine has been shown to react with tetrafluoroterephthaloyl chloride to yield (XVIII) (ref.9). It has now been found that the N-potassium derivative in ethereal solution at room temperature may replace the N-lithio compound in the above reaction. The pale yellow N-potassium compound is readily obtained from a solution of the secondary amine in ethanolic potassium hydroxide.



(XVIII)

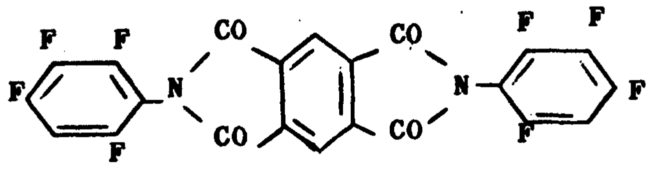


(XIX)

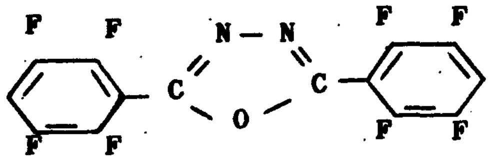
It was required to prepare the isomer (XIX) of (XVIII) as a model compound more directly relevant to a subsequent polymer preparation. A dark green material was obtained from the solution of 1,4-di(pentafluoroanilino)-2,3,5,6-tetrafluorobenzene in ethanolic potassium hydroxide. An ethereal solution of this material was treated with pentafluorobenzoyl chloride, to yield a red solution which contained unchanged acid chloride after standing overnight, and after a subsequent $5\frac{1}{2}$ hour under reflux. The reaction product yielded a small amount of starting diamine as the only pure isolable compound.

When the diamine was treated with sodium hydride in ether, followed by pentafluorobenzoyl chloride, a compound was obtained which is believed to be the required bis(tertiary amide) (XIX). The elemental analysis is not very satisfactory, and confirmation of structure is required by further analysis and molecular weight determination.

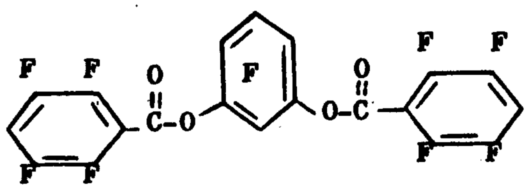
Polyfluoro model compounds containing nuclear hydrogen



(XX)



(XXI)

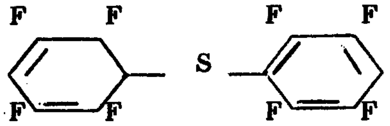


(XXII)

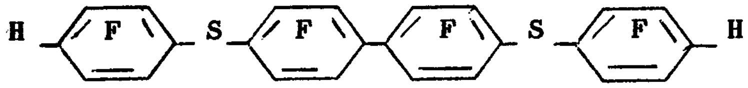
The compounds (XX- XXII) were synthesised by the standard methods that have already been employed for their analogues (refs.10 and 11). They were required (a) to determine the effect on thermal stability of nuclearly bound H in polyfluoro structures, (b) to provide standards containing H for mass spectrometric investigation of residual H in perfluoro model compounds already prepared. It is to be noted that compound (XXII) had an incorrect molecular weight : see Table 1, note (iii).

Residual Hydrogen in Perfluoro Model Compounds

In addition to the polyfluoro compounds (XX - XXII), the compounds (XXIII) and (XXIV) have been provided by Imperial Smelting Corporation. These were submitted as standards along with a number of perfluoro compounds, to Dr.R.I.Reed of Glasgow University for mass spectrometric analysis for traces of hydrogen.



(XXIII)

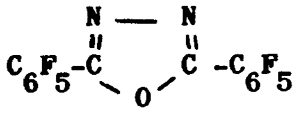
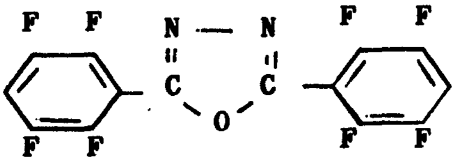
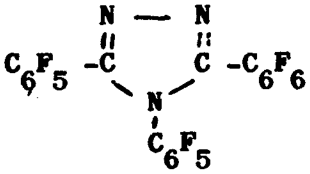
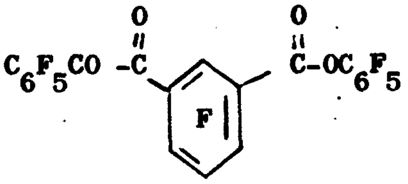
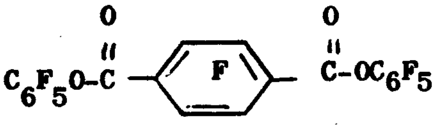
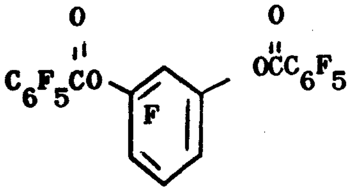


(XXIV)

The results obtained so far are shown in Table 1, together with the T_D values. The method of analysis enabled a quantity of hydrogen as low as 0.02% to be detected. A dash in Table 1 indicates that the compound was free from hydrogenic impurity down to this level; an asterisk indicates that there was a trace only, above the 0.02% level. Notes to the Table indicate the possibility of H in two other compounds at about the 0.02% level.

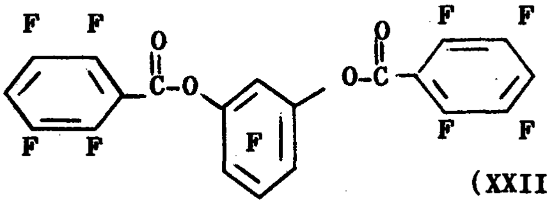
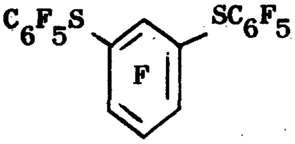
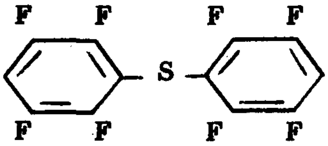
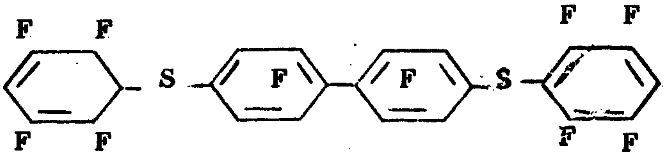
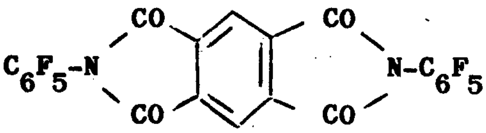
The T_D value is somewhat lowered by substitution of H for F in the compounds examined. Hence the indications are that there would have to be an appreciable amount of such polyfluoro compound present as impurity in order to depress the T_D of the analogous perfluoro compound. Such an amount would easily be shown by the mass spectrometric analysis, and probably also by a curve in place of the straight line obtained in the plot of the log dp/dt against T^{-1}. Therefore it seems unlikely that the T_D values hitherto obtained for fluoro model compounds prepared in this programme are artificially lowered by the presence of hydrogenic impurities.

TABLE I.

	H-impurity	T_D
	-	327°C
 (XXI)	Note (i)	313°C
	Note (i)	305°C
	-	300°C
	-	318 - 314°C
	*	304°C

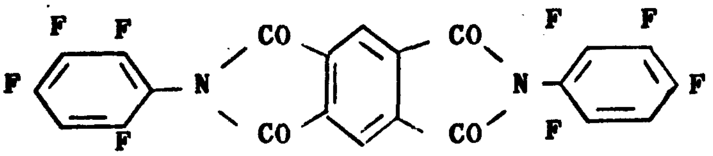
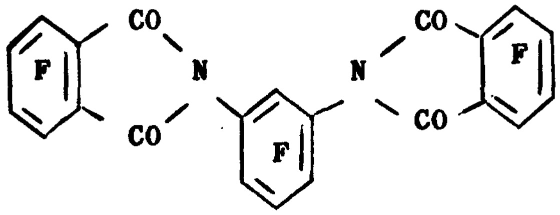
(continued)

TABLE 1. (continued)

	H-impurity	**T_D**
 (XXII)	Note (iii)	Not available
	-	324°C
	Note (ii)	328°C
 (XXIII)	-	(b.p. too low for T_D determination)
 (XXIV)	Not determined	349°C
	-	418°C

(continued)

TABLE 1. (continued)

	H-impurity	T_D
 (XX)	Note (ii)	396°C
	*	318°C

Notes to Table I

(i) The mass spectrum could not be interpreted sufficiently well enough to determine if there was H as impurity.

(ii) If H-impurity is present, it is in very small amount.

(iii) Massspectrometry indicates M.W. 592 (Calc. M.W. 534)

2. POLYMER SYNTHESES AND THERMO-OXIDATIVE STABILITY

Polybenzoxazoles

Poly(2,2'-m-phenylene-6,6'-bibenzoxazole) was prepared in polyphosphoric acid from isophthalic acid and 3,3'-dihydroxybenzidine or 3,3'-dihydroxybenzidine dihydrochloride as described in the literature (ref.2). The two methods gave polymer of inherent viscosity 0.07 and 0.28 dl/g., respectively.

The perfluoro dihydrochloride was employed in an attempt to prepare a polybenzoxazole from tetrafluoroisophthalic or tetrafluoroterephthalic acid, again in polyphosphoric acid. No polymer was obtained, the reaction products being soluble in sodium bicarbonate or methanol.

Polycarbonates

Previous preparations of polycarbonates from phosgene and dihydric phenols, by the interfacial condensation method, gave polymers of low inherent viscosities. An attempt to prepare the bischloroformate of 4,4'-dihydroxyoctafluorobiphenyl yielded polymeric material.

As a consequence of the above results (ref.11), other attempts have been made to obtain polycarbonates of higher inherent viscosities. Hydrogenic polycarbonates were synthesised with the intention of applying the most suitable methods to the preparation of perfluorinated polycarbonates.

Poly(m-phenylene carbonate)

(a) A mixture of m-phenylene bischloroformate and resorcinol was heated at 200° for 6 hr. The polymer had an inherent viscosity 0.18 dl/g. in N,N-dimethylacetamide.

(b) Resorcinol in sodium hydroxide solution was treated with m-phenylene bischloroformate in tetrachloroethane by the interfacial condensation method, to yield polycarbonate of inherent viscosity 0.17 dl/g. in N,N-dimethylacetamide or 0.19 dl/g. in dimethylsulphoxide.

Heating this polymer at 250°/0.3mm. gave a hard rubbery material of lower inherent viscosity (0.06 dl/g.). The solution for the viscosity determination had to be made up hot owing to poor solubility. It is possible that heating in the dimethyl sulphoxide degraded the polymer.

(c) Resorcinol and m-phenylene bischloroformate with aqueous sodium bicarbonate/tetrachloroethane gave, by the interfacial condensation method, a polycarbonate of inherent viscosity 0.23 dl/g. in N,N-dimethylacetamide.

(d) As in (c) but employing calcium carbonate in place of sodium bicarbonate: inherent viscosity 0.09 dl/g. in N,N-dimethylacetamide.

(e) m-phenylene bischloroformate was added in small portions to a solution of resorcinol in N,N-dimethylacetamide. A diluted portion of the mixture had an inherent viscosity 0.06 dl/g. It was also found that m-phenylene bischloroformate reacts vigorously with the solvent alone.

(f) Resorcinol and m-phenylene bischloroformate in refluxing tetrachloroethane yielded no polycarbonate.

(g) Resorcinol and m-phenylene bischloroformate in refluxing nitrobenzene gave polycarbonate of 0.19 dl/g. inherent viscosity in N,N-dimethylacetamide. With completely anhydrous nitrobenzene a higher figure may be obtained.

Poly(p-phenylene carbonate)

Hydroquinone in normal sodium hydroxide was treated with p-phenylene bischloroformate in tetrachloroethane, by the interfacial condensation method. The polycarbonate was insoluble in organic solvents. The low inherent viscosity, 0.051 dl/g., determined from 0.5% solution in concentrated sulphuric acid, may have been due to possible degradation occurring when the polymer was dissolved in the warm acid.

From the above experiments it would seem that the best methods to employ for the preparation of perfluorinated polycarbonates from bischloroformates and dihydric phenols, to obtain higher inherent viscosities than formerly, would be the following.

(i) The interfacial condensation method with sodium bicarbonate as base.

(ii) Solution polymerisation in refluxing nitrobenzene.

(iii) Melt polymerisation.

It would appear to be unlikely that even a weakly basic solvent could be used for solution polymerisation; cf. the result of treating resorcinol with m-phenylene bischloroformate in anhydrous N,N-dimethylacetamide. It was found that the chloroformate reacts vigorously with this solvent alone, after an induction period of a few minutes.

By method (i) no polymer was obtained when tetrafluorohydroquinone/ tetrafluoro-p-phenylene bischloroformate or tetrafluororesorcinol/tetrafluoro-m-phenylene bischloroformate were employed. With the latter reagents by methods (ii) and (iii) dark products were obtained which were partially soluble in dimethylacetamide and having inherent viscosities ca. 2.0 dl/g. However, these viscosity determinations may be very inaccurate owing to the high dilution and poor solubility of the polymer.

Polyhydrazides/Polyoxadiazoles

Low inherent viscosities have been obtained (ca. 0.2 or less) for the polyhydrazides described earlier (ref.11). Attention has been turned to obtaining pure and dry solvent as well as pure reagents. The earlier preparations of polyhydrazides employed solvent that contained small amounts of water.

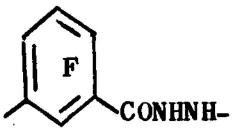
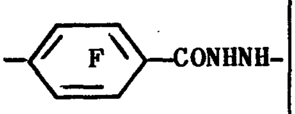
N,N-Dimethylacetamide (DMAC) was fractionally distilled and dried over molecular sieve. Gas chromatography indicated there to be only one component, and the infra-red spectrum gave no indication of OH or NH absorption. This solvent is therefore probably pure and anhydrous. Hexamethylphosphoramide (HMP) was similarly purified and dried, but was also treated with a polymeric acid chloride to remove impurity having NH absorbance in the infra-red. These solvents were used in the polymerisations described below.

The experimental conditions were first investigated for hydrogenic polymers. The addition of isophthaloyl chloride in HMP to 'anhydrous' (95+%) hydrazine in HMP afforded polyhydrazide of inherent viscosity 0.12 dl/g. This is no improvement on previous techniques (ref.11) where the same reagents were used, but in DMAC containing a trace of water.poly(tetrafluoroisophthalhydrazide)prepared previously (ref.11) had an inherent viscosity 0.086 dl/g., and 0.11 dl/g. has now been attained in HMP. Similarly poly(tetrafluoroterephthalhydrazide) had an inherent viscosity 0.11 dl/g. prepared in HMP from tetrafluoroterephthaloyl chloride and 95+% hydrazine.

By using dihydrazides an anhydrous system was more readily obtained. Thus isophthalhydrazide/isophthaloyl chloride in HMP yielded polymer of inherent viscosity 0.27 dl/g. and in DMAC 0.30 dl/g. was attained. Polymer gelled from the reaction in DMAC but not from the reaction in HMP, where the reagents were in more concentrated solution. In both cases the polymer was precipitated by dilution of the reaction mixture with water and was collected by filtration. The perfluoro analogue of this polymer was not obtained in this way because tetrafluoroisophthalhydrazide has not yet been synthesised. However, tetrafluoroterephthalhydrazide (ref.11) yielded polyhydrazide of inherent viscosity 0.29 dl/g. when treated with tetrafluoroterephthaloyl chloride in DMAC. In this reaction the perfluoro polymer separated out of the reaction mixture and was collected by filtration. It should be noted however, that this polyhydrazide has some solubility in such solvents as DMAC, whereas poly(terephthalhydrazide) is insoluble in all the organic solvents tried (ref.11 and cf. ref.12).

The characteristics of the above polyhydrazides are summarised in Table 2.

Table 2.

No.	Polyhydrazide	Method of preparation	Solvent in preparation	Inherent Viscosity
PH1		A	HMP	0.27
PH2		A	DMA	0.30
PH3		B	HMP	0.12
PH4		B	HMP	0.11
PH5		A	DMA	0.29
PH6		B	HMP	0.11

Notes to Table 2.

Method A : diacid chloride/dihydrazide

Method B : diacid chloride/hydrazine

Thermogravimetric analysis in air was carried out, and the results obtained for PH 2, PH 4, and PH 5 are given in Diagram 1. The rate of heating was ca. 1° per minute. It will be seen that whereas the hydrogenic polyhydrazide PH 2 loses water of hydration up to 255°, followed by cyclodehydration to stable polyoxadiazole and eventual decomposition at ca.420°, the perfluoro polyhydrazides PH 4 and PH 5 appear to lose water of hydration up to ca.255°, but thereafter decompose, and decomposition is proceeding rapidly at 350°. In the cases of PH 4 and PH 5 there seems to be no formation of stable perfluoro polyoxadiazole. This low thermo-oxidative stability of perfluoropolyhydrazides is not inconsistent with the low T_D values obtained for perfluoro model compounds which contain the NH or NHCO group, and the low thermo-oxidative stability of a perfluoro poly(sec. amide) (cf.ref.10 and ref.11). In addition a recent publication has shown that a polybenzimidazole containing both the endocyclic NH group and a perfluoroalkylene chain has thermal instability (ref.13).

As the T_D values for perfluoro oxadiazoles are approximately equal to those of their hydrogenic analogues it might be assumed that the perfluoro polyoxadiazoles would compare better with the hydrogenic polyoxadiazoles, than do the perfluoro polyhydrazides with the hydrogenic polyhydrazides, in terms of thermo-oxidative stability. Therefore the polyhydrazides PH 2 and PH 5 were heated at 256° in a nitrogen stream for 5.5 hour in an attempt to cyclodehydrate to the oxadiazole structure, prior to carrying out TGA (air). In addition PH 5 was heated at 256° for seven hours in vacuo prior to carrying out TGA (air). The TGA (air) results are shown in Diagram 2, where it is seen that the perfluoro polymer is still considerably less stable than the hydrogenic polymer. The polymers obtained by treating the polyhydrazides PH 2 and PH 5 at 256° were however, essentially still polyhydrazides as shown by elemental analyses and by the presence of NH absorbtion in the infra-red. The curves for the hydrogenic polymer in Diagrams 1 and 2 show that water of cyclodehydration has not been completely eliminated until a temperature of ca. 340° has been attained. Hence a prior cyclodehydration at ca.300° is indicated in order to obtain polyoxadiazole from polyhydrazide. However, this temperature may well be too high for perfluoro polyhydrazides for it was noted that they are already becoming deep brown at 256° in nitrogen or in vacuo, whereas the hydrogenic polyhydrazides retain their pale cream colour at this temperature. The preparation of perfluoro polyoxadiazoles, therefore, remains to be examined further.

Polyamic Acids/Polyimides

In view of the low inherent viscosities obtained for polyamic acids derived from pyromellitic dianhydride and perfluoro diamines, emphasis has been placed on obtaining pure reagents and solvents.

N,N-Dimethylacetamide was dried over molecular sieve, fractionally distilled and stored over molecular sieve.

Pyromellitic dianhydride was recrystallised three times from acetic anhydride and resublimed three times.

The perfluoro diamines originated as follows (a) - (e) :-

(a) Tetrafluoro-p-phenylene diamine (ex I.S.C.), obtained from tetrafluoroterephthalic acid by a Schmidt reaction, and of 98.9% purity by g.c. (two impurities of shorter retention time), was employed in the polymerisation.

(b) Tetrafluoro-m-phenylene diamine (ex I.S.C.), obtained by the procedure of D.G.Holland (ref.14) and of 99.2% purity by g.c. (two impurities of shorter retention time) was resublimed in vacuo three times.

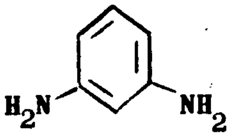
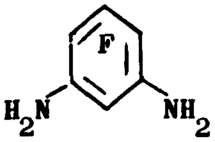
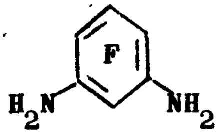
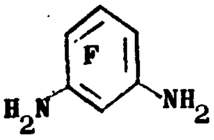
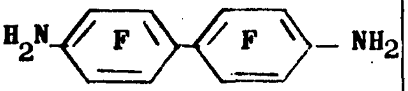
(c) Tetrafluoro-m-phenylene diamine (ex I.S.C.), obtained by the procedure of D.G.Holland, and of 99+% purity by g.c. (0.6% impurity of longer retention time) was resublimed three times in vacuo.

(d) Tetrafluoro-m-phenylene diamine of ca. 85% purity (ex I.S.C.), and containing ca.5% ortho and 10% para isomers was treated with phthalic anhydride to yield m-diphthalimido-tetrafluorobenzene. Hydrazinolysis in ethanol afforded pure (by g.c.) tetrafluoro-m-phenylene diamine, which was resublimed before use, to remove traces of solvent.

(e) Octafluorobenzidine of 98% purity by g.c. (2% of impurity with a longer retention time) ex I.S.C. was recrystallised from benzene and from petrol, but there was no improvement in the purity. The recrystallised diamine was resublimed twice before use.

Each of the above samples of diamine was treated in dimethylacetamide solution with pyromellitic dianhydride: see Table 3. In all cases but one a low inherent viscosity was obtained, i.e. less than 0.1 dl/g. In the case of a polyamic derived from tetrafluoro-m-phenylene diamine (b) an inherent viscosity of 0.2 was obtained. To check on the quality of the dianhydride and solvent, a polymerisation was carried out with m- and p-phenylene diamine, the experimental conditions being the same as in the reactions with the perfluoro diamines. Inherent viscosities of 1.4 and 2.4 dl/g. were obtained, showing that the perfluoro diamines were not satisfactory in this type of polymerisation.

Table 3. Polyimides

No.	Diamine treated with PMDA in DMAC	Inherent Viscosity (dl/g)	Reaction Temp./Time
PI (1)		1.4 (falling to 1.24 on standing)	Room temp./31 hr.
PI (2)	 Sample (b)	0.098	Room temp./18 hr. and 50°/8 hr.
PI (3)		0.2	50°/102 hr.
PI (4)	 Sample (c)	0.085	Room temp. and 60°/6hr.
PI (5)		0.06	Room temp.(and reversed addition of reagents)
PI (6)	 Sample (d)	0.08	Room temp. (and viscosity then decreased at 60°/4 hr.)
PI (7)		2.4	Room temp.
PI (8)	 Sample (a)	0.08	Room temp./12 days and 60°/4hr.
PI (9)		0.05	As for PI (2)
PI (10)		0.044	50°/24 hr.

The low reactivity of tetrafluoro-p-phenylene diamine as against that of p-phenylene diamine, towards phthalic anhydride was demonstrated in dimethylacetamide solution. Whilst there was a gradual colour change in the case of the perfluoro diamine no heat was liberated. In the case of the hydrogenic diamine there was an immediate colour change, and heat was liberated. Further, the anhydride absorbance at 1850 cm^{-1} rapidly disappeared in the latter case, but in the former it persisted, although gradually reducing. During a period of 70 hours this absorbance decreased to 45% of the initial value at a temperature varying from 22° to 28°.

The low reactivity of octafluorobenzidine towards pyromellitic dianhydride in DMAC at 50° was demonstrated. The infra-red absorbance of the anhydride group was measured at intervals of time. After 90 hours the absorbance of the anhydride in the sample solution had disappeared while that of the blank (a solution of pyromellitic dianhydride in dimethylacetamide) had risen, due to increased cell length caused by attack of solution, and to evaporation of solvent. Another polyamic acid solution was prepared in higher concentration, the inherent viscosity being measured at intervals. After 4 hours at 50°, the inherent viscosity was 0.04 dl/g. and this rose to 0.044 dl/g. after a total of 24 hours at 50°C. During a further 66 hours at 25°C the inherent viscosity did not rise further. Part of the polyamic acid solution was converted to the polyimide by heating on a shallow tray under nitrogen, at 160°C for 2 hours and then at 300°C for 2 hours. The polyimide PI 10 was obtained as a powdery deposit with no film formation.

The polyamic acids were converted to polyimides by removal of solvent and then heating at 300°, as described in the Experimental. It will be seen from Diagram 3 that the thermo-oxidative stability of PI(9) is considerably lower than that of the hydrogenic polyimide PI(1), and lower than that of PI(2). The relatively low thermo-oxidative stability of PI(9) is not inconsistent with a low molecular weight, but may also be due to the large amount of NH and NH_2 groups which are suggested by the infra-red absorbance. The polyimides PI(1) and PI(2) also exhibit NH absorbance in the infra-red, but to a lesser extent. It may be that more complete cyclodehydration to polyimide occurred under the TGA conditions at the slow rate of heating of ca. 1°/minute in the case of PI(1) and PI(2). This could be important, for when the perfluoro polyimide PI(2) was heated rapidly (6°/minute in air) to 400° and then maintained at 400°, it proved to be less thermo-oxidatively stable than the hydrogenic analogue PI (1). * However, an examination of Diagram 3 will also show that even at 1°/minute the rate of loss of weight is greater for PI (2) than for PI(1) at 400°, but the curves in general suggest that the thermo-oxidative stabilities of these two polymers are not greatly different.

* The rates of weight loss under these conditions at 400° were 0.23% per hour for PI(1) and 0.79% per hour for PI(2).

3. THERMAL STABILITY OF MODEL COMPOUNDS

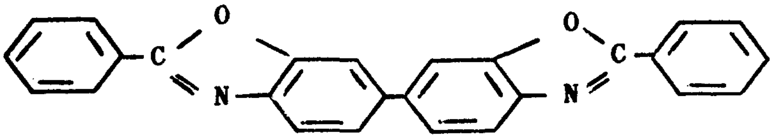
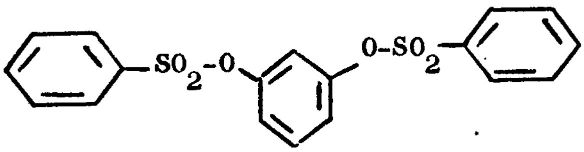
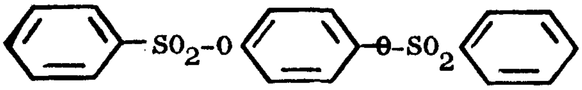
Table 4 lists the perfluoro and hydrogenic compounds synthesised, and compares the thermal decomposition temperatures which were obtained as described by Blake et al (ref.15), in nitrogen. The thermal decomposition temperatures of compounds containing CH and CF in the same aromatic ring are given in Table 1, and those of the perfluoro compounds synthesised earlier in this programme have been reported earlier (ref.11).

Although the perfluoro bibenzoxazole has a lower T_D than its hydrogenic analogue, this is still relatively high, and therefore this structure should be incorporated into polymers for determination of thermo-oxidative stability. From the results obtained for perfluoro sulphonates and the dithiocarbonate, it would not seem that polymers incorporating these structures would be stable much above 200°. On the otherhand the perfluoro bis(tertiary amide) structure may be suitable for incorporation into polymers, but preparative difficulties might be encountered in the light of experience gained with the model compound.

Table 4.

THERMAL DECOMPOSITION TEMPERATURES

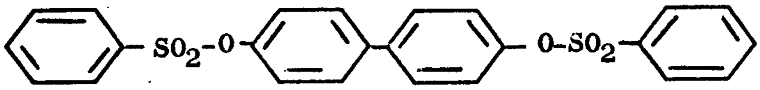
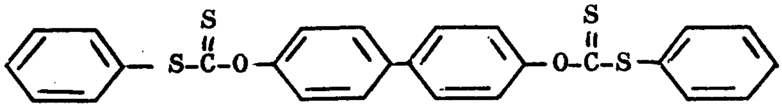
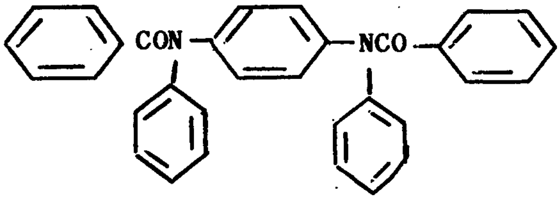
Thermal decomposition temperatures were determined for the compounds listed in Table 4 (T_D, the temperature at which there is 0.84 mm Hg min^{-1} increase of vapour pressure in a nitrogen atmosphere: ref.15)

Skeletal Structure	Hydrogenic Compound T_D	Perfluorinated Compound T_D
	420°C	380°C *
	266°C	200°C
	236°C	214°c

* The partially fluorinated analgoue (III) had T_D 326°

Table 4.
(continued)

THERMAL DECOMPOSITION TEMPERATURES

Skeletal Structure	Hydrogenic Compound T_D	Perfluorinated Compound T_D
	246°C	217°C
	186°C	194°C
	334°C	340°C

D. EXPERIMENTAL

Note Where molecular weights are quoted they have been obtained by osmometry, unless otherwise stated.

1. HETEROCYCLICS (AND INTERMEDIATES)

2,2'-Diphenyl-6,6'-bibenzoxazole (II)

(a) Direct preparation with benzoylchloride

3,3'-Dihydroxybenzidine (10.8 g.; 0.05 mole) and benzoyl chloride (50 g.; 0.36 mole) were heated at 250° (bath) for five hours. The excess of benzoyl chloride was distilled off, and the residue was extracted with methanol and then with hot benzene, cooled and filtered. The crude bis-benzoxazole (17.7 g.) was washed with a little cold benzene and dried (91% yield based on the diamine), m.p. 250-254°. (Literature m.p. 249-250°, ref. 1).

Recrystallisation from chlorobenzene gave 2,2'-diphenyl-6,6'-bibenzoxazole as glistening white plates (12.8 g.), m.p. 252-4°.

Calc. for $C_{26}H_{16}N_2O_2$:	C, 80.4;	H, 4.12;	N, 7.22;	M.W. 388
Found :	C, 79.1;	H, 4.0 ;	N, 6.2 ;	M.W. 391 (Rest method)
	80.0;	4.2 ;	5.4	

The infra-red spectrum showed the presence of -C = N-, cyclic -O- and trisubstituted benzene, and the absence of -OH, -NH- and NH_2 groups.

(b) Direct preparation from benzoic acid (ref. 2)

A solution of 3,3'-dihydroxybenzidine (4.32 g. : 0.002 mole) in polyphosphoric acid (100 g.; 80% P_2O_5) was heated to 120° under nitrogen. Benzoic acid (4.88 g. : 0.004 mole) was added, the mixture was stirred at 120° for 10 hours, poured into water and filtered. The grey solid was washed with sodium bicarbonate solution (twice), water, and methanol, and dried at reduced pressure, yielding crude product (6.5 g. : 84% yield), m.p. 249-252°, which was recrystallised from benzene/ethanol to give white plates (4.2 g.), m.p. 254-255°.

(c) Via dibenzoyl derivative of 3,3'-dihydroxybenzidine

Preparation of the dibenzoyl derivative.

3,3'-Dihydroxybenzidine (8.65 g. : 0.04 mole), N,N-diethylaniline (15 g. : 0.1 mole) and benzoyl chloride (11.9 g. : 0.085 mole) were dissolved in anhydrous ether (200 ml.), and were stirred at room temperature for 8 hours, and the suspension was filtered. Evaporation of the filtrate gave a small amount of liquid which appeared to consist of benzoyl chloride and N,N-diethylaniline. The solid collected by filtration was washed with water until the washings were free from chloride and dried at 100°/15 mm. to yield the pale green benzoyl derivative (14.4 g. : 85% yield), m.p. >400°.

Cyclisation of the dibenzoyl derivative of 3,3'-dihydroxybenzidine.

(i) By heat.

A small amount of the dibenzoyl derivative of 3,3'-dihydroxybenzidine was heated in a test tube over a low flame. Water was evolved and the material turned black. The cool residue was extracted with boiling chlorobenzene, to yield 2,2'-diphenyl-6,6'-bibenzoxazole, m.p. 249-252°.

(ii) With thionyl chloride.

The dibenzoyl derivative (1 g.) and thionyl chloride (10 ml.) were stirred at 160° (bath) for 5 hours. The reaction mixture was poured into water, and the solid was collected by filtration, washed with sodium bicarbonate solution, water, and methanol, and dried. The brown solid (0.65 g.), m.p. 220-230°, was recrystallised from chlorobenzene to give the bibenzoxazole (0.48 g.) m.p. 248-252°.

(iii)With polyphosphoric acid.

The dibenzoyl derivative (1 g.) and polyphosphoric acid (10 ml.) were heated for 5 hours at 160° (bath). The mixture was poured into water and filtered. The white solid collected by filtration was washed with sodium bicarbonate solution, water, and methanol, and dried, to yield the bibenzoxazole (0.61 g.), m.p. 242-248°.

2,2'-Diphenyl-4,4',5,5',7,7'-hexafluoro-6,6'-bibenzoxazole (IV)

A mixture of 3,3'-dihydroxyhexafluorobenzidine (3.24 g. : 0.01 mole) and benzoyl chloride (14.1 g. : 0.10 mole) was heated at 200° for 5 hours, cooled and triturated with cold petrol ether. The brown solid (8.3 g.), m.p. 55-170° was collected by filtration. A portion (0.3 g.), m.p. 348-351°, was insoluble in hot benzene. The benzene-soluble material was recovered by evaporation of the solvent, and fractionally recrystallised from a mixture of benzene and petrol, or from ethanol, but no pure products were obtained. The product of m.p. 348-351° was recrystallised three times from chlorobenzene to yield a compound, m.p. 351.5-352°. The infra-red spectrum of this material is not inconsistent with the proposed bibenzoxazole structure.

Anal. Calc. for $C_{26}H_{10}F_6N_2O_2$: C, 62.9; H, 2.0; F, 23.0; N, 5.6
Found : C, 62.2; H, 2.6; F, 22.2; N, 5.4.

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

(a) Attempted condensation of 3,3'-dihydroxybenzidine with pentafluorobenzoic acid.

Pentafluorobenzoic acid (5.41 g. : 0.0256 mole) was added to a solution of 3,3'-dihydroxybenzidine (2.76 g. : 0.0128 mole) in polyphosphoric acid (100 g. : 80% P_2O_5) at 120° under nitrogen. The mixture was stirred at 120° for 10 hours, with pentafluorobenzoic acid subliming, allowed to cool and poured into ice and water. The solid collected by filtration was unreacted pentafluorobenzoic acid, m.p. 102-105°. The filtrate was buffered to pH 6, but no further solid separated.

(b) Via intermediate (X) from 3,3'-dihydroxybenzidine and pentafluorobenzoyl chloride at 250°.

3,3'-Dihydroxybenzidine (4.32 g. : 0.02 mole) was heated at 200° with pentafluorobenzoyl chloride (11.53 g. : 0.05 mole). After 2 hours a further 5 g. of pentafluorobenzoyl chloride was added and the temperature of the mixture was raised to 250° for 8 hours, during which time it gradually became more fluid. Benzene (100 ml.) was added to the mixture, the solid (10.6 g.), m.p. 279-282°, was collected by filtration, and recrystallised from chlorobenzene to give white fluffy crystals (8.1 g.), m.p. 289-291°.

The infra-red spectrum of this compound (X) is inconsistent with the bibenzoxazole structure: there are >NH and >C=O absorption bands. It was doubtful if -OH is present.

Calc. for $C_{26}H_{10}F_{10}N_2O_4$ Di(pentafluorobenzoyl derivative)
C, 51.6; H, 1.7; F, 31.5; N, 4.6; M.W. 604
Calc. for $C_{33}H_9F_{15}N_2O_5$ (Tripentafluorobenzoyl derivative)
C, 49.7; H, 1.1; F, 35.7; N, 3.5; M.W. 798
Found : C, 49.1; H, 1.0; F, 36.8; N, 3.0; M.W. 755 (Rast.)
C, 48.8; H, 1.3; F, 37.4; N, 3.2.

The product was assumed to be a pentafluorobenzoyl derivative of 3,3'-dihydroxybenzidine. When treated with polyphosphoric acid at 200° for 6 hr., phosphorus pentoxide at 150° for 5 hr., or thionyl chloride under reflux for 5 hr., no cyclisation appeared to take place, and the starting material was largely recovered in each case. Treatment of the product (0.5 g.) with conc. sulphuric acid at 150° for 5 hr., followed by adding the solution to water, yielded a grey solid (0.05 g.), m.p. >400°.

When (X) (1.56 g.) was heated at 340-360° for 3 minutes water and a sublimate were evolved. The cooled buff-coloured solid (1.12 g.) was boiled with ethanol (50 ml.) and the suspension was filtered hot. The cold filtrate deposited off-white crystals (0.07 g.), m.p. 190-198°. The ethanol-insoluble material (0.71 g.), m.p. 217-230°, was recrystallised from benzene to give white solid (0.5 g.), m.p. 232.5-233.5°. The infrared spectrum of this latter product is not inconsistent with 2,2'-di (pentafluorophenyl)6,6'-bibenzoxazole.

Calc. for $C_{26}H_6F_{10}N_2O_6$: C, 55.0; H, 1.1; F, 33.4; N, 4.9; M.W. 568
Found : C,54.8; H, 0.9; F, 33.1; N, 4.9; M.W. 515
(Rough value due to low solubility)

(c) Via the di(pentafluorobenzoyl) derivative (XI) of 3,3'-dihydroxybenzidine.

N,N-Diethylaniline (3.3 g. : 0.022 mole) was added over 15 min. to pentafluorobenzoyl chloride (4.6 g. : 0.02 mole and 3,3'-dihydroxybenzidine (2.46 g. : 0.01 mole) in anhydrous ether (100 ml.). The mixture was stirred at room temperature for 5 hours and filtered. Evaporation of the filtrate gave a mixture of N,N-diethylaniline and its hydrochloride and pentafluorobenzoyl chloride, but the solid collected by filtration was washed with water until the washings were free from chloride, and dried. The green residue (3.3 g.), m.p. ca. 305° (decomp.) was assumed to be a di(pentafluorobenzoyl) derivative of 3,3'-dihydroxybenzidine. An attempt to cyclise this derivative by heating for 16 hours at 250° with polyphosphoric acid gave only unreacted starting material.

A small amount of the dibenzoyl derivative (XI) was heated over a low flame. Considerable charring occurred. The solid was extracted with benzene, and evaporation of the extract gave a trace of solid, m.p. 210-223°. This appeared to be the bibenzoxazole described under (b), as shown by mixed m.p.

Compounds isolated from the reactions of 3,3'-dihydroxy-2,2',5,5',6,6'-hexafluorobenzidine with pentafluorobenzoyl chloride

(a) Compound V

3,3'-Dihydroxy-hexafluorobenzidine, m.p. 191-192° (4.1 g. : 0.0127 mole) and pentafluorobenzoyl chloride (21 g. : 0.091 mole) was heated at 230° (bath) for nine hours. The excess of pentafluorobenzoyl chloride was distilled off, and the residual brown solid was dissolved in hot methanol. The methanol solution was evaporated to dryness and the residue was recrystallised from benzene (25 ml.) to yield white solid (1.35 g.), m.p. 266-271°. Recrystallisation from a large volume of benzene gave fluffy white solid (1.08 g.), m.p. 271-274°. Another recrystallisation raised the melting point to 274-275.5°.

Calc. for $C_{26}F_{16}N_2O_2$: C, 46.2; H, 0.0; F, 44.9; N, 4.14; M.W. 676
Found : C, 42.7; H, 1.5; F, 47.4; N, 2.7; M.W. 808 (Rast method)
C, 44.0; H, 0.10; F, 48.5; N, 2.30;

The infra-red spectrum showed a >C=O function and the presence of a conjugated >C=N- band, but there was no evidence for >NH, $-NH_2$, -OH, $>CH_2$ or CH_3 groups. The compound was insufficiently soluble for N.M.R. examination.

The benzene mother liquor from the first recrystallisation was diluted with petrol (60-80°) to yield buff-coloured powder (1.7 g.), m.p. 100-120°. Recrystallisation from aqueous ethanol raised the melting point to 108-130°, but yielded no pure compound.

(b) Compound VI

A smaller scale preparation was repeated as in (a) but without the use of methanol in case reaction had occurred between the original product and this solvent in (a).

3,3'-Dihydroxy-hexafluorobenzidine, m.p. 191-192°, (1 g.) and pentafluorobenzoyl chloride (5 g.) after 5 hours at 230° gave a brown sticky solid, m.p. 65-75°. Recrystallisation from benzene/petrol (60-80°) gave white solid (1 g.), m.p. 99-102°.

Part of this material was boiled with methanol and the solution evaporated to dryness. There was no change in melting point.

Calc. for $C_{26}F_{16}N_2O_2$: C, 46.2; H, 0.00; F, 44.9; N, 4.14; M.W.676

Calc. for $C_{26}H_4F_{16}N_2O_4$: C, 43.8; H, 0.57; F, 42.7; N, 3.93; M.W.712

Found : C, 43.1; H, 0.45; F, 46.6; N, 2.1; M.W.625(Rast)
C, 43.9; H, 0.08; F, 48.4; N, 2.11;

The infra-red spectrum shows the presence of a strong >C=O function, and a conjugated >C=N bond, and the absence of >NH, $-NH_2$, -OH, $>CH_2$ or $-CH_3$ absorption. The N.M.R. spectrum indicated the absence of H, and therefore of NH.

(c) Compounds V and VII

3,3'-Dihydroxy hexafluorobenzidine, m.p. 181-5°, decomp. (8.57 g.:0.0265 mole) and pentafluorobenzoyl chloride (35 g.:0.152 mole) were heated for 5 hours at 230° and then for 5 hours at 250°. The excess of pentafluorobenzoyl chloride was distilled off and the cold residue recrystallised from aqueous ethanol to give a first crop of white crystals (12.7 g.), m.p. 262-270°, a second crop (2.1 g.), m.p. 200-250°, and a third crop (4.6 g.), m.p. 315-325°. A small part of the first crop was recrystallised from ethanol gave white crystals, m.p. 271-273° (mixed m.p. with V prepared in (a), 272-275°). The third crop recrystallised from ethanol, m.p. 323-325°, had a mixed m.p. with VII, (prepared below), 325-328°.

(d) Di(pentafluorobenzoyl) derivative (VIII) of 3,3'-dihydroxy-2,2',5,5',6,6'-hexafluorobenzidine

3,3'-Dihydroxy-hexafluorobenzidine (1 g.:0.031 mole, m.p. 191-5°) pentafluorobenzoyl chloride (1.5 g.:0.065 mole), N,N-diethylaniline (0.5 g.), and ether (20 ml.) were stirred for six hours at 20°. The diethylaniline hydrochloride was filtered off and the filtrate evaporated to dryness to give buff-coloured solid (0.8 g.), m.p. 276-280°. Washing with a little cold benzene followed by recrystallisation from aqueous ethanol gave a compound (0.38 g.), m.p. 298-300°.

Calc. for $C_{26}H_4F_{16}N_2O_4$: C, 43.8; H, 0.56; N, 3.93; F, 42.7; M.W.712

Found : C, 43.63; H, 0.35; N, 3.77; F, 39.93; M.W.704

The infra-red spectrum did not indicate whether or not this was an O- or an N- pentafluorobenzoyl derivative.

(e) Di(pentafluorobenzoyl) derivative (VII) of 3,3'-dihydroxy-hexafluorobenzidine

Pentafluorobenzoyl chloride (6.9 g.: 0.03 mole) was added to a solution of 3,3'-dihydroxy hexafluorobenzidine (4.86 g.: 0.015 mole; m.p. 181-5° decomp.) in anhydrous ether (50 ml.), followed by a solution of N,N-diethylaniline (5.2 g.:0.035 mole) in anhydrous ether (50 ml.). After stirring for 5 hours the ether solution was decanted from the semi-solid, and evaporated to give a gum (1.9 g.), m.p. 51-75°, which was recrystallised three times from aqueous ethanol to yield a white solid (0.5 g.), m.p. 320-330°. The ether-insoluble material was washed free of chloride with water and fractionally recrystallised from aqueous ethanol to give two compounds:

(VII) 2.4 g. m.p. 329-330°

	C	H	F	N	Cl	M.W.
Calc. for $C_{26}H_4F_{16}N_2O_4$:	C, 43.8;	H, 0.6;	F, 42.7;	N, 3.9;	Cl, 0.0;	M.W. 712
Found :	C, 44.0;	H, 0.7;	F, 37.4;	N, 4.1;	Cl, 0.0;	M.W.582
	C, 45.3;	H, 0.9;		N, 3.5;		
	C, 43.7;	H, 0.6;		N, 3.9;		

(IX) 0.6 g. m.p. 224-225° (decomp.)

	C	H	F	N	Cl	M.W.
Found :	C, 43.1;	H, 1.2;	F, 37.5;	N, 5.5;	Cl, 0.2:	M.W.462

2,2'-Di(pentafluorophenyl)-4,4',5,5',7,7'-hexafluoro-6,6'-bibenzoxazole (I)

(a) Attempted cyclisation of (VII) in polyphosphoric acid

The fluorobenzoyl derivative (VII) (2 g.) was stirred with polyphosphoric acid (50 g.) at 120° under nitrogen for 2 hours but the solid was not "wetted". Dimethyl formamide (5 ml.) was added and the mixture was heated at 120° for a further 20 hours, when part of the solid dissolved. The mixture was poured into water to yield starting material (1.9 g.), m.p. 332-334°, collected by filtration (mixed m.p. with starting material was 330-333°).

(b) Pyrolytic cyclisation of (VII) to (I)

The fluorobenzoyl derivative (VII) (0.83 g.) was heated at 350° for 3 minutes. The cold residue (0.67 g.) was recrystallised twice from methylated spirits to give the perfluorobibenzoxazole (0.1 g.) m.p. 186-190°.

(c) Pyrolytic cyclisation of (V) to (I)

The intermediate (V) (2.4 g.) was heated at 350° for 4 minutes. The residue (2.1 g.) was recrystallised from aqueous ethanol to give impure starting material (0.4 g., m.p. 210-217°), and off-white solid (0.78 g.) m.p. 166-169° (resolidifying and remelting at 188°). The latter was recrystallised from benzene and benzene/petrol (60-80°) to give fluffy white crystals of the perfluoro bibenzoxazole, m.p. 192.5-193.5°.

Calc. for $C_{26}F_{16}N_2O_2$: C, 46.2; H, 0.0; F, 44.9; N, 4.1;

Found : C, 46.35; H, 0.0; F, 44.8; N, 4.3;

C, 46.1; H, 0.0; N, 4.3;

Decafluorobenzanilide

Pentafluorobenzoyl chloride (11.53 g.:0.05 mole) and pentafluoroaniline (9.15 g.:0.05 mole) were dissolved in anhydrous ether (150 ml.) and N,N-diethylaniline (9 g.:0.06 mole) added. After stirring for 4 hours, the diethylaniline hydrochloride was filtered off and the ether was distilled from the filtrate to leave a pale yellow residue, m.p. 140-155°. This was recrystallised from ethanol/petrol ether (60-80°) to give white needles (6.4 g.) m.p. 180-181.5° (cf. m.p. 183-5°; Part I of this report).

Calc. for $C_{13}F_{10}HNO$: C, 41.4; F, 50.4; H, 0.27; N, 3.71;

Found : C, 41.3; F, 54.0; H, 0.24; N, 3.97;

Attempted cyclisations of decafluorobenzanilide

(a) In N,N-Diethylaniline

Decafluorobenzanilide (0.5 g.) was stirred with N,N-diethylaniline (20 ml.) at 100° for 10 hours. The diethylaniline was distilled off at reduced pressure to leave unreacted starting material (0.34 g.), m.p. 172-179°.

(b) In pyridine

When pyridine was used instead of N,N-diethylaniline the product was a black brittle solid, m.p. 170-180°, from which starting material was the only pure substance obtained by recrystallisation.

(c) In hexamethylphosphoramide

Decafluorobenzanilide (0.5 g.) was stirred with hexamethylphosphoramide (10 ml.) at 100° for 10 hours. The solvent was distilled off at reduced pressure, and last traces removed by heating the residue at 100°/0.1 mm. for 5 hours. The product (0.41 g.) was a sticky solid, m.p. 100-115°. After recrystallisation from aqueous ethanol (twice) and petrol ether (60-80°)/benzene (twice) a white solid (0.1 g.), m.p. 163-170° was obtained.

A further quantity of crude material was prepared and purification was attempted by adsorption chromatography on alumina from an ethanolic solution. All of the solid fractions obtained had wide melting ranges.

2,5-Di(2,3,5,6-tetrafluorophenyl)-1,3,4-oxadiazole

2,3,5,6-Tetrafluorobenzoyl chloride (12.8 g.) was added to N/1 NaOH (125 ml.) stirred at 5°, followed immediately by hydrazine hydrate (1.35 ml.) in water (10 ml.) over ca. 5 min. The temperature was maintained at 5-10° and the mixture was stirred at this temperature for 30 min., followed by 2 hours, during which time room temperature was attained. The mixture was acidified with conc. hydrochloric acid (6 ml.), with the temperature below 20°, filtered, and the solid collected was washed free of acid, and dried. The crude substance (8.3 g.), m.p. 267-8°, was recrystallised from aqueous methanol to yield N,N'-di(tetrafluorobenzoyl)hydrazine (5.4 g.), m.p. 272-3° (unchanged on further recrystallisation).

Calc. for $C_{14}H_4F_8N_2O_2$: C, 43.7; H, 1.05; F, 39.6; N, 7.3;

Found : C, 43.5; H, 1.13; F, 39.3; N, 7.5;

The above product (3 g.) was heated with phosphoryl chloride (60 ml.) on the steam bath for 3 hr. The mixture was distilled to dryness under reduced pressure to yield a gum which crystallised from ethanol. Recrystallisation from ethanol gave the oxadiazole (2.5 g.), m.p. 167-8°.

Calc. for $C_{14}H_2F_8N_2O$: C, 45.9; H, 0.55; F, 41.5; N, 7.7; M.W. 366

Found : C, 45.9; H, 0.65; F, 41.1; N, 7.9; M.W. 366

2. SULPHONATES

1,3-Di(phenylsulphonyloxy)benzene

A solution of resorcinol (11 g.: 0.1 mole) in water (100 ml.) was made slightly alkaline with 2N sodium hydroxide solution and shaken whilst benzene sulphonyl chloride (40 g. : 0.227 mole) was added in small amounts. Sodium hydroxide was added at intervals, to keep the mixture alkaline during and after the addition, whilst the mixture was shaken for 1 hour. A white oil separated, which did not solidify on standing overnight. The supernatant liquid was decanted and the oil was shaken with a large excess of 5N sodium hydroxide solution. After two hours, solid was filtered off, washed with caustic soda solution and then with water until neutral. Two recrystallisations from ethanol gave white crystalline sulphonate (24.8 g.), m.p. 54.5-55.5°. (Literature m.p. 69-70°; ref. 5).

Calc. for $C_{18}H_{14}O_6S_2$: C, 55.4; H, 3.6; O, 24.6; S, 16.5; M.W. 390

Found : C, 55.3; H, 3.4; O, 24.5; S, 16.3; M.W. 393

1,4-Di(phenylsulphonyloxy)benzene

The method and scale were as for the 1,3-derivative. Two recrystallisations from ethanol gave white needles (21.0 g.), m.p. 119-120° (Literature m.p. 120-121°. ref. 5).

Calc. for $C_{18}H_{14}O_6S_2$: C, 55.35; H, 3.62; O, 24.60; S, 16.45; M.W. 390

Found : C, 55.5; H, 3.5; O, 24.7; S, 16.4; M.W. 390

4,4'-Di(phenylsulphonyloxy)biphenyl

A suspension of 4,4'-dihydroxybiphenyl (1.9 g.: 0.01 mole) in water (100 ml.) was made slightly alkaline with sodium hydroxide. Benzene sulphonyl chloride (5 g.: 0.036 mole) was added in small amounts at a time with shaking, and the mixture was kept alkaline with sodium hydroxide. After three hours shaking, the solid was filtered off and recrystallised from ethanol to yield needles of 4,4'-di(phenylsulphonyloxy)-biphenyl (2.76 g.), m.p. 152.5-153.5°. (Lit. m.p. 148°; ref. 6).

Calc. for $C_{24}H_{18}O_6S_2$: C, 61.8; H, 3.87; S, 13.7; O, 20.6; M.W. 466

Found : C, 61.3; H, 3.7; S, 14.1;

C, 63.1; H, 4.3; S, 13.15; O, 19.6; M.W. 470

1,3-Di(pentafluorophenylsulphonyloxy)tetrafluorobenzene

Tetrafluoro resorcinol (1.82 g.: 0.01 mole), pentafluorobenzene sulphonyl chloride (5.4 g.: 0.0203 mole), N,N-diethyl aniline (3 g.), and benzene (50 ml.) were shaken for four hours at room temperature. The precipitated diethylaniline hydrochloride was filtered off, and the filtrate was washed with sodium hydroxide, dilute hydrochloric acid and three times with water. The benzene was distilled off and the residue was recrystallised from ethanol to give glistening white plates (3.83 g.: 60% yield), m.p. 112-113°.

Calc. for $C_{18}F_{14}O_6S_2$: C, 33.7; F, 41.4; S, 10.0; M.W. 642

Found : C, 33.8; F, 43.85; S, 12.4;

C, 33.8; F, 43.9; S, 12.4; M.W. 635

1,4-Di(pentafluorophenylsulphonyloxy)tetrafluorobenzene

Tetrafluorohydroquinone (4.3 g.: 0.0236 mole), pentafluorobenzenesulphonyl chloride (12.6 g.: 0.047 mole), N,N-diethyl aniline (7.1 g.), and benzene (100 ml.) were shaken for four hours. The mixture was filtered, and the filtrate was washed with sodium hydroxide solution, dilute hydrochloric acid, and three times with water. The benzene solution was evaporated to dryness to give white solid (4.0 g.), m.p. 130-152°. The solid collected by filtration was similarly washed with water, sodium hydroxide, hydrochloric acid, and water and the residue (7.1 g.), m.p. 157-160°, combined with the other solid product. Recrystallisation from benzene gave glistening plates (9.8 g.: 51% yield), m.p. 159-160.5°. A small second crop (0.64 g.), m.p. 158-160° was obtained.

Calc. for $C_{18}F_{14}O_6S_2$: C, 33.7; F, 41.4; S, 10.0; M.W. 642

Found : C, 33.54; F, 45.00; S, 13.20;
(Repeat) : C, 34.8; F, 41.5; S, 11.5; M.W. 635

4,4'-Di(pentafluorophenylsulphonyloxy)octafluorobiphenyl

4,4'-Dihydroxyoctafluorobiphenyl (3.3 g.: 0.01 mole), pentafluorophenylsulphonyl chloride (5.5 g.: 0.0206 mole), N,N-diethylaniline (5.0 g.) and benzene (100 ml.) were shaken for 4 hours and the diethyl aniline hydrochloride was filtered off. The filtrate was washed with sodium hydroxide solution, dilute hydrochloric acid, and water. The benzene was distilled off and the residual solid was recrystallised from ethanol to give white crystals (5.14 g.: 65% yield), m.p. 151-152.5°.

Calc. for $C_{24}F_{18}O_6S_2$: C, 36.5; F, 43.3; S, 8.1; M.W. 790

Found : C, 36.75; F, 45.6; S, 10.0; M.W. 763

(Repeat) : C, 36.0; F, 40.2; S, 9.4;

3. DITHIOCARBONATES (AND INTERMEDIATES)

Attempted preparations of potassium pentafluorophenylxanthate

Pentafluorophenol (10 g.), potassium hydroxide (20 g.), carbon disulphide (25 g.), and ethanol (80 ml.) were heated at 50-55°C for six hours. The cooled solution was filtered from a small amount of solid and distilled to small volume, to yield orange needles (8 g.), m.p. above 400°.

Calc. for $C_7F_5OS_2K$: C, 28.20; H, 0.00; F, 31.85; S, 21.48; K, 13.09;

Found : C, 8.06; H, 0.96; F, 0.98; S, 2.14; K, 51.45;

The mother liquors, evaporated to dryness, gave a mixture of orange and white solid (11.0 g.), m.p. above 400°. The residue contained an excess of potassium hydroxide.

An attempt was made to prepare the p-nitrobenzyl ester from the orange needles by means of p-nitrobenzyl bromide in aqueous ethanol. The small amount of solid was collected by filtration and recrystallised from ethanol, and from chloroform, to give a pale yellow solid, m.p. 158-9°.

Calc. for $C_{14}H_6F_5O_3NS$: C, 42.30; F, 23.93; H, 2.03; N, 3.52; S, 16.14;

Found : C, 54.91; F, 2.78; H, 3.98; N, 8.74; S, 9.65;

Phenyl dithiochloroformate (ref. 7)

A solution of sodium hydroxide (4 g.: 0.1 mole) in water (50 ml.) was added dropwise to a stirred solution of thiophenol (11.0 g.: 0.1 mole) and thiophosgene (11.5 g.: 0.1 mole) in chloroform (100 ml.) at room temperature. Heat of reaction caused the chloroform to reflux. The mixture was cooled by means of a water bath, and stirred for five hours, the chloroform layer was separated, dried (magnesium sulphate), and the chloroform and excess of thiophosgene was distilled off. The residue was distilled in vacuo to yield phenyl dithiochloroformate (12.96 g., 69% yield) boiling at 65-68°/0.25 mm. (Lit. b.p. 104°/13 mm.)

O,S-Diphenyl dithiocarbonate (XIV)

A suspension of dry potassium phenate (6.6 g.: 0.05 mole) in absolute ethanol (50 ml.) was stirred vigorously, while a solution of phenyl dithiochloroformate (9.5 g.: 0.05 mole) in ethanol (50 ml.) was added. After the mixture had been stirred for five hours, potassium chloride was filtered off, and the ethanol was distilled under reduced pressure to leave a viscous red liquid which solidified on standing. Three recrystallisations from aqueous ethanol gave yellow needles (3.53 g., 29% yield), m.p. 43.5-44.5°.

The literature (ref. 7) melting point of the O,S-diphenyldithiocarbonate is 51°, and the melting point of S,S-diphenyl dithiocarbonate $C_6H_5S.C.O.S.C_6H_5$ is 43°; thus it is possible that isomerisation has occurred from the O,S- to the S,S-diphenyl ester.

Calc. for $C_{13}H_{10}OS_2$: C, 63.4; H, 4.1; S, 26.0; O, 6.5;

Found : C, 63.5; H, 4.3; S, 26.0; O, 6.4;

Pentafluorophenyl dithiochloroformate

A suspension of potassium pentafluorothiophenate (3.57 g.: 0.015 mole) in chloroform (20 ml.) was added in small portions to a solution of thiophosgene (1.75 g.: 0.015 mole) in chloroform (50 ml.). After the mixture had been stirred for 5 hours, potassium chloride was filtered off, and the chloroform was distilled off. The residue was distilled in vacuo, the main fraction (2.62 g., 63% yield) boiling at 61-63°/1 mm. being collected as the required pentafluorophenyl dithiochloroformate.

O,S-Di(pentafluorophenyl)dithiocarbonate (XIII)

A solution of pentafluorophenyl dithiochloroformate (2.62 g.: 0.0094 mole) in ethanol (20 ml.) was added to a stirred suspension of potassium pentafluorophenate (2.09 g.: 0.0094 mole) in ethanol (30 ml.). After the mixture had been stirred for 5 hours, the potassium chloride was separated by filtration and the ethanol was distilled off. The residue was recrystallised from aqueous ethanol to give pale yellow crystals (1.51 g., 38% yield) m.p. 97.5-98.5°.

Calc. for $C_{13}F_{10}OS_2$: C, 36.6; F, 44.6; S, 15.0; H, 0.00;

Found : C, 36.7; F, 44.9; S, 15.0; H, 0.13;

O,O-(4,4'-Biphenylylene) di (S-phenyl dithiocarbonate) (XVI)

A solution of phenyl dithiochloroformate (5.65 g.: 0.03 mole) in ethanol (50 ml.) was added to a stirred suspension of the di-potassium salt of 4,4'-dihydroxybiphenyl (3.92 g.: 0.015 mole) in ethanol (50 ml.). After 4 hours, the solid was filtered off and washed free of chloride with water. The filtrate was distilled to remove the ethanol, leaving a sticky yellow solid which was recrystallised from aqueous ethanol to give an off-white solid (0.3 g.) m.p. 168°, having an elemental analysis for O-4(4'-hydroxybiphenylyl) S-phenyl dithiocarbonate.

Calc. for $C_{19}H_{14}O_2S_2$: C, 67.4; H, 4.1; O, 9.5; S, 18.9;

Found : C, 67.4; H, 4.3; O, 9.63; S, 18.8;

The solid filtered from the reaction mixture, was recrystallised from benzene to give a pale yellow solid (0.67 g.) m.p. 195.5-196°.

A repeat preparation gave a higher yield of this material but with m.p. 195-197°. Both products were combined and recrystallised from benzene to give glistening lemon yellow crystals, m.p. 197.5-198°.

Calc. for $C_{26}H_{18}O_2S_4$: C, 63.6; H, 3.7; O, 6.5; S, 26.1;

Found : C, 63.8; H, 3.6; O, 6.6; S, 26.0;

O,O-(4,4'-Octafluorobiphenylylene) di(S-pentafluorophenyl dithiocarbonate (XV)

A solution of pentafluorophenyl dithiochloroformate (3.35 g.: 0.012 mole) in ethanol (50 ml.) was added during five minutes to a well stirred suspension of the di-potassium salt of 4,4'-dihydroxy-octafluorobiphenyl (2.43 g.: 0.006 mole) in ethanol (50 ml.). After stirring for a further 3 hours, the solid was collected by filtration, washed free of potassium chloride with water, and dried. The off-white crystals (3.2 g.) m.p. 155-157° obtained were recrystallised from benzene/ethanol to give glistening crystals (1.7 g.) m.p. 160.5-161.5°.

Calc. for $C_{26}F_{18}O_2S_4$: C, 38.3; F, 42.0; S, 15.75;
Found : C, 39.9; F, 42.1; S, 17.6;

4. BIS(TERTIARY AMIDES)

N,N,N',N'-Tetra(pentafluorophenyl)tetrafluoroterephthaldiamide

Potassium hydroxide (0.272 g.: 4.84 millimole) in ethanol (3 ml.) was added to decafluorodiphenylamine (1.694 g.: 4.85 millimole) in ethanol (4 ml.), and the ethanol was removed by distillation under reduced pressure at room temperature to yield the pale green-yellow potassium salt, which was dissolved in ether (40 ml.) and treated with tetrafluoroterephthaloyl chloride (0.632 g.: 2.3 millimole). The mixture was stirred for 2 hr., with precipitation of potassium chloride, and kept overnight, at room temperature. The precipitate was collected by filtration, washed with dilute hydrochloric acid, followed by water until free of acid, and dried. The crude product (1.36 g., 62% yield) was recrystallised from xylene to yield the bis(tertiary amide), m.p. 289-291° (the mixed m.p. with product previously prepared, ref. 11, page 91, was undepressed).

N,N'-Di(pentafluorobenzoyl)-N,N'-di(pentafluorophenyl)-2,3,5,6-tetrafluorophenylene diamine

(a) Attempted preparation (via K salt of diamine)

Ethanolic potassium hydroxide (0.224 g. KOH: 4.0 millimole, in 10 ml. ethanol) was added to a solution of N,N'-di(pentafluorophenyl)-tetrafluoro-p-phenylene diamine (1.024 g.: 2.0 millimole) in ethanol (16 ml.). The ethanol was removed by distillation under reduced pressure, with gentle warming, and the dark green residue was dissolved in anhydrous ether (30 ml.). The ethereal solution was treated with pentafluorobenzoyl chloride (0.967 g.: 4.2 millimole) in ether (10 ml.), and the mixture was stirred overnight at room temperature. Solid which separated was collected by filtration, and soluble in water, was discarded. The red ethereal solution was refluxed for 5.5 hr. and washed with dilute hydrochloric acid, followed by dilute sodium hydroxide and water, and dried (Na_2SO_4). Removal of the ether by distillation yielded a dark red wax which was recrystallised from petrol (b.p. 100-120°) to yield the starting diamine (0.2 g.), m.p. 178°.

(b) Via Na salt of diamine

N,N'-Di(pentafluorophenyl)tetrafluoro-p-phenylene diamine (5.379 g.) in ether (60 ml.) was added to a suspension of sodium hydride (0.504 g.) in ether (75 ml.) which was prepared under nitrogen. The green solution was refluxed for 2 hr., pentafluorobenzoyl chloride (4.482 g.) was added, the solution turning grey, and then pink during refluxing (2 hr.). The solid was collected by filtration, washed with ether, water, and dilute hydrochloric acid, and with water until free of acid, to yield crude product (8.4 g.), m.p. 282-3°. Recrystallisation from aqueous dimethylacetamide gave pink crystals, m.p. 283-4° which was recrystallised from methyl ethyl ketone to yield a white product (5.8 g.) m.p. 283-4°.

Calc. for $C_{32}F_{24}N_2O_2$: C, 42.7; H, 0.0; F, 50.7; N, 3.11;

Found : C, 43.7; H, 0.26; F, 44.5; N, 3.45;

C, 42.4; H, 0.11; N, 2.93;

5. IMIDES

N,N'-Di(2,3,4,6-tetrafluorophenyl)pyromellitimide

Pyromellitic dianhydride (2.0 g.), 2,3,4,6-tetrafluoroaniline (3.37 g.) and glacial acetic acid (24 ml.) were refluxed for 4 hr. Solid began to separate before the reactants had completely dissolved. The cooled mixture was filtered, and the product (3.8 g.) m.p. 270° was recrystallised twice from benzene to yield pure imide (2.6 g.), m.p. 270.5-271°.

Calc. for $C_{22}H_2F_8N_2O_4$: C, 51.75; H, 0.40; F, 29.8; N, 5.5;

Found : C, 51.5; H, 0.58; F, 32.0; N, 5.9;

The compound was too insoluble for a determination of M.W. by osmometry. Despite the poor analysis for fluorine it was shown to have the correct M.W., by mass spectrometry (result by Dr.R.I.Reed of Glasgow University).

6. ESTERS (AND ACID CHLORIDES)

2,3,5,6-Tetrafluorobenzoyl chloride

The acid (24.7 g., ex I.S.C., m.p. 146-9°), thionyl chloride (65 ml.), and dimethylformamide (0.5 ml.) were refluxed for 24 hr. The mixture was distilled under reduced pressure (b.p. 65.5°/16 mm.), and redistilled to yield the acid chloride (22 g.), b.p. 163°/760 mm.

1,3-Di(2,3,5,6-Tetrafluorobenzoyloxy)-2,4,5,6-tetrafluorobenzene

Tetrafluororesorcinol (1.73 g.) in benzene (40 ml.) was azeotropically dried, with removal of a small amount of the benzene by distillation. Tetrafluorobenzoylchloride (4.17 g.) and N,N-diethylaniline (3.15 ml.) were added, and the solution was refluxed for 3 hr. Colour changes to yellow, through green, then yellow were noted. The turbid solution was diluted with benzene and washed with dilute hydrochloric acid, sodium bicarbonate, and then with water. Removal of the benzene by distillation yielded an oil which crystallised from a mixture of benzene and petrol to yield the ester (3.3 g.), m.p. 68-68.5°.

Calc. for $C_{20}H_2F_{12}O_4$: C, 45.0; H, 0.38; F, 42.7; M.W. 534

Found : C, 45.2; H, 0.11; F, 42.6; M.W. 592

7. POLYBENZOXAZOLES

Poly(2,2'-m-phenylene-6,6'-bibenzoxazole)

(a) From the free base.

3,3'-Dihydroxybenzidine (1.45 g.: 0.0067 mole) was heated at 200° under a stream of nitrogen with polyphosphoric acid until a clear solution was obtained. Isophthalic acid (0.83 g.: 0.005 mole) was added and heating continued for 30 minutes. The hot solution was poured into water and the precipitated polymer filtered off, washed with water, sodium bicarbonate solution, water and finally methanol before drying at 100°/1 mm. to give a grey solid (0.2 g.). The inherent viscosity of a 0.2% w/v solution in concentrated sulphuric acid at 30° was 0.07 dl/g.

(b) From the dihydrochloride. (ref. 3)

The dihydrochloride was prepared by adding an excess of concentrated hydrochloric acid to a solution of the diamine in the minimum of dilute hydrochloric acid. It was recrystallised from hot water. For the polymerisation, as in (a), the 3,3'-dihydroxybenzidine dihydrochloride (1.45 g.: 0.005 mole) was dissolved in polyphosphoric acid (60 g.) at 200° and isophthalic acid (0.83 g.: 0.005 mole) added. After working up a grey polymeric material (1.5 g.) was obtained. The inherent viscosity of a 0.2% w/v solution in concentrated sulphuric acid was 0.28 dl/g.

Poly(2,2'-tetrafluoro-m-phenylene-4,4',5,5',7,7'-hexafluoro-6,6'-bibenzoxazole). (Attempted Preparation)

Dry HCl gas was passed into an ethereal solution of the free base to yield 3,3'-dihydroxy-hexafluorobenzidine dihydrochloride (not analysed).

3,3'-dihydroxyhexafluorobenzidine dihydrochloride (0.374 g.: 0.00094 mole) and polyphosphoric acid (100 g.) were heated at 200° under a slow stream of nitrogen until a clear solution was obtained. Tetrafluoroisophthalic acid (0.274 g.: 0.00094 mole) was added and heating continued for 1 hour. The hot solution was poured into water and the brown solid was collected by filtration, and washed successively with sodium bicarbonate, water, and methanol to leave no residue.

Poly(2,2'-tetrafluoro-p-phenylene-4,4',5,5',7,7'-hexafluoro-6,6'-bibenzoxazole). (Attempted Preparation)

A mixture of perfluoro 3,3'-dihydroxybenzidine dihydrochloride (1.59 g.: 0.004 mole) and polyphosphoric acid (100 g.) was stirred at 200° under a stream of nitrogen until a clear solution was obtained. Tetrafluoroterephthalic acid (0.95 g.: 0.004 mole) was added and after heating a further hour, the hot solution was poured into water. The precipitate was washed with water, sodium bicarbonate solution and methanol, when all dissolved.

8. POLYCARBONATES (AND CHLOROFORMATES)

Tetrafluorophenylene-1,3-bis chloroformate

Tetrafluororesorcinol (99+% pure) was azeotropically dried in benzene and recrystallised from benzene. This (16.6 g.: 0.091 mole) was added to a solution of phosgene (47 g.) in anhydrous ether (80 ml.) at 0-5°. A solution of N,N-diethylaniline (26 ml.) in anhydrous ether (80 ml.) was added over 30 minutes and the mixture was stirred for 24 hours, before filtering off the diethylaniline hydrochloride. The ether was distilled from the filtrate to leave a pale brown liquid (27.8 g.: 99% yield). This was distilled at reduced pressure, to give a main fraction (17.7 g.), b.p. 76.5-78°/3 mm. Crystals (3 g.), m.p. 78-85°, which separated on standing, were collected by filtration and recrystallised from benzene/petrol ether (60-80°) to give white needles, m.p. 78-80°, with an infra-red spectrum consistent with the structure tetrafluororesorcinol.

Calc. for $C_6H_2F_4O_2$: C, 39.6; H, 1.1; F, 41.8; Cl, 0.0;

Found : C, 35.8; H, 2.3; F, 40.4; Cl, 0.0;

The infra-red spectrum of the distillate is consistent with this being the required bischloroformate, but there is a small amount of absorption due to -OH.

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

Found : C, 31.5; H, 0.0; F, 25.0; Cl, 23.0;

A larger quantity of the bischloroformate was prepared from less pure tetrafluororesorcinol which may have contained a small amount of hydrogenic impurity. This tetrafluororesorcinol and its bischloroformate were used in the examination of methods for the preparation of polycarbonates.

m-Phenylene bis(chloroformate)

Resorcinol (27.2 g.: 0.247 mole) was added to phosgene (53 g.: 0.535 mole) in anhydrous ether (250 ml.) at 0-5°, and whilst the mixture was stirred at 0-5°, N,N-diethylaniline (80 ml.) in ether (100 ml.) was added during 30 min. The mixture was kept overnight, the diethylaniline hydrochloride was separated by filtration, and the ether was distilled off, to yield crude m-phenylene bis(chloroformate) (52 g.), m.p. 45-60°. Recrystallisation from petrol (40-60°) gave cream coloured crystals (45.5 g.: 78% theoretical), m.p. 47-8° (Lit. m.p. 46°; ref. 16).

p-Phenylene bis(chloroformate)

Hydroquinone (0.247 mole) was treated as for resorcinol above, to yield crude material (51 g.), m.p. 98-100°. Recrystallisation afforded p-phenylene bis(chloroformate) (44 g.: 76% yield), m.p. 102-3° (Lit. m.p. 100°; ref. 5. Lit. m.p. 102.5-103.5°; ref. 17).

Poly (m-phenylene carbonate)

(a) By melt polymerisation

Resorcinol (5.5 g.; 0.05 mole) and m-phenylene bis(chloroformate) (12.25 g.; 0.05 mole) were kept at 200°/6 hr. When cool the flask was broken to obtain the polymer which was crushed to a fine powder, and heated at 100°/15 mm. for 5 hr. to remove hydrogen chloride and other volatiles.

Calc. for $C_7H_4O_3$: C, 61.8; H, 2.96; Cl, 0.00;

Found : C, 60.9; H, 3.57; Cl, 1.33;

The inherent viscosity at 30° determined from 0.5% solution in N,N-dimethylacetamide was 0.18 dl/g.

(b) By interfacial condensation in tetrachloroethane/aqueous sodium hydroxide

Resorcinol (5.5 g.; 0.05 mole) in normal sodium hydroxide (100 ml.) and m-phenylene bis(chloroformate) (14.1 g.; 0.06 mole) in sym.-tetrachloroethane (120 ml.), were stirred together. The thick emulsion was diluted with water (70 ml.), and was stirred for 24 hours, with the addition of sodium hydroxide as required to maintain alkalinity. The mixture was added to acetone (400 ml.), the polymer was collected by filtration and washed with water and acetone. Heating at 100°/10 mm. for several hours gave the pale yellow polycarbonate (13.5 g.) free from volatiles.

Found: C, 60.22; H, 3.00; Cl, 1.04; O, 33.5; Total: 97.76%

The inherent viscosity at 30°C for 0.5% solution was 0.19 dl/g. in dimethyl sulphoxide and 0.17 dl/g. in N,N-dimethylacetamide.

The poly(m-phenylene carbonate) (5 g.) was heated at 250°/0.3 mm. for 5 hours. The product was a hard rubber-like substance, which could not be removed from the flask. On breaking the flask, the polymer and glass could not be separated. A small amount of glass-free polymer was removed from the centre of the mass and dissolved in hot dimethyl sulphoxide. An inherent viscosity 0.06 dl/g. was obtained at 30° i.e. a decrease in viscosity from 0.19 dl/g.

(c) By interfacial polycondensation in tetrachloroethane/aqueous sodium bicarbonate

Resorcinol (3.3 g.; 0.03 mole), water (70 ml.), and sodium bicarbonate (10 g.) were stirred vigorously. A solution of m-phenylene bis(chloroformate) (8.0 g.; 0.035 mole) in sym.-tetrachloroethane (70 ml.) was added, and stirring was continued for 24 hours. The mixture was poured into acetone and the polymer was collected by filtration, washed with dilute hydrochloric acid and with water, and dried at 120°/5 mm. The cream coloured polycarbonate (7.8 g.) had an inherent viscosity 0.23 dl/g. at 30°, determined in 0.5% solution in dimethylacetamide.

Found: C, 60.6; H, 3.0; Cl, 1.14;

(d) By interfacial polycondensation in tetrachloroethane/aqueous calcium carbonate

The method and scale were the same as in (c) except that the sodium bicarbonate (10 g.) was replaced by calcium carbonate (10 g.). The cream coloured polymer (3.6 g.) had an inherent viscosity 0.086 dl/g. at 30° in 0.5% solution in N,N-dimethylacetamide.

Found: C, 58.05; H, 2.67; Cl, 2.97;

(e) In N,N-dimethylacetamide

(i) Behaviour of m-phenylene bis(chloroformate) in dimethylacetamide

A solution of m-phenylene bis(chloroformate) in dimethylacetamide was prepared. After about five minutes, there was a vigorous exothermic reaction, with much evolution of acidic vapour, and the solution became brown and viscous. Heating at 100° for 2 hours did not appear to increase the viscosity. The solution was poured into cold water, to give a sticky solid. After standing overnight this had changed to a thick yellow oil.

(ii) Polymerisation

m-Phenylene bis(chloroformate) (4.7 g.; 0.02 mole) was added in small portions to resorcinol (2.2 g.; 0.02 mole) in N,N-dimethylacetamide (50 ml.). When the reaction had subsided (30 minutes), the inherent viscosity was determined, and again after maintaining the solution at 100° for 15 hours. There was only a slight increase to 0.06 dl/g. over this period.

(f) In tetrachloroethane

Resorcinol (2.2 g.: 0.02 mole) was partly dissolved in tetrachloroethane (20 ml.) and a solution of m-phenylene bis-(chloroformate) (4.7 g.: 0.02 mole) in tetrachloroethane (20 ml.) was added. There was no temperature rise and solution was incomplete. Tetrachloroethane (40 ml.) was added and the mixture was refluxed for 2 hour periods, cooling each time to check that the amount of insoluble material was decreasing. After a total of 16 hours refluxing only a small amount of insoluble material remained and the cold solution was poured into acetone. No polymer was precipitated even on dilution with water.

(g) In nitrobenzene

Resorcinol (2.2 g.;0.02 mole) in nitrobenzene (20 ml.) was mixed with a solution of m-phenylene bis(chloroformate) (4.7 g.; 0.02 mole) in nitrobenzene (20 ml.). There was no temperature rise, but solution was complete in 5 minutes. The solution was refluxed, when hydrogen chloride was evolved and the viscosity of the solution increased. After 15 hours refluxing, the viscosity had become constant, and the nitrobenzene was removed by distillation. The water was decanted, and the residue ground up, washed with water, and with acetone, and dried at 100°/8 mm. The polymer (3.85 g.) was obtained as a brownish-grey powder of inherent viscosity 0.19 dl/g. determined from a 0.5% solution in N,N-dimethylacetamide at 30°.

Poly(p-phenylene carbonate)

p-Phenylene bis(chloroformate) (14.1 g.: 0.06 mole) in sym.-tetrachloroethane (120 ml.) was added to a rapidly stirred solution of hydroquinone (5.5 g.; 0.05 mole) in normal sodium hydroxide. The emulsion was stirred for 24 hours, added to acetone, and the polymer was collected by filtration, washed with water, acetone, and dried at 120°/10 mm. The polymer (12.2 g.), a cream coloured powder, insoluble in dimethyl sulphoxide and in hexamethylphosphoramide, had an inherent viscosity 0.05 dl/g. at 30° from a 0.5% solution in 98% sulphuric acid.

Found: C, 57.9; H, 3.5; Cl, 0.41; O, 31.2;

[There was a grey residue (0.163 mg.) from the combustion of 4.070 mg.]

Poly(tetrafluoro-m-phenylene carbonate)

(a) Interfacial polycondensation

Tetrafluororesorcinol (1.82 g.; 0.01 mole) was stirred vigorously with sodium bicarbonate (10 g.) in water (60 ml.) and a solution of tetrafluorophenylene-1,3-bis chloroformate (3.07 g.:0.01 mole) in tetrachloroethane (60 ml.) was added. After stirring for 24 hours, the mixture was poured into acetone, and the solution was diluted with water. There was no precipitate.

(b) Solution polymerisation in nitrobenzene

A solution of tetrafluororesorcinol (1.82g. ; 0.01 mole) in dry nitrobenzene (20 ml.) was added to a solution of tetrafluorophenylene-1,3-bis chloroformate (3.07 g.: 0.01 mole) in dry nitrobenzene (20 ml.) and the resulting solution refluxed (bath) for 6 hours. The nitrobenzene was steam distilled and the residual solid was collected by filtration, washed with water, acetone, and dried at 100°/0.2 mm. to give a black brittle solid (0.034 g.).

Part of the polymer (0.0198 g.) was heated with dimethyl acetamide (10 ml.) and the insolubles filtered off. Only a small amount (0.0018 g.) had dissolved and the inherent viscosity of this solution at 30°C was 2.1 dl/g.

(c) Melt polymerisation

A mixture of tetrafluororesorcinol (1.82 g.: 0.01 mole) and tetrafluorophenylene-1,3-bis chloroformate (3.07 g.; 0.01 mole) was heated at 200° (bath) for 6 hours. The cold reaction mixture was extracted with acetone. The residue (0.0123 g.) was a black brittle solid. A small amount (0.0021 g.) of this dissolved in dimethyl acetamide (20 ml.). The inherent viscosity at 30° was 2.1 dl/g.

9. POLYHYDRAZIDES/POLYOXADIAZOLES (cf. Ref. 19)

Where N,N-dimethylacetamide (DMAC) was employed as a solvent, it was purified as described under Section 10 of Experimental.

Hexamethylphosphoramide (ex Aldrich Chemical Co.) was redistilled in vacuo, dried over molecular sieve and treated with a polymeric acid chloride (10 g.) on the steam bath for 2 hours. The polymer was separated by filtration and the hexamethylphosphoramide was redistilled (b.p. 112°/13 mm.). The polymeric acid chloride referred to above was prepared by treating anhydrous Amberlite IRC-50 ion exchange resin with thionyl chloride. This acid chloride was employed to remove traces of material exhibiting NH absorbance in the I.R. The HMP was stored over molecular sieve.

PH(1) Isophthaldihydrazide/Isophthaloyl chloride

Following the method of PH(5), but employing the hydrazide and acid chloride in HMP, an inherent viscosity 0.27 dl/g. was obtained.

PH(2) Isophthaldihydrazide/Isophthaloyl chloride

Employing DMAC in place of HMP an inherent viscosity 0.3 dl/g. was obtained. Gelling occurred with 25 mmole hydrazide and 24.33 mmole chloride. No more chloride was added. Isolation was as for pH 5.

PH(3) Hydrazine/Isophthaloyl chloride

Isophthaloyl chloride (2.13 g.) in HMP (15 ml.) was added dropwise over 35 min. to anhydrous hydrazine (0.33 ml.) in HMP (20 ml.) at 5-10°. The polyhydrazide was precipitated, after four days at room temperature, by adding the solution to water (120 ml.) at 5°. The cream coloured polyhydrazide (1.5 g.) had an inherent viscosity 0.12 dl/g. at 30° from 0.5% solution in dimethyl sulphoxide.

PH(4) Hydrazine/Tetrafluoroisophthaloyl chloride

Tetrafluoroisophthaloyl chloride (2.90 g.) in HMP (15 ml.) gave a pale yellow solution which was added to anhydrous hydrazine (0.33 ml.), etc., and the mixture of solid plus liquid exactly as described under PH(6) yielded cream coloured polyhydrazide (2.0 g.), inherent viscosity 0.11 dl/g. from a 0.5% solution in dimethyl sulphoxide at 30°.

PH(5) Tetrafluoroterephthaldihydrazide/Tetrafluoroterephthaloyl chloride

It was intended to add the acid chloride portionwise to the solution of the hydrazide, but because the polymer began to separate from solution, this plan was modified, as follows.

The acid chloride (256.1 mg. ; 9.31 millimole) in DMAC (10 ml.) was added to the hydrazide (266 mg.: 10.0 millimole) in DMAC (50 ml.), with a rise in temperature from 18° to 36°. Whilst the acid chloride was being washed from the dropping funnel into the polymer solution by DMAC (10 ml.) polymer began to separate as shown by the formation of turbidity. The remainder of the acid chloride (18.9 mg.; 0.69 millimole) in DMAC (10 ml.) was added ca. 10 min. after the first addition and was washed from the dropping funnel into the mixture by DMAC (10 ml.).

The mixture was stirred for 4 hours, kept overnight, and the precipitated polymer was filtered off, washed with DMAC and with water until free of chloride ion. The polyhydrazide (3.8 g.) changed from cream to a pale yellow on drying at 100°/0.8 mm. Inherent viscosity at 30° from a 0.5% solution in dimethyl sulphoxide : 0.29 dl/g. No softening point was noted up to 400°, but the polymer became dark brown at elevated temperature.

PH(6) Hydrazine/Tetrafluoroterephthaloyl chloride

Tetrafluoroterephthaloyl chloride (2.9 g.) in HMP (15 ml.) gave a yellow solution which changed to cherry red on standing. This was added dropwise to a stirred solution of anhydrous hydrazine (0.33 ml.) in HMP (20 ml.) over 35 min. at 5-10°.

During the early part of the addition white solid separated. The mixture was stirred for a further 2 hours and kept for four days before adding to water (120 ml.) at 5° (temperature rise to 21° on mixing). The polymer was collected by filtration and was washed free of acid by trituration with water before drying at 100°/0.1 mm., to yield polyhydrazide (2.3 g.) as a cream coloured material of inherent viscosity 0.11 dl/g. determined from a 0.5% solution in dimethyl sulphoxide at 30°.

10. POLYAMIC ACIDS/POLYIMIDES

The references (a)-(e) in experiments PI(1)-PI(9) refer to the samples of perfluoro diamines described in Part 3 of the Discussion. The diamine from the amination of pentafluoroaniline, referred to under (d) in Part 3 (Polyamic Acids/Polyimides) was purified as follows:

Tetrafluoro-m-phenylene diamine prepared from pentafluoroaniline and ammonia has been shown to contain the o- and p- isomers (ref. 11, p.87). This material (32.4 g.), phthalic anhydride (59.4 g.) and glacial acetic acid (450 ml.) were stirred under reflux for 2.1/4 hr. The mixture was cooled, and the white crystals were collected by filtration, washed with glacial acetic acid (50 ml.) and the dark filtrates were discarded.

The above crude diphthaloyl derivative was stirred under reflux with glacial acetic acid (1000 ml.) and filtered hot. The solid collected (25 g.), m.p. 325-7°, was washed free of acid with water, and dried. The filtrates yielded impure product, (16.4 g.), m.p. 319°, softening at 312°.

The purer fraction was recrystallised from 2-ethoxyethanol to yield m-diphthalimidotetrafluorobenzene (21.7 g.), m.p. 327-327.5°, m.p. unchanged on further recrystallisation.

Calc. for $C_{22}H_8F_4N_2O_4$: C, 60.0; H, 1.83; F, 17.3; N, 6.37;

Found : C, 60.1; H, 1.99; F, 17.3; N, 6.50;

This product (14.5 g.), ethanol (350 ml.) and hydrazine hydrate (4.0 ml.) were boiled for 40 min. Initially a solution was formed, from which crystals separated. The mixture was distilled to dryness, and the residue was partitioned between ether and dilute sodium hydroxide. The ethereal solution was washed free of alkali; dried ($MgSO_4$). A considerable proportion of the ethereal solution was accidentally lost, so that the yield of diamine (3.2 g.), m.p. 131-2° (Lit. m.p. 129.5-131°, ref. 18) obtained by distilling to dryness, was artificially low.

No impurities were detected in this diamine by the gas chromatographic conditions previously employed to detect o- and p- isomers in other samples. The diamine was sublimed at 70°/0.5 mm. to remove possible traces of volatiles that had not been removed by the distillation to dryness.

Purification of N,N-dimethylacetamide

Dimethylacetamide (ex British Drug Houses) was dried over Linde Molecular Sieve 5A, fractionally distilled (the fraction of b.p. 61°/15 mm. was collected) and stored over molecular sieve.

Purification of pyromellitic dianhydride (PMDA)

Pyromellitic dianhydride (ex Koch-Light) was recrystallised twice from acetic anhydride, resublimed twice, recrystallised from redistilled acetic anhydride and resublimed.

PI(1) PMDA/m-phenylene diamine

The polyamic acid was prepared by the technique described previously (ref. 11, page 109). The major part (5.1743 g.: 23.72 millimoles) of the powdered PMDA was added to a well stirred solution of redistilled m-phenylene diamine (2.7077 g.: 25.07 millimoles) in dimethylacetamide (100 ml.) and the remainder of the PMDA (0.291 g.: 1.35 millimoles) was added in small portions at intervals. Just before each addition a 1 ml. sample was withdrawn from the mixture, weighed, made up to 10 ml. with dimethyl acetamide, and the inherent viscosity of this solution was determined.

The inherent viscosity increased from 0.30 dl/g. to a maximum of 1.40 dl/g. as shown in Table 5.

TABLE 5

Pyromellitic Dianhydride		Molar Ratio	Time of stirring of Polymer Solution at room temperature after addition	Inherent Viscosity dl/g.
Total Wt. (g)	Total Moles	PMDA/AMINE		
5.1743	0.02372	0.9465	2½ hours	0.30
5.2645	0.02414	0.9632	3 hours	0.37
5.3397	0.02448	0.9768	18 hours	0.45
5.4101	0.02480	0.9896	4 hours	0.72
5.4655	0.02507	1.00	4 hours	1.40
			70 hours	1.24

On standing 70 hr. the inherent viscosity reduced to 1.24 dl/g. Removal of the solvent by distillation from a flask at reduced pressure on the steam bath was not satisfactory, in that an intractable hard resin was obtained. A portion was extracted from the mass and converted to polyimide at 300°/15 mm. for 6 hr.

A second part of the polyamic acid solution was evaporated in a nitrogen stream at 20° rising to 300°, followed by conversion to polyimide in nitrogen at 300° for two hours. This polymer still contained traces of NH, detected by absorbance in the infra-red; it is designated PI(1) in Table 3.

PI(2) PMDA/Tetrafluoro-m-phenylene diamine

Tetrafluoro-m-phenylene diamine (b) of purity 99.2%, in dimethylacetamide, was treated with PMDA as described under PI(1) and PI(8). The inherent viscosity was ca. 0.085 dl/g., and this value increased to 0.098 dl/g. on maintaining the solution at 45-50° for 8 hours. The polyamic acid was converted to polyimide as for PI(1) but the elemental analysis suggests incomplete cyclodehydration.

Calc. for $C_{16}H_2F_4N_2O_4$: C, 53.05; H, 0.55; N, 7.75;

Calc. for $C_{16}H_4F_4N_2O_5$: C, 50.5; H, 1.06; N, 7.4;

Found : C, 51.4; H, 0.82; N, 8.0;

PI(3) PMDA/Tetrafluoro-m-phenylene diamine

Using the same concentration of reagents as in PI(2), an equivalent of PMDA was added to the diamine (b) in DMAC at 50°. The solution was stirred at 50° and the inherent viscosity was determined at intervals.

Time elapsed	Inherent Viscosity
28 hours	0.18 dl/g.
49 hours	0.23 dl/g.
102 hours	0.20 dl/g.

PI(4) PMDA/Tetrafluoro-m-phenylene diamine

As for PI(2) but employing diamine (c) of 99+% purity, an inherent viscosity of 0.065 dl/g. was obtained. This value increased to 0.085 dl/g. on maintaining the solution at 60° for 6 hours.

PI(5) PMDA/Tetrafluoro-m-phenylene diamine

The diamine (c) was added in controlled amounts to the PMDA in DMAC at room temperature. By this reversal of the usual order of addition an inherent viscosity 0.06 dl/g. was obtained when equivalent amounts of the two reagents were present.

PI(6) PMDA/Tetrafluoro-m-phenylene diamine

As for PI(2) but employing diamine (d) of apparently 100% purity. An inherent viscosity ca. 0.08 dl/g. was obtained, which decreased on heating the solution at 60° for 4 hours.

PI(7) PMDA/p-Phenylene diamine

As for PI(1) to give a polyamic acid of inherent viscosity 2.4 dl/g. The polyimide was obtained by evaporation of the solvent from a film at a temperature rising to 180°, in nitrogen, followed by 2 hours at 300°.

PI(8) PMDA/Tetrafluoro-p-phenylene diamine

Tetrafluoro-p-phenylene diamine [2.708 g.; 15.04 millimoles; purity 98.9%, (a)] in dimethylacetamide (100 ml.) was treated with PMDA

(3.054 g.; 14.01 millimoles) and subsequently five additions of PMDA were made to bring the final weight of PMDA to 3.336 g. The inherent viscosity rose slowly to ca. 0.08 dl/g., reaching this maximum over twelve days, i.e. ten days after the final addition. There was no increase in viscosity when this solution was heated at 60° for 4 hours.

PI(9) PMDA/Octafluorobenzidine

As for PI(2) but employing octafluorobenzidine (e), an inherent viscosity 0.05 dl/g. was obtained, i.e. only a marginal increase over the initial 0.04 dl/g. was caused by further additions of PMDA. The polyamic acid was converted to polyimide as for PI(1), but there may have been incomplete cyclodehydration.

Calc. for $C_{22}H_2F_8N_2O_4$: C, 51.75; H, 0.4; N, 5.5;

Calc. for $C_{22}H_4F_8N_2O_5$: C, 50.0; H, 0.76; N, 5.3;

Found : C, 50.3; H, 0.7; N, 6.75;

PI(10) Reactivity of octafluorobenzidine towards PMDA in DMAC

(i) A mixture of pyromellitic dianhydride (0.2181 g.: 0.01 mole), octafluorobenzidine (0.3282 g.; 0.01 mole) and dimethyl acetamide (50 ml.) was stirred at 50°, 5 ml. samples being taken at intervals and the infra-red absorbance of the anhydride group at 1850 cm^{-1} measured. For comparison, a solution of pyromellitic dianhydride (0.2181 g.) in dimethyl acetamide (50 ml.) was treated in a similar manner.

Time at 50° (hours)	Absorbance due to anhydride group	
	Blank	Reaction mixture
0	0.10	0.11
18	0.11	0.13
24	0.12	
42	0.12	0.09
66	0.13	0.04
90	0.13	0.0

The increase in absorbance of the blank appears to be mainly due to attack on the cell plates by the solution causing an increase in cell length. This effect must also be allowed for in the absorbance figures for the reaction mixture.

(ii) Another polyamic acid solution was prepared at ten times the above concentration and the inherent viscosity was measured at intervals rising from 0.044 dl/g. after 4 hours at 50° to 0.44 after 24 hours at 50°. The viscosity remained constant during a further 66 hours at 25°. Part of the polyamic acid solution was converted to the polyimide by heating on a shallow tray under nitrogen, at 160° for 2 hours and then at 300° for 2 hours. The polyimide was obtained as a powdery deposit with no film formation.

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PART III

FLUIDS

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A. INTRODUCTION

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

In this report work on syntheses of perfluoro-(1,3-bis(octyl)-benzene), perfluoro-(3,3'-bis(n-butyl)biphenyl), perfluoro-(1,6-diphenyl-hexane), and perfluoro-n-propyl pentafluorophenyl sulphide is described.

B. SUMMARY

2,3,4,6-Tetrafluorophenyl-lithium and perfluoro-octanal at -70° gave perfluoroheptyl 2,3,4,6-tetrafluorophenyl carbinol in 48% yield. With two moles of n-butyl lithium and one mole of perfluoro-octanal this carbinol gave 2,4,5,6-tetrafluorophenylene-1,3-bis(perfluoroheptyl carbinol) which was oxidised to perfluoro-(1,3-bis(octanoyl)benzene).

Lithiation of 3,3'-dihydro-octafluorobiphenyl and reaction of the organometallic compound with perfluorobutyraldehyde at -70° gave 3,3'-bis(1-hydroxy-2,2,3,3,4,4,4-heptafluorobutyl)octafluorobiphenyl (96% crude yield). Oxidation of this dihydroxy-compound gave perfluoro-(3,3'-bis(n-butyryl)biphenyl) in 42% yield.

The reaction between pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride in ether appears to have given perfluoro-(1,4-bis(benzoyl)butane) in 70% yield.

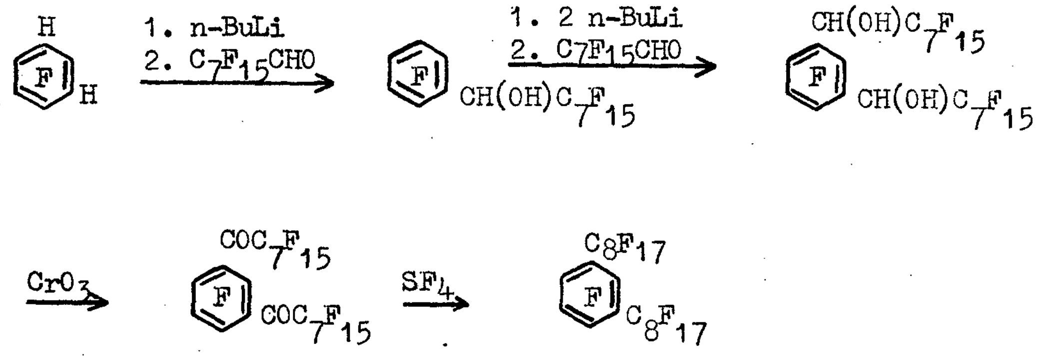
Attempts to form perfluoro-n-propyl pentafluorophenyl sulphide by reaction of cuprous pentafluorothiophenate with heptafluoro-1-iodopropane in dimethylformamide solution have not been successful.

C. DISCUSSION

1. PERFLUORO-(1,3-BIS(OCTYL)BENZENE) (I)

One type of compound to be prepared for evaluation as a thermally stable fluid is a perfluoro(dialkyl benzene), (ref. 1). Compound (I) was selected for synthesis, but initial experiments were carried out on the synthesis of a perfluoro(monoalkylbenzene) to test methods of preparation.

An attempted synthesis of perfluoro(octylbenzene), by treatment of perfluoro(octanoylbenzene) with sulphur tetrafluoride, failed because perfluoro(octanoylbenzene) could not be prepared by direct reaction of methyl perfluoro-octanoate with pentafluorophenylmagnesium bromide (ref. 2). However, reaction between pentafluorophenyl-lithium and perfluoro-octanal gave perfluoroheptyl pentafluorophenyl carbinol in 49% yield and it thus seems likely that the following route for the preparation of (I) will succeed:-

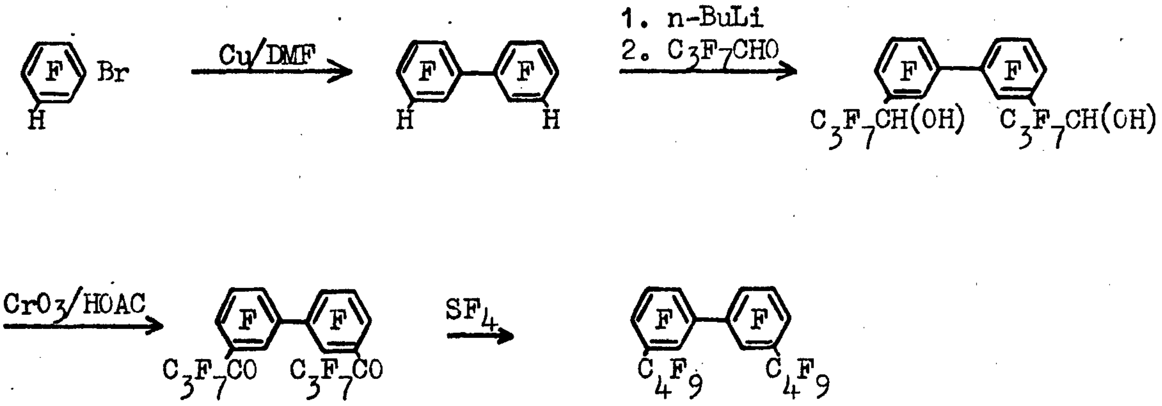


The perfluoro-octanal required for this synthesis was prepared by reduction of methyl perfluoro-octanoate with lithium aluminium hydride (ref. 3) and dehydration of the aldehydrol formed by distillation from concentrated sulphuric acid. Difficulty was encountered in getting aldehyde of better than 90% purity. The ester from which it was obtained was of about 88% purity (when analysed on a polypropylene glycol/celite column) and the impurities could not be removed by distillation. They may be isomeric or homologous esters derived from other carboxylic acids present in commercial perfluoro-octanoic acid.

1,2,3,5-Tetrafluorobenzene was metalated with one equivalent of n-butyl-lithium at -70° and the monolithio-compound was treated with perfluoro-octanal giving perfluoroheptyl 2,3,4,6-tetrafluorophenyl carbinol in 45% yield. The carbinol was treated with two equivalents of n-butyl-lithium and one equivalent of perfluoro-octanal in tetrahydrofuran at -70° giving 2,3,4,6-tetrafluorophenylene-1,3-bis(perfluoroheptylcarbinol) in 31% yield. Oxidation of this compound with chromium trioxide in acetic acid gave a 48% yield of perfluoro-(1,3-bis(octanoyl)benzene). The sequence is being repeated to produce more of (I) before the final stage of the reaction is investigated.

2. PERFLUORO-(3,3'-BIS(n-BUTYL)BIPHENYL) (II)

A second type of compound to be evaluated as a thermally stable fluid is a perfluoro(dialkylbiphenyl) (ref. 1) and the synthesis of II is being carried out using the following reaction sequence:-



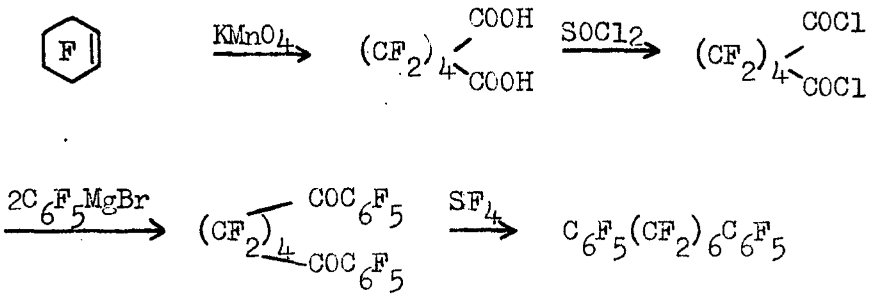
3,3'-Dihydro-octafluorobiphenyl was prepared in 63% yield and 99+% purity by an Ullmann reaction on 2,3,4,6-tetrafluorobromobenzene. Treatment of this compound with two equivalents of n-butyl-lithium in hexane/tetrahydrofuran at -70° apparently yielded the 3,3'-dilithio-derivative since the absence of butyl-lithium was demonstrated by a negative Gilman Colour Test IIA (ref. 4). Reaction of the dilithio-compound with heptafluorobutyraldehyde, prepared in 68% yield by lithium aluminium hydride reduction of methyl heptafluorobutyrate (ref. 3), gave the viscous 3,3'-bis(1-hydroxy-2,2,3,3,4,4,4-heptafluorobutyl)octafluorobiphenyl in 96% crude yield. Attempts to purify this material by distillation and crystallisation were not successful and the crude material was therefore oxidised with the large excess of chromium trioxide in acetic acid found necessary in trial experiments. Perfluoro-(3,3'-bis(n-butyryl)biphenyl) was obtained in 42% yield and 92% purity. An analytical sample was obtained by re-distillation and the use of preparative scale gas chromatography.

Treatment of a sample of 92% purity (II) with phenylhydrazine gave a vigorous reaction and a product with a sharp melting point was isolated. This is probably the bis(phenylhydrazone) but an unsatisfactory carbon analysis was obtained.

The action of sulphur tetrafluoride on II is now under investigation in order to complete the synthesis.

3. PERFLUORO(1,6-DIPHENYLHEXANE) (III)

A third type of structure for evaluation as a thermally stable fluid (ref. 1) is a perfluoro-(α,ω-bis(phenyl)alkane). As a first example of this type, the synthesis of (III) was begun since starting materials were fairly readily available. The proposed reaction sequence is:-



Oxidation of decafluorocyclohexene with potassium permanganate in acetone (ref. 5) gave octafluoroadipic acid in 42 and 53% yields in two experiments. An attempted synthesis of the penultimate compound in the sequence above by direct reaction of the acid with two equivalents of pentafluorophenylmagnesium bromide failed. (Other workers (ref. 6) have successfully reacted phenylmagnesium bromide with octafluoradipic acid to give a diketone.) Treatment of octafluoroadipic acid with thionyl chloride in the presence of potassium hydroxide (ref. 7) gave octafluoroadipoyl chloride in yields of 56 and 69%. Reaction of pentafluorophenylmagnesium bromide with octafluoroadipoyl chloride in ether then gave a 70% yield of 99+% pure material which has an infra-red spectrum in accord with the expected perfluoro-(1,4-bis(benzoyl)butane) structure. Confirmation of this structure by elemental analysis is awaited.

A reaction between pentafluorophenylmagnesium bromide and octafluoroadipoyl chloride in tetrahydrofuran yielded a neutral product, believed to be a di(tertiary alcohol) formed by further Grignard attack on the first formed diketone, and an acidic product which may be perfluoro-(5-benzoylpentanoic acid). This reaction will be further investigated since the latter compound may prove to be a useful intermediate for further fluid syntheses.

4. PERFLUORO-n-PROPYL PENTAFLUOROPHENYL SULPHIDE (IV)

Several reactions proposed for the preparation of compounds containing fluoroalkyl chains linked via a sulphur atom to a fluorinated aromatic ring (ref. 1) involve the reaction of a cuprous salt of the appropriate polyfluorothiophenol with a fluoroalkyl iodide. Similar reactions using fluoroaryl bromides are known (ref. 8). The reaction of heptafluoro-1-iodopropane with cuprous pentafluorothiophenate was investigated first. In an initial reaction carried out with equimolar quantities of reagents in dimethylformamide solution at 150-155°, little, if any, of (IV) was formed. The iodide was recovered only in small yield (3.2%) and the main product was volatile material which, although not analysed, was thought to be hexafluoropropene or heptafluoropropane. The latter compound could easily arise from formation of the heptafluoro-n-propyl radical by thermal dissociation of the iodide and subsequent hydrogen abstraction from dimethylformamide. In a second reaction, carried out at 100°, a negligible amount of very volatile material was formed but 45% of the cuprous pentafluorothiophenate was recovered. Again little, if any, of (IV) appeared to have been formed.

At this stage octafluoroadipic acid became available (see 3 above) and was converted to its disilver salt in 96% yield. Reaction of this with elemental iodine (ref. 9) has given 1,4-di-iodo-octafluorobutane in 36% yield. This di-iodide has a boiling point of 150° and is a more convenient starting material than heptafluoro-1-iodopropane which has to be sealed in glass ampoules for reactions at about 150°.

D. EXPERIMENTAL

1. PERFLUOROHEPTYL PENTAFLUOROPHENYL CARBINOL

a. Attempted preparation from methyl perfluoro-octanoate and pentafluorophenylmagnesium bromide

(1) Methyl perfluoro-octanoate

Perfluoro-octanoic acid (250g., 0.604 mole), methanol (21.3g., 0.687 mole), and 98% sulphuric acid (39.6g., 0.396 mole) were heated under reflux for 5 hours. The mixture was cooled, the organic layer was separated and dried ($CaCl_2$). The dry liquid was distilled through a 6 inch column packed with Dixon gauzes giving methyl perfluoro-octanoate (131.9g.), b.p. 159-164°/761 mm. The combined lower- and higher-boiling fractions (87.2g.) were again esterified giving a further quantity of the ester. The combined products (185g., 71.5%) were methyl perfluoro-octanoate, $n_D^{19.5}$ 1.3060, infra-red spectrum No. 3772. The purity determined by gas chromatography (dinonyl phthalate at 100°) was 99%.

Anal. Calc. for $C_9H_3F_{15}O_2$: C, 25.2; H, 0.7; F, 66.6%

Found: C, 24.1; H, 1.1; F, 65.4

Methyl perfluoro-octanoate (improved method)

Perfluoro-octanoic acid (433.5g., 1.047 mole), AnalaR methanol (36.7g., 1.145 mole) and sulphuric acid (98.4%, 104.4g., 1.048 mole) were stirred and boiled for 4½ hours until the vapour temperature (154°) and liquid temperature (157°) rose no higher. The mixture was cooled and the two layers were separated. The lower organic layer was distilled twice giving the ester (340.1g., 76%), b.p. 157-164°, and unchanged acid (64.2g., 15%), b.p. 190-195°.

The conversion of acid to ester is 89%. The ester was of 88% purity and contained 5 impurities of lower gas chromatography retention time and 3 of higher retention time (polypropylene glycol, 100°, 2 metre column).

(2) Reaction of methyl perfluoro-octanoate with pentafluorophenylmagnesium bromide

A solution of methyl perfluoro-octanoate (14.22g., 0.033 mole) in ether (25 ml.) was added over 40 minutes to the Grignard reagent prepared from magnesium (0.8g., 0.033g. atom) and bromopentafluorobenzene (8.23g., 0.033 ml.) in ether (35 ml.). The mixture was stirred at -70° for 1 hour, then warmed to room temperature and stirred overnight, then acidified with 2$\underline{N}$ sulphuric acid (55 ml.). Distillation of the dried organic layer gave methyl perfluoro-octanoate (9.3g.) and then perfluoro-octanoic acid containing a trace of an impurity, possibly the desired ketone.

b. Preparation from perfluoro-octanal and pentafluorophenyl-lithium

(1) Perfluoro-octanal hydrate

Lithium aluminium hydride (4.24g., 0.113 mole) was stirred for 2 hours with dry ether (141 ml.). The resulting suspension was added during 2 hours into a solution of methyl perfluoro-octanoate (176.4g., 0.412 mole) in ether (219 ml.) kept at -60 to -65°. When the addition was complete ethanol (11 ml., 0.193 mole) was added. The mixture was allowed to warm to room temperature and was then poured onto a mixture of crushed ice (500g.) and sulphuric acid (32 ml., s.g. 1.84). The aqueous layer was extracted with ether (3 x 50 ml.). The ether was distilled then the aldehyde hydrate (163g.) was distilled at 137-140°/700 mm.

(2) Perfluoro-octanal

Perfluoro-octanal hydrate (122.7g.) was heated with sulphuric acid (60 ml.) giving perfluoro-octanal (98.3g., 74.5% yield from methyl perfluoro-octanoate), b.p. 120-122°, 90% pure by gas chromatography, I.R. spectrum No. 3888. Redistillation did not improve the purity of the aldehyde. The impurities are probably derived from isomeric acids present in the commercial perfluoro-octanoic acid starting material. This aldehyde was used for the preparations now described.

(3) Perfluoroheptyl pentafluorophenyl carbinol

Pentafluorobenzene (3.50g., 0.0208 mole) dissolved in tetrahydrofuran (10 ml.) was added, under nitrogen, to a hexane solution of n-butyl-lithium (9.75 ml., 2.12N) in tetrahydrofuran (25 ml.) at -70°. The mixture was stirred at -70° for 30 minutes, then perfluoro-octanal (8.20g., 0.0208 mole) was added. After stirring the mixture for 30 minutes at -70° it was allowed to warm to room temperature and acidified with 1N hydrochloric acid (55 ml.). The aqueous layer was extracted with methylene chloride, the extract combined with the organic layer, and dried. Distillation of the extract gave perfluoroheptyl pentafluorophenyl carbinol (5.2g., 49%), b.p. 84-90°/0.3 mm., m.p. 46-48°, of 96% purity by gas chromatography. (I.R. No. 4020).

Anal. Calc. for $C_{14}H_2F_{20}O$: C, 29.7; H, 0.35; F, 67.1%

Found: C, 29.6; H, 0.30; F, 66.8

2. PERFLUORO-1,3-BIS(OCTANOYL)BENZENE

(1) Perfluoroheptyl-2,3,4,6-tetrafluorophenyl carbinol

1,2,3,5-Tetrafluorobenzene (11.02g., 0.0736 mole) in ether (175 ml.) was kept at -70° while n-butyl lithium (35 ml. of a 2N solution in hexane) was added. After 30 minutes, a solution of perfluoro-octanal (29g., 0.0736 mole) in ether (25 ml.) was added. The product was isolated in the manner described above and distilled to give perfluoroheptyl 2,3,4,6-tetrafluorophenyl carbinol, b.p. 71-75°/0.25 mm., (95% purity, 16.4g., 48%). I.R. No. 3983.

Anal. Calc. for $C_{14}H_3F_{19}O$: C, 30.7; H, 0.6; F, 65.9%

Found: C, 31.8; H, 1.5; F, 65.5

(2) 2,4,5,6-Tetrafluorophenylene-1,3-bis(perfluoroheptyl carbinol)

Using the procedure described above, perfluoroheptyl 2,3,4,6-tetrafluorophenyl carbinol (13.83g., 0.0253 mole), n-butyl lithium (24.2 ml., 2.1N in hexane, 0.0506 mole) and perfluoro-octanal (10.02g., 0.0253 mole) were reacted in tetrahydrofuran (75 ml.) at -70°. Distillation of the products gave:

(i) perfluoroheptyl 2,3,4,6-tetrafluorophenyl carbinol (4.9g.), b.p. 66-68°/0.4 mm.

(ii) 2,4,5,6-tetrafluorophenylene-1,3-bis(perfluoroheptyl carbinol) (7.33g., 30.7%), b.p. 160-180°/0.25 mm.

Fraction (ii) was redistilled to give an analytical sample. I.R. No. 3990a.

Anal. Calc. for $C_{22}H_4F_{34}O_2$: C, 28.0; H, 0.42; F, 68.2%

Found: C, 29.2; H, 0.6; F, 66.2

(3) Perfluoro-(1,3-bis(octanoyl)benzene)

A solution of chromium trioxide (2.0g., 0.020 mole) in acetic acid (25 ml.) and water (5 ml.) was added over 45 minutes to a solution of 2,4,5,6-tetrafluorophenylene-1,3-bis(perfluoroheptyl carbinol) (7.361g., 0.0078 mole) in acetic acid (25 ml.) at 50-60°. The mixture was heated to 80° during 1 hour, then cooled and diluted with water (200 ml.). The product separated as a lower layer. The aqueous layer was extracted with methylene chloride (3 x 5 ml.), and the combined organic layers were dried and distilled to yield 1,3-bis(perfluoro-octanoyl)-2,4,5,6-tetrafluorobenzene (3.5g., 47.8%), b.p. 123-125°/0.25 mm., which crystallised on being kept. It was recrystallised at 0° from light petroleum (b.p. 40-60°) to give the diketone, m.p. 38.5-40°. I.R. No. 4158.

Anal. Calc. for $C_{22}F_{34}O_2$: C, 28.1; H, 0.0; F, 68.5%

Found: C, 28.5; H, 0.3; F, 67.6

3. PERFLUORO-(3,3'-BIS(n-BUTYRYL)BIPHENYL)

(1) 2,3,4,6-Tetrafluorobromobenzene

To a stirred, boiling solution of 1,3-dibromotetrafluorobenzene (308g., 1.0 mole) in glacial acetic acid (500 ml.) was added 90% purity zinc powder (72.7g., 1.0 mole) in portions over 1 hour. External heating was stopped during the addition but was applied for a further $\frac{3}{4}$ hour after the addition was complete. Steam distillation yielded an organic liquid which was water washed (3 x 200 ml.), dried ($MgSO_4$), and distilled through a 1' helices-packed column yielding a main fraction (168.5g., 74%) of 99+% 2,3,4,6-tetrafluorobromobenzene, b.p. 141-142°.

(2) 3,3'-Dihydro-octafluorobiphenyl

2,3,4,6-Tetrafluorobromobenzene (165g., 0.72 mole) and copper bronze (50.2g., 0.79g. atom) were stirred in boiling dry dimethylformamide for 6 hours. The mixture was steam distilled for 12 hours giving crude product (85g.), m.p. 56-62°, which was fractionally distilled to yield a main fraction (68g.), b.p. 92-98°/12 mm. of 3,3'-dihydro-octafluorobiphenyl, 99+% pure by gas chromatography. Yield 63%.

(3) Methyl heptafluorobutyrate

n-Heptafluorobutyric acid (214g., 1.0 mole) and concentrated sulphuric acid (98g., 1.0 mole) were stirred together while dry methanol (34g., 1.06 mole) was slowly added. The mixture was boiled and stirred for 4 hours, then distilled giving a main fraction (211.3g., 92.5%), b.p. 80-82°, of methyl heptafluorobutyrate, 99+% purity by gas chromatography.

(4) Heptafluorobutyraldehyde

A solution of methyl heptafluorobutyrate (228g., 1.0 mole) in dry ether (200 ml.) was stirred under nitrogen at -70° while a slurry of lithium aluminium hydride (10.55g., 0.28 mole) in ether (300 ml.) was added portionwise in $1\frac{1}{4}$ hours. The temperature was kept at -60° to -70° throughout the addition and the solution was then stirred at -70° for a further $\frac{1}{2}$ hour. 95% ethanol (25 ml.) was added dropwise and the solution allowed to warm to -10°, then it was poured onto crushed ice (500g.). Concentrated sulphuric acid (30 ml.) was added and the ether layer was separated. The residual aqueous layer was ether extracted (4 x 200 ml.). The ether solutions were combined and dried ($MgSO_4$), then the ether was distilled leaving a residue of heptafluorobutyraldehyde hydrate (218g., 100%).

To part of the aldehyde hydrate (70.0g., 0.324 mole) was added concentrated sulphuric acid (50 ml.). The vigorously stirred mixture was heated to 90° and the evolved aldehyde collected in two traps cooled in dry-ice. The crude product was redistilled yielding heptafluorobutyraldehyde (43.3g., 68%) b.p. 30-32°.

(5) Reaction of 3,3'-dilithio-octafluorobiphenyl with heptafluorobutyraldehyde

To a stirred solution of n-butyl-lithium (13.0g., 0.203 mole) in hexane (95 ml.) and tetrahydrofuran (250 ml.) at -70° was slowly added in 35 minutes a solution of 3,3'-dihydro-octafluorobiphenyl (29.8g., 0.10 mole) in tetrahydrofuran (50 ml.). The solution was stirred at -70° for $1\frac{1}{2}$ hour. Gilman Colour Test IIA was then negative. A solution of heptafluorobutyraldehyde (40.7g., 0.21 mole) in tetrahydrofuran (50 ml.) at -70° was slowly added to the stirred dilithio-compound in 30 minutes from a cooled funnel. A small quantity of a clear gel remained in the funnel when the addition was complete. The reaction mixture was stirred at -70° for a further 45 minutes, then allowed to warm to room temperature, the creamy suspension dissolving to give a clear brown solution. The mixture was acidified with 6N hydrochloric acid (250 ml.) and the phases separated. The aqueous layer was ether extracted (4 x 100 ml.), the extracts added to the organic layer, the combined solution dried ($MgSO_4$), and the solvent removed on a water bath. The residue was heated at 100°/50-100 mm. for 3 hours to remove residual solvent. At room temperature the residue (66.5g.) was a brown gum. An attempt to distil 10g. at 175°/0.2 mm. yielded only a small quantity of solvent and a residual gum (9.45g.).

A small quantity of this gum was dissolved in ethanol and reprecipitated by the addition of water. Slow evaporation of the solvents then gave a brittle resin which was crushed to a buff powder and dried in vacuo, m.p. 39-43° (softening range).

Anal. Calc. for $C_{20}H_4F_{22}O_2$: C, 34.6; H, 0.6; F, 60.2%

Found: C, 35.5; H, 0.9; F, 57.7

The infra-red spectrum of this material (No. 3727) had absorption bands assigned to -OH, -CH and fluorinated aromatic ring.

(6) Perfluoro-(3,3'-bis(n-butyryl)biphenyl)

(a) Small-scale oxidation of 3,3'-bis(1-hydroxy-2,2,3,3,4,4,4-heptafluorobutyl)octafluorobiphenyl

To a stirred solution of the dialcohol (6.38g., 0.009 mole) from the previous experiment in glacial acetic acid (15 ml.) at 80° was added a solution of chromium trioxide (1.5g., 0.015 mole) in glacial acetic acid (20 ml.) and water (5 ml.) over 25 minutes. The dark green solution formed was heated at 80-90° for a further $1\frac{1}{4}$ hours. When cool it was poured into stirred crushed ice (100g.). A viscous, organic layer was separated and the aqueous solution was extracted with ether (3 x 50 ml.). The extracts and the viscous liquid were combined, water washed, dried (Hi-Drite) and the ether evaporated. The viscous, pale green residue was kept at 60-70°/0.5 mm. for 1 hours and then weighed 5.11g. An infra-red spectrum showed the presence of C = 0 absorptions but some hydroxyl absorptions were still present.

(b) Large-scale oxidation using a greater excess of oxidising agent

A solution of 3,3'-bis(1-hydroxy-2,2,3,3,4,4,4-heptafluorobutyl)octafluorobiphenyl (53g., 0.076 mole), in glacial acetic acid (120 ml.) was stirred at 100° while a solution of chromium trioxide (25.0g.) in glacial acetic acid (250 ml.) and water (40 ml.) was added over $1\frac{1}{2}$ hours. Heating was continued for $3\frac{1}{2}$ hours, a further quantity of chromium trioxide (5g.) in glacial acetic acid (50 ml.) and water (5 ml.) being added towards the end. The mixture was poured into water ($1\frac{1}{2}$ litres), a pale green oil separating out. This was run off and added to ether extracts (5 x 200 ml.) of the aqueous layer. The ether solution was water washed (2 x 100 ml.), dried (Hi-Drite), then distilled leaving a green residue (48.2g.). Distillation of this residue at 3.5 mm. yielded a viscous liquid (25.01g.), b.p. 135-138°, of 88% purity by gas chromatography. Redistillation of this material through a Vigreux column yielded 92% pure material (18.44g.), b.p. 146-150°/6 mm. Further attempts to purify this material by fractional distillation using a semi-micro unit failed; the best fraction, b.p. 142-144°/5 mm., was 97.6% pure by gas chromatographic analysis. Final purification of a part of this fraction was effected by preparative scale gas chromatography using a 20' x $\frac{3}{8}$" column, packed with Apiezon grease on celite, at 200°. The main product from this separation was dried ($MgSO_4$) and distilled in vacuo yielding material of 99.7% purity by gas chromatographic analysis. I.R. No. 4143.

Anal. Calc. for $C_{20}F_{22}O_2$: C, 34.8; H, 0.0; F, 60.6%

Found: C, 34.9; H, 0.0; F, 58.3

(N.B. We find that fluorine values in compounds containing $-CF_3$ groups are frequently found to be low when decomposition by the "oxygen-flask" method is used.)

When a small quantity of the 92% pure diketone was warmed with phenylhydrazine a vigorous reaction occurred. The product, after three recrystallisations from ethanol/toluene, had m.p. 275-277° but analytical values for a bis(phenylhydrazone) were poor.

Anal. Calc. for $C_{32}H_{12}F_{22}N_4$: C, 44.2; H, 1.4%

Found: C, 45.1; H, 1.1

A further attempt to prepare a larger quantity of this derivative in glacial acetic acid solution gave an uncrystallisable red oil.

4. PERFLUORO-(1,4-BIS(BENZOYL)BUTANE)

a. Attempted preparation from octafluoroadipic acid and pentafluorophenylmagnesium bromide

(1) Octafluoroadipic acid

To a stirred solution of AnalaR potassium permanganate (63g., 0.4 mole) in dry acetone (1 litre) at 0°, was added decafluorocyclohexene (100g. of 97.4% purity; 0.37 mole) over 1 hour, the temperature not rising above +5°. The solution was stirred at 5° for a further hour. Water (1 litre) was added and the acetone was removed at reduced pressure on a water bath at 50-60°. The brown solution was decolourised with sulphur dioxide, acidified with 5N-sulphuric acid (100 ml.), and ether extracted (3 x 100 ml., 3 x 150 ml.). Evaporation of the dried extracts in vacuo yielded a solid (84.5g.) which was recrystallised from benzene (1500 ml.) giving white crystals of octafluoroadipic acid (45g., 42%), m.p. 127-129° (sealed tube). Barbour et al. cited m.p. 133-134° (ref. 10).

In a second similar preparation the acid was obtained in 53% yield.

(2) Reaction between octafluoroadipic acid and pentafluorophenylmagnesium bromide

A solution of pentafluorophenylmagnesium bromide was prepared from bromopentafluorobenzene (44.5g., 0.18 mole) and magnesium turnings (4.82g., 0.198g. atom) in ether (75 ml.). To this stirred solution was added octafluoroadipic acid (8.70g., 0.03 mole) in ether (60 ml.), the temperature being maintained at 10°. After the addition, the solution was stirred and boiled for 1 hour, then poured into 6N hydrochloric acid (70 ml.). The ether layer was separated, combined with ether extracts (3 x 50 ml.) of the aqueous residue, and dried. Distillation of ether solution yielded only pentafluorobenzene (15.6g., 0.093 mole) and a solid residue (5.35g.) which was shown by its infra-red spectrum to be octafluoroadipic acid.

b. Attempted preparation from octafluoroadipoyl chloride and pentafluorophenylmagnesium bromide

(1) Octafluoroadipoyl chloride

Octafluoroadipic acid (29g., 0.1 mole), thionyl chloride (74.6g., 0.63 mole), and crushed potassium hydroxide (0.5g.) were heated and stirred at 100° for 8 hours. By distillation of the mixture through a 6" Vigreux column octafluoroadipoyl chloride (22.5g., 69%), b.p. 131-132°, was isolated. The infra-red spectrum (No. 4061) was consistent with the acid chloride structure, but gas chromatographic analysis is not yet possible since the material has not eluted from any column so far tried.

A second preparation gave the acid chloride in 56% yield.

(2) Reaction of octafluoroadipoyl chloride with pentafluorophenylmagnesium bromide

(a) In tetrahydrofuran solution

A stirred suspension of magnesium turnings (1.99g., 0.08g. atom) in dry tetrahydrofuran (30 ml.) under nitrogen was activated at 20° by the addition of ca. 0.25 ml. of 1,2-dibromoethane, then cooled to -5° (internal temperature). Bromopentafluorobenzene (9.96g., 0.041 mole) was added over 20 minutes, the internal temperature being kept at 0-5° by intermittent cooling. After stirring the solution at 0° for 1 hour it was filtered under nitrogen into a dropping funnel then added (in 45 minutes) to a solution of octafluoroadipoyl chloride (6.60g., 0.02 mole) in dry tetrahydrofuran (25 ml.). The solution was allowed to stand at ambient temperature for 24 hours, then acidified with 4N sulphuric acid (40 ml.) and poured into water (240 ml.). A yellow oil separated. It was water washed (2 x 20 ml.) then extracted with 1% sodium carbonate solution. The neutral liquid remaining was dried ($MgSO_4$) and weighed 3.56g. The sodium carbonate washings were acidified with 4N sulphuric acid to yield an acidic organic liquid which was separated off and dried ($MgSO_4$). Yield 5.48g.

The infra-red spectrum (No. 4109) of the neutral product showed absorptions for a highly fluorinated aromatic ring and for bonded hydroxyl. Little carbonyl absorption was evident. This material may contain the di(tertiary alcohol) which could be formed in this reaction.

The infra-red spectrum (No. 4110) of the acid product showed absorptions for a highly fluorinated aromatic ring, for bonded hydroxyl and for carbonyl. This material may contain the monocarboxylic acid formed by Grignard attack on only one of the two acid chloride groups present in octafluoroadipoyl chloride.

(b) In ether solution

To a stirred solution of pentafluorophenylmagnesium bromide, prepared from magnesium turnings (2.12g., 0.087g. atom) and bromopentafluorobenzene (20.0g., 0.081 mole) in ether (50 ml.), at 0°, was added a solution of octafluoroadipoyl chloride (13.1g., 0.04 mole) in ether (25 ml.) during 1¼ hours. The reaction was mildly exothermic and the temperature of the mixture was kept at 0-5° by applied cooling. The reaction mixture was kept at ambient temperature for 24 hours then poured into 2.5N sulphuric acid (40 ml.). The ether layer was separated off, water washed and dried (Hi-Drite). Distillation of the ether yielded a residue (23.5g.) which was distilled at 0.1 mm. yielding three fractions, (i) b.p. 94-100° (4.23g.), (ii) b.p. 100-104° (5.11g.), (iii) b.p. 104-110° (11.42g.) and a residue (1.3g.). Fractions (ii) and (iii) were identical and 99+% pure by gas chromatographic analysis. An infra-red spectrum (No. 4149B) of fraction (ii) showed absorptions for a highly fluorinated ring, carbonyl and -C-F. A trace of bound -OH was evident. Confirmation of the perfluoro-(1,4-bis(benzoyl)butane) structure by elemental analysis is awaited.

5. PERFLUORO-n-PROPYL PENTAFLUOROPHENYL SULPHIDE

(a) Reaction between cuprous pentafluorothiophenate and 1-iodoheptafluoropropane at 155°

Cuprous pentafluorothiophenate (6.6g., 0.025 mole), 1-iodoheptafluoropropane (7.3g., 0.025 mole) and dimethylformamide (35 ml.) were shaken and heated in a sealed tube at 150-155° for 7½ hours. Volatile product (3.5g.), vented from the unsealed tube, was collected at -78° then allowed to warm to 0°. A small residue (0.27g.) of 1-iodoheptafluoropropane was left. The residual reaction product was poured into water (150 ml.) yielding a suspension which was filtered off, dried, and exhaustively ether extracted (30 hours). Evaporation of the dried extracts gave a brown paste (1.04g.) which contained two main components present to the extent of 45% and 36%. These were not identified but an infra-red spectrum of this residue (No. 4005) contained a band at ca. 860 cm.$^{-1}$ which may be attributed to a sulphur bridge.

(b) Reaction between cuprous pentafluorothiophenate and 1-iodoheptafluoropropane at 100°

The same quantities of reagents were used as in (a) above but the sealed tube was shaken and heated at 100° for 7 hours. A negligible amount of volatile material was liberated when the tube was opened and no material distilled out when the tube was kept at 100° for 2 hours then at 150° for 15 minutes. The hot solution was filtered and insoluble unreacted cuprous pentafluorothiophenate collected (3.01g.) (identified by an infra-red spectrum). The green filtrate was poured into water (175 ml.) giving a yellow precipitate which was filtered off, dried, and exhaustively ether extracted. Removal of the ether from the dried extracts gave liquid (1.13g.) from which ether and dimethylformamide were distilled to leave a residue (0.39g.) having a similar infra-red spectrum to that of the residue in the first reaction.

6. 1,4-DI-IODO-OCTAFLUOROBUTANE

(1) Disilver octafluoroadipate

To a solution of octafluoroadipic acid (29.0g., 0.1 mole) in water (75 ml.) at 100° was added freshly precipitated moist 'silver oxide', (prepared from silver nitrate (34g., 0.2 mole) and AR sodium hydroxide (8g., 0.2 mole) in 300 ml. water), over 1½ hours. The solution was heated at 100° for 2½ hours, then filtered hot and evaporated to dryness in vacuo in subdued light to give disilver octafluoroadipate (48.5g., 96%).

(2) 1,4-Di-iodo-octafluorobutane

In a vertical pyrex trap was placed iodine (56.6g., 0.22 mole), a layer of phosphoric oxide, a layer of glass wool, and dry disilver octafluoroadipate (48.5g., 0.096 mole). The trap exit was connected to two traps, the first cooled in ice-water, the second in alcohol/dry-ice mixture and thence via a tube packed with potassium hydroxide pellets to a manometer and oil pump. The reactants were heated at 160-170° at 200 mm. for 3 hours and the product, together with much iodine, was collected in the two cooled traps. Yield 26.7g. (61%). The material was washed with sodium thiosulphate solution and water, then dried and distilled at 25 mm. A main fraction (16.0g.), b.p. 50-52°/ 25 mm., was 97% pure 1,4-di-iodo-octafluorobutane, (analysis by gas chromatography).

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PART IV

FLUOROCARBON FLUIDS

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Introduction

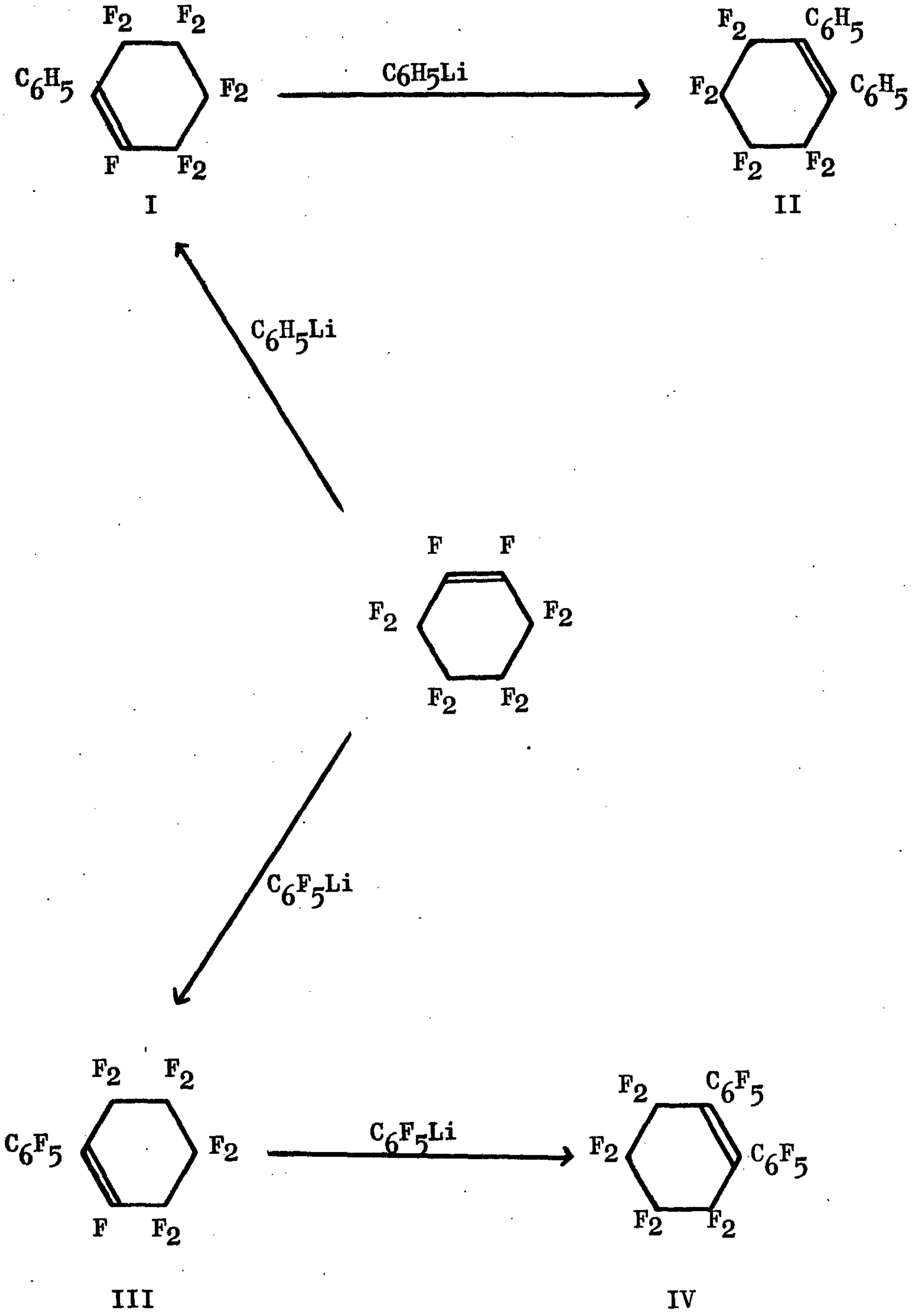
This work has been directed towards the preparation of model compounds containing perfluorocyclohexyl rings joined in various ways and containing perfluoroalkyl substituents, for investigation of their physical and chemical properties.

Summary

The reactions of phenyl and pentafluorophenyl lithium with decafluorocyclohexene, o- and p- perfluoroxylene have been studied. Precursors of the desired compounds have been obtained and their fluorination with cobaltic fluoride has been started.

Discussion

The reactions of organo-lithium reagents with fluoro-olefins have been reported[1-3] previously and appeared useful in the synthesis of the desired model compounds. In most cases using cyclic olefins two alkyl or aryl groups have been introduced in a 1,2-relationship.[2,3] Nucleophilic substitutions of perfluoro-



F2 F2
C6H5
F2
F F2
I
C6H5Li
F2 C6H5
F2
C6H5
F2 F2
II
C6H5Li
F F
F2
F2
F2 F2
C6F5Li
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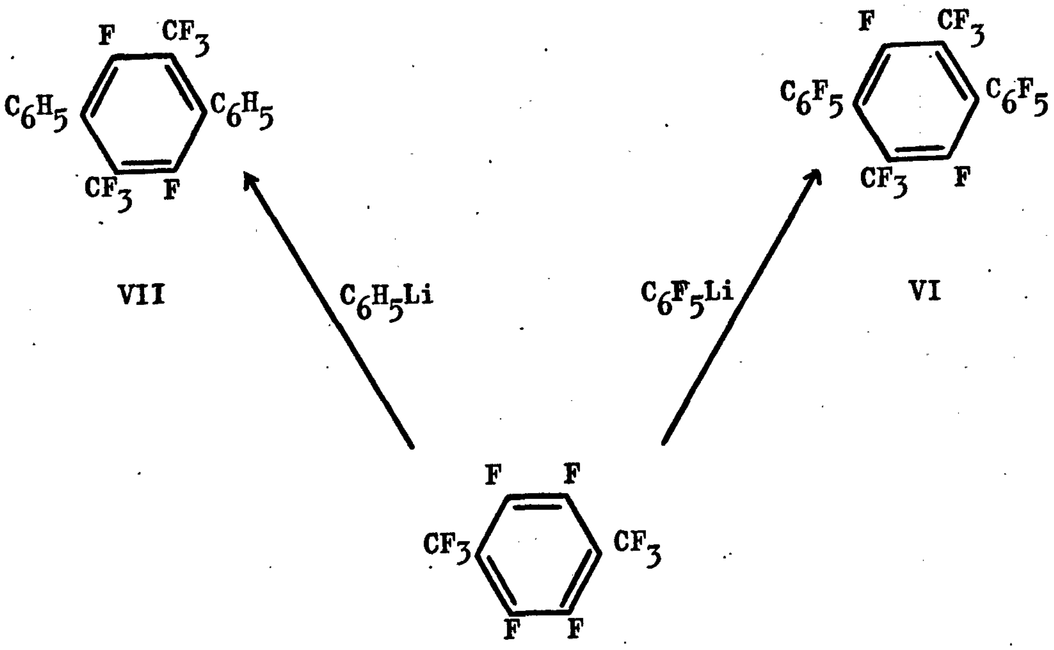
F2
C6F5
F2 F2
IV


F
CF3
C6H5
C6H5
CF3
F
VII
C6H5Li
F
CF3
C6F5
C6F5
CF3
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CF3
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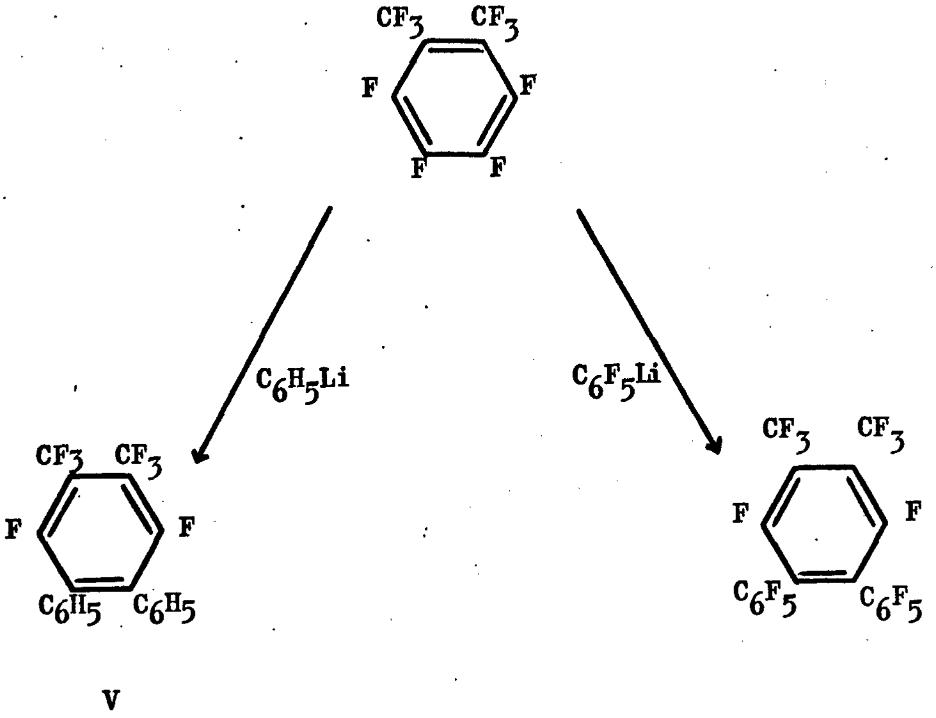
F


CF3
CF3
F
F
F
F
C6H5Li
C6F5Li
CF3
CF3
F
F
C6H5
C6H5
V
CF3
CF3
F
F
C6F5
C6F5

aryl systems by organo-lithium reagents have also been reported[4] and also offered routes to the desired compounds. Therefore, both processes have been investigated.

Decafluorocyclohexene readily undergoes reactions with nucleophilic reagents[3,5] and we have investigated its reactions with phenyl and pentafluorophenyl lithium. With decafluorocyclohexene in ether solution phenyl lithium gave a liquid which was shown by comparison with a compound from the Ullman reaction between 1-bromononafluorocyclohexene and bromobenzene,[6] to be 1-phenyl-nonafluorocyclohexene (I). Further reaction of compound (I) with phenyl lithium gave a crystalline solid which analysed for a bis-phenyl octafluorocyclohexene. Reactions of aryl lithium reagents with cyclic fluoro-olefins usually give 1,2-di-substituted products[2,3] and this, together with spectroscopic evidence indicated that the compound was 1,2-bis(phenyl)octafluorocyclohexene (II). Both (I) and (II) were fairly resistant to oxidation by potassium permanganate.

In a similar reaction, but using pentafluorophenyl lithium, two products were obtained in reasonable yield, which were shown to be 1-(pentafluorophenyl)nonafluorocyclohexene (III) and 1,2-bis(pentafluorophenyl)octafluorocyclohexene (IV). These compounds were very resistant to oxidation by a variety of oxidising agents, presumably due to steric factors preventing the oxidant from reaching the double bond.

Fluorination of compounds (I) - (IV) has been started, each giving a major component and work is currently in progress to isolate and characterise these products.

The introduction of trifluoromethyl groups into polyfluorocyclo-alkane systems usually lowers the melting point significantly (cf. C_6F_{12} and $C_6F_{11}CF_3$). Hence, the introduction of trifluoromethyl groups into systems similar to the fluorination products of (I) - (IV) was of interest to the project.

An obvious way to introduce the CF_3- group was to use the perfluoroxylenes as substrates. Nucleophilic substitutions of these compounds have been studied;[7] the fluorine atoms para to the trifluoromethyl groups are usually displaced first. Thus, by using the isomeric perfluoroxylenes a range of compounds can be produced. Reaction of perfluoro-o-xylene with pentafluorophenyl lithium has already been done,[4] a similar reaction but using phenyl lithium gave 3',6'-difluoro-4',5'-bis(trifluoromethyl)-o-terphenyl (V).[7] None of the diphenyl could be detected, presumably because the diphenyl produced in the first step of the reaction is more reactive than the xylene.

Similar reactions with perfluoro-p-xylene gave, respectively, 3',6'-bis(trifluoromethyl)decafluoro-p-terphenyl (VI) and 2',5'-difluoro-3',6'-bis(trifluoromethyl)-p-terphenyl (VII).[6] The orientations of these compounds were indicated by ^{19}F and ^{1}H n.m.r. spectroscopy and by analogy with orientations which can be established chemically.[6]

Fluorination of (V) and (VI) with cobaltic fluoride gave a mixture of products with one major component. Work is in progress to identify this and the minor components.

Another approach to the synthesis of polyfluorocycloalkyl compounds is in the Ullmann reaction from bromopolyfluorocyclalkenes. This reaction has been used previously[6] as mentioned above. Work has commenced on this project using decafluorocyclohexene as starting material. Reduction of the latter[8] gave 1H-nonafluorocyclohexene in good yield and bromination of the latter is now being studied.

Experimental

Reaction of phenyl lithium with decafluorocyclohexene

A solution of phenyl lithium in ether (104 ml., 0·081 g./ml.) was added to a solution of decafluorocyclohexene (26·2 g.) in dry ether (100 ml.) stirred under nitrogen at 0°. The reaction mixture was stirred at 15° for 2 hr. when dilute hydrochloric acid (100 ml.) was added. The aqueous layer was extracted with ether (2 x 100 ml.), the ether layer and extracts combined, dried ($MgSO_4$) and the ether distilled, through a 6" vacuum jacketed column packed with glass helices, to leave a brown oil (24·0 g.). Analytical gas chromatography indicated a mixture of four components one of long retention time. Separation of a portion (8 g.) of the mixture by preparative g.l.c. gave (i) benzene and bromobenzene (0·3 g. total); (ii) 1-phenylnonafluorocyclohexene (4·5 g.);[6] (iii) a solid (0·1 g.) believed to be diphenyl; (iv) a solid (3·0 g.) (see below).

Reaction of 1-phenylnonafluorocyclohexene with phenyl lithium

A solution of phenyl lithium in ether (15·5 ml., 0·081 g./ml.) was added to a stirred solution of 1-phenylnonafluorocyclohexene (3·8 g.) in dry ether (10 ml.) under an atmosphere of nitrogen. The reaction mixture was stirred for 2 hr. at 15° and then heated under reflux for 2 hr., dilute hydrochloric acid (100 ml.) was added, the ether layer and the combined ether extracts (2 x 100 ml.) of the aqueous layer were dried ($MgSO_4$) and the ether distilled off to leave a brown liquid (2·0 g.). Analytical gas chromatography showed two main components, 1-phenylnonafluorocyclohexene and the longer retained component indicated above. Distillation *in vacuo* gave an oily liquid (0·9 g.) which deposited crystals of *1,2-diphenyloctafluorocyclohexene*, m.p. 42-43° on standing.

Calc. for $C_{18}H_{10}F_8$: C, 57·2; H, 2·6%

Found C, 57·2; H, 2·6%

In a similar experiment but using 2 moles of phenyl lithium a similar mixture of products (22·5 g.) was obtained which gave on separation 1-phenylnonafluorocyclohexene (8 g.) and 1,2-diphenyloctafluorocyclohexene (2·5 g.).

Reaction of pentafluorophenyl lithium and decafluorocyclohexene

A solution of decafluorocyclohexene (26·2 g.) in dry ether (60 ml.) was added at -78° to a solution of pentafluorophenyl lithium (from pentafluorobenzene, 16·8 g.) in dry ether (100 ml.) the reaction mixture was stirred at -76° for 10 hr. then the temperature was raised to -40° and the mixture maintained this temperature for 4 days. After this time it was allowed to attain room temperature and water (50 ml.) and dilute sulphuric acid (100 ml.) were added. The ether layer and the combined extracts of the aqueous layer (2 x 100 ml.) were dried ($MgSO_4$) and the ether distilled to leave a viscous brown oil (42 g.). On standing overnight crystals (5·8 g.), m.p. 132-133° separated. Repeated recrystallisation from ethanol gave 1,2-bispentafluorophenyl-octafluorocyclohexene (3·2 g.) m.p. 138° identical to that previously described.[4] Separation by g.l.c. of a portion (10 g.) of the mother liquors gave (1) pentafluorobenzene (0·5 g.); (2) 1-pentafluorophenylnonafluorocyclohexene (2·9 g.); (3) 1,2-bispentafluorophenyloctafluorocyclohexene (0·5 g.); (4 and 5) two unidentified components in trace amounts.

Reaction of phenyl lithium and decafluoro-p-xylene

Phenyl lithium in ether (225 ml., 0·075 g., PhLi/ml.) was slowly added to decafluoro-p-xylene (28·6 g.) in dry ether (100 ml.), stirred at 0° under nitrogen. The reaction mixture was stirred at 0° for 3 hr. and then kept at 15° for 24 hr., dilute sulphuric acid (100 ml.) was added and the ether layer separated. The aqueous layer was extracted continuously with ether for 24 hr., the ether layer combined, dried ($MgSO_4$) and the ether distilled off to leave a white solid (29·0 g.). Recrystallisation from petroleum ether (b.p. 100-120°) gave 2',5'-difluoro-3',6'-bis(trifluoromethyl)-p-terphenyl (18·0 g.) m.p. 233° (cited[7] 234-5°). No diphenyls could be detected.

The reaction of pentafluorophenyl lithium and decafluoro-p-xylene

Decafluoro-p-xylene (14·3 g.) in dry ether (60 ml.) was added with stirring under an atmosphere of nitrogen to a solution of pentafluorophenyl lithium (from pentafluorobenzene, 16·8 g.) in ether/n-heptane (3:1, 200 ml.) at -78°. The solution was stirred at -78° for 10 hr., warmed to -40° and maintained at this temperature for 4 days. The solution was warmed to 15° and water (20 ml.) and dilute sulphuric acid (100 ml.) added. The ether layer and the combined extracts (2 x 100 ml.) of the aqueous layer were dried ($MgSO_4$) and the ether distilled to give a yellow syrup from which a white crystalline solid (7 g.) was formed on standing. Recrystallisation from petroleum ether (100-120°) gave 2'5'-difluoro-3',6'-bistrifluoromethyldecafluoro-p-terphenyl, m.p. 173-174°.

Calc. for $C_{20}F_{18}$: C, 41·2; F, 58·8%

Found: C, 41·4; F, 59·1%

The mother liquor gave 2H-nonafluorodiphenyl and a trace of a compound which had the expected spectral properties of the mono substitution product.

Reaction of phenyl lithium and decafluoro-o-xylene

Phenyl lithium in ether (78·1 ml., 0·075 g. PhLi/ml.) was added to decafluoro-o-xylene (10·0 g.) in ether (100 ml.) at 0° in an atmosphere of nitrogen. The solution was stirred at 0° for 9 1/2 hr., kept at 5° for 4 days, and then allowed to attain room temperature. Water (20 ml.) and dilute sulphuric acid (100 ml.) were then added, the ether layer washed with dilute sulphuric acid (2 x 100 ml.), dried ($MgSO_4$) and the ether evaporated to leave a brown oil (15·8 g.) which gave white crystals (3·5 g.) on standing. Recrystallisation of the latter from petroleum ether (100-120°) gave 3',6'-difluoro-4',5'-bis(trifluoromethyl)-o-terphenyl, m.p. 99-100°

Calc. for $C_{20}H_{10}F_8$: C, 59·7; H, 2·4%

Found: C, 59·6; H, 2·5%

Separation of the mother liquors by preparative gas chromatography gave a crystalline solid, m.p. 65-66° (2·1 g.) which gave 3,4-bis(trifluoromethyl)-2,5,6-trifluorobiphenyl (2·0 g.) m.p. 66° (from petrol).

Calc. for $C_{14}H_5F_9$: C, 48·8; H, 1·5%

Found: C, 48·9; H, 1·4%

and a further quantity of the disubstituted product above (2·3 g.).

The reaction of pentafluorophenyl lithium and decafluoro-o-xylene

n-Butyl lithium in n-hexane (29·8 ml., 0·15 g. BuLi/ml.) and ether (50 ml.) was rapidly added to pentafluorobenzene (11·7 g.) in dry ether at -76° under nitrogen. After the mixture had been stirred for 1/2 hr. decafluoro-o-xylene (10·0 g.) in dry ether (60 ml.) was rapidly added and the solution stirred for 11 hr. The solution was kept at -40° for 4 days, allowed to attain room temperature, and water (20 ml.) and dilute sulphuric acid (100 ml.) was added. The ether layer was washed with dilute sulphuric acid (2 x 100 ml.), dried ($MgSO_4$) and the ether evaporated to give a light brown liquid (30 g.). On standing crystals of 4',5'-bis(trifluoromethyl)decafluoro-o-terphenyl (1·7 g.) were deposited identical with an authentic sample.[3] The residue was shown to be mainly the same compound, about 95% pure.

Reduction of decafluorocyclohexene with sodium borohydride

A suspension of sodium borohydride (3·8 g.) in dry diglyme (100 ml.), was slowly added to a mixture of decafluorocyclohexene (52·4 g.) in dry diglyme (50 ml.) at 0°. The addition was stopped when all the decafluorocyclohexene had been consumed, as shown by gas chromatography. Water (100 ml.) was slowly added to the reaction mixtre and the lower organic layer (45·5 g.)

separated. Separation of a portion (30 g.) of this liquid by preparative gas chromatography gave (i) 1H-nonafluorocyclohexene (15·5 g.); (ii) 2H-nonafluorocyclohexene (1·0 g.); and a mixture of dihydro-octafluorocyclohexenes (1·5 g.).

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PART V

FLUORINATED HETEROCYCLIC COMPOUNDS

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A. INTRODUCTION

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

B. SUMMARY

Pentachloropyridine has been prepared by three different methods. The first method is the now well established one of heating together dry pyridine and an excess of phosphorus pentachloride in a stainless steel autoclave at 300°C.[1,2] The second method consists of chlorination of pyridine with elemental chlorine in the presence of catalytic amounts (2·5% by weight) of antimony trichloride. Reaction of the partially chlorinated pyridines obtained with excess phosphorus pentachloride in a steel autoclave at 300° yields pentachloropyridine. The third method used was the one reported by Roedig and Grohe[3] in which hexachloro-2-cyclopentenone is first reacted with liquid ammonia at -50° to yield the amide of pentachloropenta-2,4-dienoic acid. Pentachloropyridine is then obtained by reaction of this amide with phosphorus pentachloride.

Pentafluoropyridine is produced by a halogen exchange reaction between pentachloropyridine and anhydrous potassium fluoride in an autoclave at 480°.[1,2]

Perfluoroisonicotinic acid has been prepared from pentafluoropyridine by the following synthesis:-[4,5]

Reaction of the tetrafluoroisonicotinyl chloride with 4-lithiotetrafluoropyridine appears to give di-tetrafluoro-4-pyridyl ketone. This reaction has just been carried out and more detailed results are not yet available.

Two fully-fluorinated ethers have been prepared from potassium pentafluorophenate and pentafluoropyridine and heptafluoroisoquinoline.

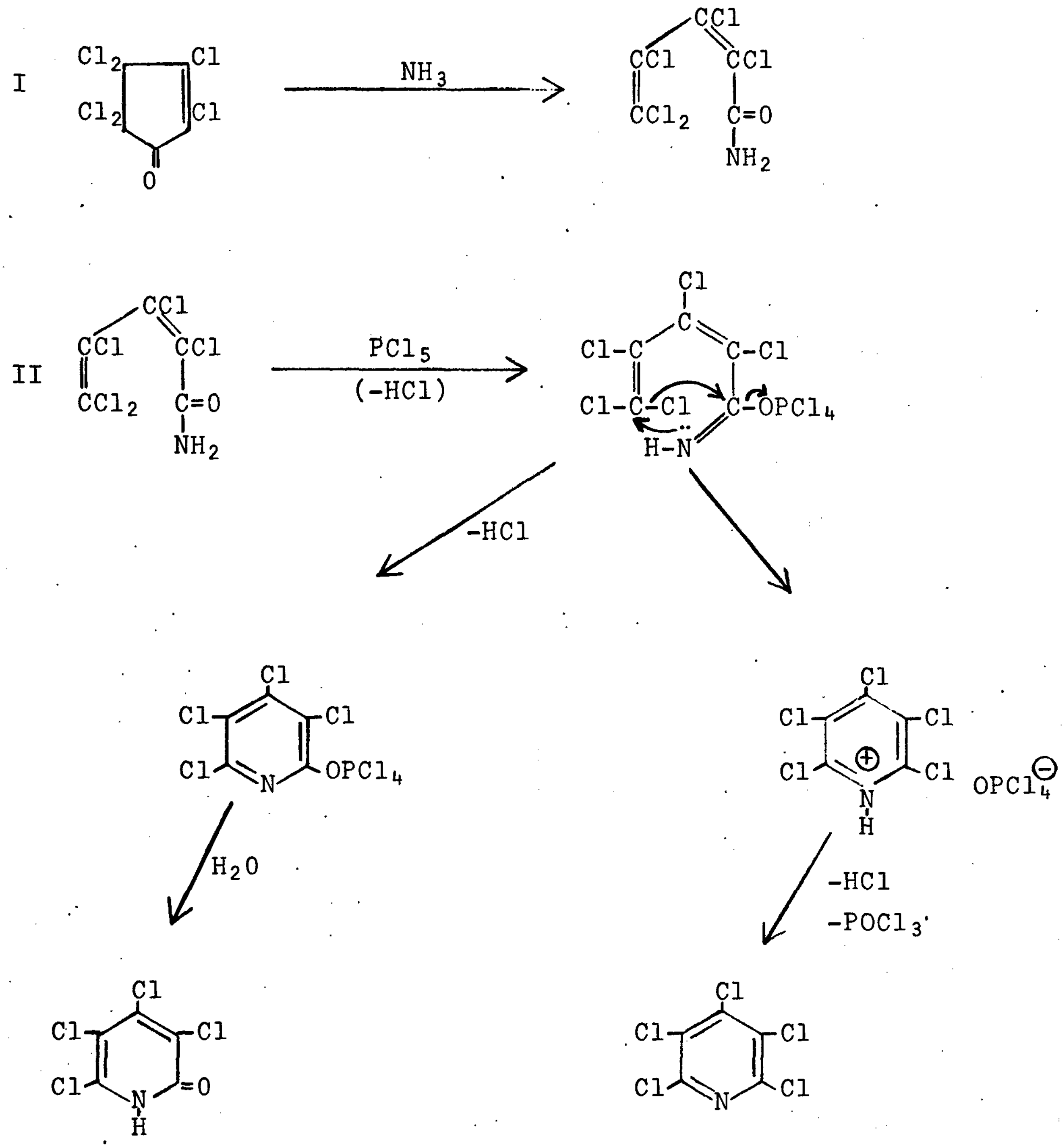
C. DISCUSSION

1. PREPARATION OF PENTACHLOROPYRIDINE

The preparation of pentachloropyridine by reaction of dry pyridine with an excess of phosphorus pentachloride in a stainless steel autoclave at 300° has occasionally proved to be hazardous. This has been due to the phosphorus pentachloride gradually eating away the copper seal which is placed in between the autoclave and its lid, and the autoclave itself and causing explosions. Provided that the autoclave and its copper seal are carefully examined after each reaction, the autoclave fitted with a nickel-sleeve, and the seal replaced when necessary, the reaction should not be hazardous. The main disadvantage with this method is that relatively little pyridine can be used in the reaction since the phosphorus pentachloride occupies most of the space in the autoclave. However this method is at present the most convenient one for the large scale preparation of pentachloropyridine.

It was thought that if the pyridine could be replaced by partially chlorinated pyridine the reaction might be less hazardous and this procedure would also allow relatively more of the pyridine species to be placed in the autoclave since less phosphorus pentachloride would be required. Consequently an investigation into the chlorination of pyridine was undertaken. In view of the successful use of chlorine, with antimony trichloride as catalyst, in preparing pentachlorobenzthiazole from monochlorobenzthiazole[7] it was decided to use these reagents. Chlorine gas was passed into dry pyridine containing antimony trichloride (2·5% by weight) and quite good yields of a mixture of di-, tri- and tetra-chloropyridines were obtained. The reactions were carried out at elevated temperatures and one of the problems was to prevent the chloropyridines distilling from the reaction mixture and cooling on the cooler parts of the reaction vessel, especially in the condenser. In an attempt to overcome this difficulty the chlorination was on occasions carried out in carbon tetrachloride solution but the yields were poor. Some of the results of these experiments are summarised in Table I. The mixtures of di-, tri- and tetra-chloropyridines produced by this method were fully chlorinated by heating with an excess of phosphorus pentachloride at 300° in a stainless steel autoclave. This reaction went smoothly. The main drawback to this method was the length of time which it took, since the partially chlorinated pyridines had to be steam distilled from the reaction mixture. Also it was found that when the scale of the primary chlorination was increased the yield of partially chlorinated pyridines decreased due to more extensive decomposition occurring.

The preparation of pentachloropyridine from hexachloro-2-cyclopentenone proceeds in two distinct stages.



The first stage involves reaction of hexachloro-2-cyclopentenone with liquid ammonia at -50° to yield the amide of pentachloropenta-2,4-dienoic acid. The yield quoted in the literature for this reaction is 87% but a

100% yield of crude amide has been shown to be possible. The second stage of the synthesis is the reaction between the amide and phosphorus pentachloride. In early experiments using the amount of phosphorus pentachloride quoted in the literature (the theoretical amount), the main product was tetrachloro-2-pyridone. However, as expected, the tetrachloro-2-pyridone was readily converted into pentachloropyridine on further treatment with phosphorus pentachloride. If a 120% excess, over the theoretical amount, of phosphorus pentachloride was used in the second stage of the reaction, a reasonable yield (48%) of pentachloropyridine was obtained in one step. The yield quoted in the literature for this stage is 67%. In recent reactions, where a 120% excess over the theoretical amount of phosphorus pentachloride was used, the product obtained had an infra-red spectrum which was almost identical with that of an authentic sample of pentachloropyridine. It also had a m.p. of 126-128° which is similar to that of pentachloropyridine (123-124°). However it could not be readily steam distilled whereas pentachloropyridine is quite steam volatile and unlike the pentachloropyridine prepared by this method in the early experiments it could not be converted into pentafluoropyridine by reaction with anhydrous potassium fluoride at elevated temperatures. Subsequent investigation showed that the supposed amide of pentachloropenta-2,4-dienoic acid produced in the recent reactions had an infra-red spectrum which differed considerably from that of the amide produced in the early reactions. Further investigations are being carried out on this problem. It is probable that the difficulties are arising from the scaling up of the process. It is much more difficult to keep a bulky reaction mixture in a large reaction vessel at a temperature of -50°C (as is required in the preparation of the unsaturated amide in the first stage) than to do the same on a small scale.

Pentachloropyridine can be readily converted into pentafluoropyridine by reaction with anhydrous potassium fluoride in an evacuated steel autoclave for 16 hrs. at 480°.

2. CONVERSION OF PENTAFLUOROPYRIDINE INTO TETRAFLUOROISONICOTINIC ACID

The first stage in the conversion of pentafluoropyridine into tetrafluoroisonicotinic acid consists of reaction of the pentafluoropyridine with excess ammonia (0·88) at 80°C to yield 4-aminotetrafluoropyridine. This reaction proceeds almost quantitatively. Diazotisation of this amine in 80% hydrofluoric acid (in order to prevent nucleophilic displacement of the fluorine atoms of 4-aminotetrafluoropyridine) at -20°, followed by reaction of the diazonium salt with cuprous bromide in hydrobromic acid converts the 4-aminotetrafluoropyridine into 4-bromotetrafluoropyridine in approx. 70% yield. Two methods are then available for the conversion of the 4-bromotetrafluoropyridine into tetrafluoroisonicotinic acid. In the first of these reaction with magnesium in tetrahydrofuran at -25° (in order to prevent polymerisation) yields tetrafluoro-4-pyridyl magnesium bromide which on carbonation gives the required acid in 60% yield. 4-Bromotetrafluoropyridine also undergoes an exchange reaction at -75° with butyl-lithium to give 4-lithiotetrafluoropyridine which can then be carbonated to produce the lithium salt of tetrafluoroisonicotinic acid. The free acid is liberated by acidification with dilute hydrochloric acid. The yield of tetrafluoroisonicotinic acid is 80%.

3. ATTEMPTED PREPARATION OF TETRAFLUOROISONICOTINYL CHLORIDE AND ITS REACTIONS

Considerable difficulty has been experienced in the attempted preparation of tetrafluoroisonicotinyl chloride. Heating tetrafluoroisonicotinic acid with an excess of thionyl chloride, under reflux, for periods of time varying from six to seventy-two hours, both in the absence and presence of dimethyl formamide in catalytic amounts, fails to convert the acid to the acid chloride. This method is similar to that described by Cummings and Lynch (Monsanto Chemicals Ltd. Progress Report, December 1964) for the preparation of pentafluorobenzoyl chloride from pentafluorobenzoic acid. The liquid product obtained boiled over the range 114-118° at 0·1 mm., but unreacted acid sublimes under these conditions and hence the product was always contaminated with unreacted acid. However, analysis of what was thought to be fairly pure sample showed the complete absence of chlorine. Reactions of the liquid were consistent with what would be expected for tetrafluoroisonicotinyl chloride e.g. reacted with ammonia to give an amide and with phenyl hydrazine to give N-phenyl-N'-tetrafluoroisonicotinyl hydrazine. The liquid is therefore probably the anhydride of tetrafluoroisonicotinic acid and the carbon analysis was consistent with that of a mixture of equal parts of unreacted acid and its anhydride. Further work is being done on this liquid.

Reaction of tetrafluoroisonicotinic acid with phosphorus pentachloride at 90° gave a liquid mixture of phosphorus oxychloride and tetrafluoroisonicotinyl chloride which was separated by vacuum distillation. The yield of pure acid chloride was about 30% but, on a larger scale, this should be much improved.

The liquid obtained from the reaction between tetrafluoroisonicotinic acid and thionyl chloride (which was assumed (wrongly) to be tetrafluoroisonicotinyl chloride) has been reacted with anhydrous hydrazine at various temperatures between -50° and room temperature using the technique which W. Cummings and E.R. Lynch used to prepare pentafluorobenzhydrazide. No reaction occurs at -50° but on warming to -20 to 0° reaction occurs. Both ether and tetrahydrofuran were used as solvents, the only obvious difference between them being that the reaction was more vigorous in ether than in tetrahydrofuran. In all cases an orange-red solid, which was only very slightly soluble in the solvent, was obtained. Removal of the solvent by filtration gave a brown solid which did not extract at all into benzene and which was very difficult to purify. Attempted purification by vacuum sublimation resulted in decomposition before sublimation occurred. The solid was very soluble in alcohols but insoluble in most other solvents. Recrystallisation even with mixed solvents was not very satisfactory. However a small amount of solid was recrystallised from meths yielding a light brown solid which decomposed at 65°. Carbon and hydrogen analysis gave results which were not consistent with the values calculated for any of the expected products of the reaction. The usual product from the reactions (the brown product) also decomposed at about 65°.

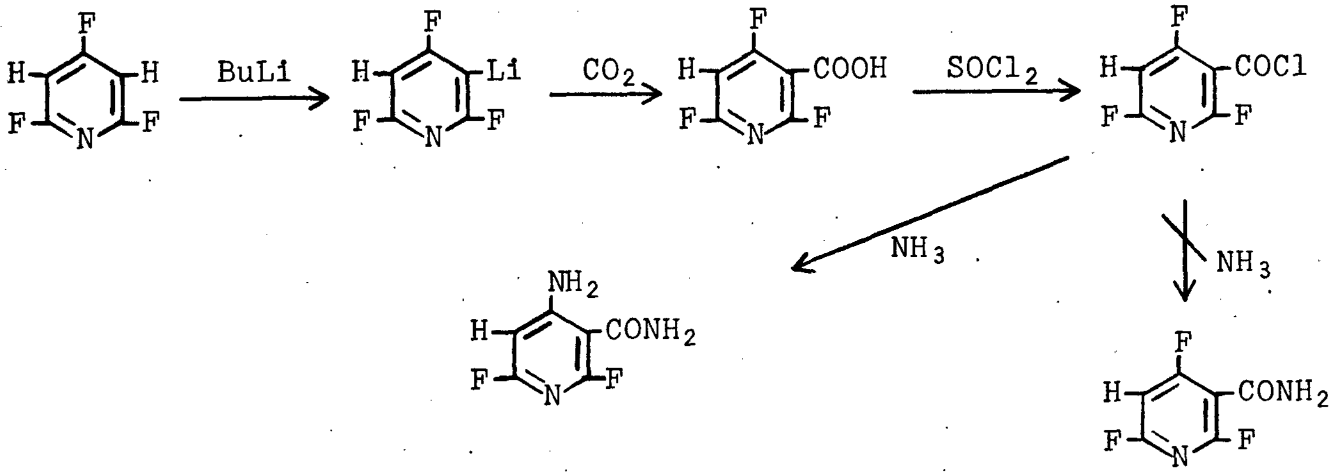
In order to obtain a cleaner product and also to favour formation of N,N'-bis(tetrafluoroisonicotinyl)hydrazine, it was decided to carry out the reaction by adding the hydrazine to the (supposed) tetrafluoroisonicotinyl chloride i.e. an excess of acid chloride is always present. This method also reduces the possibility of nucleophilic replacement of the pyridine ring fluorine atoms by hydrazine. The solid obtained was similar in appearance to the products obtained when the acid chloride was added to the hydrazine but it had a much higher decomposition point (about 130°). The properties of this solid were similar to those of N,N'-bis(pentafluorobenzoyl)hydrazine i.e. insoluble in benzene, soluble in alcohols, but the solid could not be satisfactorily recrystallised. This compound could be N,N'-bis(tetrafluoroisonicotinyl)hydrazine but it needs further investigation.

Since a clean product was not obtained in the reactions of the (supposed) tetrafluoroisonicotinyl chloride with hydrazine it was decided to carry out the reaction with a less reactive hydrazine species in the hope of obtaining a product which could be purified more easily. This was accomplished by using phenylhydrazine as the hydrazine species. Two solid products were obtained. One, which was insoluble in ether, has not been fully identified but has been shown to contain a 4-substituted tetrafluoropyridine nucleus and also a phenyl group. One would have expected to obtain phenylhydrazine hydrochloride from the reaction and this would be expected to be insoluble in ether. The solid which was insoluble in ether is definitely not this compound. The solid which was soluble in ether was isolated, purified by recrystallisation from hexane/meths/carbon tetrachloride and identified as N-phenyl-N'-tetrafluoroisonicotinyl hydrazine by elemental analysis, its infra-red spectrum and its mass spectrum. It was obtained in 50% yield.

Tetrafluoroisonicotinamide has been prepared in 31% yield by reaction of the (supposed) tetrafluoroisonicotinyl chloride with anhydrous ammonia in benzene. The poor yield is probably due incomplete reaction between tetrafluoroisonicotinic acid and thionyl chloride in the first stage of the reaction.

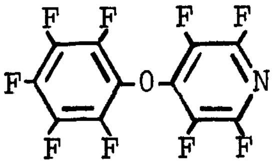
4. ATTEMPTED PREPARATION OF 2,4,6-TRIFLUORONICOTINAMIDE

An attempted preparation of 2,4,6-trifluoronicotinamide from 2,4,6-trifluoronicotinic acid was carried out using the same method which was used for the preparation of tetrafluoroisonicotinamide. The expected product was 2,4,6-trifluoronicotinamide but from the analytical figures the product appears to be 4-amino-2,6-difluoronicotinamide. This is not really surprising since the 2,4,6-trifluoronicotinic acid has a reactive (towards nucleophilic displacement) fluorine atom in position 4. The presence of the ortho carbonyl group will increase the reactivity of the 4-flucrine atom towards nucleophiles such as ammonia.

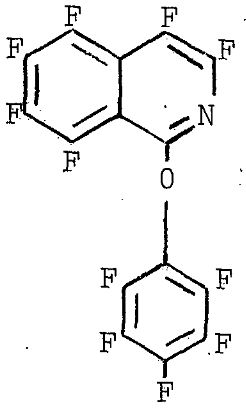


5. PREPARATION OF FULLY-FLUORINATED ETHERS

Anhydrous potassium pentafluorophenate reacted readily when refluxed with pentafluoropyridine or heptafluoroisoquinoline in tetrahydrofuran solution to give ethers which, judging from the normal reactions of these heterocycles, will have the structures



and



respectively. Similar reactions have been tried using the monohydrate of the potassium salt of 4-hydroxy tetrafluoropyridine. Derivatives have been obtained in low yield but reaction is sluggish and the experiments will be repeated with the anhydrous potassium salt.

D. EXPERIMENTAL

Chlorination of Pyridine with Phosphorus Pentachloride.

Dry pyridine (100 g.) and phosphorus pentachloride (2,500 g.) were placed in a stainless steel autoclave fitted with a nickel liner. The autoclave was heated to 300° for 24 hrs., the temperature being measured by means of a thermocouple inserted into a thermometer well which reached down inside the autoclave. Thus the walls of the autoclave were at a temperature in excess of 300°. After allowing the autoclave to cool to room temperature the hydrogen chloride generated during the reaction was released before the autoclave was opened. Excess phosphorus pentachloride was hydrolysed with ice. When this was complete the organic product was steam distilled. The solid product was filtered off and dried (200 g.). Fractional distillation gave tetrachloropyridines (~60 g.) and pentachloropyridine (~140 g.).

Chlorination of Pyridine with Chlorine.

In a typical experiment a flask fitted with stirrer, water condenser and gas lead was purged with dry nitrogen and then charged with dry pyridine (170 g., 2·15 mole) and antimony trichloride (4·25 g.). Chlorine gas (756 g., 10·7 mole) was passed through the pyridine, first at 100° and then the temperature of the reaction vessel was gradually raised to 160°. When the refluxing liquid became solid the water condenser was replaced by an air condenser. When the required amount of chlorine had been passed into the reaction mixture it was allowed to cool, water was added and then it was steam distilled. The distillate was extracted with methylene chloride. Removal of the solvent from the dried extracts yielded an oily liquid (257·5 g.) which deposited some white crystals on cooling and whose composition was determined by analytical scale gas liquid chromatography as being

dichloropyridine	19	
trichloropyridine	47	mole %
tetrachloropyridine	34	

Chlorination of Chloropyridines with Phosphorus Pentachloride.

A stainless steel autoclave (1 l.) fitted with a nickel liner was charged with chloropyridines of average molecular formula $C_5H_{2.4}Cl_{2.6}N$ (150 g., 0·85 mole) and phosphorus pentachloride (900 g., 4·3 mole) and was then heated to 270° for 12 hrs., then to 305° for 6 hr. After allowing the autoclave to cool to room temperature, the hydrogen chloride generated during the reaction was released before the vessel was opened. The excess phosphorus pentachloride was then slowly hydrolysed by adding it to crushed ice. When this was complete the organic product was steam distilled. The solid product was filtered from the distillate, dried by azeotropic distillation of the water with benzene, and fractionated to give tetrachloropyridines ($\sim$50 g.) and pentachloropyridine ($\sim$100 g.).

Preparation of Pentachloropyridine from hexachloro-2-cyclopentenone (1).

Liquid ammonia (330 cc.) and dry ether (450 cc.) were placed in a flanged glass vessel (2 l.), cooled to -50° and stirred vigorously. Hexachloro-2-cyclopentenone (300 g.) was slowly added and the mixture stirred at -50° for a further hour. The mixture was then allowed to warm to room temperature and the ether distilled off. The solid obtained was washed well with water and dried in an oven (90°) for a short while. 260 g. of the crude amide of pentachloropenta-2,4-dienoic acid were obtained (m.p. 107-108°, lit. 111-112°, yield -93%).

The crude amide (240 g.) in dry benzene (215 cc.) was cooled to 0° and stirred while phosphorus pentachloride (200 g.) was slowly added. Immediate evolution of hydrogen chloride occurred. After stirring the mixture for 2 hrs. at 0°, it was raised to 80° and maintained at this temperature for 6 hrs. After distilling off the benzene the mixture was heated to 160° for 4 hrs. On cooling to room temperature the excess phosphorus pentachloride was hydrolysed with ice and the solid obtained was filtered off, washed with water and dried in an oven (105 g.). Repeated recrystallisation from meths yielded only solid of m.p. 190-200. This solid appeared to be mainly tetrachloro-2-pyridone (lit. m.p. 224-225°).

Some of the above solid (7·3 g.) was heated with phosphorus pentachloride (14 g.) at 160° for 4 hrs. On cooling to room temperature the excess phosphorus pentachloride was hydrolysed with ice. The solid obtained was filtered off, washed with water and dried in an oven (7·0 g.). Recrystallisation from meths yielded almost pure pentachloropyridine (m.p. 118-119°, lit. 124°), identified by comparison of its infra-red spectrum with that of an authentic sample.

Preparation of Pentachloropyridine from Hexachloro-2-cyclopentenone (2).

Liquid ammonia (1 l.) in dry ether (1·28 l.) was placed in a flanged glass vessel (5 l.) fitted with stirrer, condenser, dropping funnel, cooled to -50° and stirred vigorously. Hexachloro-2-cyclopentenone (880 g.) was slowly added, the temperature being maintained at -50°. After 1 hr. the temperature was allowed to rise slowly to room temperature. The ether was distilled off leaving a brown solid which was washed with water and dried to give the crude amide (820 g., 100%; m.p. 105°, lit. 111-112°).

The amide (820 g.) in dry benzene (750 ccs.) was stirred at 0° and phosphorus pentachloride (1 Kg.) slowly added. Immediate evolution of hydrogen chloride took place. The mixture was stirred at room temperature until complete solution occurred (2 hrs.). It was then heated under reflux for 6 hrs. After the benzene had been distilled off phosphorus pentachloride (500 g.) was added and the mixture heated to 160° for 4 hrs. On cooling to room temperature, the excess phosphorus pentachloride was hydrolysed with ice and the solid obtained filtered off, washed with water and dried by azeotropic distillation with benzene. The hot solution was filtered in order to remove red phosphorus and evaporation of the filtrate yielded a dirty brown solid. Distillation gave almost pure pentachloropyridine (370 g., 48·4%; m.p. 123°, lit. 124°).

Both this and the pentachloropyridine produced in the previous experiment were readily converted into pentafluoropyridine by reaction with potassium fluoride but, as stated in the discussion, further samples of pentachloropyridine prepared in this way would not react with potassium fluoride.

Conversion of Pentachloropyridine into Pentafluoropyridine.

In a typical experiment, an autoclave (120 ml.) was charged with pentachloropyridine (20 g., 0·079 mole) and anhydrous potassium fluoride (60 g., 1·04 mole) and evacuated before being heated to 480° for 20 hr. When the reaction vessel was still hot, the product (13 g.) was distilled from it under vacuum. The composition of the product (determined by analytical scale G.L.C.) was pentafluoropyridine 70, monochlorotetrafluoropyridine 25, and dichlorotrifluoropyridine 5 mole %. The products from several reactions were combined and fractionated through a concentric tube column.

SYNTHESIS OF TETRAFLUOROISONICOTINIC ACID

1. Preparation of 4-aminotetrafluoropyridine.

Pentafluoropyridine (10 g., 0·059 mole) and ammonia (20 ml; 0·88 s.g.) were placed in a Carius tube and the tube evacuated and sealed. The tube was heated to 80° for 5 hrs. On cooling to room temperature the organic layer solidified. The tube was opened and water added to the mixture which was then extracted with ether. Distillation of the dried ($MgSO_4$) ether extracts afforded a white crystalline material (8·8 g., 90%). Sublimation under reduced pressure and recrystallisation from light petroleum (b.p. 80-100°) gave 4-aminotetrafluoropyridine m.p. 85-86°.

2. Preparation of 4-bromotetrafluoropyridine from 4-aminotetrafluoropyridine.

4-Aminotetrafluoropyridine (12 g.) was dissolved in hydrofluoric acid (80 ml.; 80% $^w/_w$), stirred and cooled to -20°. Sodium nitrite (12 g.) was added over a period of 30 mins. Freshly prepared cuprous bromide (made by dissolving the water washed precipitate from 60 g. copper sulphate + 40 g. potassium bromide + 20 g. sodium sulphite, in 40 ml. of hydrobromic acid (48% $^w/_w$)) was added to the diazotised amine over a period of 30 mins. at a temperature of -20 to -25°. After a further 30 mins. stirring during which the temperature rose to room temperature, the mixture was diluted with water (1 l.). The mixture was extracted with methylene chloride, the extracts dried ($MgSO_4$) and the solvent distilled off. Distillation of the residual liquid from phosphorus pentoxide yielded 4-bromotetrafluoropyridine (12·3 g., 73·9%, b.p. 138-142°, lit. 134-135°).

3. Conversion of 4-bromotetrafluoropyridine to tetrafluoroisonicotinic acid.

(a) Via tetrafluoro-4-pyridylmagnesium bromide.

A three necked flask fitted with stirrer, dropping funnel, condenser and containing magnesium (4 g.) and dry tetrahydrofuran (40 ml.) was purged with dry nitrogen and cooled to -25°. A solution of 4-bromotetrafluoropyridine (20 g.) in dry tetrahydrofuran (10 ml.) was added over 45 mins. After a short time the reaction commenced. The reaction mixture was allowed to warm to -10 to 0° and was then maintained at this temperature for 1·5 hours before dry carbon dioxide was bubbled through the solution for 2 hrs. at -10°. Dilute sulphuric acid was then added and when all the excess magnesium had dissolved the mixture was extracted with ether. The extracts were dried ($MgSO_4$), the solvent was removed by distillation and from the residue a white solid (10·1 g., 62%) was sublimed under reduced pressure. Recrystallisation from hexane afforded tetrafluoroisonicotinic acid m.p. 104-105°.

(b) Via 4-lithiotetrafluoropyridine.

4-Bromotetrafluoropyridine (2 g., 8·75 m.mole) in dry ether (15 ml.) was added over a period of 1 hr. at -75° to a solution of butyl-lithium (3·5 ml., 8·75 m.mole) in ether (15 ml.) under dry nitrogen. The solution was then carbonated for 1 hr. during which the temperature rose to room temperature. Water was then added in order to dissolve the lithium salt of tetrafluoroisonicotinic acid which had precipitated. The solution was then acidified with dilute hydrochloric acid and ether extracted. The ether extract was dried ($MgSO_4$) and after the solvent had been removed, sublimation under reduced pressure afforded the tetrafluoroisonicotinic acid (1·35 g., 80%).

Reaction of Tetrafluoroisonicotinic acid with Thionyl Chloride.

Tetrafluoroisonicotinic acid (1 g.) was heated under reflux with thionyl chloride (10 ml.) for 16 hrs. The excess thionyl chloride was then removed by distillation under reduced pressure. The residual liquid was then distilled under reduced pressure (0·1 mm.) to give a green liquid (0·7 g., b.p. 114-118°). Some unreacted acid solidified in the condenser during the distillation. The infra-red spectrum of the liquid obtained showed the presence of a hydroxyl group (due to unreacted acid).

Elemental analysis of what was thought to be a fairly pure sample of green liquid (produced as above) gave:-

	C: 37·6;	F: 43·6;	Cl: nil
Calculated for C_6F_4ClON	C: 33·7;	F: 35·6;	Cl: 16·6
Calculated for $C_{12}F_8N_2O_3$	C: 38·7;	F: 40·9;	Cl: nil

This liquid reacted as tetrafluoroisonicotinyl chloride would be expected to react e.g. gave an amide by reaction with ammonia, and a phenylhydrazide by reaction with phenylhydrazine. An obvious conclusion to draw from this is that the liquid is the anhydride of tetrafluoroisonicotinic acid. This compound would be expected to react in a similar manner to the acid chloride and the carbon analysis is consistent with a 50:50 mixture of anhydride and unreacted acid.

Reaction of (supposed) Tetrafluoroisonicotinyl chloride[+] with anhydrous hydrazine in tetrahydrofuran*

Tetrafluoroisonicotinyl chloride[+] (0·7 g.) in tetrahydrofuran (10 ml.) was added over 20 mins. to anhydrous hydrazine (1 ml.) in tetrahydrofuran (10 ml.) at -10°. The solution was stirred for a further 20 mins. at -10°

and then for 40 mins. during which the temperature rose to room temperature.

The orange yellow solid obtained was filtered off and an unsatisfactory recrystallisation from meths yielded a light brown solid (0· 2 g.) which decomposed at 65°. Its infra-red spectrum showed a broad peak stretching from 2·7 —— 3·7μ, which is probably due to N-H absorption, the broadness being due to hydrogen bonding.

Elemental analysis gave	C: 28·3;	H: 3·67
Calculated for tetrafluoroisonicotinylhydrazine	C: 34·5;	H: 1·44
Calculated for bis(tetrafluoroisonicotinyl)-hydrazine	C: 37·3;	H: 0·50

Since the hydrogen content is high it must be assumed that some nucleophilic substitution of the ring fluorine atoms by hydrazine has occurred.

*This is essentially the method reported for the preparation of pentafluorobenzhydrazide in Monsanto Chemicals Ltd. Research Department's progress report, December 1964, on highly fluorinated aromatic compounds and polymers by W. Cummings and E.R. Lynch.

Reaction of (supposed) Tetrafluoroisonicotinyl chloride⁺ with anhydrous hydrazine in ether.

Tetrafluoroisonicotinyl chloride$^+$ (2·6 g.) in ether (25 ml.) was stirred at room temperature. Anhydrous hydrazine (1 ml.) in ether (10 ml.) was added over 15 mins. The ether began to reflux due to an exothermic reaction occurring. After a further 45 mins. stirring, the orange red solid which formed was filtered off, 3·5 g. of dry solid being obtained. It could not be satisfactorily recrystallised but it was found to be very soluble in alcohols but insoluble in other solvents. The infra-red spectrum was similar to that of the solid obtained in the previous experiment but this solid did not decompose till 130°.

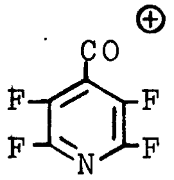
Preparation of N-Phenyl-N'-Tetrafluoroisonicotinylhydrazine.

Tetrafluoroisonicotinyl chloride[+] (0·45 g.) in ether (10 mls.) was stirred at room temperature. Phenyl hydrazine (0·5 g.) was added over 15 mins. and then the mixture stirred for a further 30 mins. A white solid soon precipitated from the brown coloured ether solution. The white solid (0·38 g.) was filtered off and recrystallised from propanol/hexane. The solid started to decompose at 130°. It has not yet been identified but has been shown to contain a tetrafluoro-4-substituted pyridine group and a phenyl group. Elemental analysis gave

C: 45·4; H: 2·96

Concentration of the ether solution gave a red and white solid. This was filtered off and washed with a little ether leaving a white solid which was recrystallised from hexane/meths/carbon tetrachloride affording N-PHENYL-N'-PERFLUOROISONICOTINYL HYDRAZINE (0·3 g., 49·8%) m.p. 175-180° (decomposition).

Calculated for $C_{12}H_7F_4N_3O$ C: 50·5; H: 2·35; M.wt. 285
Found C: 50·5; H: 2·45; M.wt. 285

The mass spectrum was as expected i.e. parent peak at 285, major peaks at 178  and 107 ($PhNHNH^+$).

[+] The tetrafluoroisonicotinyl chloride referred to is the liquid obtained from the reaction between thionyl chloride and tetrafluoroisonicotinic acid.

Preparation of Tetrafluoroisonicotinamide.

Tetrafluoroisonicotinic acid (0·66 g.) was heated under reflux with thionyl chloride (11 ml.) for 12 hrs. Excess thionyl chloride was removed by distillation under reduced pressure. Dry benzene (15 ml.) was then added and anhydrous ammonia bubbled through the solution for 10 mins. The benzene was distilled off leaving a light brown solid which was washed with a little water, dried, and sublimed under reduced pressure to give a white solid (0·2 g., 31%). Recrystallisation from carbon tetrachloride afforded TETRAFLUOROISONICOTINAMIDE m.p. 96-97°.

Calculated for $C_6H_2F_4N_2O$ C: 37·1; H: 1·03; F: 39·15
Found C: 37·0; H: 1·08; F: 38·8

Attempted preparation of 2,4,6-trifluoronicotinamide.

2,4,6-Trifluoronicotinic acid (0·3 g.) was heated with thionyl chloride (6 ml.) under reflux for 12 hrs. The excess thionyl chloride was removed by distillation under reduced pressure. Dry benzene (10 ml.) was then added and anhydrous ammonia bubbled through the solution for 10 mins. at room temperature. Sublimation under reduced pressure of the brown solid obtained after the benzene had been distilled off, afforded a white solid (0·08 g.) which was thrice recrystallised from water yielding a white solid m.p. 166·5-167·5°.

Calculated for $C_6H_3F_3N_2O$ C: 40·9; H: 1·7
for $C_6H_5F_2N_3O$ C: 41·6; H: 2·9
Found C: 41·2; H: 3·1

The product is thus almost certainly 4-amino-2,6-difluoronicotinamide.

The Preparation of Tetrafluoroisonicotinyl Chloride.

Tetrafluoroisonicotinic acid (5 g.) and phosphorus pentachloride (6·1 g.; 10% excess) were heated together to 90° for 6 hrs. A clear liquid product (5·0 g.) was obtained by distillation. This liquid was redistilled at 13 mms. pressure affording three fractions

1. b.p. 40-51° (2·10 g.)
2. b.p. 51-52° (1·75 g.)
3. residue (0·75 g.)

Analysis of fraction 2 gave C: 33·4; F: 35·4; Cl: 17·1

Calculated for C_6F_4ClNO C: 33·7; F: 35·6; Cl: 16·6

Fraction 2 is therefore TETRAFLUOROISONICOTINYL CHLORIDE. The yield based on weight of fraction 2 is 32% but the true yield is almost certainly higher than this since the infra-red spectra of fractions 1 and 3 indicate the presence of tetrafluoroisonicotinyl chloride.

Nonafluoro(pyridyl-4-phenyl)ether.

Anhydrous potassium pentafluorophenate (1·38 g., 6·2 m.moles), pentafluoropyridine (1·00g., 5·9 m.moles) and dry tetrahydrofuran (10 ml.) were refluxed together for 4 hours. The potassium salt dissolved in the tetrahydrofuran and a brown precipitate was formed. The product was poured into water and extracted with ether (5 x 30 ml.). The ethereal extract was dried ($MgSO_4$) and evaporated to leave a colourless liquid and a small amount of white solid. This product was shown by gas-liquid chromatography (silicone grease at 200°) to contain mainly reaction product together with small amounts of unchanged pentafluoropyridine and pentafluorophenol. A small shoulder on the product peak presumably indicated the presence of a little of 2-isomer (< 5%). The perfluoropyridyl-4-phenyl ether (0·26 g.) was isolated by preparative scale gas-liquid chromatography.

Found C, 38·9; F, 50·6%

$C_{11}F_9NO$ requires C, 39·6; F, 51·3%

It is intended to attempt the preparation on a larger scale to try to separate the ether by distillation in vacuo. On attempted distillation at room temperature slight darkening occurs. The compound boils at 102° at 15 mm. F^{19} n.m.r. spectroscopy indicated that the compound was the 4-isomer.

Octafluoro-4,4'-dipyridyl Ether.

The monohydrate of the potassium salt of tetrafluoro-4-hydroxypyridine (1·38 g.) and pentafluoropyridine (1·00 g.) were refluxed in 20 ml. of tetrahydrofuran for 8 hours. The solution became yellow in colour after ½ hr. and a brown precipitate of potassium fluoride was slowly formed. The reaction mixture was poured into 200 ml. of water and extracted with ether (3 x 50 ml.). The ethereal layer was shaken with dilute sodium carbonate solution to remove any unchanged tetrafluoro-4-hydroxypyridine, dried ($MgSO_4$) and evaporated to leave 0·5 g. of product which was shown to be a new compound by gas-liquid chromatography (silicone grease at 200°). Attempts to purify the product proved difficult because of the small amount and the reaction will be tried again on a larger scale.

Undecafluoro(phenyl-isoquinolyl)ether.

Anhydrous potassium pentafluorophenate (0·666 g., 3 m.mole) and heptafluoroisoquinoline (0·765 g., 3 m.mole) and tetrahydrofuran (10 ml.) were refluxed for 1½ hours. The reaction mixture quickly darkened to give 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 unchanged heptafluoroisoquinoline, at 40°C to remove a little unchanged pentafluorophenol and at 80°C to sublime the product. The white solid was recrystallised from methanol to give a solid which melted sharply at 124°C.

Found C, 42·6%; F, 49·6%

$C_{15}F_{11}NO$ requires C, 42·9%; F, 49·9%

Yield 0·756 g. (62%)

Table 1

Preparation of Pentachloropyridine

Reactant and experiment number	Temp. °C	Wt. of starting material (gms.)	Wt. of chlorine (gms.)	Wt. of product obtained (gms.)	Composition of Product Mole % Di-chloro	Tri-chloro	Tetra-chloro	Penta-chloro	Average Formula of product	% yield based on average molecular formula
1 Pyridine	160	120 (1·5 moles)	535 (7·5 moles)	137·5	37·5 (31·0)	36·3 (37·1)	26·2 (31·9)	-	$C_5H_{2\cdot1}Cl_{2\cdot9}N$	51·7
2 Pyridine	160	170 (2·15 moles)	756 (10·75 moles)	257·5	19·2 (15·1)	47·0 (45·7)	33·8 (39·2)	-	$C_5H_{1\cdot8}Cl_{3\cdot2}N$	60·6
3 Pyridine	200	180 (2·28 moles)	1222 (17·2 moles)	208·4	61·2 (55·7)	35·9 (40·3)	2·2 (3·1)	0·6 (0·9)		Some product was lost which was relatively richer in tri- and tetra-chloro-pyridines
4 Chloro* pyridines in CCl_4	95	145 (0·725 moles)	197 (2·8 moles)	127·5	30·0 (24·4)	41·9 (42·0)	28·1 (33·6)	-	$C_5H_{1\cdot9}Cl_{3\cdot1}N$	-
5 Pyridine in CCl_4	110	160 (2·0 moles)	781 (11·0 moles)	38·0	31·8 (26·5)	50·7 (52·1)	17·5 (21·4)	-	$C_5H_{2\cdot1}Cl_{2\cdot9}N$	10·7

* The composition of the starting material for this expt. was $C_5H_{1\cdot8}Cl_{3\cdot2}N$

Figures in parentheses are weight %.

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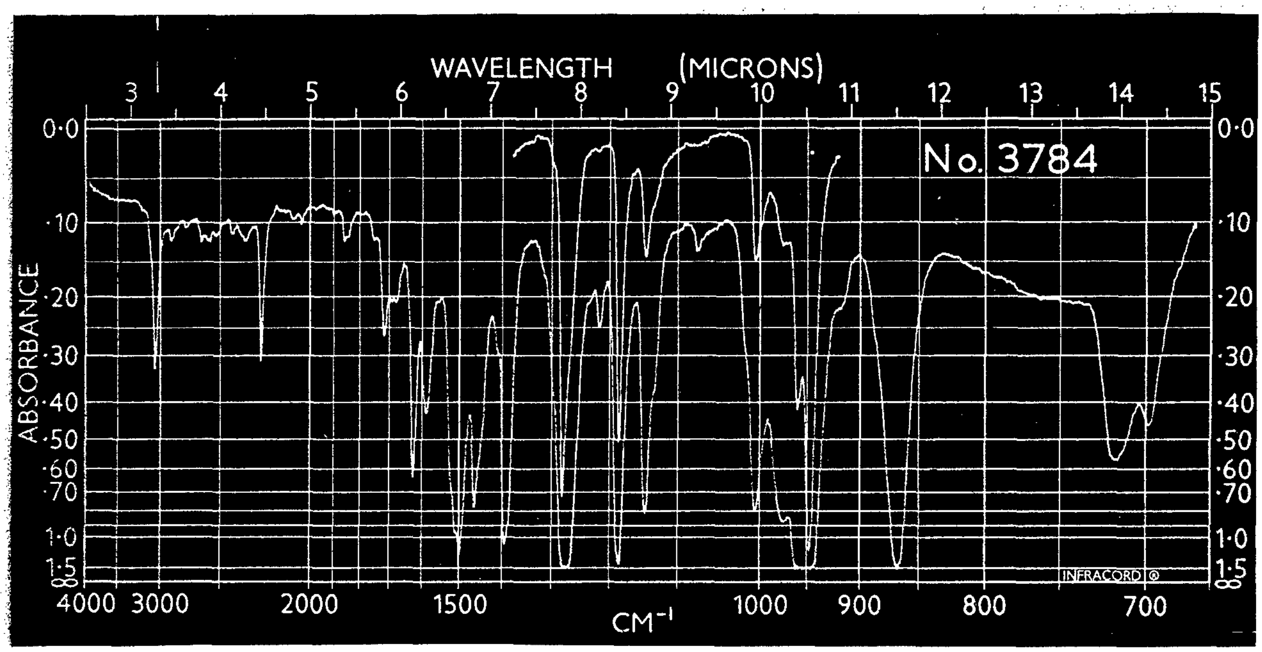
1. R.D. Chambers, J. Hutchinson, W.K.R. Musgrave, J., 1964, 3573.
2. Banks, Haszeldine, Latham and Young, J., 1965, 594.
3. Roedig, Grohe, Ber., 1965, 98, 923.
4. Chambers, Hutchinson, Musgrave, J., 1964, 3736.
5. Chambers, Hutchinson, Musgrave, J., 1965, 5040.
6. J. Hutchinson, private communication.
7. Farbenfabriken Bayer, A.G., Ger. Pat. 1,168,911; Chem. Abs., 1964, 61, 3073.
8. Chambers, Drakesmith and Musgrave, J., 1965, 5045.

APPENDIX I

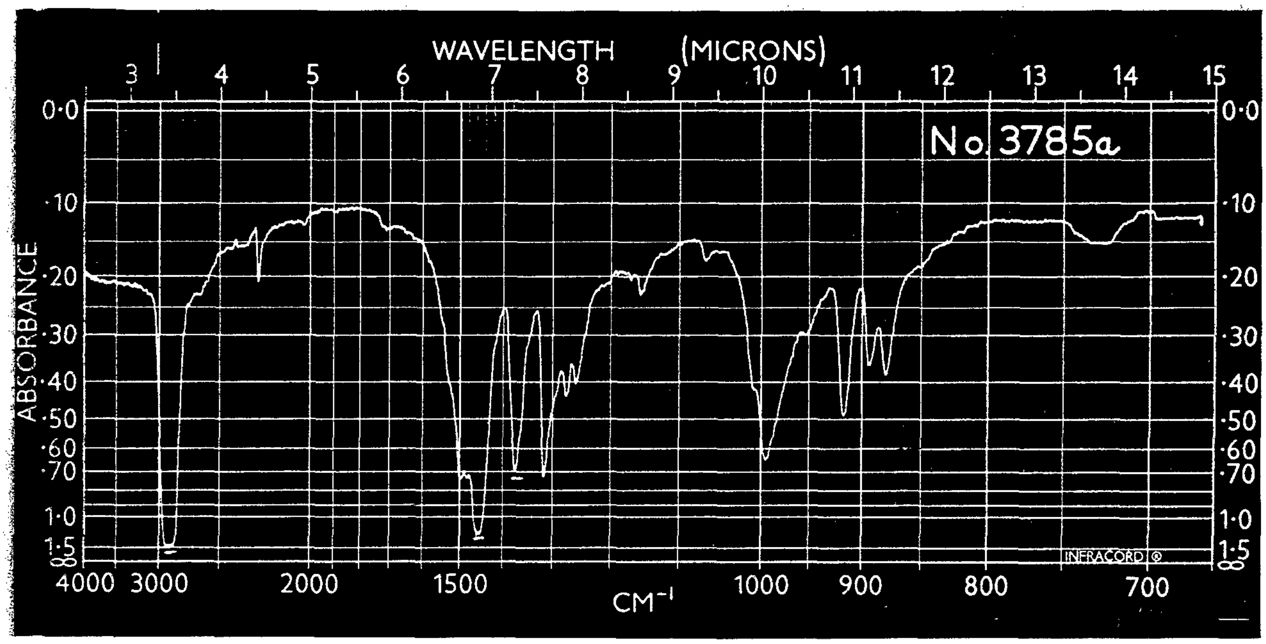
Infrared Spectra Referred to in Part I

No.	
3784	2,3,5,6-Tetrafluorobenzonitrile (in CCl_4)
3785a	Tetrafluoroterephthalodinitrile (Nujol mull)
3845	Tetrafluoroterephthalic acid (KBr disc)
3805	2,3,5,6-Tetrafluorobenzoic acid (in $CHCl_3$)
3434	3-Bromoheptafluorotoluene (thin film)
3428	3-Cyanoheptafluorotoluene (thin film)
3630	Heptafluoro-m-toluic acid (in CCl_4)
3487	3-Fluoro-6-hydroxy durene (in CCl_4)
4055	Difluoro-bis(methoxycarbonyl)xylene (in CCl_4)
4014	2,5-Difluoro-3,4,6-tris(methoxycarbonyl)toluene (in CCl_4)
4091	Difluoroxylene dicarboxylic acid (KBr disc)
4095	Difluorotoluene-3,4,6-tricarboxylic acid (KBr disc)
4127	Difluoropyromellitic acid (KBr disc)
4134	Barium difluoropyromellitate (KBr disc)
4083	1,2,4,5-Tetra(bromomethyl)-3,6-difluorobenzene (in $CHCl_3$)
4090	Unknown product from oxidation of 1,2,4,5-tetra(bromomethyl)-3,6-difluorodurene (KBr disc)
3483	3-Hydrazino-2,4,5,6-tetrafluoroaniline (in $CHCl_3$)
3642	Acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone (in CCl_3CN)
3641	Tetrafluoro-m-phenylenediamine (in CCl_4)
3543	Tetrafluoro-p-phenylenediamine (in $CHCl_3$)

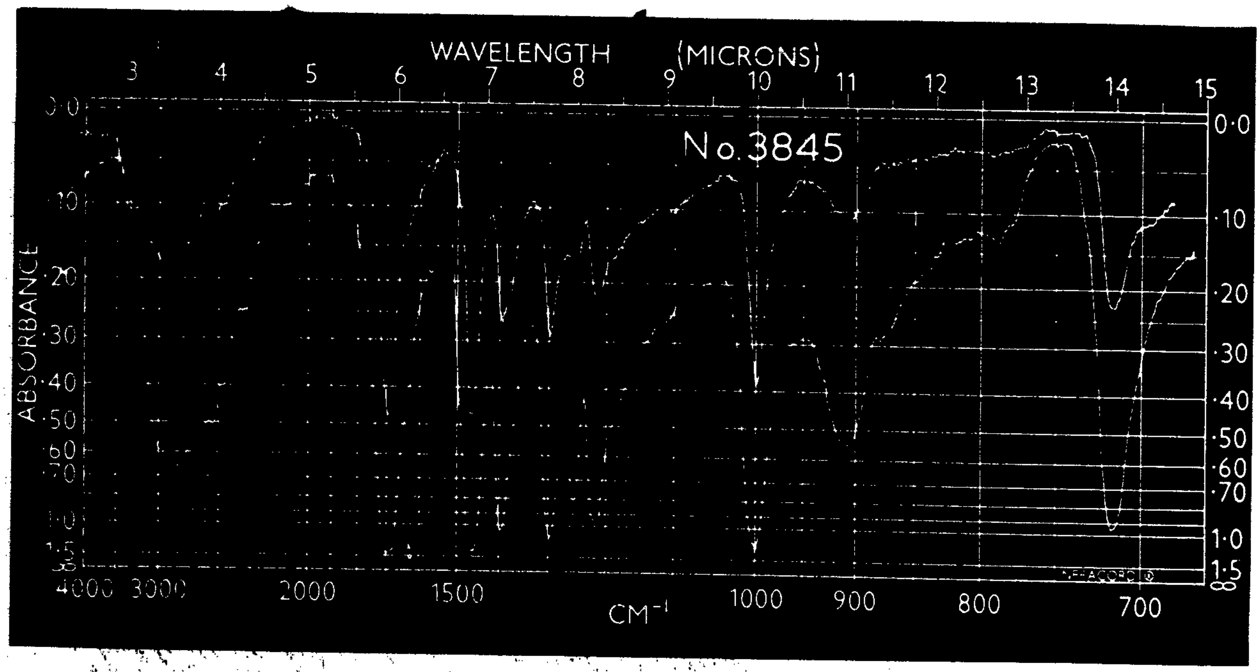
3424	Decafluorobenzanilide (in $CHCl_3$)
3449	N-(pentafluorophenyl)pentafluorobenzimidoyl chloride (in CCl_4)
3735	1,4-Bis(pentafluoroanilino)tetrafluorobenzene (in CCl_3CN)
3710	4-Aminononafluorodiphenylamine (in CCl_4)
3382	2,3,4,6-Tetrafluoroaniline (thin film)
3422	3,3'-Bis(pentafluorobenzamido)-4,4'-dinitrohexafluorobiphenyl
3849a	3,3'-Bis(pentafluorobenzamido)-4,4'-diaminohexafluorobiphenyl (KBr disc)
3823	Tetrafluororesorcinol (in CCl_4)
3837	Tetrafluororesorcinol (KBr disc)
3921	Tetrafluororesorcinol (KBr disc)
3670a	Tetrafluorocatechol (in CCl_4)
4022	4,4'-Bis(2,3,5,6-tetrafluorophenylthio)octafluorobiphenyl (in CCl_4)
3472	Tetrafluorobenzene-1,4-dithiol (in CCl_4)



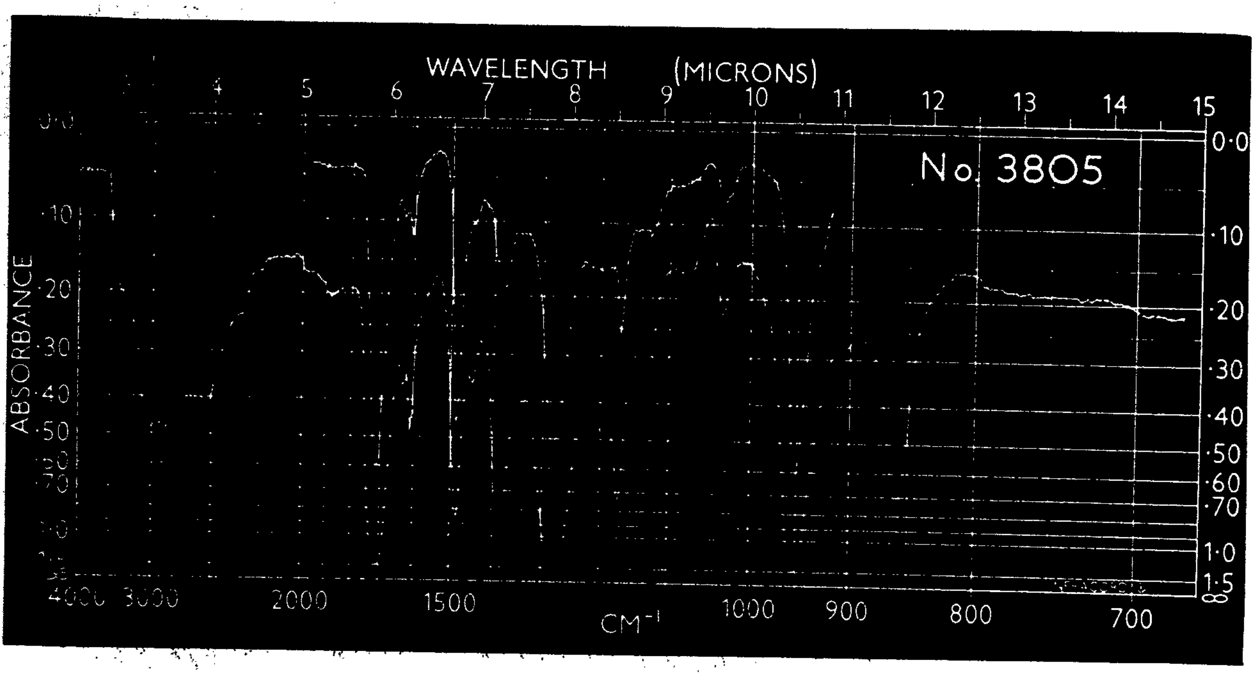
Spectrum No. 3784 2,3,5,6-Tetrafluorobenzonitrile (in CCl_4)



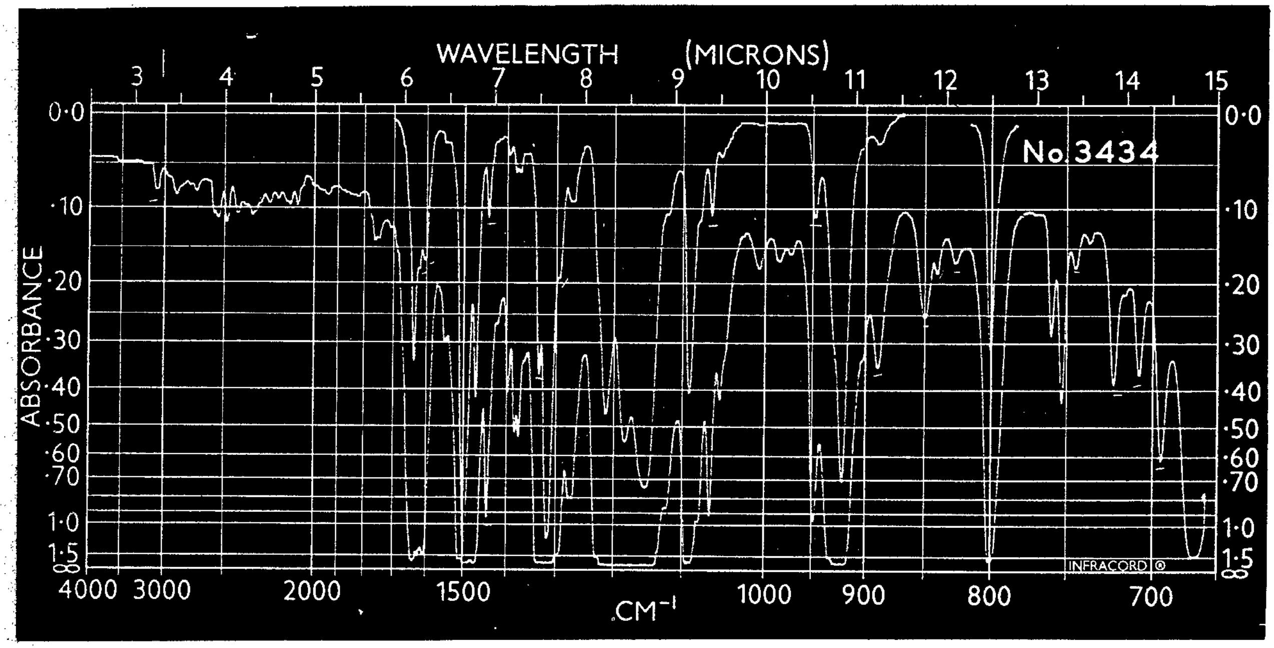
Spectrum No. 3785a Tetrafluoroterephthalodinitrile (Nujol mull)



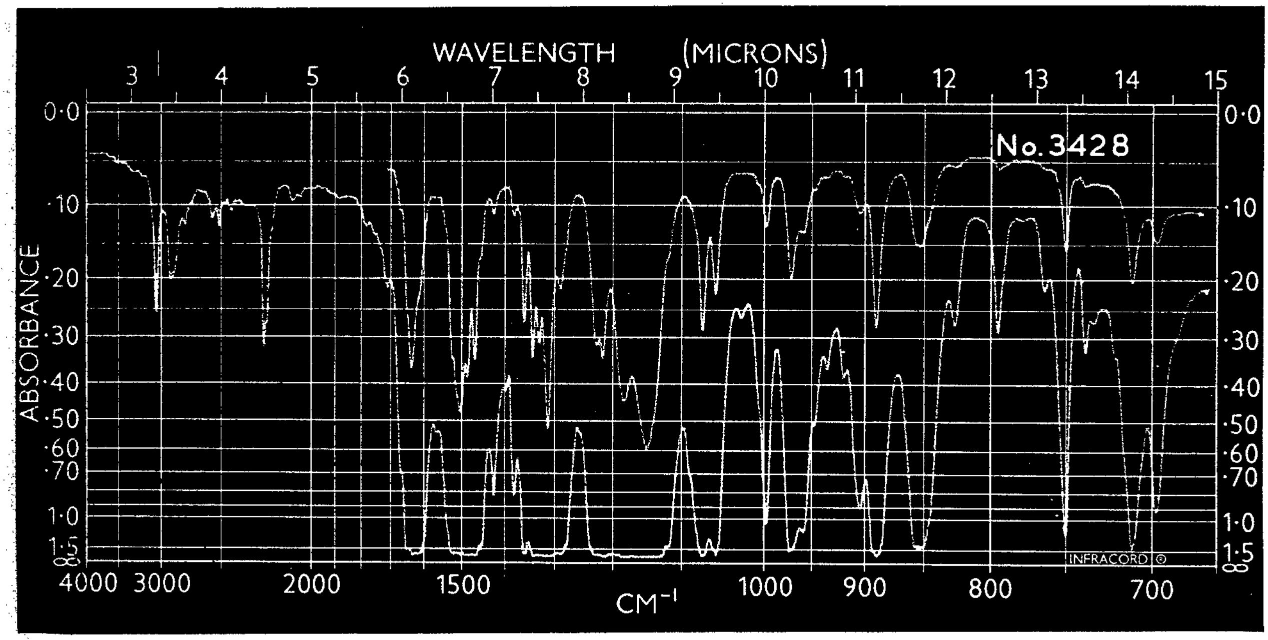
Spectrum No. 3845 Tetrafluoroterephthalic acid (KBr disc)



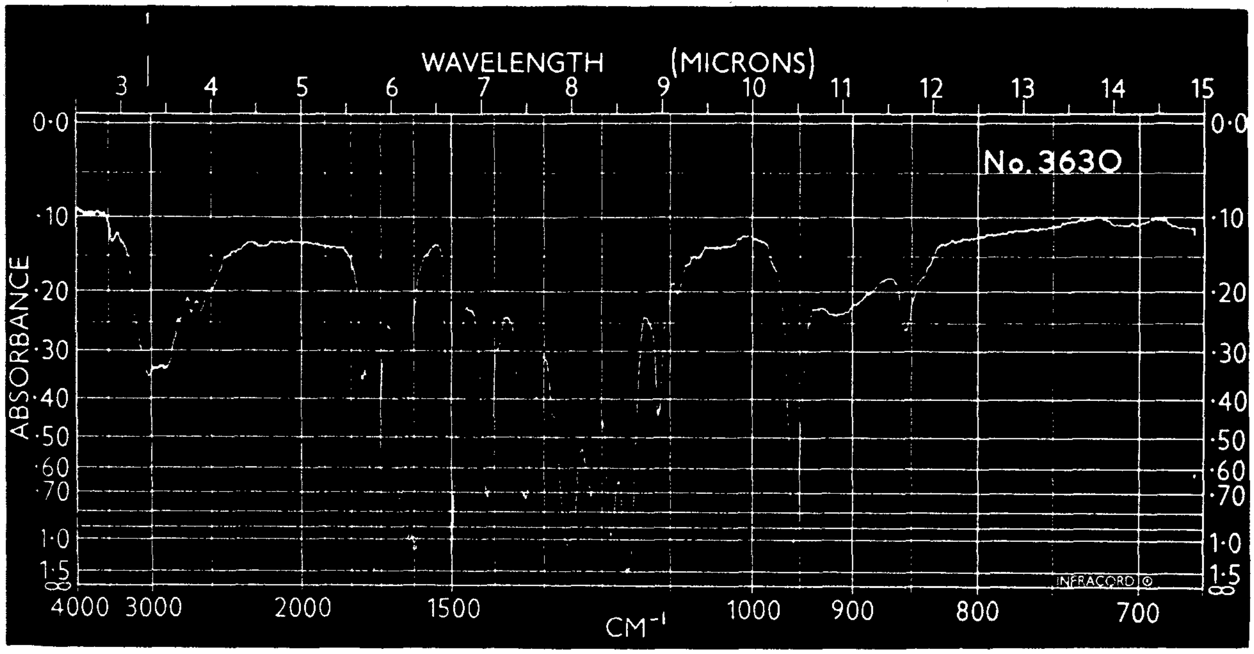
Spectrum No. 3805 2,3,5,6-Tetrafluorobenzoic acid (in $CHCl_3$)



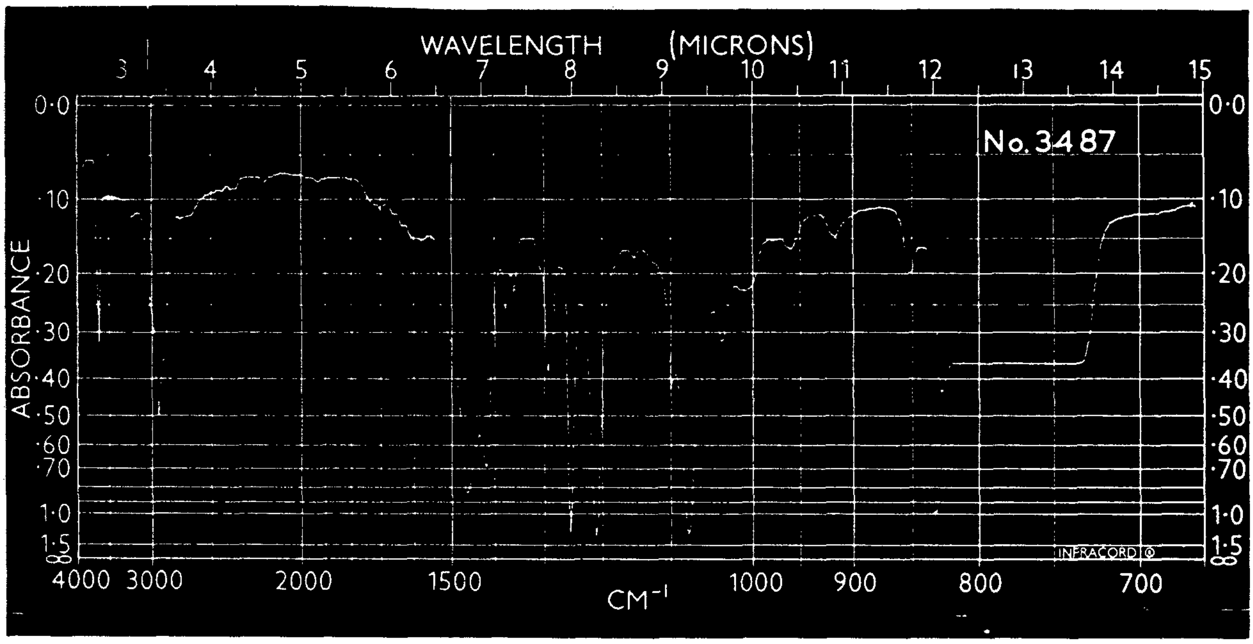
Spectrum No. 3434 3-Bromoheptafluorotoluene (thin film)



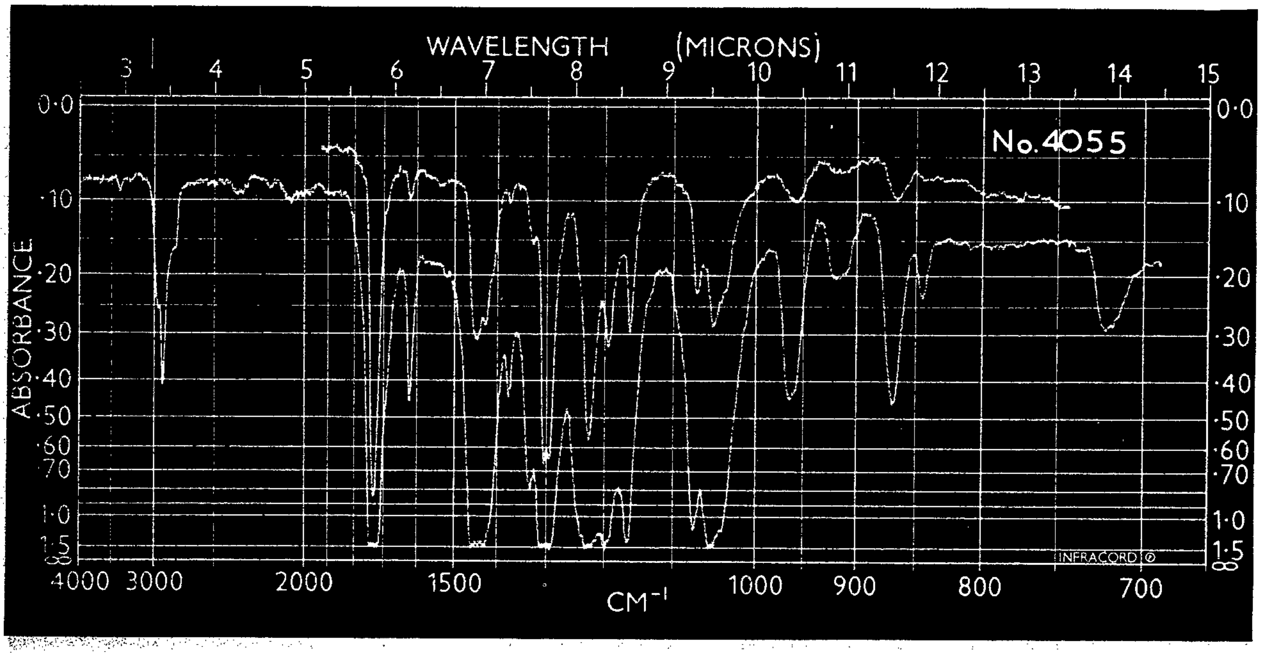
Spectrum No. 3428 3-Cyanoheptafluorotoluene (thin film)



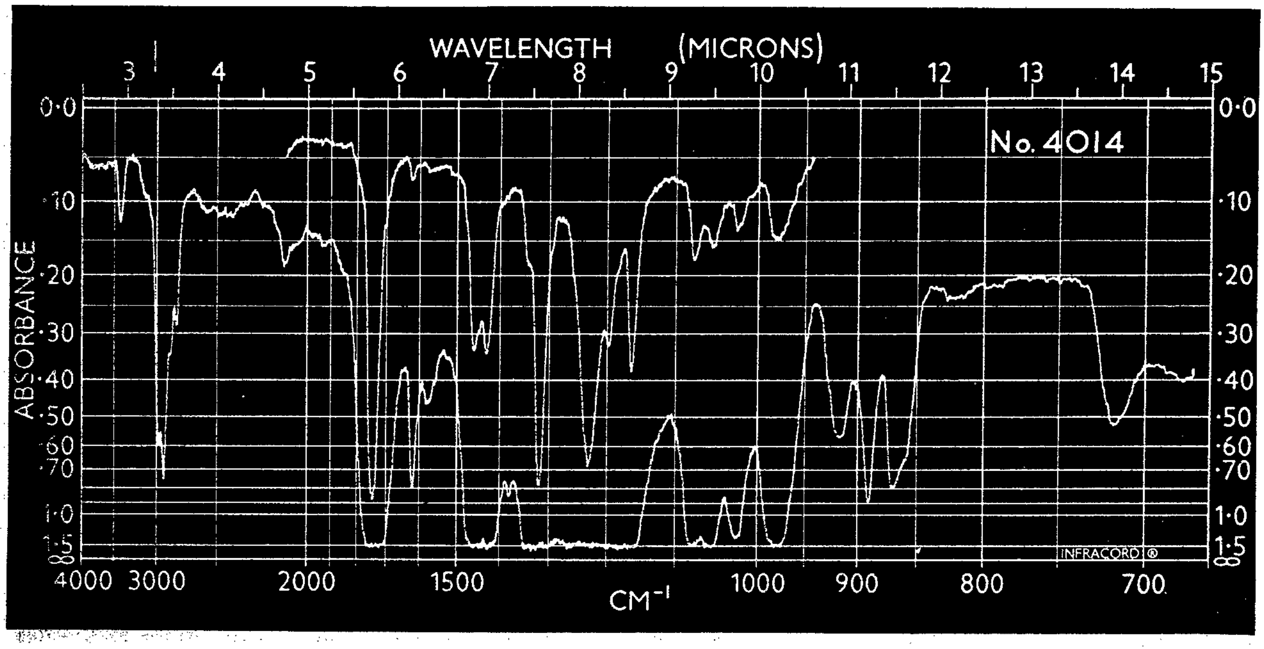
Spectrum No. 3630 Heptafluoro-m-toluic acid (in CCl_4)



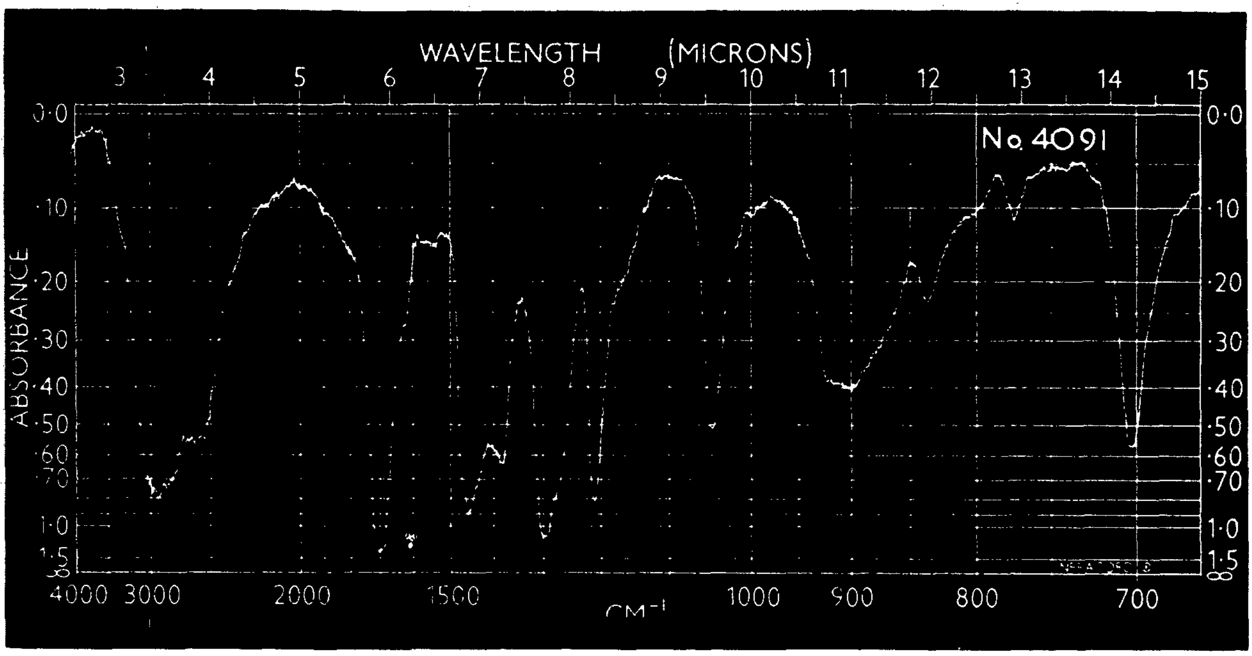
Spectrum No. 3487 3-Fluoro-6-hydroxy durene (in CCl_4)



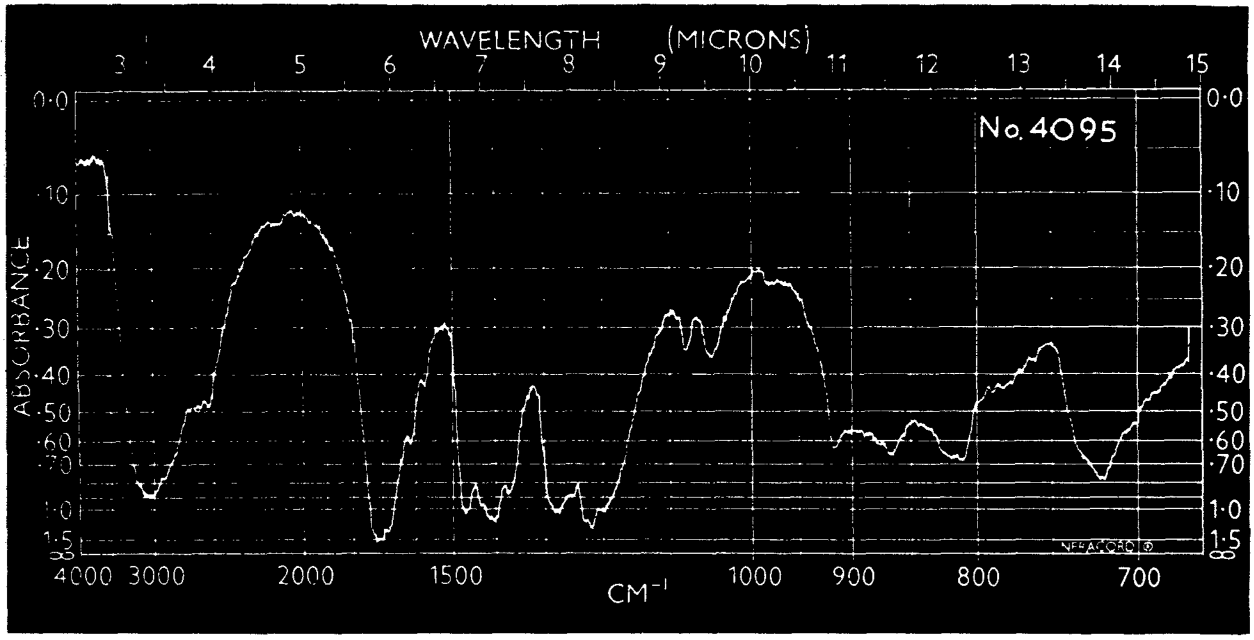
Spectrum No. 4055 Difluoro-bis(methoxycarbonyl)xylene (in CCl_4)



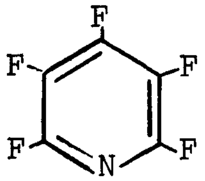
Spectrum No. 4014 2,5-Difluoro-3,4,6-tris(methoxycarbonyl)-toluene (in CCl_4)

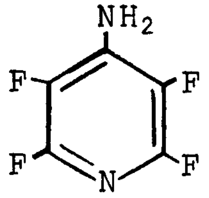


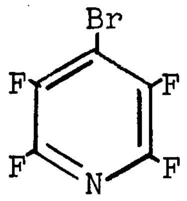
Spectrum No. 4091 Difluoroxylene dicarboxylic acid (KBr disc)

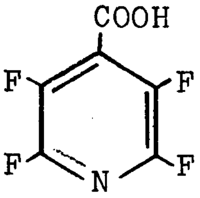


Spectrum No. 4095 Difluorotoluene-3,4,6-tricarboxylic acid (KBr disc)







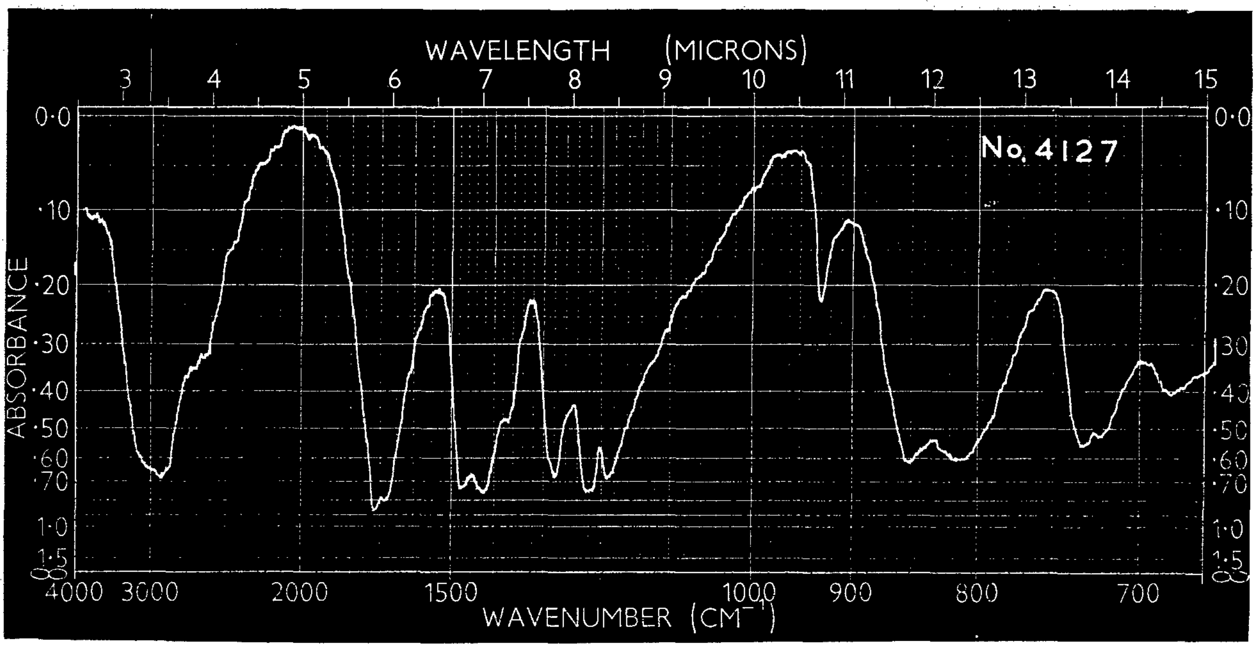


The final stage of the synthesis can be carried out either by carbonation of tetrafluoro-4-pyridyl magnesium bromide (prepared by reaction of 4-bromotetrafluoropyridine with magnesium in tetrahydrofuran) or by reaction of 4-bromotetrafluoropyridine with butyl-lithium followed by carbonation of the 4-lithiotetrafluoropyridine produced.[6] The latter reaction goes in better yield (80%) than the former (60%).

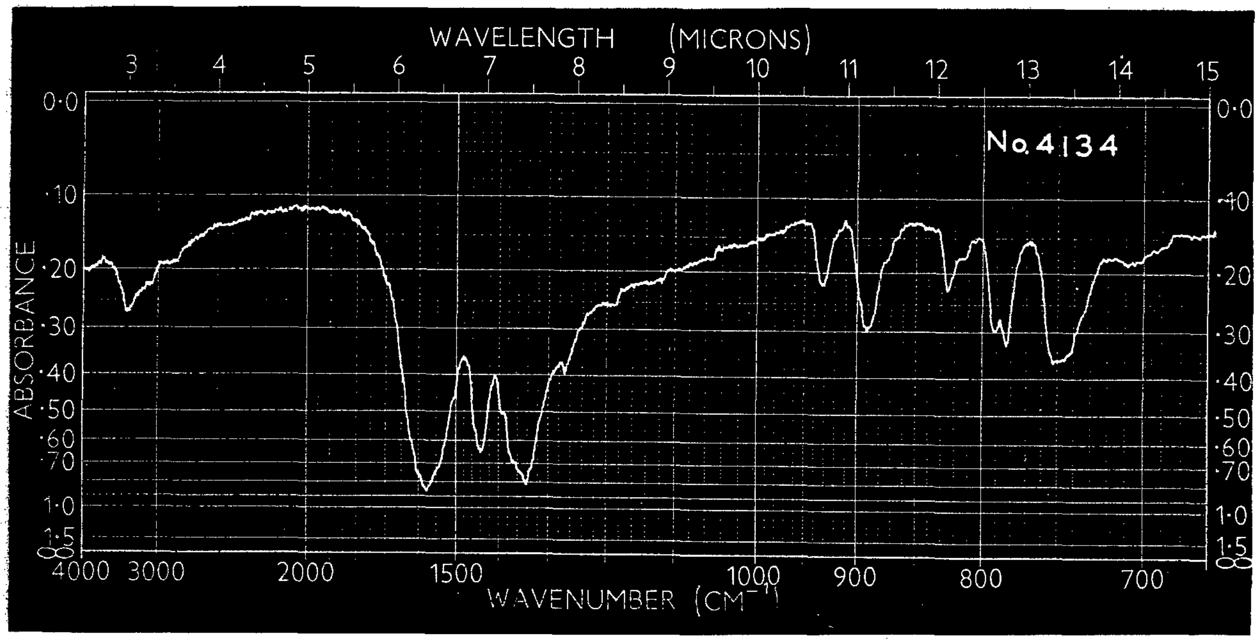
The reaction between perfluoroisonicotinic acid and thionyl chloride at 80°, both in the absence and presence of catalytic amounts of dimethyl formamide, does not go to completion for reaction times of up to 72 hrs. Perfluoroisonicotinyl chloride is not obtained. The reaction product appears to be a mixture of unreacted perfluoroisonicotinic acid and its anhydride. The perfluoroisonicotinyl chloride can however be obtained by reacting the acid with phosphorus pentachloride at 90°C.

The product from the reaction between thionyl chloride and perfluoroisonicotinic acid has been reacted with anhydrous hydrazine at various temperatures between -50° and room temperature.

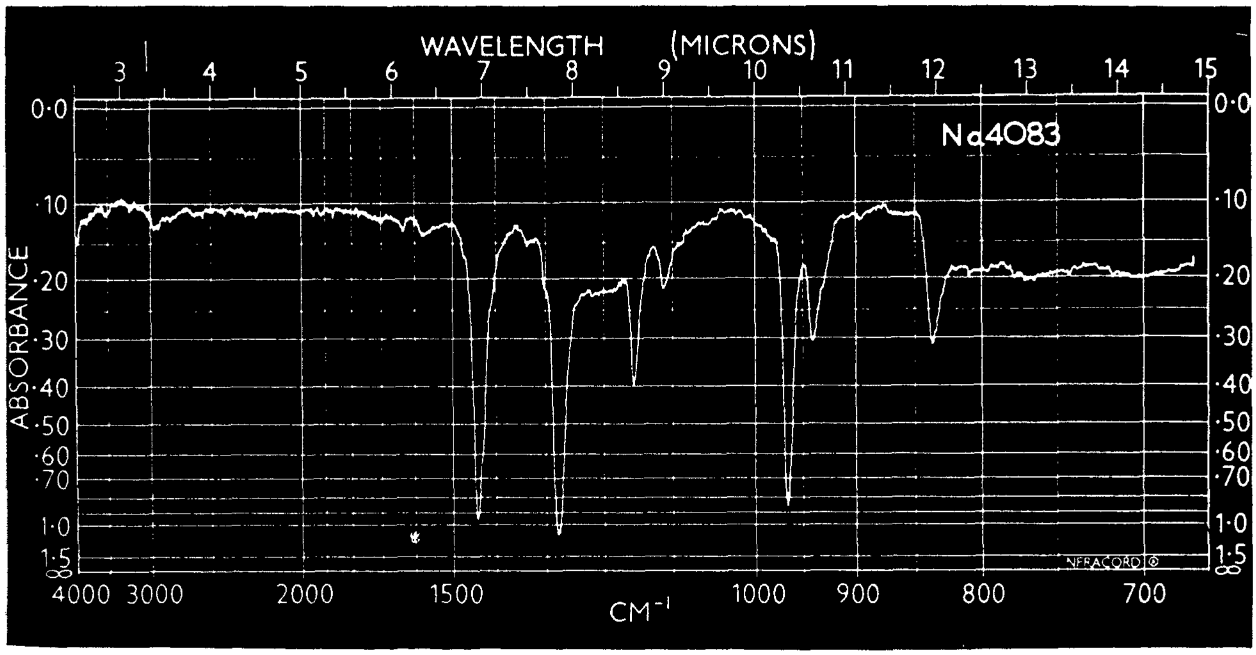
Perfluoroisonicotinamide and N-phenyl-N'-perfluoroisonicotinyl hydrazine have been prepared and the attempted preparation of 2,4,6-trifluoronicotinamide has been carried out; the product appeared to be 4-amino-2,6-difluoronicotinamide.



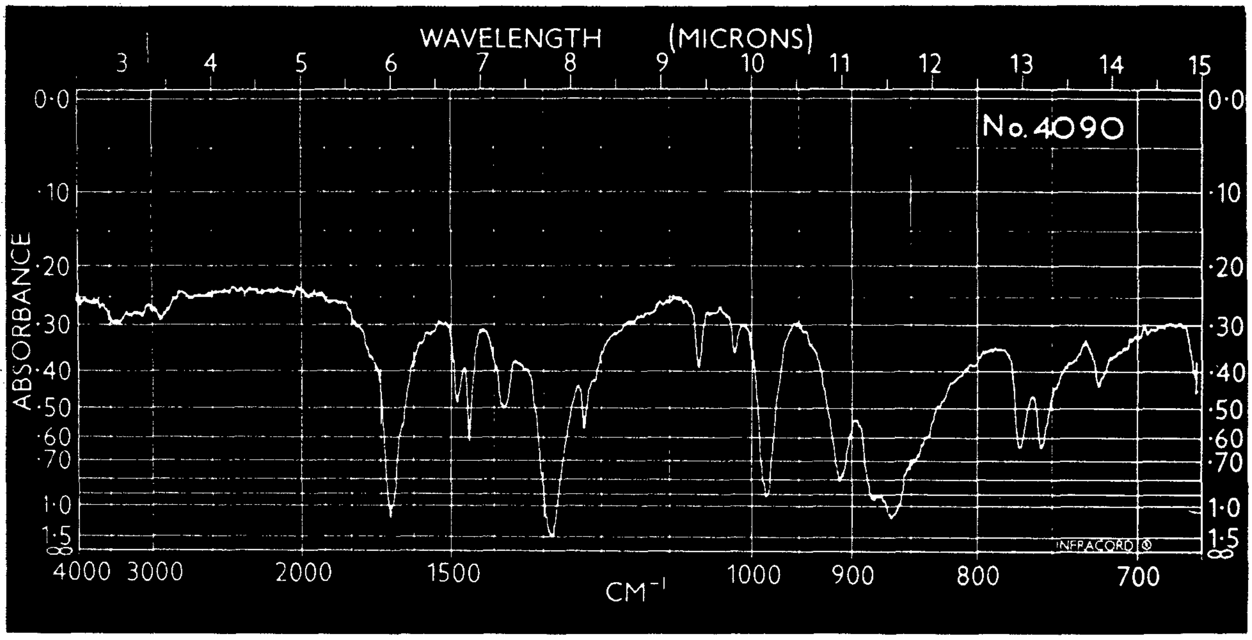
Spectrum No. 4127 Difluoropyromellitic acid (KBr disc)



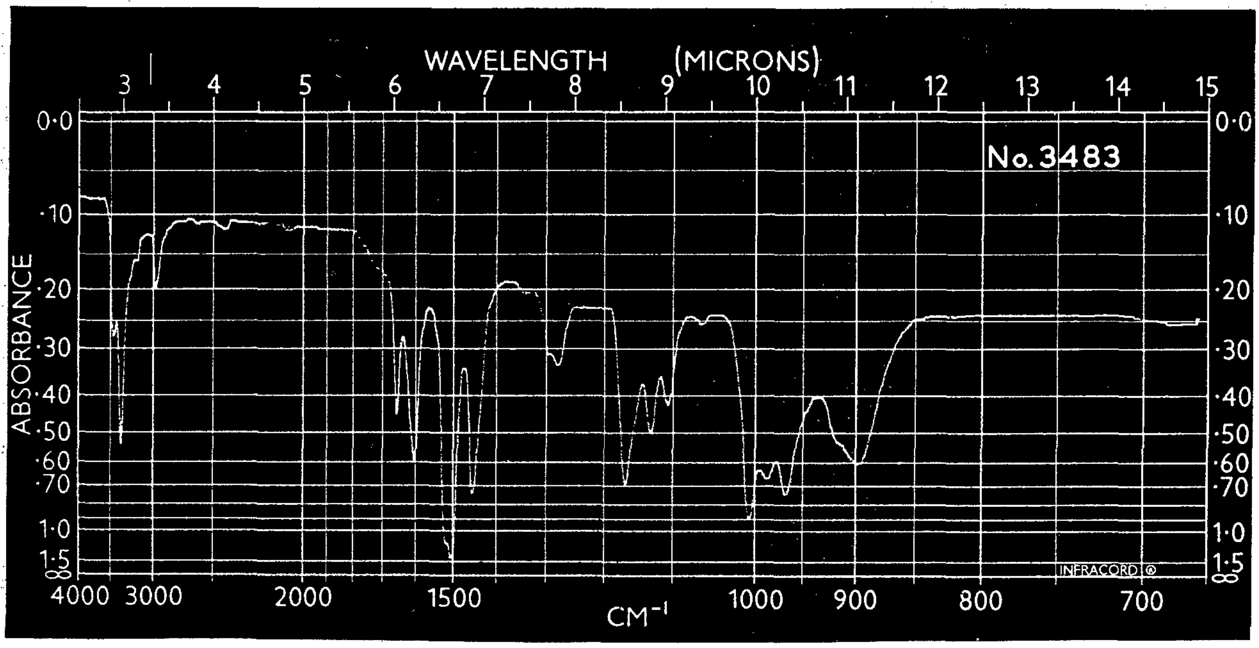
Spectrum No. 4134 Barium difluoropyromellitate (KBr disc)



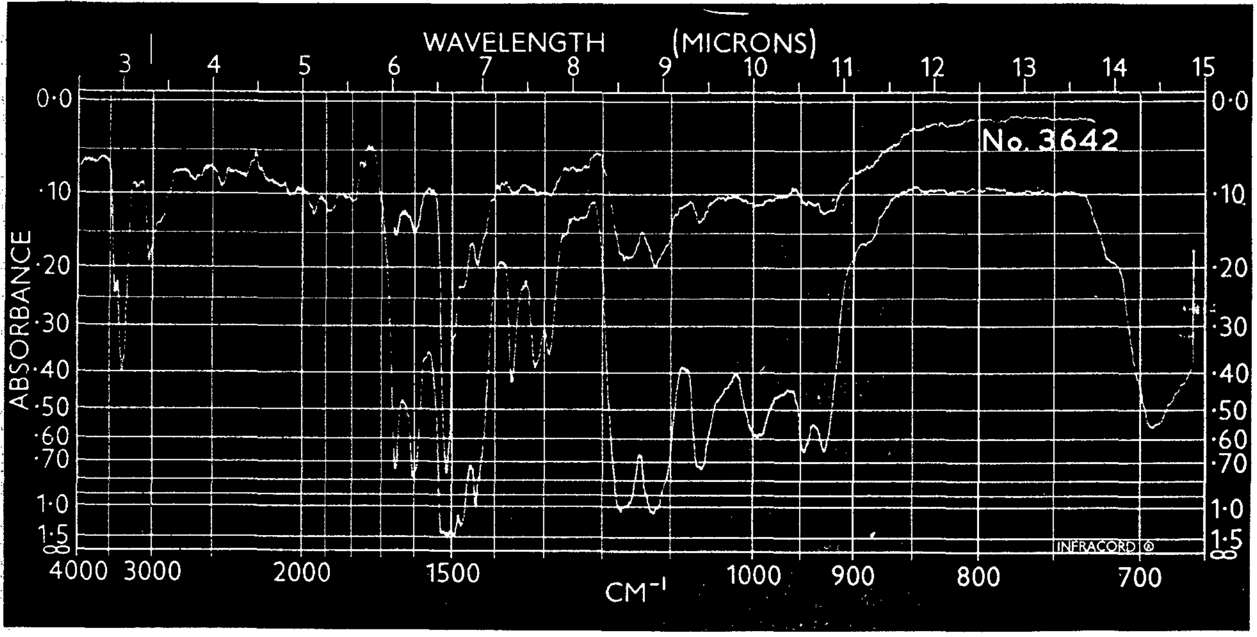
Spectrum No. 4083 1,2,4,5-Tetra(bromomethyl)-3,6-difluorobenzene (in $CHCl_3$)



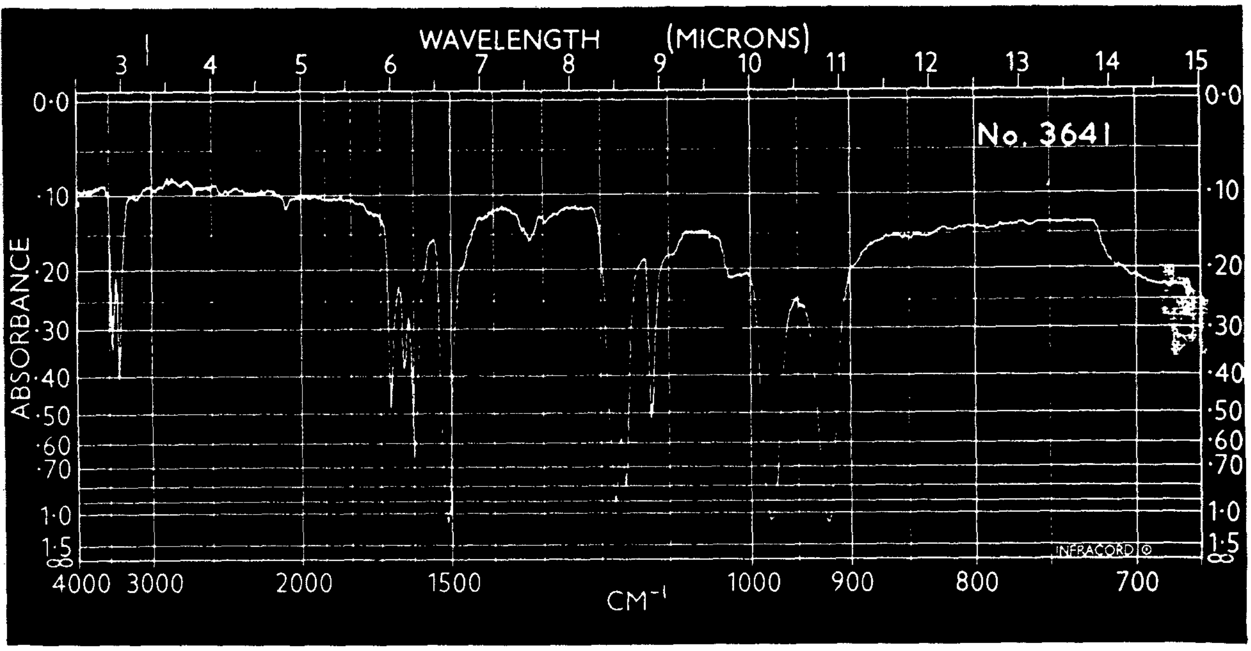
Spectrum No. 4090 Unknown product from oxidation of 1,2,4,5-tetra(bromomethyl)-3,6-difluorodurene (KBr disc)



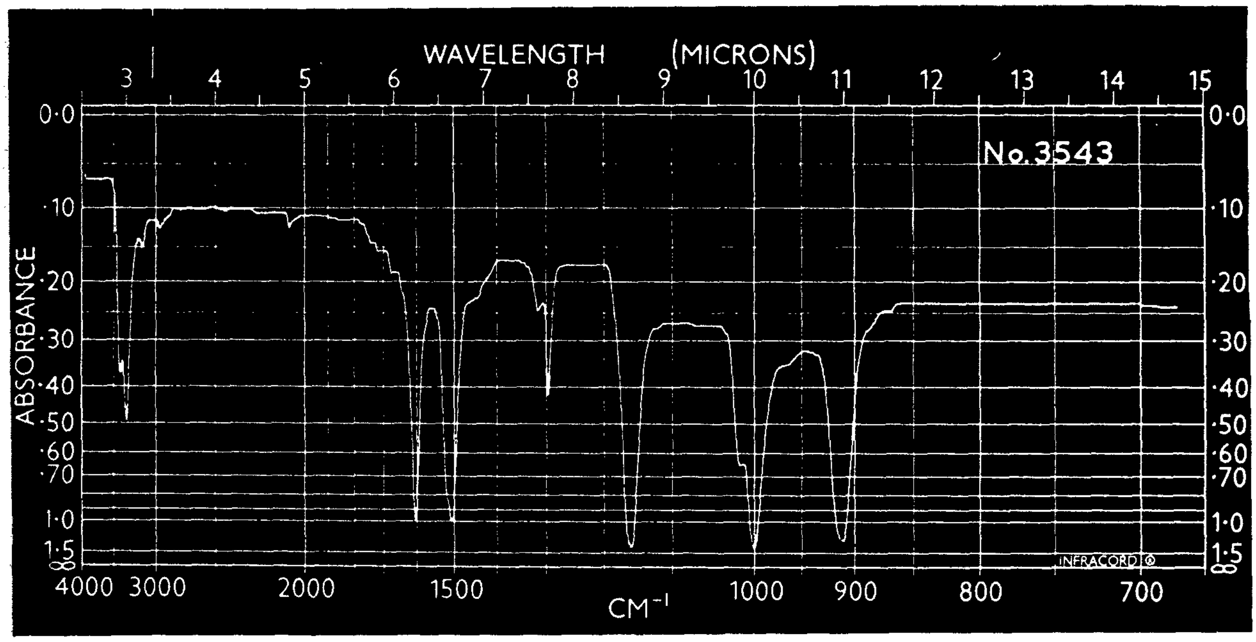
Spectrum No. 3483 3-Hydrazino-2,4,5,6-tetrafluoroaniline (in $CHCl_3$)



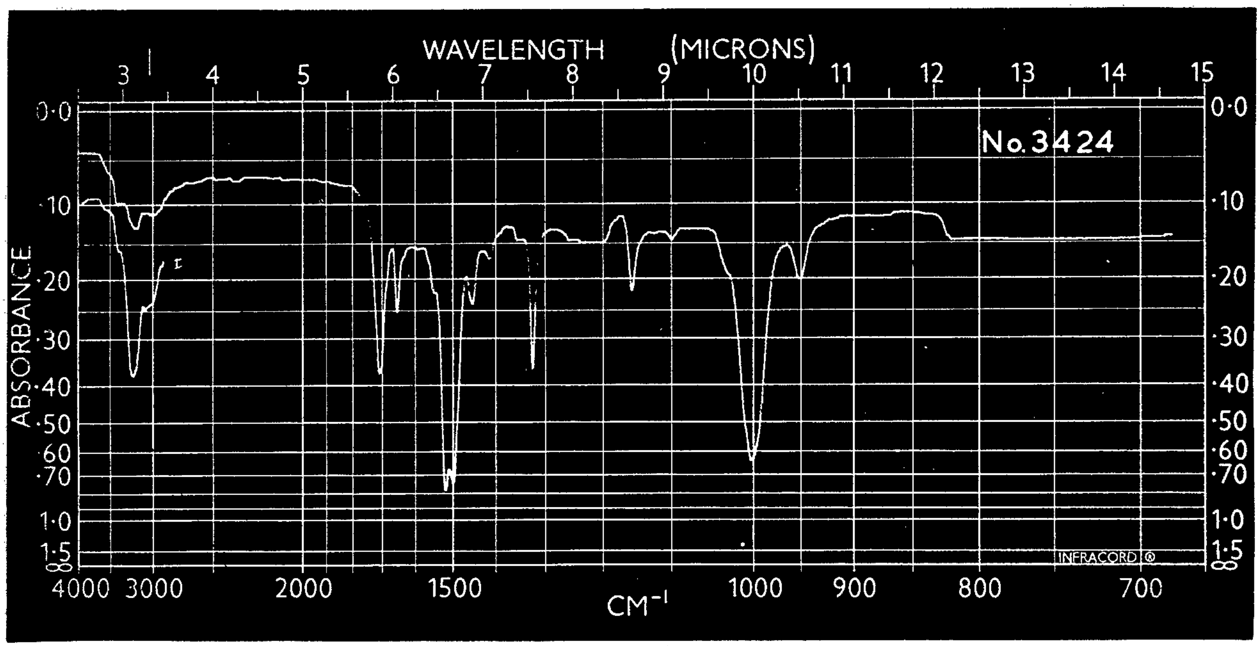
Spectrum No. 3642 Acetophenone 3-amino-2,4,5,6-tetrafluorophenylhydrazone (in CCl_3CN)



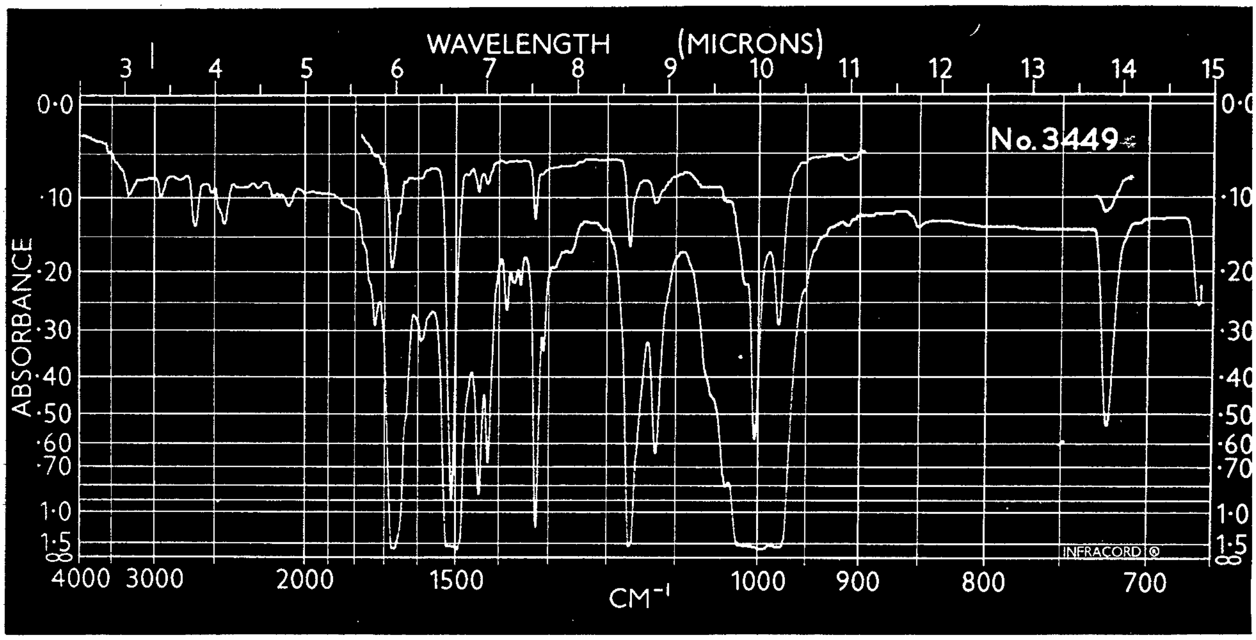
Spectrum No. 3641 Tetrafluoro-m-phenylenediamine (in CCl_4)



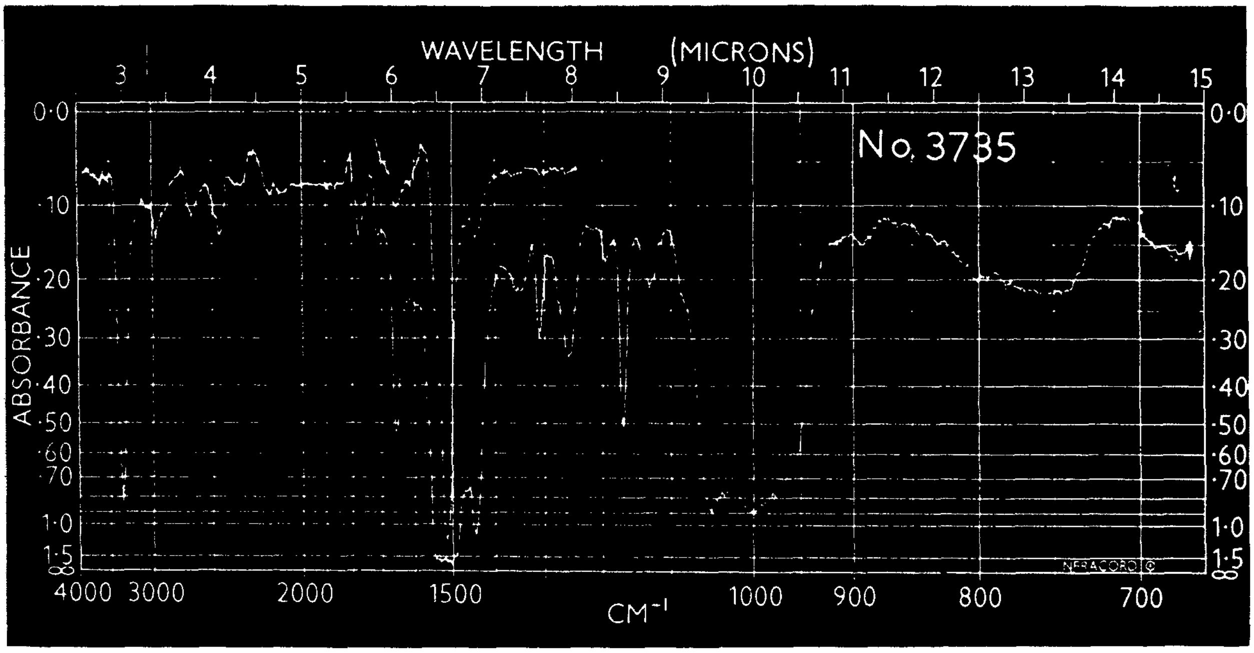
Spectrum No. 3543 Tetrafluoro-p-phenylenediamine (in $CHCl_3$)



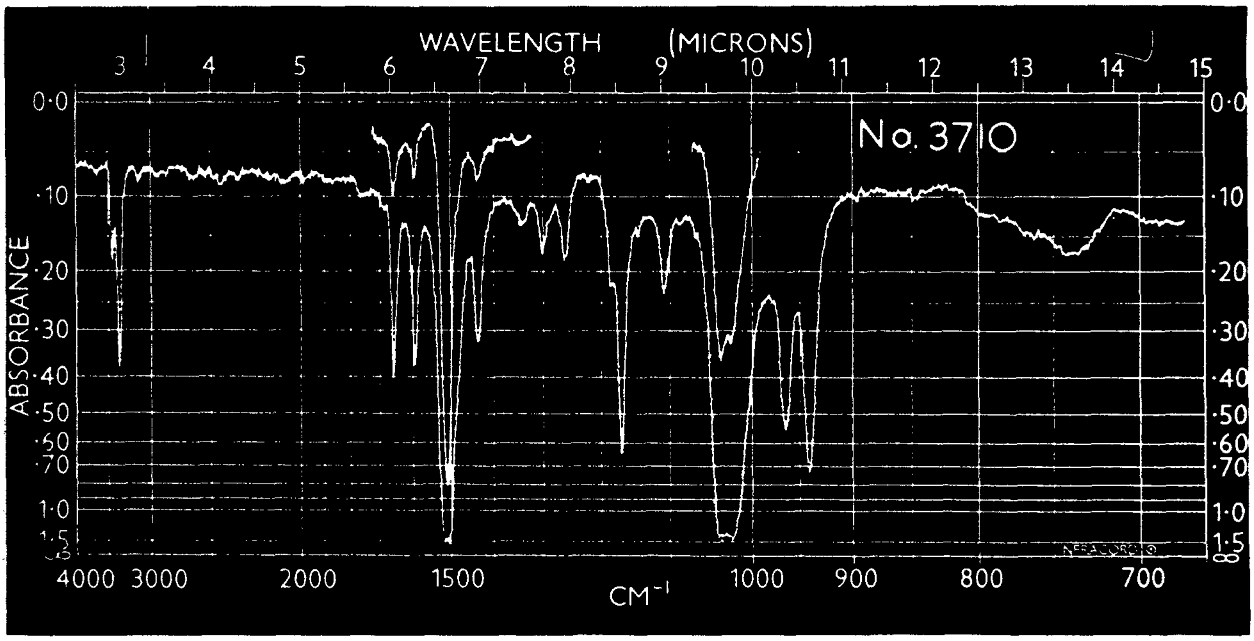
Spectrum No. 3424 Decafluorobenzanilide (in $CHCl_3$)



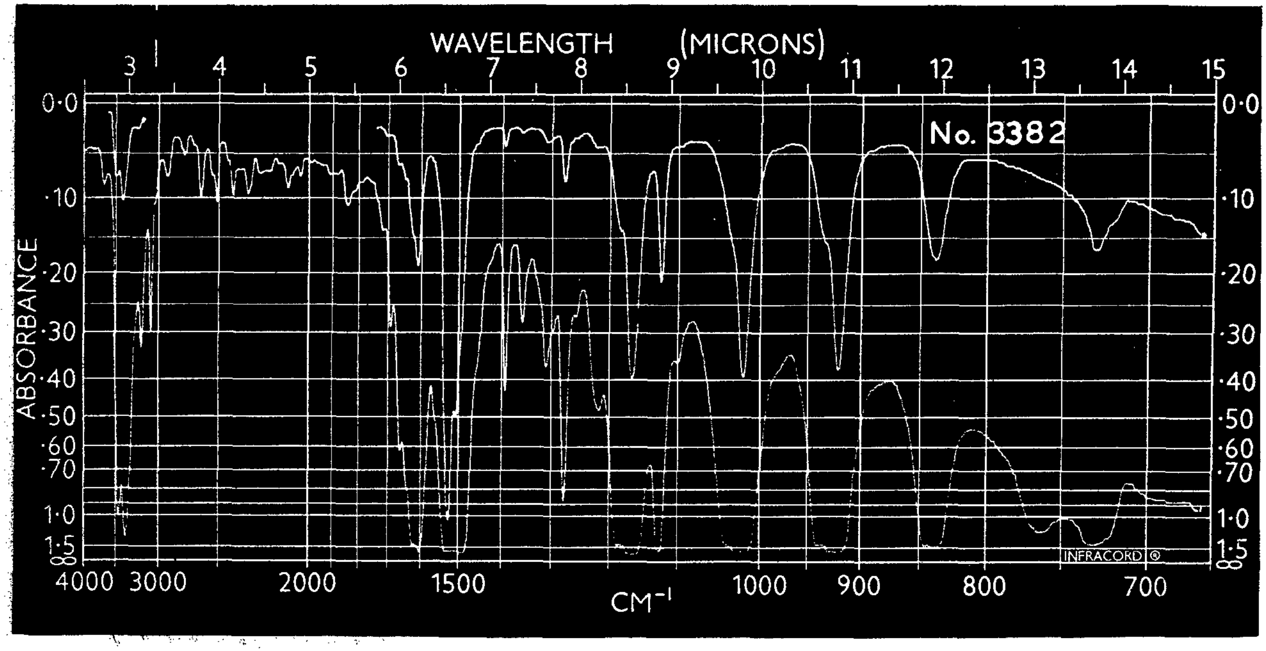
Spectrum No. 3449 N-(pentafluorophenyl)pentafluorobenzimidoyl chloride (in CCl_4)



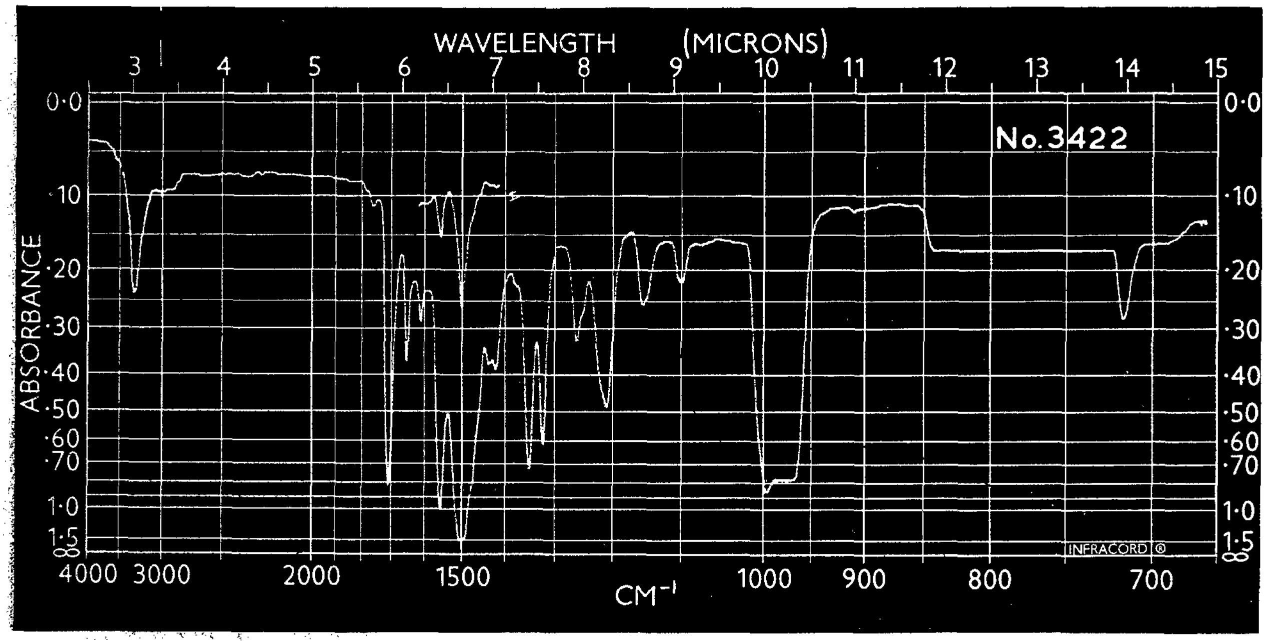
Spectrum No. 3735 1,4-Bis(pentafluoroanilino)tetrafluorobenzene (in CCl_3CN)



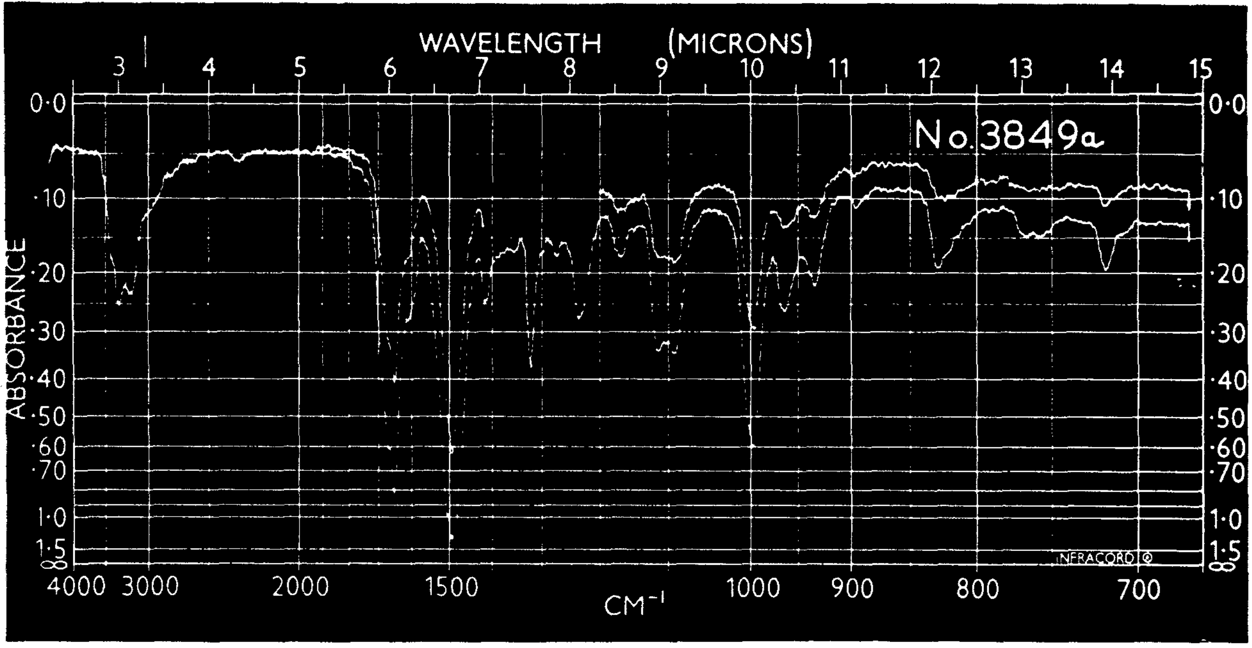
Spectrum No. 3710 4-Aminononafluorodiphenylamine (in CCl_4)



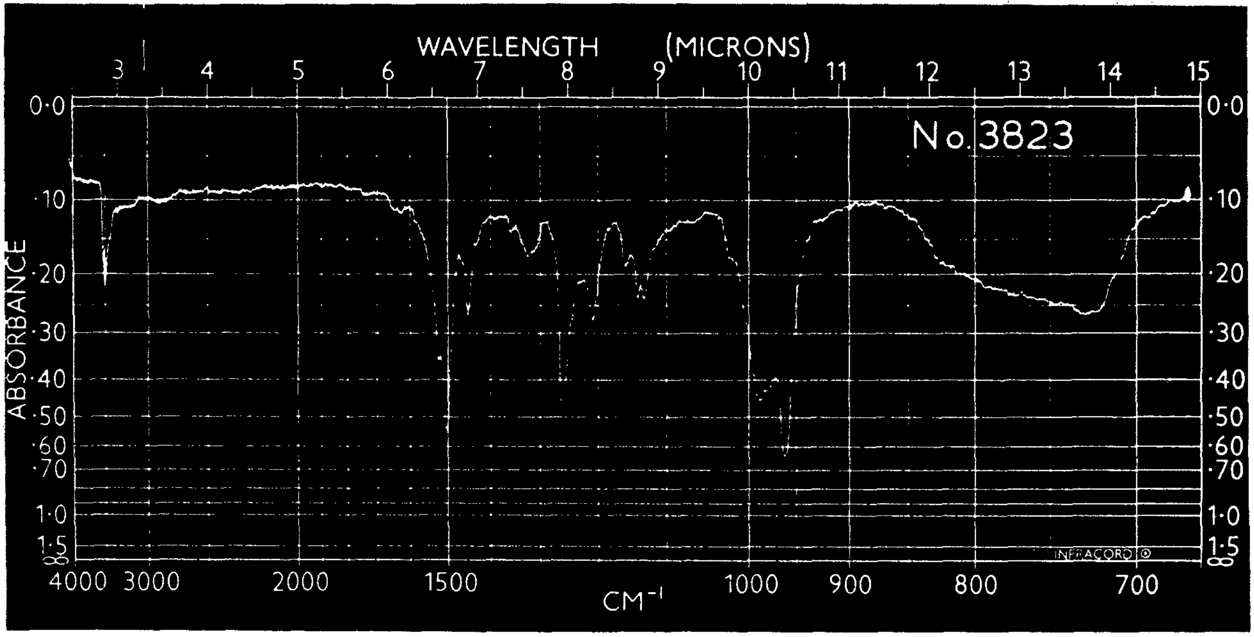
Spectrum No. 3382 2,3,4,6-Tetrafluoroaniline (thin film)



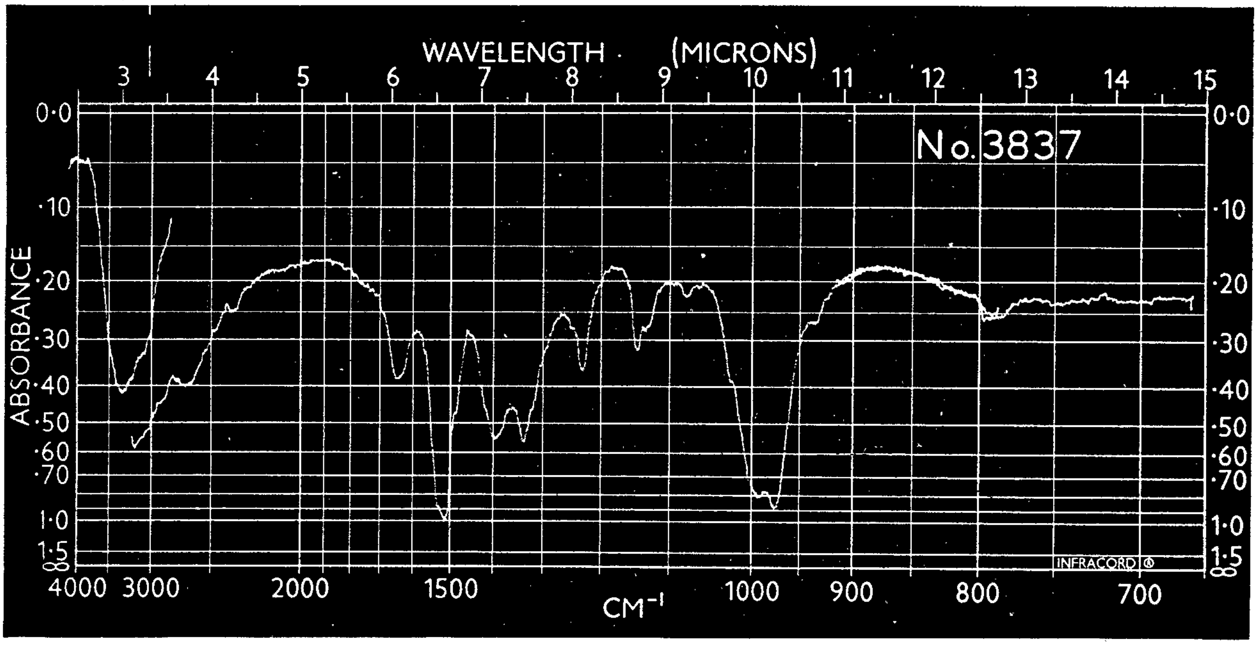
Spectrum No. 3422 3,3'-Bis(pentafluorobenzamido)-4,4'-dinitrohexafluorobiphenyl



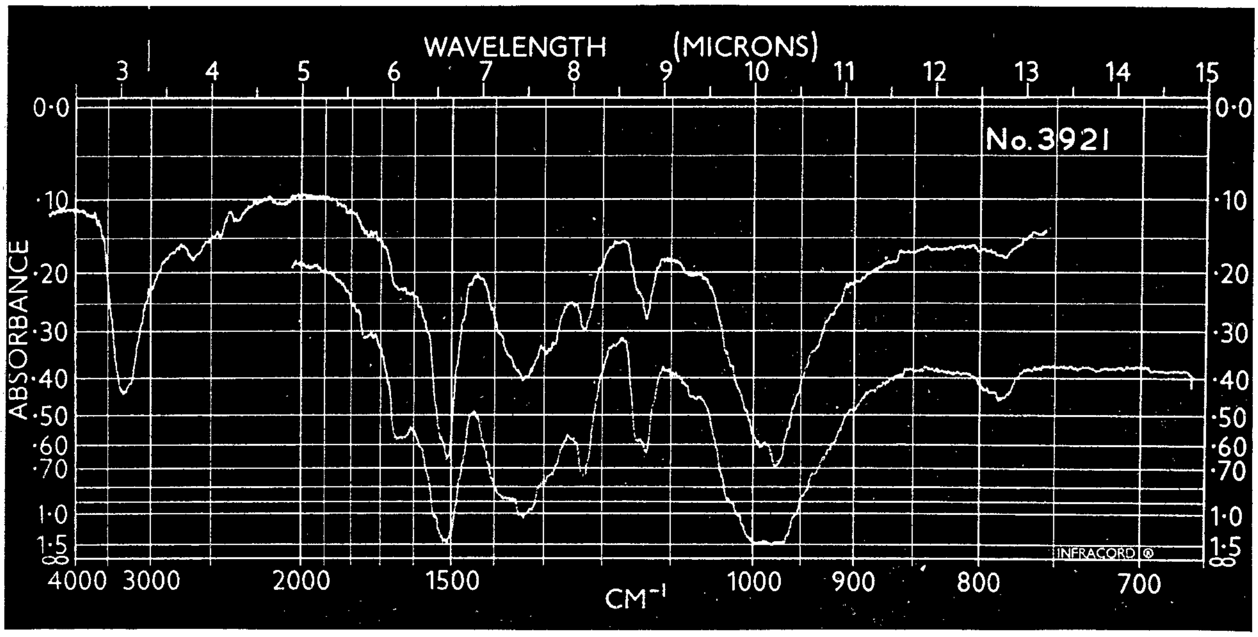
Spectrum No. 3849a 3,3'-Bis(pentafluorobenzamido)-4,4'-diaminohexafluorobiphenyl (KBr disc)



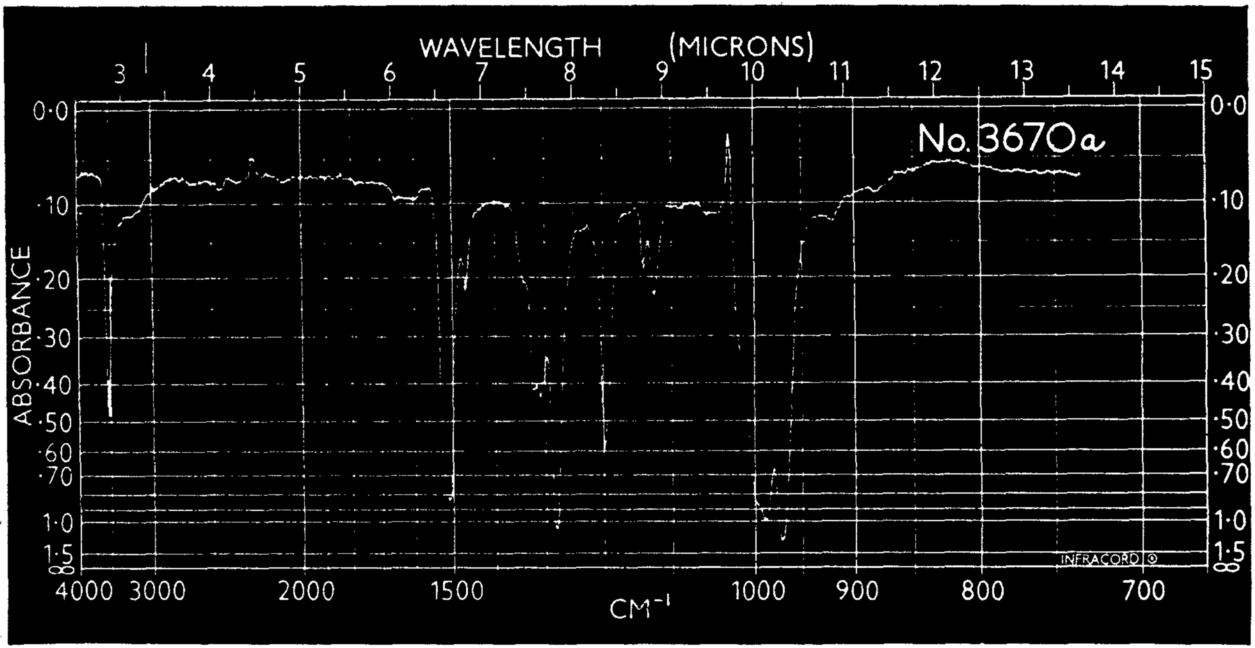
Spectrum No. 3823 Tetrafluororesorcinol (in CCl_4)



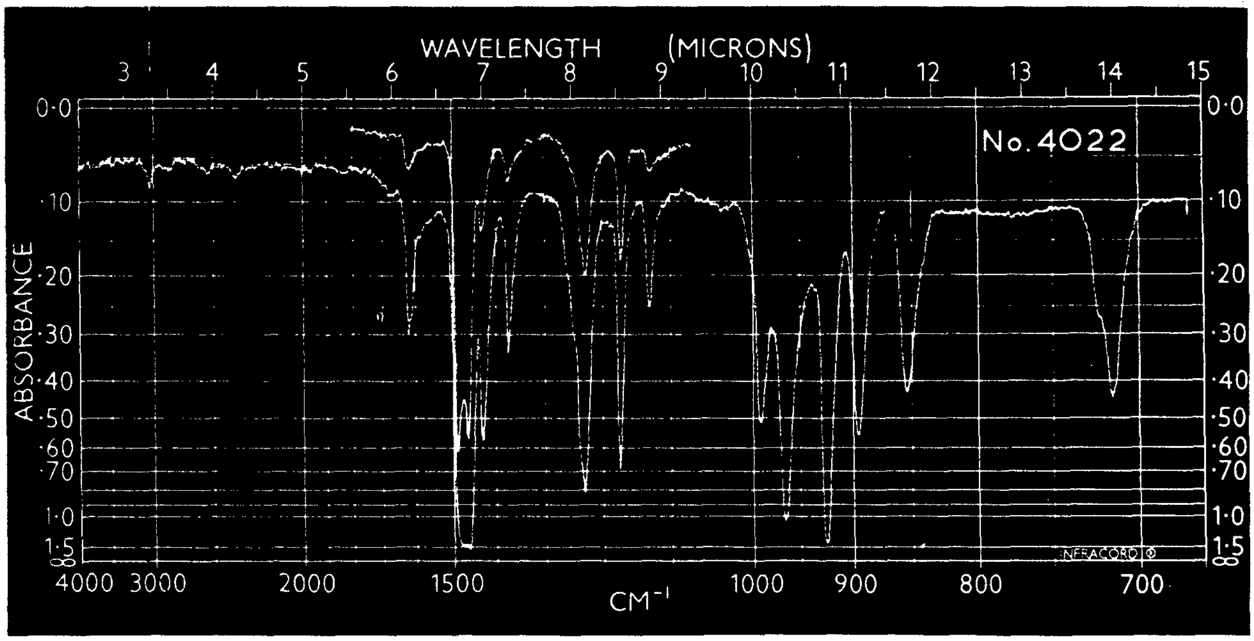
Spectrum No. 3837 Tetrafluororesorcinol (KBr disc)



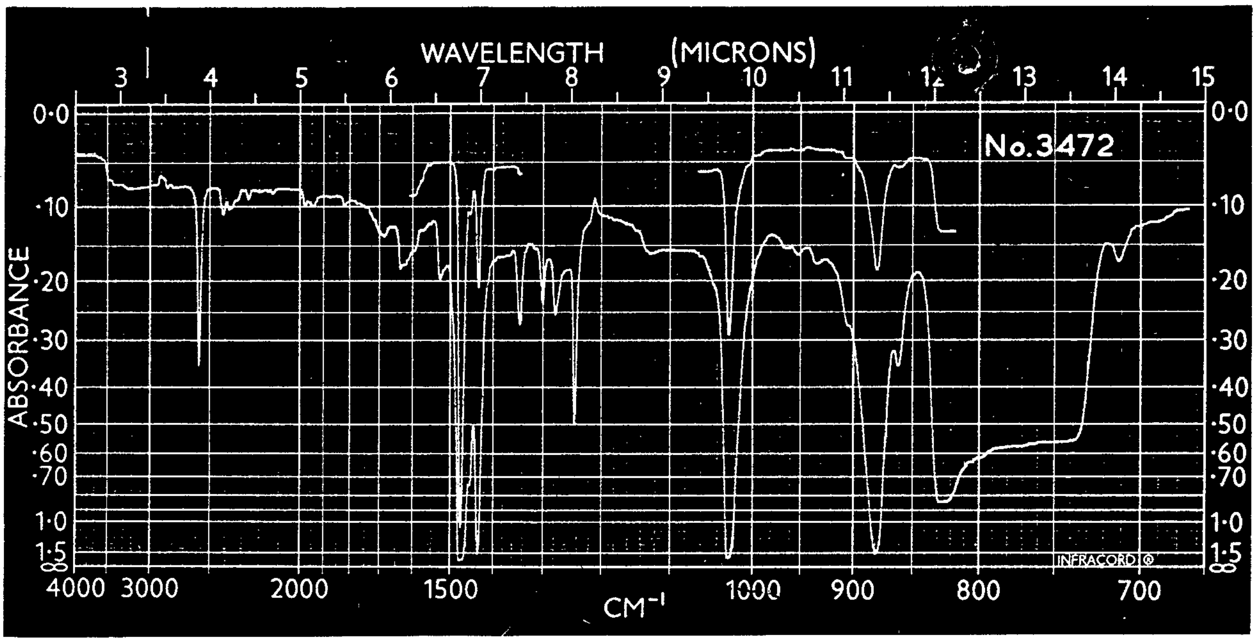
Spectrum No. 3921 Tetrafluororesorcinol (KBr disc)



Spectrum No. 3670a Tetrafluorocatechol (in CCl_4)



Spectrum No. 4022 4,4'-Bis(2,3,5,6-tetrafluorophenylthio)-octafluorobiphenyl (in CCl_4)



Spectrum No. 3472 Tetrafluorobenzene-1,4-dithiol (in CCl_4)

APPENDIX IIA

Diagrams 1 - 3 are TGA curves for polyhydrazides and polyimides, determined in air. The Stanton HTD thermobalance was employed at a rate of heating of ca. 0.5°/minute up to 200°C and 1°/minute above 200°C.

Diagram 1

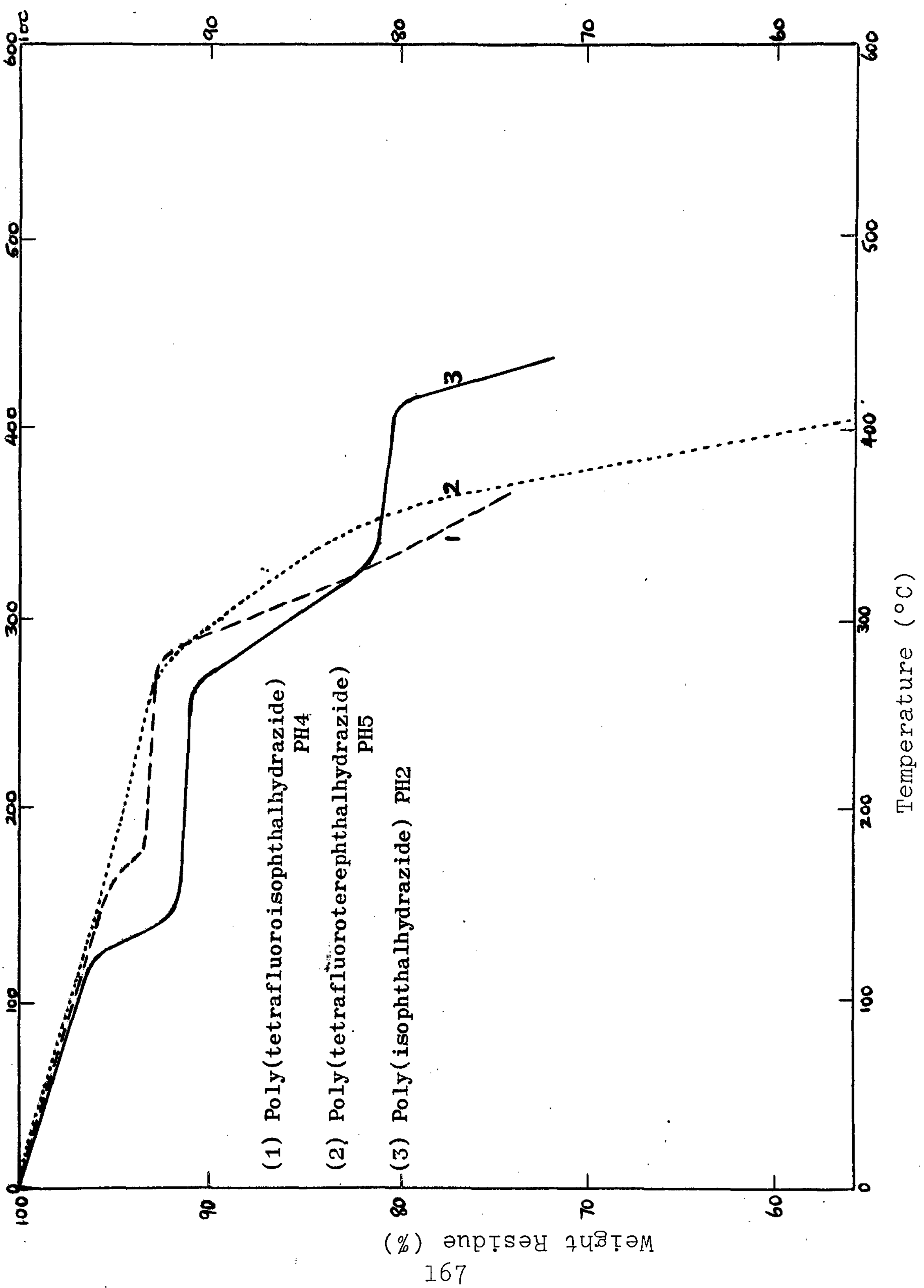

(1) Poly(tetrafluoroisophthalhydrazide) PH4
(2) Poly(tetrafluoroterephthalhydrazide) PH5
(3) Poly(isophthalhydrazide) PH2
1
2
3
Temperature (°C)
Weight Residue (%)
0
100
200
300
400
500
600
100
90
80
70
60

Diagram 2

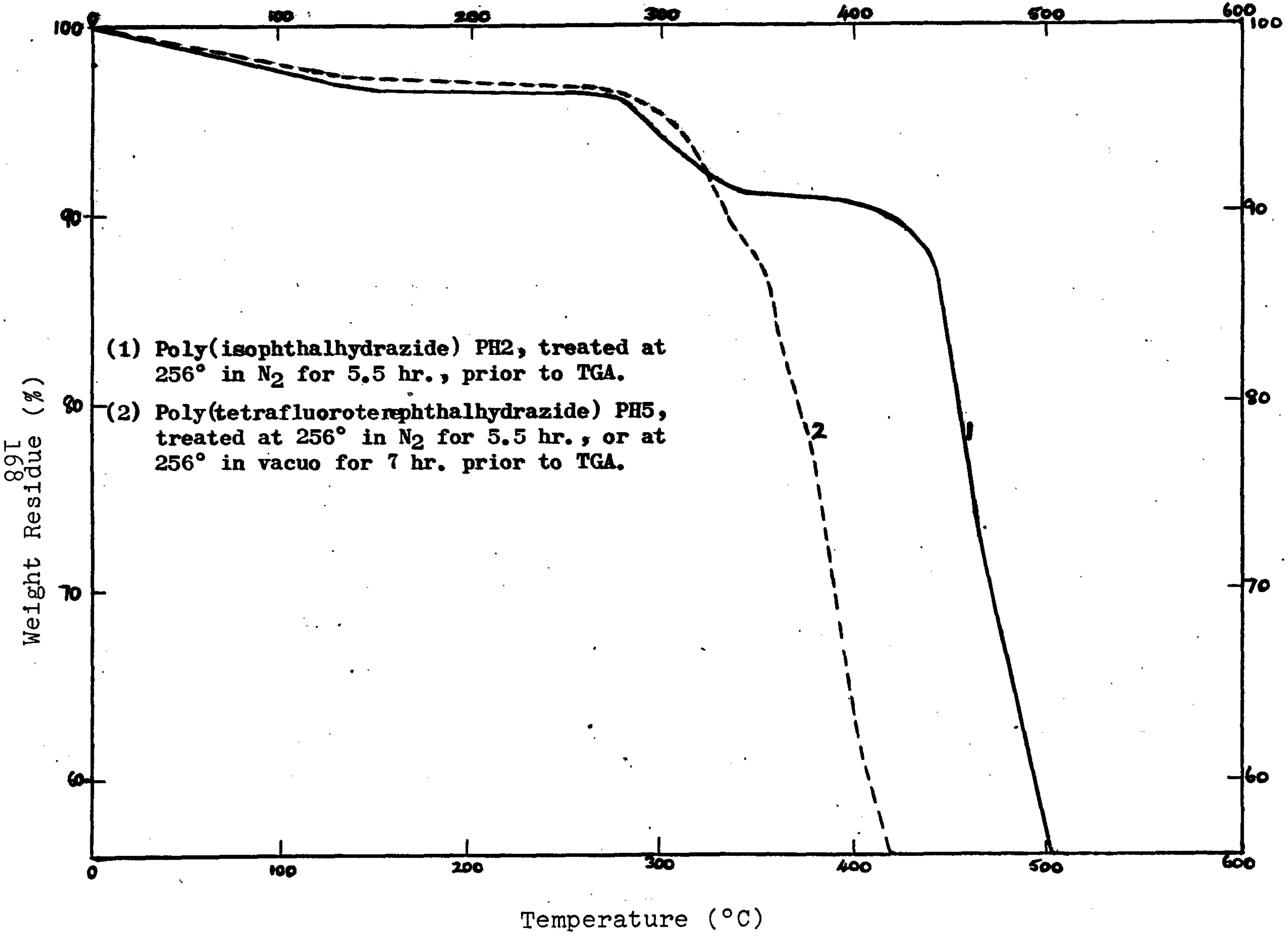
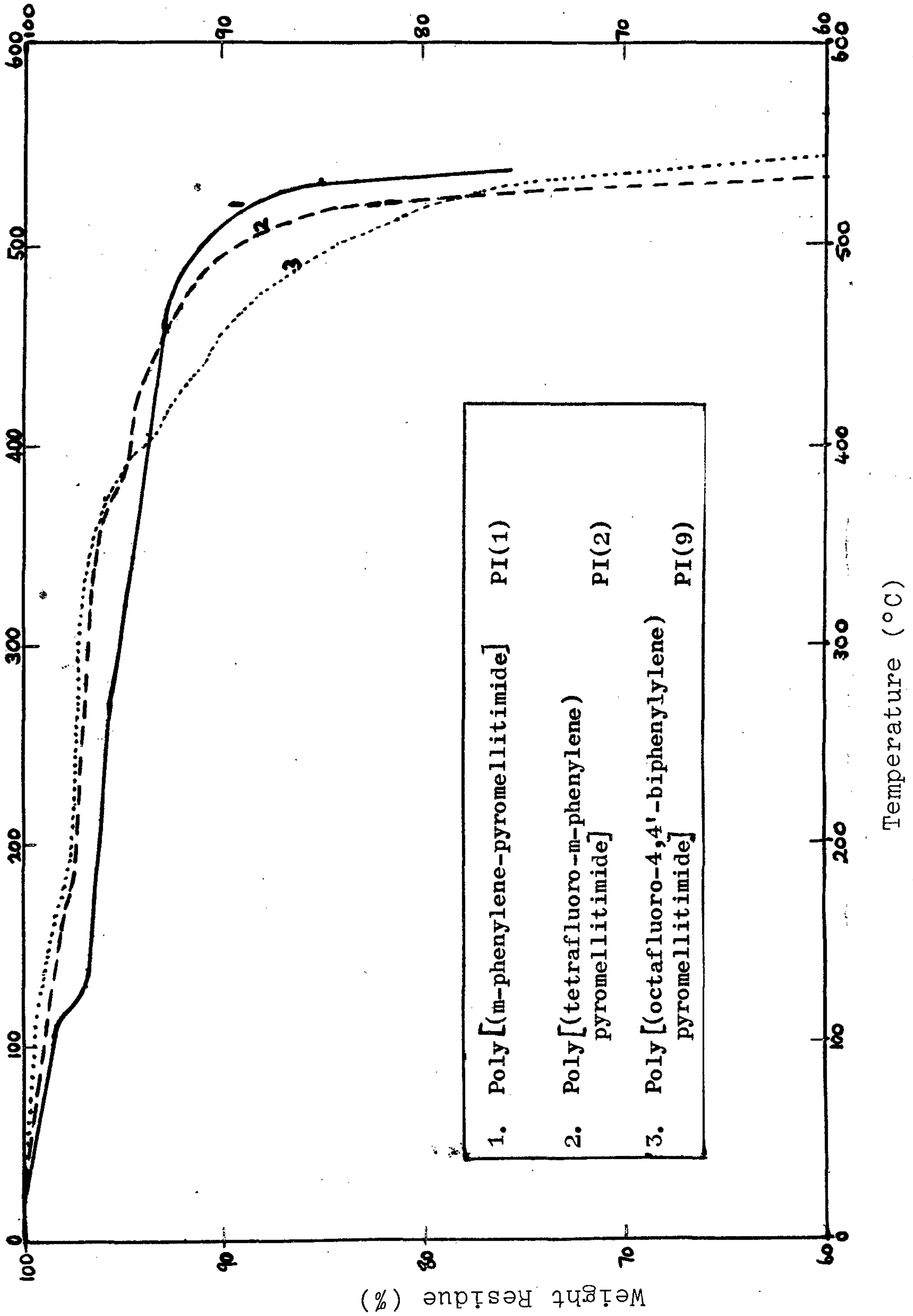

100
90
80
70
60
0
100
200
300
400
500
600
1
2
(1) Poly(isophthalhydrazide) PH2, treated at 256° in N_2 for 5.5 hr., prior to TGA.
(2) Poly(tetrafluoroterephthalhydrazide) PH5, treated at 256° in N_2 for 5.5 hr., or at 256° in vacuo for 7 hr. prior to TGA.
Weight Residue (%)
Temperature (°C)

Diagram 3



1. Poly[(m-phenylene-pyromellitimide] PI(1)
2. Poly[(tetrafluoro-m-phenylene) pyromellitimide] PI(2)
3. Poly[(octafluoro-4,4'-biphenylylene) pyromellitimide] PI(9)
1
2
3
Temperature (°C)
Weight Residue (%)
0
100
200
300
400
500
600
100
90
80
70
60

APPENDIX IIB

The infra-red spectra of compounds reported in Part II

No.	Compound	Wavelength μ	Medium
589	1,3-Di(phenylsulphonyloxy)benzene	2 - 15	KCl disc.
590	1,4-Di(phenylsulphonyloxy)benzene	2 - 15	KCl disc
591	4,4'-Di(phenylsulphonyloxy)-biphenyl	2 - 15	KCl disc
592	1,3-Di(pentafluorophenylsulphonyloxy) tetrafluorobenzene	2 - 15	KCl disc
593	1,4-Di(pentafluorophenylsulphonyloxy) tetrafluorobenzene	2 - 15	KCl disc
594	4,4'-Di(pentafluorophenylsulphonyloxy) octafluorobiphenyl	2 - 15	KCl disc
SAE 51	2,2'-Diphenyl - 6,6'-bibenzoxazole (II)	2.5 - 8 7.5 -25	KBr disc KBr disc
1256	2,2'-Di(pentafluorophenyl)-6,6'-bibenzoxazole (III)	2.5 - 8 7.5 - 25	KBr disc KBr disc
1300	2,2'-Diphenyl-hexafluoro-6,6'-bibenzoxazole (IV)	2.5 - 8 7.5 - 25	KBr disc KBr disc
1301	2,2'-Di(pentafluorophenyl)-hexafluoro-6,6'-bibenzoxazole (I)	2.5 - 8 7.5 - 25	KBr disc KBr disc
SAE 53	Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxyhexafluorobenzidine (V)	2.5 - 8 7.5 - 25	KBr disc KBr disc
SAE 52	Ditto (VI)	2.5 - 8 7.5 - 25	Nujol mull on NaCl Nujol mull on NaCl
1057	Ditto (VII)	2.5 - 8 7.5 - 25	KBr disc KBr disc
507	Ditto (VIII)	2 - 15	Nujol mull
1381	Ditto (IX)	2.5 - 8 7.5 - 25	KBr disc KBr disc

(continued)

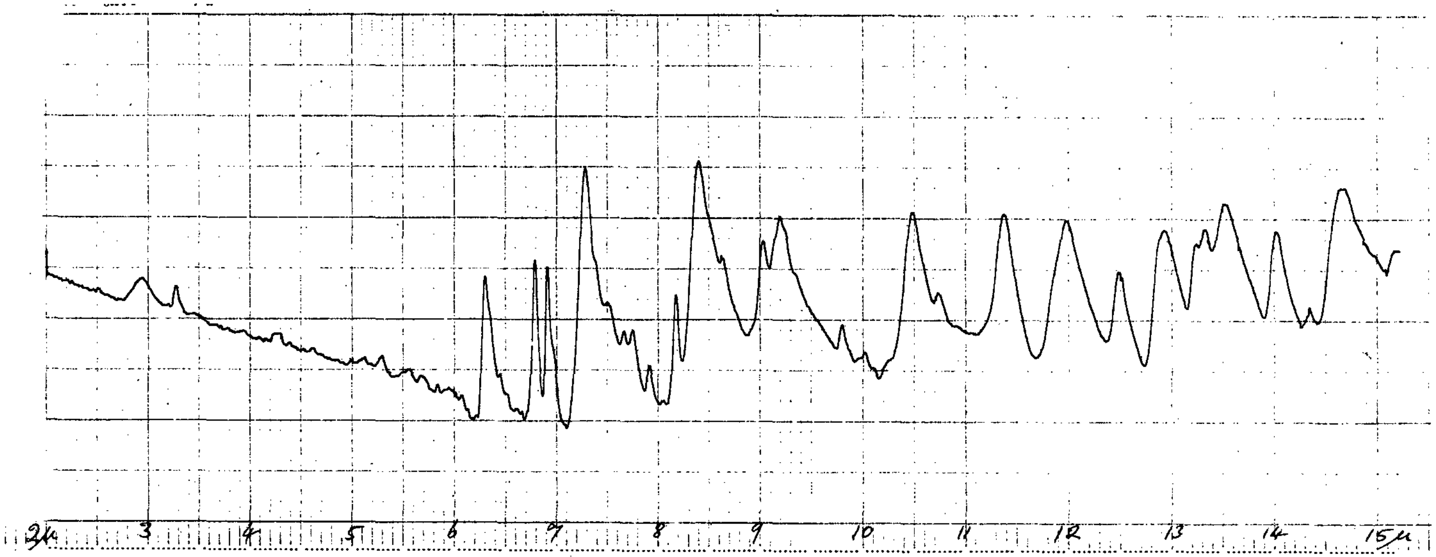
APPENDIX IIB (continued)

No.	Compound	Wavelength μ	Medium
1099	Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxybenzidine (X)	2.5 - 8	Nujol mull on NaCl
		7.5 - 25	Nujol mull on on NaCl
		2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1440	Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxybenzidine (XI)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1408	O,S-Di(pentafluorophenyl)-dithiocarbonate (XIII)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1407	O,S-Diphenyldithiocarbonate (XIV)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1410	O,O-(4,4'-Octafluorobiphenylylene) di(S-pentafluorophenyl dithiocarbonate) (XV)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1409	O,O-(4,4'-Biphenylylene)-di(S-phenyldithiocarbonate) (XVI)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1083	Tetrafluoro-m-phenylene bischloroformate	2.5 - 8	Film on NaCl
		7.5 - 25	Film on NaCl
1126	N,N'-Di(pentafluorobenzoyl)-N,N'-di(pentafluorophenyl)-2,3,5,6-tetrafluorophenylene diamine (XIX)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
901	N,N'-Di(2,3,4,6-tetrafluorophenyl)pyromellitimide (XX)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
949	2,5-Di(2,3,5,6-tetrafluorophenyl)-1,3,4-oxadiazole (XXI)	2.5 - 8	Nujol mull on NaCl
		7.5 - 25	Nujol mull on NaCl

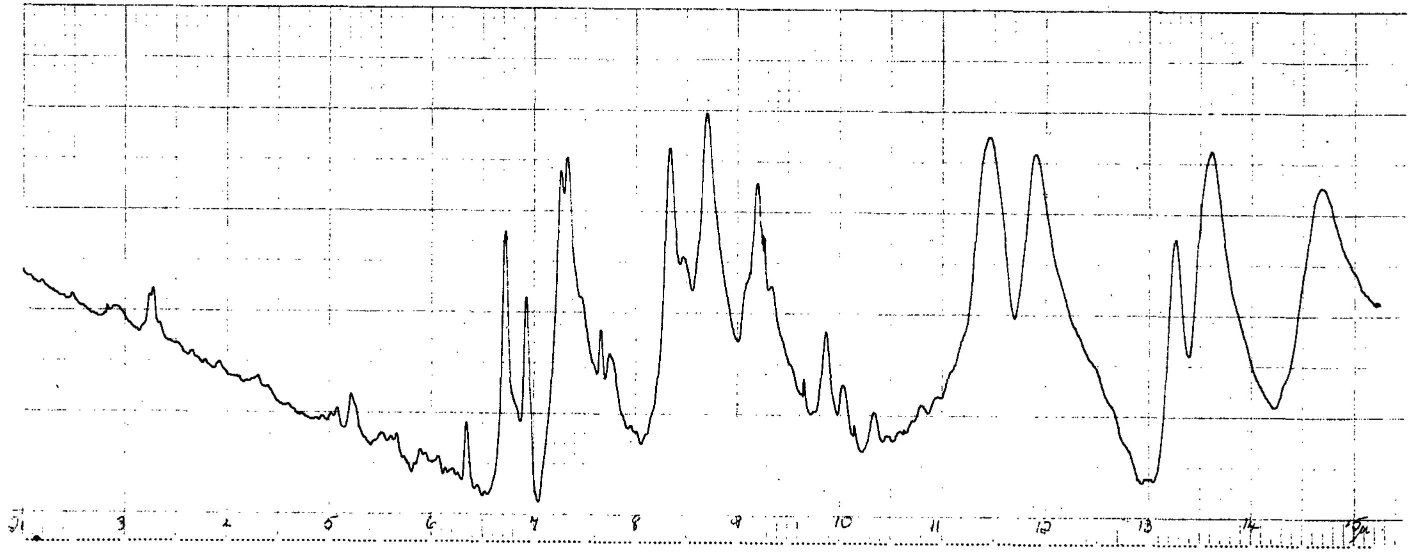
(continued)

APPENDIX IIB (continued)

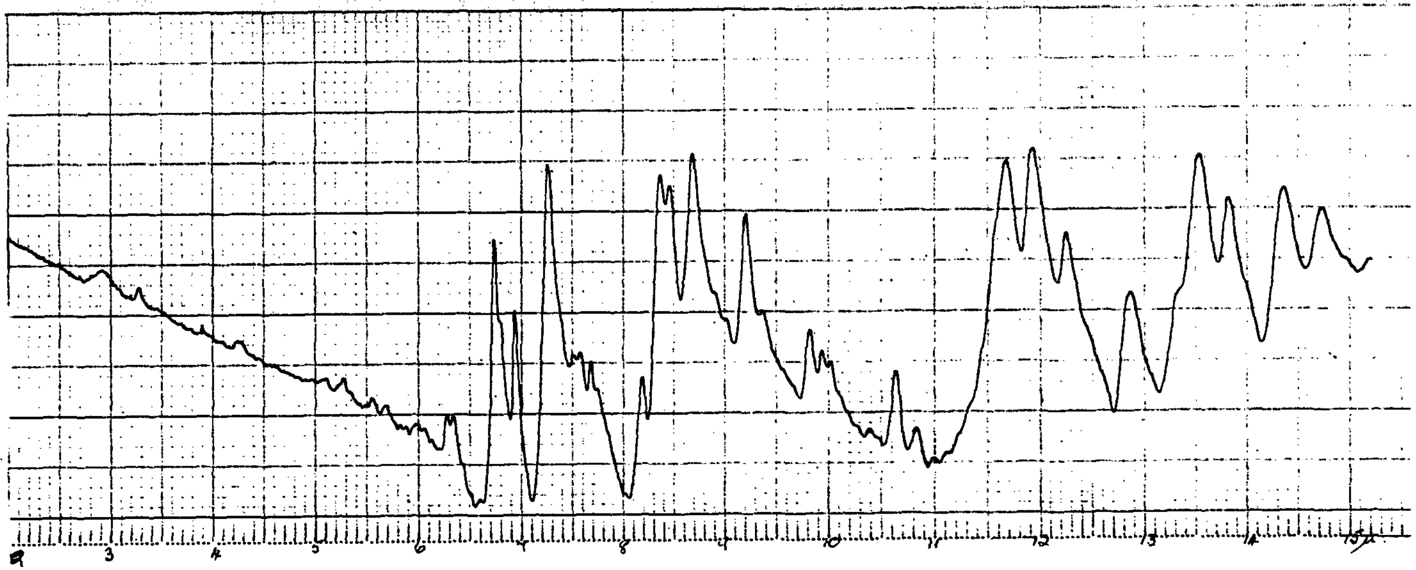
No.	Compound	Wavelength µ	Medium
950	Hydrazide precursor of (XXI)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
		2.5 - 8	Nujol mull on NaCl
		7.5 - 25	Nujol mull on NaCl
1117	1,3-Di(2,3,5,6-Tetrafluorobenzoyloxy)-2,4,5,6-tetrafluorobenzene (XXII)	2 - 15	KCl disc
1058	Poly(m-phenylenepyromellitimide) (P.I. (1))	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1060	Poly[(tetrafluoro-m-phenylene)-pyromellitimide (P.I.(2))	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1061	Poly[octafluoro-4,4'-biphenylylene)pyromellitimide] (P.I.(9))	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1106	Poly(isophthalhydrazide)(PH2)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1424	Poly(tetrafluoroisophthalhydrazide) (PH 4)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
		2.5 - 8	Nujol on NaCl
		7.5 - 25	Nujol on NaCl
1067	Poly(tetrafluoroterephthalhydrazide (PH 5)	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1069	Poly(tetrafluoroterephthalhydrazide) (PH 5) after 5.5 hour at 256°C in N_2	2.5 - 8	KBr disc
		7.5 - 25	KBr disc
1108	Poly(isophthalhydrazide) (PH 2) after 5.5 hour at 256° in N_2	2.5 - 8	KBr disc
		7.5 - 25	KBr disc



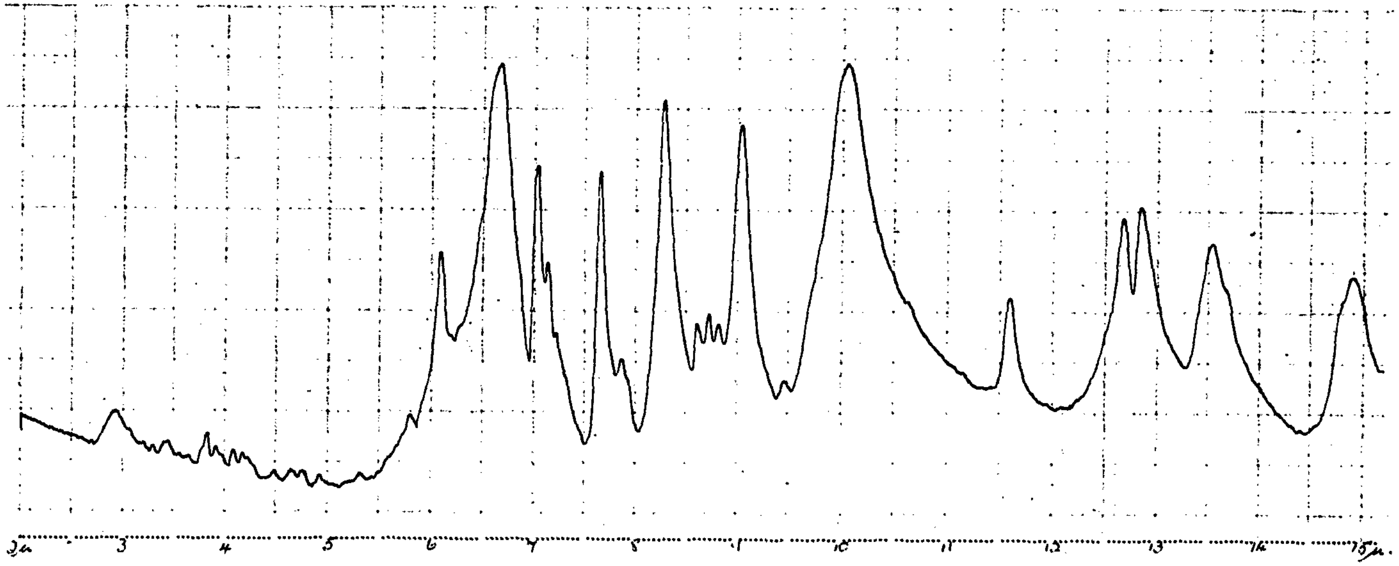
Spectrum No. 589 1,3-Di(phenylsulphonyloxy)benzene



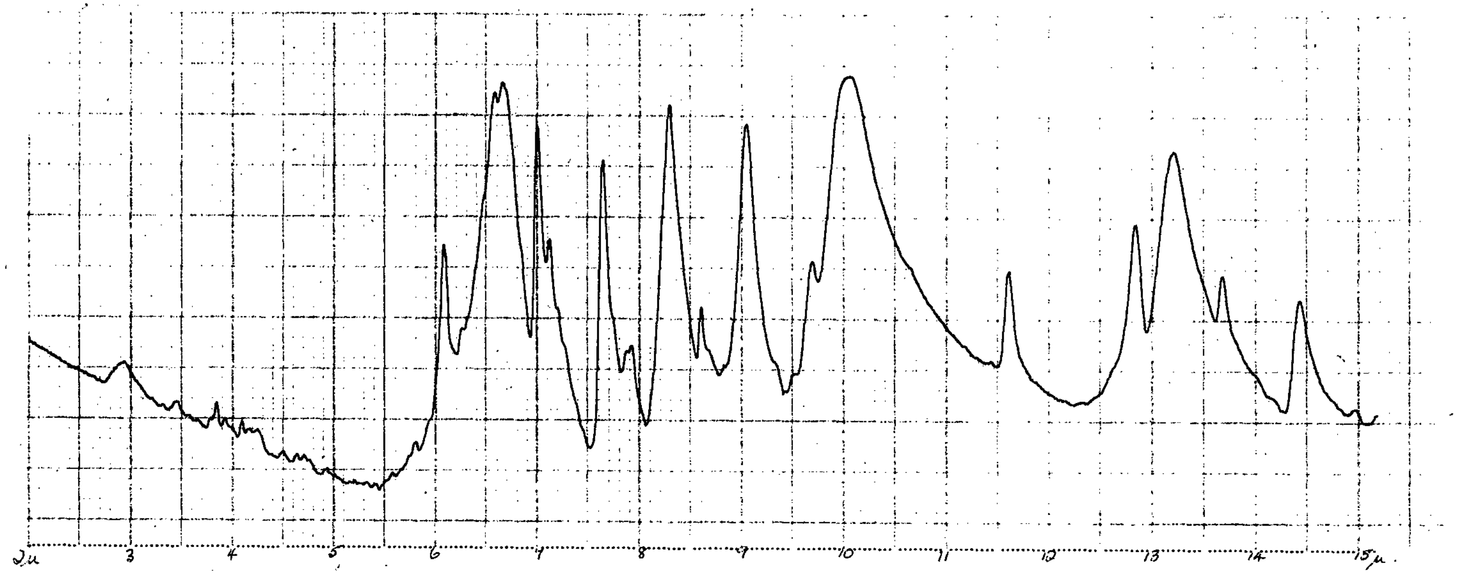
Spectrum No. 590 1,4-Di(phenylsulphonyloxy)benzene



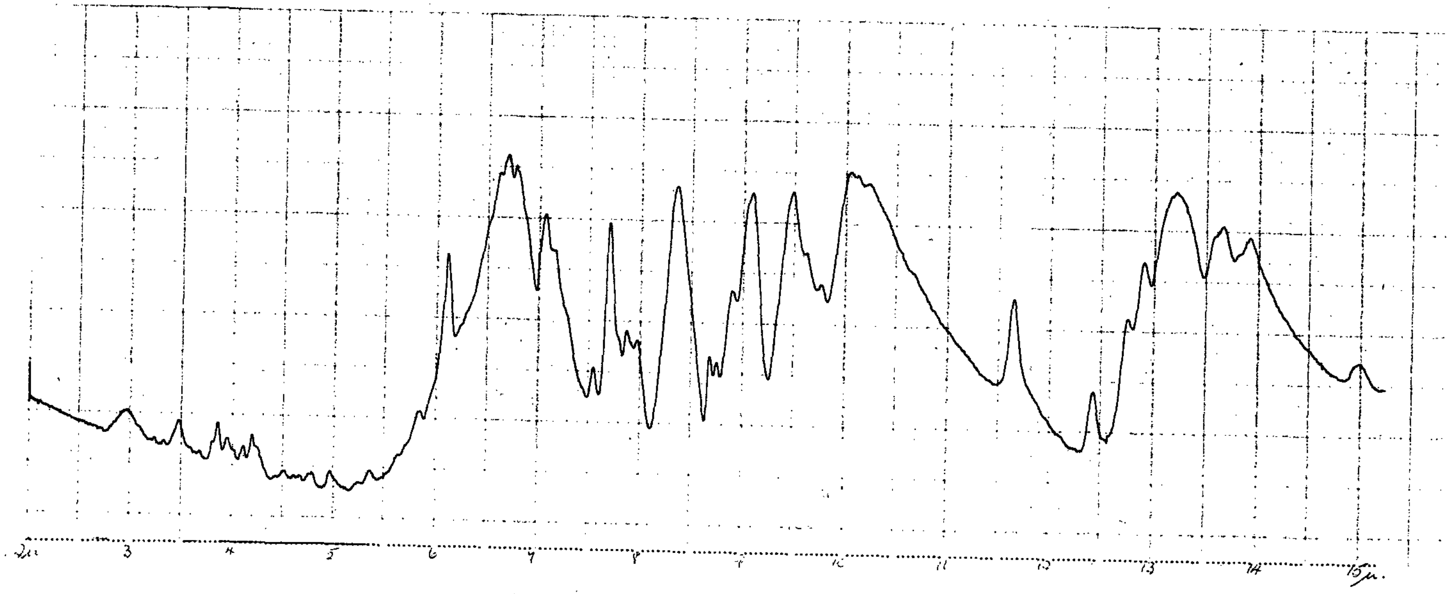
Spectrum No. 591 4,4'-Di(phenylsulphonyloxy)biphenyl



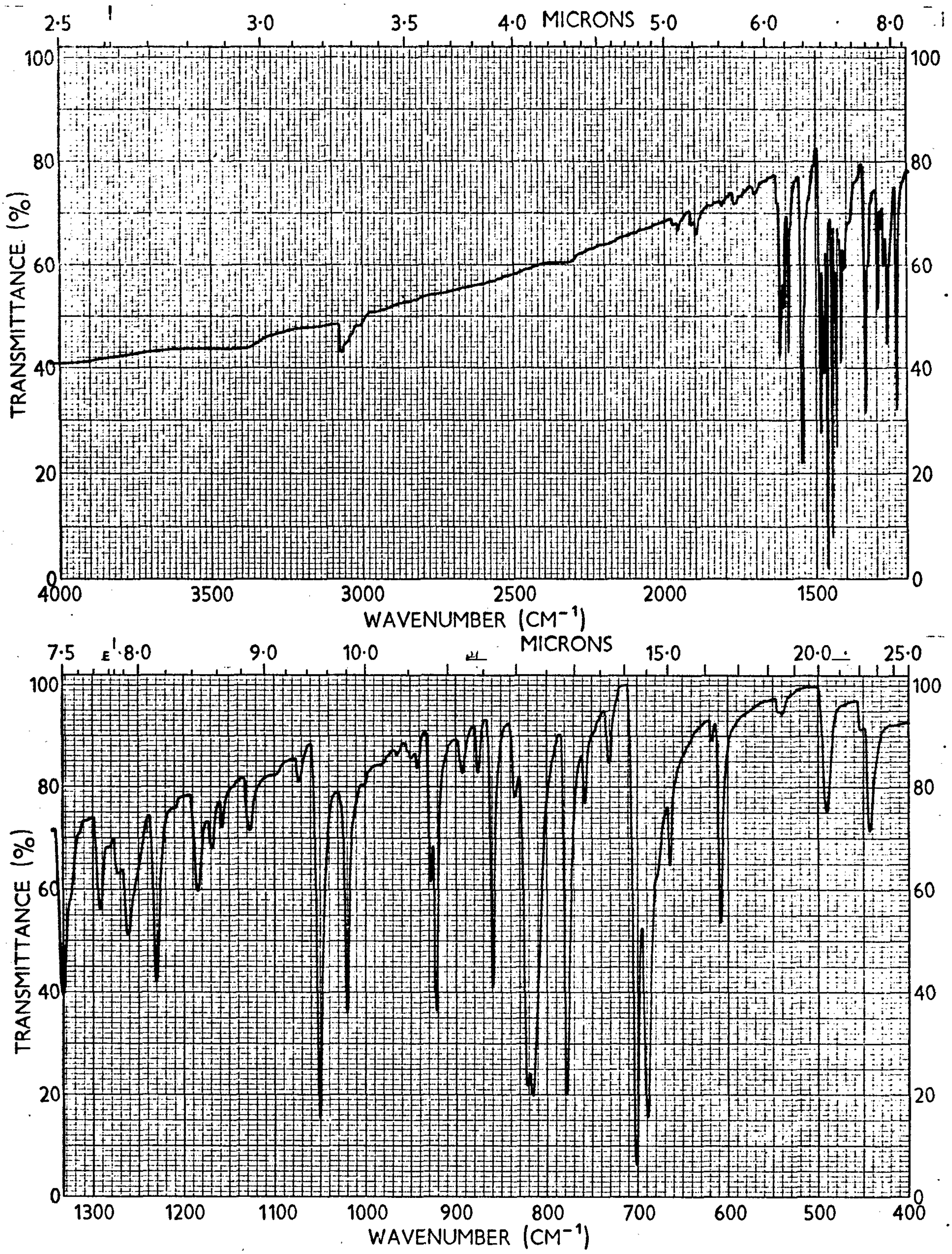
Spectrum No. 592 1,3-Di(pentafluorophenylsulphonyloxy)tetrafluorobenzene



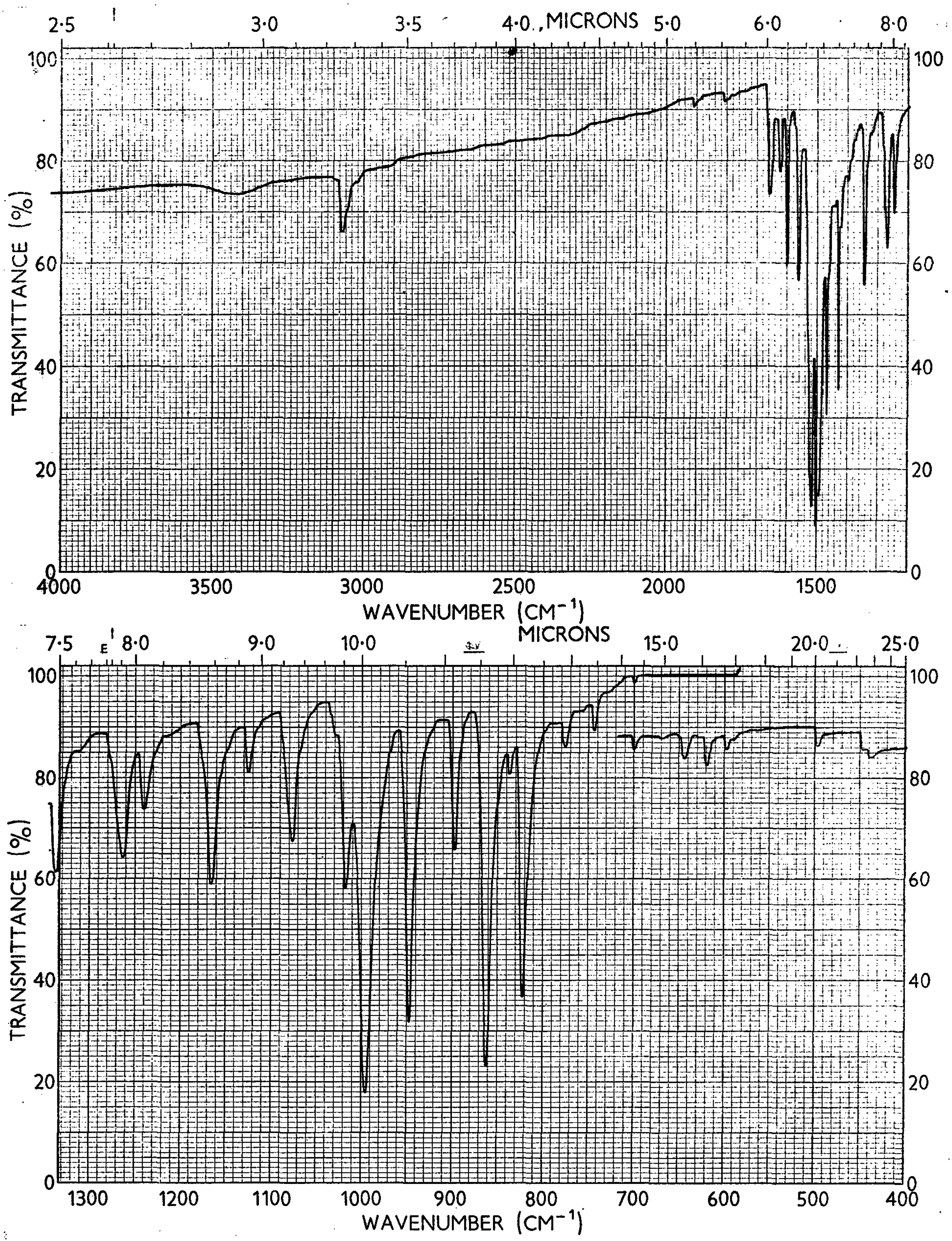
Spectrum No. 593 1,4-Di(pentafluorophenylsulphonyloxy)tetrafluorobenzene



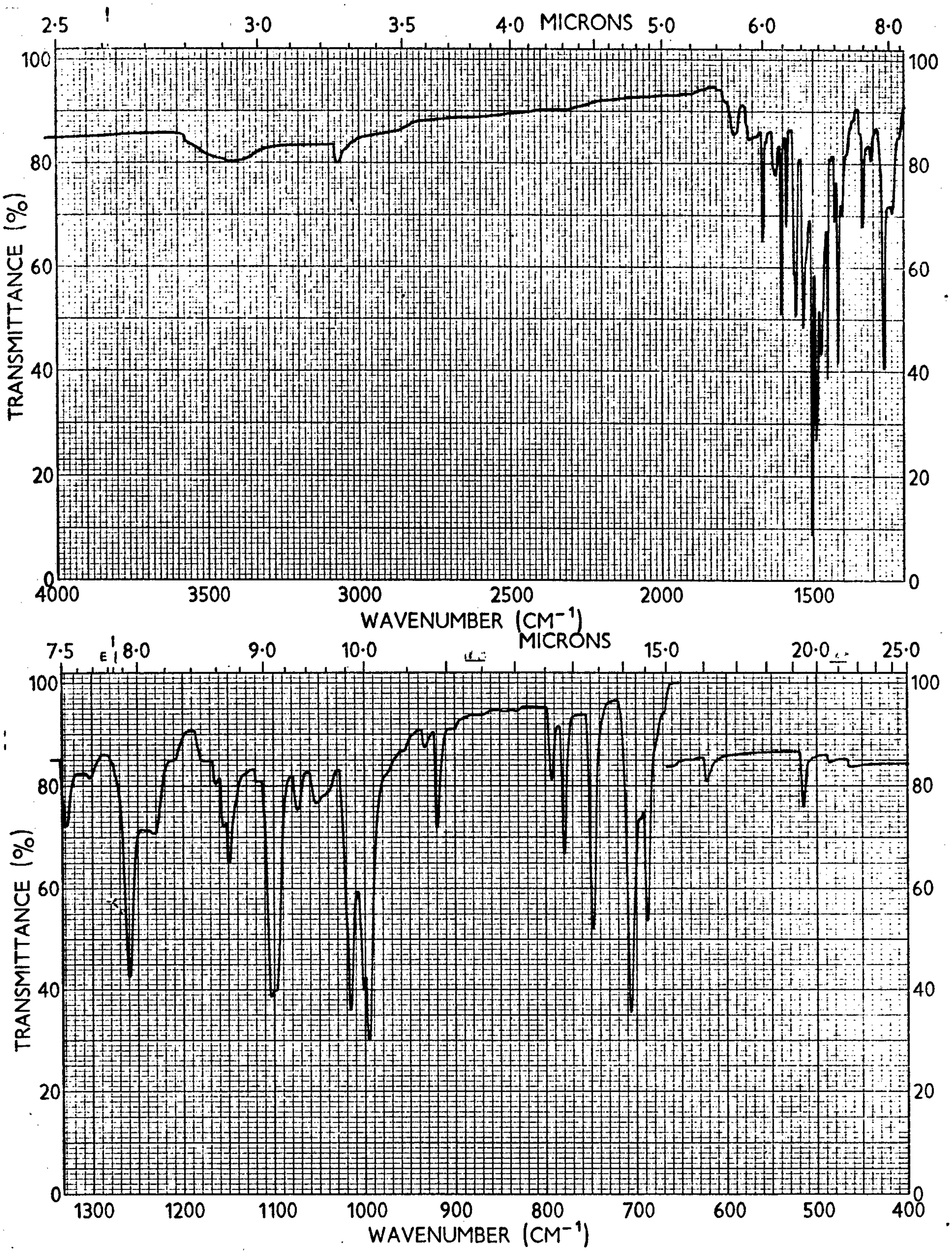
Spectrum No. 594 4,4'-Di(pentafluorophenylsulphonyloxy)octafluorobiphenyl



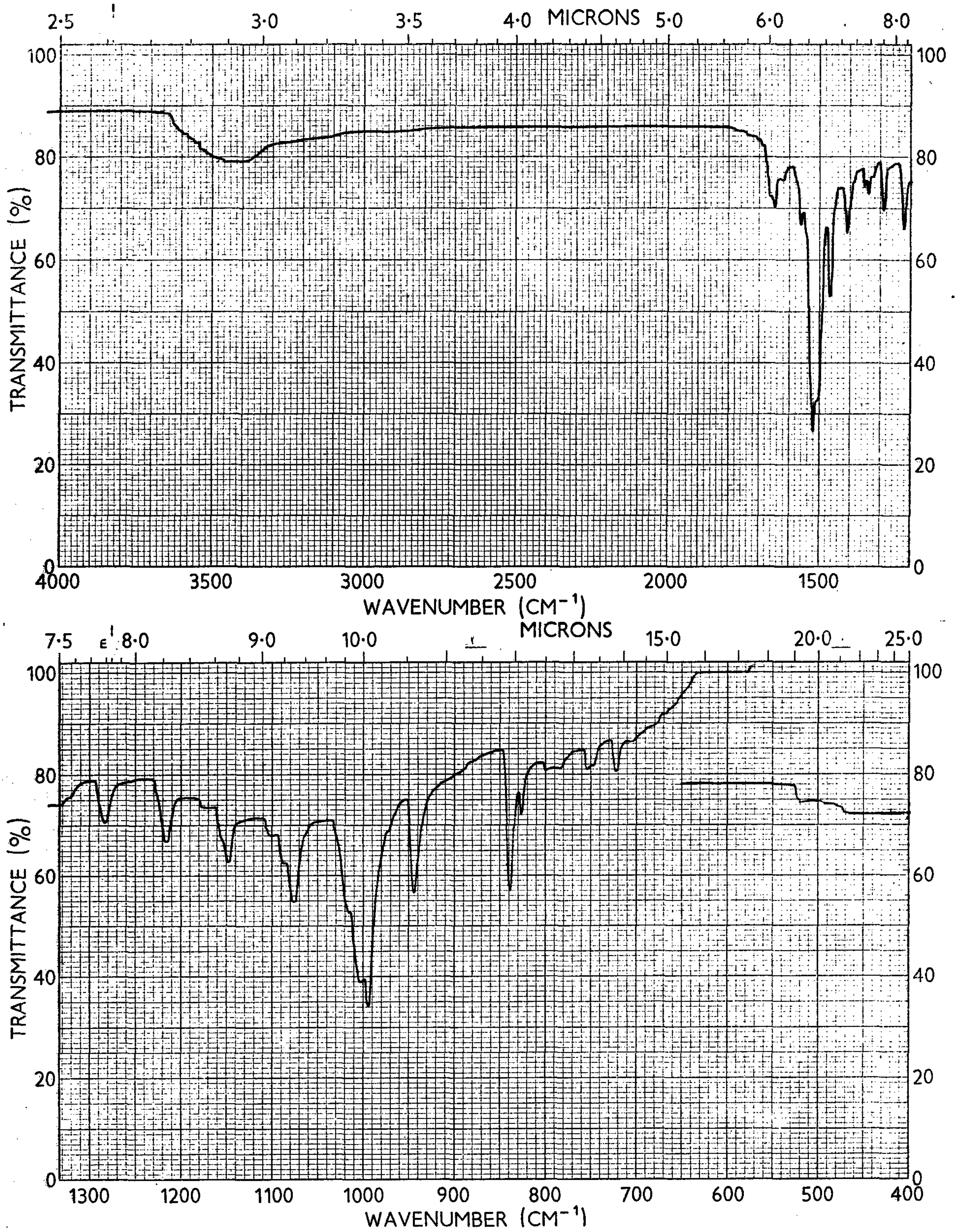
Spectrum No. SAE 51 2,2'-Diphenyl-6,6'-bibenzoxazole (II)



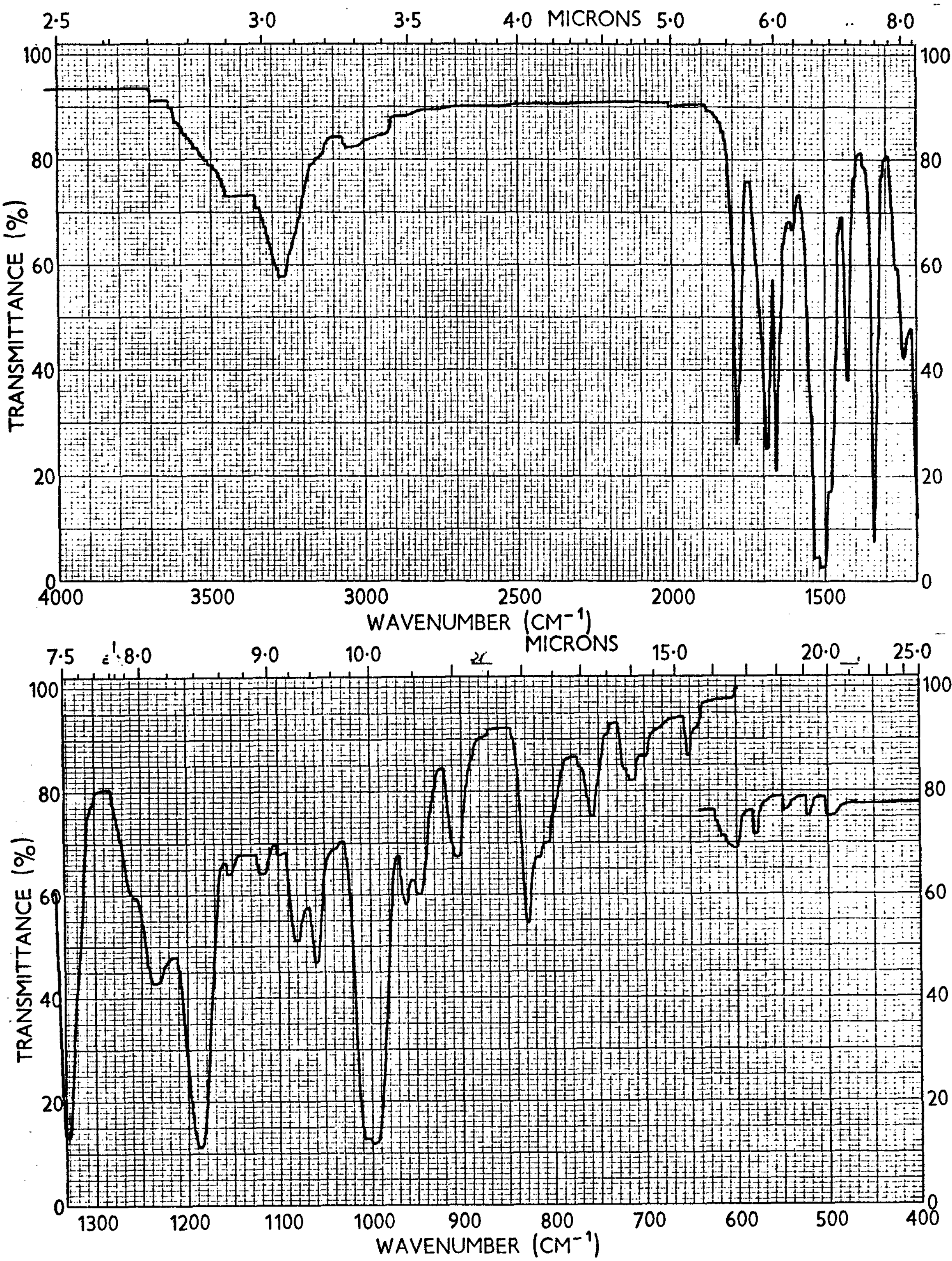
Spectrum No. 1256 2,2'-Di(pentafluorophenyl)-6,6'-bibenzoxazole (III)



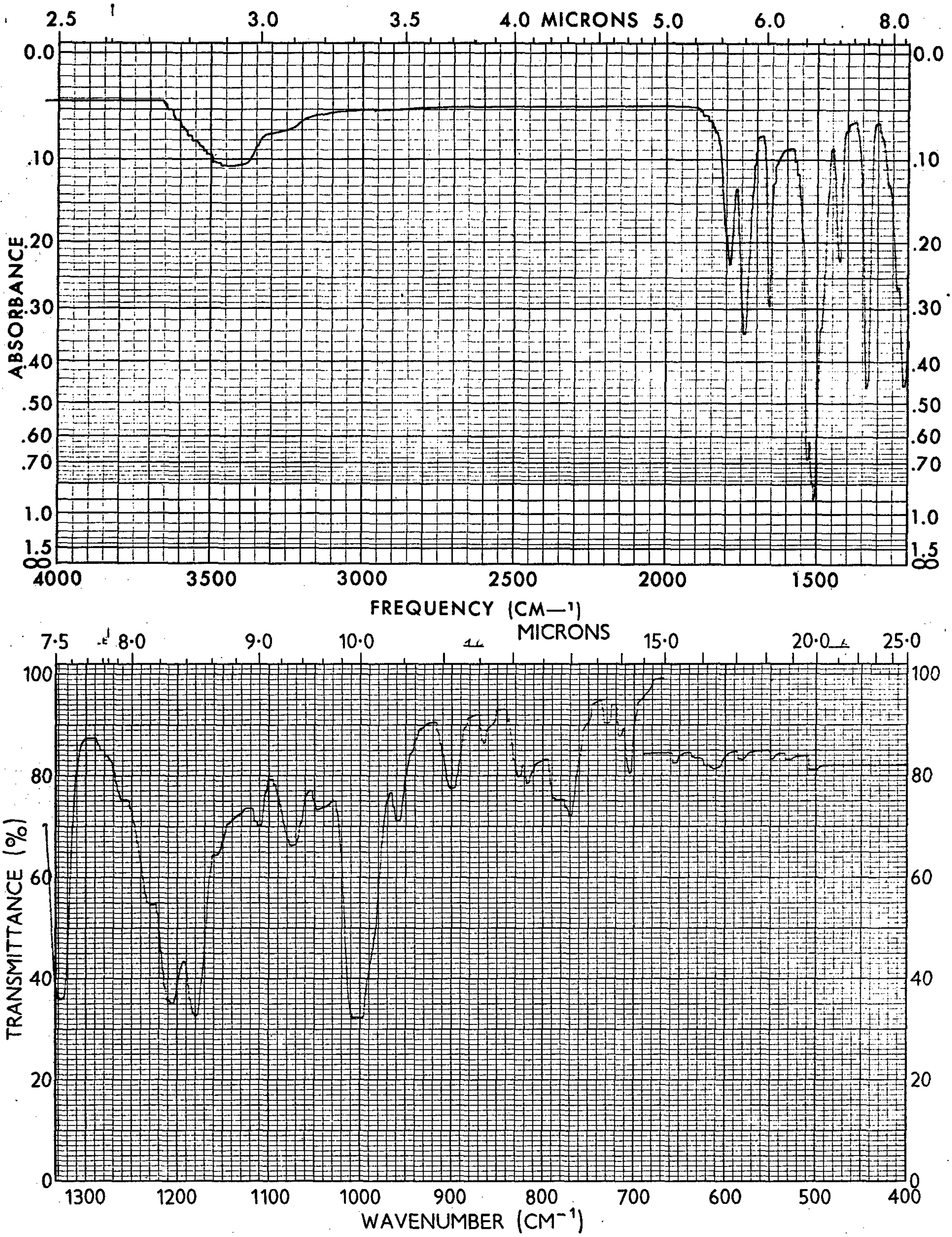
Spectrum No. 1300   2,2'-Diphenyl-hexafluoro-6,6'-bibenzoxazole (IV)



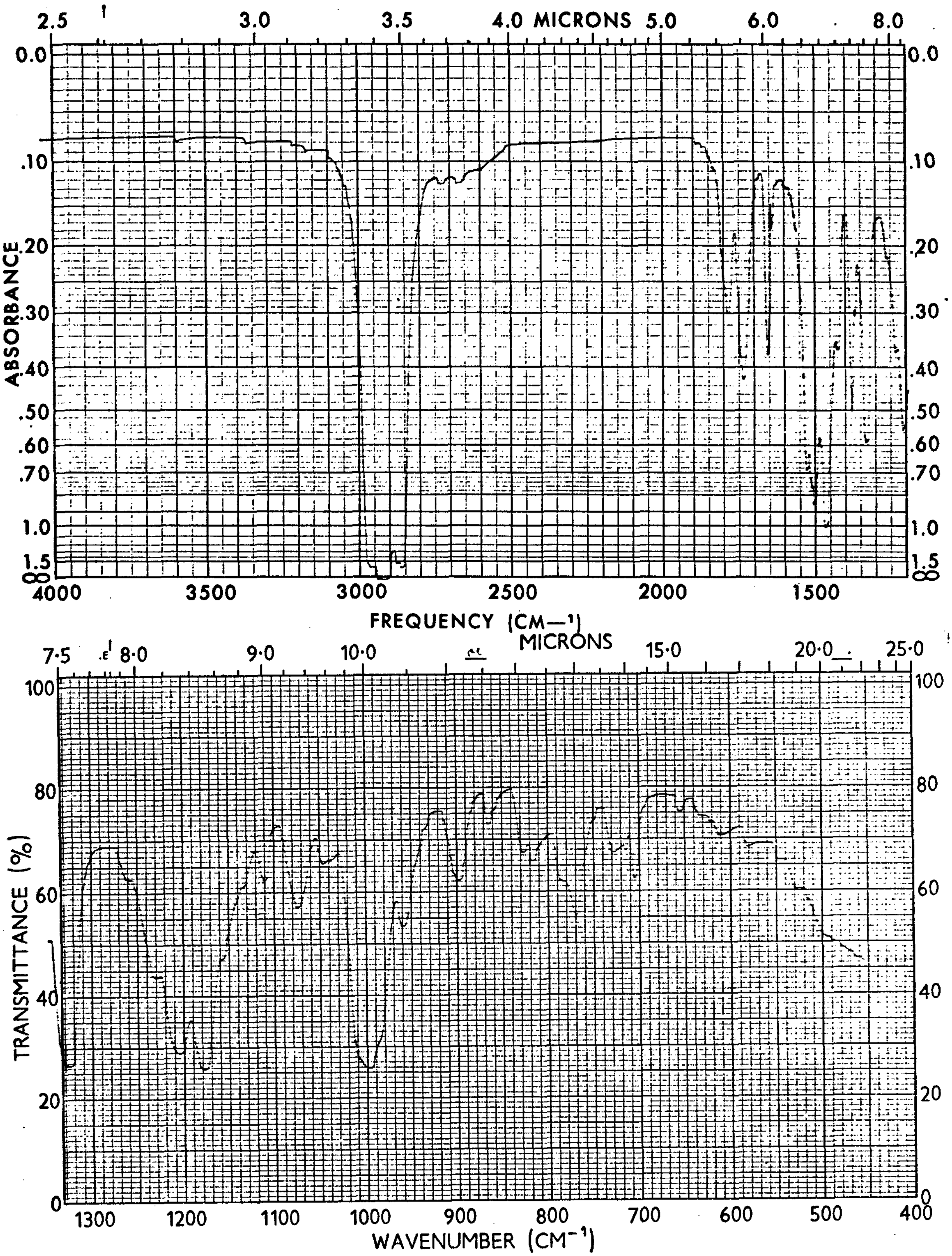
Spectrum No. 1301 2,2'-Di(pentafluorophenyl)hexafluoro-6,6'-bibenzoxazole (I)



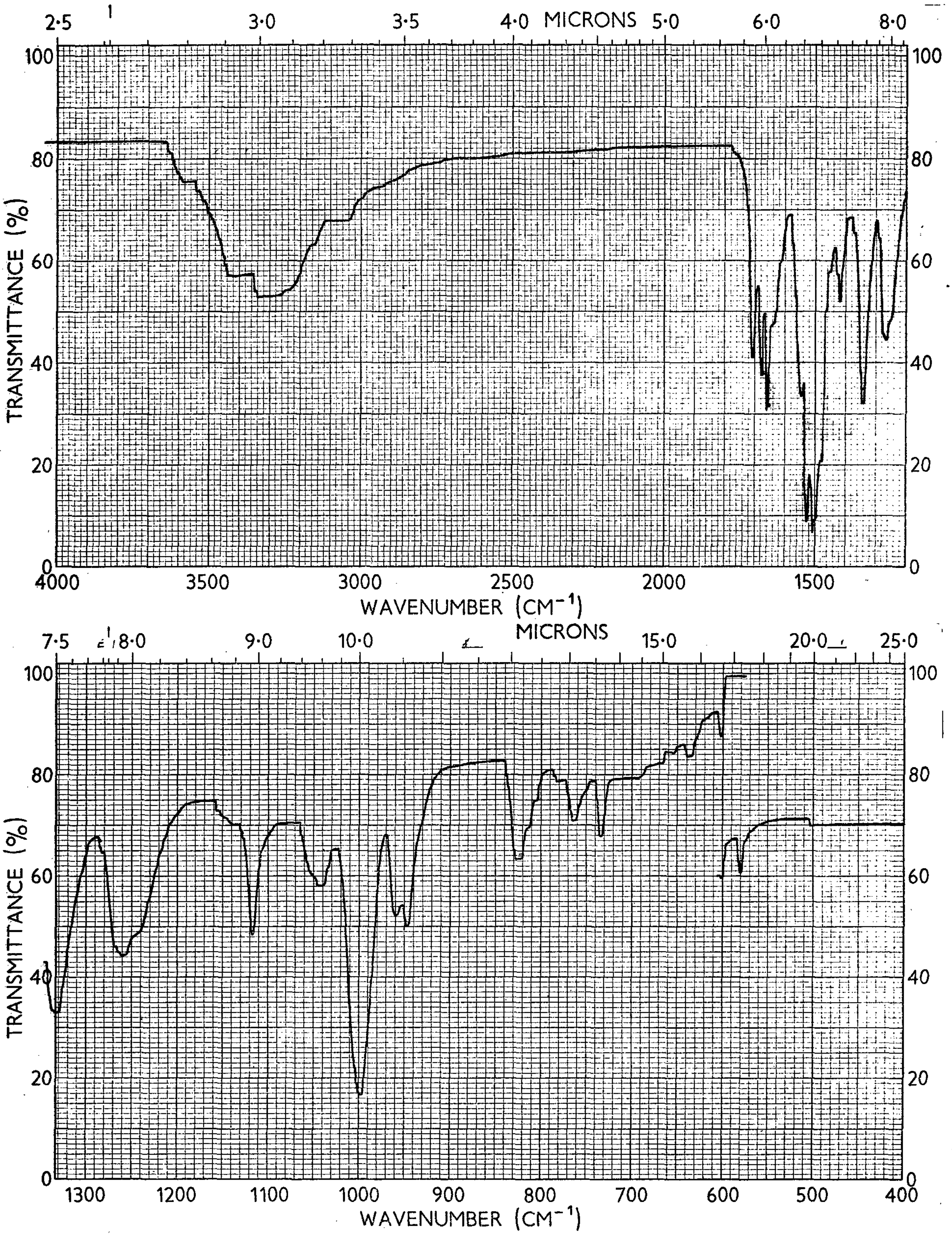
Spectrum No. SAE 53 Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxyhexafluorobenzidine (V)



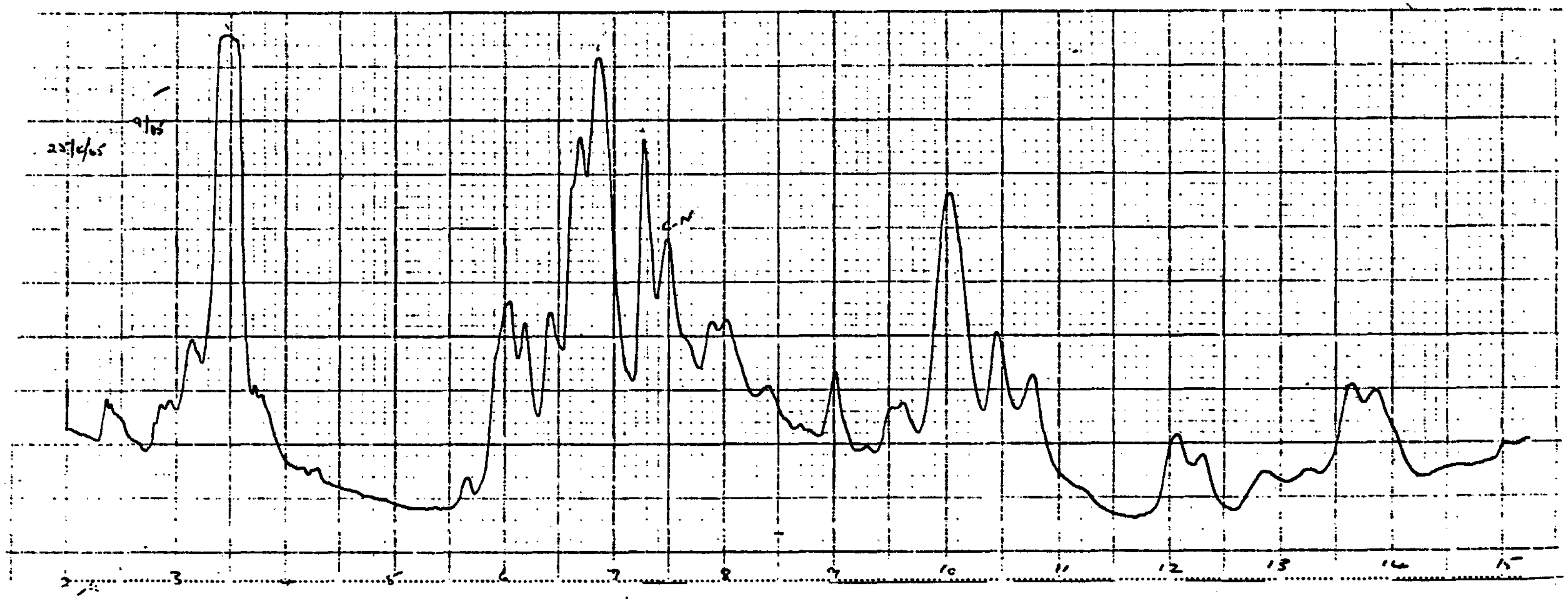
Spectrum No. SAE 52   Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxyhexafluorobenzidine (VI)



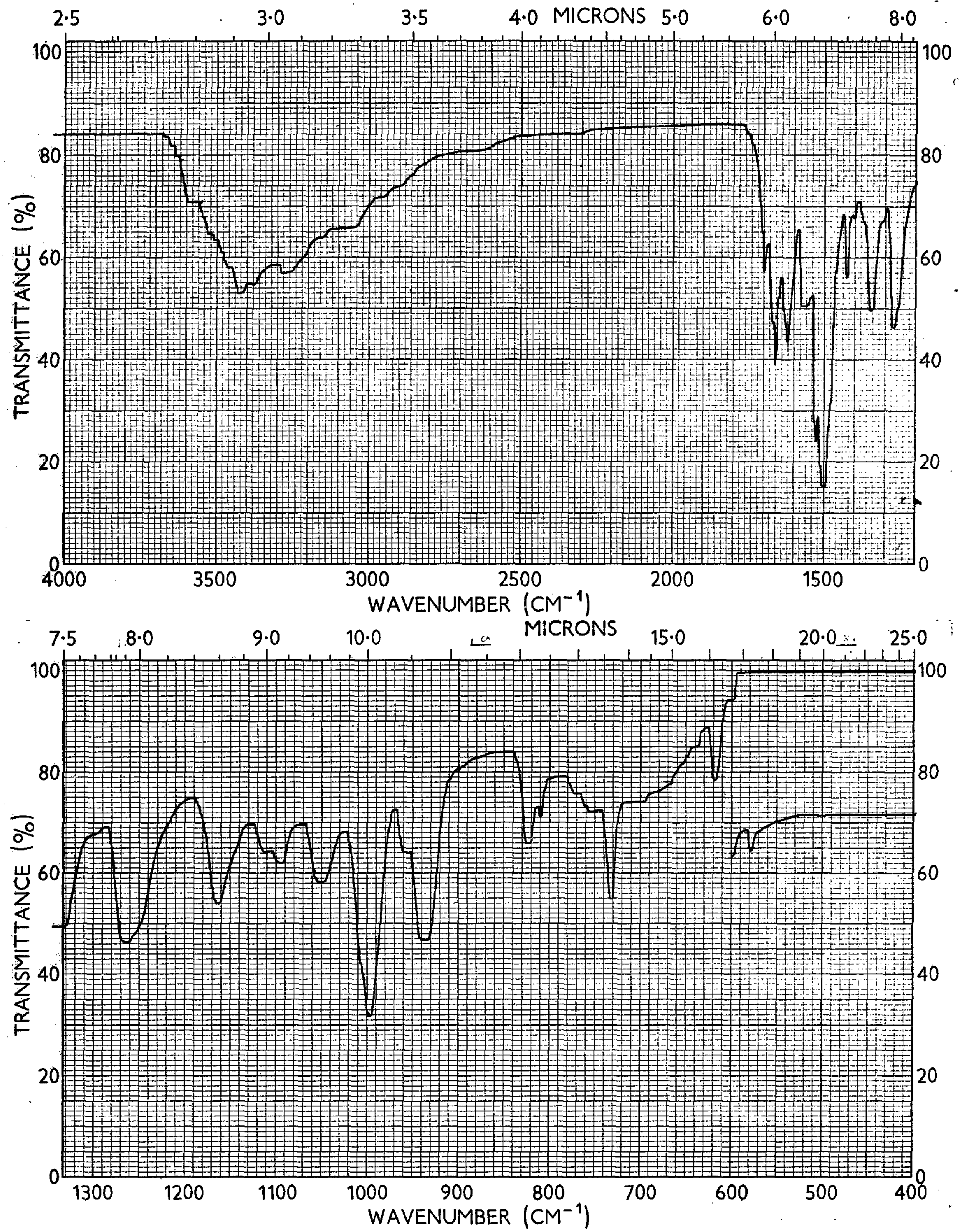
Spectrum No. SAE 52 Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxyhexafluorobenzidine (VI)



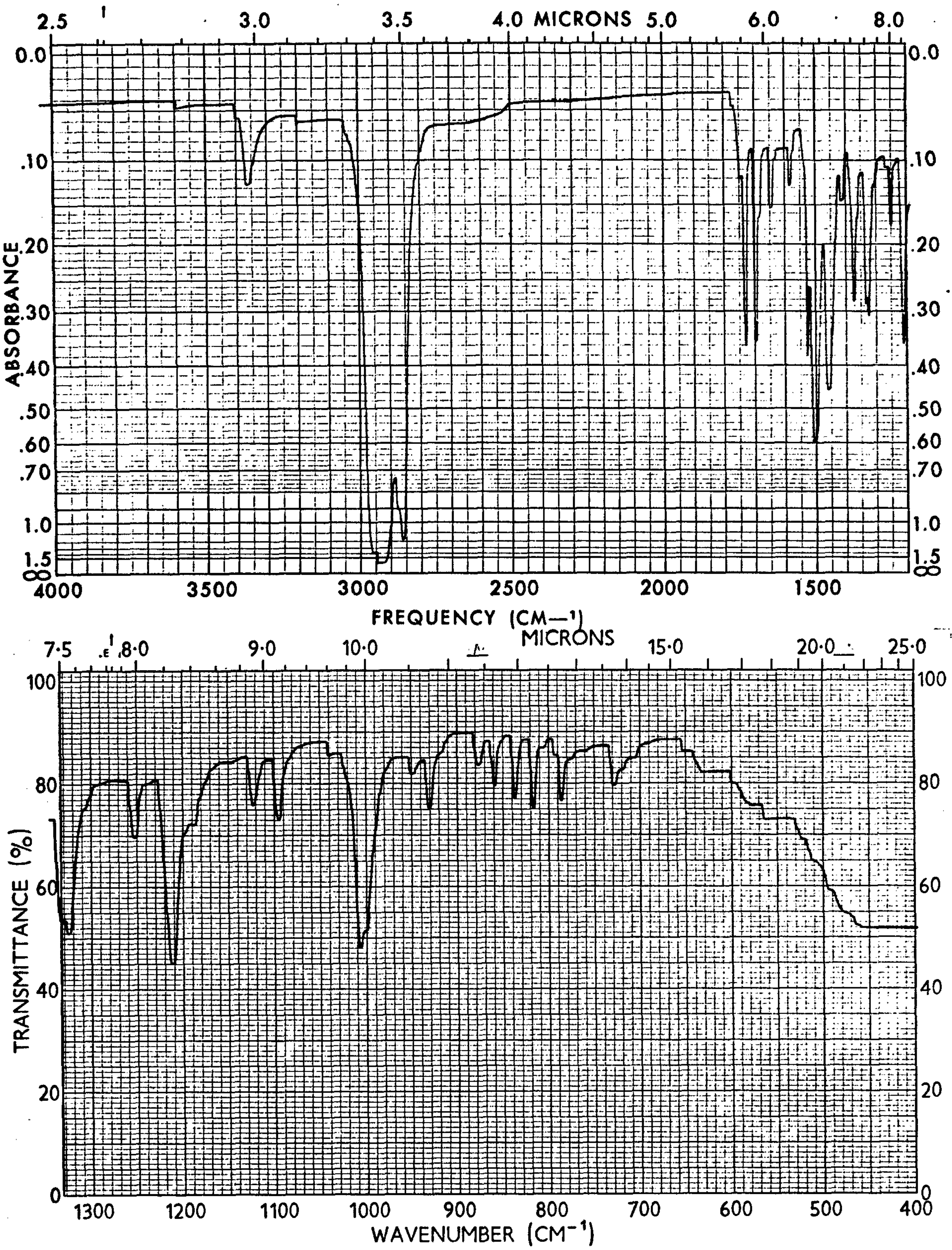
Spectrum No. 1057 Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxyhexafluorobenzidine (VII)



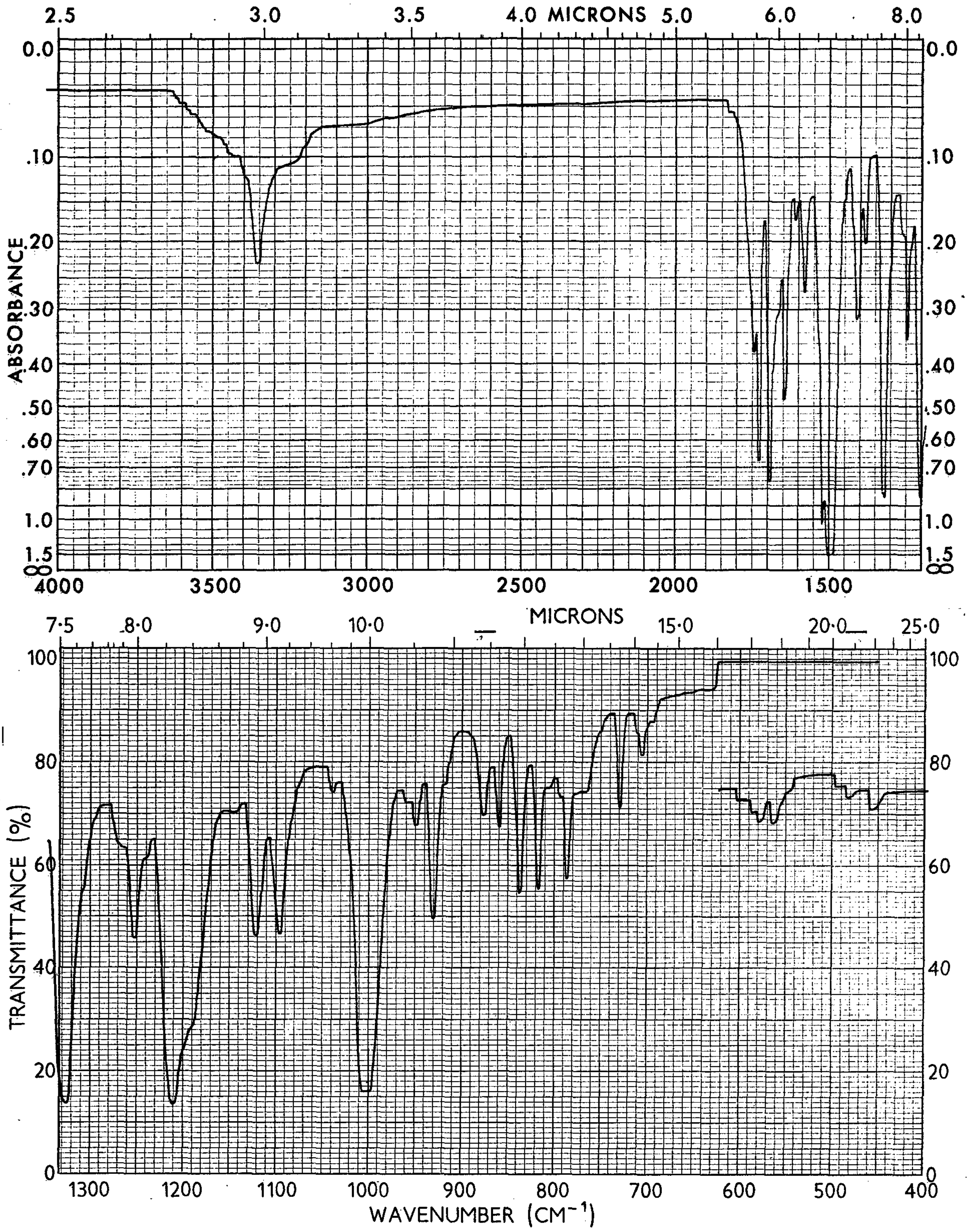
Spectrum No. 507 Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxyhexafluorobenzidine (VIII)



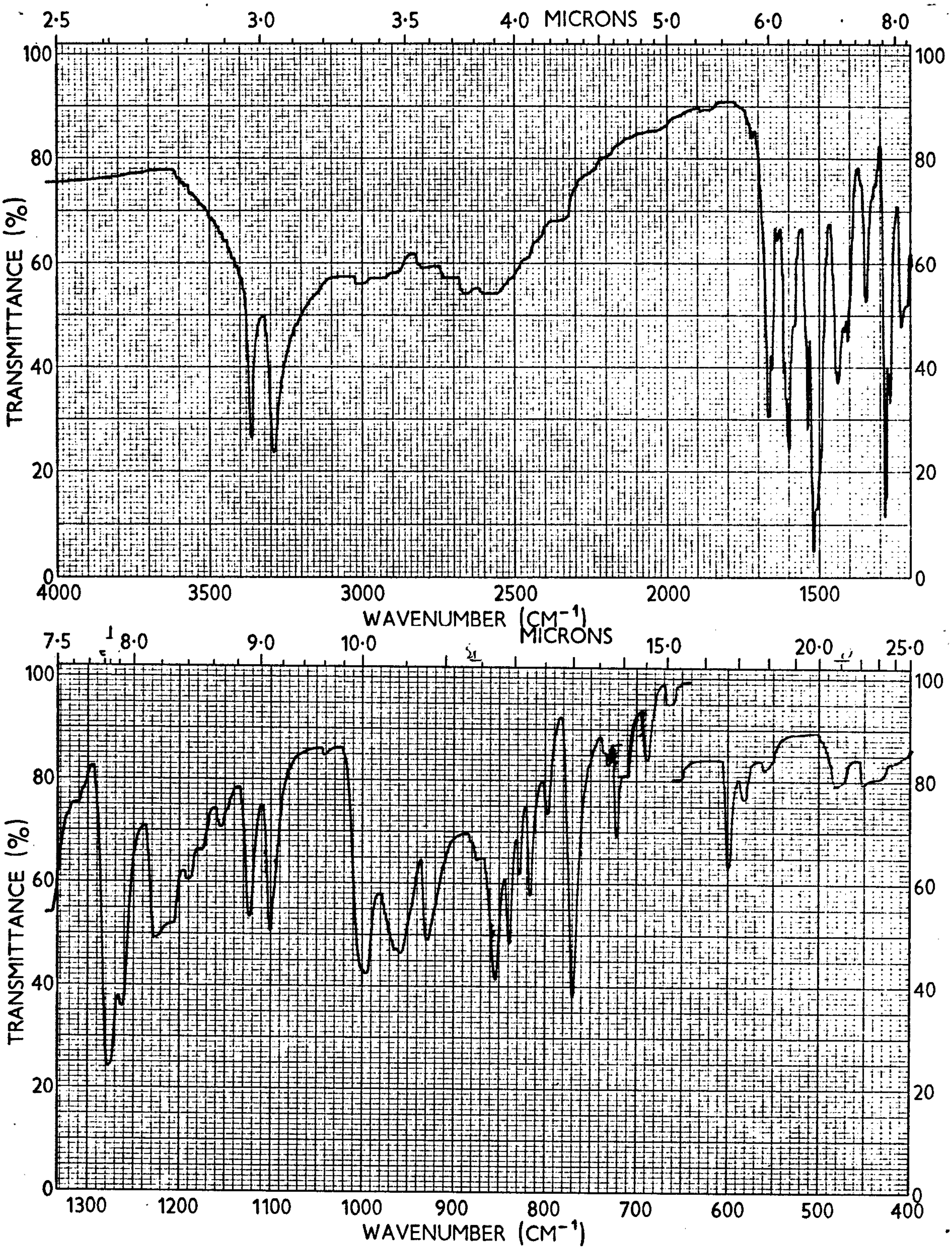
Spectrum No. 1381 Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxyhexafluorobenzidine (IX)



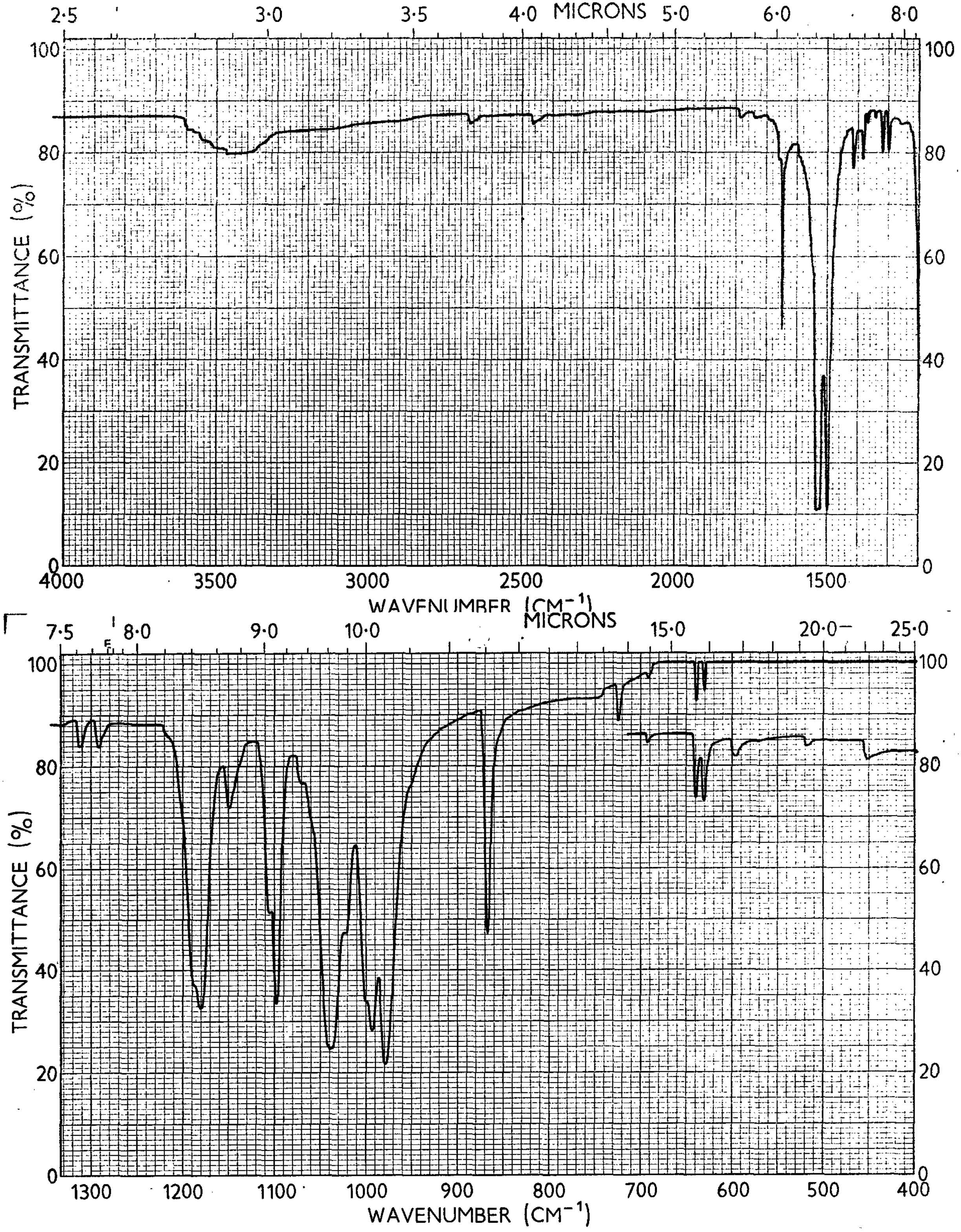
Spectrum No. 1099 Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxybenzidine (X)



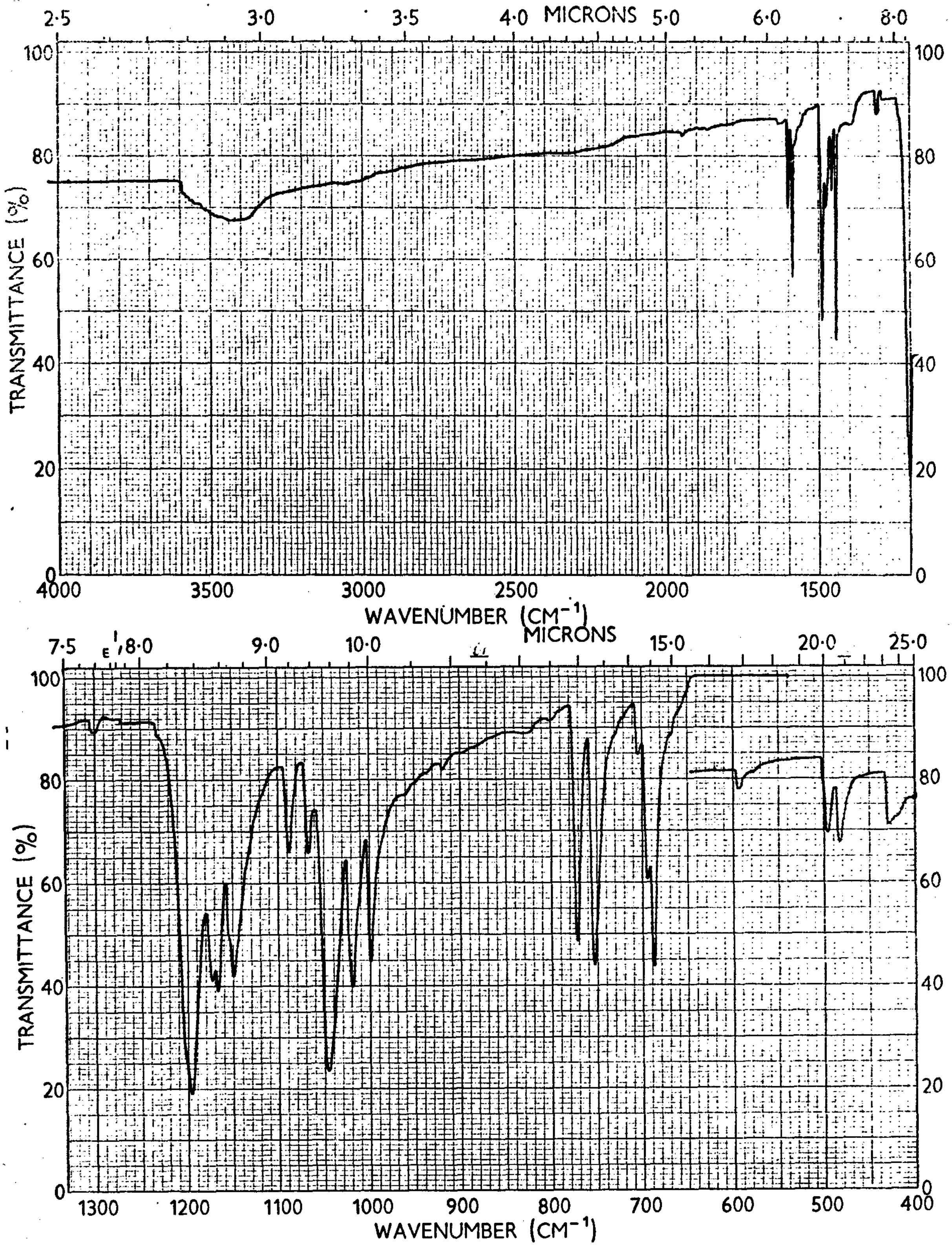
Spectrum No. 1099 Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxybenzidine (X)



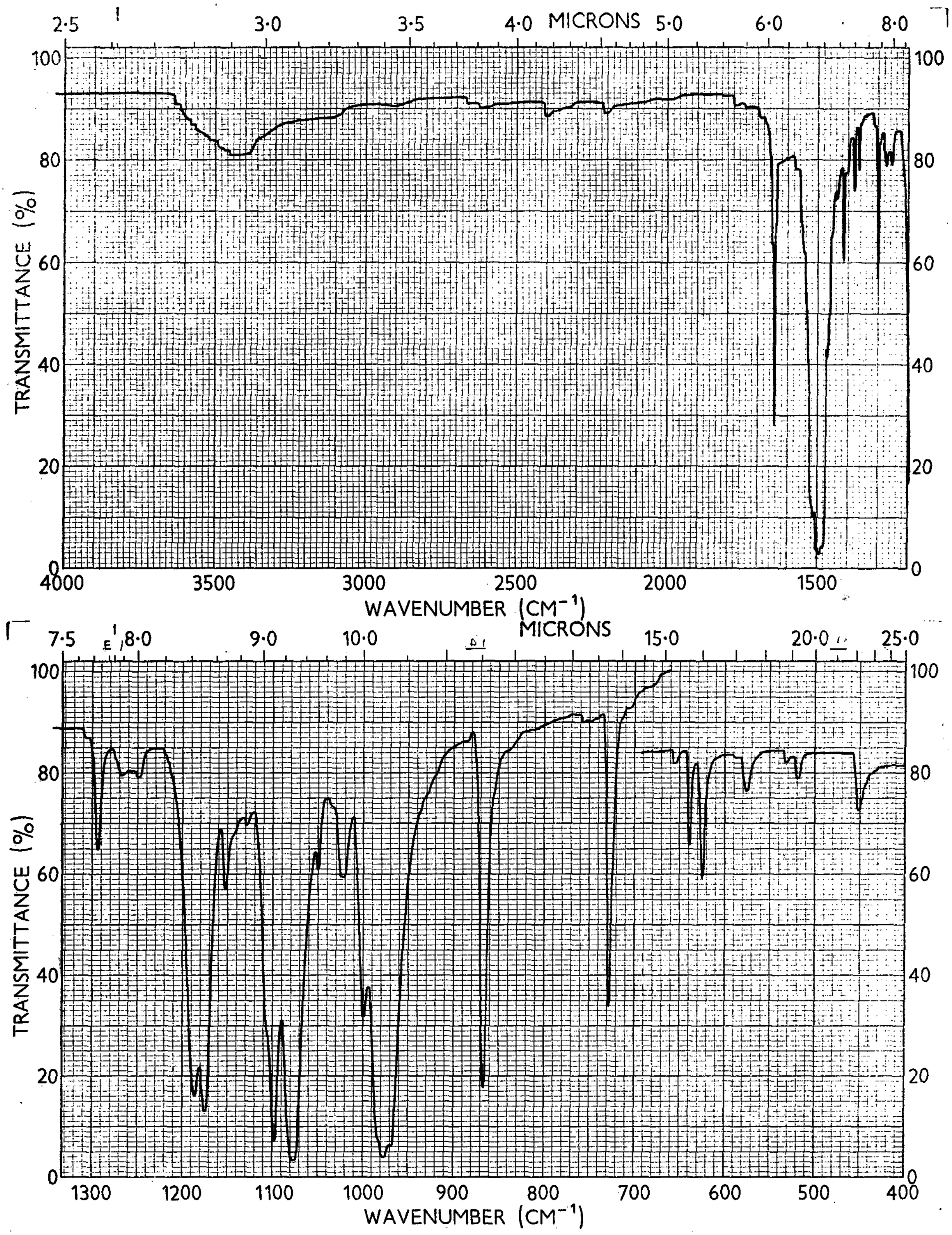
Spectrum No. 1440   Reaction product of pentafluorobenzoyl chloride and 3,3'-dihydroxybenzidine (XI)



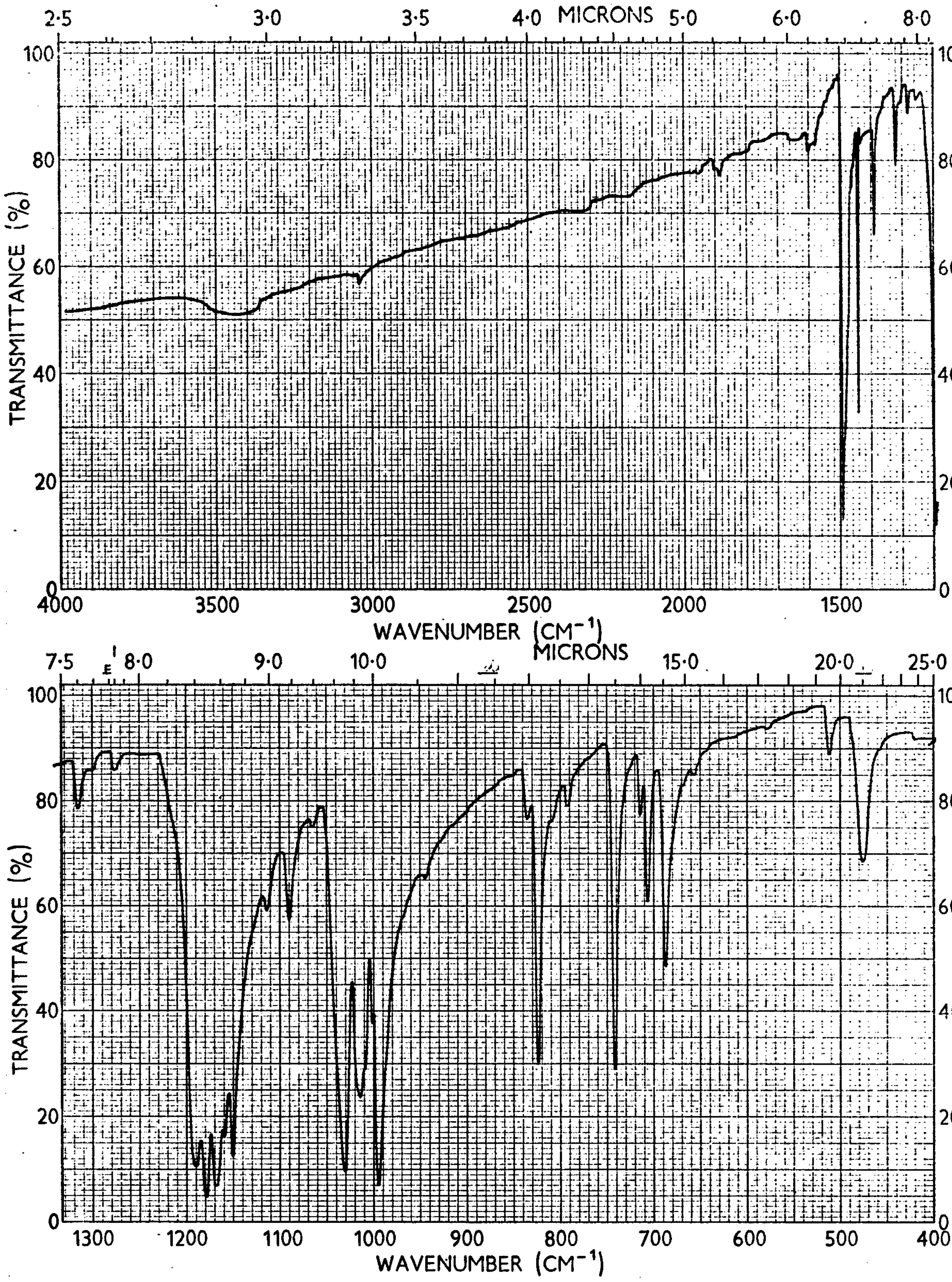
Spectrum No. 1408 O,S-Di(pentafluorophenyl)dithiocarbonate (XIII)



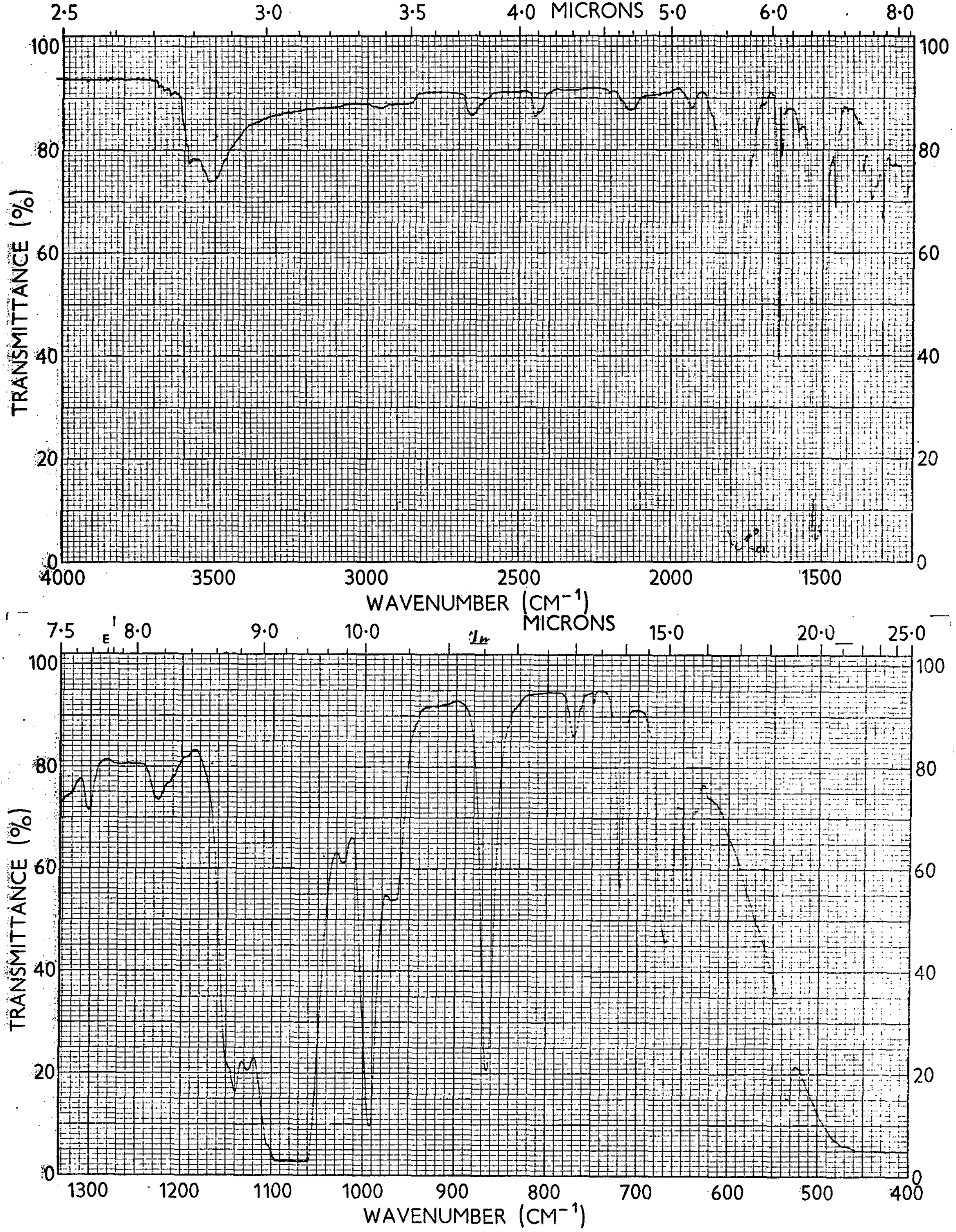
Spectrum No. 1407 O,S-Diphenyldithiocarbonate (XIV)



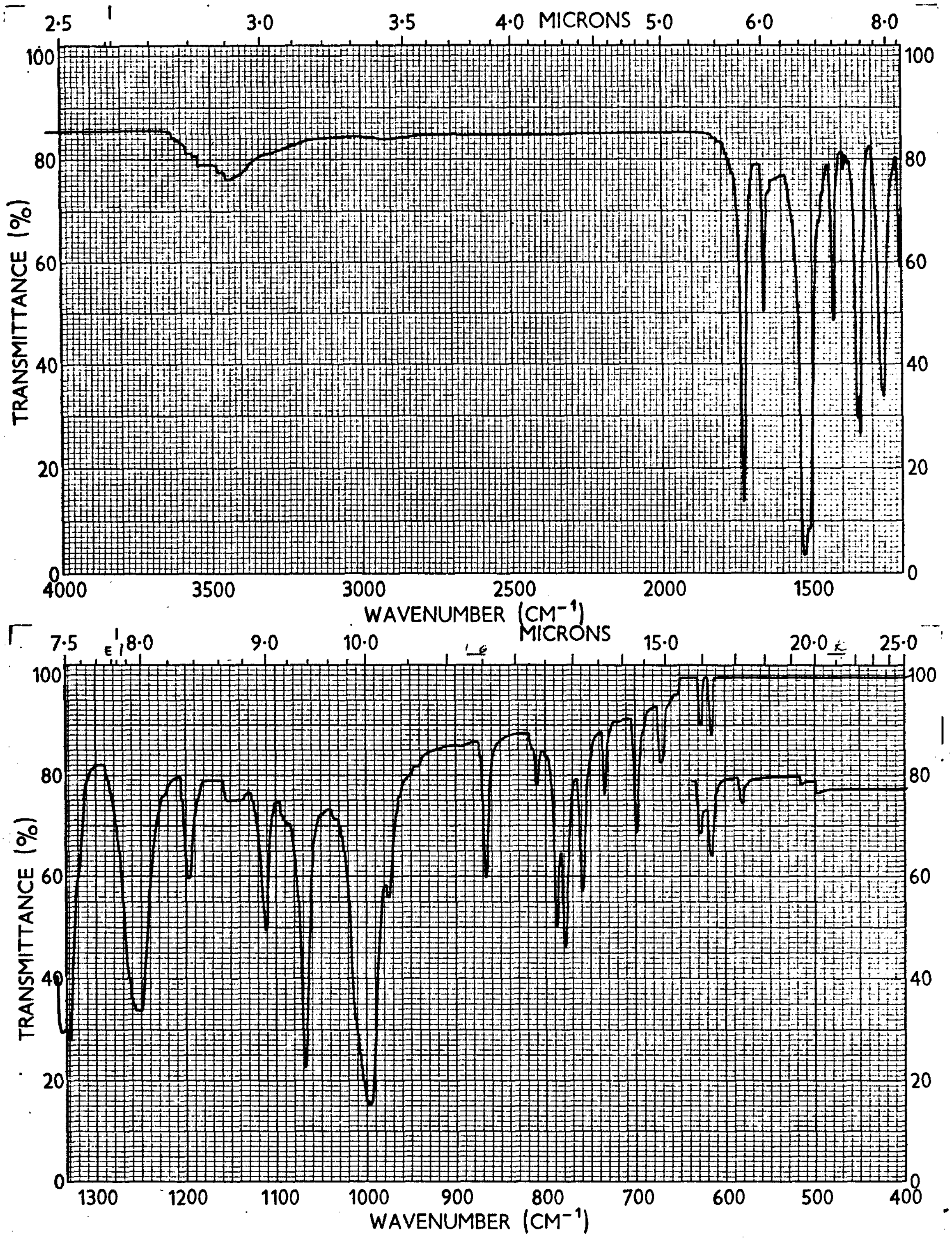
Spectrum No. 1410 0,0-(4,4'-Octafluorobiphenylylene)
di(S-pentafluorophenyl dithiocarbonate)
(XV)



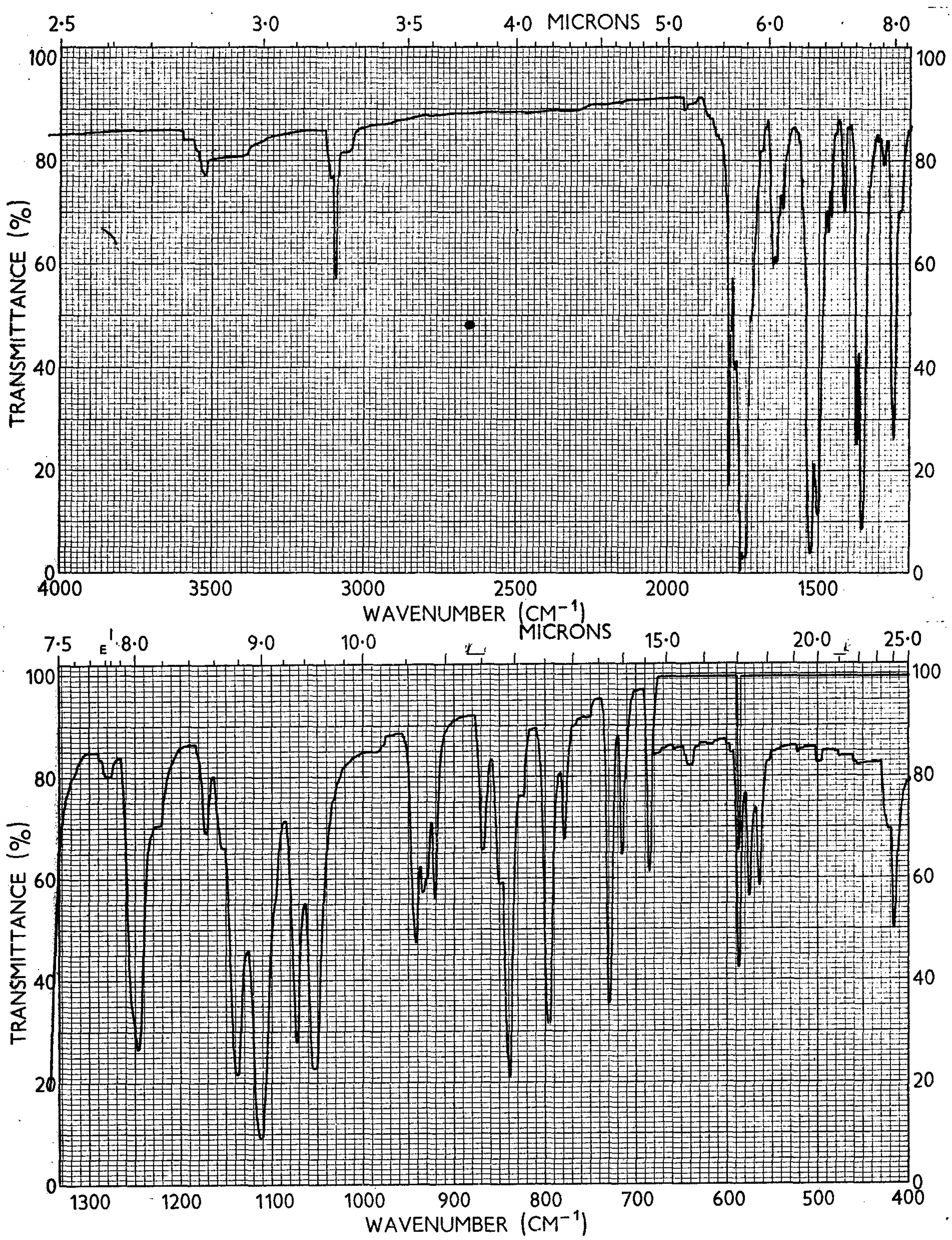
Spectrum No. 1409 0,0-(4,4'-Biphenylylene) di(S-phenyl-dithiocarbonate) (XVI)



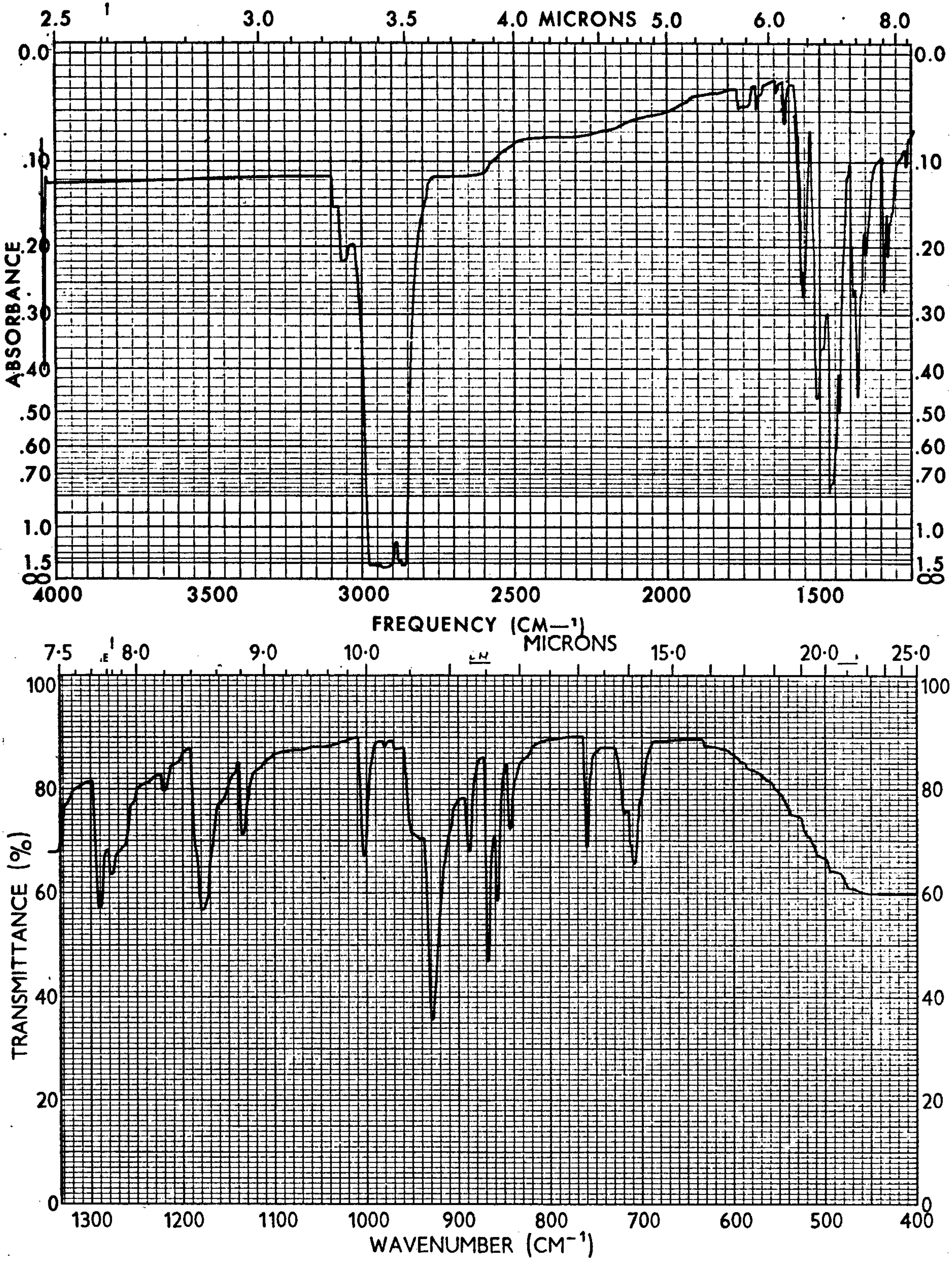
Spectrum No. 1083 Tetrafluoro-m-phenylene bischloroformate



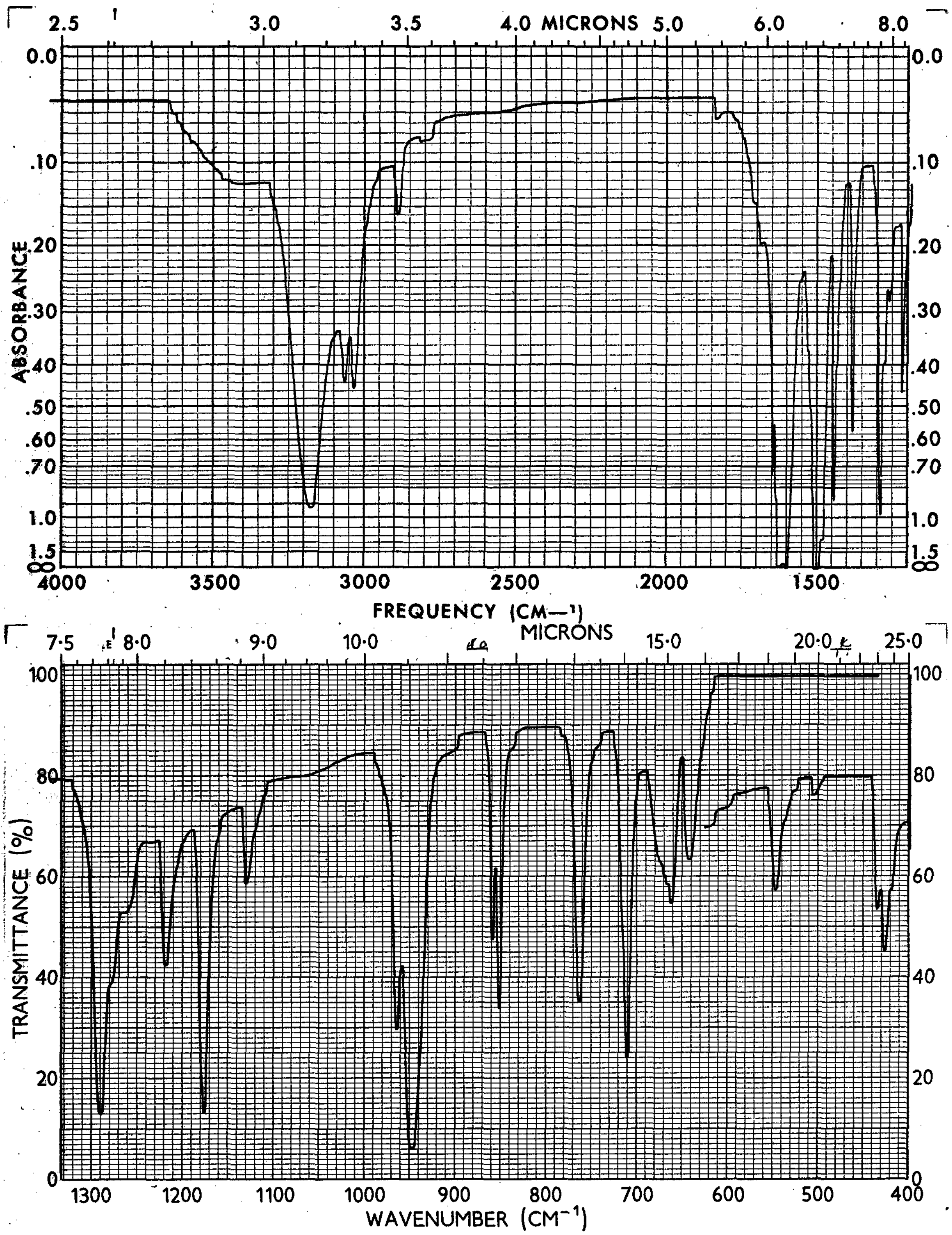
Spectrum No. 1126 N,N'-Di(pentafluorobenzoyl)-N,N'-di-(pentafluorophenyl)-2,3,5,6-tetrafluorophenylene diamine (XIX)



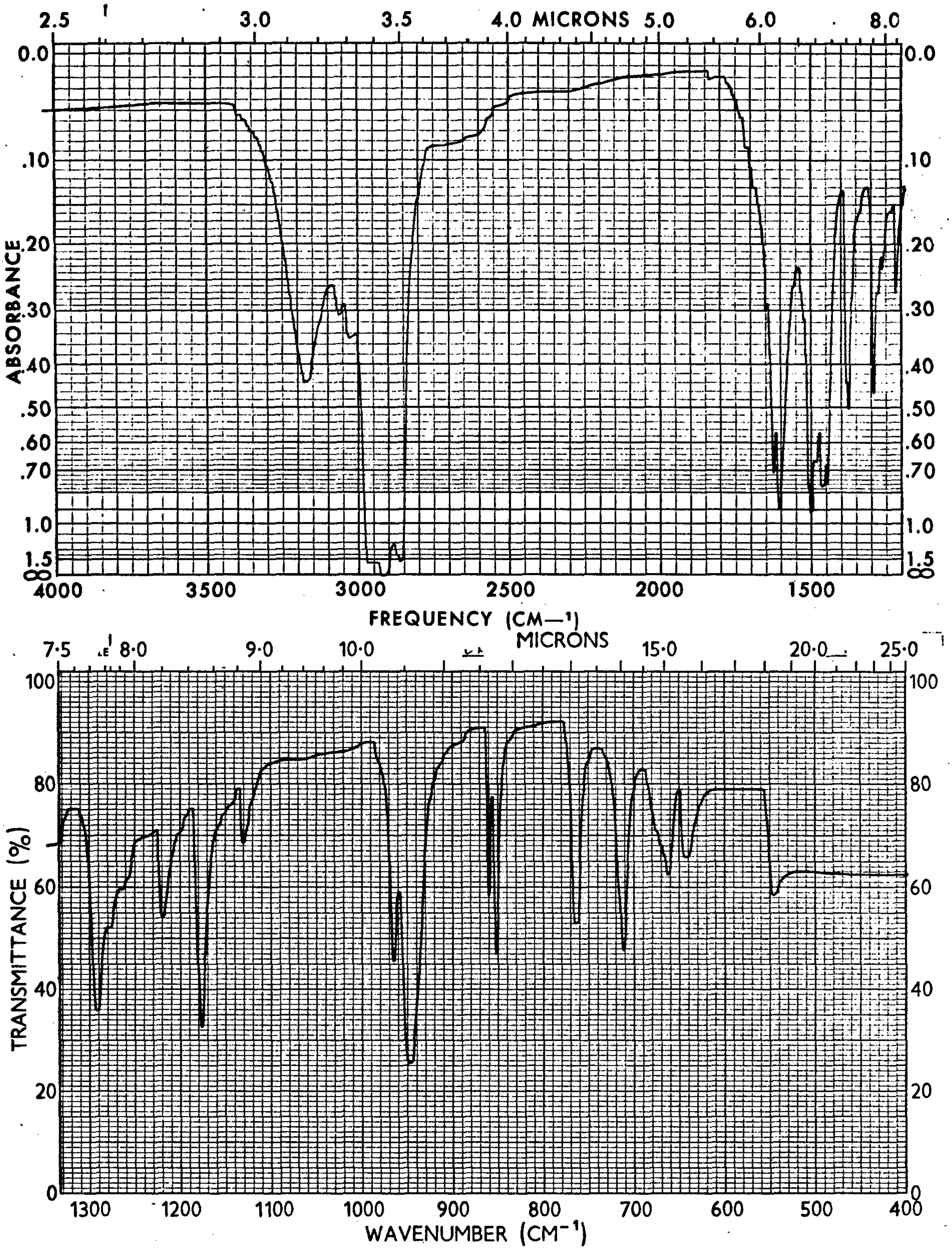
Spectrum No. 901 N,N'-Di(2,3,4,6-tetrafluorophenyl)-
pyromellitimide (XX)



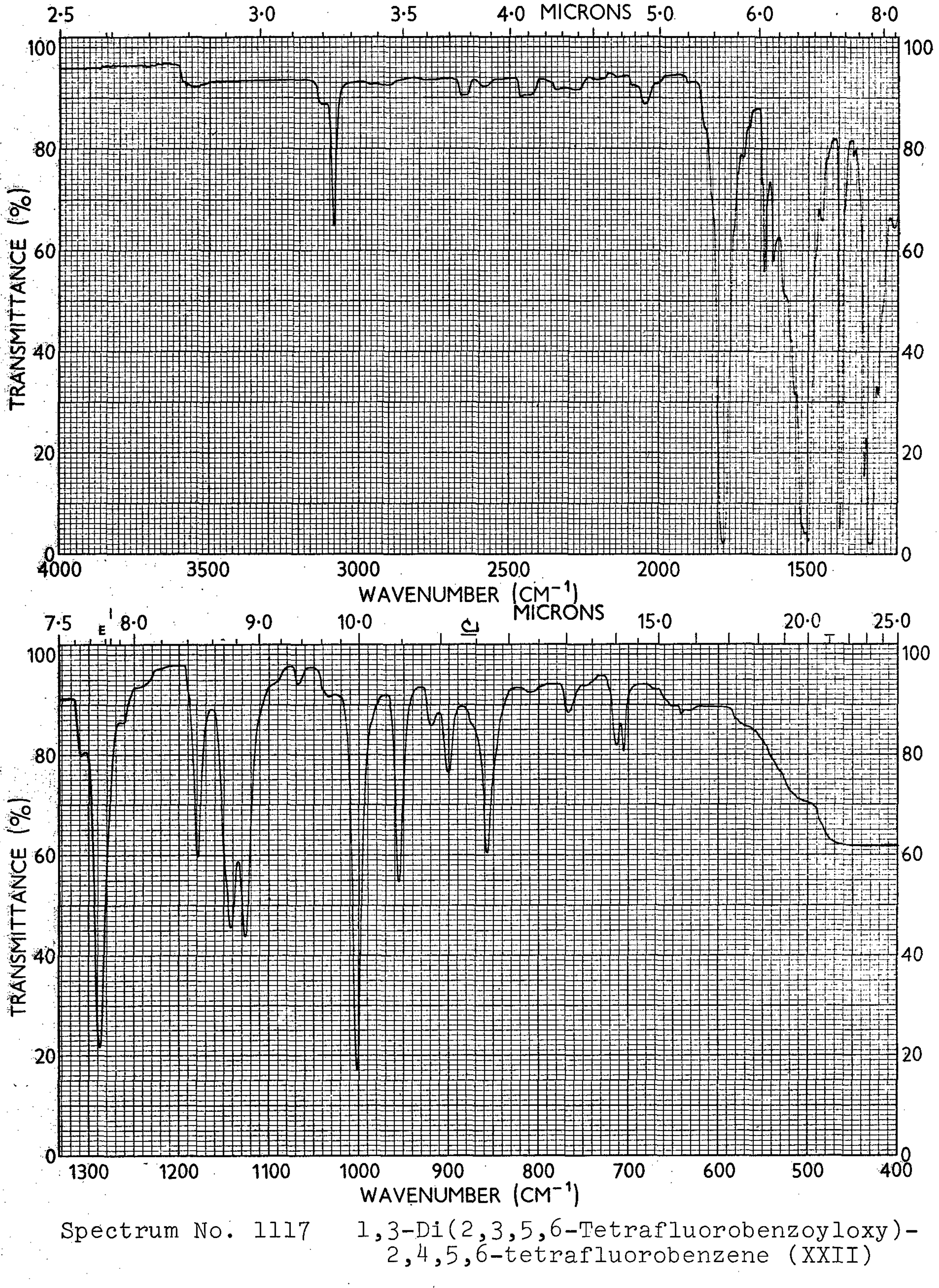
Spectrum No. 949 2,5-Di(2,3,5,6-tetrafluorophenyl)-
1,3,4-oxadiazole (XXI)



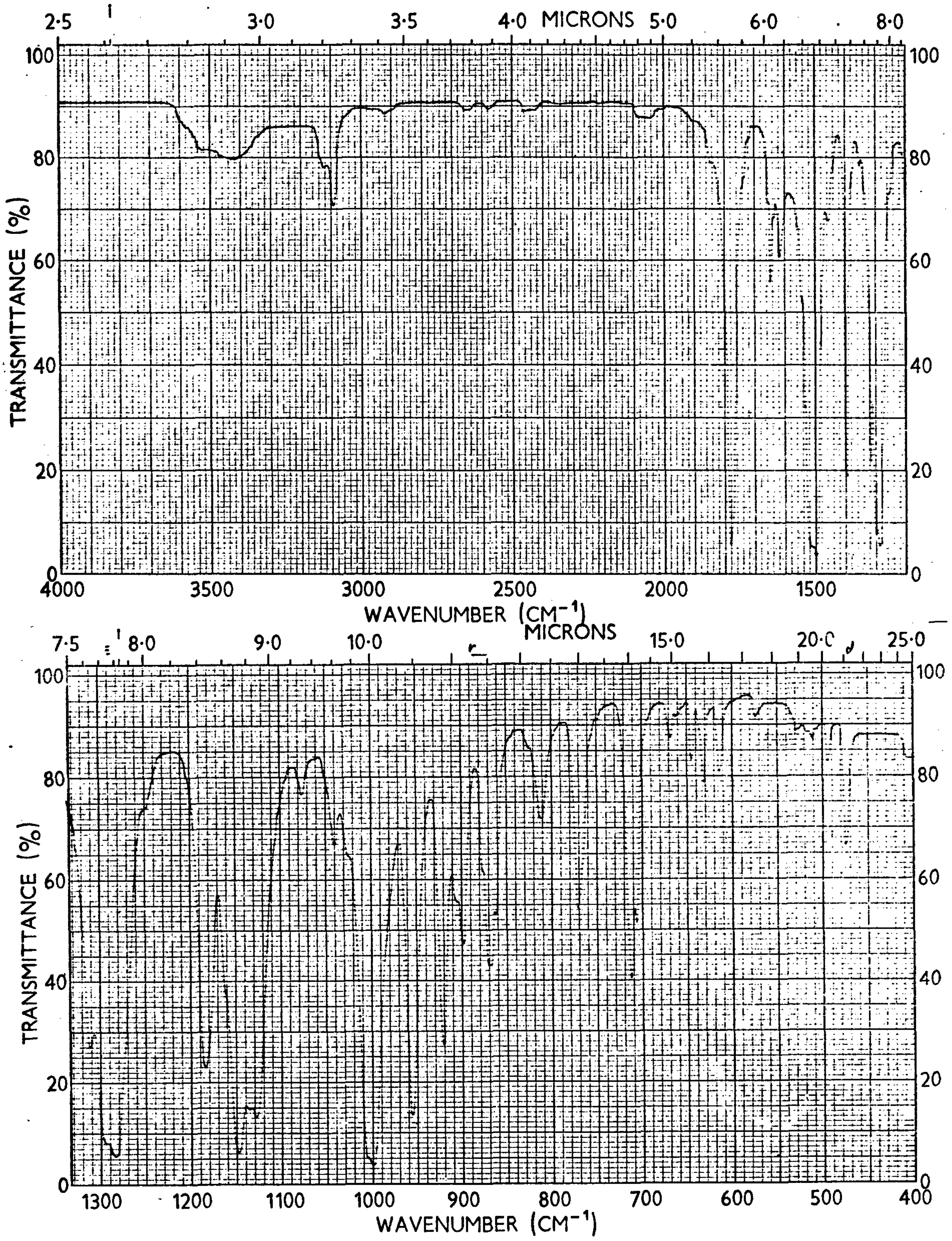
Spectrum No. 950 Hydrazide precursor of (XXI)



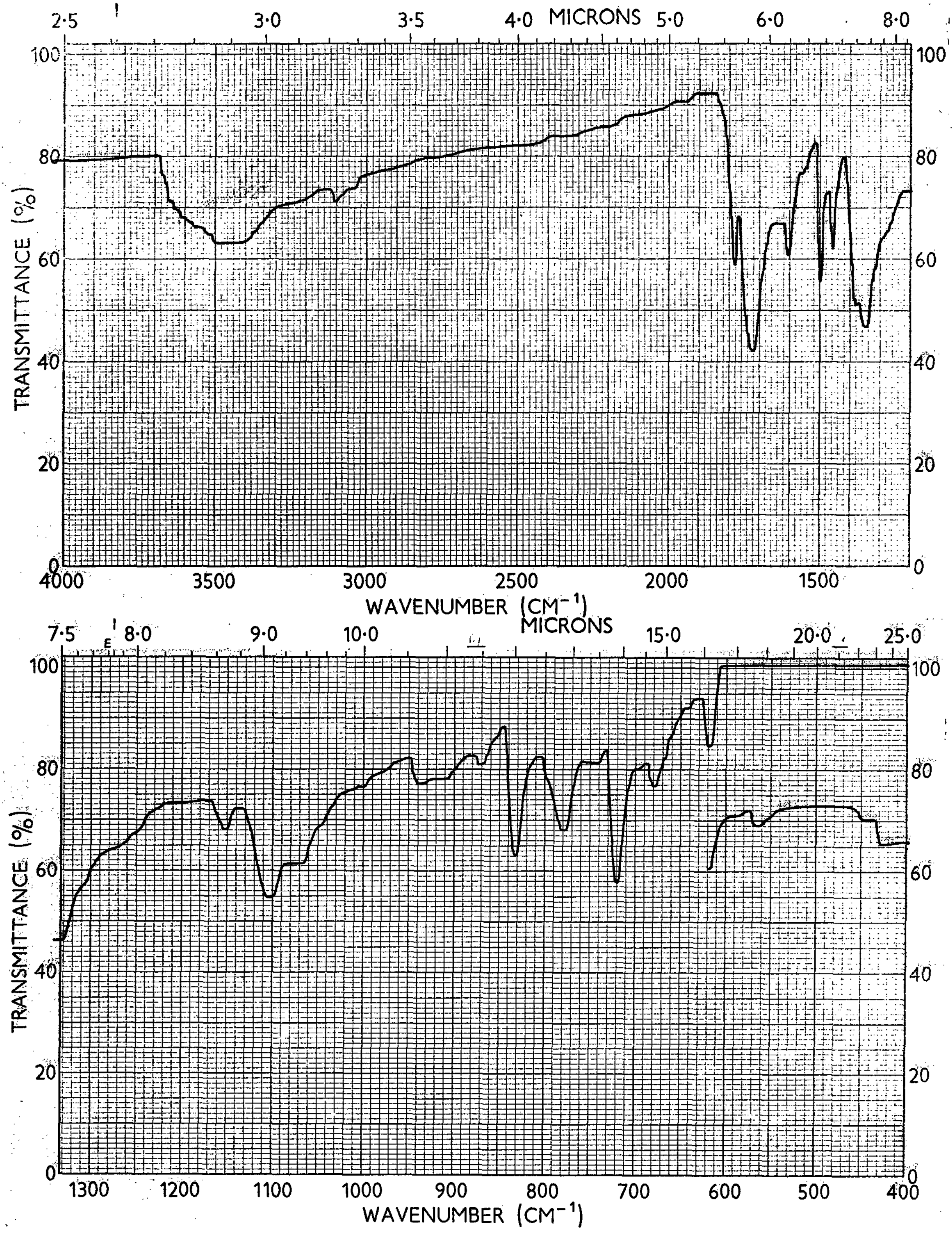
Spectrum No. 950 Hydrazide precursor of (XXI)



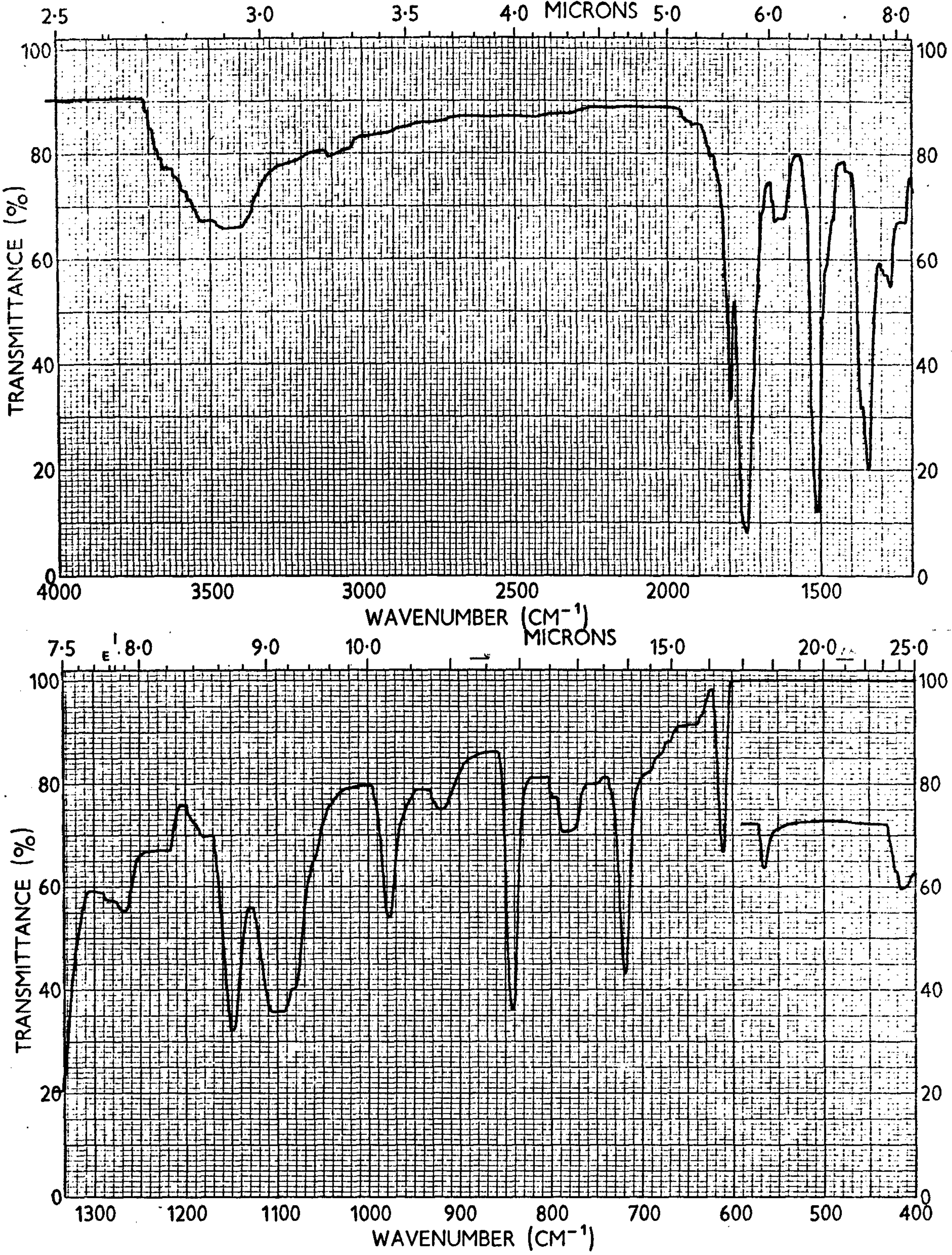
Spectrum No. 1117 1,3-Di(2,3,5,6-Tetrafluorobenzoyloxy)-
2,4,5,6-tetrafluorobenzene (XXII)



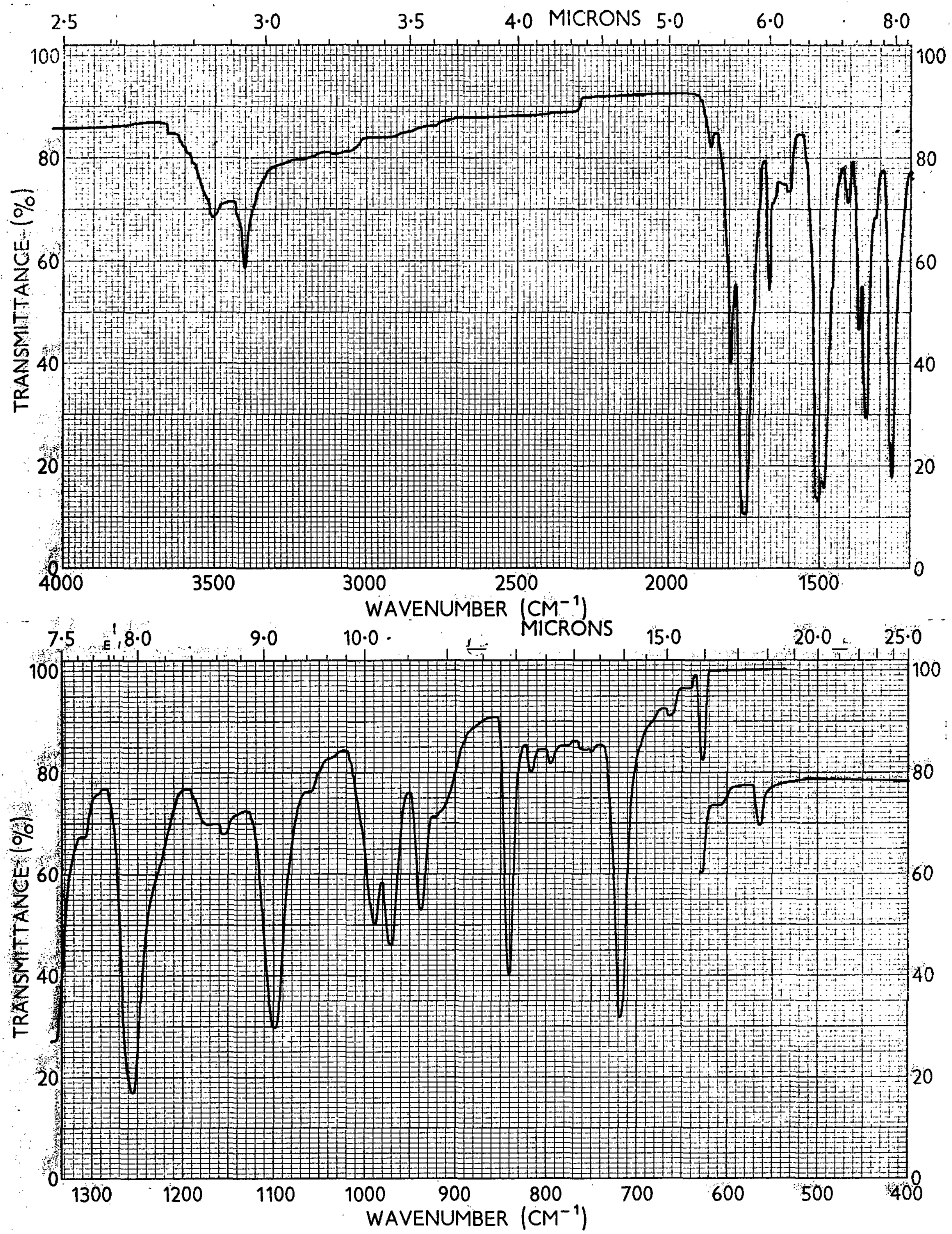
Spectrum No. 1117 1,3-Di(2,3,5,6-Tetrafluorobenzoyloxy)-2,4,5,6-tetrafluorobenzene (XXII)



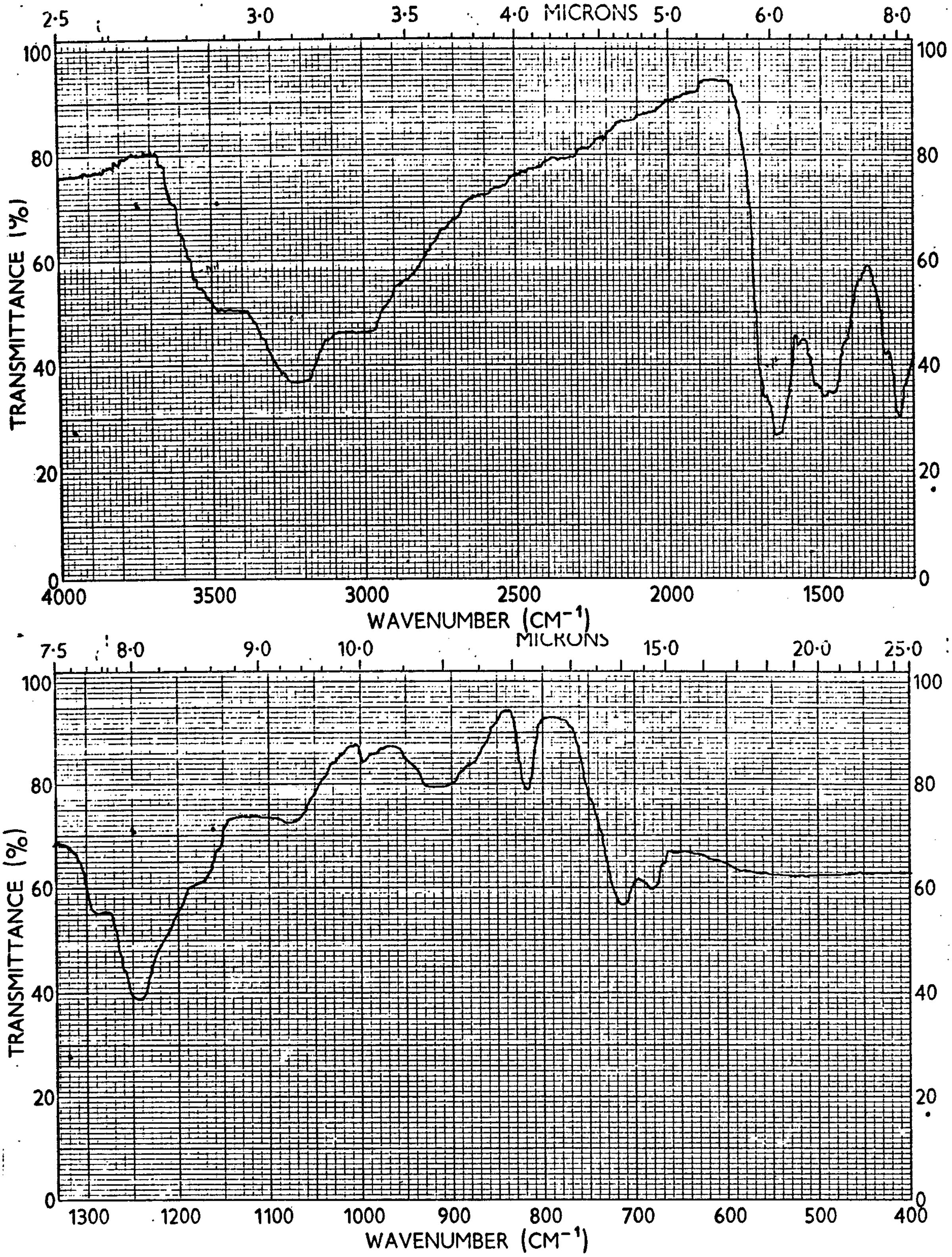
Spectrum No. 1058 Poly(m-phenylenepyromellitimide)
(P.I. (1))



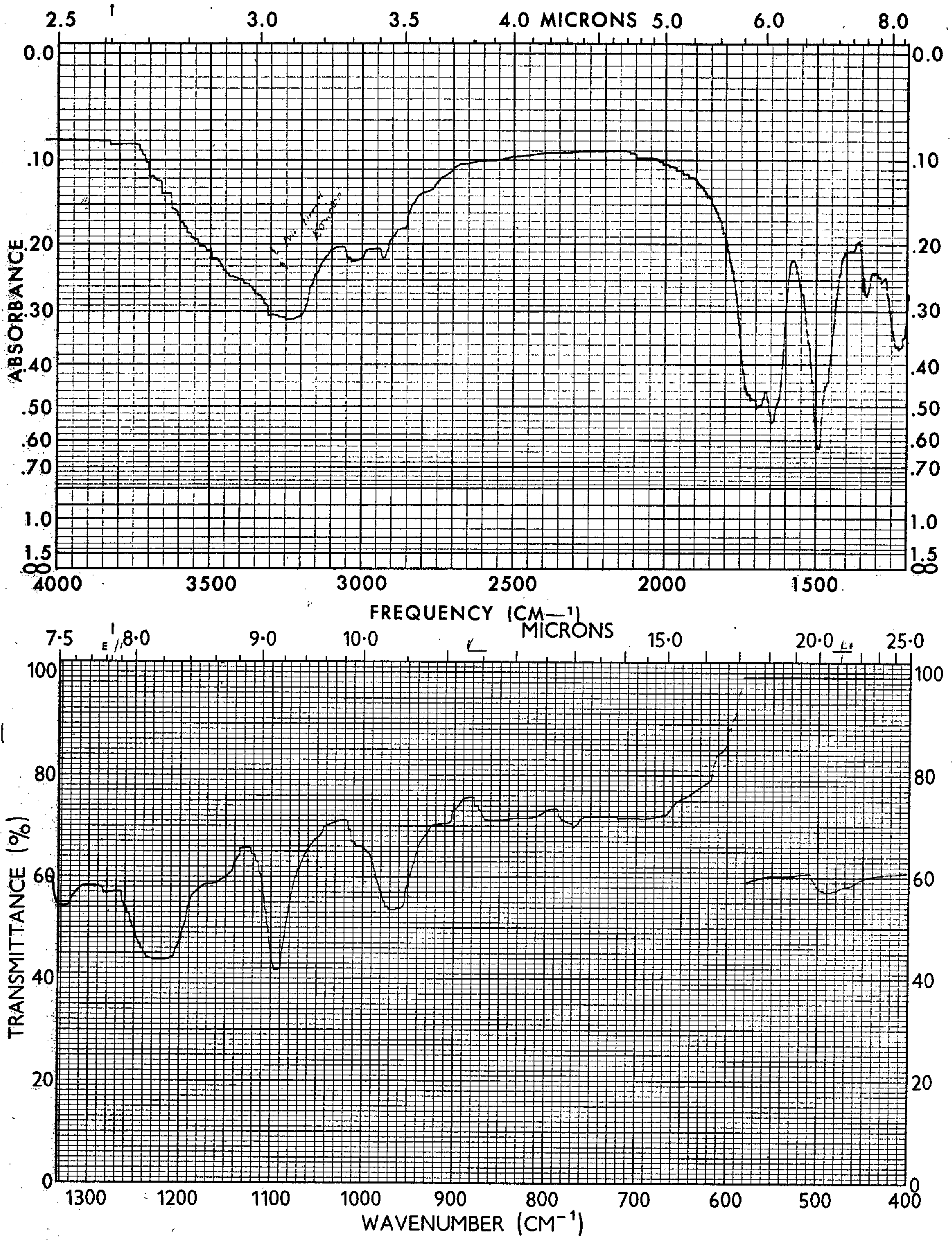
Spectrum No. 1060 Poly[(tetrafluoro-m-phenylene)-
pyromellitimide](P.I. (2))



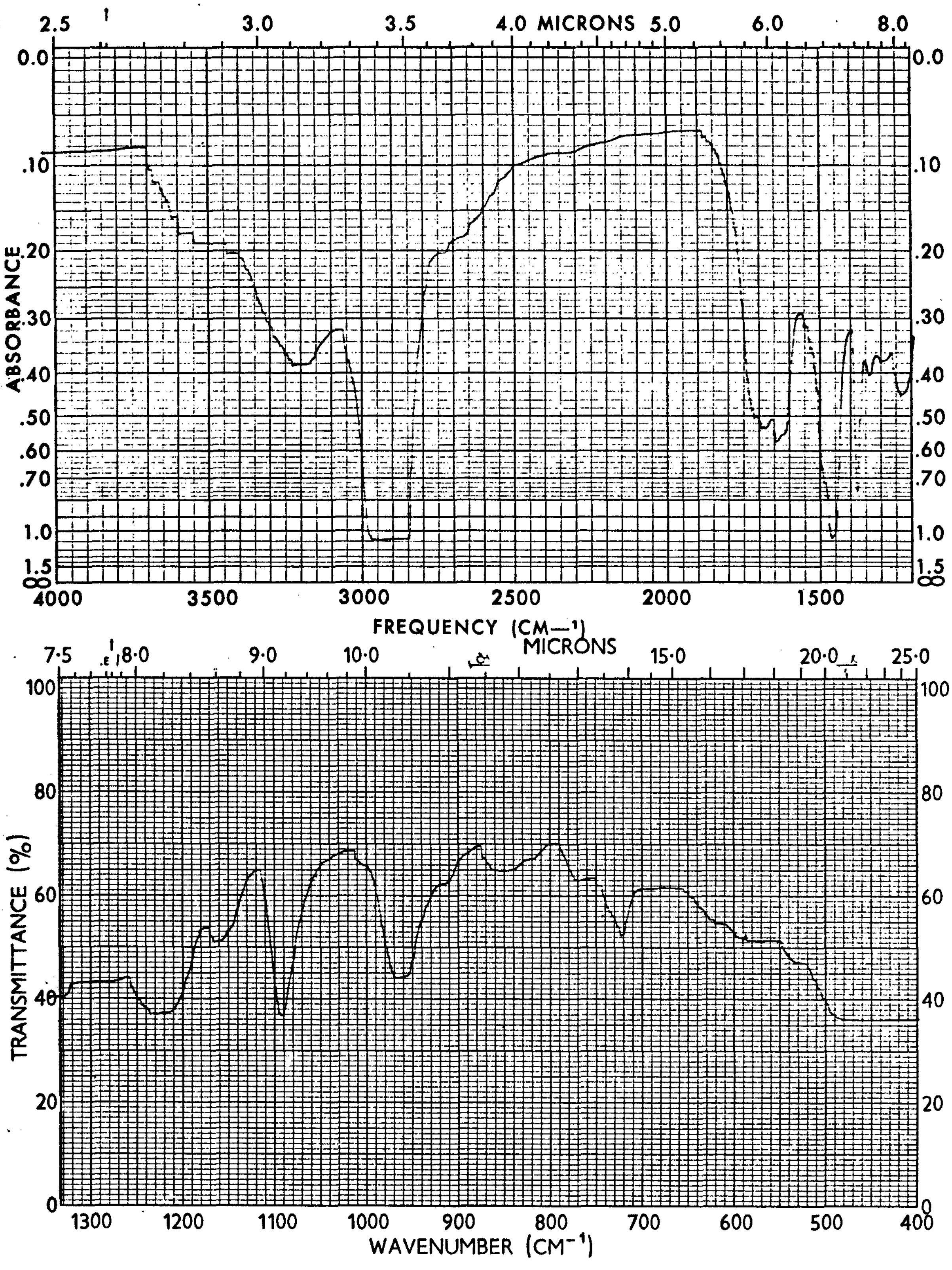
Spectrum No. 1061 Poly[(octafluoro-4,4'-biphenylylene)-
pyromellitimide] (P.I. (9))



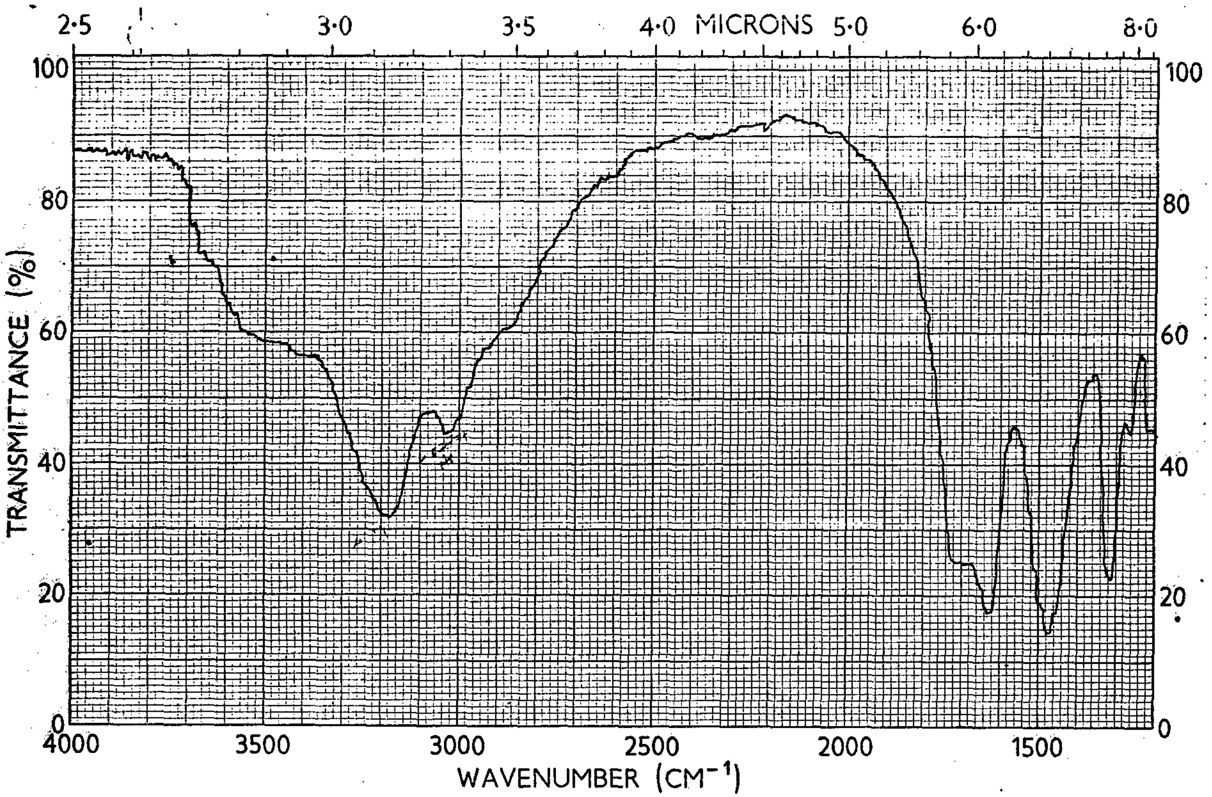
Spectrum No. 1106 Poly(isophthalhydrazide) (PH_2)

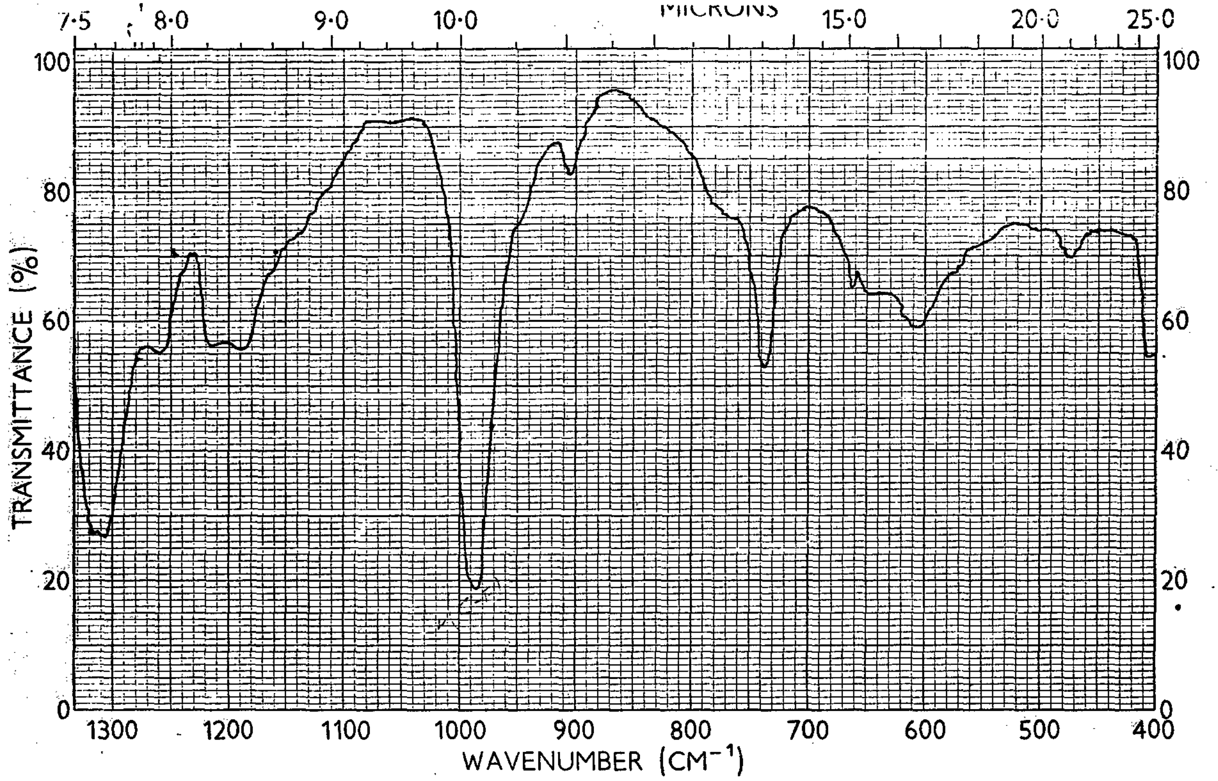


Spectrum No. 1424 Poly(tetrafluoroisophthalhydrazide)
(PH 4)

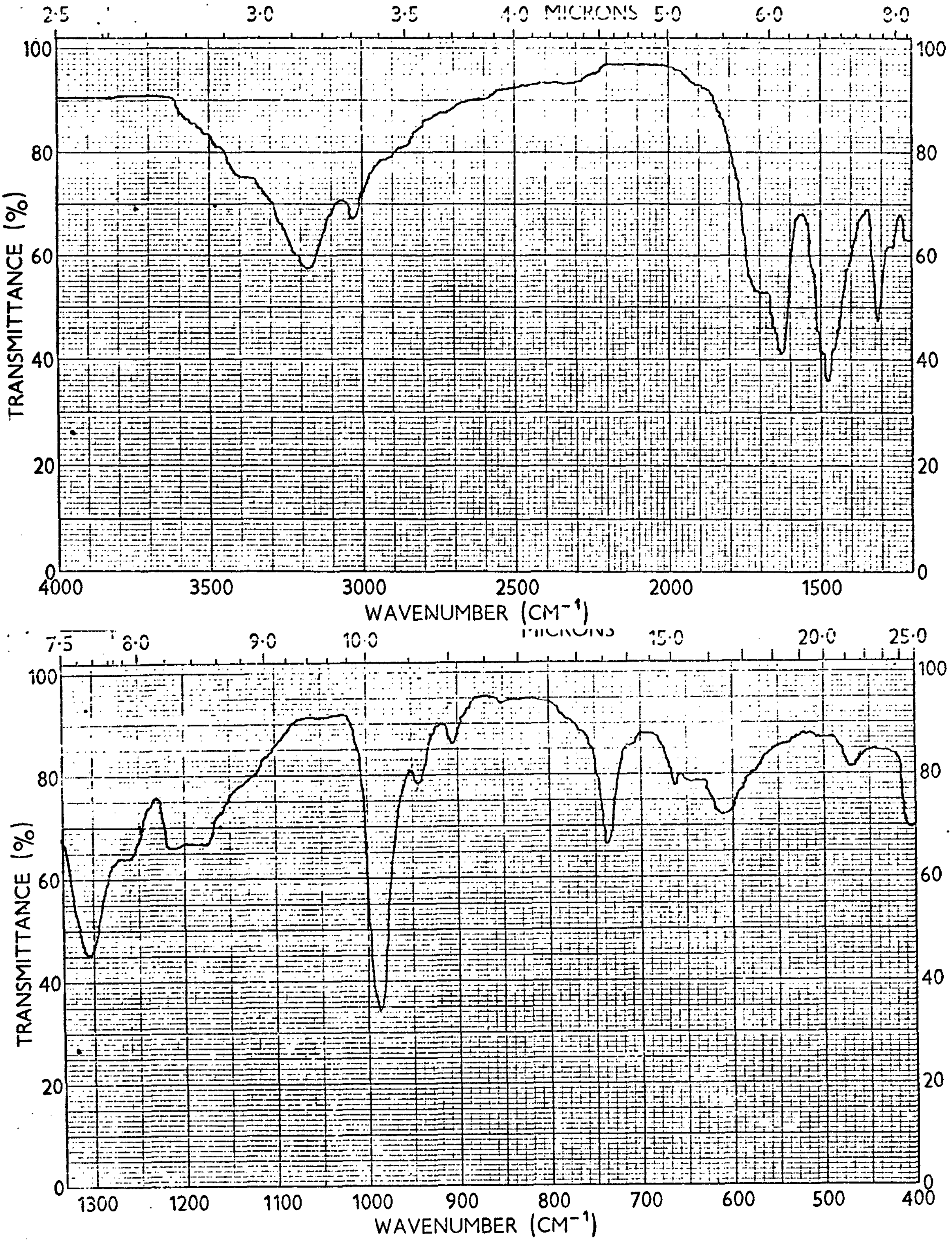


Spectrum No. 1424 Poly(tetrafluoroisophthalhydrazide)
(PH 4)

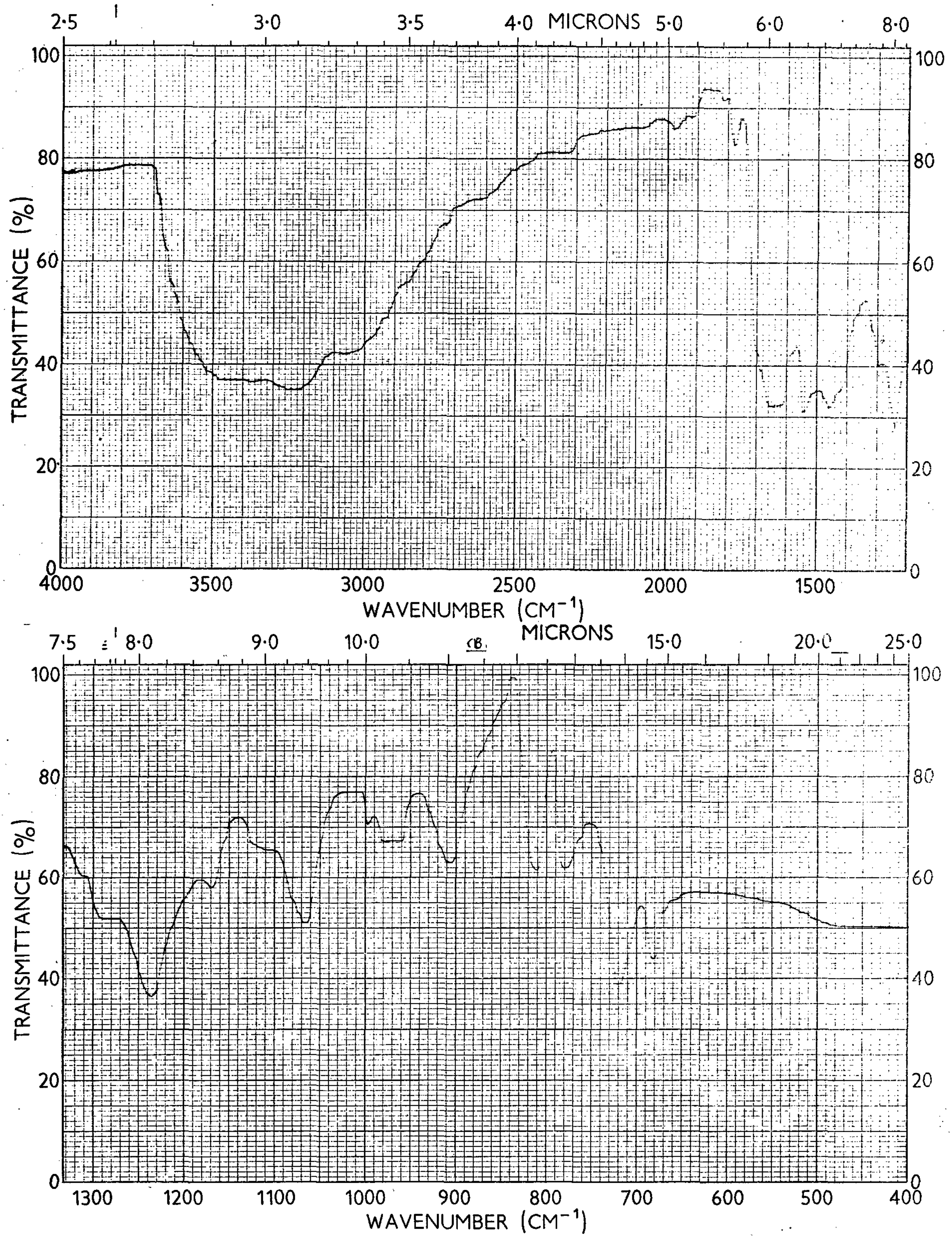




Spectrum No. 1067   Poly(tetrafluoroterephthalhydrazide
(PH 5)



Spectrum No. 1069 Poly(tetrafluoroterephthalhydrazide) (PH 5) after 5.5 hour at 256°C in N_2

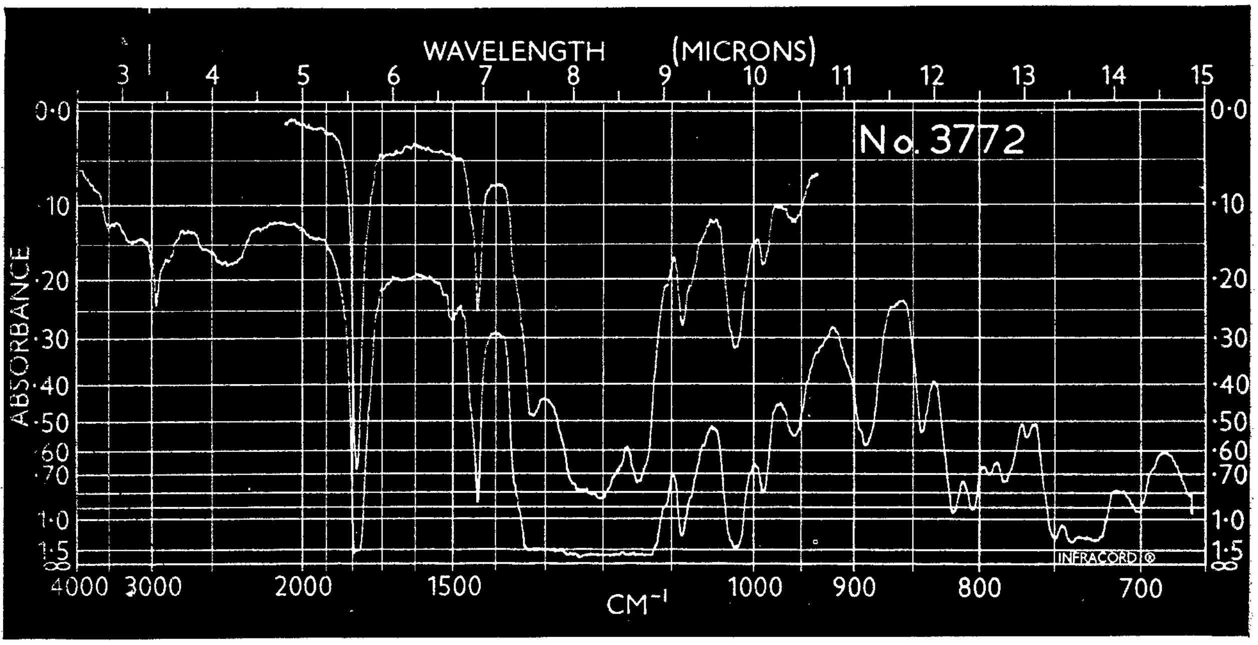


Spectrum No. 1108 Poly(isophthalhydrazide) (PH 2) after 5.5 hour at 256° in N_2

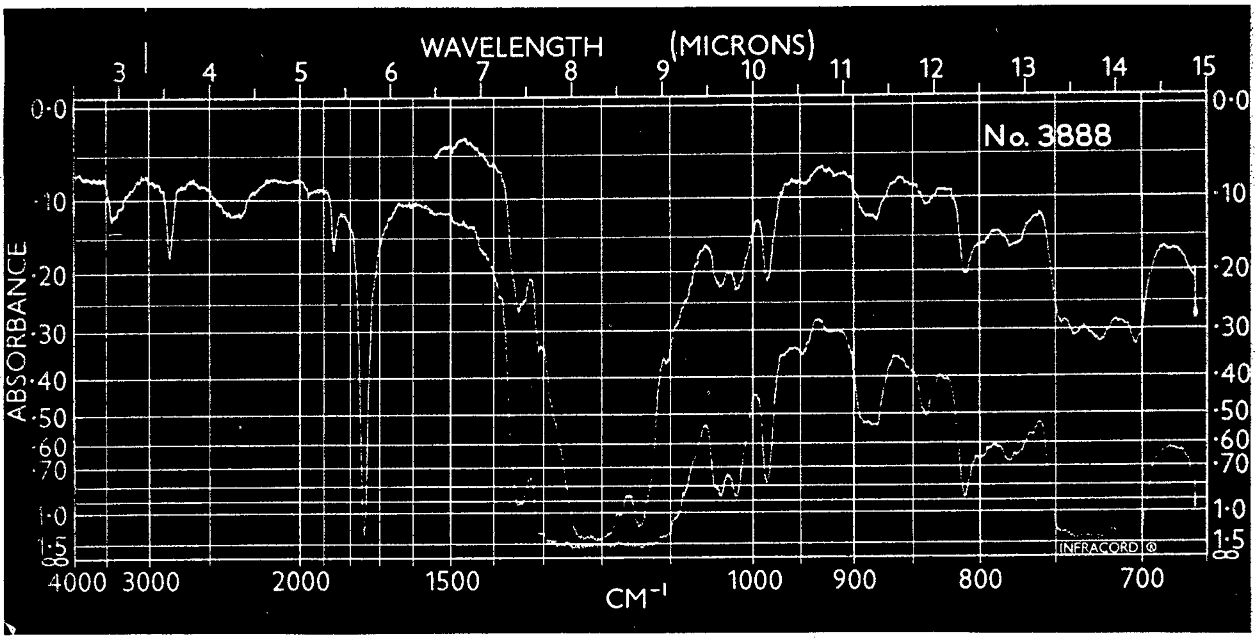
APPENDIX III

Infrared Spectra Referred to in Part III

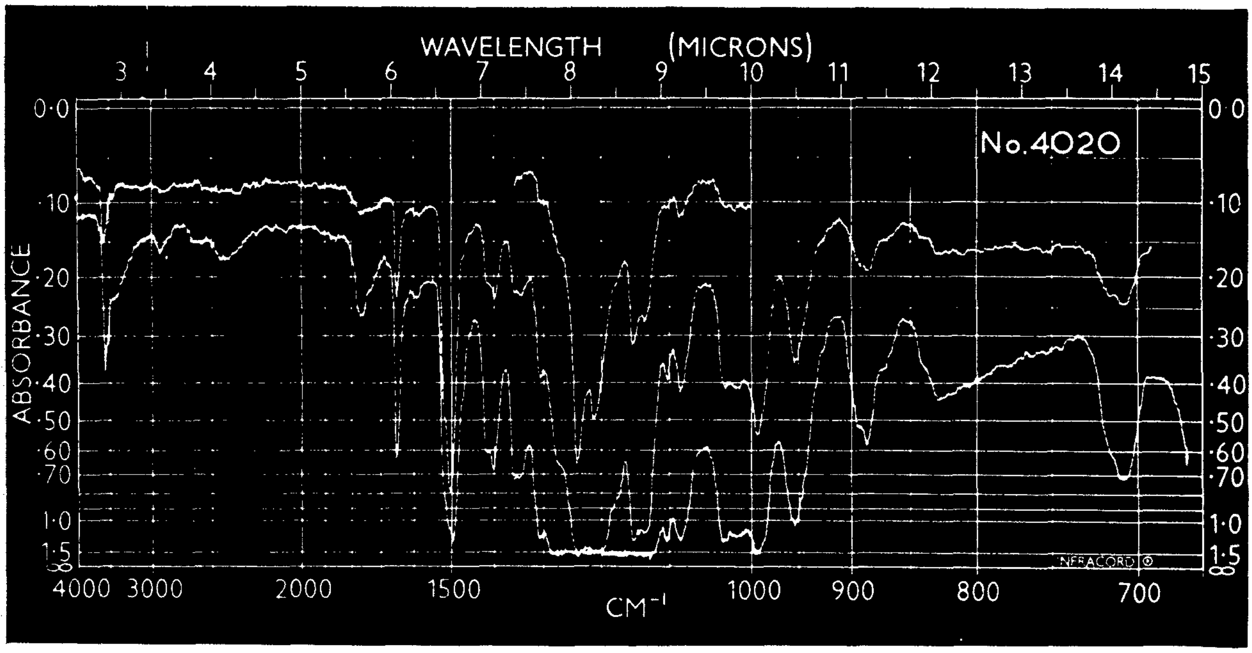
No.	
3772	Methyl perfluoro-octanoate (thin film)
3888	Perfluoro-octanal (thin film)
4020	Perfluoroheptyl pentafluorophenyl carbinol (in CCl_4)
3983	Perfluoroheptyl 2,3,4,6-tetrafluorophenyl carbinol (thin film)
3990a	2,4,5,6-Tetrafluorophenylene-1,3-bis(perfluoroheptyl carbinol) (thin film)
4158	1,3-Bis(perfluoro-octanoyl)tetrafluorobenzene (thin film)
3727	Impure 3,3'-bis(1-hydroxy-2,2,3,3,4,4,4-heptafluorobutyl)-octafluorobiphenyl (in CCl_4)
4143	3,3'-Bis(heptafluoro-n-butyryl)octafluorobiphenyl (thin film)
4061	Octafluoroadipoyl chloride (thin film)
4109	Neutral product from reaction between octafluoroadipoyl chloride and pentafluorophenylmagnesium bromide (thin film)
4110	Acid product from reaction between octafluoroadipoyl chloride and pentafluorophenylmagnesium bromide (thin film)
4149B	Suspected perfluoro(1,4-bis(benzoyl)butane) (thin film)
4005	Reaction product from heptafluoro-1-iodopropane and cuprous pentafluorothiophenate (in CCl_4)



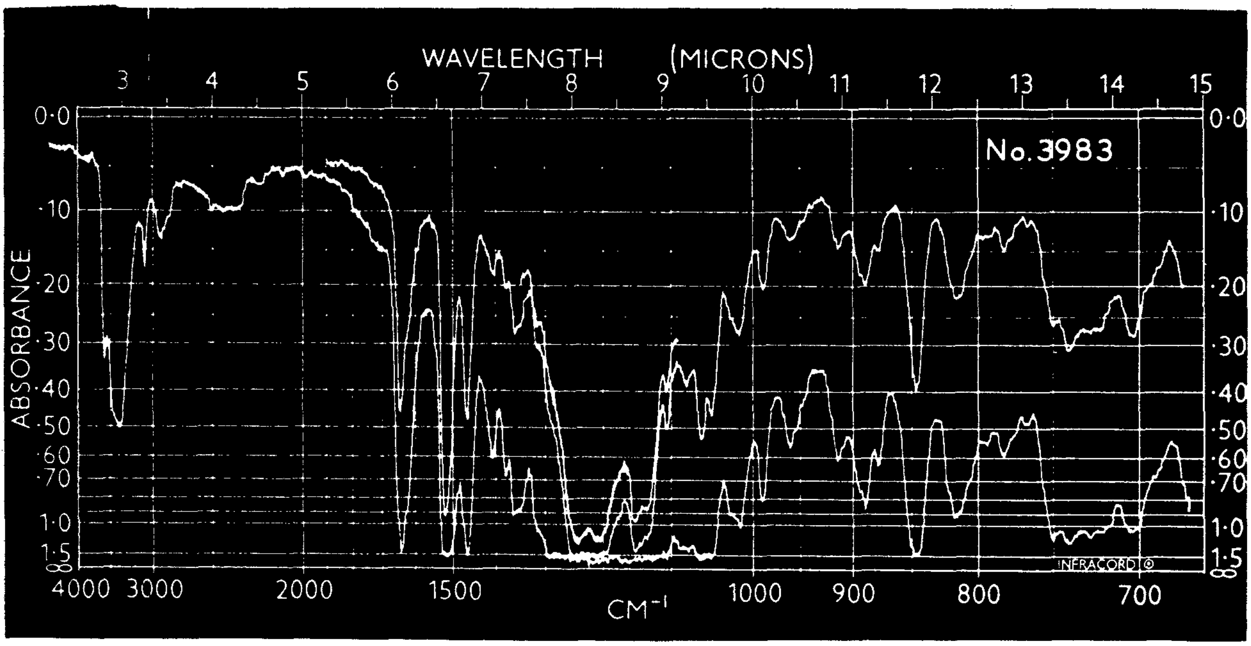
Spectrum No. 3772 Methyl perfluoro-octanoate (thin film)



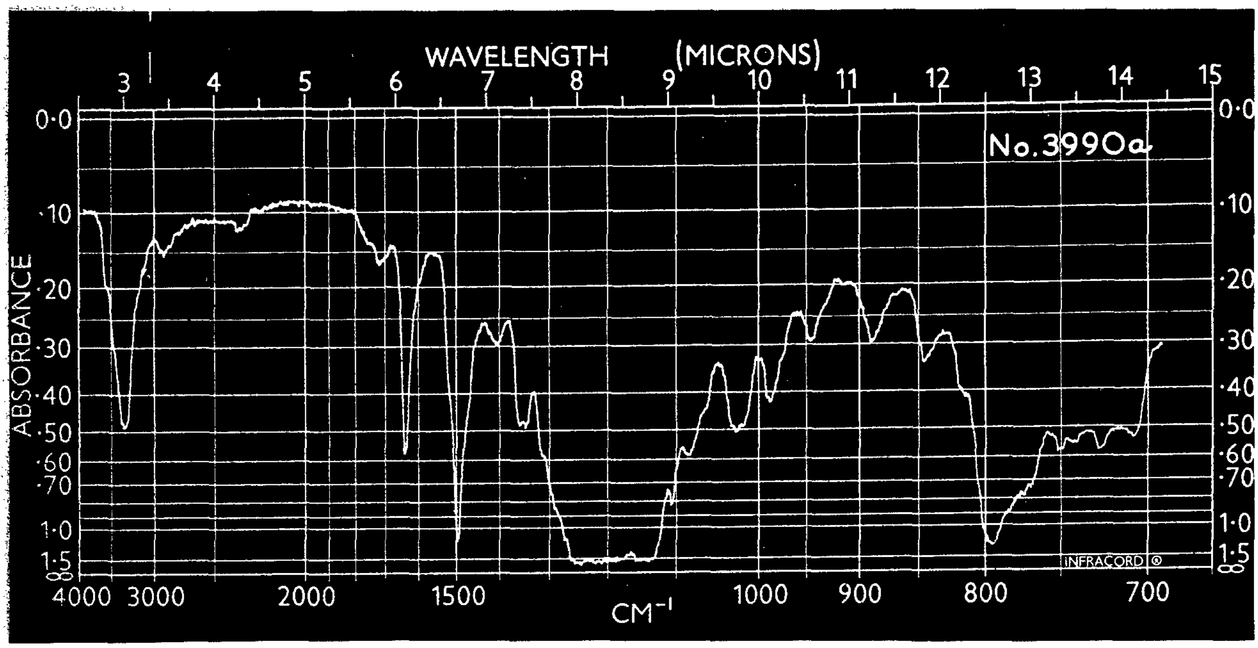
Spectrum No. 3888 Perfluoro-octanal (thin film)



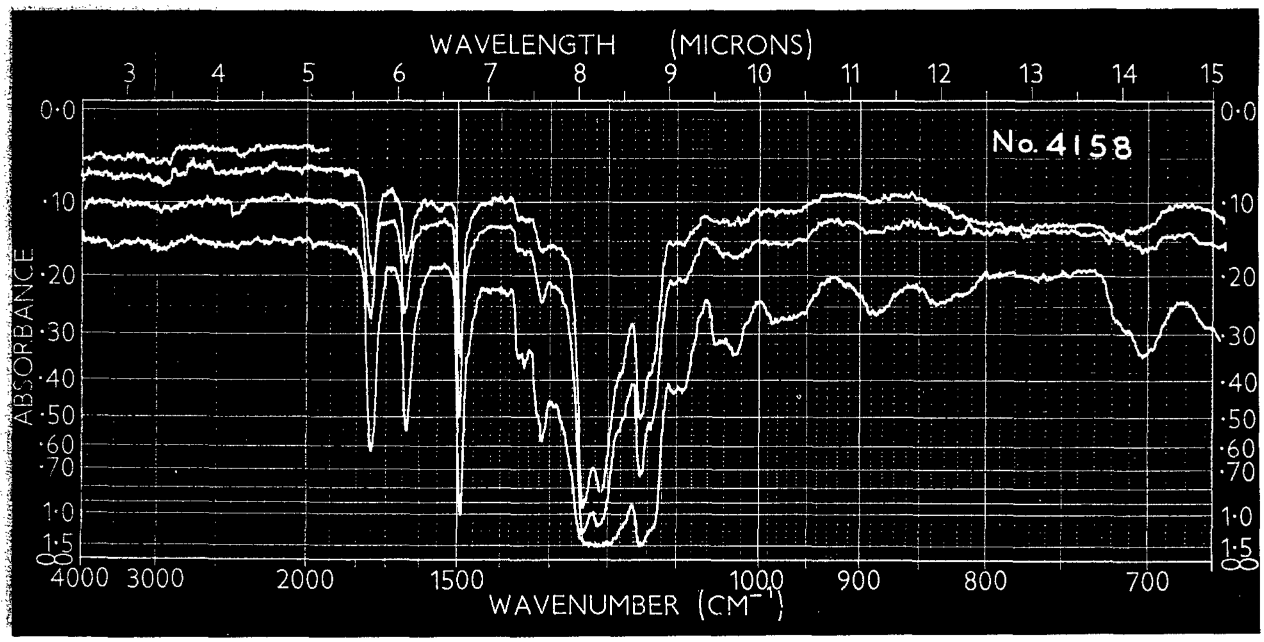
Spectrum No. 4020 Perfluoroheptyl pentafluorophenyl carbinol (in CCl_4)



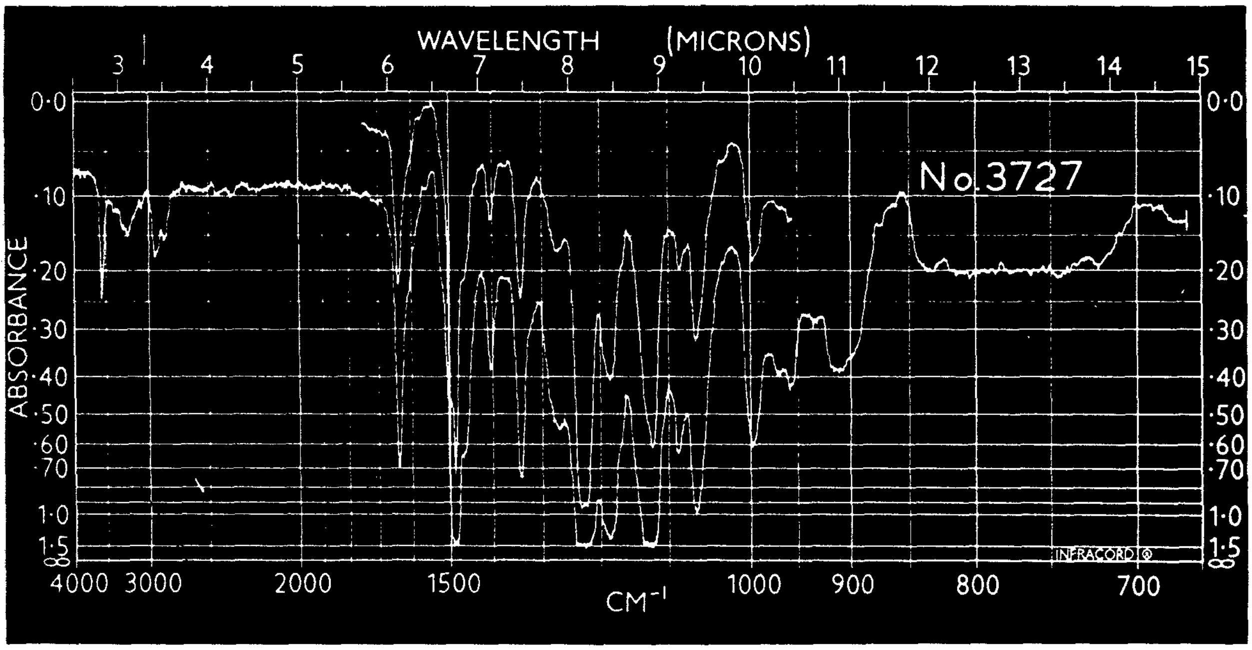
Spectrum No. 3983 Perfluoroheptyl 2,3,4,6-tetrafluorophenyl carbinol (thin film)



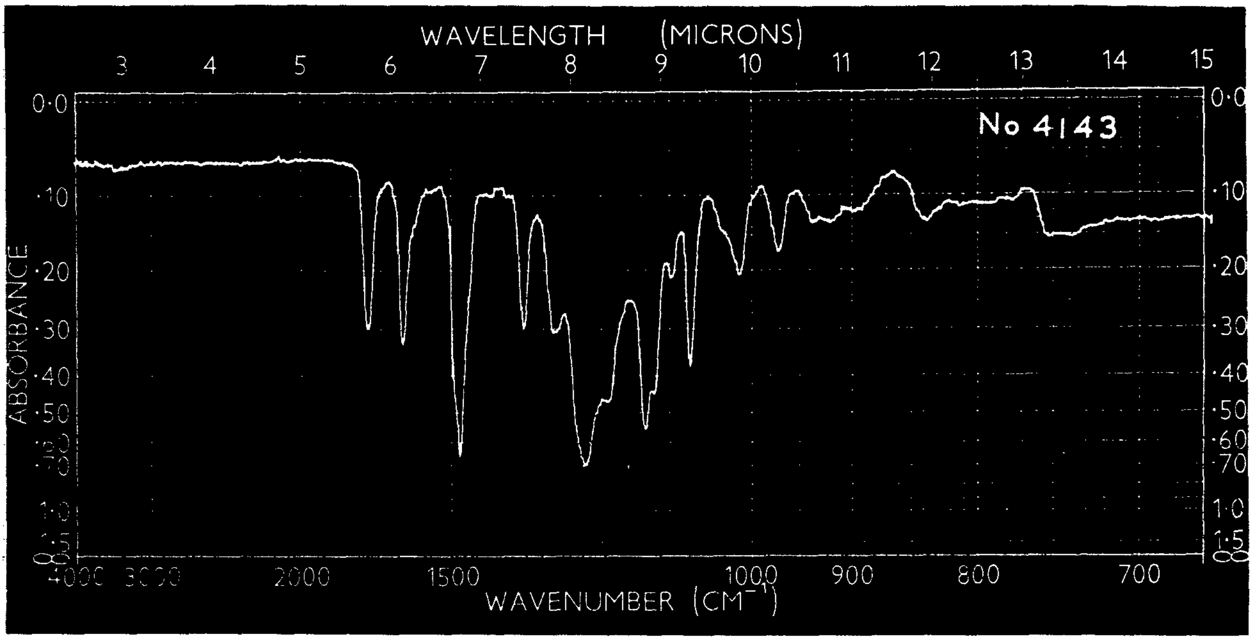
Spectrum No. 3990a 2,4,5,6-Tetrafluorophenylene-1,3-bis(perfluoroheptyl carbinol) (thin film)



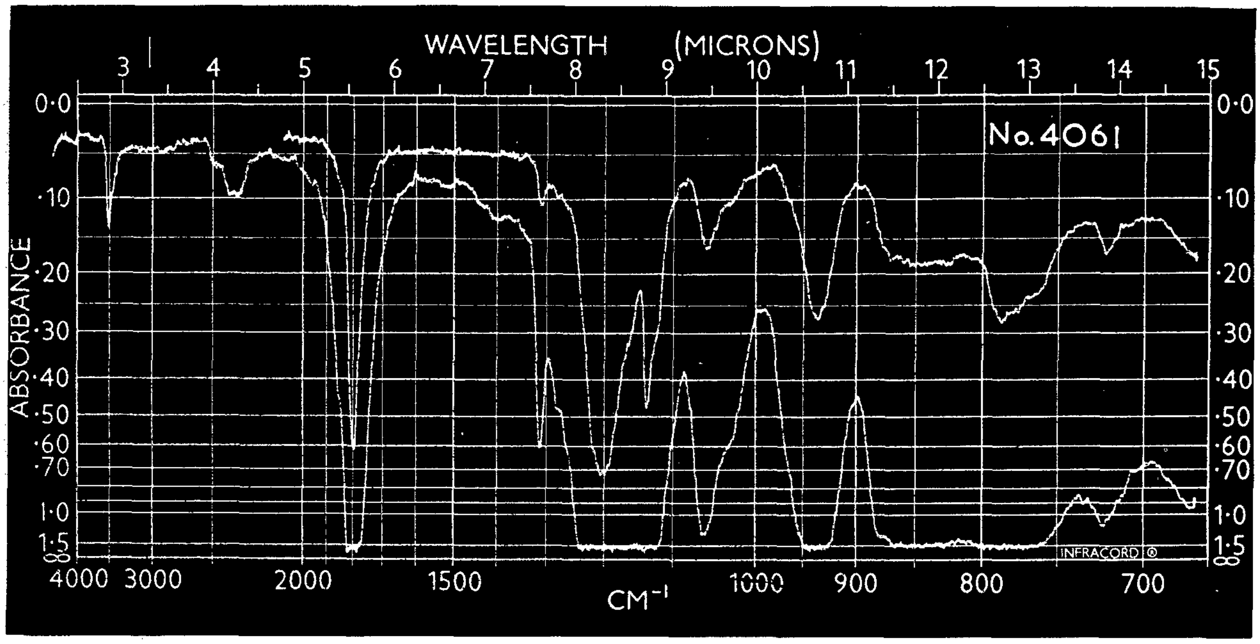
Spectrum No. 4158 1,3-Bis(perfluoro-octanoyl)tetrafluorobenzene (thin film)



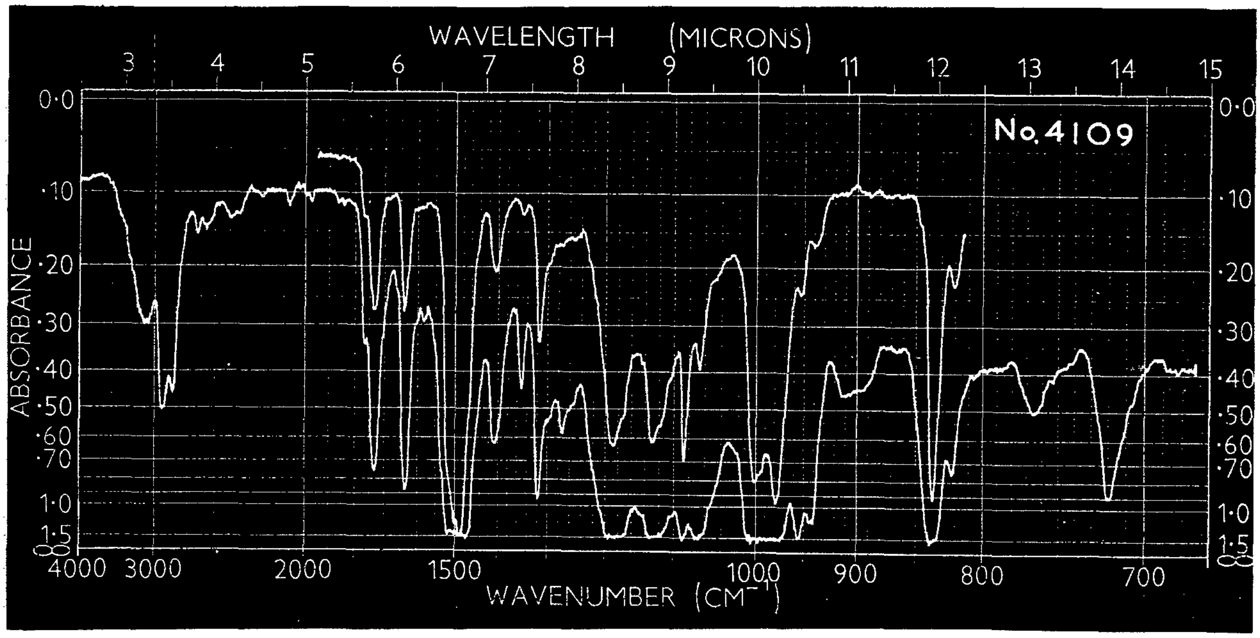
Spectrum No. 3727 Impure 3,3'-bis(1-hydroxy-2,2,3,3,4,4,4-heptafluorobutyl)octafluorobiphenyl (in CCl_4)



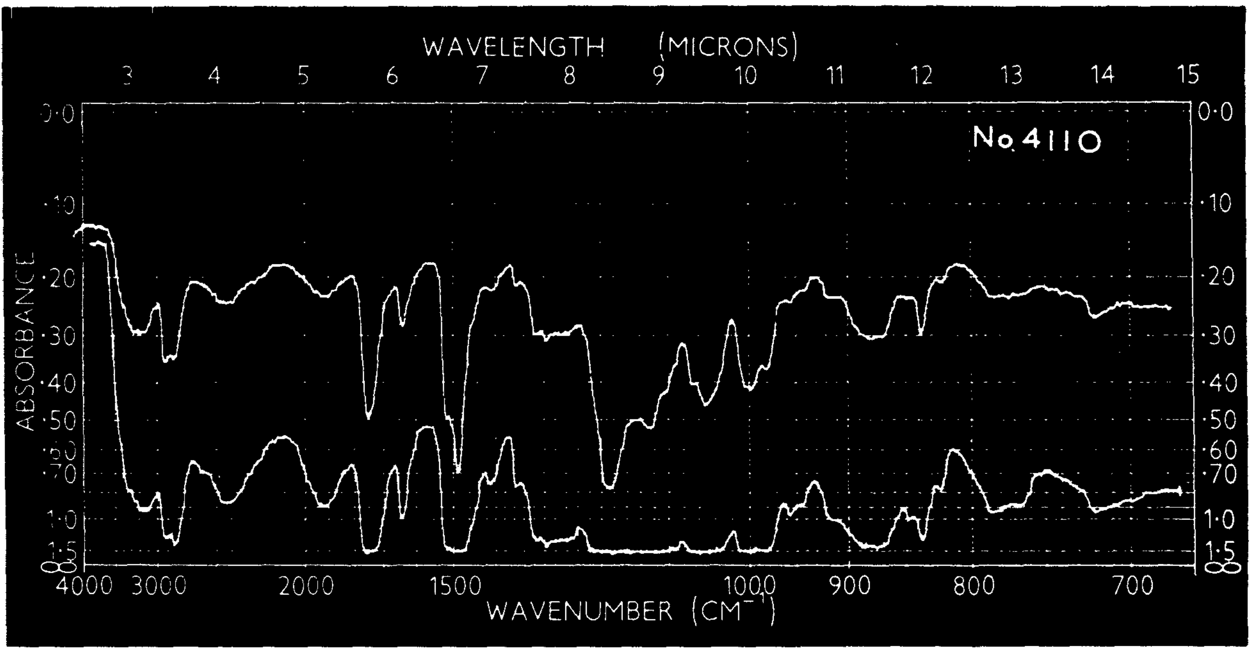
Spectrum No. 4143 3,3'-Bis(heptafluoro-n-butyryl)octafluorobiphenyl (thin film)



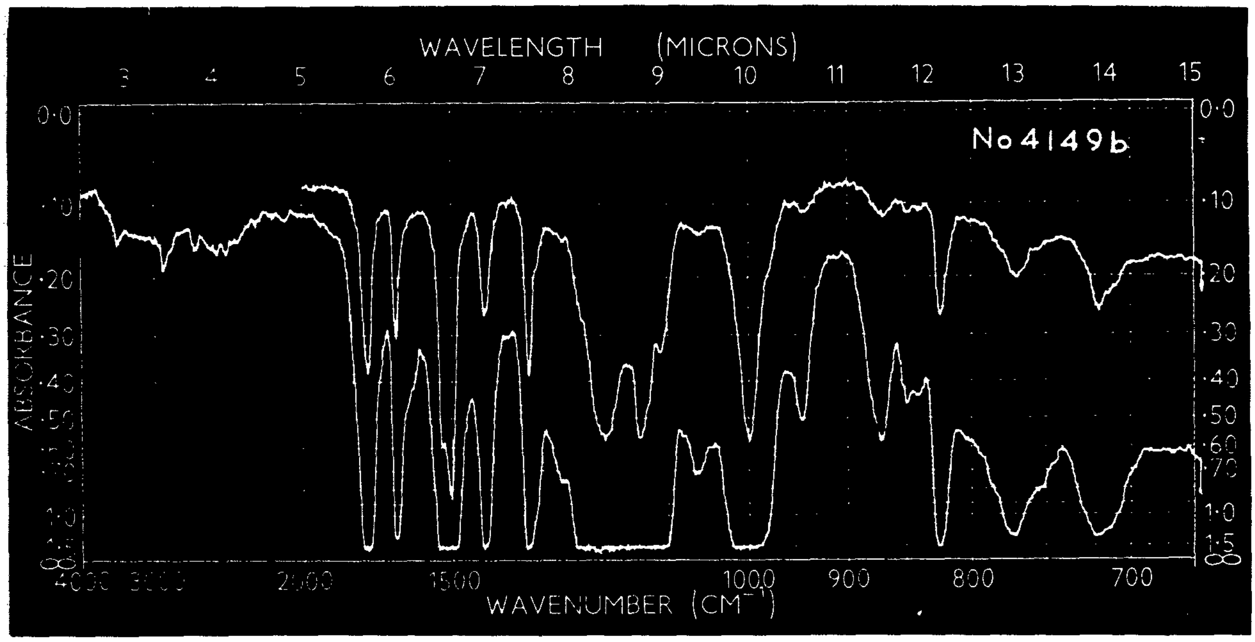
Spectrum No. 4061 Octafluoroadipoyl chloride (thin film)



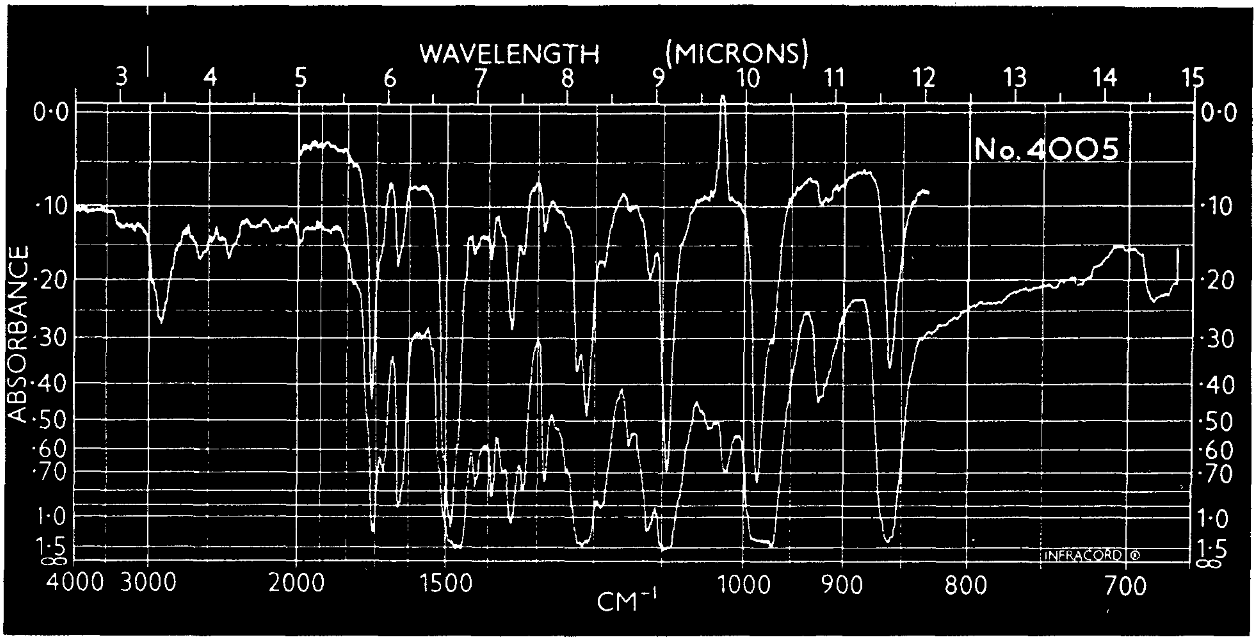
Spectrum No. 4109 Neutral product from reaction between octafluoroadipoyl chloride and pentafluorophenylmagnesium bromide (thin film)



Spectrum No. 4110 Acid product from reaction between octafluoroadipoyl chloride and pentafluorophenylmagnesium bromide (thin film)



Spectrum No. 4149B Suspected perfluoro(1,4-bis(benzoyl)-butane) (thin film)

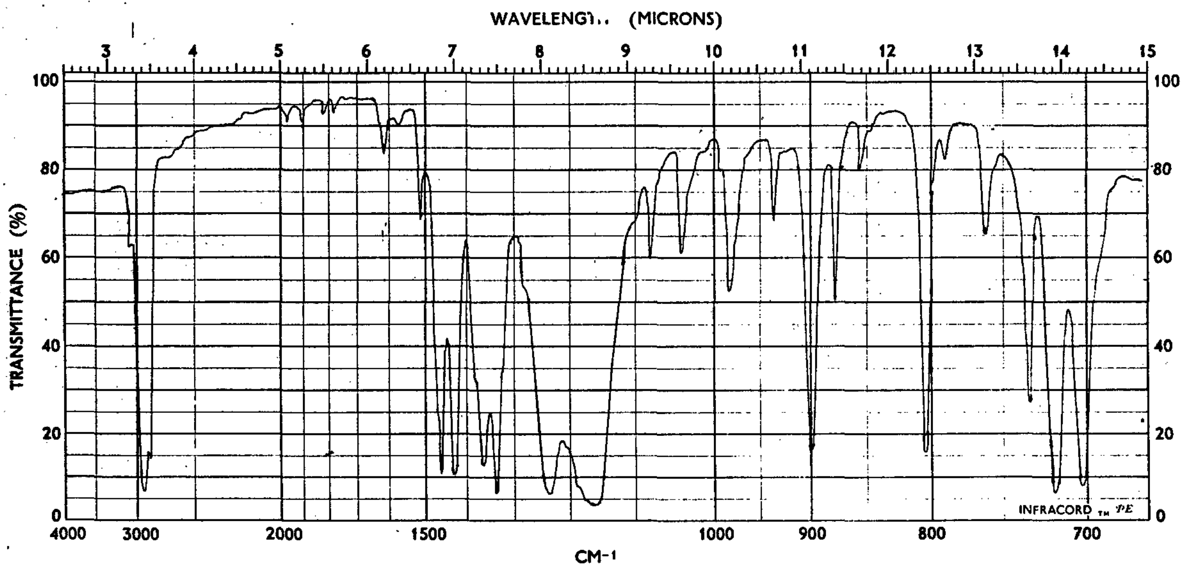


Spectrum No. 4005 Reaction product from heptafluoro-1-iodopropane and cuprous pentafluorothiophenate (in CCl_4)

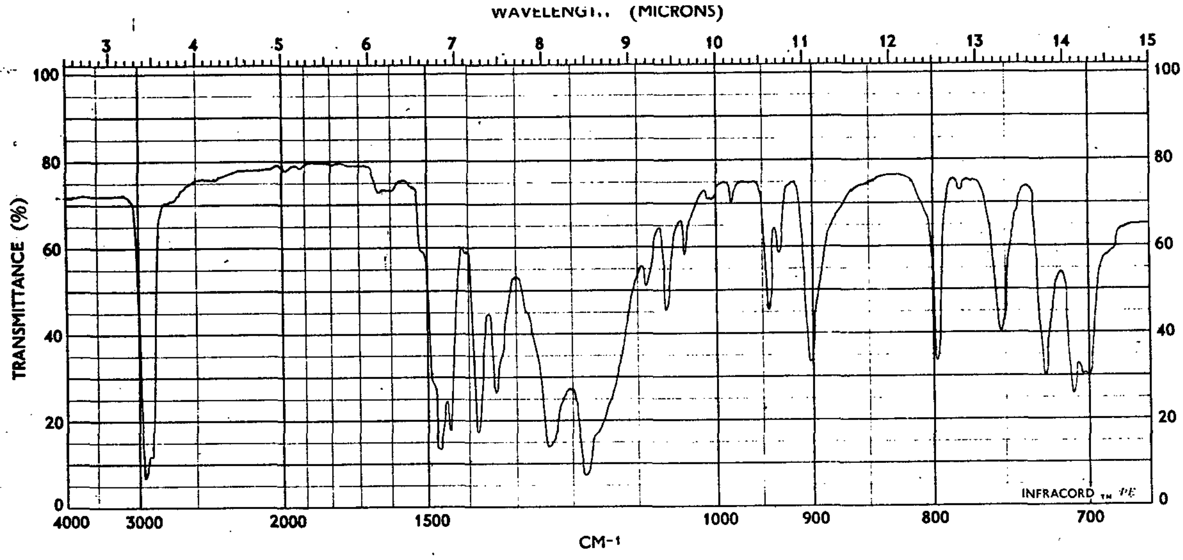
APPENDIX IV

Infra-red spectra of new compounds referred to in Part IV.

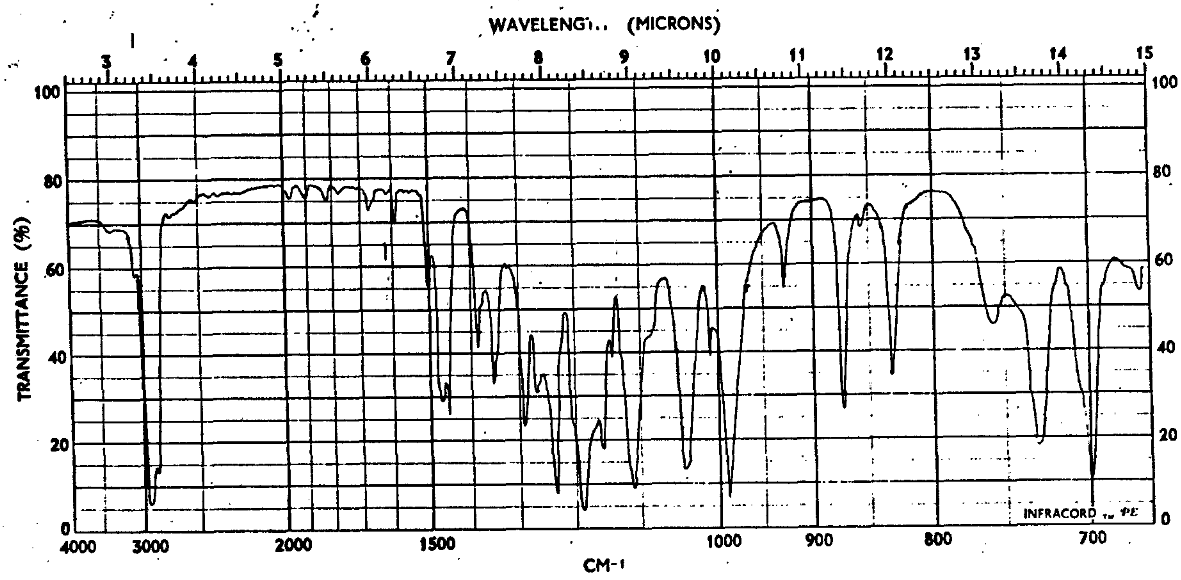
1. 3',6'-Difluoro-4',5'-bis(trifluoromethyl)-o-terphenyl (V)
2. 3,4-Bis(trifluoromethyl)-2,5,6-trifluorobiphenyl
3. 1,2-Bis(phenyl)octafluorocyclohexene (II)
4. 3',6'-Bis(trifluoromethyl)decafluoro-p-terphenyl (VI)



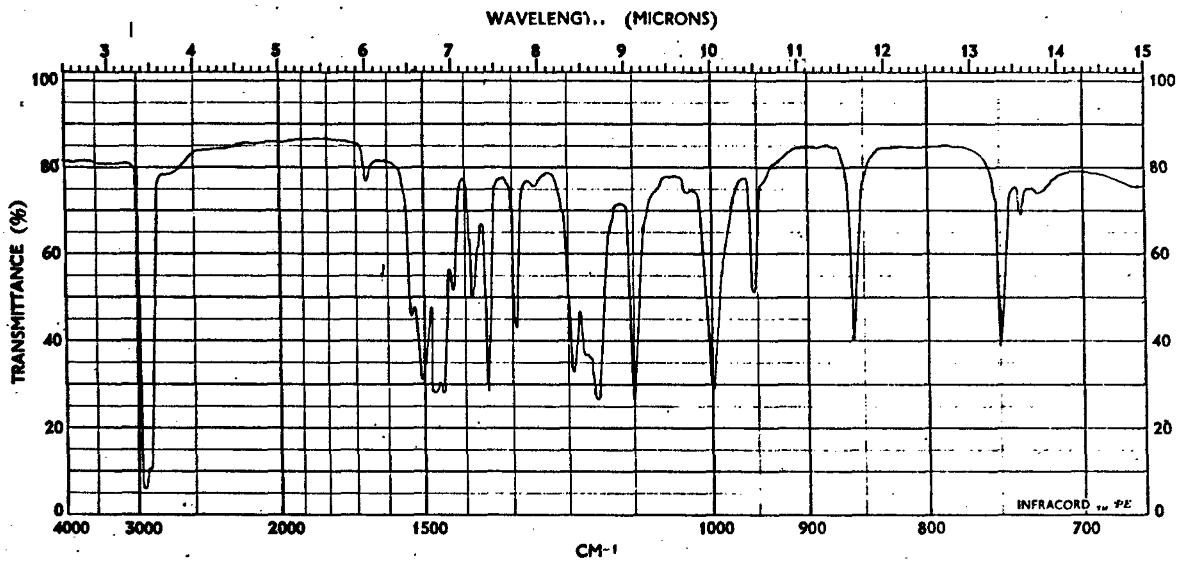
Spectrum No. 1. 3',6'-Difluoro-4',5'-bis(trifluoromethyl)-o-terpehnyl (V)



Spectrum No. 2 3,4-Bis(trifluoromethyl)-2,5,6-trifluorobiphenyl



Spectrum No. 3. 1,2-Bis(phenyl)octafluorocyclohexene (II)



Spectrum No. 4. 3',6'-Bis(trifluoromethyl)decafluoro-p-terphenyl (VI)

APPENDIX V

Spectra referred to in Part V

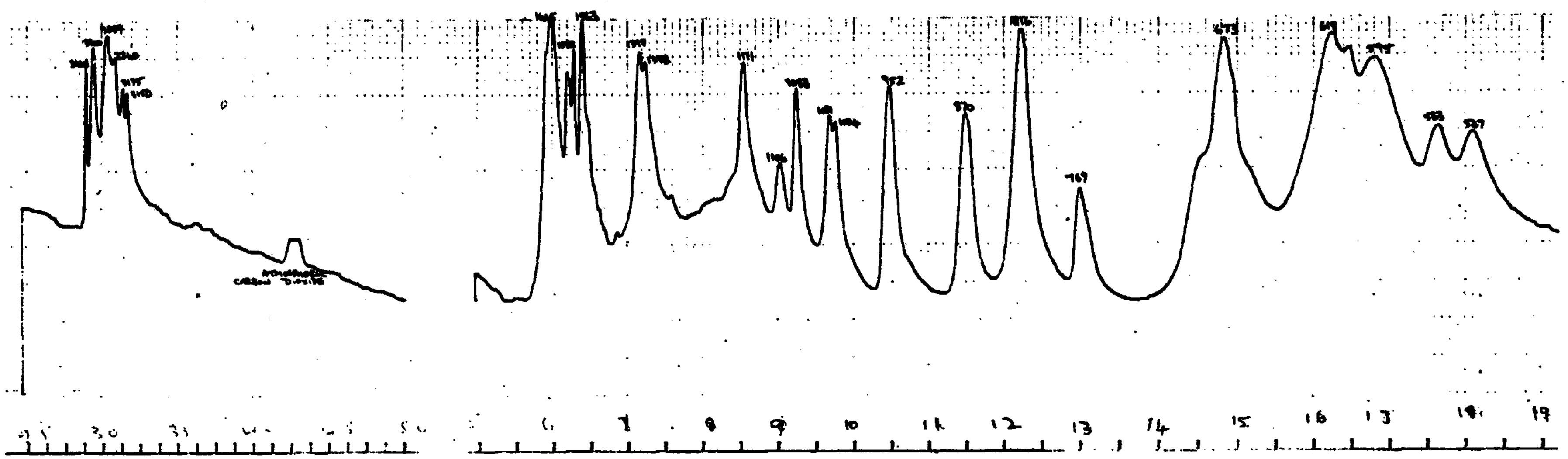
Amide of Pentachloropenta-2,5-dienoic Acid.

Tetrafluoro-isonicotinamide.

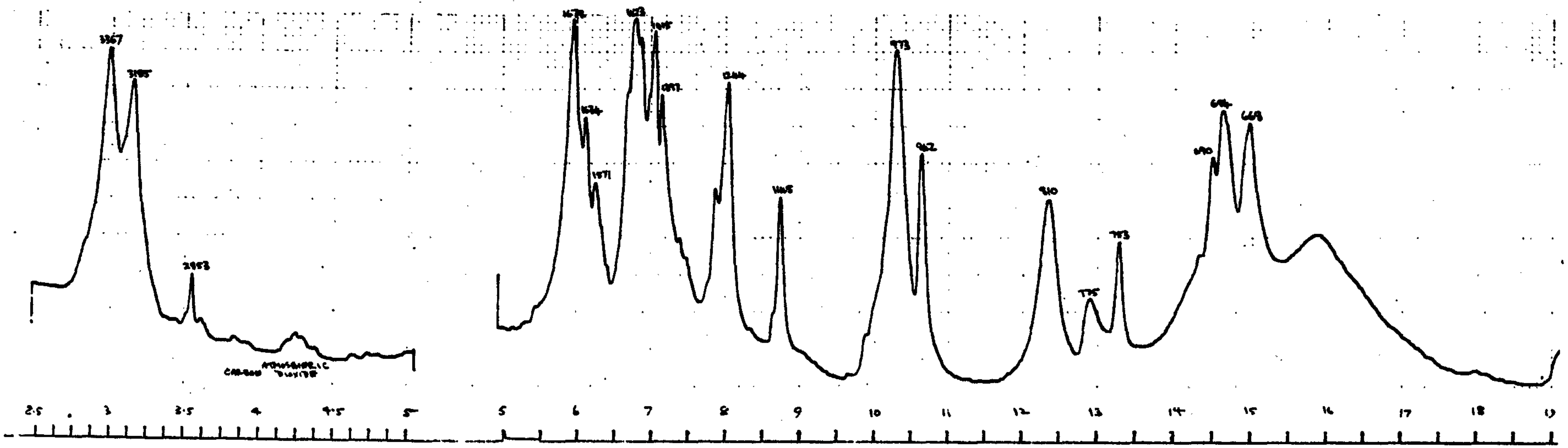
Phenylhydrazide of Tetrafluoroisonicotinic Acid.

Tetrafluoroisonicotinoyl Chloride.

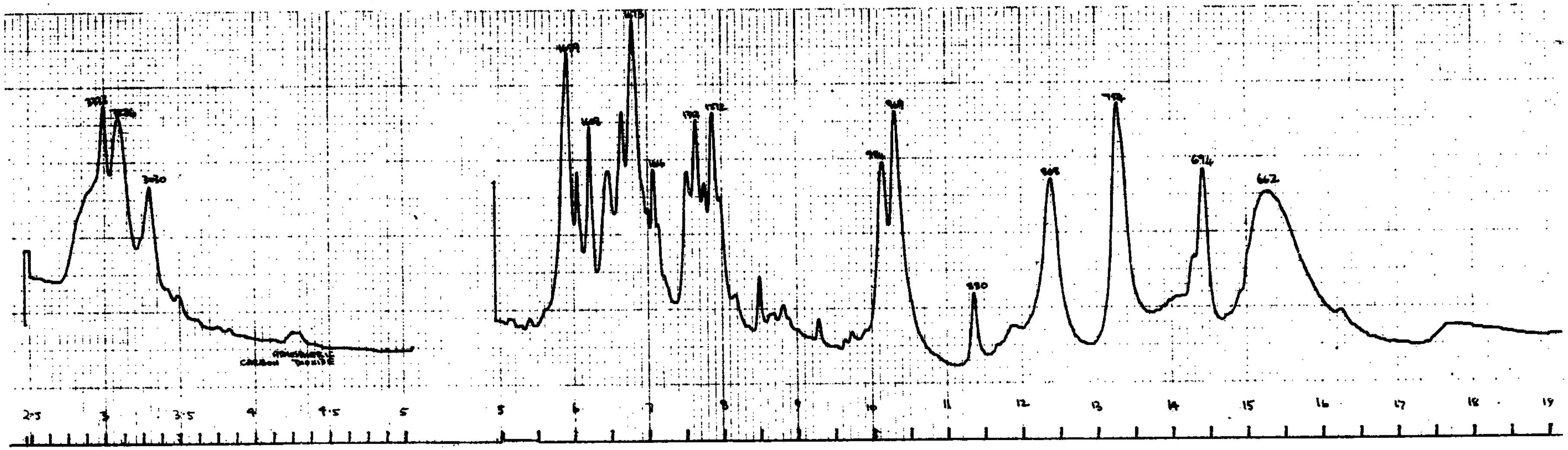
Undecafluoro-(phenyl-1-isoquinolyl)ether.



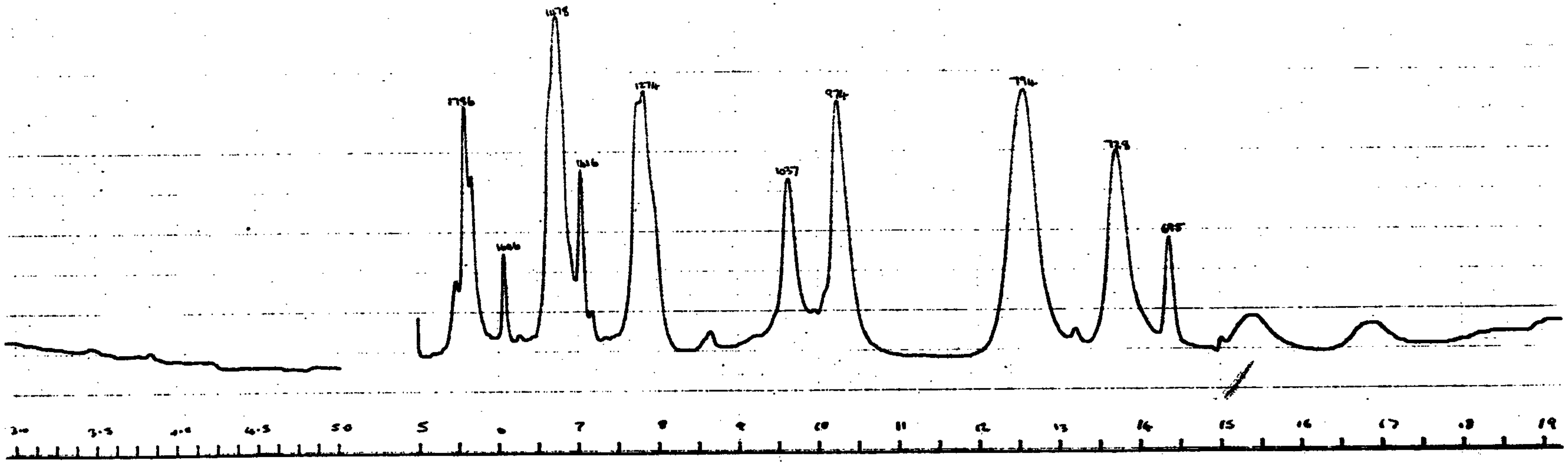
Amide of Pentachloropenta-2,5-dienoic Acid



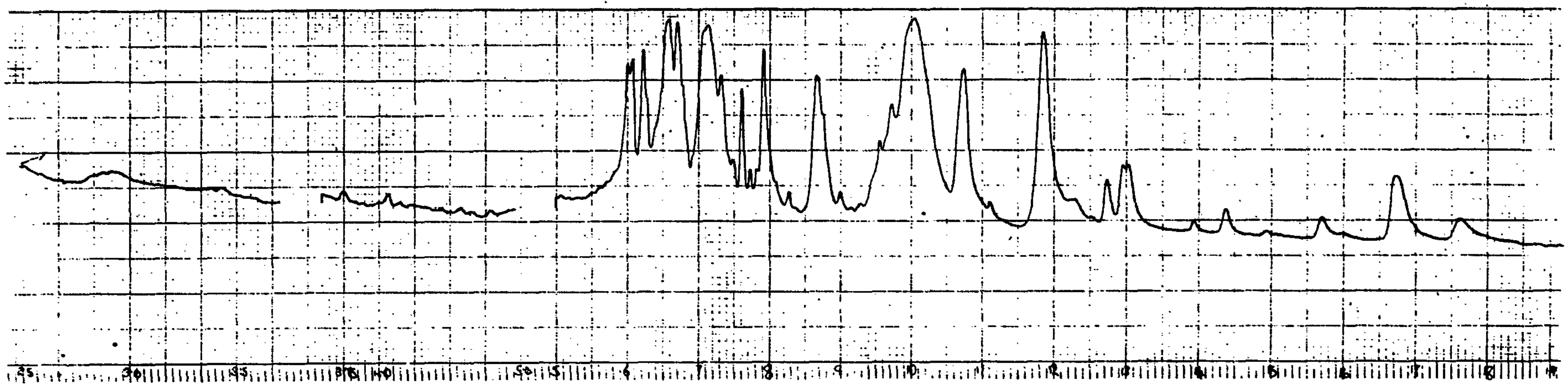
Tetrafluoro-isonicotinamide



Phenylhydrazide of Tetrafluoroisonicotinic Acid



Tetrafluoroisonicotinoyl Chloride



Undecafluoro-(phenyl-1-isoquinolyl)ether

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13. ABSTRACT

Preparations and synthetic studies have been carried out on difluoropyromellitic acid, tetrafluoroisophthalic acid, tetrafluorophenylene diamines, 3,3',4,4'-tetra-substituted-hexafluorobiphenyls, tetrafluororesorcinol, sulphides, dithiols, and 2,3,5,6-tetrafluorobenzoic acid. The above, with other perfluorinated aromatic compounds were employed in the synthesis of perfluorinated aromatic model compounds and polymers. The hydrogenic analogues were also prepared for comparison of thermal and thermo-oxidative stabilities. Model compound structures include bibenzoxazoles, oxadiazoles, sulphonic esters, dithiocarbonates, amides, and imides, for which thermal decomposition temperatures are reported. Polymer structures include carbonates, hydrazides, and imides. Synthetic routes to perfluoro aralkyl compounds are being investigated. Starting materials are tetrafluorobenzene, octafluorobiphenyl, and perfluoroaliphatic aldehydes. Synthetic routes to perfluoro cyclohexyls via reactions of phenyl and pentafluorophenyl lithium with decafluorocyclohexene and o- and p- perfluoroxylene have been studied. Studies have been made of routes to pentachloropyridine, for the exchange reaction with potassium fluoride to yield pentafluoropyridine. The reaction of pentafluoropyridine or heptafluoroisoquinoline with potassium pentafluorophenate or the potassium salt of 4-hydroxytetrafluoropyridine appears to have yielded the appropriate ethers.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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