

UNCLASSIFIED

AD NUMBER
AD815443
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution: Further dissemination only as directed by Air Force Materials Laboratory, Polymer Branch, Nonmetallic Materials Division, Attn: MANP, Wright-Patterson AFB, OH 45433, March 1967, or higher DoD authority.
AUTHORITY
AFML ltr, 7 Dec 1972

THIS PAGE IS UNCLASSIFIED

AFML-TR-67-19

AD0815443

OFFICIAL FILE COPY

FLUOROAROMATIC CHEMISTRY: THE REACTIONS AND KINETICS OF SODIUM PENTAFLUOROPHENOLATE WITH SUBSTITUTED PENTAFLUOROBENZENES

RALPH J. DePASQUALE, 1/LT, USAF
CHRIST TAMBORSKI

TECHNICAL REPORT AFML-TR-67-19

MARCH 1967

This document may be further distributed by any holder only with specific prior approval of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (MANP), Wright-Patterson Air Force Base, Ohio 45433.

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



OFFICIAL FILE COPY

BEST AVAILABLE COPY

20040302140

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned to the Research and Technology Division unless return is required by security considerations, contractual obligations, or notice on a specific document.

**FLUOROAROMATIC CHEMISTRY: THE REACTIONS AND
KINETICS OF SODIUM PENTAFLUOROPHENOLATE
WITH SUBSTITUTED PENTAFLUOROBENZENES**

*RALPH J. DePASQUALE, 1/LT, USAF
CHRIST TAMBORSKI*

This document may be further distributed by any holder only with specific prior approval of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (MANP), Wright-Patterson Air Force Base, Ohio 45433.

FOREWORD

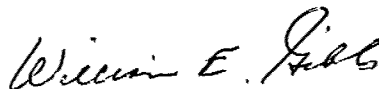
This report was prepared by the Polymer Branch of the Nonmetallic Materials Division, Air Force Materials Laboratory. The work was conducted under Project No. 7340, "Non-metallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with 1/Lt Ralph J. DePasquale, Ph.D., and Christ Tamborski, Ph.D., Project Engineers.

This report covers research conducted from November 1965 to November 1966. The manuscript was released by the authors in November 1966 for publication as a technical report.

The authors are indebted to the Analytical Branch, Materials Physics Division and its contractors for elemental analysis and nuclear magnetic resonance studies. The F^{19} nmr spectra were interpreted by John Pustinger, Jr., and J.E. Strobel of the Monsanto Research Corporation, Dayton, Ohio.

This work was supported, in part, by the Air Force Materials Laboratory Director's Discretionary Funds.

This technical report has been reviewed and is approved.



WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

Sodium pentafluorophenolate and sodium 4-hydroxytetrafluorophenolate were synthesized and shown to react with a series of substituted pentafluorobenzenes. Reaction conditions were chosen to maximize the kinetically controlled product, viz phenolate substitution at the position para to the functional group. Small percentages of side products derived from ortho or both ortho and para displacement were generally observed. Polysubstitution products could be obtained in fair yield when pentafluorobenzonitrile was used as the substrate.

The relative rates for the reaction of eight substituted pentafluorobenzenes with sodium pentafluorophenolate were measured. The differences in rate between substituents were relatively large. This was further demonstrated by the linear plot of log (relative rate) vs Hammett's σ_p which gave a slope of about 7.5.

(This abstract may be further distributed by any holder only with specific prior approval of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (MANP), Wright-Patterson Air Force Base, Ohio 45433.)

TABLE OF CONTENTS

SECTION	PAGE
I INTRODUCTION	1
II DISCUSSION	2
1. Preparation of the Sodium Salts of Pentafluoro- and 4-Hydrotetrafluorophenol	2
2. Reactions of Perfluorophenol Salts With Decafluorobiphenyl	2
3. Reactions of Sodium Pentafluorophenolate With Monosubstituted Hexafluorobenzene	3
4. Spectral Properties of 4-Substituted Nonofluorodiphenyl Ethers	8
5. Kinetics	8
III EXPERIMENTAL	12
1. Sodium 4-Hydropentafluorophenolate (Ib)	12
2. 4-(4-Hydrotetrafluorophenoxy)-Nonafluorobiphenyl (II)	12
3. Sodium Pentafluorophenolate (Ia)	13
4. 4,4'-Bis(pentafluorophenoxy)octafluorobiphenyl (V)	13
5. 4-Bromononafluorodiphenyl Ether (VI)	14
6. 4-Chlorononafluorodiphenyl Ether (XI)	15
7. 4-Cyanononafluorodiphenyl Ether (XIV)	15
8. Reaction of Pentafluorobenzonitrile With Sodium Pentafluorophenolate-Multiple Substitution	16
9. 4-Trifluoromethylnonafluorodiphenyl Ether (XVIII)	17
10. Ethyl Pentafluorobenzoate	17
11. 4-Carboethoxynonafluorodiphenyl Ether (XIX)	17
12. 4-Nonafluorodiphenyl Ether Carboxylic Acid (XXI)	18
13. Decafluorodiphenyl Ether (XXII)	18
14. 4-Hydrnonafluorodiphenyl Ether (XXIII)	18
15. Reaction of Iodopentafluorobenzene With Sodium Pentafluorophenolate	19

TABLE OF CONTENTS (CONT'D)

SECTION	PAGE
16. The Polymerization of Sodium Pentafluorophenolate	20
17. Kinetics	20
REFERENCES	21
INFRARED SPECTRA (FIGURE 1)	25

ILLUSTRATIONS

FIGURE		PAGE
1.	Sodium Pentafluorophenolate Ia (KBr)	25
2.	4-Hydrotetrafluorophenolate Ib (KBr)	26
3.	4-(4-Hydrotetrafluorophenoxy)-nonafluorobiphenyl II (KBr)	27
4.	4,4-Bis-(4-Hydrotetrafluorophenoxy)-octafluorobiphenyl III (KBr)	28
5.	4-Pentafluorophenoxy-nonafluorobiphenyl IV (KBr)	29
6.	4,4'-Dipentafluorophenoxyoctafluorobiphenyl V (KBr)	30
7.	4-Bromononafluorodiphenyl Ether VI (KBr)	31
8.	2-Bromononafluorodiphenyl Ether IX (film)	32
9.	4-Bromotetrafluoro-N,N-dimethylaniline VII (film)	33
10.	4-Chlorononafluorodiphenyl Ether XI (KBr)	34
11.	4-Cyanononafluorodiphenyl Ether XIV (KBr)	35
12.	2,4-Dipentafluorophenoxytrifluorobenzonitrile XV (KBr)	36
13.	2,4,6-Tripentafluorophenyldifluorobenzonitrile XVI (KBr)	37
14.	4-Trifluoromethylnonafluorodiphenyl Ether XVI (KBr)	38
15.	Ethylpentafluorobenzoate (film)	39
16.	4-Carboethoxynonafluorodiphenyl Ether XIX (KBr)	40
17.	4-Nonafluorodiphenyl Ether Carboxylic Acid Sodium Salt XX (KBr)	41
18.	4-Nonafluorodiphenyl Ether Carboxylic Acid XXI (KBr)	42
19.	Decafluorodiphenyl Ether XXII (KBr)	43
20.	4-Hydrononafluorodiphenyl Ether XXIII (KBr)	44
21.	2-Pentafluorophenoxypropanone XXIV (film)	45

SECTION I

INTRODUCTION

One of the research programs in the Air Force Materials Laboratory on thermally and oxidatively stable fluids and polymers has centered on the synthesis of perfluoroaromatic compounds.

From previous work it was discovered that perfluoropolyphenylene polymers possess a high degree of thermal stability. It is unfortunate that the polymer's insolubility limits its applications. The intractable character in systems of this type can be attributed in part to the rigidity of the polymer chain. If the flexibility of the polymer can be enhanced by substituting an oxygen atom between successive phenyl rings, a perfluoropolyphenyl ether polymer would seem to be attractive. Furthermore, low molecular weight hydrocarbon polyphenyl ethers serve as excellent fluids.

This report describes the preparation of model perfluorodiphenyl ether compounds. Further work on the synthesis of low and high molecular weight perfluoropolyphenyl ether polymers is now in progress.

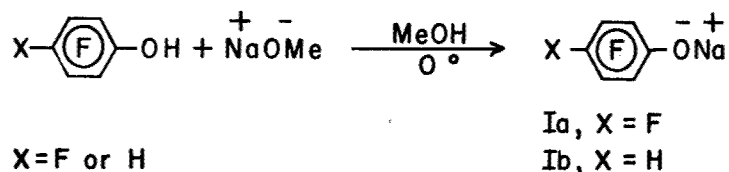
SECTION II

DISCUSSION

1. PREPARATION OF THE SODIUM SALTS OF PENTAFLUORO- AND 4-HYDROTETRAFLUOROPHENOL

The reactions of sodium and potassium phenolate with hexafluorobenzene and decafluorophenyl have been reported (Reference 1). Attempts to react the perfluoroanalogs of these salts with perfluoroaromatic substrates gave low yields of products (References 2 and 3). This was attributed to the electronic effects of a perfluoroaromatic nucleus which would render a perfluorophenolate anion a poor nucleophile. Regardless of substrate, the bulk of a nucleophile at the reactive site could also determine reactivity. Reasoning that a hydrated (or alcoholated) salt of a perfluorophenol would be a poorer nucleophile than its "free" analog, the anhydrous sodium salts of 4-hydrotetrafluoro- and pentafluorophenol were prepared.

Sodium methoxide at 0°C* smoothly converted these phenols to their corresponding salts.



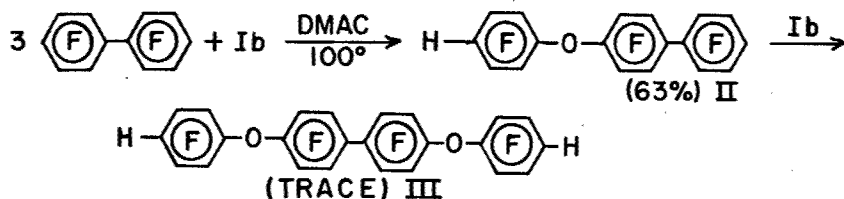
As expected, proton transfer from the phenol to methoxide was much faster than base-substitution on the perfluoroaromatic nucleus.

The two salts, isolated as white powdery solids, were heated in a vacuum oven to remove any residual methanol.

2. REACTIONS OF PERFLUOROPHENOL SALTS WITH DECAFLUOROBIPHENYL

a. 4-(4-Hydrotetrafluorophenoxy)-nonafluorobiphenyl (II)

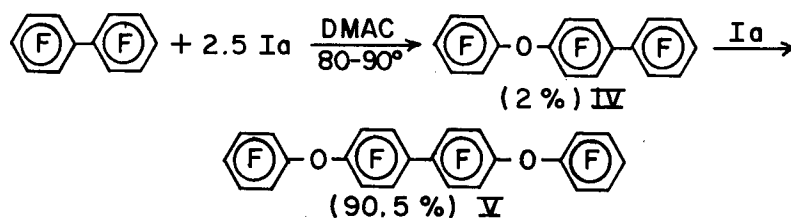
By reacting a threefold excess of decafluorobiphenyl with Ib in N,N-dimethylacetamide (DMAC), a 63 percent yield of 4-(4-hydrotetrafluorophenoxy)-nonafluorobiphenyl (II) was obtained. Traces of the bis-compound III existed in the crude reaction mixture.



b. 4,4'-Bis(pentafluorophenoxy)-octafluorobiphenyl (V)

In an experiment similar to the above, V was isolated in a 90.5 percent yield by reacting a 2.5-fold excess of Ia with decafluorobiphenyl. Approximately 2 percent of the monosubstituted biphenyl, IV, was identified in the crude reaction mixture.

*All temperatures cited are degrees centigrade.



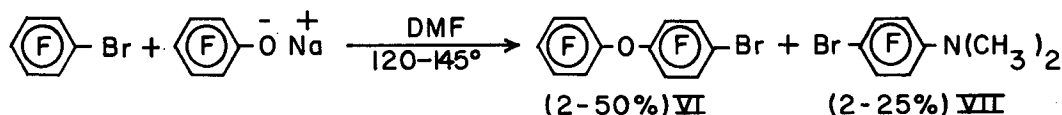
The Hammett substituent constant σ_p predicts that the reaction rates of Ia and Ib on the same substrate would be of similar orders of magnitude. Trial experiments, where Ia and Ib were reacted with decafluorobiphenyl under similar conditions verify the prediction. These reactions appear to go to completion at approximately the same time. Therefore, one would expect that the reaction of Ia with decafluorobiphenyl to give V and of Ib with decafluorobiphenyl to give III, as the major products, could be achieved by appropriately changing the stoichiometry of the reactants.

3. REACTIONS OF SODIUM PENTAFLUOROPHENOLATE WITH MONOSUBSTITUTED HEXAFLUOROBENZENE

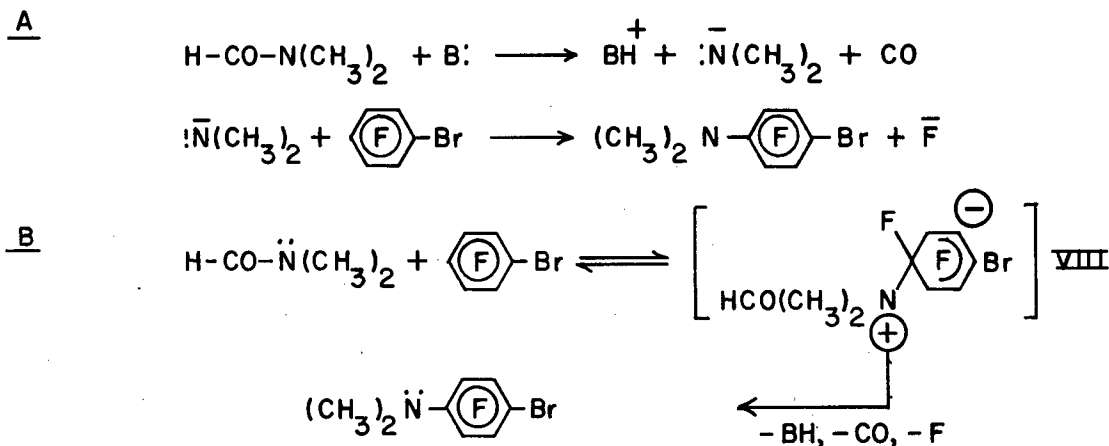
a. 4-Bromononafluorodiphenyl Ether (VI)

4-Bromononafluorodiphenyl ether (VI) was the first in a series of monosubstituted perfluorophenyl ethers that was prepared by the action of sodium pentafluorophenolate on a substituted pentafluorobenzene. Experiments varying reaction parameters (solvent, mole ratio of reactants, temperature, and time) were carried out in order to obtain the optimum yield of VI. Table I summarizes the results.

In dimethylformamide (DMF), varying yields of VI were obtained in addition to an undesirable side product VII.



Competing with the reaction forming VI was a side reaction that incorporated solvent into the perfluoroaromatic nucleus VII. This side reaction was found to be base-catalyzed since VII was formed faster and in higher yields in the presence of sodium pentafluorophenolate (see Table I). Two reasonable mechanisms for the side reaction can be offered.



Mechanism B is attractive since the positive charge on the nitrogen atom should enhance the departure of the formyl proton of VIII relative to the same proton in DMF. It is not surprising that by changing the solvent to DMAC, VII is no longer detectable. It is evident from Table I that DMAC is the solvent of choice for these reactions.

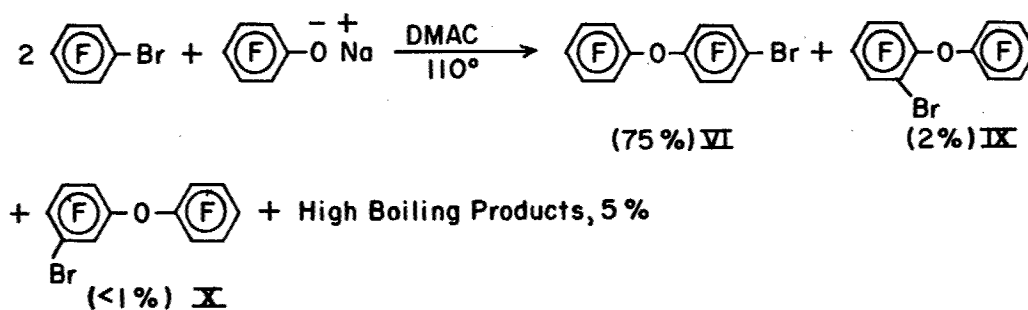
High boiling products were detectable in the crude mixtures of both the DMF and DMAC reactions. These products are probably isomeric terphenyl ethers which can be minimized by (1) using a twofold excess of the substituted pentafluorobenzenes to the fluorophenoxide anion and (2) lowering reaction temperatures.

Two peaks consistently flanked (preceded and followed) VI on analyzing the crude reaction mixtures by vapor phase chromatography (vpc). These peaks were barely separable from VI which suggests their isomeric nature. Their sum area was approximately equivalent (DMAC, 110°) to 3 percent of VI. Tedious separation of the first (of the three) peak by preparative vpc afforded a colorless viscous oil whose infrared and F^{19} nuclear magnetic resonance (nmr) spectra were recorded. The F^{19} nmr spectrum had absorptions at 79.3 ppm (area 2) 83.0 ppm (area 1), and 84.9 ppm (area 2), whose multiplets and relative areas were characteristic of a pentafluorophenoxy group. The three remaining multiplets resonated at 52.7 ppm (doublet with fine structure, area 1), 77.2 ppm (broad distorted doublet, area 2) and 80.4 ppm (complicated multiplet, area 1). By irradiating the 77.2 ppm doublet, the absorption at 52.7 ppm resolved into a sharp doublet ($J \sim 21$ cps). Assuming that this product is isomeric, the spectrum is more consistent with structure IX than structure X. Both F7 and F8 in X would be expected to resonate at 53 ± 3 ppm.



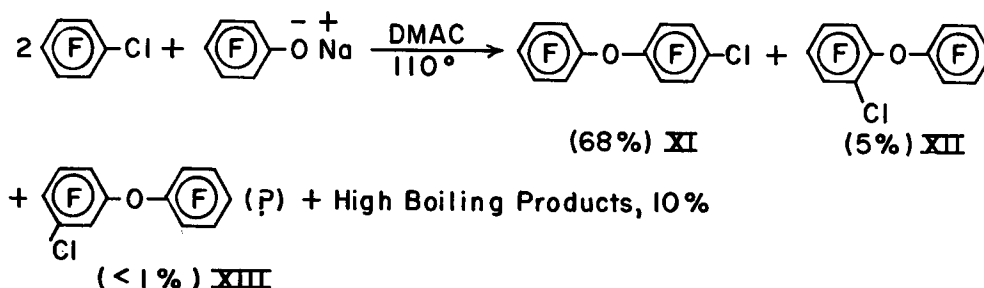
The following assignments were made: F₁(52.7 ppm), F_{2,2'}(77.2 ppm), F₃(79.3 ppm), F₄(80.4 ppm), F₅(83.0 ppm), F₆(84.9 ppm).

The overall scheme for the reaction is



b. 4-Chlorononafluorodiphenyl Ether (XI)

Reaction of chloropentafluorobenzene with sodium pentafluorophenolate in DMAC gave 4-chlorononafluorodiphenyl ether (XI) in 68 percent yield. Analysis of the crude reaction mixture (vpc) revealed three peaks of similar retention times in a 6:94: < 1 ratio, respectively (in the bromopentafluorobenzene reaction, the analogous ratio was 3:97: < 1). This is consistent with the assignment of the first peak to 2-chlorononafluorodiphenyl ether (XII) since it is well documented that chloropentafluorobenzene has a greater ortho:para ratio than bromopentafluorobenzene in nucleophilic substitution reactions (References 4 and 5).

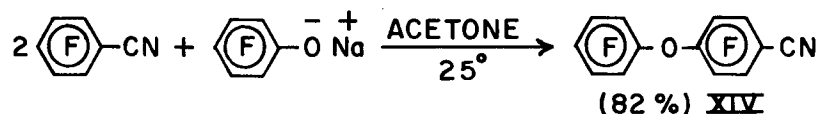


The assignment of the peak following XI to the meta-diphenyl ether XIII seems reasonable but speculative.

It is worthy to note that decafluorodiphenyl ether was absent from both the bromo and chloropentafluorobenzene reactions. This infers that the transition state leading to VI or XI has a lower energy of activation than the transition state affording decafluorodiphenyl ether. A ratio of decafluorodiphenyl ether to VI or XI of 1:99 corresponds to a ΔE^* of approximately 3 Kcal (110°).

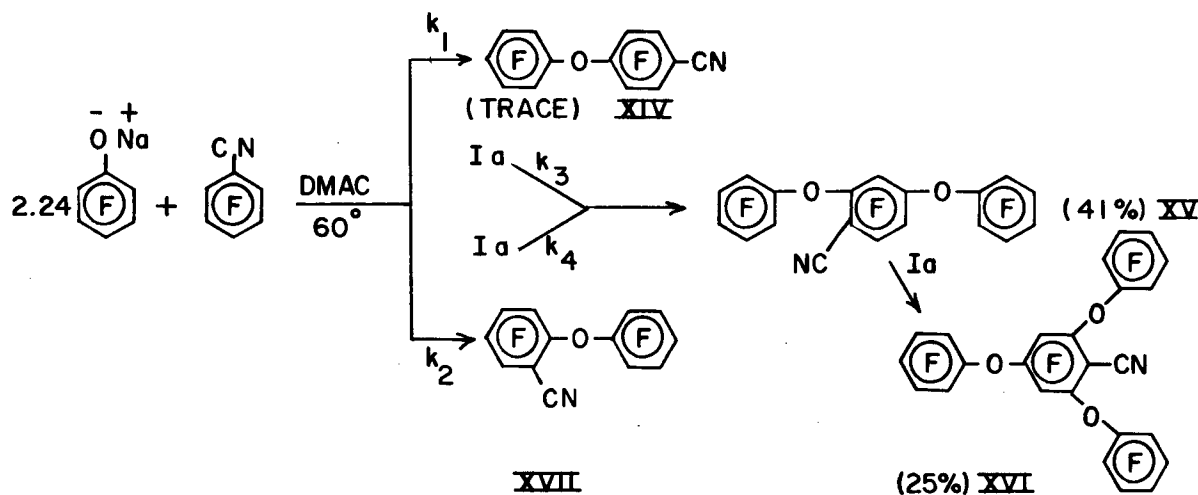
c. 4-Cyanononafluorodiphenyl Ether (XIV)

4-Cyanononafluorodiphenyl ether (XIV) was synthesized in an 82 percent yield by reacting a twofold excess of pentafluorobenzonitrile with sodium pentafluorophenolate in acetone at room temperature. Less than 2 percent of isomers and high boiling products was detected under these conditions.



A preliminary experiment using equimolar amounts of reactants (70°, DMAC) showed an unusual abundance of polysubstitution products. An experiment was then devised to isolate and identify these products.

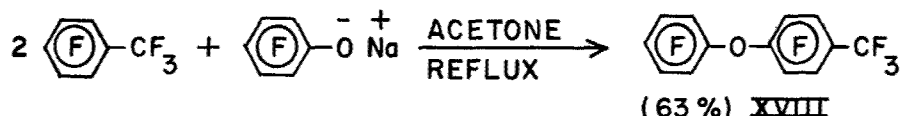
When 2.24 equivalents of sodium pentafluorophenolate was reacted with one equivalent of pentafluorobenzonitrile (60° in DMAC), two high boiling products were formed which were identified as XV and XVI. As the reaction proceeded, XIV and a peak (vpc) just preceding it, XVII, increased in concentration and then diminished. Their ratio was relatively constant (ca 10:1 respectively) during the initial stages of the reaction. However, as XV appeared, this ratio became progressively larger, implying that XVII is consumed faster than XIV. This phenomenon can be rationalized by the following scheme, where $k_1 > k_2$ and $k_4 > k_3$.



From the facile polysubstitution found in this scheme it is evident that the nitrile group is a strong activator for nucleophilic substitution reactions.

d. 4-Trifluoromethylnonafluorodiphenyl Ether (XVIII)

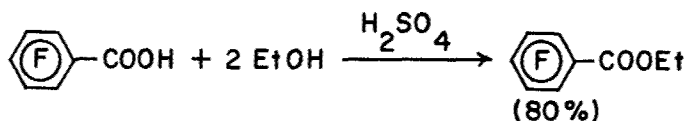
When a twofold excess of octafluorotoluene to sodium pentafluorophenolate was refluxed in acetone, 4-trifluoromethylnonafluorodiphenyl ether (XVIII) was isolated in 63 percent yield. Traces (1%) of side products were detectable (vpc) in the crude reaction mixture. When



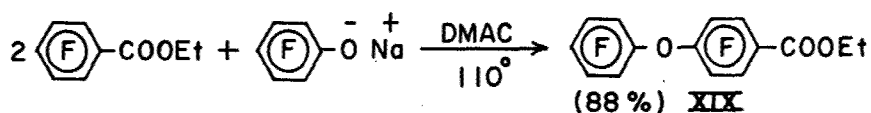
this reaction was attempted at room temperature, no appreciable product was formed in 24 hours. By using a 1.5 equivalent excess of octafluorotoluene to sodium pentafluorophenolate at 110° in DMAC and 80 percent yield of XVIII was obtained.

e. 4-Carboethoxynonafluorodiphenyl Ether (XIX) and Its Related Acid

Ethyl pentafluorobenzoate was prepared in an 80 percent yield from its corresponding acid via an acid-catalyzed esterification.

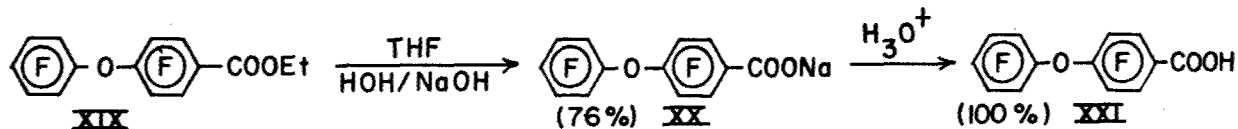


By reacting this ester with sodium pentafluorophenolate, 4-carboethoxynonafluorodiphenyl ether (XIX) was isolated in an 88 percent yield.



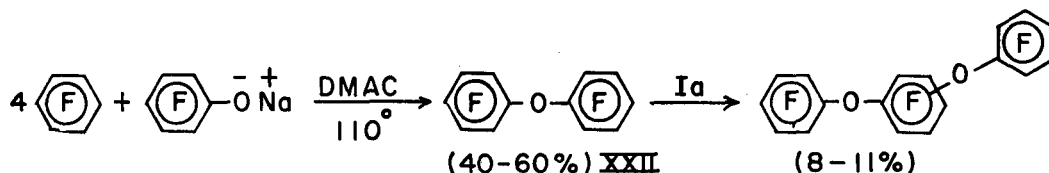
Only traces (<1%) of isomeric or high boiling products (vpc) were detected in the crude reaction mixture. It is not surprising that the ortho positions in the starting ester (ortho to COOC₂H₅ group) are unreactive; the carboethoxy group can provide a considerable amount of nonbonded interaction to an approaching nucleophile.

The ester XIX was easily hydrolyzed in aqueous basic tetrahydrofuran (THF) to the acid via the salt XX which could be isolated.



f. Decafluorodiphenyl Ether (XXII)

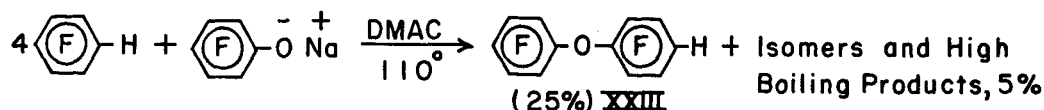
Decafluorodiphenyl ether (XXII) was prepared in yields ranging from 40 to 60 percent by reacting a fourfold excess of hexafluorobenzene with sodium pentafluorophenolate. This excess was necessary to reduce the yield of high boiling products (probably terphenyl ethers). About 10 percent of these by-products were isolated. This fact encourages future attempts to synthesize perfluoropolyphenyl ether polymers.



Since isomers of XXII are impossible, the peaks (vpc) that usually accompany these reactions (flanking the major product) were undetectable.

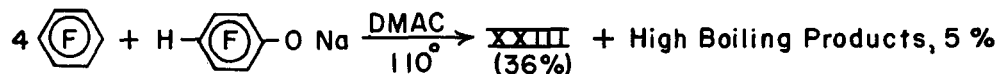
g. 4-Hydrononafluorodiphenyl Ether (XXIII)

4-Hydrononafluorodiphenyl ether was synthesized in a low yield (25%) by the action of sodium pentafluorophenolate on a fourfold excess of pentafluorobenzene. The reaction mixture was composed of ca 5 percent isomers and other high boiling material. Continued heating did not affect the yield. Apparently, the reaction does not go to completion under these conditions.



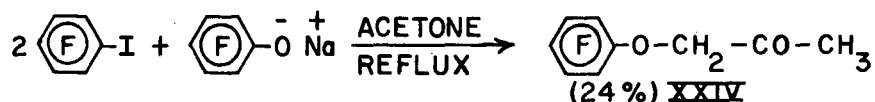
Hydropentafluorobenzene seems to be the limit for observing a reaction between a substituted pentafluorobenzene and sodium pentafluorophenolate.

XXIII was also prepared (isomer free) in a 36 percent yield by reacting hexafluorobenzene with 4-hydrotetrafluorophenolate.

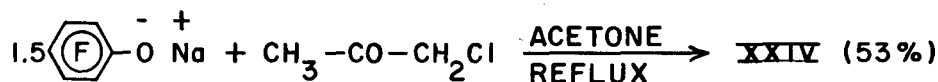


h. Reaction of Iodopentafluorobenzene With Sodium Pentafluorophenolate

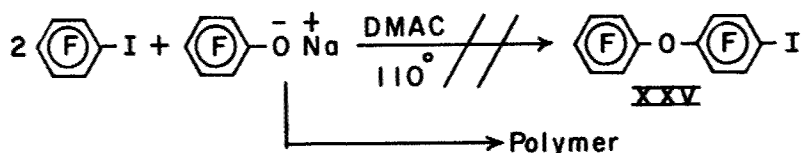
In the reactions of sodium pentafluorophenolate with halopentafluorobenzenes (I, Br, Cl, F), the iodo-compound is anomalous. The reaction between two equivalents of iodopentafluorobenzene and sodium pentafluorophenolate in acetone afforded one product, XXIV.



This product could arise via a facile $\text{S}_{\text{N}}2$ reaction of phenolate ion with iodoacetone. The presence or mode of formation of iodoacetone was not established. Compound XXIV was also synthesized by an alternate route.



Attempts to obtain 4-iodononafluorodiphenyl ether (XXV) in DMAC at elevated temperatures afforded a polymer.



Further work with iodopentafluorobenzene was arrested.

i. Stability of Sodium Pentafluorophenolate

When sodium pentafluorophenolate was refluxed in DMAC for 19 hours, the bulk of it was recovered as the phenol (75%) after acidification. A dark brittle polymer was also obtained.

It seems reasonable, therefore, to assume that little, if any, of the salt polymerized during the reactions which afforded substituted nonafluorobiphenyl ethers.

4. SPECTRAL PROPERTIES OF 4-SUBSTITUTED NONAFLUORODIPHENYL ETHERS

The infrared spectra of the monosubstituted nonafluorodiphenyl ethers had characteristic bands at $6.7 \pm 1.1 \mu$ (C=C), $8.6 \pm 1.1 \mu$ (Ar-O), and $9.8 \pm 2.2 \mu$ (C-F).

The 40 mc F^{19} nmr spectra (see Table II) of the ethers demonstrated typical pentafluorophenoxy absorptions at $+78.5 \pm 1.5$ ppm, $+82 \pm 2$ ppm, $+84.5 \pm 2.5$ ppm (CCl_4 or Me_2CO relative to trifluoroacetic acid (TFAA)). The remaining parts of these spectra basically exhibited AA'XX' patterns. Couplings were reported wherever possible.

5. KINETICS

The relative rates of reaction between seven pairs of monosubstituted pentafluorobenzenes were measured. The results are given below:

$$\frac{k_{\text{C}_6\text{F}_5\text{CN}}}{k_{\text{C}_6\text{F}_5\text{CF}_3}} = 39 (47^\circ)$$

$$\frac{k_{\text{C}_6\text{F}_5\text{Br}}}{k_{\text{C}_6\text{F}_5\text{Cl}}} = 1.2 (106^\circ)$$

$$\frac{k_{\text{C}_6\text{F}_5\text{CF}_3}}{k_{\text{C}_6\text{F}_5\text{CO}_2\text{Et}}} = 8.2 (106^\circ)$$

$$\frac{k_{\text{C}_6\text{F}_5\text{Cl}}}{k_{\text{C}_6\text{F}_6}} = 32 (\text{actual } 5.4, 106^\circ)$$

$$\frac{k_{\text{C}_6\text{F}_5\text{CO}_2\text{Et}}}{k_{(\text{C}_6\text{F}_5)_2}} = 4.0 (\text{actual } 2.0, 106^\circ)$$

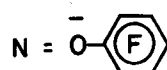
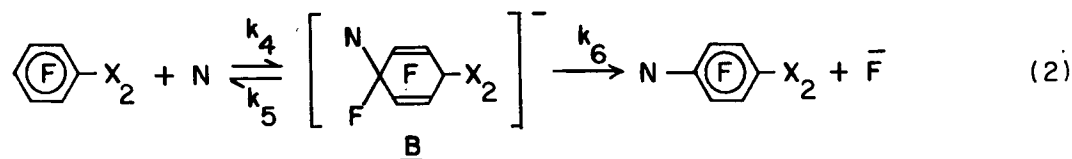
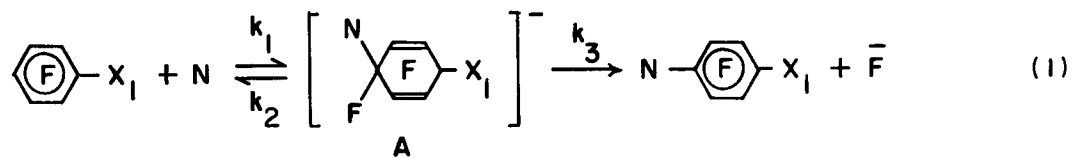
$$\frac{k_{\text{C}_6\text{F}_6}}{k_{\text{C}_6\text{F}_5\text{H}}} = .91 (\text{actual } 5.5, 106^\circ)$$

$$\frac{k_{\text{C}_6\text{F}_5\text{CO}_2\text{Et}}}{k_{\text{C}_6\text{F}_5\text{Br}}} = 75 (106^\circ)$$

$\frac{C_6F_5X}{}$	Rel Rate
CF_3	2.4×10^4
CO_2Et	2.9×10^3
C_6F_5	7.3×10^2
Br	39
Cl	32
H	1
F	.91

The rate expression utilized was derived accordingly:

Given the paths for two substituted pentafluorobenzenes



$$\frac{d \left[\text{N} \text{---} \text{C}_6\text{F}_4\text{X}_1 \right]}{dt} = k_3 \text{A} \quad (3)$$

$$\frac{d \left[\text{N} \text{---} \text{C}_6\text{F}_4\text{X}_2 \right]}{dt} = k_6 \text{B} \quad (4)$$

Applying the steady state hypothesis (Reference 6) to intermediates A and B, one obtains:

$$[\text{A}] = \frac{k_1 \left[\text{C}_6\text{F}_5\text{X}_1 \right] [\text{N}]}{k_2 + k_3} ; \quad [\text{B}] = \frac{k_4 \left[\text{C}_6\text{F}_5\text{X}_2 \right] [\text{N}]}{k_5 + k_6}$$

Dividing Equation 3 by Equation 4 and substituting for A and B the expression

$$\frac{d \left[\text{N}-\text{C}_6\text{H}_4\text{X}_1 \right]}{d \left[\text{N}-\text{C}_6\text{H}_4\text{X}_2 \right]} = \frac{K \left[\text{C}_6\text{H}_5\text{X}_1 \right]}{\left[\text{C}_6\text{H}_5\text{X}_2 \right]} ; K = \frac{k_1 k_3 (k_5 + k_6)}{k_4 k_6 (k_2 + k_3)} \quad (5)$$

is obtained.

Assuming that [A] and [B] at any time (t) is negligible to

$$\begin{aligned} & \left[\text{C}_6\text{H}_5\text{X}_1 \right], \left[\text{C}_6\text{H}_5\text{X}_2 \right] \text{ and } \left[\text{N}-\text{C}_6\text{H}_4\text{X}_1 \right], \left[\text{N}-\text{C}_6\text{H}_4\text{X}_2 \right] \text{ it follows that} \\ & \left[\text{C}_6\text{H}_5\text{X}_1 \right]_t = \left[\text{C}_6\text{H}_5\text{X}_1 \right]_0 - \left[\text{N}-\text{C}_6\text{H}_4\text{X}_1 \right] \text{ and} \\ & \left[\text{C}_6\text{H}_5\text{X}_2 \right]_t = \left[\text{C}_6\text{H}_5\text{X}_2 \right]_0 - \left[\text{N}-\text{C}_6\text{H}_4\text{X}_2 \right] \end{aligned}$$

Substitution into Equation 5 and integrating gives the rate expression:

$$K = \frac{\text{Log} \frac{\left[\text{C}_6\text{H}_5\text{X}_1 \right]_0 - \left[\text{N}-\text{C}_6\text{H}_4\text{X}_1 \right]}{\left[\text{C}_6\text{H}_5\text{X}_1 \right]_0}}{\text{Log} \frac{\left[\text{C}_6\text{H}_5\text{X}_2 \right]_0 - \left[\text{N}-\text{C}_6\text{H}_4\text{X}_2 \right]}{\left[\text{C}_6\text{H}_5\text{X}_2 \right]_0}} = \text{Relative Rate of Reaction}$$

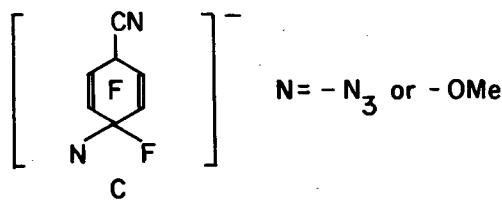
The concentrations of $\text{N}-\text{C}_6\text{H}_4\text{X}_1$ and $\text{N}-\text{C}_6\text{H}_4\text{X}_2$ were measured by vpc using triphenylmethane as a standard. No allowance was made for the substitution of fluorine atoms ortho or meta to X since substitution of this type in our system is minor. In essence, therefore, the rates tabulated are the relative rates of formation of the para isomers.

Six of the reactions (pairs) were analyzed when they had proceeded between 25 and 90 percent completion. The last (fluorine-hydrogen) was measured during its early stages (11-19%) to assure that aliquots were withdrawn before the hydropentafluorobenzene/pentafluorophenoxide reaction terminated (this reaction did not go to completion).

A plot of $\log k$ (relative rate) against the Hammett σ_p gives a straight line with $\rho = 7.5$. From the graph the σ_p of a pentafluorophenyl group can be estimated at +0.4 (COOH = +0.406). The

large magnitude of ρ is a striking reflection of the delocalization demanded by the intermediate carbanion A or B (Equations 1 and 2, respectively). In the pentafluorophenoxide monofunctional pentafluorobenzene reactions studied para substitution predominated. With chloro and bromopentafluorobenzene as substituents, the ortho:para:meta substitution ratios were 6:94:<1 and 3:97:<1, respectively. In these reactions, the ortho:para and the meta:para ratios are smaller than those obtained using methoxide as the nucleophile (References 4 and 7). This is consistent with the intuitive expectation that the more reactive nucleophile (methoxide) should be less selective. A change in nucleophile from methoxide to pentafluorophenoxide would also be expected to decrease the ortho:para ratio from steric considerations. For CF_3 , $\text{CO}_2\text{C}_2\text{H}_5$, and C_6F_5 substituents, para substitution greater than 98 percent was observed.

At high temperature the pentafluorobenzonitrile-pentafluorophenolate reaction was extremely rapid, and formed a considerable amount of isomeric and polysubstituted products. By dropping the temperature to 47°C , side products of this type were inappreciable (<10%). The reactions of this substrate were much faster than anticipated. It would not be surprising if k_2 (Equation 1, $\text{X} = \text{CN}$) is of the same order of magnitude as k_3 . It would be instructive if intermediates like C could be isolated in similar reactions.



SECTION III

EXPERIMENTAL

Melting points were determined in a Buche (oil bath) apparatus. Boiling points and melting points are uncorrected. The F^{19} nmr spectra were recorded on a Varian V-4300-2 DP spectrometer at 40.0 mc/s. Chemical shifts are reported in ppm from external TFAA. Carbon tetrachloride was used as the solvent unless otherwise stated. The H^1 nmr spectra were recorded on a Varian A-60 spectrometer in carbon tetrachloride. Chemical shifts are reported as ppm from the internal standard tetramethylsilane (TMS). Infrared spectra were run on a Perkin-Elmer "Infracord" spectrophotometer as KBr pellets or as liquid films. Vapor phase chromatography analysis was done on an F & M model 500 instrument using a helium flow of 60 cc per minute, 6' x 1/4" column, 20 percent Apiezon L on 60 to 80 mesh Chromasorb W and programmed from 100° to 275° (21° per minute) after which it was held at this temperature.

1. SODIUM 4-HYDRO-PENTAFLUOROPHENOLATE (Ib)

Sodium metal (11.5 g, 0.500 g/at.) was dissolved in 700 ml of absolute methanol. To the methoxide solution which was cooled to -10° (methanol-ice), 4-hydro-tetrafluorophenol (83.0 g, 0.500 mole) dissolved in 100 ml of methanol, was added dropwise with stirring over a one-hour period. The temperature was maintained at -10° to 0°. At the completion of the addition, an aspirator was attached to the system and the methanol was removed at reduced pressure (ca 20 mm). The white solid that remained was triturated with 300 ml of chloroform and dried in a vacuum oven (70° at 1 mm) until no further weight loss was noticed. The white salt, mp over 350°, was soluble in water and most polar organic solvents (yield 98-100%).

2. 4-(4-HYDROTETRAFLUOROPHENOXY)-NONAFLUOROBIPHENYL (II)

Decafluorobiphenyl (155 g, 0.411 mole) was dissolved in 500 ml of DMAC. To this stirred solution sodium 4-hydro-tetrafluorophenolate (25.8 g, 0.137 mole) was added in an atmosphere of nitrogen. The reaction mixture was heated to 100° and maintained at this temperature for 3.5 hours. A sample of the mixture withdrawn and analyzed by vpc indicated two peaks (besides solvent) decafluorobiphenyl and the desired product. There was also a trace (< 2%) of a higher boiling component which was identified as a disubstituted biphenyl. The ratio of the peaks was unchanged when the reaction mixture was heated for another hour. The cooled mixture was added to 1500 ml of distilled water and the solid that settled was filtered, dried, and fractionally sublimed (30°/.5 mm and 100°/.5 mm). The first sublimate consisted of ca 90 percent decafluorobiphenyl and 10 percent of the desired product II. The residue from the first sublimation was placed in a flask and heated at reduced pressure (100°/.3 mm) to remove the last traces of decafluorobiphenyl. On cooling the residue, 32.0 g of an off-white solid, mp 58° to 60°, was obtained. A pure white sample mp 61° to 63°, was obtained by eluting a petroleum ether (30°-60°) solution of the residue from an alumina column with petroleum ether (30°-60°).

From the first sublimate (90:10 mixture), an additional 9.6 g of product II (98% pure) was obtained by recrystallization from methanol (to remove the decafluorobiphenyl) and further sublimation. The overall yield of the desired compound II was 63 percent.

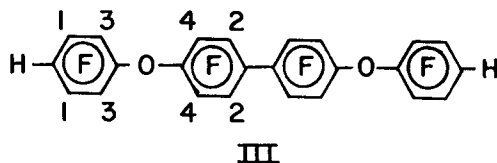
Analysis—Calcd for $C_{18}HF_{13}O$: C, 45.00; H, 0.21. Found: C, 44.93; H, 0.26.

The H^1 nmr spectrum of this compound exhibited a triplet of triplets centered at 7.0 ppm with orthofluoro/hydrogen and metafluoro/hydrogen coupling constants of 9.8 and 7.0 cps, respectively.

In a preliminary experiment equimolar amounts of decafluorobiphenyl and sodium 4-hydrotetrafluorophenolate under similar reaction conditions gave rise to a mixture of mono- and disubstituted perfluorobiphenyls II and III. Separation was achieved by careful alumina chromatography; the disubstituted perfluorobiphenyl III had a mp of 106° to 108°.

Analysis—Calcd for $C_{24}H_2F_{16}O_2$: C, 46.00; H, 0.32, mw, 626. Found: C, 46.03; H, 0.49, mw 626 (mass spectrum).

The H^1 nmr spectrum of III was exactly the same as the monosubstituted product II. Its F^{19} nmr spectrum had multiplets at 59.0 ppm (area 1) and 76.7 ppm (area 1) which were assigned to the fluorine atoms at positions 1-2 and 3-4.



3. SODIUM PENTAFLUOROPHENOLATE (Ia)

The procedure for the preparation of sodium 4-hydropentafluorophenolate was followed. A white-powdery salt, mp 320° (d), was obtained in a 95 to 100 percent yield.

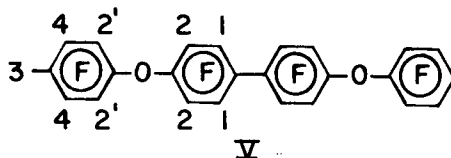
4. 4,4' BIS(PENTAFLUOROPHENOXY)OCTAFLUOROBIPHENYL (V)

In a nitrogen atmosphere, sodium pentafluorophenolate (25.88 g, 0.125 mole), decafluorobiphenyl (16.7 g, 0.050 mole), and 600 ml of DMAC were stirred and heated between 80° to 90°. The reaction was followed by vpc. After 140 hours at this temperature, two peaks were obtained in a 2 (shorter retention time, compound IV): 98 area ratio. The reaction mixture was cooled and added to 1500 ml of water. The tan solid that precipitated was filtered and dried (27.5 g) mp 161° to 165°.

The aqueous DMAC solution was extracted with chloroform (3 x 100 ml). The extracts were combined, extracted with water (4 x 100 ml), dried ($MgSO_4$), and evaporated to dryness. The dark residue that remained was triturated with cold methanol and filtered leaving 3.5 g of a tan solid, mp 160° to 165°, which was combined with the previous batch (total 31.0 g, 90.5%). This crude material was dissolved in methylene chloride, placed on an alumina column and eluted with methylene chloride. Recrystallization from ethanol/benzene gave an analytical sample, mp 170° to 171°.

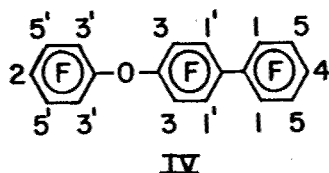
Analysis—Calcd for $C_{24}F_{18}O_2$: C, 43.53; F, 51.64. Found: C, 43.44; F, 51.75.

The F^{19} nmr spectrum consisted of four multiplets at 58.9 ppm (area 2), 77.5 ppm (area 4), 80.3 ppm (area 1) and 85.0 ppm (area 2) which were assigned to the fluorine substituents at the 1, 2-2', 3, and 4 positions, respectively.



A trial experiment gave a mixture of mono- and disubstituted pentafluorophenoxyperfluorobiphenyls. The monosubstituted isomer, IV, mp 57° to 59°, was isolated and characterized. Its molecular weight was 498 (mass spectrum).

Its F^{19} nmr spectrum had a multiplet at 58.4 ppm (area 4), triplet at 70.9 ppm (area 1, $JF_{25'} \sim 20$ cps), multiplet at 77.0 ppm (area 4), triplet at 79.9 ppm (area 1, $JF_{45'} \sim 20$ cps) and a multiplet at 82.0 (area 4). These resonances were assigned to the fluorine atoms at positions 1-1', 2, 3-3', 4, and 5-5', respectively.



5. 4-BROMONONAFLUORODIPHENYL ETHER (VI)

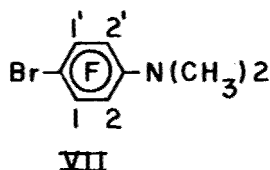
Method A. In a nitrogen atmosphere, bromopentafluorobenzene (11.95 g, 0.0480 mole), sodium pentafluorophenolate (10.0 g, 0.0480 mole), and 250 ml of DMF were heated at 120° for 18 hours. The mixture was cooled and added to 500 ml of distilled water. The aqueous DMF solution was extracted with benzene (or 30°-60° petroleum ether) (4 x 100 ml) and the combined dried extracts were concentrated. The residue, consisting of DMF, unreacted bromopentafluorobenzene, and a high boiling product, were distilled at reduced pressure (40°-50° at 15 mm) to remove DMF and unreacted starting material. After cooling, the residue that solidified was dissolved in and eluted from a short alumina column with petroleum ether (30°-60°). Recrystallization from methanol (or 95% ethanol) yielded 5.0 g (25%) of a white crystalline solid, mp 85° to 86°.

Analysis—Calcd for $C_{12}F_9OBr$: C, 35.06; F, 41.66; Br, 19.44. Found: C, 34.98; F, 41.67; Br, 19.25.

Method B. In an atmosphere of nitrogen, sodium pentafluorophenolate (5.0 g, 0.026 mole), bromopentafluorobenzene (5.9 g, 0.024 mole), and 125 ml of DMF were stirred and heated to 145°. The reaction was monitored by vpc. After four hours, three peaks were observed; unreacted starting material, VII and the desired bromoether, VI. As the reaction continued, the starting material and bromoether peaks decreased while product VII increased. After 20 hours, analysis by vpc revealed the presence of only one major peak, VII. Traces of bromopentafluorobenzene and the bromoether were detectable. The reaction mixture was cooled and added to 750 ml of distilled water. The aqueous DMF solution was extracted with methylene chloride (3 x 100 ml). The combined methylene chloride extracts were extracted with water (4 x 50 ml), dried ($MgSO_4$) and evaporated to dryness leaving a dark, oily residue. The residue was distilled at reduced pressure yielding 1.5 g (24%) VII, of a colorless oil, bp 52° at 1 mm. The tars that remained in the pot were discarded.

The H^1 nmr spectrum of VII exhibited a triplet ($J = 2$ cps) at 2.92 ppm which is characteristic for dimethylamino group flanked by two fluorines.

From this spectrum and elemental analysis, a structure for VII was assigned:



Analysis—Calcd for $C_8H_6F_4BrN$: C, 35.32; H, 2.23; F, 27.94; Br, 29.37; N, 5.15. Found: C, 35.71; H, 2.27; F, 28.14; Br, 29.38; N, 5.02.

The F^{19} nmr spectrum of VII displayed a 10-line resonance (half of an $AA'XX'$ pattern) centered at 56.1 ppm (area 1) and a symmetrical but more complicated multiplet centered at 70.0 ppm (area 1). By irradiating methyl protons, the absorption at 70.0 ppm simplified into the other half of an $AA'XX'$ pattern. The experimentally derived coupling constants are $J_{12} = 20.7$ cps, $J_{12}' = 6.4$ cps, $J_{11}' = 4.6$ cps, and $J_{22}' = 2.6$ cps.

VII was independently prepared by refluxing bromopentafluorobenzene in DMF for 72 hours. The yield was low (ca 15%) since the reaction did not go to completion.

Method C. To 100 ml of DMAC was added sodium pentafluorophenolate (3.5 g, 0.017 mole) and bromopentafluorobenzene (8.4 g, 0.034 mole) in a nitrogen atmosphere. The mixture was stirred and heated to 110° and maintained at this temperature until the product peak (vpc) no longer increased (ca 9 hrs). The reaction was cooled and the mixture was added to 500 ml of distilled water. The aqueous DMAC was extracted with benzene (or 30°-60° petroleum ether) (3 x 100 ml), and the combined extracts were extracted with water (3 x 100 ml), dried ($MgSO_4$), and evaporated to dryness leaving 5.7 g (70%) of 95 to 98 percent 4-bromononafluorodiphenyl ether, mp 79° to 82°. By eluting this solid from a short alumina column (30°-60° petroleum ether) a pure white solid, mp 82° to 84°, was obtained.

6. 4-CHLORONONAFLUORODIPHENYL ETHER (XI)

In an atmosphere of nitrogen, sodium pentafluorophenolate (10.4 g, 0.0520 mole), chloropentafluorobenzene (21.2 g, 0.104 mole), and 300 ml of DMAC were stirred and heated to 110°. After 15 hours the analyzed reaction mixture showed two peaks (vpc ca 6:94 ratio). The mixture was cooled and added to 1 liter of distilled water. The oily layer that settled to the bottom of the aqueous DMAC solution was separated, taken up in benzene, and concentrated at reduced pressure, depositing an off-white solid (11.2 g), mp 65° to 69°, that consisted of a 6:94 ratio of two products (probably isomers, vpc). The aqueous DMAC solution was further extracted with benzene (3 x 100 ml) and the combined extracts were concentrated leaving 2.1 g of an oil from which 1.5 g of additional product could be obtained. (The total weight of crude product was 12.7 g (68%)). This mixture was purified by elution with petroleum ether (30°-60°) from a short alumina column and recrystallized from methanol to a mp of 74° to 75°.

Analysis—Calcd for $C_{12}F_9OC1$: C, 39.32; F, 46.65; Cl, 9.67. Found: C, 39.54; F, 46.45; Cl, 9.9. The F^{19} nmr data is presented in Table II.

7. 4-CYANONONAFLUORODIPHENYL ETHER (XIV)

Pentafluorobenzonitrile (20.0 g, 0.104 mole), sodium pentafluorophenolate (10.4 g, 0.0520 mole), and 200 ml of anhydrous acetone were stirred together at room temperature under a helium atmosphere, until the reactant (C_6F_5CN) and product peaks (vpc) remained constant. Less than two percent of side products were present in this crude reaction mixture. The solvent was evaporated and the unreacted pentafluorobenzonitrile was removed by distillation at reduced pressure (25° at 1 mm). The residue was triturated with petroleum ether (30° to 60°) and filtered to remove 1.7 g of inorganic salts. Concentration of the filtrate deposited an off-white solid which was recrystallized from methanol-water (40:3) to obtain 12.3 g of a white solid, mp 61° to 62°.

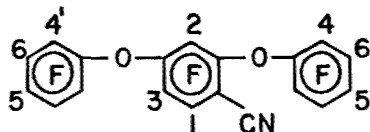
The mother liquor was concentrated leaving 4.8 g of a solid. This crude material was dissolved in petroleum ether (30°-60°) and eluted from an alumina column with petroleum ether (30°-60°). Further recrystallization (methanol-water) yielded 2.8 g of product, mp 59° to 62° (15.1 g total, 82% yield). A vpc trace of the combined solids showed less than one percent impurity (probably isomeric).

Analysis—Calcd for $C_{13}F_9NO$: C, 43.72; F, 47.88; N, 3.92. Found: C, 43.73; F 47.62; N, 3.95.

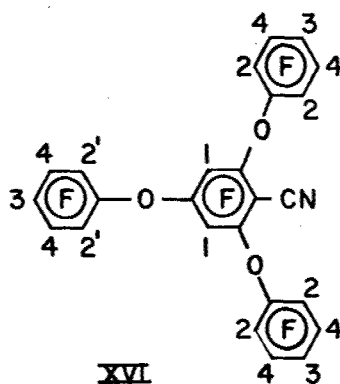
8. REACTION OF PENTAFLUOROBENZONITRILE WITH SODIUM PENTAFLUOROPHENOLATE—MULTIPLE SUBSTITUTION

Pentafluorobenzonitrile (3.27 g, 0.0170 mole) and sodium pentafluorophenolate (7.83 g., 0.0380 mole) were added to DMAC (100 ml) kept under an atmosphere of nitrogen. The reaction mixture was maintained at 60° for 18 hours. Analysis (vpc) revealed the presence of 4-cyanononafluorodiphenyl ether (less than 2%) and two higher boiling components. The reaction mixture was cooled and filtered. The filtrate was then added to 300 ml of distilled water, causing a solid to precipitate. The aqueous DMAC solution was decanted, the solid was washed with water and cold methanol, respectively, and then dried. This crude material, 7.9 g, had a melting point range of 130° to 150°.

The solid was stirred in 80 ml of refluxing hexane and filtered while hot leaving 3.2 g of an insoluble fraction. Recrystallization from petroleum ether (90°–120°) deposited 2.9 g (25%) of a white crystalline solid, mp 184° to 185°. Structure XVI was proposed for this high melting component.



XV



XVI

Analysis—Calcd for $C_{25}F_{17}O_3N$: C, 43.82; F, 47.14; N, 2.04. Found: C, 43.94; F, 46.85, N, 2.36.

The hexane soluble fraction was concentrated and eluted from a short alumina column with hexane. Concentration of the solvent left 3.7 g (41%) of a colorless oil that solidified on standing, mp 70° to 72°.

Analysis—Calcd for $C_{19}F_{13}O_2N$: C, 43.78; F, 47.39; N, 2.69. Found: C, 43.89; F, 47.01; N, 2.71.

The F_{19} nmr spectrum of XVI (acetone) exhibited a broad singlet at 70.0 ppm (area 2) which on an expanded scale showed three distinct lines with two more (quintet) barely distinguishable. This band was assigned F_1 coupled to F_2 and $F_{2'}$. At 74.9 ppm (area 6) was a three-band multiplet (with fine structure) which is believed to be composed of two sets of superimposable doublets, F_2 and $F_{2'}$, the former being more deshielded due to the inductive and anisotropic influences of the cyano group. The remaining absorptions, distorted triplet (area 3) at 83.4 ppm, and a triplet with fine structure (area 6) at 86.4 ppm, were assigned F_3 and F_4 , respectively. The experimental coupling constants are $F_{12} \sim F_{12'} \sim 4$ cps, $F_{24} \sim 21$ cps, $F_{34} \sim 21$ cps, and $F_{23} \sim F_{23'} \sim 3$ cps.

The nmr data indicates that restricted rotation appears to be negligible due to the J_{12} coupling symmetry.

The F_{19} nmr spectrum of XV (acetone) exhibited a doublet of doublets at 55.6 ppm (area 1) assigned F_1 ($JF_{12} \sim 21$ cps, $JF_{13} \sim 10$ cps), a doublet of quintets centered at 71.8 ppm (area 1)

assigned F₂ (JF₂₃ ~ JF₂₄ ~ 4 cps), and a broad multiplet (area 1) centered at 76.1 ppm assigned to F₃. The remaining adsorptions at 76.9 ppm (area 4), 83.0 ppm (area 2), and 85.8 ppm (area 4) were assigned F₄-F_{4'}, F₅, and F₆, respectively. Similar to the spectrum of XVI the band at 76.9 ppm consisted of two sets of superimposable doublets.

9. 4-TRIFLUOROMETHYLNONAFLUORODIPHENYL ETHER (XVIII)

In an atmosphere of nitrogen, sodium pentafluorophenolate (3.3 g, 0.016 mole), octafluorotoluene (7.7 g, 0.033 mole) and 80 ml of anhydrous acetone were stirred at reflux for six days. The reaction mixture was cooled, the acetone and unreacted starting material were removed in vacuo, leaving 6.2 g of a white solid. This material was triturated with petroleum ether (30°-60°), filtered, and the filtrate was passed through a short alumina column. After removing the solvent, 4.1 g (63%) of the product, mp 62° to 63° (ca 99%, one component by vpc), was obtained.

Analysis—Calcd for C₁₃F₁₂O: C, 39.02; F, 56.98. Found: C, 39.15; F, 56.32. The F¹⁹ nmr data is presented in Table II.

10. ETHYL PENTAFLUOROBENZOATE

Absolute ethanol (46.0 g, 1.00 mole) and concentrated sulfuric acid (15.2 g) were added to a refluxing benzene solution (200 ml) of pentafluorobenzoic acid (106 g, 0.500 mole). The mixture was refluxed for 18 hours and then cooled. After adding 200 ml of diethyl ether two layers separated. The organic layer was washed until the water extracts were neutral to litmus, dried over MgSO₄, and concentrated, leaving 96.0 g of a light yellow fluid (80%) which was basically one component (96%vpc). Distillation at reduced pressure, bp 47° to 48° at 1 mm, yielded a colorless ester with a banana oil odor.

The H¹ nmr spectrum of the ester was typical for a carboethoxy group having a quartet centered at 4.45 ppm (area 2) and a triplet centered at 1.42 ppm (area 3, J = 7 cps).

An infrared spectrum (film) exhibited a carbonyl band at 5.7 μ .

11. 4-CARBOETHOXYNONAFLUORODIPHENYL ETHER (XIX)

Sodium pentafluorophenolate (16.4 g, 0.052 mole), ethylpentafluorobenzoate (33.6 g, 0.104 mole), and 300 ml of DMAC were heated to 110° and maintained at that temperature for two to three hours. The mixture was then cooled and added to 1 liter of distilled water. The oil that settled was separated and distilled at reduced pressure. Unreacted ester (16.1 g, 99+% purity by vpc) was recovered. The residue, 17.4 g, mp 45° to 46°, solidified on cooling.

The aqueous DMAC solution was extracted with benzene (or 30°-60° petroleum ether) (3 x 100 ml), the combined extracts were extracted with water (3 x 100 ml) and concentrated leaving 3.5 g of an oil. Distillation of the oil at reduced pressure removed unreacted ester and left a solid residue (1.0 g), mp 44° to 47°, which was combined with the above similar fraction (total 18.4 g, 88%). The solid was dissolved in and eluted from a short alumina column with petroleum ether (30°-60°) to give an analytical sample, mp 46° to 47°.

Analysis—Calcd for C₁₅H₅F₉O₃: C, 44.57; H, 1.25; F, 42.31. Found: C, 44.68, H, 1.30, F, 41.87.

The H¹ nmr spectrum of this ester was virtually identical to that of ethylpentafluorobenzoate. The F¹⁹ nmr data is presented in Table II.

12. 4-NONAFLUORODIPHENYL ETHER CARBOXYLIC ACID (XXI)

To 4-carboethoxynonafluorodiphenyl ether (4.4 g, 0.011 mole), dissolved in 100 ml of THF, was added sodium hydroxide (0.90 g, 0.025 mole) dissolved in 20 ml of water. The mixture was stirred at room temperature for ca 72 hours. After evaporation of the solvent, 50 ml of water was added, and the solution was filtered. The solid obtained was dried in a vacuum oven and weighed 3.3 g (76%), mp 305° to 308° (with decomposition). It was proven to be the sodium salt of the desired acid, XX. The above aqueous filtrate was acidified to pH of 1 (HCl) and extracted with ether (3 x 30 ml). The combined extracts were dried (MgSO₄) and concentrated depositing a pinkish-white solid. The solid was recrystallized twice from petroleum ether (90°-120°) to give 0.43 g (10.5%) of an analytical sample, mp 168° to 169°.

Analysis—Calcd for C₁₃HF₉O₃: C, 41.51; H, 0.27; F, 45.46. Found: C, 45.23; H, 0.36; F, 45.74.

The sodium salt was quantitatively converted to the acid by dissolving it in hot water, adding concentrated HCl to pH of 1, filtering and drying.

The F¹⁹ nmr spectrum (acetone) of the acid exhibited bands at 63.2, 80.0, 83.8, and 86.7 ppm whose areas and assignments were the same as the corresponding ethylester.

13. DECAFLUORODIPHENYL ETHER (XXII)

In an atmosphere of nitrogen, sodium pentafluorophenolate, (55.1 g, 0.250 mole), hexafluorobenzene (176 g, 1.00 mole), and 700 ml of DMAC were stirred and heated to 110°. Aliquots were periodically withdrawn from the reaction mixture and analyzed by vpc. The reaction was terminated when the product peak no longer increased (ca 24 hrs). The mixture was added to 3 liters of distilled water, the bottom layer was removed, extracted with water, dried, and concentrated, depositing 56.0 g of a tan solid, mp 55° to 58°. The aqueous DMAC solution was extracted with petroleum ether (30°-60°) (3 x 250 ml) and the combined extracts were extracted with water (3 x 100 ml), dried, and concentrated, leaving 3.1 g of crude product, mp 54° to 59°. Analysis (vpc) of the combined solids showed decafluorodiphenyl ether of approximately 85 percent purity which corresponds to a 59 percent yield. Sublimation of the crude product (65°-70° at 0.2 mm) afforded decafluorodiphenylether, mp 70° to 73° (Reference 2, mp 72°). The residue was further sublimed at 130° at 0.2 mm to give a white solid, mp 142° to 150°, which is suspected to be perfluoroterphenyl ethers (8-11%).

The infrared spectrum and retention time (vpc) of the synthetic ether was identical to those of an authentic sample.

The F¹⁹ nmr data is presented in Table II.

14. 4-HYDRONONAFLUORODIPHENYL ETHER (XXIII)

Method A. Under a nitrogen atmosphere sodium pentafluorophenolate (3.5 g, 0.017 mole), pentafluorobenzene (11.4 g, 0.068 mole), and 100 ml of DMAC were heated to 110° and maintained at that temperature for two days. The usual work-up was followed as described for compound XXII. The crude product was purified by sublimation to obtain 1.41 g (25%) of a white crystalline solid, mp 54° to 55°.

Method B. Under a nitrogen atmosphere, 150 ml of DMAC, sodium 4-hydropentafluorophenolate (7.0 g, 0.037 mole), and hexafluorobenzene (25.2 g, 0.136 mole), were stirred and heated to 110°. After 24 hours the reaction mixture was cooled and added to 450 ml of distilled water. The bottom layer was separated and concentrated leaving a white solid. The solid was triturated with petroleum ether (30°-60°) and filtered. The insoluble material 0.6 g, mp 138° to

142°, was 85 percent one component (vpc, probably a terphenyl ether). The filtrate was dissolved in and eluted from a short alumina column with petroleum ether (30°-60°) and after evaporation of the solvent deposited 4.4 g (36%) of the desired product, mp 54° to 56°, whose purity was estimated at 98+ percent (vpc).

Analysis—Calcd for $C_{12}H_9FO$: C, 43.39; H, 0.30; F, 51.49. Found: C, 43.35; H, 0.33; F, 51.58.

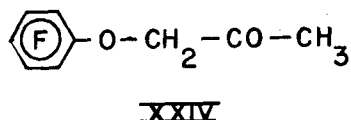
The H^1 nmr spectrum exhibited a triplet of triplets centered at 7.0 ppm with orthofluorine and metafluorine-hydrogen coupling constants of 10 and 6.7 cps, respectively. For F^{19} nmr see Table II.

15. REACTION OF IODOPENTAFLUOROBENZENE WITH SODIUM PENTAFLUOROPHENOLATE

Method A. In an atmosphere of nitrogen, sodium pentafluorophenolate (10.4 g, 0.0520 mole), iodopentafluorobenzene (30.6 g, 0.104 mole), and 200 ml of acetone were stirred at reflux for one week. Analysis of the reaction mixture (vpc) revealed the presence of one reaction product, XXIV. The solvent was removed and the residue (liquid and solid) was filtered. The solid was identified as sodium pentafluorophenolate. The filtrate was distilled at reduced pressure. The first fraction, bp 35° to 65° at 1 mm (32.0 g), consisted of primarily iodopentafluorobenzene, the second fraction bp 70° to 75° at 1 mm (3.0 g), was 98 percent one component (vpc).

An infrared spectrum of the liquid contained CH and C = O bands at 3.3 and 5.7 μ in addition to the usual perfluoroaromatic bands. It was apparent that solvent was incorporated into the perfluoroaromatic nucleus. Its molecular weight was 240 (mass spectrum).

The H^1 nmr spectrum of this compound exhibited a broad singlet at 4.7 ppm (area 2) and a sharp singlet at 2.2 ppm (area 3). On an expanded scale the broad singlet appeared as a triplet ($J \sim 1$ cps). The F^{19} nmr spectrum showed complicated multiplets centered at 79.5 ppm (area 2) and 85.9 ppm (area 3). Irradiation of the high field multiplet gave a broad singlet at 79.5 ppm. Irradiation of the low field signal gave a multiplet at 85.9 ppm which was reminiscent of an AB₂ pattern. The following structure was proposed:



The low field multiplet was assigned to the fluorine atoms at the ortho position.

Analysis—Calcd for $C_9H_5F_5O_2$: C, 45.00; H, 2.08; F, 39.58. Found: C, 44.36; H, 2.04; F, 39.74.

By reacting chloro-2-propanone (5.0 g, 0.054 mole) with sodium pentafluorophenolate (16.2 g, 0.081 mole) for eight hours in refluxing acetone, a 53 percent yield of XXIV was obtained, bp 62°/0.25 mm.

Method B. The same procedure as in Method A was followed using DMAC as solvent (125°-140°) for three days. By following the reaction by vpc no major increase was noticed in spite of the disappearance of starting material. After work-up only intractable material was isolated.

16. THE POLYMERIZATION OF SODIUM PENTAFLUOROPHENOLATE

Sodium pentafluorophenolate (10.0 g, 0.0498 mole) was refluxed in 100 ml of DMAC for 19 hours in a nitrogen atmosphere. After the usual work-up, 1.4 g of a brittle, dark polymer (completely molten at 180°) and 8.0 g (90% pure, vpc) of pentafluorophenol (obtained after acidification) were the only insoluble products.

17. KINETICS

The relative rates of reaction between seven pairs of monosubstituted hexafluorobenzenes were measured and correlated. The stoichiometry utilized in each experiment is listed in Table III.

The reaction vessel was purged with nitrogen and immersed in a thermostated oil bath. The solvent and the two substituted pentafluorobenzene compounds were added and allowed to attain oil bath temperature. To the stirred solution, sodium pentafluorophenolate was introduced; 1.0 ml aliquots were periodically withdrawn, added to a standard, and analyzed by vpc. From the areas of the two substituted biphenyl ethers (standardized with triphenylmethane) the relative rates were calculated.

For each experiment three to five aliquots were withdrawn at different reaction times, and relative rates were calculated for each aliquot. The average relative rate was recorded (there was not more than a 5% deviation from run to run).

Experiments 1 and 2 were quenched by cooling in dry-ice-acetone. Since a freshly prepared solution of pentafluorobenzonitrile (the most reactive) and sodium pentafluorophenolate in DMAC showed no trace of product when analyzed by vpc, chemical quenching seemed necessary.

REFERENCES

1. E.S. Blake, G.A. Richardson, J.A. Webster, and R.E. De Brunner, Monsanto Research Corporation, Fire Resistant High Temperature Hydraulic Fluids, ASD-TDR-62-405, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.
2. E.S. Blake, G.A. Richardson, J.A. Webster, Monsanto Research Corporation, High Temperature Fire Resistant Fluids, RTD-TDR-63-4186.
3. W.J. Pummer and L.A. Wall, Decafluorodiphenyl Ether and Related Polymers, NBS Report Number 7782.
4. J. Burdon, Tetrahedron, 21, 3373 (1965).
5. K.C. Ito and J. Miller, 19, 423-36 (1966).
6. This hypothesis has been applied to kinetics of this type, S.G. Cohen, et al. Progress in Physical Organic Chemistry, Vol 1, Interscience Publishers, New York, N.Y., p 52 (1963).
7. L.A. Wall, et al., J. Res. Nat'l. Bur. Stand., 67A, 481 (1963).

TABLE I
REACTIONS OF BROMOPENTAFLUOROBENZENE WITH SODIUM PENTAFLUOROPHENOLATE

Mole Ratio $C_6F_5Br:C_6F_5ONa$	Solvent	Temp (°C)	Time (hrs)	VI (Percent)	Side Products	Comments
1:1	DMF	120	18	25*	VII (2%) HBP Polymer	Not to completion ---
1:3	DMF	145	4.5	2**		---
3:1	DMF	145	4.5	50**	VII (2%)	---
1:0	DMF	145	72	---	VII* (10%)	Not to completion
1:1	DMF	145	20	trace	VII* (24%)	---
1:1	HBE	150	10	trace	---	---
3:1	HBE	150	10	trace	---	---
1:1	DMAC	120	24	40*	HBP** (20%)	No VII
2:1	DMAC	110	8	75*	HBP** (5%)	No VII
2:1	Me ₂ CO	reflux	44	trace	---	---

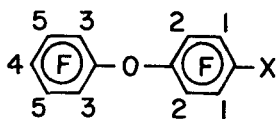
HBP = higher boiling products

* = isolated

** = estimated by vpc

HBE = $CH_3OCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_3$

TABLE II

 F^{19} NMR SPECTRA OF 4-SUBSTITUTED NONOFLUORODIPHENYL ETHERS

X	Chemical Shift of Fluorines ppm (multiplicities)				
	1	2	3	4	5
CN	53.2(m)	75.0(m)	76.8(bd)	78.6(dt)	82.0(dtf)
CF ₃	62.3(m)	78.5(m)	78.5(m)	81.0(dt)	84.2(dtf)
	CF ₃ (-23.2, triplet)				
CO ₂ Et	61.0(m)	78.3(m)	78.3(m)	81.0(dt)	83.8(dtf)
Br	54.8(m)	78.1(m)	79.0(bd)	82.0(dt)	84.5(dtf)
Cl	61.7(m)	78.0(m)	78.0(bd)	80.9(dt)	83.5(dtf)
F	--	--	78.4(bd)	81.1(dt)	83.7(dtf)
H	59.5(m)	78.3(bd)	78.3(bd)	80.7(dt)	83.2(dtf)

m = multiplet

bd = broad doublet

dt = distorted triplet

dtf = distorted triplet with fine structure

TABLE III
STOICHIOMETRY OF THE RELATIVE RATE REACTIONS

Experiment	X ₁	C ₆ F ₅ X ₁ equivalents	X ₂	C ₆ F ₅ X ₂ equivalents	C ₆ F ₅ ONa (equivalents)	DMAC (ml)	Temp °C
1	CN	0.00533	CF ₃	0.01600	0.00533	19.0	47
2	CF ₃	0.0256	CO ₂ Et	0.0527	0.0170	60.0	106
3	CO ₂ Et	0.0255	C ₆ F ₅	0.0680	0.0170	60.0	106
4	CO ₂ Et	0.0255	Br	0.0680	0.0170	60.0	106
5	Br	0.0425	Cl	0.0850	0.0170	60.0	106
6	Cl	0.0510	F	0.0850	0.0170	60.0	106
7	F	0.0340	H	0.0680	0.0170	60.0	106

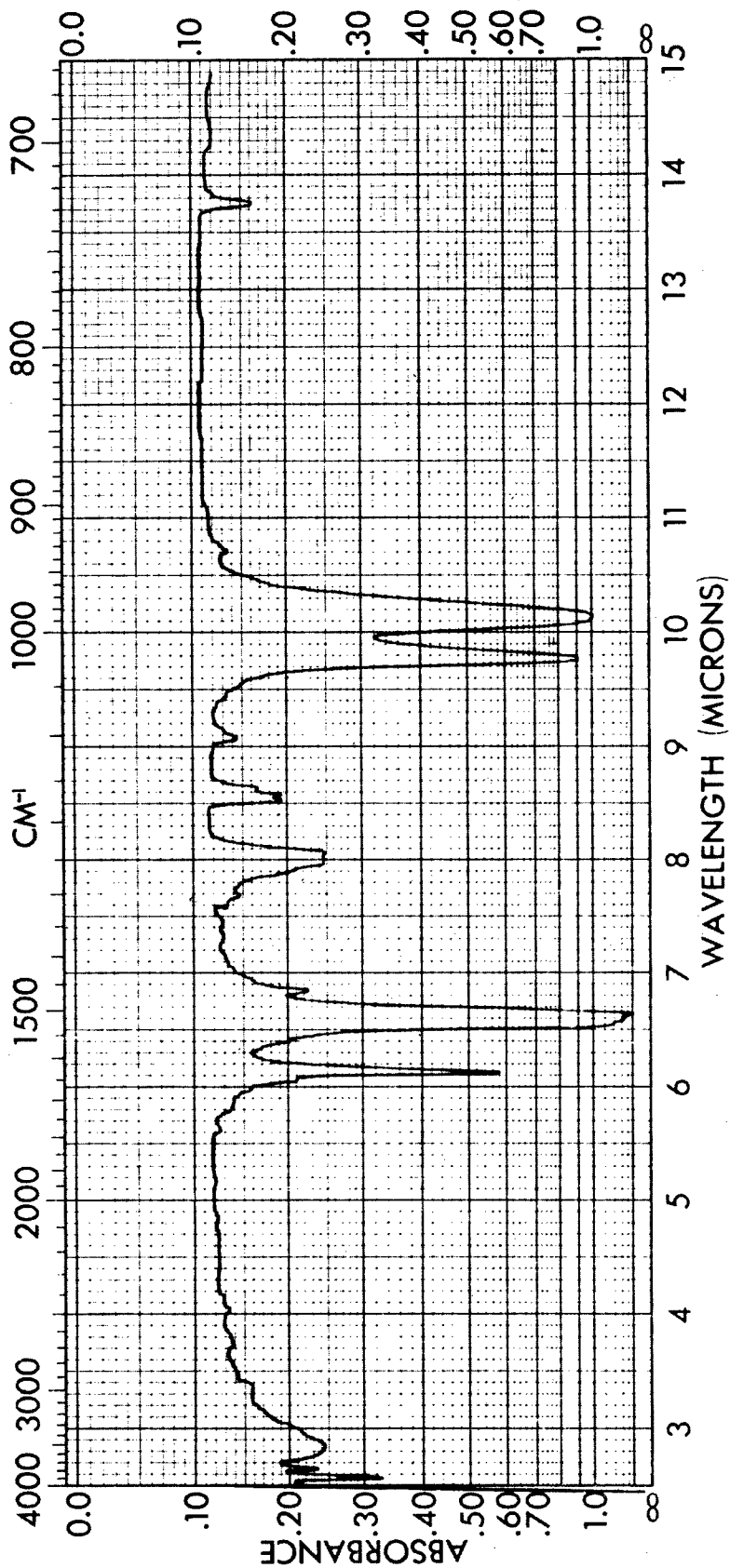


Figure 1. Sodium Pentafluorophenolate Ia (KBr)

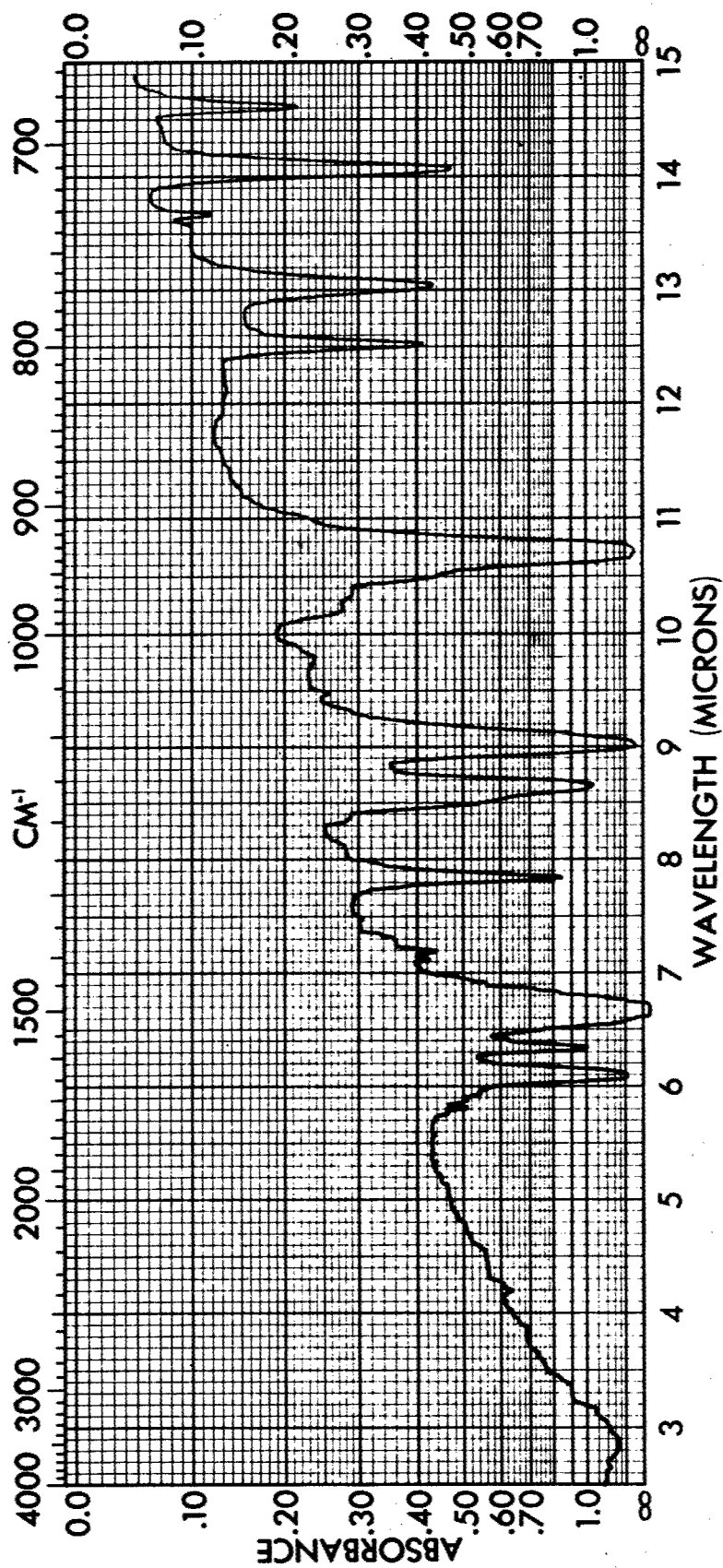


Figure 2. 4-Hydrotetrafluorophenolate Ib (KBr)

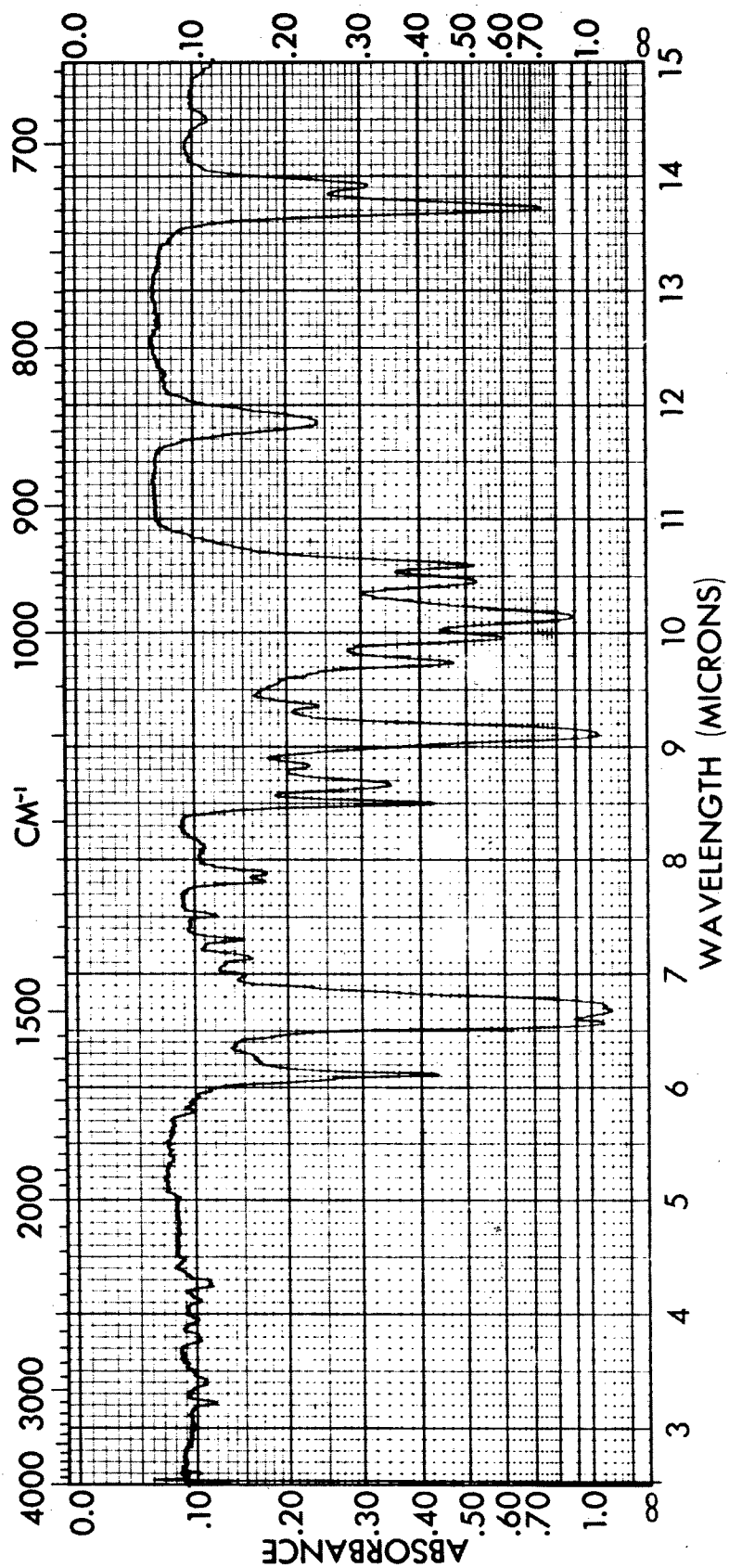


Figure 3. 4-(4-Hydrotetrafluorophenoxy)-nonafluorobiphenyl II (KBr)

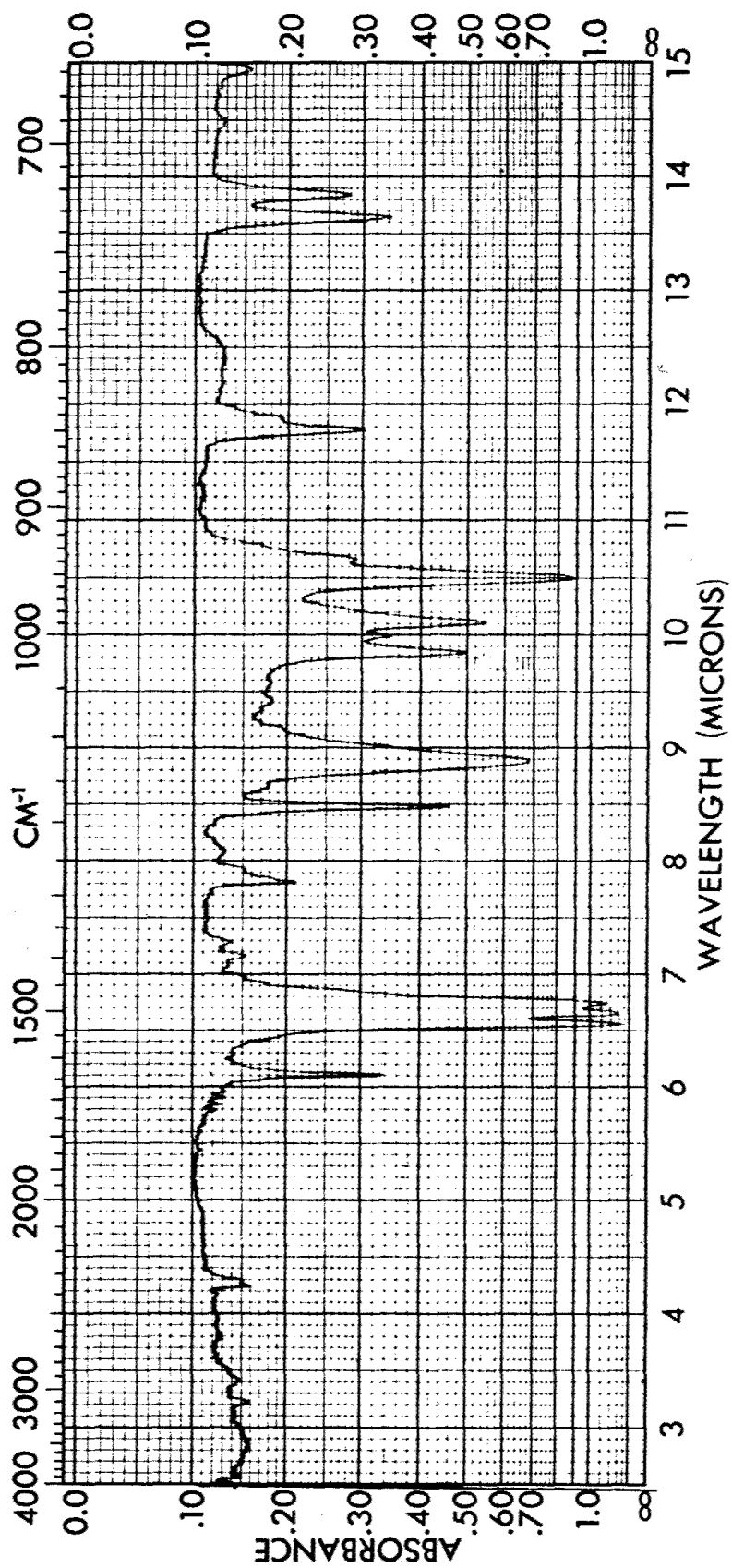


Figure 4. 4,4-Bis-(4-Hydroxytetrafluorophenoxy)-octafluorobiphenyl III (KBr)

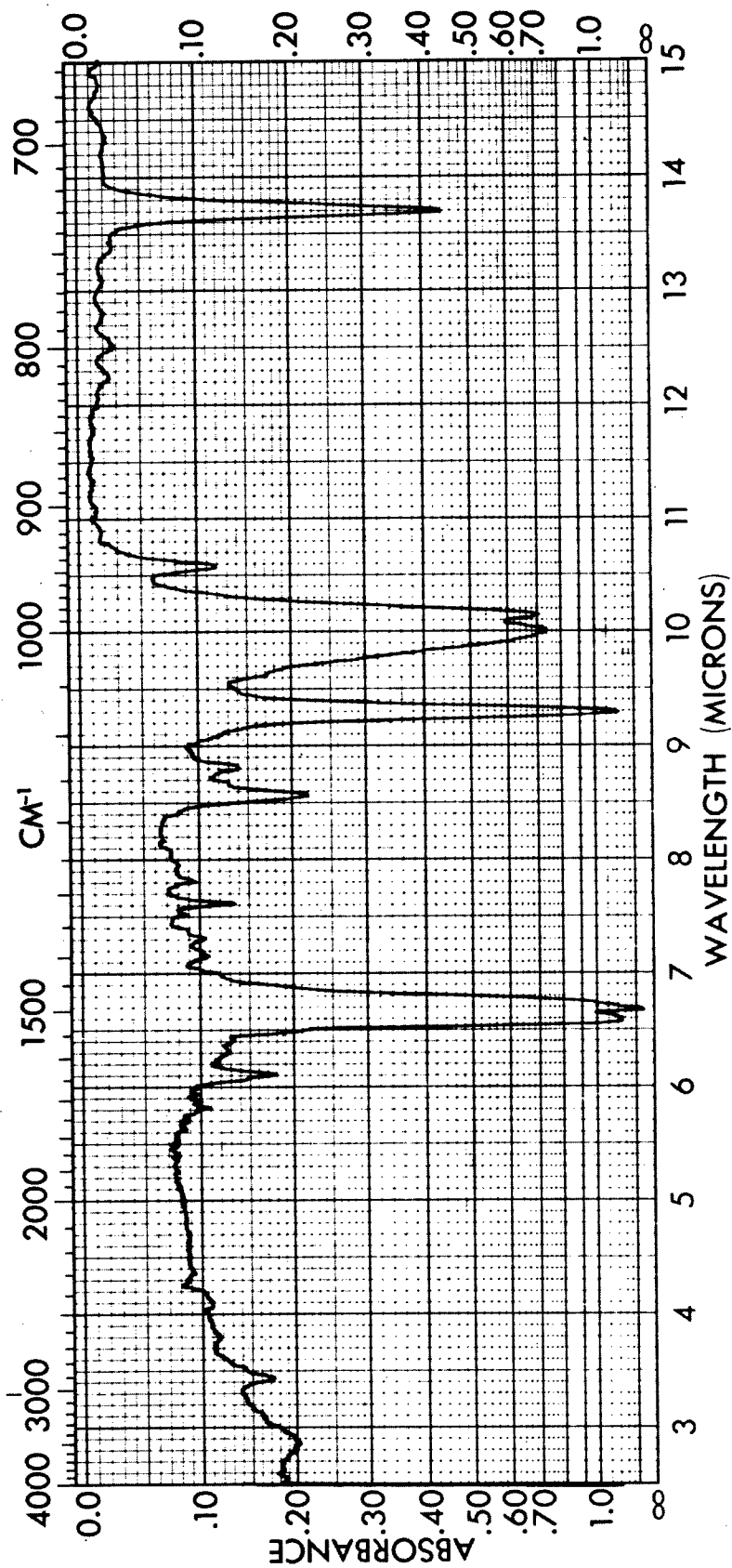


Figure 5. 4-Pentafluorophenoxynonafluorobiphenyl IV (KBr)

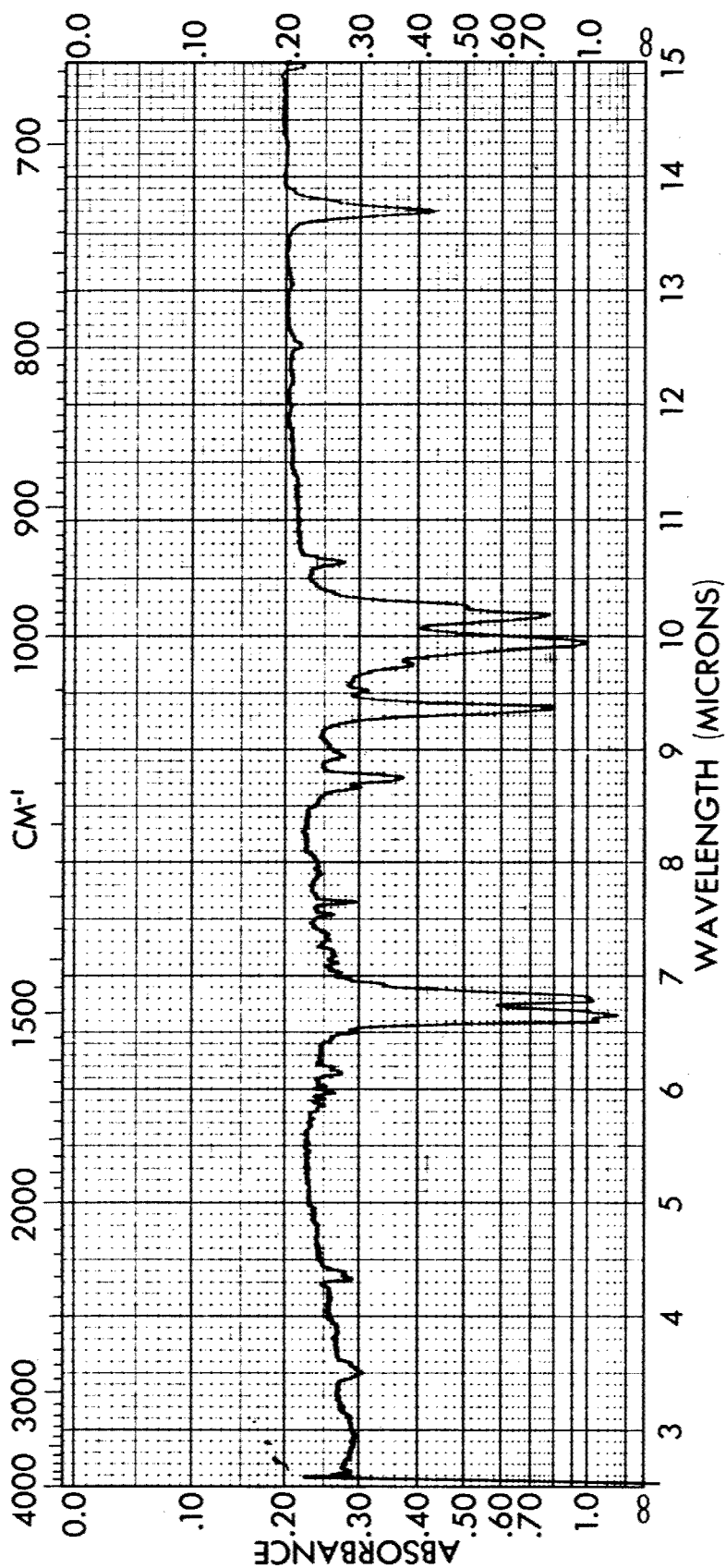


Figure 6. 4, 4' - Dipentafluorophenoxyoctafluorobiphenyl V (KBr)

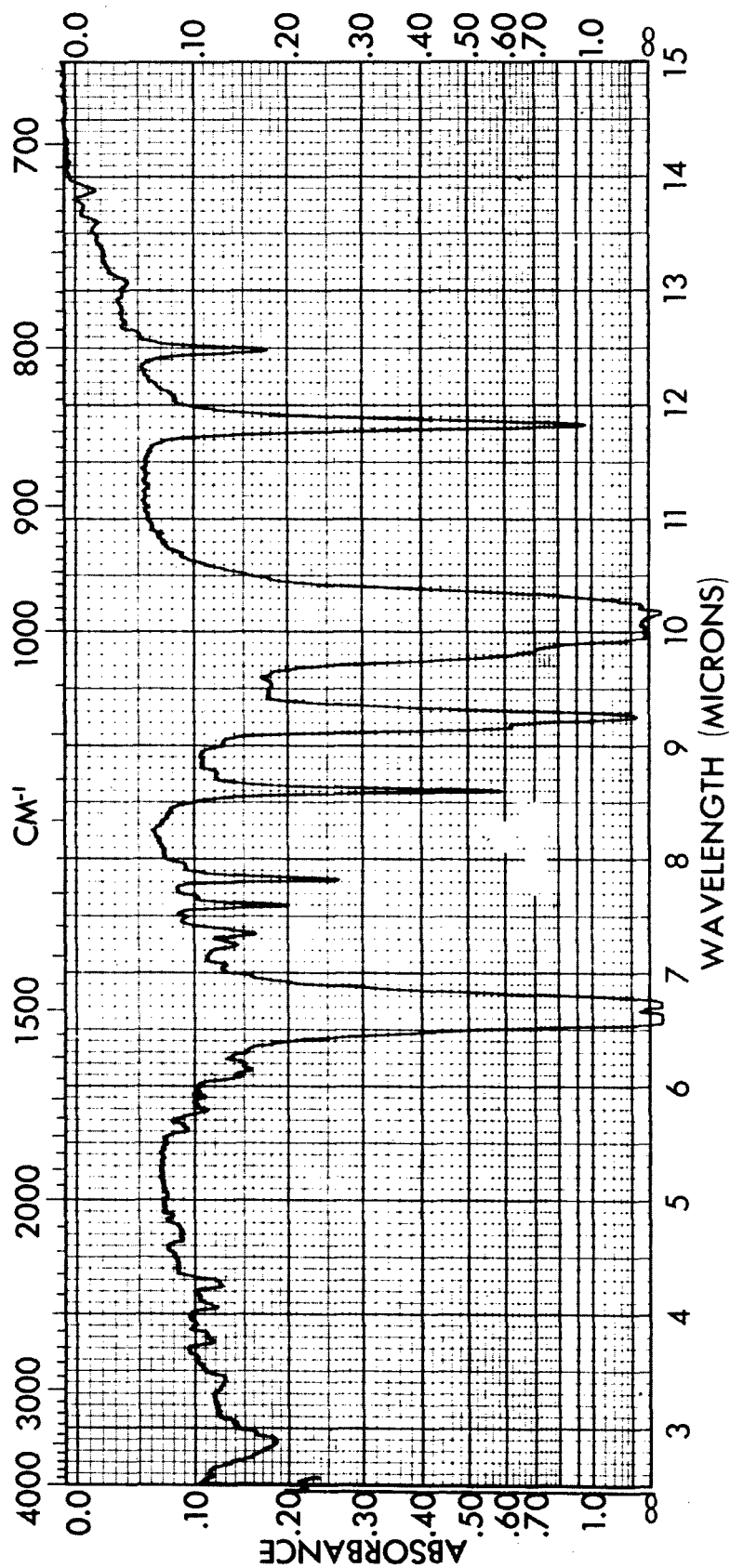


Figure 7. 4-Bromononafluorodiphenyl Ether VI (KBr)

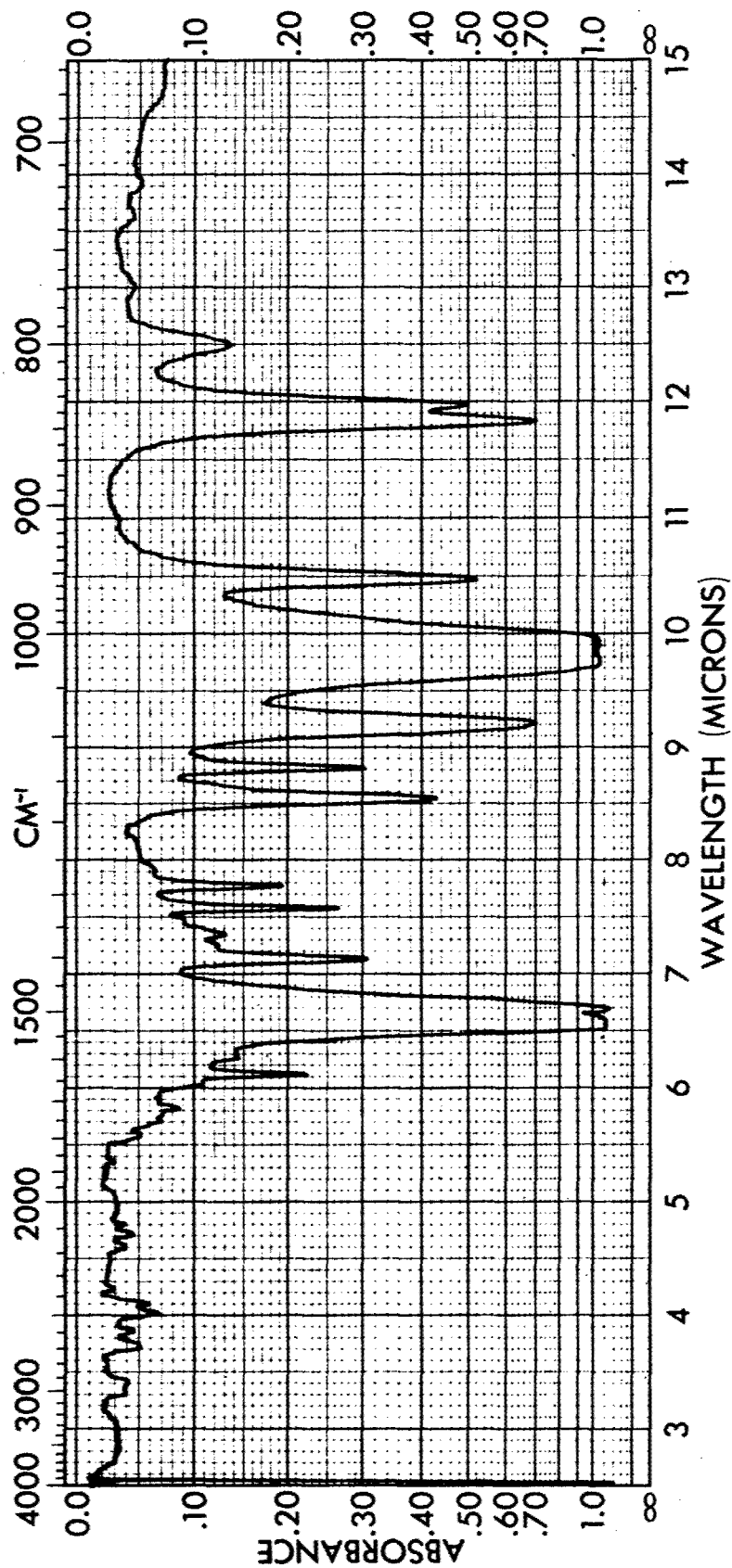


Figure 8. 2-Bromononafluorodiphenyl Ether IX (film)

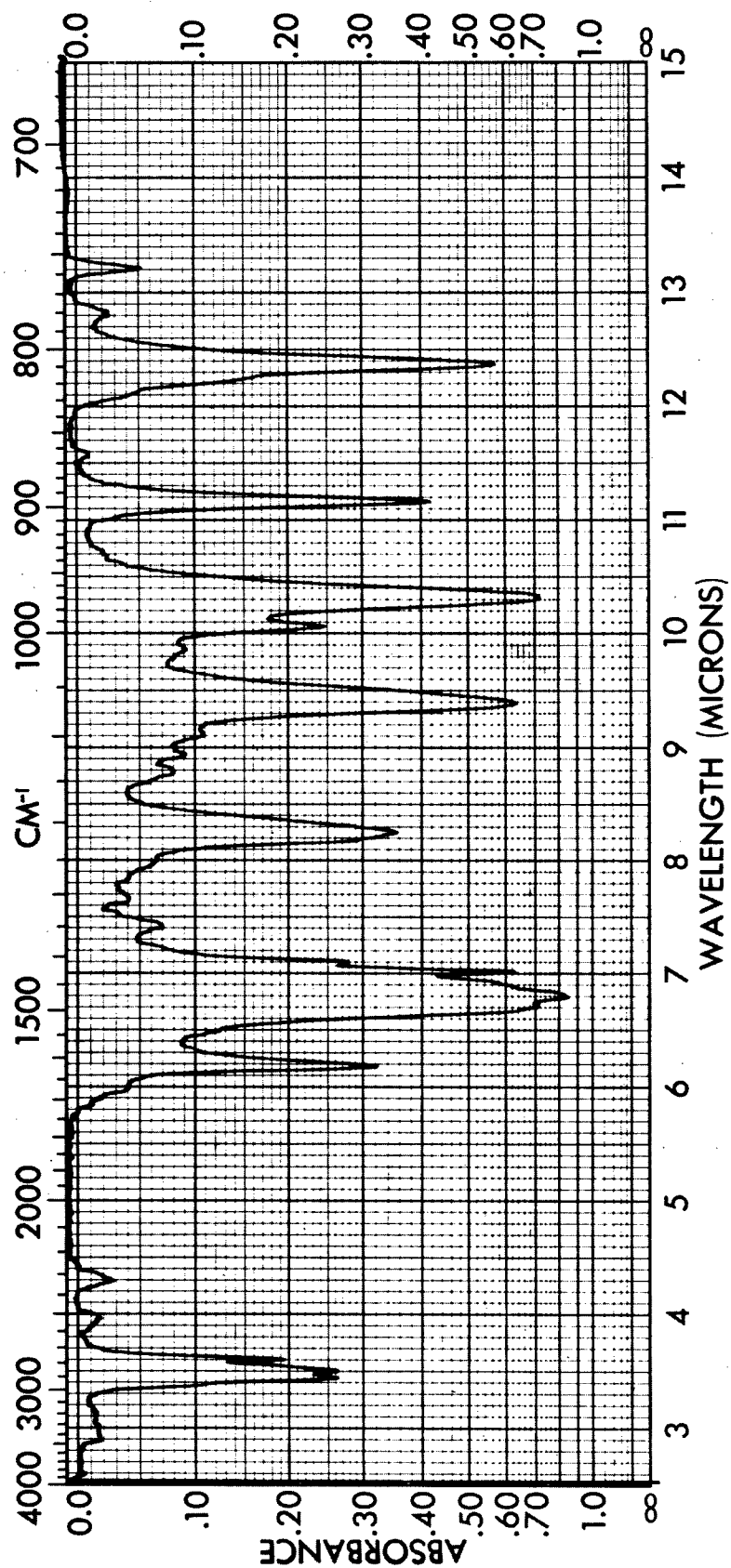


Figure 9. 4-Bromotehafluoro-N,N-dimethylaniline VII (film)

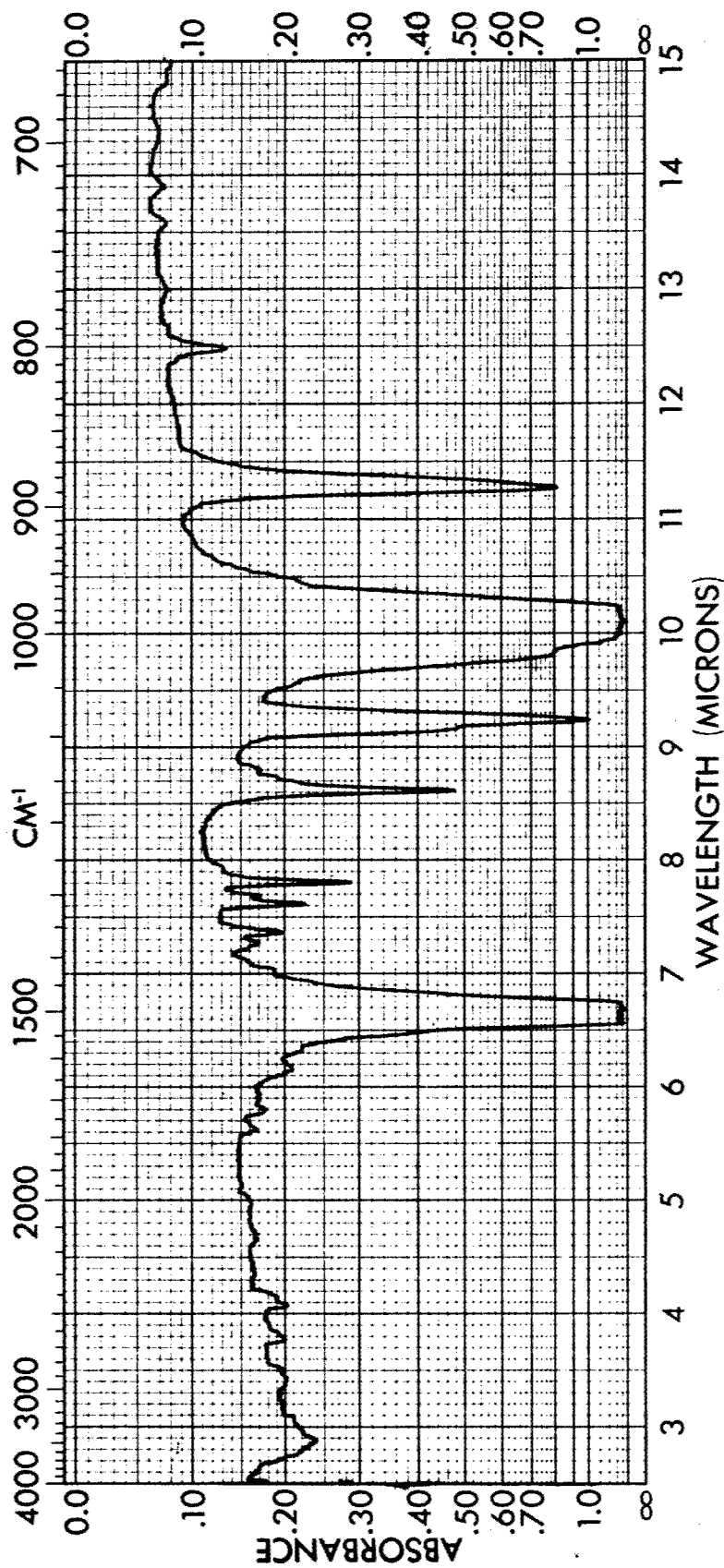


Figure 10. 4-Chlorononafluorodiphenyl Ether XI (KBr)

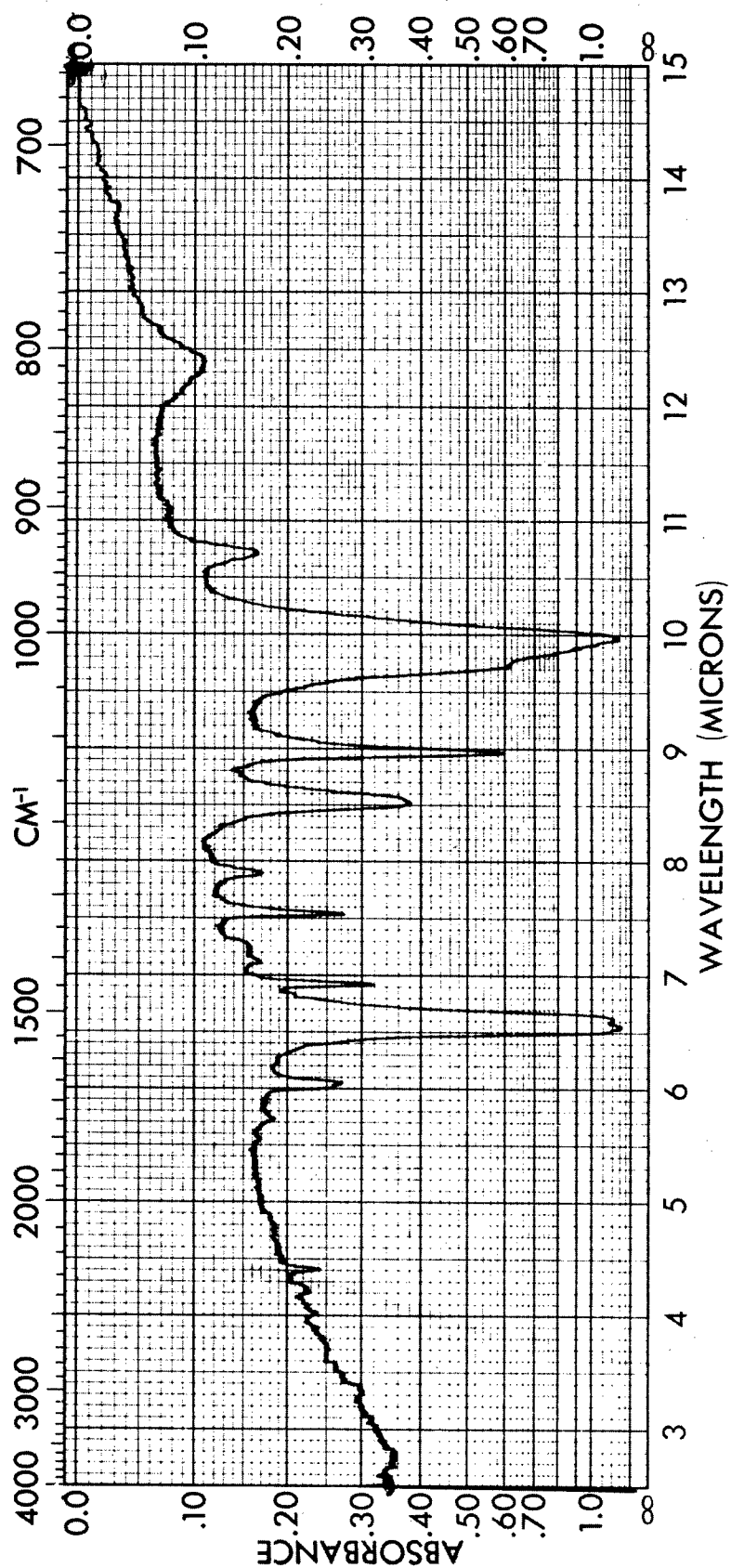


Figure 11. 4-Cyanononafluorodiphenyl Ether XIV (KBr)

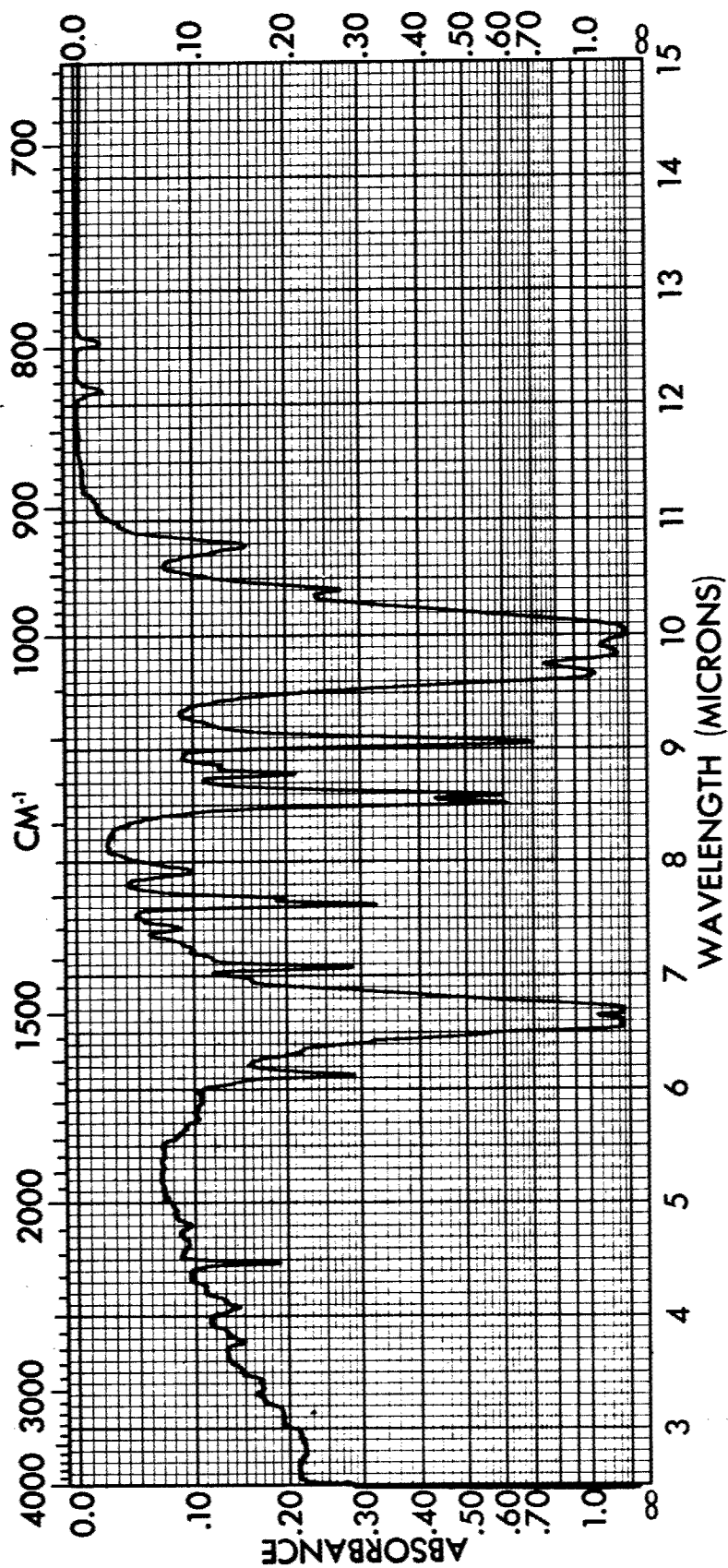


Figure 12. 2,4-Dipentafluorophenoxytrifluorobenzonitrile XV (KBr)

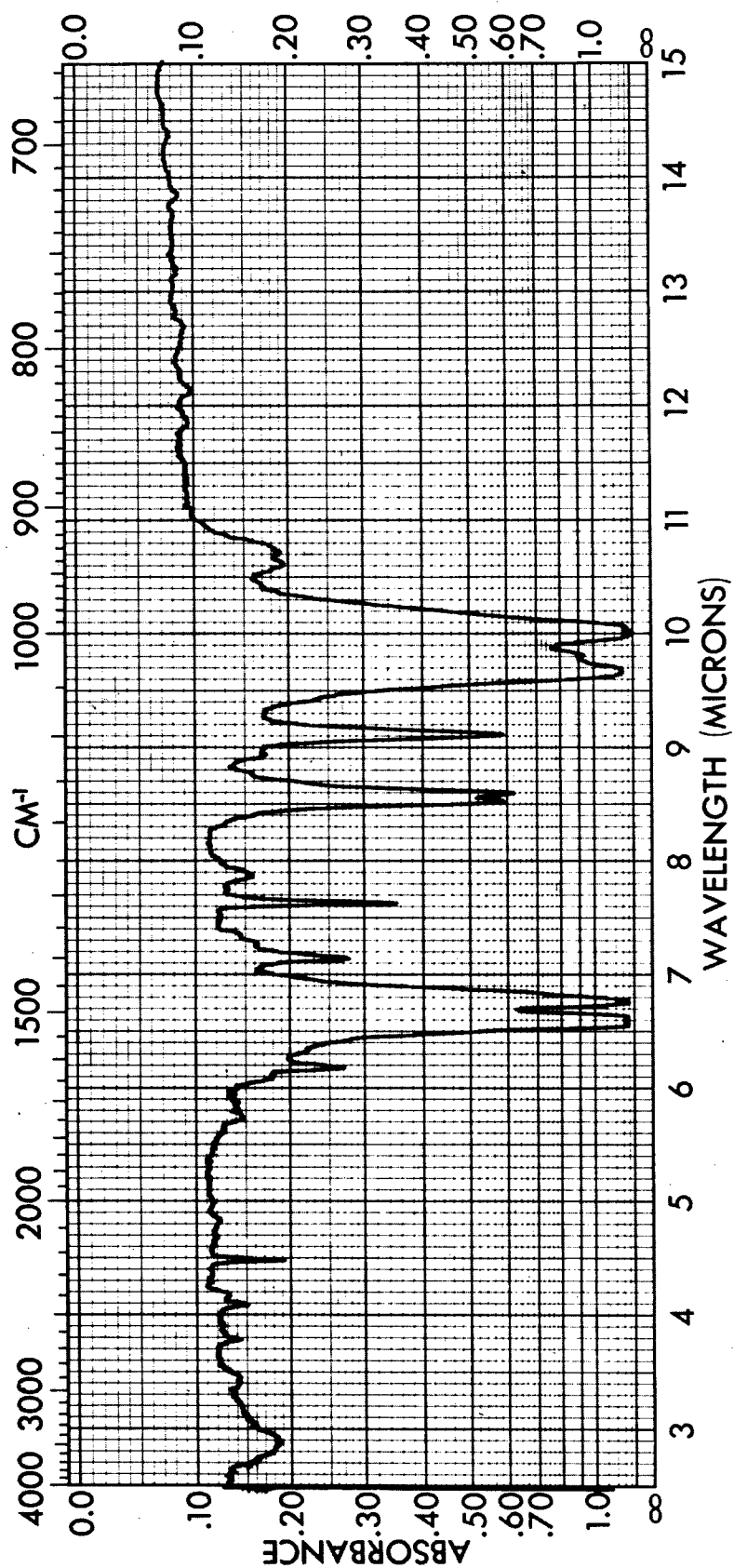


Figure 13. 2,4,6-Tripentafluorophenoxydifluorobenzonitrile XVI (KBr)

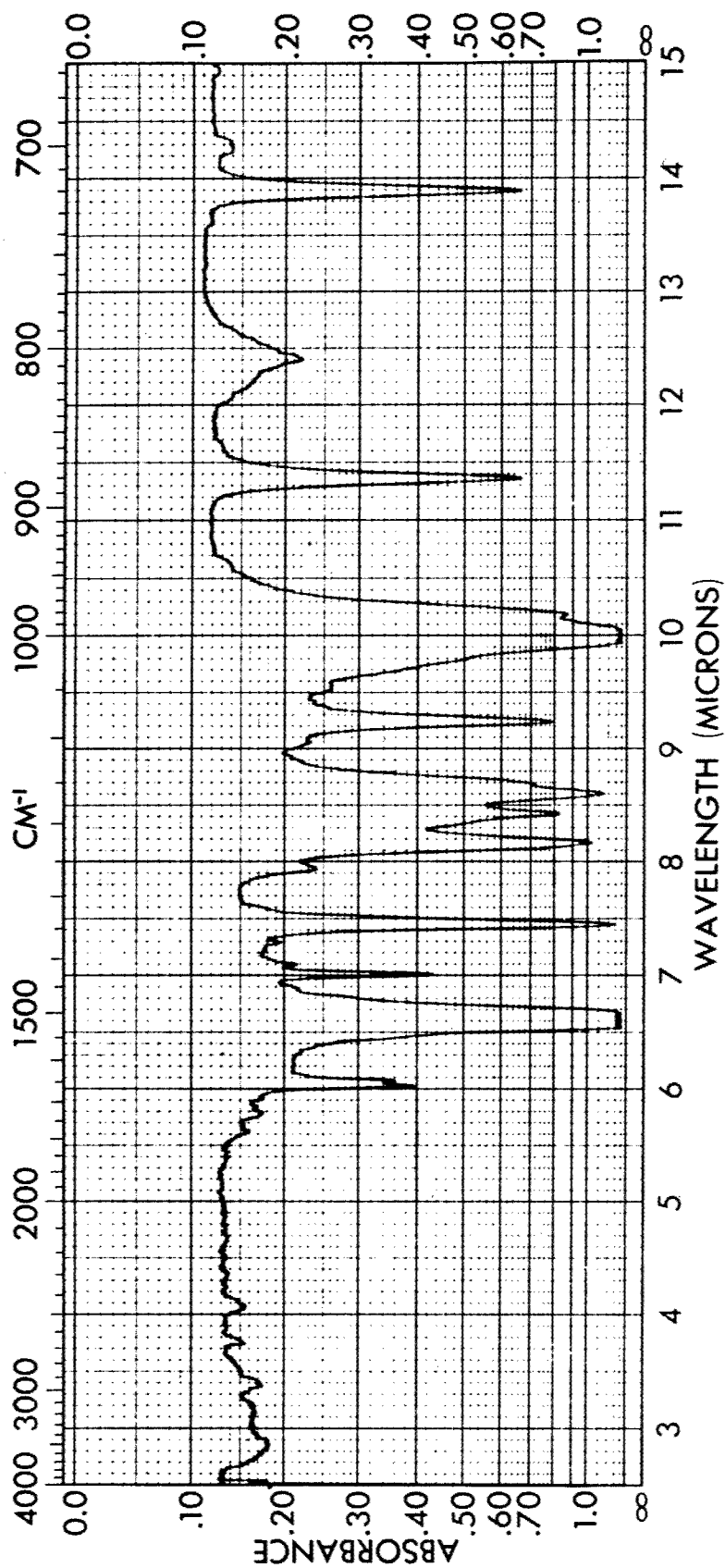


Figure 14. 4-Trifluoromethylnonafluorodiphenyl Ether XVI (KBr)

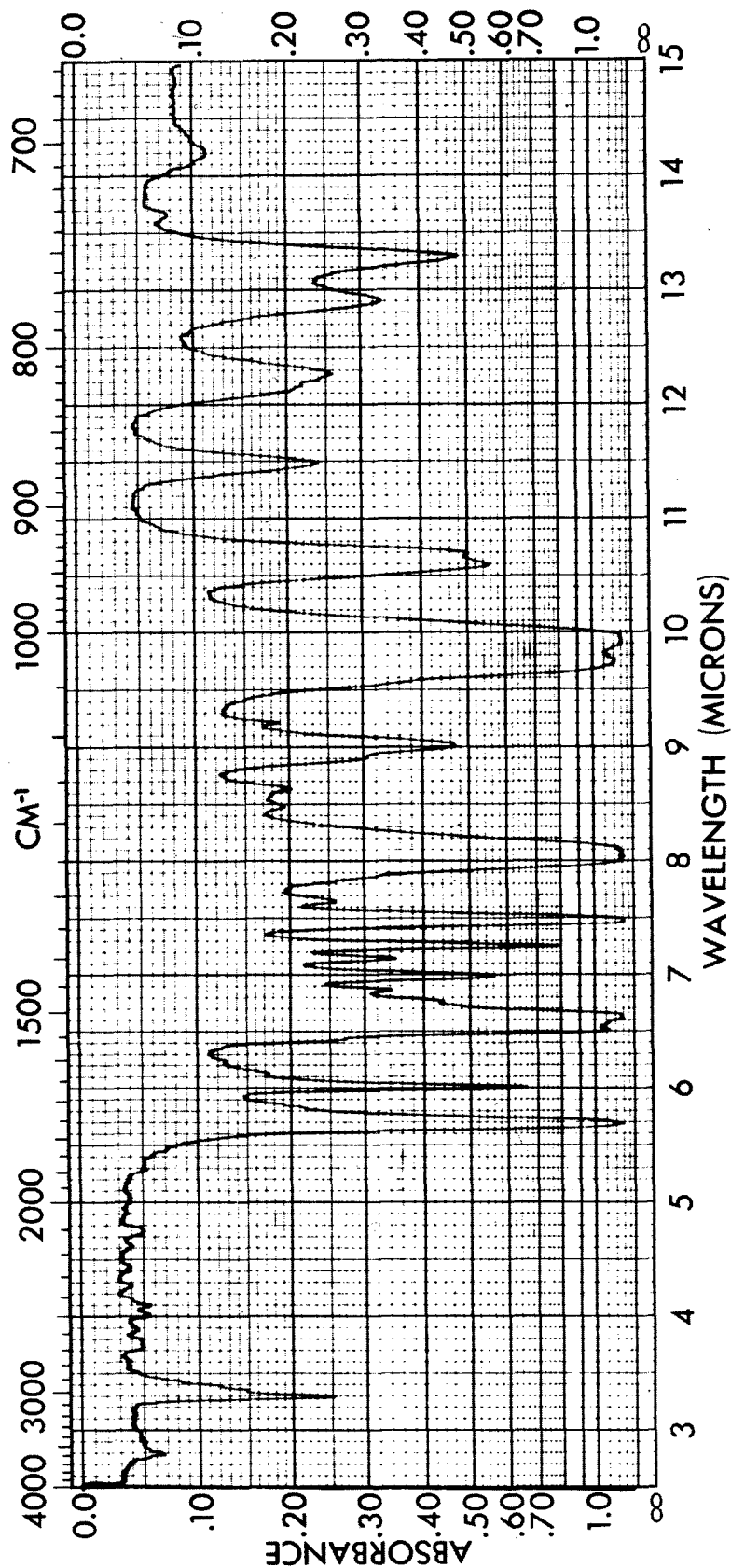


Figure 15. Ethylpentaffluorobenzoate (film)

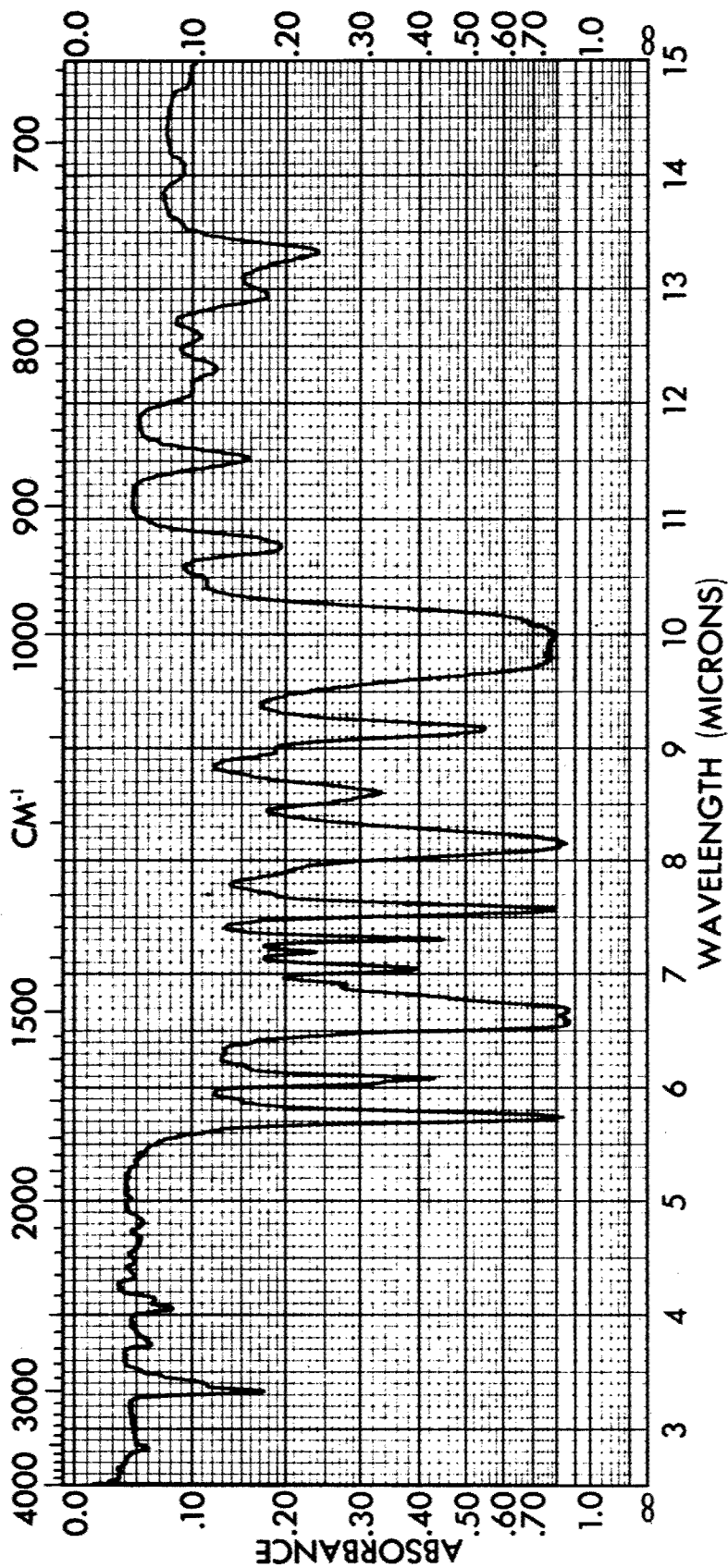


Figure 16. 4-Carboethoxynonafluorodiphenyl Ether XIX (KBr)

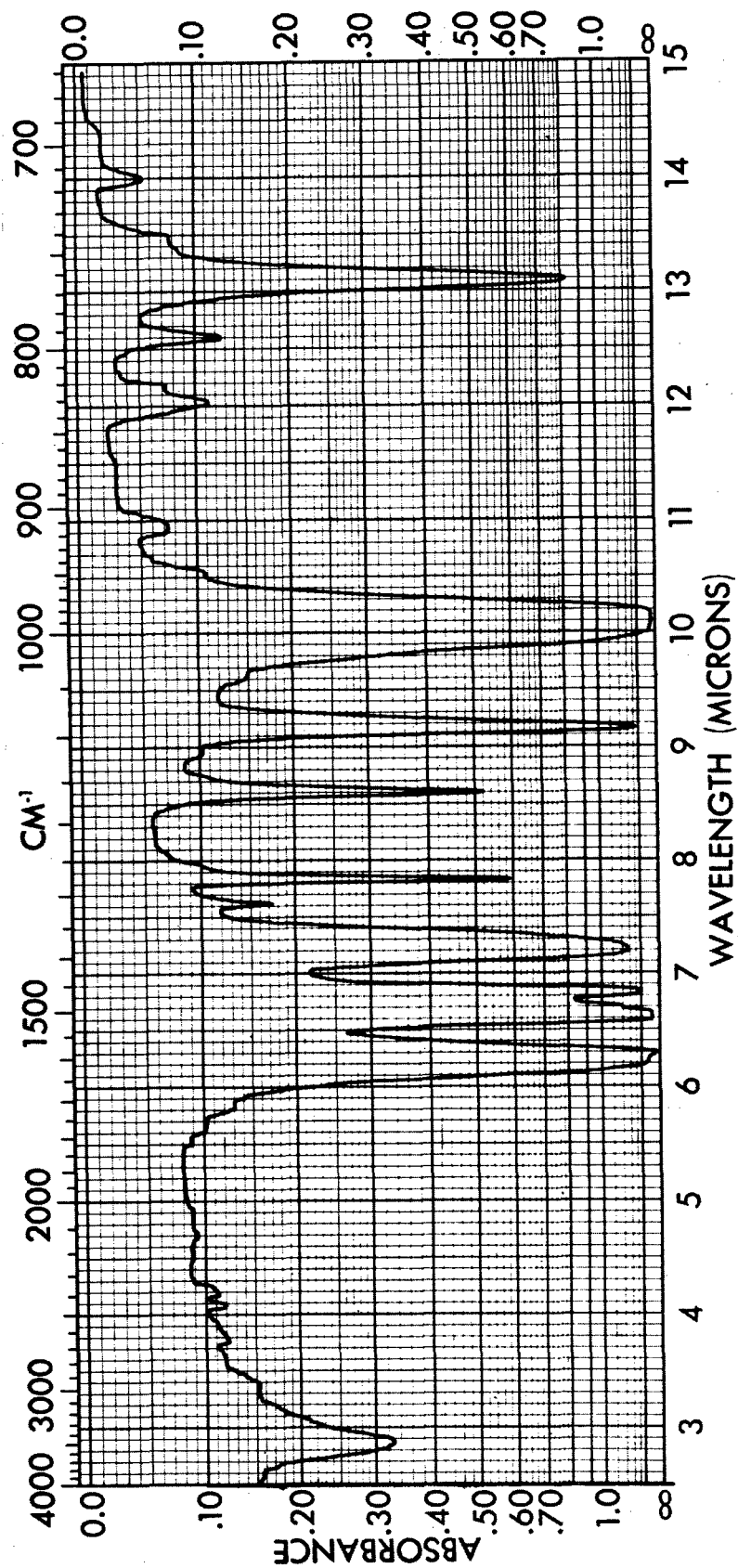


Figure 17. 4-Nonafluorodiphenyl Ether Carboxylic Acid Sodium Salt XX(KBr)

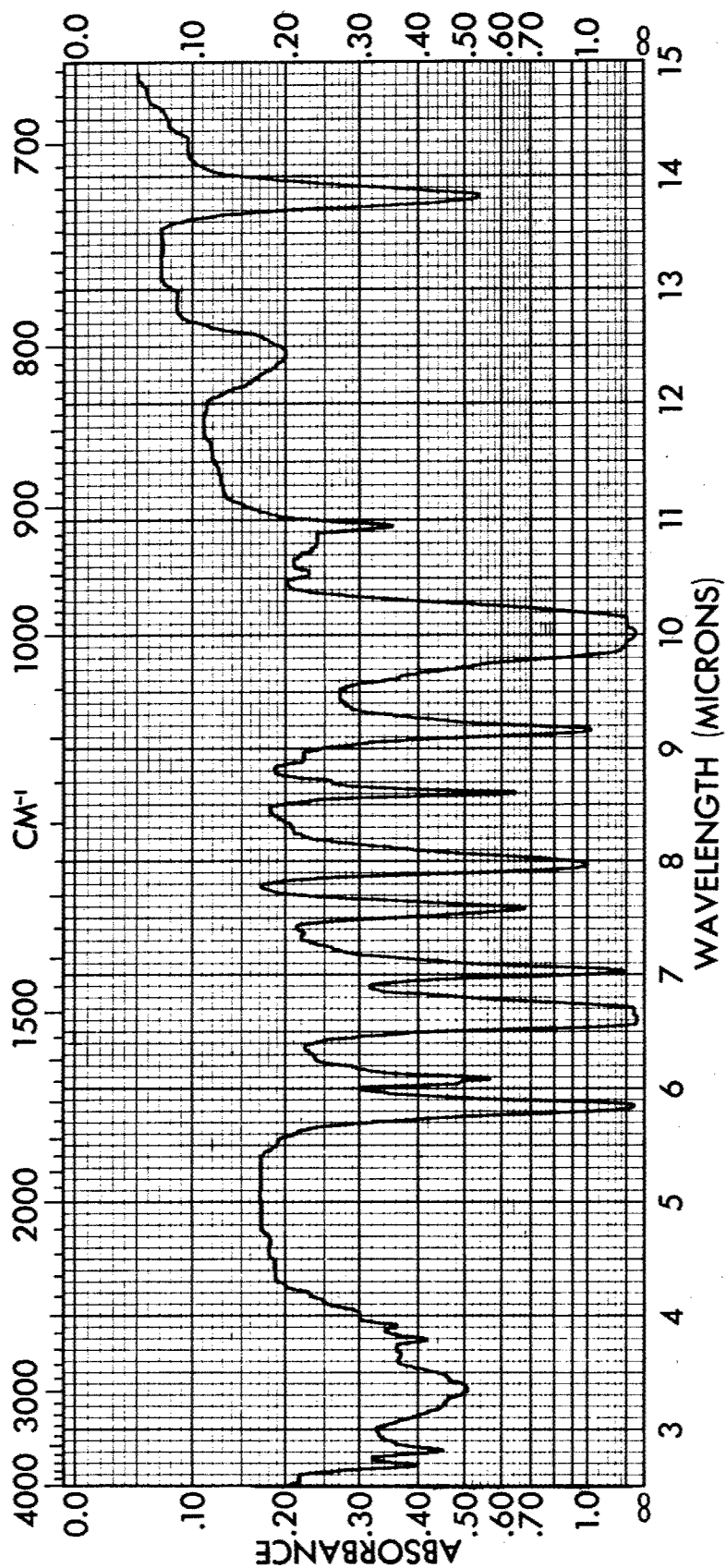


Figure 18. 4-Nonafluorodiphenyl Ether Carboxylic Acid XXI (KBr)

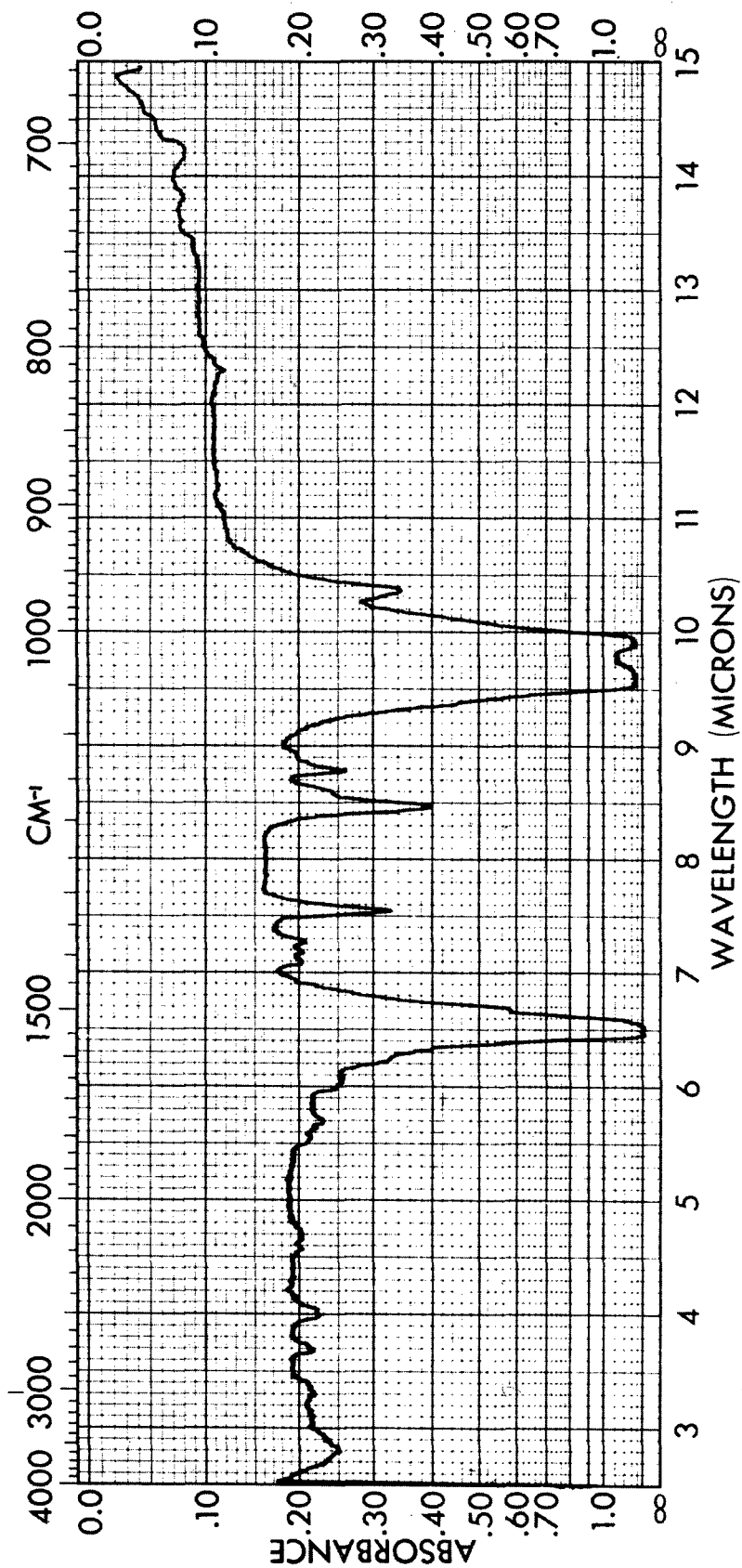


Figure 19. Decafluorodiphenyl Ether XXII (KBr)

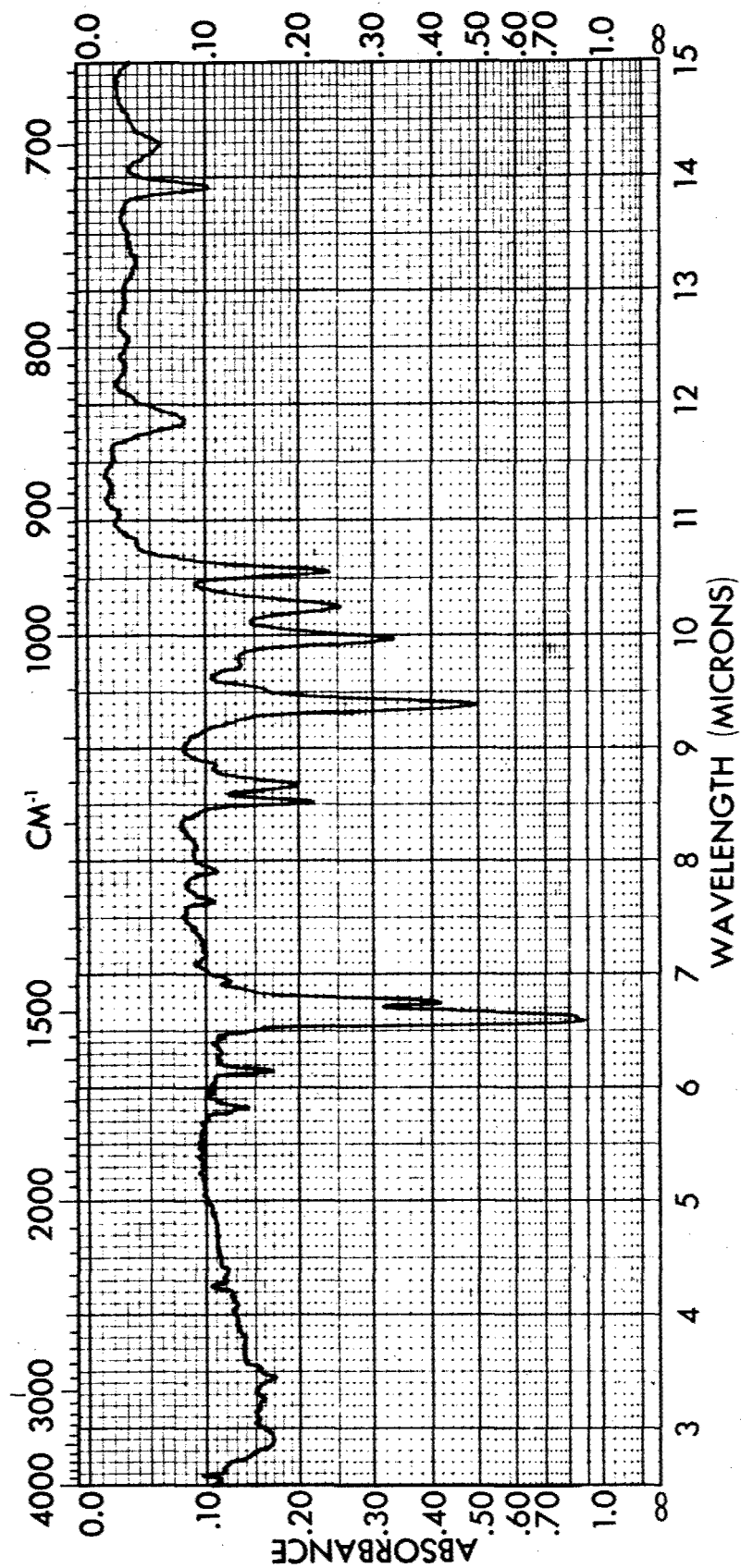


Figure 20. 4-Hydrononafluorodiphenyl Ether XXIII (KBr)

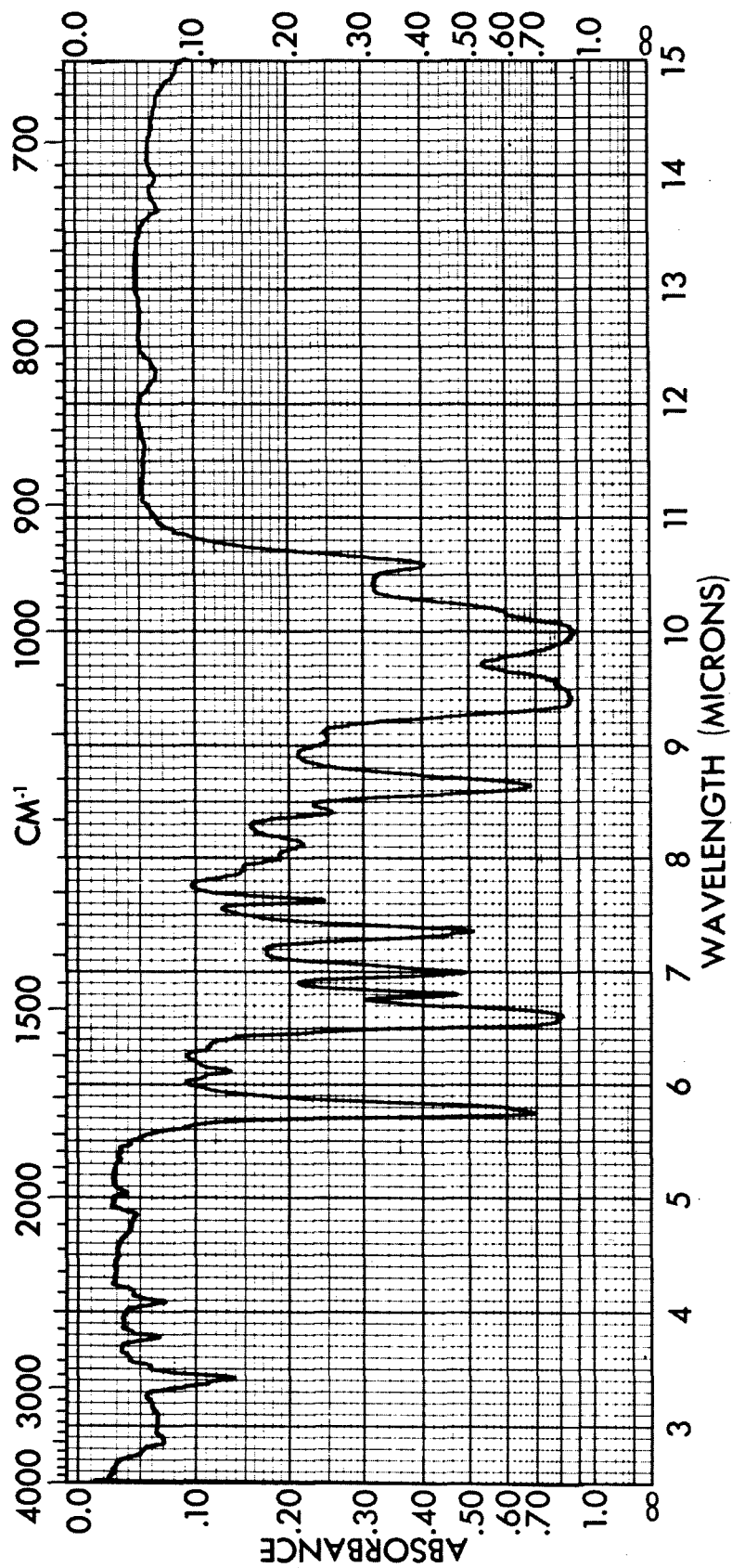


Figure 21. 2-Pentafluorophenoxypropanone XXIV (film)

UNCLASSIFIED

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio		2a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED	
		2b. GROUP	
3. REPORT TITLE FLUOROAROMATIC CHEMISTRY: THE REACTIONS AND KINETICS OF SODIUM PENTAFLUOROPHENOLATE WITH SUBSTITUTED PENTAFLUOROBENZENES			
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) November 1965 - November 1966			
5. AUTHOR(S) (Last name, first name, initial) DePasquale, Ralph J., 1/Lt, USAF; Tamborski, Christ			
6. REPORT DATE March 1967		7a. TOTAL NO. OF PAGES 54	7b. NO. OF REFS 7
8a. CONTRACT OR GRANT NO.		9a. ORIGINATOR'S REPORT NUMBER(S) AFML-TR-67-19	
b. PROJECT NO. 7340			
c. Task No. 734004		9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
d.			
10. AVAILABILITY/LIMITATION NOTICES This document may be further distributed by any holder <u>only</u> with specific prior approval of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (MANP), Wright-Patterson Air Force Base, Ohio 45433.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson AFB, Ohio	
13. ABSTRACT Sodium pentafluorophenolate and sodium 4-hydrotetrafluorophenolate were synthesized and shown to react with a series of substituted pentafluorobenzenes. Reaction conditions were chosen to maximize the kinetically controlled product, viz phenolate substitution at the position para to the functional group. Small percentages of side products derived from <u>ortho</u> or both <u>ortho</u> and <u>para</u> displacement were generally observed. Polysubstitution products could be obtained in fair yield when pentafluorobenzonitrile was used as the substrate. The relative rates for the reaction of eight substituted pentafluorobenzenes with sodium pentafluorophenolate were measured. The differences in rate between substituents were relatively large. This was further demonstrated by the linear plot of log (relative rate) vs Hammett's σ_p which gave a slope of about 7.5. (This abstract may be further distributed by any holder <u>only</u> with specific prior approval of the Polymer Branch, Nonmetallic Materials Division, Air Force Materials Laboratory (MANP), Wright-Patterson Air Force Base, Ohio 45433.			

DD FORM 1473
1 JAN 64

UNCLASSIFIED

Security Classification

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Sodium Pentafluorophenolate						
Nonofluorodiphenyl Ether						

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through _____."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through _____."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through _____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (paying for) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

UNCLASSIFIED

Security Classification