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SYNTHESIS OF PERFLUOROALIPHATIC ETHER MONOMERS

PCR, Inc.

Gainesville, Florida 32602

July 1977

TECHNICAL REPORT AFML-TR-77-99

Final Report for Period February 1976 – January 1977

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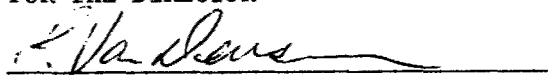WRIGHT-PATTERSON AIR FORCE BASE, OHIO   45433

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This technical report has been reviewed and is approved for publication.

A. J. SICREE
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FOR THE DIRECTOR

R. L. VAN DEUSEN, Chief
Polymer Branch
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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

Perfluoroalkyl ether α,ω-diiodides were hydrolyzed in fuming sulfuric acid to the corresponding symmetrical diacyl fluorides. Under certain conditions the intermediate hydrolysis product ω-iodoacyl fluoride was obtained as the major product. Addition of tetrafluoroethylene oxide to the diacyl fluorides gave a series of oligomer diacyl fluorides.

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PREFACE

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LIST OF ABBREVIATIONS

HFPO   Hexafluoropropylene oxide

TFEO   Tetrafluoroethylene oxide

HFGF   Hexafluoroglutaryl fluoride

OXF   Oxalyl fluoride

TFE   Tetrafluoroethylene

Throughout this report perfluoroalkylene oxide α,ω-diacyl fluorides of the general structure

$$
\overset{O}{\overset{\|}{F}}\overset{R_f}{\overset{|}{C}}CF(OCF_2\overset{R_f}{\overset{|}{C}}F)_m O(CF_2)_{x+2}O(\overset{R_f}{\overset{|}{C}}FCF_2O)_n \overset{R_f O}{\overset{|\ \|}{C}}FCF
$$
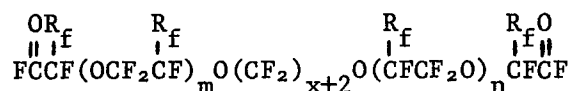
are referred to as EDAF's (Ether Diacyl Fluoride).

The parent diacyl fluoride is designated by a letter in parenthesis: (G) denotes HFGF and (O) denotes OXF.

The number of epoxide units added to the parent acyl fluoride is designated with a number followed by a letter denoting the specific epoxide: p denotes HFPO and e denotes TFEO.

Thus 5p-EDAF(O) has the structure with $m + n = 3$, $R_f = CF_3$ and $x = 0$. Similarly 2e-EDAF(G) has the structure with $m + n = 0$, $R_f = F$ and $x = 3$.

SECTION I

INTRODUCTION

Technological advances in space research have created a critical need for new and improved materials for use in aircraft and missiles. These materials must function under extreme environmental conditions and serve a variety of purposes. In preparing materials to meet these requirements, particularly polymeric materials, it is necessary to obtain monomers which, on the basis of both empirical and theoretical evidence, can be polymerized to give new materials exhibiting the desired properties.

In general, replacement of hydrogen with fluorine on a polymer chain results in dramatic changes in properties of the polymer. The fluorocarbon analogs of hydrocarbon polymers exhibit greatly improved thermal, oxidative and chemical stability. However, associated with these beneficial changes in properties is an increase in polymer backbone rigidity with consequent increase in the polymer glass transition temperature.[1] In order to increase the flexibility of the polymer chain while retaining the good high temperature resistance and chemical properties of fluorocarbon polymers, current research is being directed toward the synthesis of fluorocarbon polymers containing heteroatoms in the polymer chain.

The increase in chain flexibility by the inclusion of heteroatoms in the polymer chain is evidenced by the low glass transition temperature of poly(thiocarbonyl fluoride), $Tg = -118°C,$[2] poly(perfluorotetramethylene) oxide, flexible at $-80°C,$[3] and nitroso rubber, $Tg = -50°C.$[4] In addition, fluids prepared from polymers derived from hexafluoropropylene oxide exhibit wide fluid ranges and are thermally and oxidatively stable.[5]

1

The object of this contract is to synthesize perfluoroaliphatic ether monomers which may be used by the Air Force Materials Laboratory in the preparation of thermally and oxidatively stable materials ranging in properties from fluids to elastomers.

The perfluoroaliphatic ether monofunctional and difunctional monomers prepared or investigated under this contract are based on oligomers derived from hexafluoropropylene oxide (HFPO) or tetrafluoroethylene oxide (TFEO).[6-11] Although the major emphasis of this program is on the synthesis of difunctional monomers, when new synthetic approaches are involved it is necessary to prepare and study monofunctional model compounds.

During this report period the major research effort was directed towards the synthesis of symmetrical perfluoroalkylether difunctional monomers.

SECTION II

DISCUSSION

The perfluoroalkylene oxide difunctional oligomers prepared under the current and previous contracts are adducts of hexafluoropropylene oxide (HFPO) to hexafluoroglutaryl fluoride (HFGF) and oxalyl fluoride (OXF) or adducts of tetrafluoroethylene oxide (TFEO) to hexafluoroglutaryl fluoride.

$$FCO(CF_2)_xCOF + n\ R_f\overline{CFCF_2O} \longrightarrow FCOCFR_f[OCF_2CFR_f)]_mO(CF_2)_{x+2}O[CFR_fCF_2O]_{m'}CFR_fCOF \quad (1)$$

$$Ia : R_f = CF_3,\ x = 3$$

$$Ib : R_f = CF_3,\ x = 0$$

$$Ic : R_f = F,\ x = 3$$
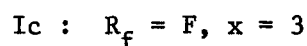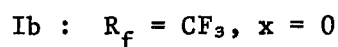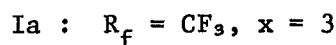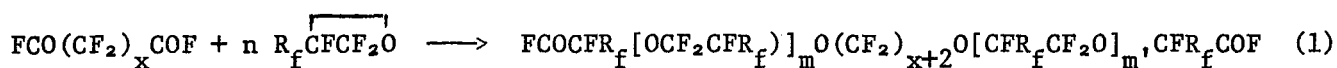
$$where\ n = m + m' + 2$$

The preparation of TFEO/OXF oligomers has been reported;[8] however, the reaction leads to a broad distribution of oligomers I (R_f = F, X = 0) and we were unable to obtain significant amounts of low molecular weight oligomers.[12,13]

Reaction 1 is not limited to HFGF and OXF, the choice of these acyl fluorides being wholly dictated by their availability and lower cost. Other perfluorodiacyl fluorides can be used and have been used, e.g., malonyl fluoride[7,14,15] succinyl fluoride,[16] and adipoyl fluoride.[14]

The product of reaction 1 is generally a mixture of oligomers which can be separated by distillation. Each oligomer of structure I, however, is also a mixture of isomers, the actual composition being determined by the nature of the acyl fluoride and epoxide and the extent of the reaction.

This is clearly seen on consideration of the 2:1 adducts (EDAF's).

The 2p-EDAF(G), Ia (m + m' = 0) is a mixture of the symmetrical isomer

$FCOCF(CF_3)O(CF_2)_5OCF(CF_3)COF$ and the unsymmetrical isomer

$FCO(CF_2)_4OCF(CF_3)CF_2OCF(CF_3)COF$ in the approximate ratio 2:1.[17] In contrast,

2e-EDAF(G), Ic (m + m'=0), has exclusively the unsymmetrical structure

$FCO(CF_2)_4OCF_2CF_2OCF_2COF$.[12]

The 2p-EDAF(O), Ib (m + m' =0), on the other hand, has almost exclusively

the symmetrical structure $FCOCF(CF_3)OCF_2CF_2OCF(CF_3)COF$.[18] Higher homologs

are more complicated mixtures of isomers, the relative composition of which

depends on the extent of the oligomerization reaction.[12,19,20]

Since these oligomers or their derivatives are intended for use as monomers

in polymerization reactions it is evident that it would be desirable to have

pure symmetrical monomers as contrasted to the hitherto available isomeric

mixtures.

A. <u>Symmetrical TFEO or HFPO Difunctional Oligomers</u>

The synthetic route to symmetrical difunctional oligomers is shown below.

$$FCO(CF_2)_xCOF \ + \ KF \ + \ ICl \qquad (x = 0 \text{ or } 3)$$

$$CF_2 = CF_2 \qquad\qquad (2)$$

$$CF_2ICF_2O(CF_2)_{x+1}COF \quad (I)$$

$$R_fCFCF_2O \qquad (R_f = F \text{ or } CF_3) \qquad (3)$$

$$CF_2ICF_2O(CF_2)_{x+2}O[CFR_fCF_2O]_nCFR_fCOF \quad (II)$$

$$\begin{aligned}&1) \ CH_3OH \qquad\qquad (4)\\ &2) \ Zn/Ac_2O\end{aligned}$$

$$CH_3OCOCFR_f[OCF_2CFR_f]_nO(CF_2)_{x+2}O(CF_2)_4O(CF_2)_{x+2}O[CFR_fCF_2O]_nCFR_fCOOCH_3 \quad (III)$$

4
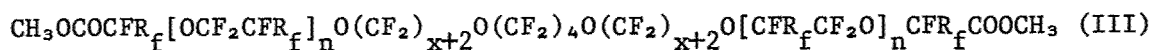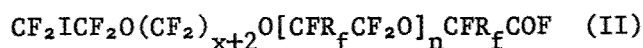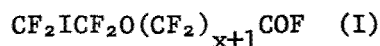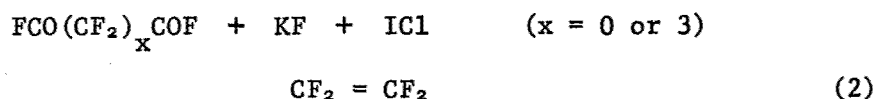
The feasibility of the above approach starting with hexafluoroglutaryl fluoride (x = 3) and hexafluoropropylene oxide (R_f = CF_3) has been demonstrated earlier and the symmetrical oligomer III (x = 3, n = 0, R_f = CF_3) was obtained and identified.[19] Conversion of the diester III to the diacid, diacyl fluoride or dinitrile can easily be accomplished by standard reactions.

The oxygen/carbon ratio of oligomers III is an important parameter related to the elastomeric properties of the final polymer. A high oxygen/carbon ratio in monomer III insures a greater flexibility of the final product, generally manifested as lower glass transition temperature (Tg). In this respect the ideal monomer III would be the one with R_f = F and x = 0. In the sequence of reactions 2 – 4 this implies starting with oxalyl fluoride (x = 0) and using TFEO (R_f = F) rather than HFPO (R_f = CF_3).

An additional requirement related to the hydrolytic stability of the final product is that the terminal acid group must be a secondary acid group rather than a primary acid. This, however, could readily be accomplished by addition of one HFPO unit to oligomer II prior to esterification and coupling.[12]

$$CF_2ICF_2O(CF_2CF_2O)_{n+1}CF_2COF \xrightarrow[\text{CsF}]{\text{HFPO}} CF_2ICF_2O(CF_2CF_2O)_{n+2}CF(CF_3)COF \quad (2a)$$

$$\text{II} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{IIa}$$
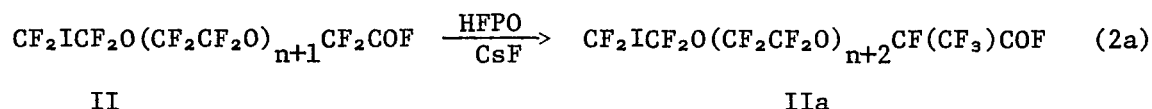
1. Preparation of $CF_2ICF_2OCF_2COF$

The title compound was prepared by addition of tetrafluoroethylene to a mixture of oxalyl fluoride, potassium fluoride and iodine monochloride in the usual manner.[12,22]

The equipment was the same as previously used,[21] a 500-ml Fischer-Porter pressure bottle. Difficulties, however, were experienced due to the low boiling point ($\sim$2°C) of oxalyl fluoride and to volatile by-products formed during the reaction. In several runs excessive pressure was developed resulting in the bursting of the reaction vessel. The following adaptations were necessary for the reaction to be carried out safely and satisfactorily.

A pressure regulator was installed on the TFE cylinder and adjusted to deliver TFE at a constant pressure of 35 psi instead of 60 psi used previously. Under these conditions pressure drop could not be used to follow the progress of the reaction. Instead, the consumption of ICl as evidenced by the gradual color change of the reaction mixture from deep red to light yellow was used as criterion of the completion of the reaction. Futhermore, the oxalyl fluoride was charged into the reactor at dry ice-acetone temperature rather than liquid nitrogen in order to reduce the stress on the glass.

The reaction mixture was transferred to a flask and the products were distilled under vacuum. Among the products of the reaction were unreacted oxalyl fluoride, carbonyl fluoride and significant amounts of the diiodide IV along with the desired product Ia.

$$FCOCOF + KF \; \underset{\longleftarrow}{\xrightarrow{\hspace{1cm}}} \; FCOCF_2O^-K^+ \tag{5}$$

$$FCOCF_2O^-K^+ \; \xrightarrow{ICl} \; FCOCF_2OI \tag{6}$$

$$FCOCF_2OI \; \xrightarrow{CF_2=CF_2} \; FCOCF_2OCF_2CF_2I \tag{7}$$
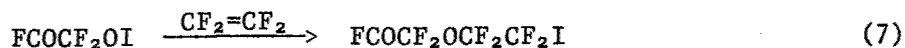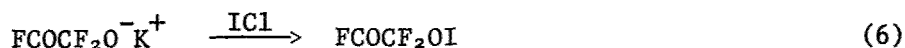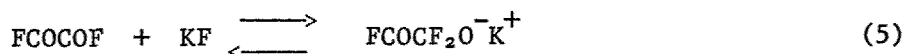
$$(Ia)$$

The diiodide IV is a normal product of the reaction, formed by further reaction of the 1:1 adduct (Ia) with KF, ICl and TFE.[21,22]

$$(Ia) + KF \xrightleftharpoons{\quad} CF_2ICF_2OCF_2CF_2O^-K^+ \tag{8}$$

$$CF_2ICF_2OCF_2CF_2O^-K \xrightarrow{ICl} CF_2ICF_2OCF_2CF_2OI \tag{9}$$

$$CF_2ICF_2OCF_2CF_2OI \xrightarrow{CF_2=CF_2} CF_2ICF_2OCF_2CF_2OCF_2CF_2I \tag{10}$$
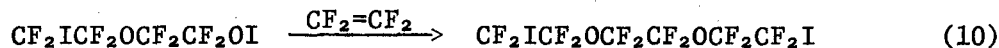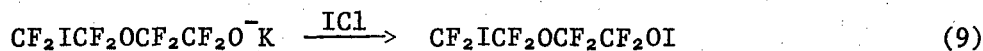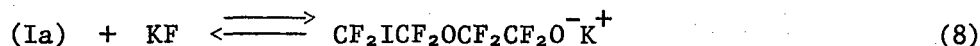
$$(IV)$$

It was found earlier, however, that by using one equivalent of KF the reaction could be directed to yield the 1:1 adduct as the major product with only minor amounts of the 2:1 adduct.[21]

The average conversion of oxalyl fluoride to Ia and IV was 11.5% and 8.0%, respectively (GLC). Actually on a weight basis more diiodide IV than monoiodide Ia was obtained. This contrasts strongly with the corresponding reaction of hexafluoroglutaryl fluoride, in which the 1:1 adduct was obtained in 32% conversion and only minor amounts of the diiodide were formed.[22] The reason for this behavior of OXF is probably due to the presence of two carbonyl groups adjacent to each other. Apparently, in this system, reaction 8 is favored over reaction 5.

2. Addition of TFEO to $CF_2ICF_2OCF_2COF$

The addition of TFEO to I was carried out in tetraglyme at $-20°C$ to $-10°C$ in the usual manner.[19]

$$CF_2ICF_2OCF_2COF + (n+1)CF_2\overset{O}{\overset{\diagup\diagdown}{CF_2}} \longrightarrow CF_2ICF_2O(CF_2CF_2O)_nCF_2COF \tag{11}$$

$$(Ia) \qquad\qquad\qquad\qquad (IIa)$$
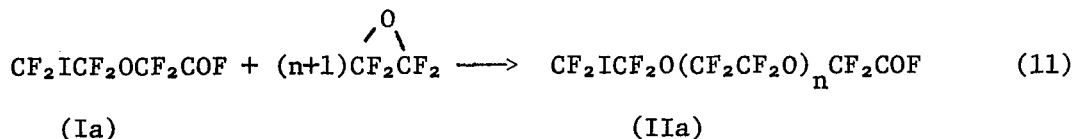
The reaction was monitored by frequent sampling and GLC analysis (Table 1). The TFEO take-up was slow and the reaction mixture was a homogeneous solution without separation of a product layer.

Inspection of the data in Table I reveals that addition of TFEO to Ia is slow and once the 1:1 adduct is formed it reacts faster with TFEO than the starting acyl fluoride Ia, thus leading to a broad distribution of oligomers IIa.

TABLE I

$$CF_2ICF_2OCF_2COF \quad + \quad (n+1)CF_2\overset{O}{\overset{/\backslash}{CF_2}} \quad \xrightarrow{CsF} \quad CF_2ICF_2O(CF_2CF_2O)_nCF_2COF$$

Ia   IIa
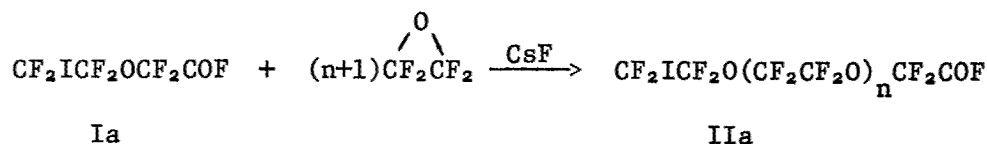
TFEO/I (mole ratio)	Product Composition (%)			
	n=0*	n=1	n=2	n=3
0.29	67.8	15.7	3.2	---
0.55	55.7	22.1	9.0	2.9
1.10	40.3	22.3	14.8	7.9
1.68	29.5	20.1	16.4	12.2

*Starting Material

The behavior of reaction (11) is similar to that of the addition of TFEO to oxalyl fluoride[12,13] and may be due to the proximity of $-CF_2I$ to the reaction site. The contrast with the addition of TFEO to HFGF[18] or of HFPO to $CF_2ICF_2O(CF_2)_4COF$[19] is striking.

The reaction was terminated when 1.68 equivalents of TFEO had been added at which point oligomers IIa with n = 1-6 were formed (see below). Some homooligomerization of TFEO did take place (5-7%), particularly at the later stages of the reaction.

The normal work-up procedure consisting of separating the fluorocarbon layer from the solvent could not be applied here since the reaction mixture was a homogeneous solution. Consequently, the product was removed from the reaction mixture under vacuum and slight heating (50°/0.3 mm). There were thus obtained 101 g of acyl fluoride having the following composition: n=0, 44.8%; n = 1, 26.9%; n = 2, 13.9%. An additional 36 g of product was obtained by methanol esterification and precipitation with water, representing a total of 85% recovery. The ester fraction had the following composition: n = 1, 5.0%; n = 2, 20.6%; n = 3, 29.5%; n = 4, 20.4%; n = 5, 8.7%; n = 6, 3.2%.

Distillation of the crude product gave a small fraction of the 1:1 adduct (IIa, n = 1), b.p. 106-110°C, and its structure was determined by NMR analysis (see Appendix, Table 3).

In view of the low specificity of the addition of TFEO to Ia, it is apparent that preparation of any given oligomer IIa by reaction 11 will be a very low yield process. This difficulty, however, could be overcome by substituting $CF_2ICF_2OCF_2CF_2OCF_2COF$ (or higher homologs) for $CF_2ICF_2OCF_2COF$ as the starting material for reaction 11. This is a common technique used successfully in the past and the data in Table 1 support this view (see Section C).

B. Hydrolysis of Perfluoroalkyl-α-ω-diiodides

It was pointed out earlier in the discussion that the 2:1 adduct of TFEO to HFGF, 2e-EDAF(G), has the unsymmetrical structure $FCO(CF_2)_4OCF_2CF_2OCF_2COF$ and, to our knowledge, there is no available synthetic method for the preparation of the symmetrical isomer $FCOCF_2O(CF_2)_5OCF_2COF$.

A slightly different situation applies to the preparation of $FCOCF_2OCF_2CF_2OCF_2COF$. Although 2e-EDAF(O) could be prepared by addition

of TFEO to OXF, the characteristics of this reaction are such that this method of preparation becomes synthetically unattractive.

A recent patent[23] disclosed the hydrolysis of perfluoroalkyl iodides $R_fCF_2CF_2I$ to acyl fluorides and it occurred to us that both 2e-EDAF(O) and symmetrical 2e-EDAF(G) could be prepared by hydrolysis of the available diiodides V.

$$CF_2ICF_2O(CF_2)_xOCF_2CF_2I \xrightarrow[\text{ZnSO}_4,\ \text{Cl}_2]{\text{H}_2\text{SO}_4\ (\text{SO}_3)} FCOCF_2O(CF_2)_xOCF_2COF \qquad (12)$$
$$\qquad\qquad V \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad VI$$
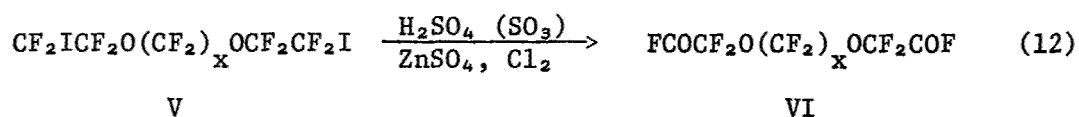
where x = 2 or 5

It was therefore of interest to investigate the feasibility of this reaction with iodides of structure V. Since methods for the preparation of perfluoroalkyl-α,ω-diiodides[13] and perfluoroalkylene oxide-α,ω-diiodides[21] are available, the scope of reaction 12, if successful, would be much broader.

1. Preparation of symmetrical 2e-EDAF's

A mixture of the diiodide V (x = 2; 0.09 mole) and $ZnSO_4$ (0.6 g) was heated to 90°C. Fuming sulfuric acid (200 g) containing 65% SO_3 by weight was then added slowly through a dropping funnel while at the same time a slow flow of chlorine was bubbled through the solution.

The temperature of the reaction mixture dropped to 70°C during the addition of sulfuric acid. After the addition of sulfuric acid was completed, the mixture was heated at 70°C and the addition of chlorine continued for 45 minutes (total chlorine, 0.04 mole).

Upon cooling to ambient temperature, the product separated as a colorless layer on top of the green colored sulfuric acid layer. It was decanted and distilled to give 2e-EDAF(O), b.p. 71-72°C, in 66.6% yield. The structure

of the product (VI, x = 2) was established by NMR and IR analysis (see Appendix, Figures 7, 8 and Tables 7 and 8).

The reaction proceeds smoothly and it is fast and complete under these conditions. There was no evidence of unreacted starting material. The isolation of the product, however, by decantation is obviously inefficient and significant amounts of the product may be lost. Consequently, the yield of the reaction is probably higher than 66%.

The symmetrical 2e-EDAF(G), b.p. 138-139°C, was prepared in a similar way by hydrolysis of the corresponding diiodide V (x=5). The structure of the product (VI, x = 5) was established by NMR and IR analysis (see Appendix, Figures 9, 10, and Table 9).

2. Controlled hydrolysis of diiodides

The conditions of hydrolysis in the above described experiments were essentially those of the patent examples[23] except that in one experiment only 22% of the recommended amount of chlorine was used. The function of chlorine was not clear to us and the results obtained raised the question of the necessity of chlorine for successful hydrolysis of the iodides.

The diiodide Va (0.6 mole) and $ZnSO_4$ (6 g) were heated at 90°C and fuming sulfuric acid (65% SO_3) was added dropwise. An exothermic reaction ensued and the rate of sulfuric acid addition was adjusted to keep the reaction temperature at 100-120°C. A total of 1,070 g of sulfuric acid was added over a period of six hours and the heating was continued for an additional 75 minutes.

$$CF_2ICF_2OCF_2CF_2OCF_2CF_2I \xrightarrow[ZnSO_4]{H_2SO_4 \ (SO_3)} \begin{array}{c} FCOCF_2OCF_2CF_2OCF_2COF \quad (VIa) \\ + \\ CF_2ICF_2OCF_2CF_2OCF_2CFO \quad (VIIa) \end{array} \quad (13)$$

Va
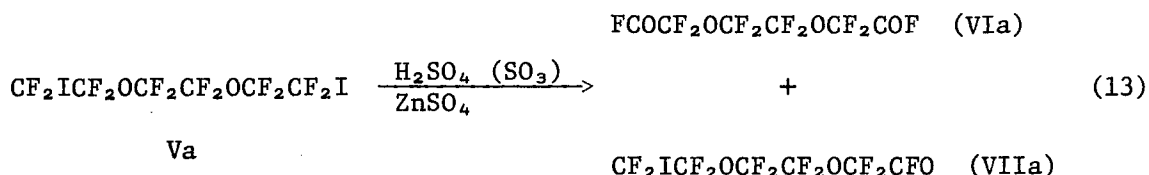
GLC analysis of the product at this point showed the following composition: Va, 37.7%; VIa, 21.7%; VIIa, 35.0%. The reaction was very clean as the above numbers indicate, the only significant impurities being two unknown peaks which appear as shoulders on the high side of peaks VIa (2.5%) and VIIa (1.8%). During the reaction, deposition of iodine was observed and an unidentified gas (SO_2?) was evolved.

The reaction mixture was heated at 85-90°C for an additional four hours. GLC analysis at this point showed the following composition: Va, 7.0%; VIa, 52.0%; VIIa, 26.3%. However the unidentified impurities mentioned above increased to 13% and the reaction was terminated. Distillation gave 71 g of 2e-EDAF(O) and intermediate fractions containing VIIa and Va.

The reaction under these conditions (no chlorine) is obviously slow and the ω-iodoacyl fluoride VIIa intermediate is one of the major products. This contrasts sharply with the course of the hydrolysis in the presence of chlorine. In the presence of chlorine the reaction is fast and complete and there is no evidence of the presence of unreacted starting material Va or the intermediate hydrolysis product VIIa among the reaction products. It appears that an oxidant like chlorine is necessary for the hydrolysis to proceed fast and to completion (is SO_3 acting as an oxidant in the absence of chlorine?).

Several aspects of reaction 13 are not clearly understood and require further investigation. It is clear, however, that this reaction is a valuable method for the controlled hydrolysis of diiodides to ω-iodoacyl fluorides.

Iodoacyl fluorides are important intermediates and the iodide VIIa, in particular, is the starting material for the preparation of $CF_2ICF_2O(CF_2CF_2O)_nCF_2COF$ oligomers, as discussed in section A-2.

12

Application of reaction 13 to diiodides of structure VIII[13] will make
available a series of perfluoroalkyl iodoacyl fluorides IX, which are not
easily prepared by other methods.

$$I(CF_2)_nI \xrightarrow[ZnSO_4]{H_2SO_4 \ (SO_3)} I(CF_2)_{n-1}COF \qquad (14)$$

$$\text{VIII} \qquad\qquad\qquad \text{IX}$$
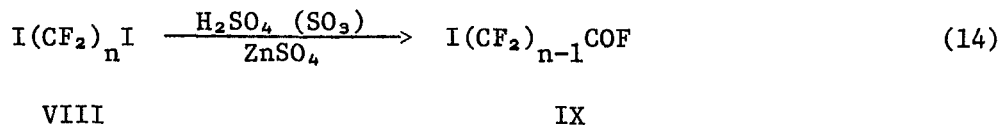
The low members of this series, n = 2-4, are of particular interest for the
preparation of symmetrical perfluoroalkylene oxide difunctional oligomers X
(see Section A).

$$CH_3OCOCFX[OCF_2CF_2]_mO(CF_2)_{2n}O[CF_2CF_2O]_mCFXCOOCH_3$$

$$X$$
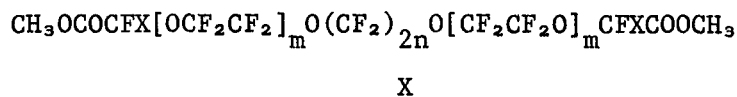
where X = F or CF_3

3. <u>Attempted hydrolysis of $CF_2BrCF_2OCF_2CF_2OCF_2CF_2Br$ (XI)</u>

An attempt was made to hydrolyze the dibromide XI to 2e-EDAF(O).

The dibromide (0.06 mole) and ZnSO_4 (0.5 g) was heated at 90°C and
fuming sulfuric acid (140 g) containing 65% of SO_3 was added slowly over a
period of 30 minutes. The mixture was then refluxed (70°C) for an additional
2 hours. IR analysis showed only starting material with no evidence of hydrolysis
product.

The mixture was refluxed (bath temperature 100-110°C) for 6 hours
while a slow flow of chlorine was bubbled through the solution (total amount
of chlorine, 3 g). IR analysis showed no evidence of hydrolysis product.
The starting material was recovered by decantation.

The dibromide was prepared in 20.7% yield from oxalyl fluoride by the same reaction used for the preparation of diiodides[19] except that bromine was substituted for ICl (see Experimental).

$$FCOCOF + 2KF + 2Br_2 \xrightarrow{CF_2=CF_2} CF_2BrCF_2OCF_2CF_2OCF_2CF_2Br \qquad (15)$$
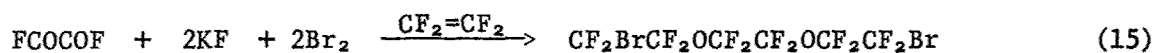
$$XI$$

C. Preparation of OXF/TFEO Oligomers

It was pointed out earlier in the discussion that addition of TFEO to OXF (reaction 1; $x = 0$, $R_f = F$) leads to a broad distribution of OXF/TFEO oligomers. Apparently, the formation of 1:1 and 2:1 adducts by addition of TFEO to OXF is a much slower reaction than the addition of TFEO to 2e-EDAF(O) thus leading to a broad distribution of oligomers. It follows that if 2e-EDAF(O) were available by an alternate method, the desired OXF/TFEO oligomers could be obtained by addition of TFEO.

$$FCOCF_2OCF_2CF_2OCF_2COF + n\ \overline{CF_2CF_2O} \xrightarrow{CsF} FCOCF_2O(CF_2CF_2O)_{n+1}CF_2COF \qquad (16)$$
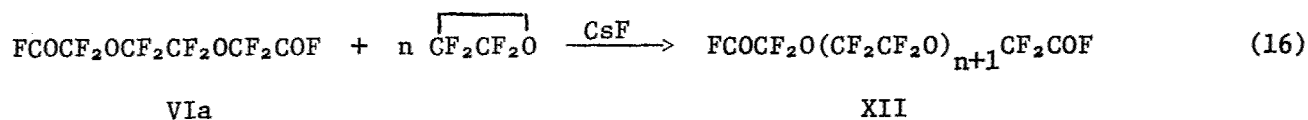
$$VIa \qquad\qquad\qquad\qquad XII$$

The addition of TFEO to 2e-EDAF(O), prepared by reaction 12, was carried out in tetraglyme at 0° to -5°C. The reaction proceeded smoothly and the results are shown in Table 2.

TABLE 2

PREPARATION OF ne-EDAF(O) OLIGOMERS

$$FCOCF_2OCF_2CF_2OCF_2COF \xrightarrow{\text{TFEO}} FCOCF_2O(CF_2CF_2O)_{n+1}CF_2COF$$
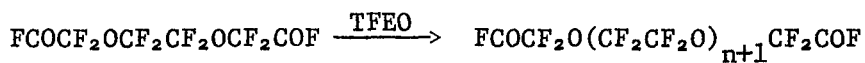
VIa   XII

TFEO/VIa (mole ratio)	Product Composition (%)					
	n=1	n=2	n=3	n=4	n=5	n=6
2	14.5	54.4	28.6	2.5	--	--
3	--	24.1	50.9	18.6	--	--
3.5		4.1	43.2	42.6	7.6	2.5

Comparison with the results obtained earlier in the attempted synthesis of oligomers XII by addition of TFEO to oxalyl fluoride[12,13] shows that reaction 16 is much more specific, leading to a narrow distribution of products which can be separated by distillation.

In a separate run TFEO (1.8 moles) was added to VIa (0.2 mole) under the same condition as above. The product had the following composition:

XII, n = 5; 7e-EDAF(O)   :   5.9%

    n = 6; 8e-EDAF(O)   :   33.7%

    n = 7; 9e-EDAF(O)   :   32.9%

    n = 8; 10e-EDAF(O)   :   8.7%

Distillation gave 8e-EDAF(O), b.p. 65-67°C/0.1 mm (Figure 12), and 9e-EDAF(O), b.p. 77-82°C/0.1 mm (Figure 13).*

The above results substantiate the reasoning presented in Section A-2 regarding the synthesis of oligomers IIa.

_____

*For an independent synthesis of these oligomers starting from perfluorooxadiacetyl fluoride see K. B. Baucom, Contract F33615-76-C-5119, Final Report (1977).

$$CF_2ICF_2OCF_2CF_2OCF_2COF \xrightarrow{\text{TFEO}} CF_2ICF_2O(CF_2CF_2O)_nCF_2COF \qquad (17)$$

VIIa   IIa
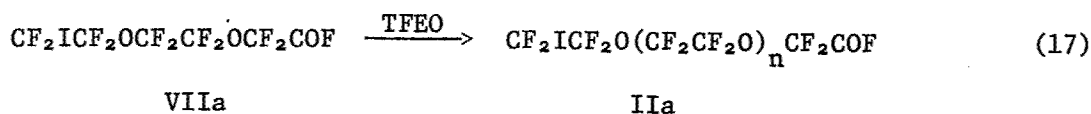
By the same token, symmetrical HFGF/TFEO oligomers XIII could be prepared by addition of TFEO to symmetrical 2e-EDAF(G) prepared by reaction 12.

$$FCOCF_2O(CF_2)_5OCF_2COF \xrightarrow{\text{TFEO}} FCOCF_2(OCF_2CF_2)_nO(CF_2)_5O(CF_2CF_2O)_nCF_2COF \qquad (18)$$

XIII

D.   Preparation of HFPO-terminated OXF/TFEO Oligomers

Oligomers XII have the desirable high oxygen/carbon ratio; however, their terminal groups are primary acid groups. For the reasons discussed earlier, secondary terminal groups are preferable and this can be accomplished by addition of one unit of HFPO to each end of oligomers XII (see section A).

$$FCOCF_2O(CF_2CF_2O)_nCF_2COF \xrightarrow{\text{HFPO}} FCOCF(CF_3)O(CF_2CF_2O)_{n+2}CF(CF_3)COF \qquad (19)$$

XII   XIV
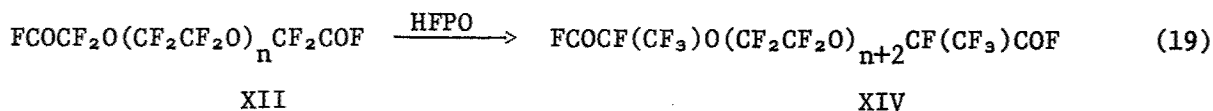
7e-EDAF(O) [XII, n =6; 0.053 mole[*]] was added to a slurry of CsF in tetraglyme. The mixture was cooled at $-5°$ to $0°C$ and HFPO was added through a vacuum manifold in the usual manner.

The reaction was monitored by GLC analysis and it was terminated when 42 g of HFPO had been added. The product was separated from the solvent layer and it had the following composition.
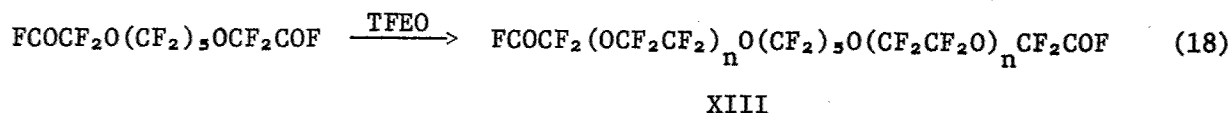
1:1 adduct	:	17.6%	
2:1 adduct (XIV, n = 6)	:	69.6%	2p-[7e-EDAF(0)]
3:1 adduct	:	12.9%	

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*Supplied by K. Baucom, Contract No. F33615-76-C-5119

The acyl fluoride XIV was converted to the nitrile via the methyl ester and amide. Distillation gave a fraction boiling at 100-106°C/1 mm, which was shown by GLC analysis to be a mixture (4.4:1) of two closely boiling components. Repeated distillations on a spinning band column did not succeed in separating the two components.

NMR analysis of the product (Appendix, Table 10) showed that it is a mixture of the isomers XV and XVI in the approximate ratio of 3-4:1. There was no evidence of other impurities present, specifically TFEO or HFPO-homooligomers.

$$NCCFO(CF_2CF_2O)_8\overset{\overset{\displaystyle CF_3}{|}}{C}FCN$$

XV

$$NCCF_2O(CF_2CF_2O)_7\overset{\overset{\displaystyle CF_3}{|}}{C}FCF_2O\overset{\overset{\displaystyle CF_3}{|}}{C}FCN$$
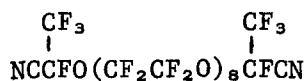
XVI

These results are surprising since on the basis of the relative reactivity of TFEO-acyl fluoride ($-OCF_2COF$) and HFPO-acyl fluorides ($-OCF(CF_3)COF$) towards addition of HFPO it would be expected that the product would be almost exclusively the symmetrical isomer XV.

Addition of HFPO to 8e-EDAF(O) was carried out in the same fashion. The reaction proceeded smoothly until all of 8e-EDAF(O) was converted to the 1:1 adduct (GLC). After t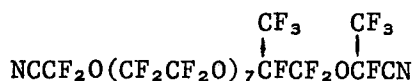his point was reached, however, further addition of HFPO resulted mostly in the formation of HFPO homooligomers, namely dimer and trimer.

After several unsuccessful attempts to force the reaction to completion, the reaction was interrupted, the fluorocarbon layer was separated from the glyme and the HFPO homooligomers were removed by distillation.

The reaction mixture (EDAF's) was added to a slurry of freshly dried CsF in glyme and the addition of HFPO was resumed at -5° to -10°. Under these conditions, the addition of HFPO was slow and accompanied by homooligomerization,

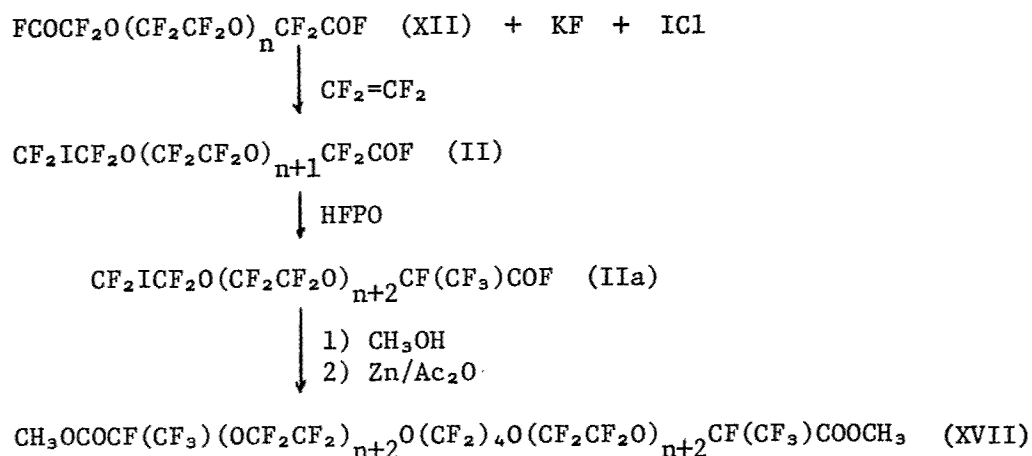which necessitated incremental addition of HFPO and removal of the HFPO homooligomers between additions.

The reaction was terminated when the ratio of 1:1 adduct to 2:1 adduct was 1.5 (GLC). The acyl fluorides were converted to the methyl esters and the product was separated from the glyme solvent by precipitation with water.

The behaviour of 8e-EDAF(O) towards HFPO addition is puzzling. On the basis of chemical reactivity, one would expect that the addition of two HFPO units would proceed smoothly. It is conceivable that the two components of the reaction product correspond to the 2:1 and 3:1 adducts rather than the 1:1 and 2:1 adducts assigned on the basis of GLC. This question could only be answered by isolation and NMR analysis of the products.

Similar results were obtained on addition of HFPO to a mixture of 9e-EDAF(O) and 10e-EDAF(O). The reaction mixture was converted to the nitriles via the ester and amide.

On the basis of the above results and our earlier results[19] relating to the preparation of 2p-[5e-EDAF(G)] and 2p-[6e-EDAF(G)], it appears that the only unambiguous synthesis of symmetrical HFPO-terminated difunctional oligomers is the coupling of ω-iodoesters, as discussed in section A-2.

Alternatively, oligomers XII could be converted to oligomers II and then to the desired symmetrical oligomers XVII as shown below.

$$FCOCF_2O(CF_2CF_2O)_nCF_2COF \quad (XII) \quad + \quad KF \quad + \quad ICl$$

$$\downarrow CF_2=CF_2$$

$$CF_2ICF_2O(CF_2CF_2O)_{n+1}CF_2COF \quad (II)$$

$$\downarrow HFPO$$

$$CF_2ICF_2O(CF_2CF_2O)_{n+2}CF(CF_3)COF \quad (IIa)$$

$$\downarrow \begin{array}{l} 1) \ CH_3OH \\ 2) \ Zn/Ac_2O \end{array}$$

$$CH_3OCOCF(CF_3)(OCF_2CF_2)_{n+2}O(CF_2)_4O(CF_2CF_2O)_{n+2}CF(CF_3)COOCH_3 \quad (XVII)$$

EXPERIMENTAL

A. Preparation of Perfluoroalkyl Ether Halides

The apparatus for the preparation of perfluoroalkylene oxide iodides and bromides consisted of three 500-ml Fischer-Porter pressure bottles connected in parallel through copper tubing to a cylinder of tetrafluoroethylene.

1. Preparation of $CF_2ICF_2OCF_2CF_2OCF_2CF_2I$

The following is a typical example. Potassium fluoride (55 g; 1.0 mole) was charged to a Fischer-Porter pressure bottle containing a magnetic stirring bar, and dried overnight at 200°C under vacuum. After the bottle was cooled to room temperature, tetraglyme (200 ml) was added and the mixture was stirred for a few minutes under vacuum.

The reaction vessel was cooled in a dry ice-acetone bath and oxalyl fluoride (45 g; 0.48 mole) was charged through a vacuum manifold. The mixture was allowed to warm up to ambient temperature and was stirred for one hour.

The reaction vessel was cooled in a dry ice-acetone bath, iodine monochloride (50 ml; 1.0 mole) was added through a syringe and the system evacuated.

The reaction vessel was connected through copper tubing to a cylinder of tetrafluoroethylene, the mixture was allowed to reach room temperature, the stirrer was turned on and TFE was pressured in at 35 psi.

The reaction was terminated, after several days, when the deep red color of the reaction mixture had turned to a light yellow color.

The excess of TFE and volatile products were vented off, the reaction mixture was poured into water, the iodine was destroyed with a solution of sodium bisulfite and the product was separated as the heavy phase.

The crude products of several runs were combined and distilled on an Oldershaw column. The average yield of the diiodide, b.p. 60-61°/13 mm, was 16%. It's IR spectrum is shown in Figure 5 and NMR spectral data in Table 5.

2. Preparation of $CF_2BrCF_2OCF_2CF_2OCF_2CF_2Br$

Potassium fluoride (55 g, 1.0 mole), tetraglyme (200 ml), oxalyl fluoride (47 g, 0.5 mole) and bromine (160 g, 1.0 mole) were charged into a 500-ml Fischer-Porter pressure bottle as described above, and TFE was pressured in at 35 psi.

Distillation gave the dibromide, b.p. 130-131°C, in 18.6% yield. Its IR spectrum is shown in Figure 6 and NMR spectral data in Table 6.

3. Preparation of $CF_2ICF_2OCF_2COF$

The preparation of the iodoacyl fluoride was essentially the same as that of the diiodide except that only half of the amount of KF (one equivalent) and ICl were used. A typical example follows.

Potassium fluoride (28 g, 0.5 mole), tetraglyme (200 ml), oxalyl fluoride (50 g, 0.53 mole) and iodine monochloride (30 ml, 0.59 mole) were charged into a 500-ml Fischer-Porter pressure bottle, and TFE was pressured in at 35 psi.

After the reaction was completed, the reaction mass was transferred into a flask and the mixture fractionated. The iodoacyl fluoride b.p. 81-84°C was obtained in 8% yield (Figure 1).

The residue of the distillation, which consisted essentially of the diiodide was washed with water and passed over a neutral Al_2O_3 column. Distillation gave the diiodide, b.p. 62-63°C/15 mm, in 11.5% yield (Figure 5).

B. Hydrolysis of Perfluoroalkyl Ether Diiodides

1. Preparation of $FCOCF_2OCF_2CF_2OCF_2COF$

a. The iodide $CF_2ICF_2OCF_2CF_2OCF_2CF_2I$ (55 g, 0.09 mole) and $ZnSO_4$ (0.6 g) were added to a three neck flask equipped with thermometer reflux condenser, magnetic stirrer, dropping funnel and a gas inlet tube.

The mixture was heated at 90°C and fuming sulfuric acid (200 g, 65% SO_3) was added while a slow flow of chlorine was bubbled through the solution. The temperature of the reaction mixture dropped to 70°C during the addition of sulfuric acid. After the addition was completed (30 minutes) the mixture was heated at 70°C and the addition of chlorine was continued for an additional 45 minutes (total chlorine: 3 g; 0.04 mole).

After cooling to ambient temperature the product separated as a clear colorless layer formed on top of the green-colored sulfuric acid layer and it was decanted. Distillation gave 15 g of the product boiling at 71-72°C (66.6% yield). Its IR spectrum is shown in Figure 7 and NMR spectral data in Table 7.

b. The iodide $CF_2ICF_2OCF_2CF_2OCF_2CF_2I$ (360 g, 0.6 mole) and $ZnSO_4$ (6 g) were heated at 90°C and fuming sulfuric acid (1,070 g, 65% SO_3) was added over a period of six hours (chlorine was not added). An exothermic reaction ensued and the rate of addition of sulfuric acid was regulated to keep the reaction temperature at 100-120°C.

After the addition of sulfuric acid was completed, the mixture was heated at this temperature for an additional 75 minutes. GLC analysis at this point showed the following composition: $FCOCF_2OCF_2CF_2OCF_2COF$, 21.7%, $CF_2ICF_2OCF_2CF_2OCF_2COF$, 35.0%; $CF_2ICF_2OCF_2CF_2OCF_2CF_2I$, 37.7%.

The mixture was heated at 85-90°C for an additional four hours at which point the product had the following composition: $FCOCF_2OCF_2CF_2OCF_2COF$, 52.0%; $CF_2ICF_2OCF_2CF_2OCF_2COF$, 26.3% and unreacted diiodide, 7.0%.

21

Distillation gave 71 g of the diacyl fluoride, b.p. 80–82°C, and intermediate fractions.

2. Preparation of $FCOCF_2O(CF_2)_5OCF_2COF$

The iodide $CF_2ICF_2O(CF_2)_5OCF_2CF_2I$ (97 g, 0.13 mole) and $ZnSO_4$ (0.7 g) were heated at 90°C and fuming sulfuric acid (300 g, 65% SO_3) was added while a flow of chlorine was passed through the solution.

After the addition was completed (60 minutes) the mixture was heated at 70–75°C and the addition of chlorine was continued for an additional 90 minutes (total chlorine 16 g, 0.23 mole).

The product was decanted. Distillation gave the diacyl fluoride, b.p. 138–139°C, in 44.6% yield. Its IR spectrum is shown in Figure 9 and NMR spectral data in Table 9.

C. Preparation of TFEO Difunctional Oligomers

1. Preparation of Tetrafluoroethylene Oxide

Tetrafluoroethylene oxide was prepared by photochemical oxidation of tetrafluoroethylene (Figure 11). A detailed description of the photochemical apparatus can be found in reference 12.

2. Addition of TFEO to $CF_2ICF_2OCF_2COF$

The iodoacyl fluoride (105 g, 0.31 mole) was added to a slurry of CsF (4 g) in tetraglyme (60 ml). A clear solution resulted after the initial exothermic reaction subsided.

The solution was cooled at −20°C to −10°C and TFEO was added slowly through a vacuum manifold under a pressure of 400–500 mm Hg. The reaction was monitored by frequent sampling and GLC analysis, and the results are shown in Table 1.

22

The product was removed from the glyme solvent under vacuum (50°C/0.3 mm). There were thus obtained 101 g of acyl fluorides with the following composition: 44.8% starting material, 26.9% 1:1 adduct and 13.9% 2:1 adduct.

An additional 36 g of product was obtained by methanol esterification of the glyme residue and precipitation with water. It had the following composition: starting material, 0.5%; 1:1 adduct, 20.6%; 2:1 adduct, 29.5%; 3:1 adduct, 20.4%; 4:1 adduct, 8.7% and 5:1 adduct, 3.2%.

3. Preparation of $CH_3OCOCF_2O(CF_2)_4OCF_2COOCH_3$

The ester $CF_2ICF_2OCF_2COOCH_3$ (32 g, 0.09 mole) was added in one portion to a mixture of acetic anhydride (25 ml), methylene chloride (50 ml) and zinc (8 g, 0.12 mole). An exothermic reaction ensued and the temperature of the mixture rose to 40°C, and a white precipitate was formed within a few minutes.

The mixture was refluxed (50°C) for four hours and stirred at ambient temperature overnight.

The reaction mixture was poured into water and the product was extracted with Freon-113. Distillation gave the product, b.p. 76-77°C/0.75 mm, identified by NMR and IR analysis (Figure 4 and Table 4).

4. Addition of TFEO to $FCOCF_2OCF_2CF_2OCF_2COF$

a. 2e-EDAF(O) [13 g; 0.04 mole] was added to a slurry of CsF (0.5 g) in tetraglyme (10 ml). The mixture was cooled at -5°C to 0°C and TFEO was added through a vacuum manifold.

The reaction was monitored by frequent sampling and GLC analysis and the results are shown in Table 2.

b. 2e-EDAF(O) [70 g; 0.2 mole] was added to a slurry of cesium fluoride (1 g) in tetraglyme (100 ml). The mixture was cooled at -5°C to 0°C and TFEO was added through a vacuum manifold.

23

The reaction was monitored by frequent sampling and it was terminated when 210 g (1.8 moles) of TFEO had been added and GLC analysis indicated the following composition: 7e-EDAF(O), 5.9%; 8e-EDAF(O), 33.7%; 9e-EDAF(O), 32.9%; 10e-EDAF(O), 8.7%.

The product (141 g) was separated from the glyme layer and was distilled to give 30 g of 8e-EDAF(O), bp 65-67°C/0.1 mm (Figure 12) and 28 g of 9e-EDAF(O), b.p. 77-82°C/0.1 mm (Figure 13) and intermediate fractions.

D.   Preparation of HFPO-terminated TFEO Oligomers

A typical example follows:

1.   Addition of HFPO to 7e-EDAF(O)

7-EDAF(O) [48 g; 0.053 mole] was added to a slurry of CsF (1 g) in tetraglyme (35 ml). The mixture was cooled at -8°C to 0°C and HFPO was added through a vacuum manifold. The reaction was monitored by frequent sampling and GLC analysis. The reaction was terminated when 42 g (0.25 mole) of HFPO had been added and the product had the following composition: 1:1 adduct, 17.6%; 2:1 adduct, 69.6%; 3:1 adduct, 12.8%.

Some HFPO homooligomers were also formed (mostly dimer) and were removed under vacuum.

2.   Conversion of the acyl fluorides to nitriles

a.   The above reaction mixture was esterified with methanol and the ester precipitated with water (82 g).

b.   The dry ester product was dissolved in Freon-113 (500 ml) and gaseous dry ammonia was bubbled through the solution.

The solvent was removed under vacuum leaving 82 g of the amide as a white waxy solid.

c.   The amide was mixed with 200 g of P_2O_5 and the mixture heated at 200–240°C/100–150 mm Hg (slight reflux).

The nitrile product was distilled off under high vacuum (67 g, 82% yield).

Distillation on a spinning band column gave 32 g of the 2:1 adduct, b.p. 106–110/1.0 mm (94% purity). GLC analysis showed that it consisted of two components in the ratio 4:1. NMR analysis showed that the two components were structural isomers (Table 10). Its IR spectrum is shown in Figure 14.
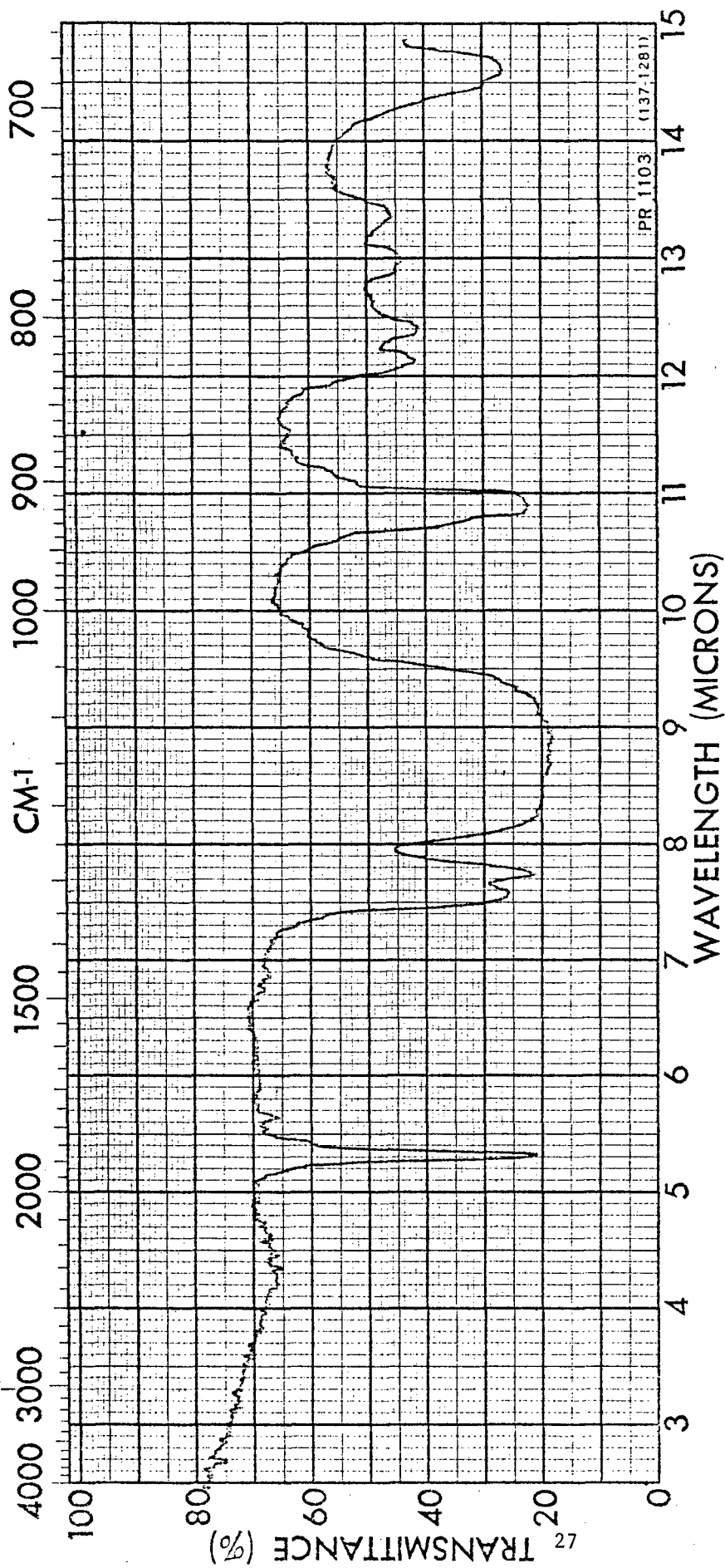
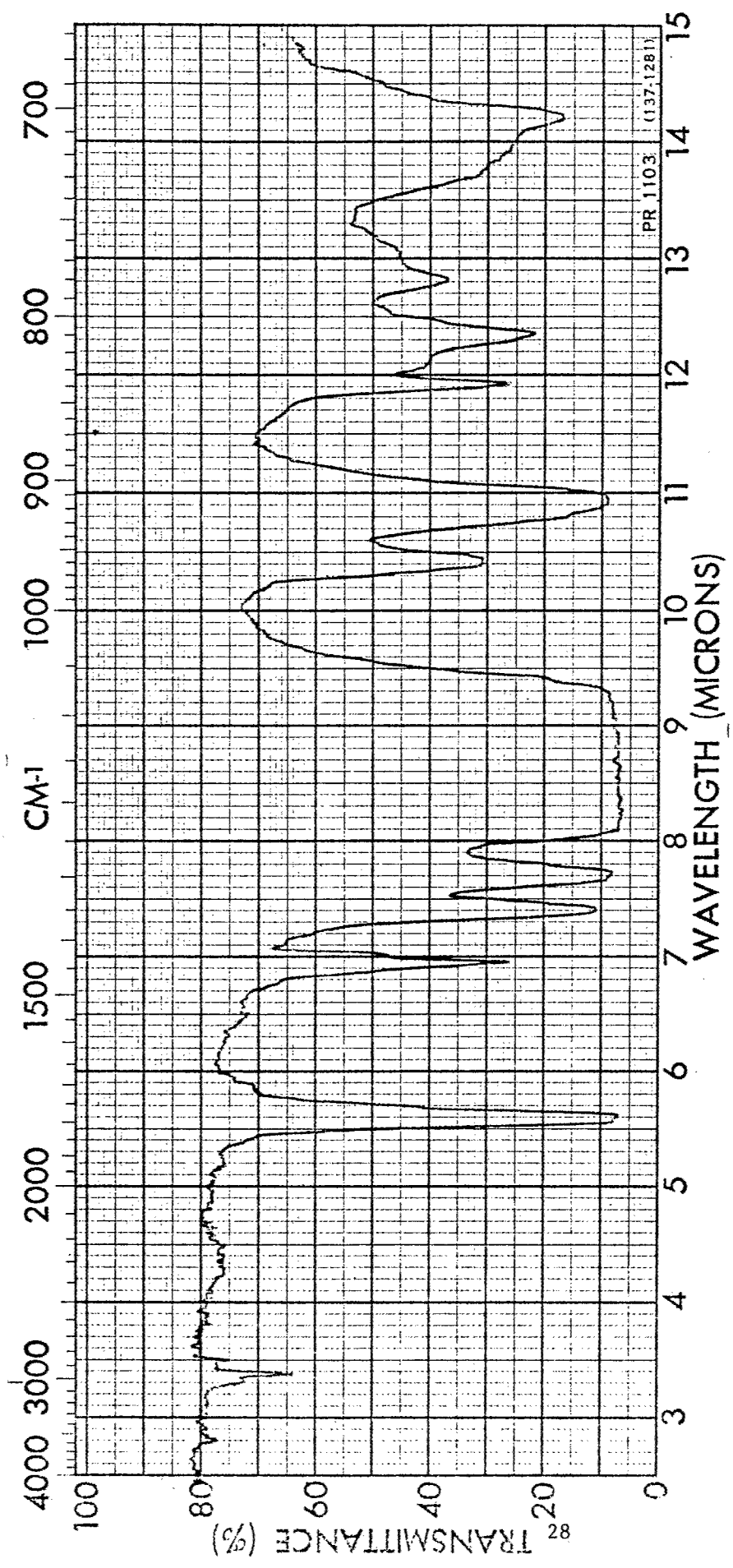APPENDIX

A. Infrared Spectra

Figure 1 – $CF_2ICF_2OCF_2COF$

Figure 2 — $CF_2ICF_2OCF_2COOCH_3$

PR 1103   (137-1281)

CM-1

WAVELENGTH (MICRONS)

TRANSMITTANCE (%)

28
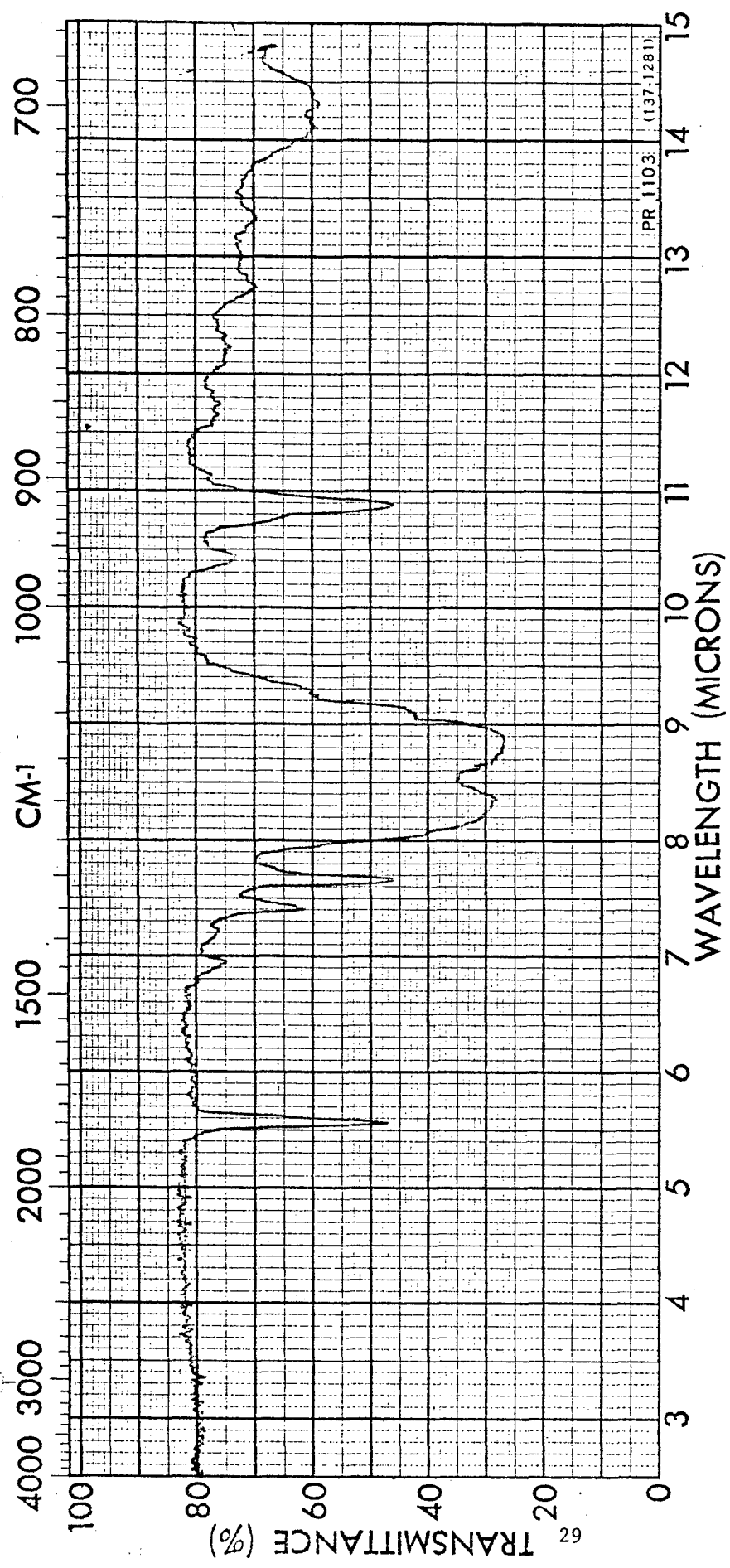
Figure 3 — $CF_2ICF_2OCF_2CF_2OCF_2COOCH_3$

29
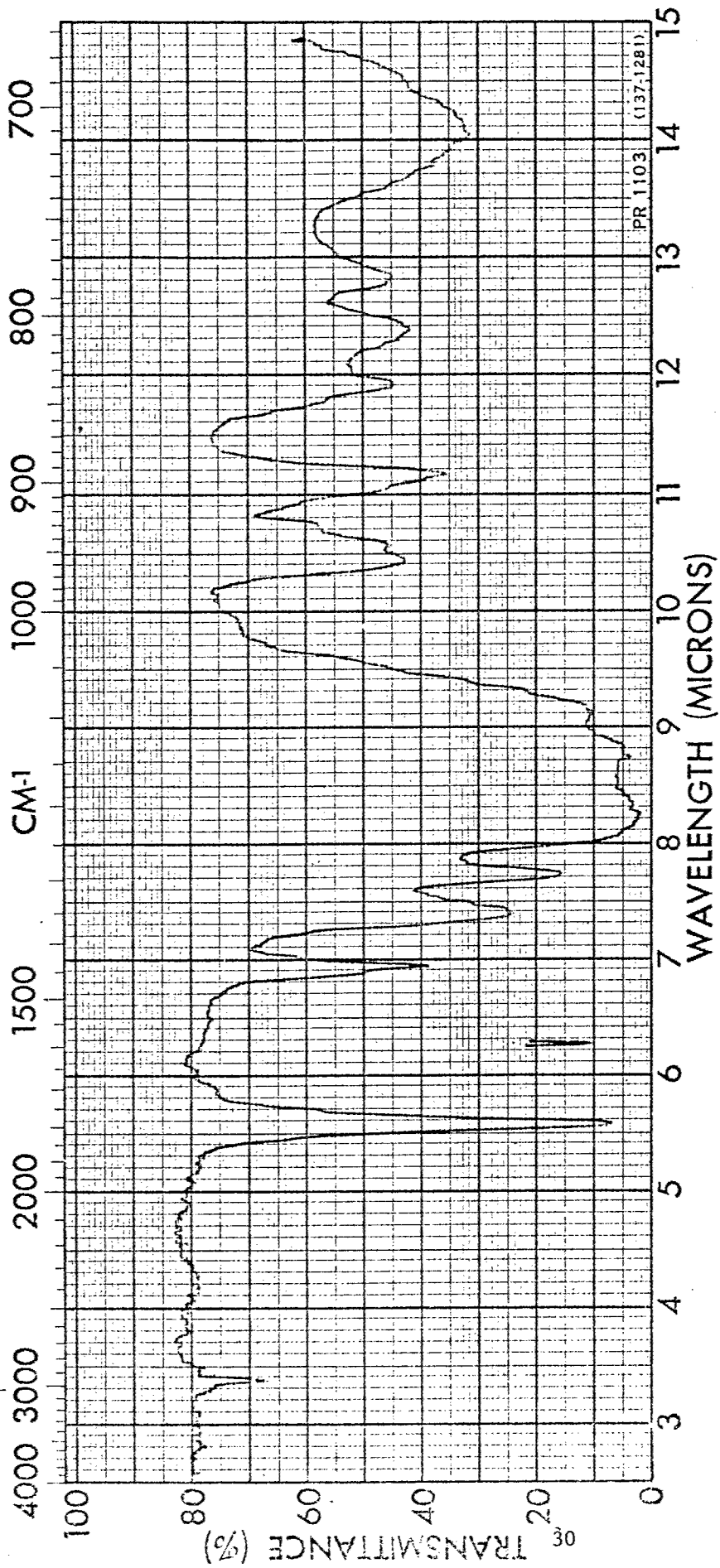
Figure 4 — $CH_3OCOCF_2O(CF_2)_4OCF_2COOCH_3$
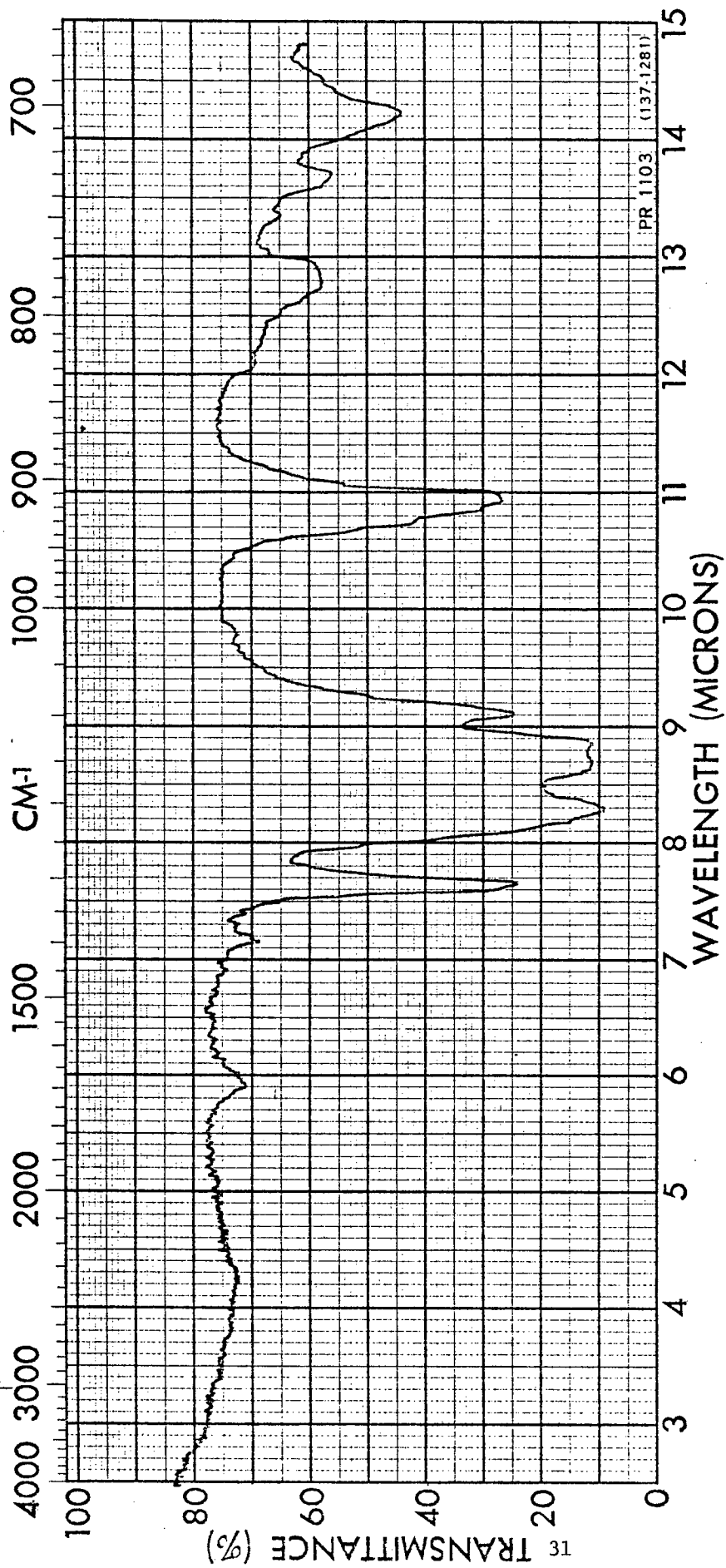
Figure 5 — CF$_2$ICF$_2$OCF$_2$CF$_2$OCF$_2$CF$_2$I

PR 1103   (137-1281)

31
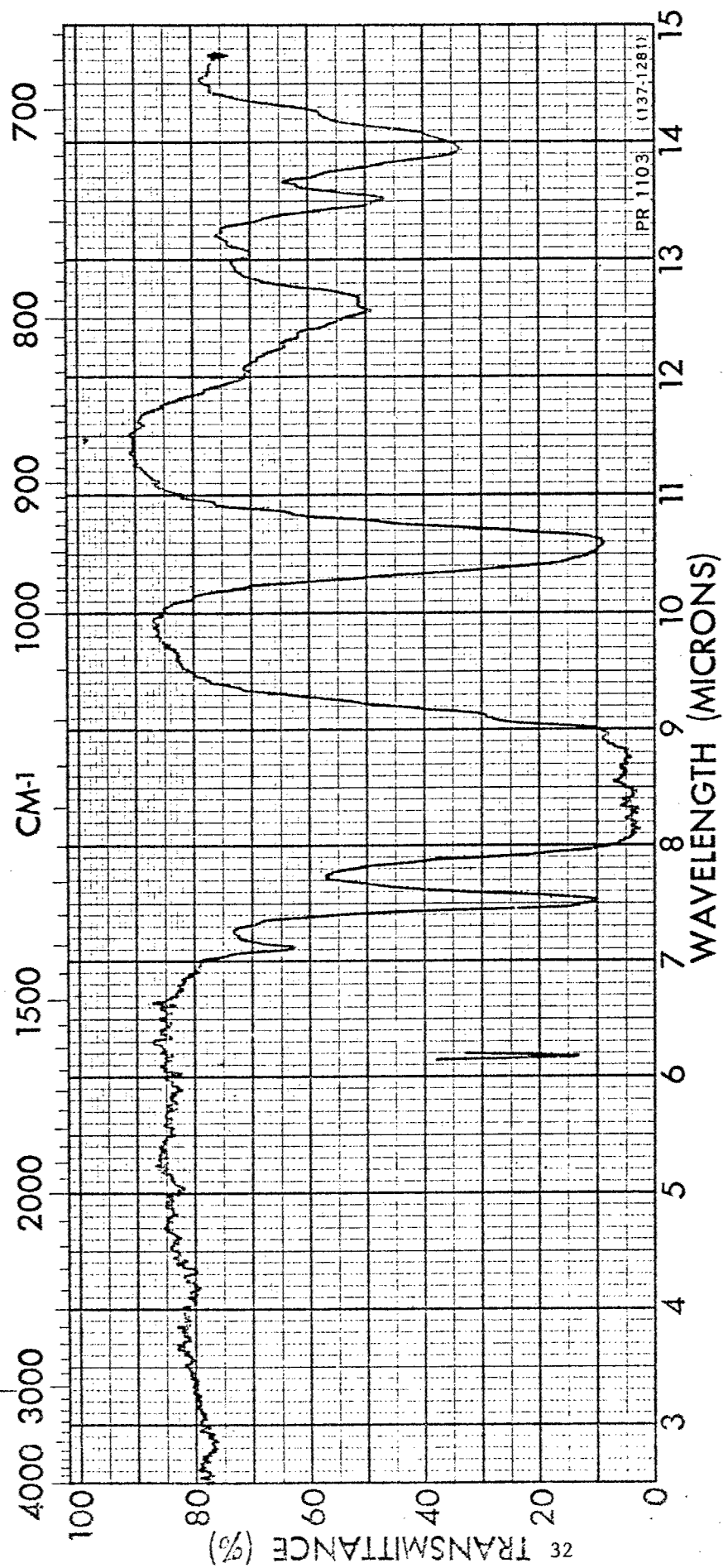
Figure 6 — $BrCF_2CF_2OCF_2CF_2OCF_2CF_2Br$
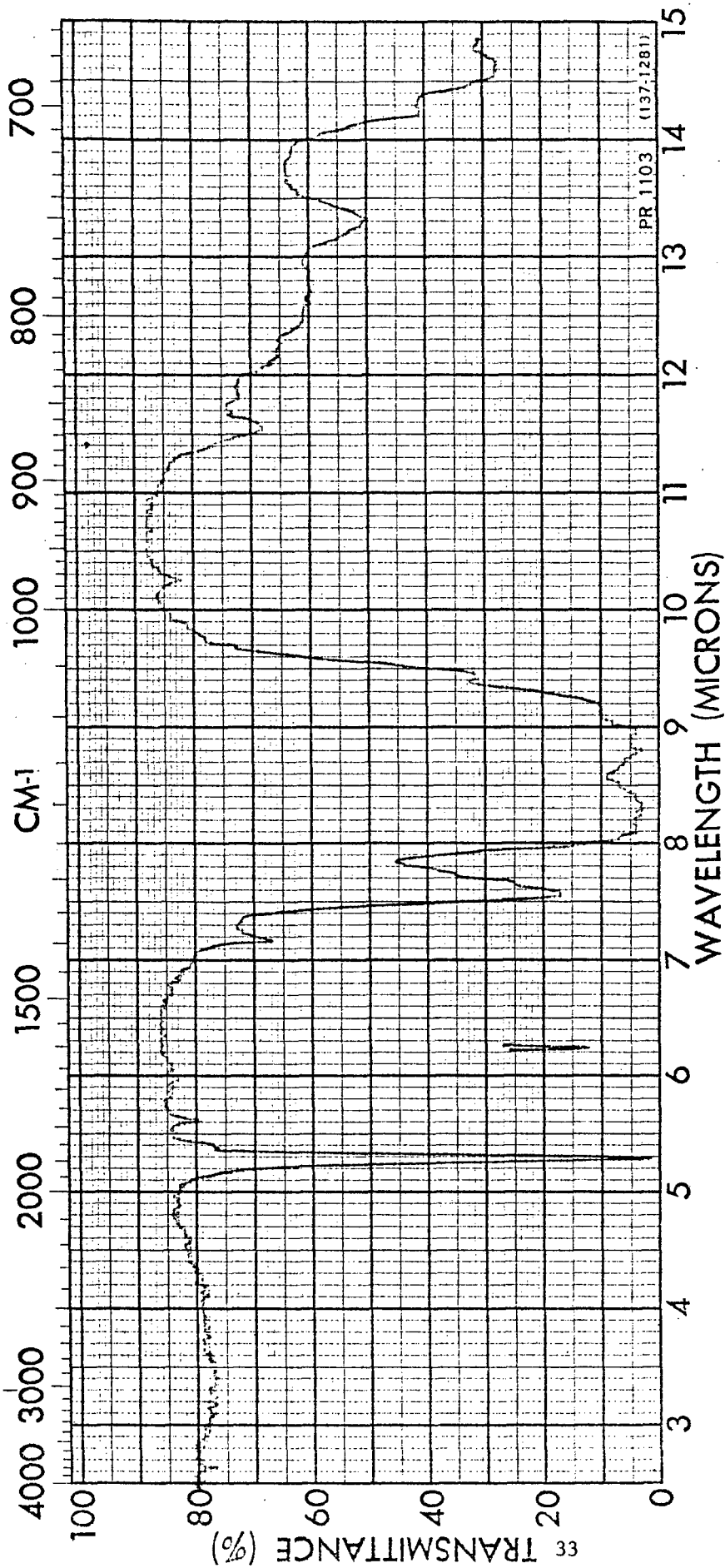
Figure 7 - FCOCF$_2$OCF$_2$CF$_2$OCF$_2$COF

33
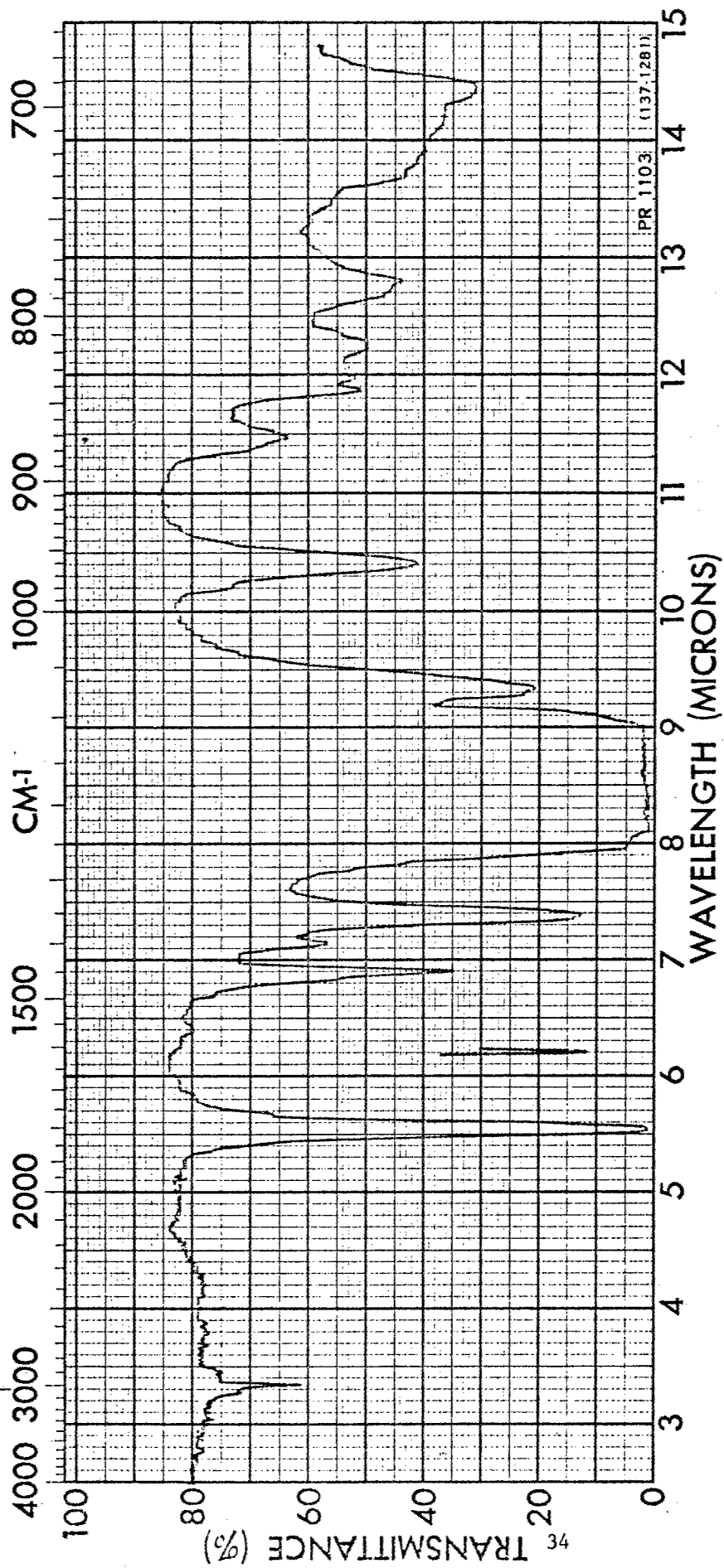
Figure 8 – CH$_3$OCOCF$_2$OCF$_2$CF$_2$OCF$_2$COOCH$_3$

Figure 9 — COFCF$_2$O(GF$_2$)$_5$OCF$_2$COF

35
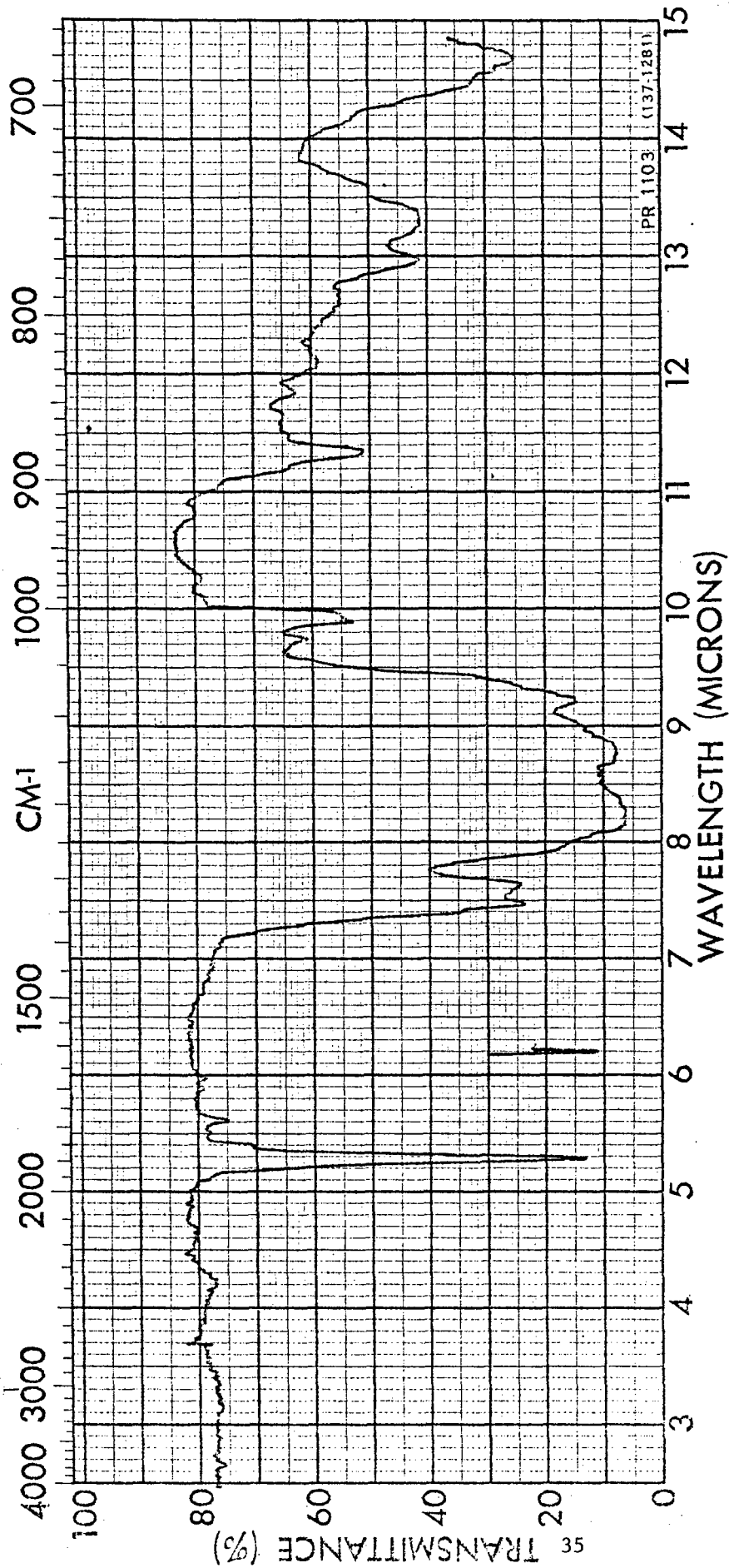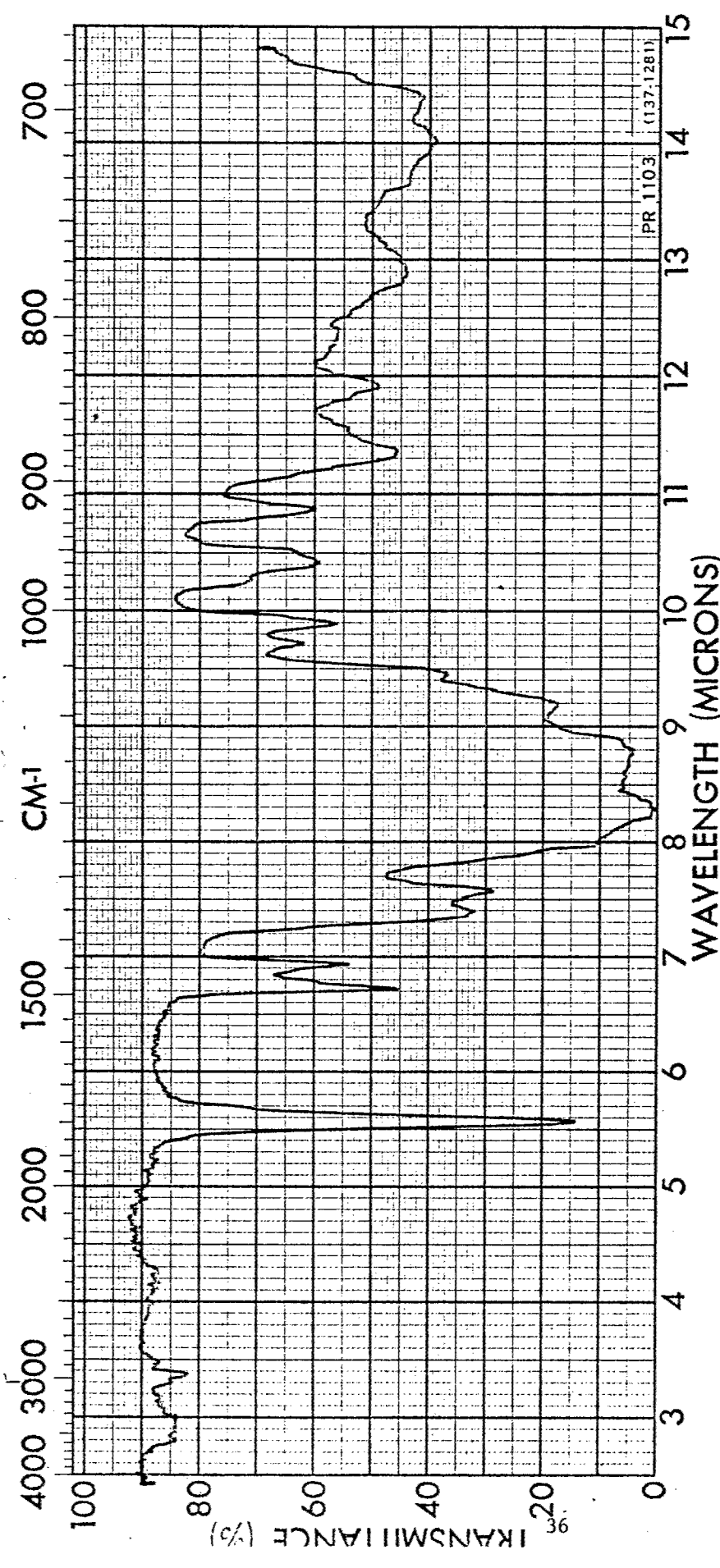
Figure 10 – $CH_3OCOCF_2O(CF_2)_5OCF_2COOCH_3$

36

Figure 11 – $CF_2\overset{\displaystyle O}{\diagdown\diagup}CF_2$

37

Figure 12 — 8e-EDAF(O)

Figure 13 -- 9e-EDAF(O)

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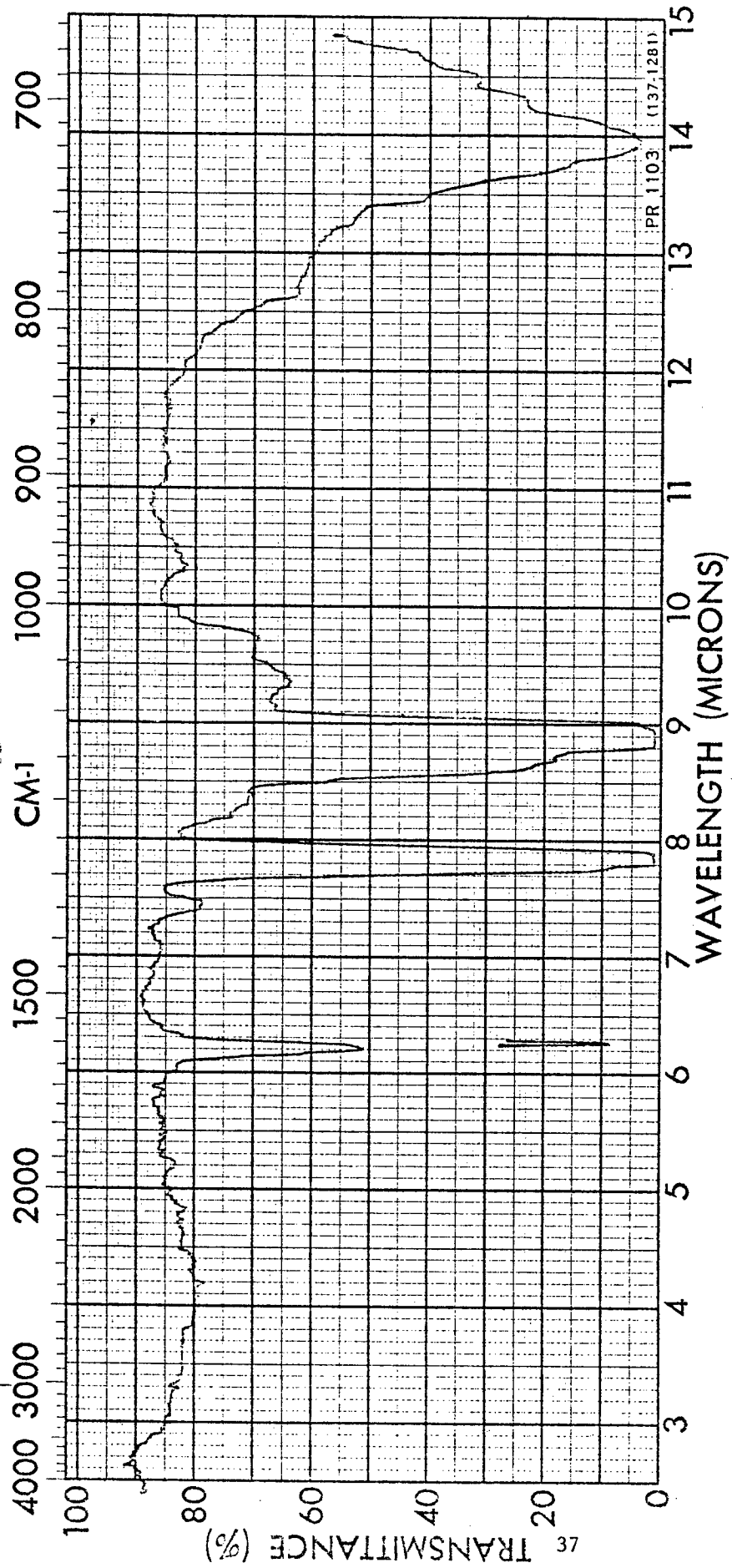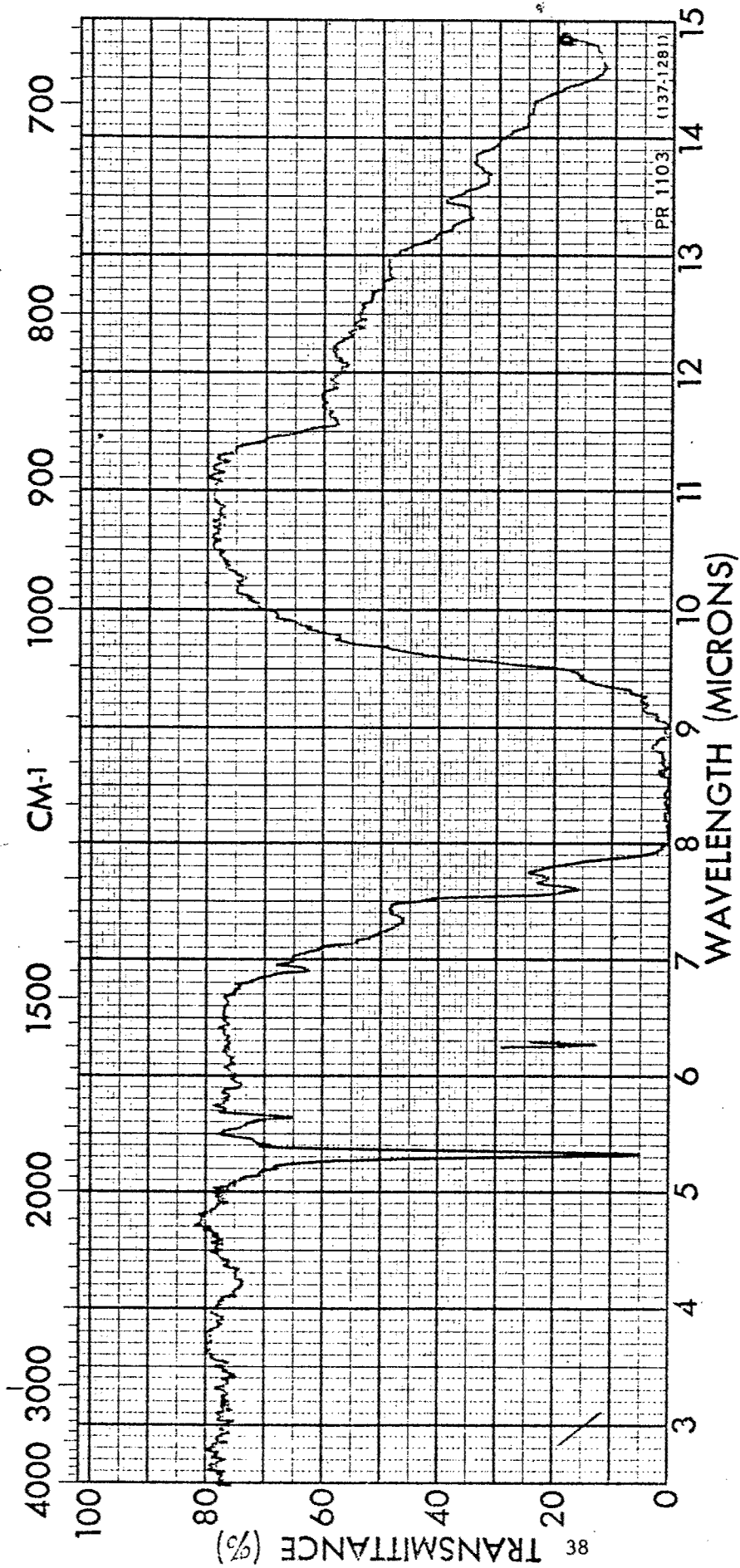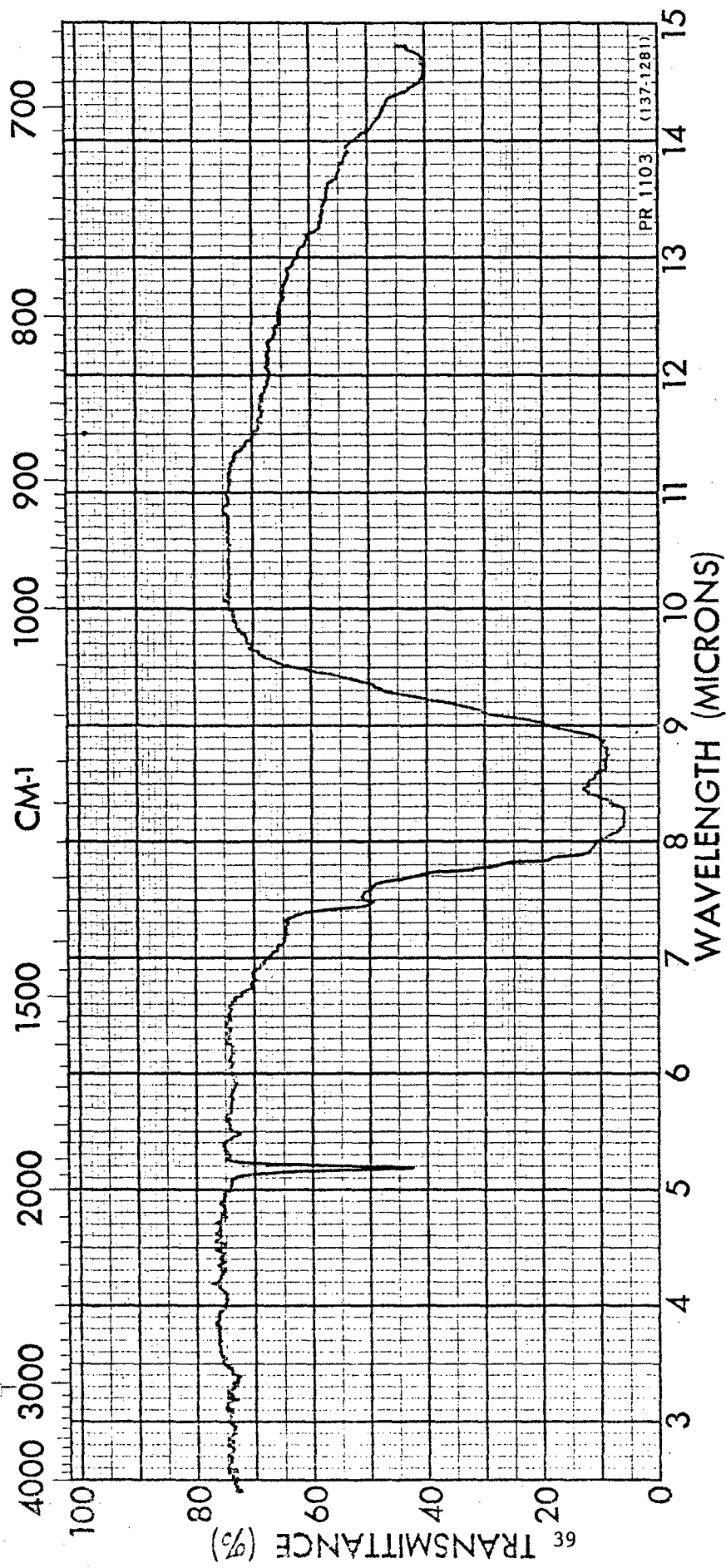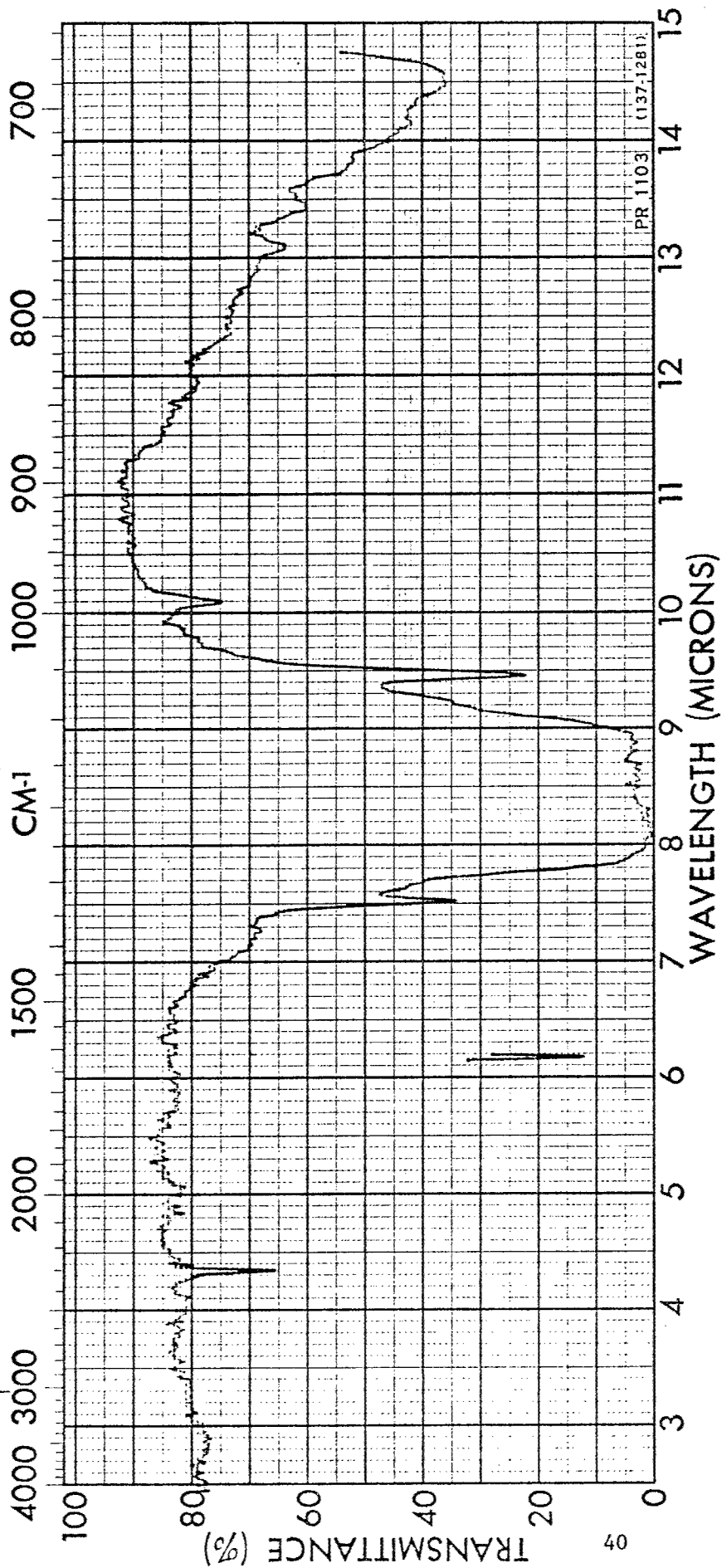
Figure 14 — 2p–[7e–EDAF(0)]–CN

B. Nuclear Magnetic Resonance Data

TABLE 3

A   C   E   D   B   G
NMR SPECTRUM OF $CF_2ICF_2OCF_2CF_2OCF_2COOCH_3$

Conditions of Spectral Determination

Nucleus	F	H
Reference	Int. $CF_2ClCFCl_2$	Ext. TMS
	(corr. to CF_3COOH)	
Frequency, Instrument	94.1, XL-100-5	

Peaks Obtained

Designation	Chem. Shift	Pattern	Rel. Area	Assignment
A	-12.9 ppm	Triplet by 6 Hz	2.0	CF_2I
B	-0.6	Triplet by 8 Hz	2.0	OCF_2 next to ester
C	+8.3	Multiplet	2.0	OCF_2 next to CF_2I
D	+10.6	Triplet by 8 Hz	2.0	OCF_2
E	+11.1	Multiplet	2.0	OCF_2
Hydrogen				
G	4.2 ppm	Singlet		$COOCH_3$

42

TABLE 4

$$\overset{\text{A}\quad\text{B}\quad\text{C}}{\text{NMR SPECTRUM OF } CH_3OCOCF_2O(CF_2CF_2)_2OCF_2COOCH_3}$$

Conditions of Spectral Determination

Nucleus	F	H
Reference	Ext. CF_3COOH	Ext. TMS
Frequency, Instrument	94.1, XL-100-15	

Peaks Obtained

Designation	Chemical Shift	Pattern	Rel. Area	Assignment
A	+0.5 ppm	Doublet by 15 Hz Doublet by 12 Hz	223	CF_2 next to ester
B	+6.1 ppm	Multiplet	224	CF_2O
C	+44.8 ppm	Triplet by 15 Hz	223	CF_2 middle
Hydrogen				
D	4.21 ppm (TMS)	Singlet		OCH_3

TABLE 5

NMR SPECTRUM OF $\overset{A}{C}F_2I\overset{B}{C}F_2O\overset{C}{C}F_2\overset{C}{C}F_2O\overset{B}{C}F_2\overset{A}{C}F_2I$

Conditions of Spectral Determination

Nucleus	F
Reference	Ext. CF_3COOH
Frequency, Instrument	94.1, XL-100-15

Peaks Obtained

Designation	Chem. Shift	Pattern	Rel. Area	Assignment
A	-13.5 ppm	Triplet by 5.5 Hz	111	CF_2I
B	+ 8.3	Multiplet	111	CF_2O next to CF_2I
C	+11.2	Multiplet	111	CF_2O

TABLE 6

$$A \quad B \quad C \quad C \quad B \quad A$$

NMR SPECTRUM OF $CF_2BrCF_2OCF_2CF_2OCF_2CF_2Br$

Conditions of Spectral Determination

Nucleus	F
Reference	Ext. CF_3COOH
Frequency, Instrument	94.1, XL-10-15

Peaks Obtained

Designation	Chem. Shift	Pattern	Rel. Area	Assignment
A	-7.3 ppm	Multiplet	69	CF_2Br
B	+9.7	Multiplet	69	CF_2 next to CF_2Br
C	+12.2	Multiplet	69	CF_2O

TABLE 7

NMR SPECTRUM OF $\overset{A}{FCO}\overset{B}{CF_2}\overset{C}{OCF_2}\overset{C}{CF_2}\overset{B}{OCF_2}\overset{A}{COF}$

Conditions of Spectral Determination

Nucleus	F
Reference	Ext. CF_3COOH
Frequency, Instrument	94.1, XL-100-15

Peaks Obtained

Desingation	Chemical Shift	Pattern	Rel. Area	Assignment
A	−89.2 ppm	Broad singlet	1.94	$\overset{\overset{\text{O}}{\|\|}}{CF}$
B	+0.7	Triplet by 11.6 Hz Doublet by 2.0 Hz	4.00	OCF_2 next to COF
C	+12.0	Pentet by 11.5 Hz	4.00	OCF_2

TABLE 8

NMR SPECTRUM OF $CH_3OCOCF_2OCF_2CF_2OCF_2COOCH_3$

Conditions of Spectral Determination

Nucleus   F

Reference   Ext. CF_3COOH

Frequency, Instrument   94.1, XL-100-15

Peaks Obtained

Designation	Chemical Shift	Pattern	Rel. Area	Designation
A	+0.70 ppm	Triplet by 11.5 Hz	3.98	OCF_2 next to ester
B	+11.6	Triplet by 11.5 Hz	4.02	OCF_2 in middle

TABLE 9

A   B   C   E   D   E   C   B   A
NMR SPECTRUM OF $FCOCF_2OCF_2CF_2CF_2CF_2CF_2OCF_2COF$

Conditions of Spectral Determination

Nucleus	F
Reference	Ext. CF_3COOH
Frequency, Instrument	94.1, XL-100-15

Peaks Obtained

Designation	Chemical Shift	Pattern	Rel. Area	Assignment
A	-89.2 ppm	Broad singlet	1.96	COF
B	+0.4	Triplet by 11 Hz Doublet by 2.5 Hz	3.96	OCF_2 next to COF
C	+6.1	Pentet by 11 Hz	4.04	OCF_2
D	+45.6	Multiplet	2.00	CF_2 in mid chain
E	+48.9	Multiplet	4.05	CF_2 flanking D

TABLE 10
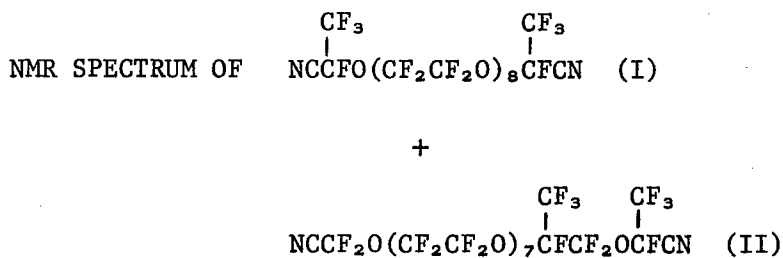
NMR SPECTRUM OF $\quad$ NCCFO$(CF_2CF_2O)_8$CFCN $\quad$ (I)
with CF_3 substituents on the two CF carbons

$$+$$

NCCF$_2$O$(CF_2CF_2O)_7$CFCF$_2$OCFCN $\quad$ (II)
with CF_3 substituents on the two CF carbons

Conditions of Spectral Determination

Nucleus	F
Reference	Ext. CF_3COOH
Frequency, Instrument	94.1, XL-100-75

Peaks Obtained

Designation	Chem. Shift	Pattern	Rel. Area	Assignment
A	-18.1 ppm	Triplet by 10 Hz	39	OCF$_2$CN (II)
B	3.8 ppm	Broad Multiplet	58	CF$_3$ next to OCF$_2$ (II)
C	5.7 ppm	Broad Singlet	34	CF$_2$O (II)
D	6.8 ppm	Broad Singlet	36	CF$_2$O (II)
E	8.0 ppm	Doublet by 5 Hz	420	CF$_3$ near CN (I and II)
FG	10.5 ppm	Doublet by 140 Hz Doublet by 17 Hz	133	F in CF$_2$O next to assym. center
H	12.3 ppm	Singlet	2100	12 CF$_2$O's in II plus 14 CF$_2$O's in I
IJ	13.4 ppm	Doublet by 140 Hz Doublet by 10 Hz	135	Other F in CF$_2$O next to assym. center
K	37.9 ppm	Multiplet	153	CF near CN (I and II)
L	68.3 ppm	Tripled by 22 Hz	23	CF next to CF$_2$O (II)

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