

NASACR-166,409

NASA CONTRACTOR REPORT 166409

NASA-CR-166409
19830001925

Synthesis of Perfluorinated Polyetheres

R. J. DePasquale
C. D. Padgett
J. R. Patton
T. Psarras

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Synthesis of Perfluorinated Polyethers

Ralph J. DePasquale
Calvin D. Padgett
Jerry R. Patton
Theodore Psarras
PCR, Inc.
Gainesville, Florida

Prepared for
Ames Research Center
under Contract NAS2-8156



National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

N83-10195[#]

FOREWORD

This report was prepared by PCR, Inc., Gainesville, Florida, under Contract No. NAS2-8156 administered by National Aeronautics and Space Administration, Ames Research Center, Moffett Field, California. Dr. Robert Rosser was the Technical Monitor for NASA.

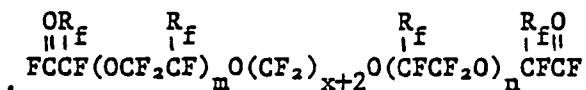
This is the Final Report under the contract and covers the period 1 April 1974 to 31 July 1977.

Personnel who have contributed to this research are Mr. C. D. Padgett and Mr. J. R. Patton, Research Chemists and Dr. R. J. De Pasquale and Dr. Theodore Psarras as Project Directors. Analyses were performed under the supervision of Dr. D. A. Warner, Director of Analytical Services.

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



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 $m + n = 3$, $R_f = \text{CF}_3$ and $x = 0$. Similarly 2e-EDAF(G) has the structure with $m + n = 0$, $R_f = \text{F}$ and $x = 3$.

ABSTRACT


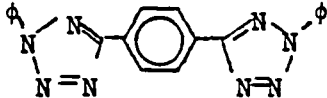
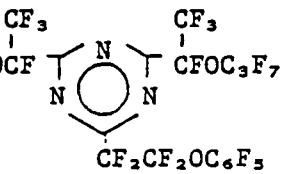
A series of highly fluorinated acetylenes was prepared and their cyclization reactions were studied.

A series of perfluoropolytriazines with $-CF_2I$ pendent groups were prepared. These materials can be cured thermally or photochemically to an elastomeric gum.

Perfluoropolytriazines with $-CN$ pendent groups were prepared. These materials can be crosslinked by reaction with terephthalonitrile oxide.

TABLE OF CONTENTS

<u>SECTION</u>		<u>Page</u>
I	INTRODUCTION	1
II	DISCUSSION	2
	A. Highly Fluorinated Acetylenes	22
	B. Perfluorinated Ether Polytriazines	11
	C. Perfluoroalkylene Ether Polytriazines with Pendent Nitrile Groups	13
	D. Perfluoroalkylene Ether Polytriazines with $-CF_2I$ Pendent Groups	18
	E. Conclusions and Recommendations	27
III	EXPERIMENTAL	29
	A. Highly Fluorinated Acetylenes	29
	1. Attempted Preparation of Fluorinated Acyl Acetylenes	29
	2. Attempted Preparation of Methyl Perfluoroalkyl Ketones Enroute to Fluorinated Acetylenes	29
	3. General Procedure for Coupling Perfluoroalkyl Iodides with Vinyl Iodides	30
	4. Attempted Synthesis of 2-(F-hexyl)biphenyl	31
	5. Conversion of $C_6F_{17}CH=CHCl$ (trans) to $C_6F_{17}C\equiv CH$	31
	6. Conversion of $R_FCH=CH\phi$ to $R_FC\equiv C\phi$ by Bromination and Dehydrohalogenation	32
	7. Preparation of Various Intermediates	33
	8. Reaction Between $C_6F_{13}C\equiv C\phi$ and ϕN_3	33
	9. Reaction Between $C_6F_{13}C\equiv C\phi$ and Butadiene	34
	10. Reaction Between $C_6F_{13}C\equiv C\phi$ and TFE	34
	11. Preparation of α -Pyrone	34

B.	Perfluoroalkylene Ether Polytriazine	35
1.	Polymerization of Dinitriles to Polytriazines by NH_3 Catalysis	35
2.	Attempted Synthesis of Low Molecular Weight Polytriazines	35
C.	Polytriazines with Pendent Nitrile Groups	36
1.	General Method	36
2.	Synthesis of $[\text{NC}(\text{CF}_2)_3\text{CO}]_2\text{O}$	36
D.	Preparation of Bis-Tetrazole	38
1.	Preparation of $\phi\text{NHN}=\text{CN}$  $\text{CH}-\text{NHN}\phi$	38
2.	Preparation of 	39
E.	Perfluoroalkylene Ether Triazines	39
1.	Preparation of $\text{C}_6\text{F}_5\text{OCF}_2\text{CF}_2\text{COF}$	39
2.	Preparation of $\text{C}_3\text{F}_7\text{OCF}-\text{C} \begin{array}{l} \text{CF}_3\text{NH} \\ \\ \text{ } \\ \text{N} \end{array} = \text{C} \begin{array}{l} \text{NH}_2 \\ \\ \text{CF}_3 \\ \\ \text{CFOC}_3\text{F}_7 \end{array}$	40
3.	Preparation of $\text{C}_3\text{F}_7\text{OCF}$  $\text{CF}_2\text{CF}_2\text{OC}_6\text{F}_5$	40
F.	Attempted Reaction of Sodium Phenoxide with p-Fluorine of Triazine Pendent Group	41
G.	Polytriazines with $-\text{CF}_2\text{I}$ Pendent Groups	42
H.	Cross-Linking of Polytriazines with Pendent $-\text{CF}_2\text{I}$ Groups	42
1.	Low Temperature Curing	42
2.	High Temperature Curing	43
I.	Preparation of $\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{COF}$	43

REFERENCES

INFRARED SPECTRA



SECTION I
INTRODUCTION

Technological advances in space research have created a critical need for new and improved materials that will function under extreme environmental conditions. In particular, sealants and elastomers are needed that will exhibit high thermal and oxidative stability (ca. 400°C), low temperature flexibility ($T_g \sim -50^\circ\text{C}$) and hydrolytic stability as well as compatibility with metals and resistance to fuels.

These stringent requirements severely limit the range of applicable chemical compositions. Poly(perfluoroalkylene oxides) of the Krytox (duPont) and Fomblin (Montedison) type, although fluids, possess high thermal and hydrolytic stability. A more versatile system which takes advantage of the high thermal stability of the perfluoroalkylene oxide structure is that of perfluoroether substituted s-triazines. All of the above systems have been extensively studied in our laboratories and the developed technology forms the basis for the approach to the solution of the sealant problem.

The approach followed in this program is to synthesize long chain perfluoroethers with functional groups ($-\text{C}\equiv\text{CH}$, $-\text{CN}$, $-\text{CF}_2\text{I}$) and to investigate methods of converting them to stable crosslinked polymers for sealant applications.

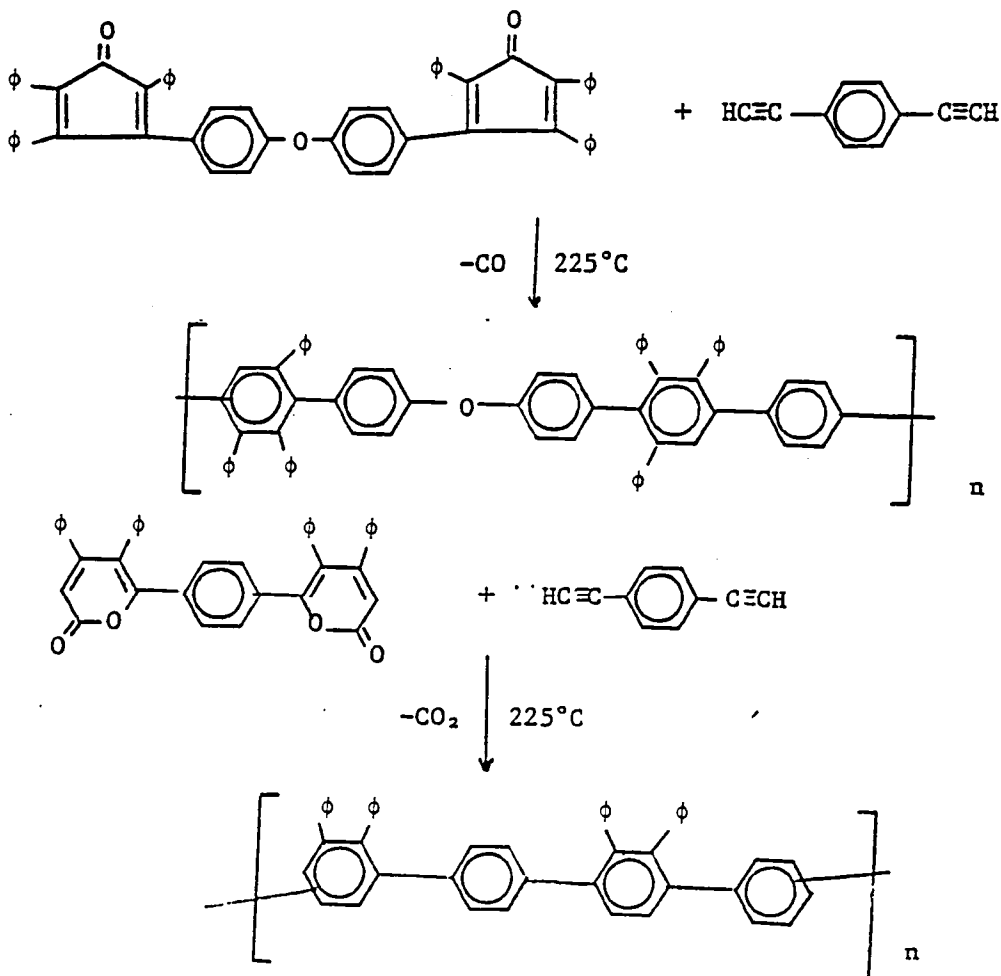
SECTION II

DISCUSSION

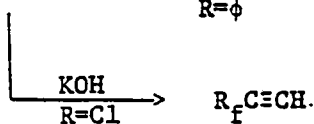
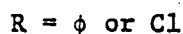
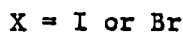
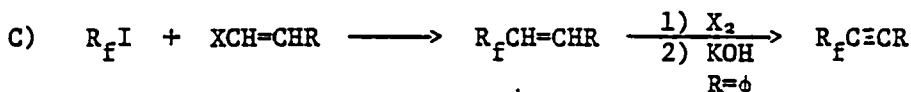
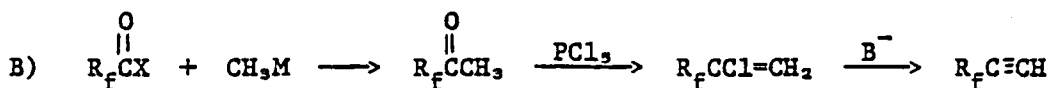
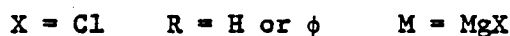
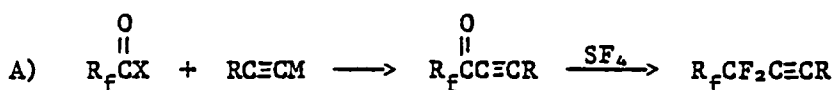
A. Highly Fluorinated Acetylenes

In search of thermally-oxidatively stable sealants,¹ perfluoroalkylene ether dinitriles were prepared and converted to fluoropolymers by reaction through the CN group (trimerization → triazines, reaction with -CNO → oxadiazoles). It was hypothesized that analogous reactions with acetylene functional groups would yield material which possesses similar thermal oxidative properties but would be superior in terms of hydrolytic stability.

Stille and co-workers prepared polymers from copolymerization between acetylenes and cyclopentadienones², or α -pyrones.³



To the best of our knowledge, highly fluorinated diacetylenes have not been reported in the literature. Routes to monoacetylenes⁴ have been reported. In general, these routes are multistep and might prove difficult to apply to the preparation of diacetylenes. Thus, we considered alternate, shorter, routes to these compounds as shown in the following schemes.



In the first sequence an acyl acetylene was prepared but in low yields. The SF₄ reaction was not attempted. In the second route it was determined that long chain perfluoroalkyl methyl ketones are difficult to isolate, due to their ease of dimerization,⁵ even under mild conditions. The third route seems most applicable to the preparation of fluorinated acetylenes.

TABLE I

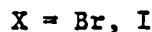
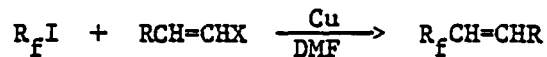
REACTIONS BETWEEN PERFLUOROALKYL IODIDES AND VINYL HALIDES

R_fI (g, mole)	Vinyl Halide (g, mole)	Cu/Bronze (g-at)	Solvent, Temp. ($^{\circ}C$) Time (hr)	Product, bp ($^{\circ}C$) (mm), yield (%)
$C_7F_{15}I$ (50, 0.10)	$ICH=CHCl$ (19, 0.10)	0.25	DMF, 120, 12	$C_7F_{15}CH=CHCl$, 75-79 (80), 64
$C_6F_{13}I$ (49, 0.12)	$\phi CH=CHBr$ (22, 0.12)	0.30	DMF, 120, 18	$C_6F_{13}CH=CH\phi$, 72-74 (1), 82
$C_8F_{17}I$ (49.3, 0.091)	$ICH=CHCl$ (28.2, 0.136)	0.39	DMF, 130, 18	$C_8F_{17}CH=CHCl$, 84-86 (32), 75
$(CF_2)_6I_2$ (11.8, 0.021)	$\phi CH=CHBr$ (10.6, 0.058)	0.30	DMF, 120, 24	$(CF_2)_6(CH=CH\phi)_2$, ^a 152-155 (0.3), 58, mp 92-96 $^{\circ}$ $I(CF_2)_6CH=CH\phi$, --, 32
$(CF_3)_2CFOCF_2CF_2I$ (50, 0.12)	$\phi CH=CHBr$ (24, 0.13)	0.60	DMAC, 100, 72	$(CF_3)_2CFOCF_2CF_2CH=CH\phi$, 64 (1), 61
$C_7F_{15}I$ (30.0, 0.061)	$CF_3CH=CHI$ (19.4, 0.088)	0.31	DMF, 90, 72	$C_7F_{15}CH=CHCF_3$, ^b 68-71 (50), 77
$C_3F_7O(CFCF_2O)_2CFI$ (25.0, 0.034)	$\phi CH=CHBr$ (8.30, 0.043)	0.17	DMAC, 120, 20	$CF_3CF_2CH=CH\phi$, ^c 72-76 (14), 4.3 g isolated

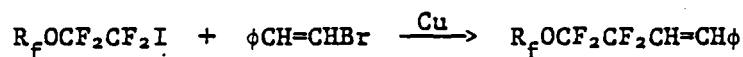
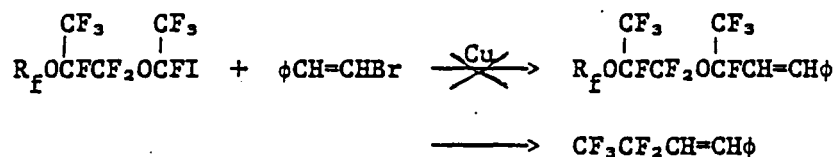
- (a) It is suggested that by employing longer reaction times, the mono iodide-styrene derivative would have been completely converted to the desired distyrene compound.
- (b) In this reaction it proves convenient to consume all of the $C_7F_{15}I$ reactant, since its b.p. is similar to that of the product.
- (c) This was the only olefinic product that could be isolated.

Perfluorovinyl Intermediates

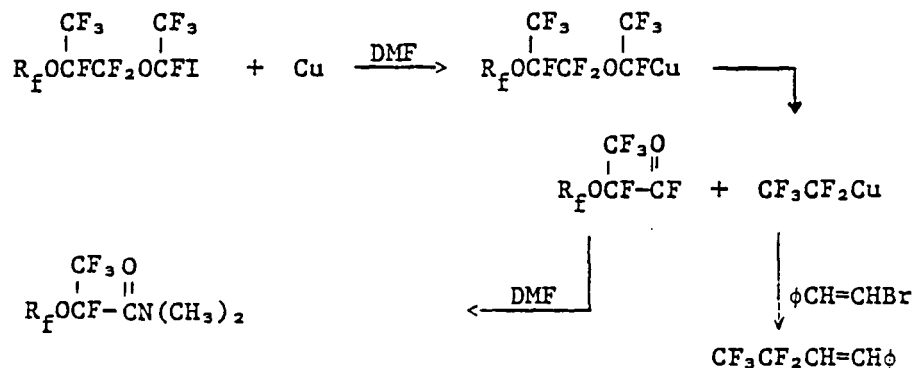
Perfluorovinyl compounds are prepared in good yield (Table I) by copper coupling experiments⁶ in dipolar aprotic solvents.



We have observed that this reaction is not general. When the alkyl iodide has an α -oxygen substituent, only degradation products occur. Compounds in which an oxygen atom appears β to the iodide afford the expected product smoothly.



With regard to the iodide containing the α oxygen substituent, it is believed⁶ that the organocopper reagent is initially formed, and then decomposes to a perfluoroethyl copper species which then reacts to give the observed product.

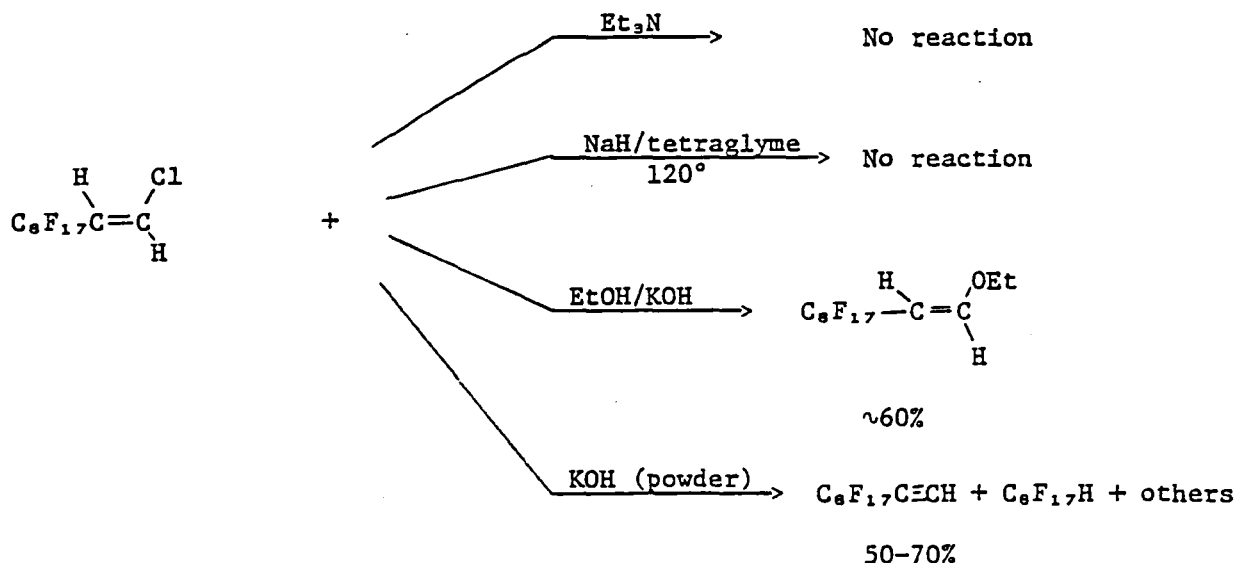


The reactions between the R_fI and vinyl halide seem stereospecific. Thus, an 80:20 mixture of trans and cis $\phi CH=CHBr$ yield roughly an 80:20 composition of trans:cis $R_fCH=CH\phi$, respectively. Reaction between either a 95:5 or 75:25 trans:cis composition of $ICH=CHCl$ and R_fI gives the expected $R_fCH=CHCl$ composition for a stereospecific reaction.

Halogenation and Dehydrohalogenation

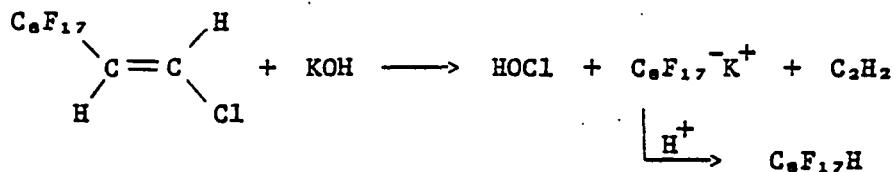
Compounds of the general structure $R_fCH=CH\phi$ brominated and dehydrohalogenate (KOH) smoothly. The end product, $R_fC\equiv C\phi$, is formed in yields ranging from 70-90% based on starting $\phi CH=CHR_f$ (see Table II, Experimental). This route was successfully applied to the preparation of, to the best of our knowledge, the first fluorinated diacetylene, $\phi C\equiv C(CF_2)_6C\equiv C\phi$.

Difficulties were encountered in dehydrohalogenating $R_fCH=CHCl$ (trans) compounds. The results of the interaction of this material with various bases are shown below.

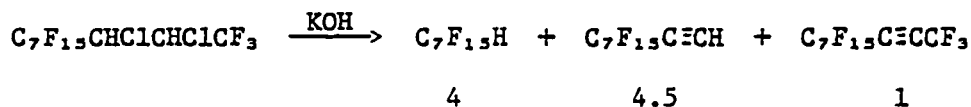


The ethoxy compound is probably formed from either of two routes: cis elimination followed by trans addition of EtO^- to the acetylene, or stereo-

specific addition-elimination. The difficulty in elimination may be due to the cis geometry of the departing H and Cl substituents. This may account for the formation of $C_6F_{17}H$ as a major by-product in the KOH dehydrohalogenation, i.e., trans elimination of a positive chlorine (Cl^+) and negative R_f fragment (R_f^-).



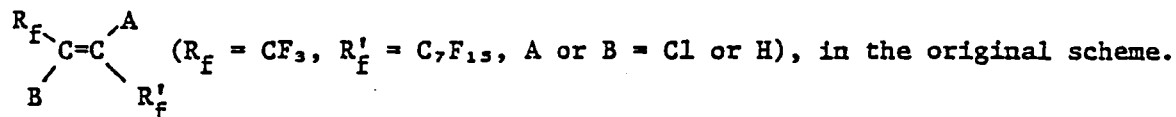
The attempted preparation of $C_7F_{15}C\equiv CCF_3$ from $C_7F_{15}CH=CHCF_3$ (trans) via halogenation and dehydrohalogenation is instructive. The trans olefin is reluctant to brominate (hv, Vycor flask); only 15% dibromide is formed after one week. In contrast, chlorination proceeded readily in a static system in pyrex. An interesting series of compounds is formed on treatment of the dichloride with KOH.



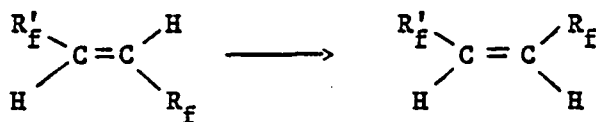
It is believed that the formation of $C_7F_{15}H$ and $C_7F_{15}C\equiv CH$ as major liquid products in this reaction is a consequence of the stereochemistry of chlorine addition and HCl elimination reactions.

Assuming a random trans or cis chlorine addition to the olefin and a random trans or cis mono elimination, four intermediate haloolefins would result.

If this explanation is found to hold for the scheme, the desired acetylene ($C_7F_{13}C\equiv CCF_3$) may be formed as the major product by starting with the cis olefin, $C_7F_{13}C=C^{CF_3}$, or isolating the trans haloolefins,

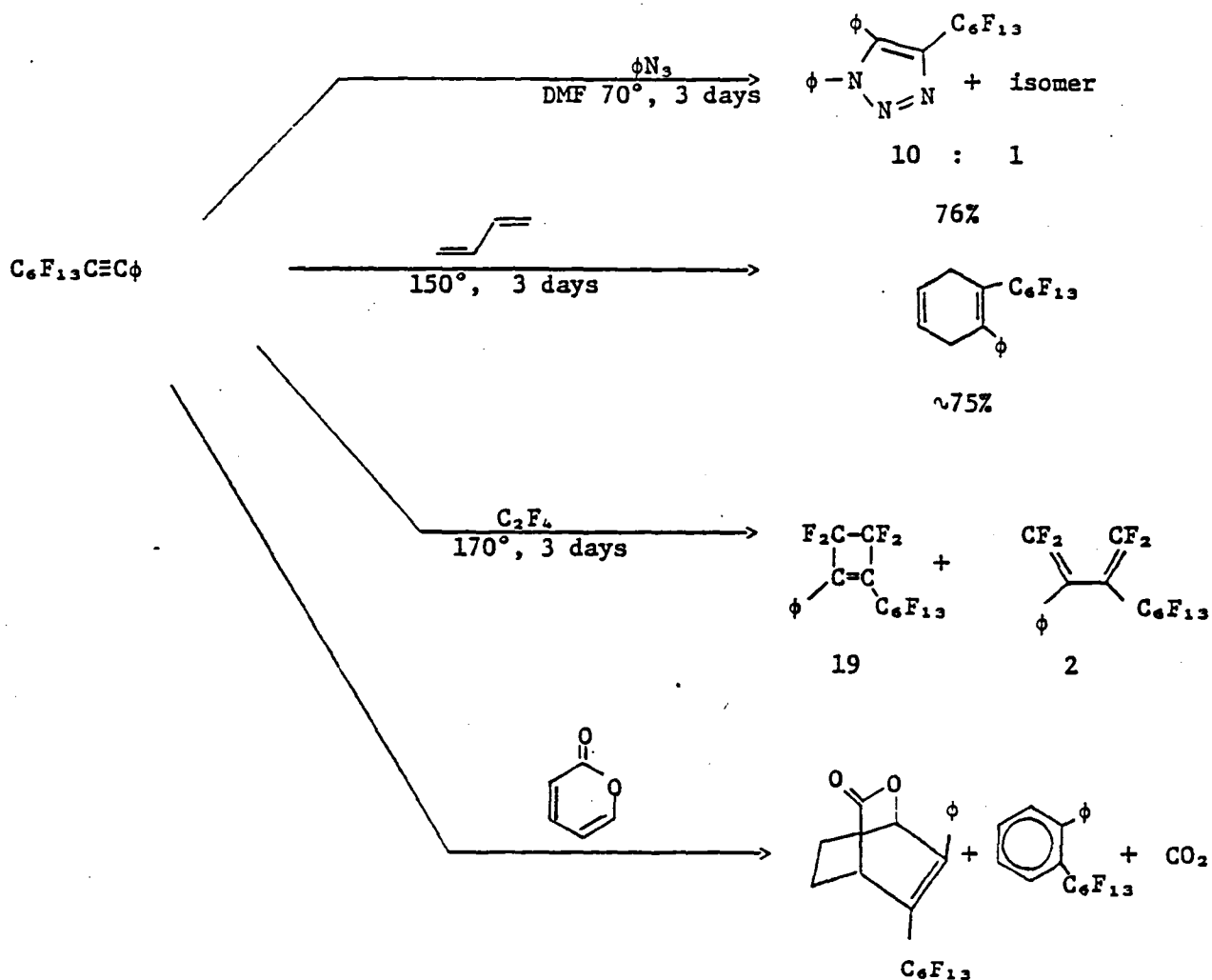


Olefin isomerization by light or nucleophiles, e.g.,

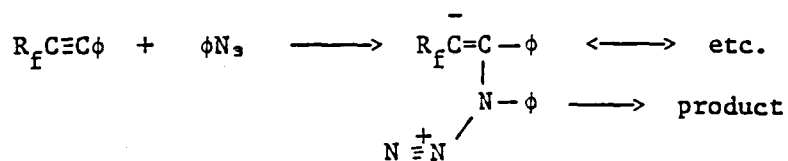


might yield the olefins of the appropriate geometry.

In order to ascertain the ability of fluorinated acetylenes to form cyclic products when reacted with a series of unsaturated substrates, reactions between an acetylene and a 1,3-dipole, diene, and reactive olefin were studied. The results are shown below.

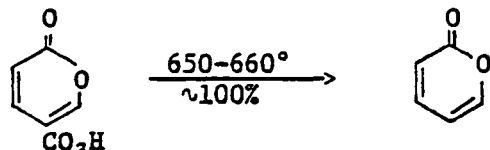


The above reactions are clean; unreacted starting material accounts for the remainder of material balance (>98%). It is notable that the 1,3-dipolar cycloaddition reaction may be step-wise with dipole intermediates intervening.



The fact that the reaction proceeds well in DMF but not in hexane would be consistent with the above hypothesis.

α -Pyrone was prepared according to a literature procedure.⁹ The

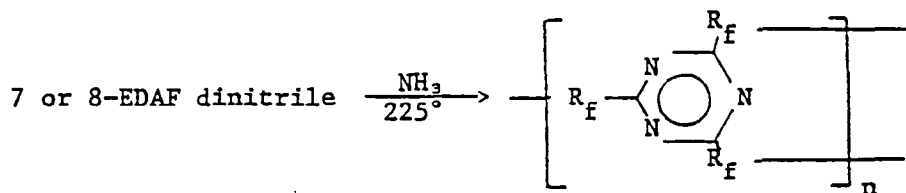


α -pyrone was then reacted with F-hexyl phenyl acetylene. In refluxing xylene both pyrone and acetylene were consumed (however, not completely) and afforded two higher boiling products (GLC). As judged by infrared the reaction gave rise to the 1:1 adduct as well as the desired aromatic.

The above results of model compound reactions indicate the feasibility of obtaining polymers by copolymerization of highly fluorinated acetylenes with appropriate substrates. However, further work in this area was discontinued due to a change in priorities of the project, as determined by the project monitor.

B. Perfluorinated Ether Polytriazines

Under an earlier contract, three-dimensional polytriazines were prepared by polymerization of 7-EDAF and 8-EDAF dinitrile at elevated temperatures in the presence of ammonia catalyst.¹ These materials, however,



had poor mechanical properties; they were cheese-like and could be easily broken.

Several attempts were made to stop the polymerization at an intermediate stage in the hope of obtaining prepolymers with unreacted nitrile groups. Such prepolymers could be crosslinked, in a second stage, with a different reagent, i.e., a bis-nitrile oxide. The results obtained, however, indicate that the polymerization reaction either goes to completion (to a gel-like material) or does not go at all. At intermediate times and temperatures, intermediate compositions could not be obtained.

It has been reported^{10,11} that polytriazines derived from perfluoroaliphatic dinitriles are tough and in some cases brittle. It was then conceivable that polymerization of a mixture of a fluoroaliphatic dinitrile with a long chain fluoroaliphatic ether dinitrile would result in a material with properties intermediate between the polytriazines derived from homooligomerization of the individual dinitriles.

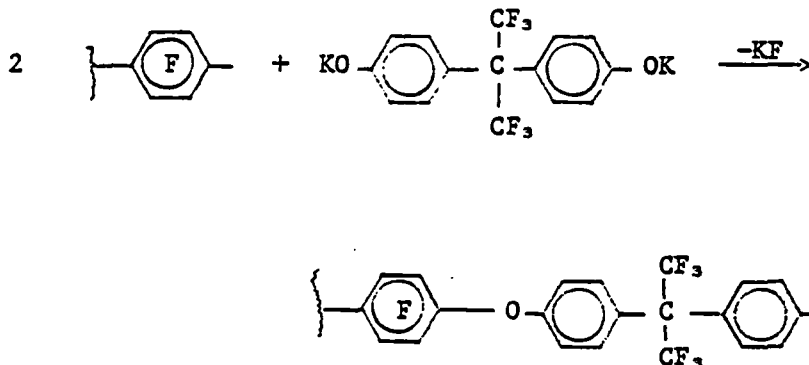
Perfluorosebaconitrile was chosen as the aliphatic component. The composition and Tg's of the these polytriazines are shown in Table II.

TABLE II
POLYTRIAZINES

<u>Dinitrile (g)</u>	<u>Dinitrile (g)</u>	<u>Tg (°K)</u>
7-EDAF Dimer	--	215
8-EDAF	--	231
7-EDAF Dimer (5 g)	<u>F</u> -Sebaconitrile (1)	283
7-EDAF Dimer (2.5 g)	<u>F</u> -Sebaconitrile (1.6)	235
--	<u>F</u> -Sebaconitrile	>373

An alternate approach to improve the properties of the polytriazines would be to add a small percentage of a monofunctional nitrile containing

a perfluorophenyl group and then crosslink or chain extend the resulting polymers through the C_6F_5 group. The dipotassium salt of hexafluoroacetone bisphenol has been used as a chain extension agent for a C_6F_5 group.¹²

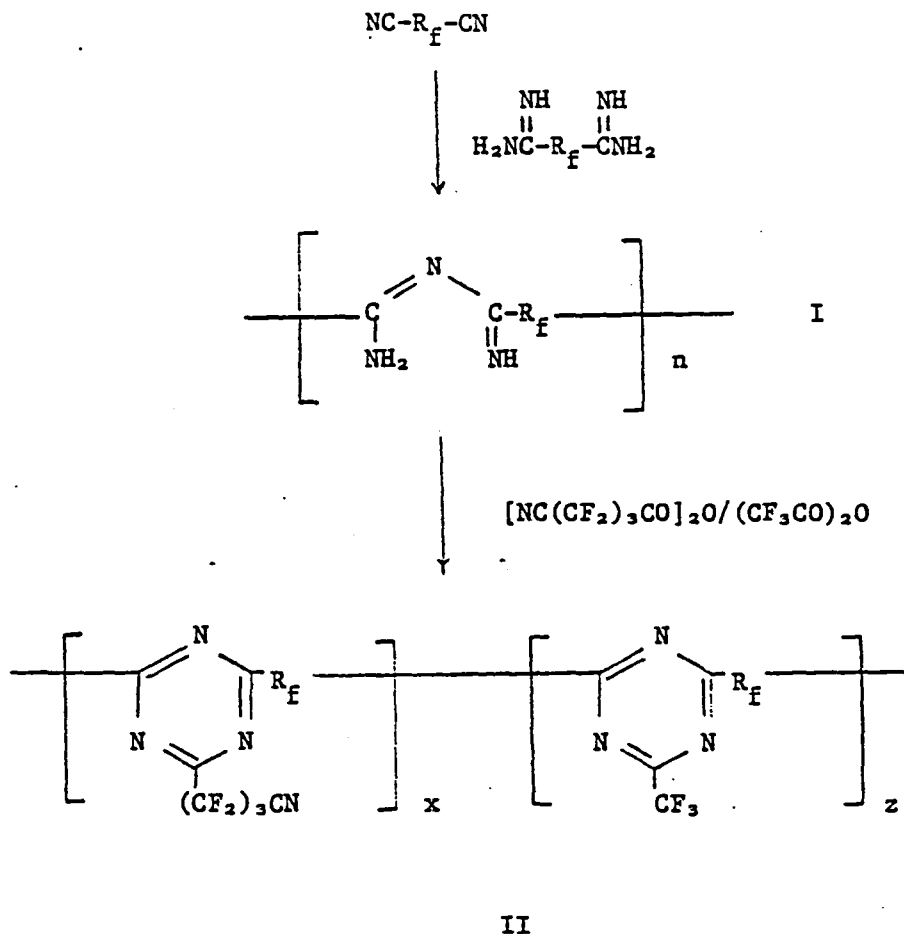


A model triazine containing a C_6F_5 pendent group was prepared and treated with sodium phenolate in an attempt to achieve fluoride displacement on the F-aromatic group. However, examination of the reaction mixture revealed that the triazine ring had been cleaved. On reexamination, it was noted that the starting material (C_6F_5O pendent triazine) which had been prepared and characterized roughly six months earlier, had decomposed on standing. This renders the results of its subsequent reaction with phenoxide meaningless.

C. Perfluoroalkylene Ether Polytriazines with Pendent Nitrile Groups

In view of the above results further work on the direct polymerization of perfluorodinitriles to polytriazines was discontinued.

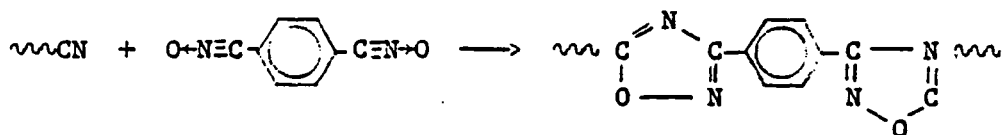
The desired polytriazines, however, with pendent nitrile groups were successfully prepared by the alternate route shown below.



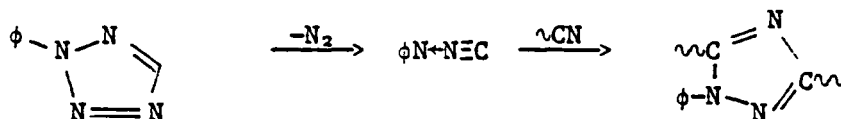
The diamidine of 8-EDAF dinitrile, dissolved in Freon E4, was added to an equivalent amount of 8-EDAF dinitrile. The resulting polyimidoylamidine I was then ring-closed to the polytriazine II with a mixture of trifluoroacetic anhydride and a nitrile-anhydride.

Two samples of the polytriazine II, $R_f = \text{CFO}(\text{CF}_2\text{CFO})_3(\text{CF}_2)_3(\text{OCFCE}_2)_3\text{OCF}-$, and an x/z ratio equal to 15/85 and 5/95, respectively, were prepared and submitted to NASA for curing and evaluation. It should be pointed out that the polytriazine polymer II is not a block copolymer; the triazine rings with pendent nitrile groups are randomly distributed over the polymer chain.

The polymer II could be crosslinked through the nitrile group by the use of an appropriate reagent. Currently, NASA is employing a dinitrile oxide to either chain extend dinitriles or crosslink polytriazines that possess pendent nitrile groups.



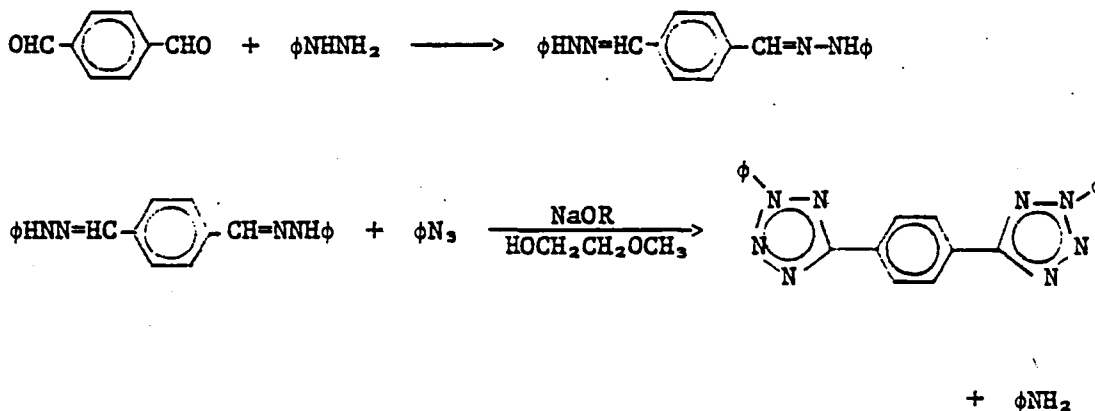
It has been reported¹³ in the literature that at elevated temperatures tetrazoles lose nitrogen affording nitrile imines in situ which subsequently react as their analogous nitrile oxides. The reaction between a bis-tetrazole and a fluorinated dinitrile has been reported to be a polymer forming reaction.¹⁴ The substitution of a bis-tetrazole for a bis-nitrile oxide in the above reaction would afford a triazole rather than an oxadiazole



linkage. While little difference in physical properties of the resulting polymer would be expected from this substitution, the use of a bis-triazole would seem to have the following advantages. The reactive intermediate is formed at elevated temperatures (>150°C) which might permit greater solubility and, consequently, higher molecular weight polymer or more effective cross-linking. Due to the in situ formation of the reactive nitrile imine, its concentration is minimal at any given time, assuming that it reacts with substrate (R_FCN) as it is formed. As a consequence, little if any homopolymerization of the bis-nitrile imine should occur. Homopolymerization of

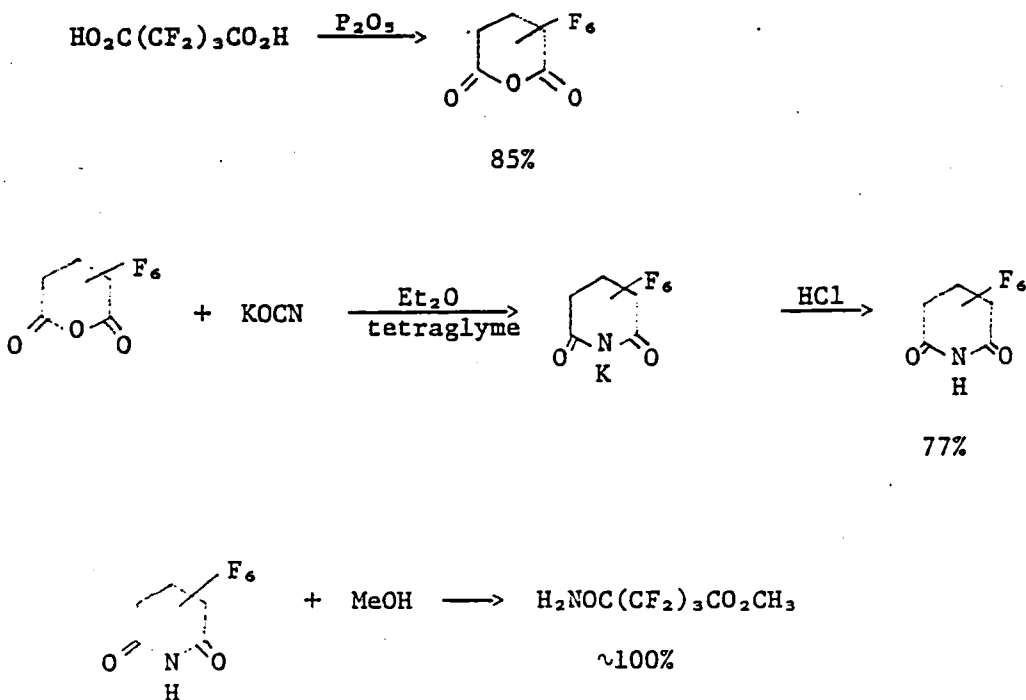
the bis-nitrile oxide is observed during related applications and leads to experimental as well as interpretive difficulties.

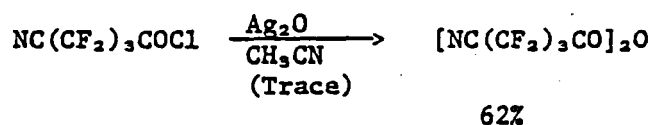
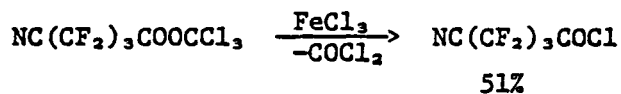
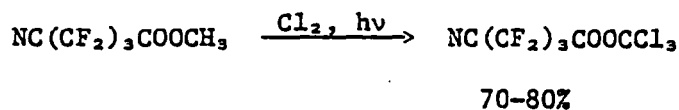
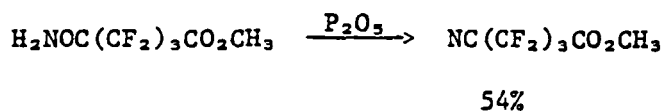
A bis-tetrazole was prepared as shown below and a sample of this material was supplied to NASA.



ω -Cyanoperfluoroalkyl Acyl Fluorides

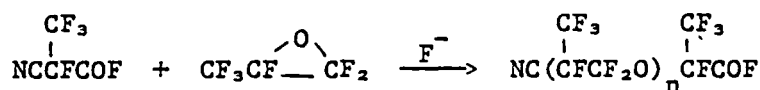
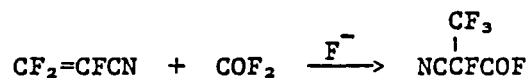
The nitrile anhydride $[\text{NC}(\text{CF}_2)_3\text{CO}]_2\text{O}$, was prepared by a modification of the Hooker Chemical Company route¹⁰ as shown below.





The imide forming reaction¹⁵ run in tetraglyme, gave a low yield (~50%) due to the difficulty in completely distilling F-glutarimide from a large quantity of tetraglyme. For this reaction to proceed, however, tetraglyme is necessary. Subsequently the reaction was repeated in Et₂O with catalytic amounts of tetraglyme and afforded a 75% yield.

The above synthesis cannot readily be extended to other nitrile-anhydrides or acyl chlorides. A more general synthesis of ω-cyanoperfluoro-alkyl acyl fluorides has been reported in the literature.¹⁶



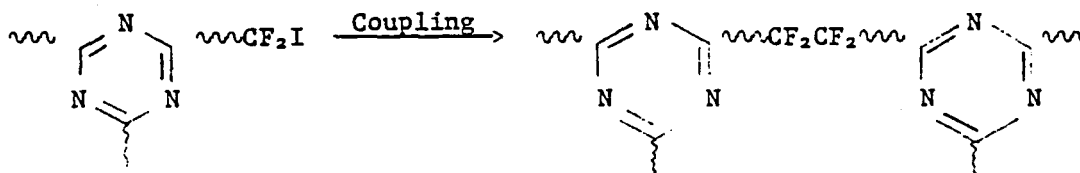
These nitrile-acyl fluorides derived from HFPO, present certain advantages over NC(CF₂)₃COCl in the preparation of polytriazines. Indeed,

it has been established that triazines derived from HFPO oligomers (secondary acyl fluorides) are hydrolytically more stable than triazines derived from TFEO oligomers (primary acyl fluorides) or from primary perfluoroalkyl acyl fluorides.¹⁷

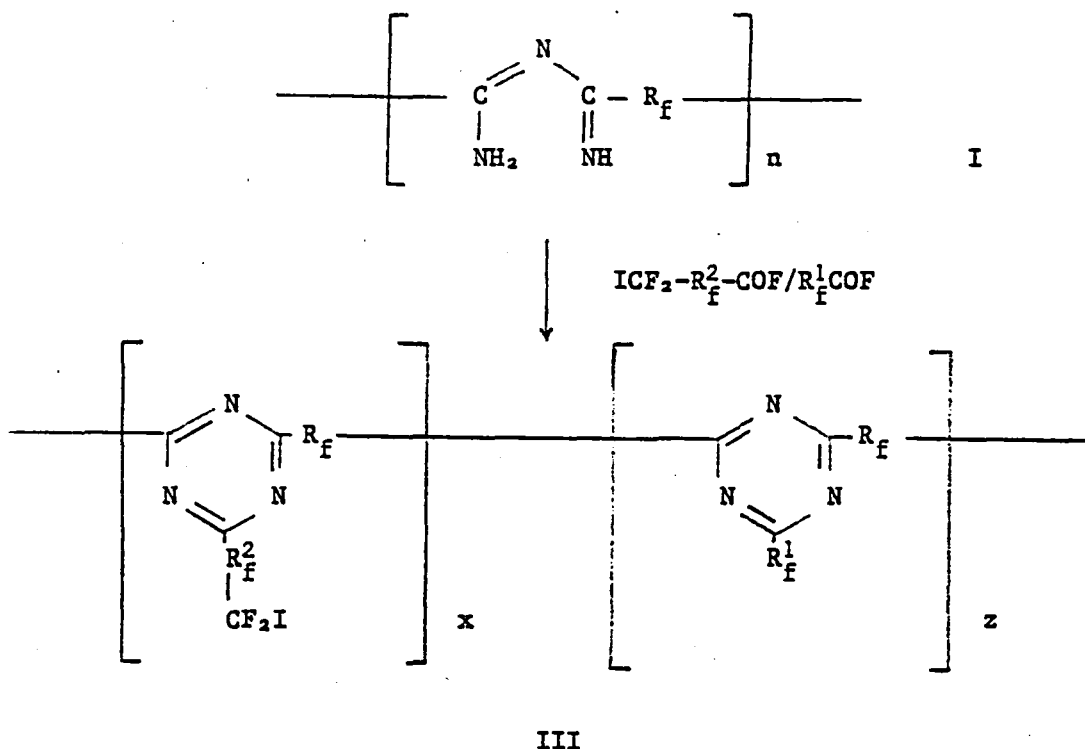
D. Perfluoroalkylene Ether Polytriazines with $-CF_2I$ Pendent Groups

The rationale for choosing the perfluoroether substituted polytriazines as the basic polymer structure is based on the demonstrated high thermal stability of this system. However, curing the polytriazine II with terephthalonitrile oxide (TPNO) introduces new functional groups into the polymer, namely the oxadiazole and phenyl rings, with an undetermined effect on the thermal as well as the hydrolytic stability of the final product.

It occurred to us that the basic structure of the polytriazine with the concomitant high thermal stability could be preserved if cross-linkable polytriazines could be made which do not require the use of an additional reagent for curing. Polytriazines with pendent $-CF_2I$ groups seem to be ideally suited for this purpose since they could be cured by u.v. irradiation, radical coupling, mercury coupling, etc., the final product being a crosslinked polytriazine.



The polytriazines with $-CF_2I$ pendent groups were prepared in the same fashion as the polytriazines with $-CF_2CN$ pendent groups, namely by ring closure of the polyimidoylamidine I with a mixture of an iodoacyl fluoride and HFPO-dimer acyl fluoride.



A variety of acyl fluorides (or anhydrides) may be used for the ring closure reaction. We have chosen, however, to use secondary acyl fluorides of the HFPO-type $[\text{R}_f\text{OCF}(\text{CF}_3)\text{CFO}]$ since it has been shown that the resulting triazines are hydrolytically more stable than triazines with primary substituents.⁷ (See also below).

A sample of the polytriazine III with $\text{R}_f^1 = \text{CF}_3\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{-}$, $\text{R}_f^2 = \text{-CF}_2\text{O}(\text{CF}_2)_3\text{OCF}(\text{CF}_3)\text{-}$ and $x/z = 15/85$ was prepared and successfully crosslinked to an elastomeric gum.

Irradiation of an aliquot of the above polytriazine with a low pressure u.v. lamp afforded an elastomeric gum ($T_g = -61^\circ\text{C}$). A similar elastomeric gum was obtained on heating an aliquot of the polytriazine at $200\text{-}230^\circ\text{C}$ ($T_g = -60^\circ\text{C}$).

There were differences in the consistency of the gums obtained by the two processes; the gum obtained from photochemical coupling appeared to be more highly cross-linked. However, since no effort was made in either

experiment to carry the reaction to completion or to determine the extent of crosslinking, these variations may be due to a difference in degree of coupling of the samples.

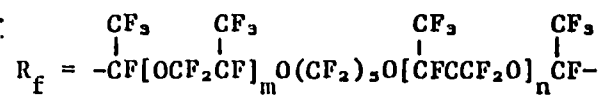
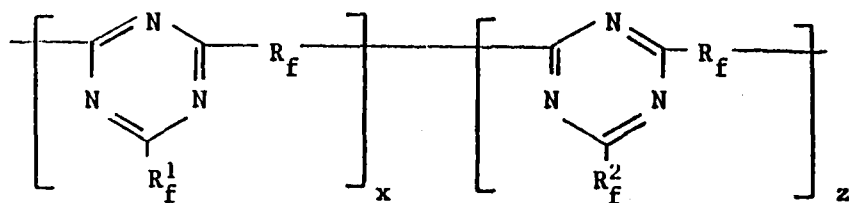
It should be pointed out in this connection that the crosslinking process which was depicted above as a simple coupling is actually a more complicated process. Work in our laboratories has shown that depending on the conditions of photochemical coupling, the radical originally formed may undergo secondary reactions which lead to other radicals and eventual coupling.¹⁸ These considerations should be kept in mind in the development of a curing process.

The percentage of crosslinking sites in the molecule is obviously critical and it may well be that the arbitrarily chosen 15% level is close to the upper limit of allowable compositions for obtaining elastomeric gums. The fact, however, that a gum was obtained, notwithstanding the limitations of the particular sample of polytriazine and the curing conditions, clearly demonstrated the validity and feasibility of this approach. A sample of this triazine was forwarded to NASA for curing and evaluation; their findings confirmed our results.

On the basis of the above results it was decided to prepare a series of polytriazines of structure III with varying lengths of the R_f group and varying proportions of $-CF_2I$ groups and study the effect of these variables on the molecular weight of the polytriazine and on the properties of the cured polymer. At the request of the Project Monitor, molecular weight determinations, curing experiments and evaluation were to be performed at NASA.

Table III shows the structure and composition of the polytriazines prepared. In each group of polytriazines with a given R_f group a small sample of the same polyimidoylamidine was ring-closed to polytriazine with

TABLE III

POLYTRIAZINES WITH $-\text{CF}_2\text{I}$ PENDENT GROUPS

Sample No.	Amount	$(R_f) \text{ m+n}$	$R_f^1 = \begin{array}{c} \text{CF}_3 \\ \\ -\text{CFOCF}_2\text{F}_7 \end{array}$	$R_f^2 = \begin{array}{c} \text{CF}_3 \\ \\ -\text{CFO}(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{I} \end{array}$
1294-43-2.1	20.0 g	2	92	8
1294-43-3.1	21.5	2	95	5
1294-43-4.1	22.0	2	88	12
1294-43-5.1*	6.7	2	$R_f^1 = R_f^2 = -\text{CF}_3$	
1294-47-1.1	19.0	4	95	5
1294-47-2.1	18.5	4	92	8
1294-47-4.1*	5.5	4	$R_f^1 = R_f^2 = -\text{CF}_3$	
1294-43-1.1**	24.5	2	92	8*
1294-57-1.1	22.8	3	85	15

TABLE III (continued)

<u>Sample No.</u>	<u>Amount</u>	<u>(R_f) mⁿ</u>	<u>R_f¹ = $\begin{array}{c} \text{CF}_3 \\ \\ -\text{CFOC}_3\text{F}_7 \end{array}$</u>	<u>R_f² = $\begin{array}{c} \text{CF}_3 \\ \\ -\text{CFO}(\text{CF}_2)_5\text{OCF}_2\text{CF}_2\text{I} \end{array}$</u>
1294-57-1.2	16.0	3	82	18
1294-57-1.3*	11.3	3	100	R _f ² = R _f ¹
1294-55-1.1	19.0	5	95	5
1294-55-1.2	17.0	5	92	8
1294-55-1.3	13.5	5	88	12
1294-55-1.4*	9.5	5	100	R _f ² = R _f ¹

* Standard for molecular weight determination.

** Inverse addition (acyl fluoride to imidoylamidine).

pure trifluoroacetic anhydride or HFPO-dimer acyl fluoride to be used for molecular weight determination. The reason for this was that the earlier attempts by NASA to determine the molecular weight of the polytriazine III gave erratic and irreproducible results attributed to inadvertent partial coupling of the sample through the $-CF_2I$ groups. Since the molecular weight of the polytriazine III is determined by the degree of polymerization of the polyimidoylamidine I, the experimental molecular weight of the standard sample (devoid of $-CF_2I$ groups) would represent the actual molecular weight of the polytriazine III.

The approach to the preparation of polytriazines with pendent groups ($-CF_2I$ or $-CF_2CN$), outlined above, rests on two assumptions: a) that the degree of polymerization of the polyimidoylamidine, hence of the polytriazine ($n = x + z$) is fairly high and b) that the reactivities of the two acyl fluorides (or anhydrides) in the ring-closure reaction are comparable. If these assumptions are valid the $-CF_2I$ groups will be randomly distributed over the polymer chain, as stated earlier.

Work at Hooker¹⁰ and at PCR¹⁹ has shown that high molecular weight polyimidoylamidines and polytriazines can be obtained by this method. Polymerization of perfluorosebacamidine with perfluorosebaconitrile (10% molar excess) followed by ring-closure with heptafluorobutyric anhydride gave a polytriazine of 32,000 molecular weight.¹⁹ Lower molecular weight polytriazines were obtained by varying the molar ratio of the reactants.¹⁹ The choice of $CF_2ICF_2O(CF_2)_5OCF(CF_3)COF$ and $CF_3CF_2CF_2OCF(CF_3)COF$ as the ring-closure reagents was dictated by the second requirement of comparable reactivity.

Nevertheless, preliminary results of molecular weight determinations, communicated to us by NASA, seem to raise questions as to the validity of

the above assumptions. High pressure liquid chromatography indicates that most of the polytriazine samples in table III are "dimers" and "trimers".

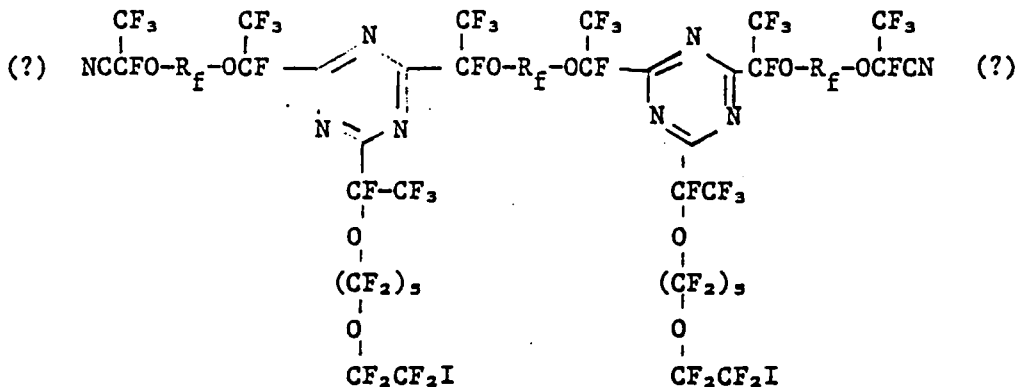
If this is generally correct, then condition a) above is obviously not satisfied. An equimolar ratio of dinitrile to diamidine was used in the preparation of the samples in Table III (Experimental Section) in order to obtain the maximum degree of polymerization. However, a number of differences exist between the present system and that of references 10 and 19, any one of which may be the cause of the indicated lower molecular weight of the obtained polytriazine: a) difference in substrate : perfluorosebaconitrile vs long chain EDAF's with the HFPO structure (secondary nitrile) b) solvent : diglyme vs Freon-113 (in some cases Freon E4), and c) ring closing reagent : anhydrides vs acyl fluorides.

It is clear that a study of the reaction of HFPO-dinitriles (EDAF's) with diamidine is required in order to establish the optimum conditions for the formation of high molecular weight polyimidoylamidine.

Perfluoroalkylene Ether Bis-Triazines with $-CF_2I$ Pendent Groups

There is an interesting implication in the HPLC results which should be explored. If the interpretation of HPLC results is correct and since we did obtain an elastomeric gum from the polytriazine III by photochemical and thermal curing,^{*} it follows that what we cured was a small fraction of the polytriazine III having the structure IV (DP = 2) or similar to that (DP = 3).

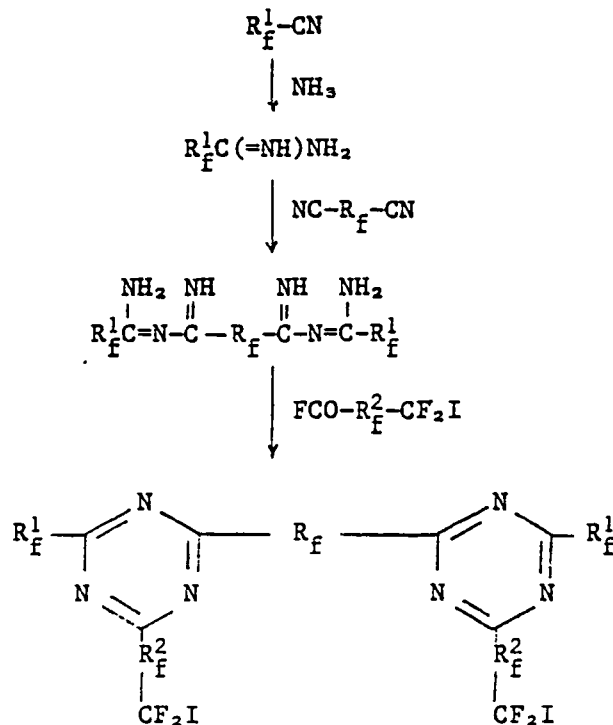
* The term "curing" is used here loosely and refers to the effect of radiation or heating on the molecular weight of the sample; it does not necessarily imply a three-dimensional structure of the resulting product.



IV

Structure IV, except for the end-groups, is a monomeric bis-triazine. Bis-triazines derived from HFPO and TFEO oligomers were studied extensively at PCR in conjunction with another contract.¹⁸

Triazines with the general structure V, the synthesis of which is outlined below, present several advantages over structure IV and its method of preparation. First, triazines V are devoid of functional end-groups. The end-groups in structure IV (nitriles or amides) are troublesome and, if left untreated, may contribute to corrosion problems. Secondly, triazines



V

V, because of their method of preparation, are pure materials as contrasted to triazines IV which constitute only a small fraction of the polytriazine samples.

With reference to the preparation of bis-triazines, more variables are available to control the molecular weight than in the synthesis of the polytriazines. These variables include:

R_F¹

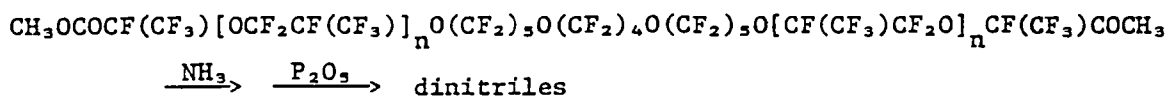
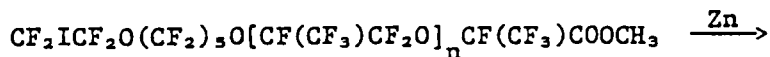
Monofunctional nitriles of the general structure $XCF_2CF_2O(CFXCF_2O)_nCFXCN$ with $n = 1 - 8$ have been prepared^{17,20} from both HFPO ($X = CF_3$) and TFEO ($X = F$).

The TFEO structure imparts greater flexibility (lower T_g) to the molecule but the HFPO structure exhibits higher hydrolytic stability.²⁰

Nitriles derived from TFEO but terminated with HFPO i.e., $C_2F_5O(CF_2CF_2O)_nCF(CF_3)CN$ combine both higher hydrolytic stability and lower T_g.¹⁷

R_F

Dinitriles derived from HFPO (EDAF's) have been prepared and used in the synthesis of polytriazines discussed earlier. Higher molecular weight diacyl fluorides, hence dinitriles, were prepared by photochemical dimerization of EDAF's.¹ A more general method, consisting of the coupling of ω-iodoesters with zinc is now available.²¹

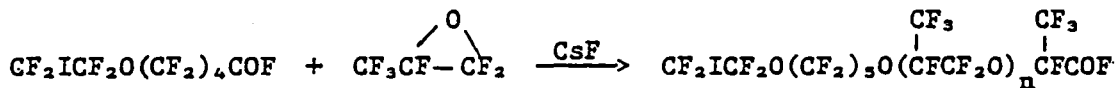
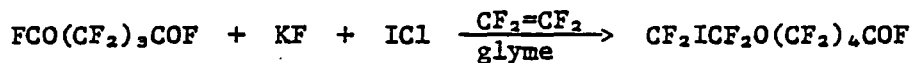


R_f²

ω -iodoacyl fluorides of the structure $\text{CF}_2\text{ICF}_2\text{O}(\text{CF}_2)_5\text{O}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n - \text{CF}(\text{CF}_3)\text{COF}$ have been prepared under the current contract. Only the first member of the series ($n = 0$) was used in the synthesis of polytriazines. However, higher homologs are more promising in the synthesis of bis-triazines.

ω -Iodoperfluoroalkylene Oxide Acyl Fluorides

The required iodoacyl fluorides were prepared by the following sequence of reactions.



A detailed discussion of these reactions can be found in reference 21.

E. Conclusions and Recommendations

The objective of this program was the preparation of long-chain perfluoropolyethers with functional pendent groups and the investigation of methods for converting these prepolymers to stable cross-linked polymers for sealant applications.

Two promising systems have emerged from this research: a) perfluoropolytriazines with -CN pendent groups (terephthalonitrile oxide crosslinking) and b) perfluoropolytriazines with -CF₂I pendent groups (thermal or photochemical curing).

Both systems are based on a polyimidoyl amidine prepolymer derived from HFPO oligomers. It is clear that, regardless of the curing method and

reagents, the properties of the final crosslinked polymer will depend largely on the molecular distribution of the polyimidoyl amidine prepolymer. Consequently, a study of the formation of polyimidoylamide is indicated. Indeed, if a polyimidoylamide of fairly high molecular weight can be prepared reproducibly there is little doubt that the corresponding polytriazine with $-CN$ or $-CF_2I$ pendent groups will yield a usable sealant on curing.

The polytriazines with $-CN$ pendent groups prepared under this contract were limited by the availability of ω -cyanoperfluoroacyl fluorides or anhydrides. Consequently, the suggested method for the preparation of ω -cyanoacyl fluorides, $NC[CF(CF_3)CF_2O]_nCF(CF_3)COF$, merits investigation. Methods for the preparation of ω -iodoacyl fluorides $ICF_2CF_2O[CF(CF_3)CF_2O]_nCF(CF_3)COF$, are available.

Another system which was briefly investigated was highly fluorinated acetylenes. The research on this subject was limited to the development of methods for the preparation of model monofunctional compounds. Further investigation of this system seems advisable.

SECTION III

EXPERIMENTAL

A. Highly Fluorinated Acetylenes

1. Attempted Preparation of Fluorinated Acyl Acetylenes

a. Acetylene was bubbled through THF (anhydrous, 200 ml) while BuMgCl (40 ml, 2.5 N, 0.1 mole) was slowly added dropwise. The temperature was maintained at 25°. The resulting solution was transferred to an addition funnel. This material was added to a THF (50 ml) solution of C₇F₁₅COCl (43.3 g, 0.1 mole) at 0°C in 2 hr. The mixture was allowed to warm to room temperature. Typical workup gave 1.9 g of distillate (b.p. 80°/15 mm) suspected to be BuCOC₇F₁₅. Bottoms (40.3 g) remained after distillation.

b. Copper phenyl acetylide (5.0 g, 0.03 mole) was added to tetraglyme (50 ml) and the resulting mixture was stirred at 25°. The addition of C₇F₁₅COCl (13.0 g, 0.03 mole) resulted in an immediate color change (yellow→grey). The mixture was filtered and phase separated. The bottom layer was added to Freon-113 (50 ml) and extracted with H₂O (3 x 25 ml). The organic phase was separated, dried and distilled. A fraction, b.p. 80°/1 mm, (1.2 g) showed the presence of a C=O (5.85μ) and a C C (4.5μ) group. Due to the poor yield (ca. 30%) further experimentation directed toward the preparation of acyl acetylenes was discontinued.

2. Attempted Preparation of Methyl Perfluoroalkyl Ketones Enroute to Fluorinated Acetylenes

a. Perfluorooctanoic acid (16.5 g, 0.04 mole) was dissolved in Et₂O (100 ml). The solution was stirred and cooled to 0° when MeMgBr (3M, 34 ml, 0.1 mole) was added dropwise over a 1.5 hr period. The mixture was hydrolyzed with aqueous HCl. Phase separation followed by extraction with

water (3 x 50 ml), drying (Na_2SO_4), and concentration left 16.8 g of a white solid which did not contain the desired ketone.

b. The above reaction was repeated using $\text{C}_7\text{F}_{13}\text{COCl}$ (0.04 mole) and Me_2CuLi (0.04 mole) as reactants. The reaction mixture was hydrolyzed with aqueous NH_4Cl ($\sim 0^\circ$) and kept cold during work up. A distillate (4.5 g, b.p. $\sim 110^\circ/\sim 1$ mm) was obtained and is believed to be $\text{C}_7\text{F}_{13}\text{COCH}=\text{CMeC}_7\text{F}_{13}$ (cis and trans). Bottoms (10.3 g) with a similar infrared as in the previous experiment remained.

3. General Procedure for Coupling Perfluoroalkyl Iodides with Vinyl Iodides

Anhydrous DMF or DMAC (200 ml) was put into a flask containing 0.4 g-at of activated copper-bronze. The solvent was degassed when the perfluoroalkyl iodide (0.1 mole) and vinyl iodide (0.1 - 0.2 mole) were added. The mixture was mechanically stirred and heated from $90-120^\circ$ (depending on the boiling points of the iodides) for roughly 24 hr. The reaction mixture was allowed to cool, pressure filtered, and the remaining liquid was added to 600 ml of H_2O . The resulting mixture was refiltered (4-7 μ frit) and extracted with Freon-113 (4 x 50). A portion of the Freon extract was used to wash the precipitate left from the previous two filtrations. The Freon layer was then extracted with H_2O (4 x 50 ml), dried (MgSO_4) and concentrated. The desired olefin was purified by distillation (see Table I).

4. Attempted Synthesis of 2-(F-hexyl)biphenyl

A 5-ml flask containing a stirring bar was fitted with a reflux condenser vented to a -183° trap and then charged with $C_6F_{13}C\equiv C\phi$ (0.997 g, 2.4 mmoles) and α -pyrone (0.231 g, 2.4 mmoles). The contents of the flask were stirred and heated at 80° for 4 hours with no apparent reaction. The reaction mixture was heated an additional 16 hours at 80° at which time it was observed that a small amount of a viscous, brown oil was being formed. An infrared spectrum of the clear, liquid portion of the product mixture showed that the relative intensities attributed to $C\equiv C$ at 4.4μ and $C=O$ at 5.7μ had now changed so that the carbonyl absorption became the stronger. A GLC of the reaction mixture showed besides starting materials and solvent two compounds which eluted after the acetylene. These are suspected to be the 1:1 adduct and the titled compound.

The clear portion of the reaction mixture was transferred to another flask where benzene and an additional 0.46 g (4.8 mmoles) of α -pyrone was added. This mixture was heated to reflux but after two days an infrared spectrum still showed the presence of unreacted acetylene. Xylene was exchanged for benzene as the solvent so as to attain a higher reflux temperature, but after an additional 24 hours another infrared spectrum still showed unreacted acetylene. A GLC of the xylene solution indicated the presence of both starting materials as well as two higher boiling products.

5. Conversion of $C_6F_{17}CH=CHCl$ (trans) to $C_6F_{17}C\equiv CH$

Powdered KOH (5.0 g) and $C_6F_{17}CH=CHCl$ (5.0 g) were charged to a 25-ml flask. The mixture was gradually heated. At 80° an exothermic reaction occurred and product began to reflux. Continuous heat was applied (oil bath to 140°) and the product was removed as it was formed, b.p. $131-134^{\circ}$

(3.3 g, 71%). Attempts to scale-up the reaction gave a vigorous exotherm that was not controllable. In an attempt to introduce the haloolefin to a KOH/mineral oil dispersion at ca. 100°, only degradation products were obtained.

6. Conversion of $R_FCH=CH\phi$ to $R_FC\equiv C\phi$ by Bromination and Dehydrohalogenation

This procedure seems general; it is exemplified by the preparation of $C_6F_{13}C\equiv C\phi$. Freon-113 (100 ml) and $C_6F_{13}CH=CH\phi$ (22.4 g, 0.054 mole) were put into a flask which was placed in the sunlight. Then Br_2 (8.7 g, 0.054 mole) diluted with Freon 113 (10 ml) was slowly added to the flask over a 0.5 hr period. The solution was stirred for 2 hr at which time essentially all the Br_2 color had dissipated. The solution was extracted with sodium thiosulfate solution, dried, and concentrated to leave 29.7 g of crude dibromide. A portion of the crude dibromide (12.9 g, 0.022 mole) was slowly added to a powdered KOH (20 g) mineral oil (30 ml) dispersion maintained at 100° under vacuum (0.2 mm). The acetylene b.p. 58-61° at 0.2 mm (7.8 g, 82% from olefin) distilled from the flask. If the fraction has a higher boiling point, it is impure with a bromoolefin (incomplete dehydrohalogenation). See Table IV for the properties of various acetylenes. Although the compound, $C_7F_{13}CH=CHCF_3$, brominated slowly, it chlorinated easily.

TABLE IV

FLUORINATED ACETYLENES

<u>Acetylene</u> ^a	<u>B.P. (°C) (mm)</u>	<u>Yield from Haloolefin (%)</u>
$C_8F_{17}C\equiv CH$	132-134	71
$C_6F_{13}C\equiv CC_6H_5$	58-61 (0.2)	84
$(CF_2)_6(C\equiv C\phi)_2$	160 (0.1)	60
$(CF_3)_2CFOCF_2CF_2C\equiv C\phi$	68-71 (18)	65
$CF_3CF_2C\equiv C\phi$	84-87 (50)	92

(a) The acetylenes have been characterized by infrared ($R_FC\equiv CH$, 3.0 μ ; $C\equiv C$, 4.65 μ ; $R_FC\equiv C\phi$, $C\equiv C$, 4.45 μ), 1H and ^{19}F NMR, and either mass spectroscopy or elemental analysis.

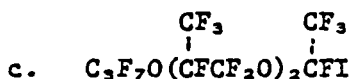
7. Preparation of Various Intermediates

a. ICH=CHCl

This material was prepared by bubbling acetylene through CH₃CN (100 ml) at 0° while ICl (100 g dissolved in 500 ml CH₃CN) was added dropwise. Usual work up gave 78 g (62%) ICH=CHCl b.p. 56-57°/90 mm (trans >95%).

b. CF₃CH=CHI

This material was prepared by an analogous procedure^{2a} used to prepare C₂F₃CH=CHI. CF₃I (96 g, 0.44 mole) and C₂H₂ (14.4 g, 0.56 mole) were charged to a 300-ml S.S. autoclave and heated at 200°/24 hr then 205°/4 hr. Distillation of the crude mixture afforded CF₃CH=CHI (trans) b.p. 72-74° (43 g, 43% yield).



This material was prepared according to a published procedure⁵ from

$\text{C}_3\text{F}_7\text{O}(\overset{\text{CF}_3}{\underset{|}{\text{C}}}\text{FCF}_2\text{O})_2\text{CFCOF}$, Na₂CO₃, and tetraglyme in a 47% yield, b.p. 115-118°/80 mm.

8. Reaction Between C₆F₁₃C≡Cφ and φN₃

The acetylene (2.0 g, 4.75 mmoles) and phenyl azide (0.57 g, 4.8 mmoles) dissolved in hexane (2.5 ml) were heated in DMF (2 ml) at 70-80° for 2 days. GLC showed two products (isomers) in a 10:1 ratio as well as unreacted acetylene. The mixture was poured into 10 ml of H₂O, extracted with Freon-113, and concentrated. The crude solid was triturated with 10 cc cold hexane and filtered to leave 1.7 g (66%) of adduct m.p. 127-130°. Recrystallization from hexane afforded an analytical sample m.p. 134-135°.

Anal. Calcd for C₂₀H₁₀F₁₃N₃: C, 44.5; H, 1.9; N, 7.75.

Found: C, 44.2; H, 2.1; N, 7.6.

The starting acetylene (0.6 g) was recovered from the hexane. The triazole had an ^1H and ^{19}F NMR consistent with its structure.

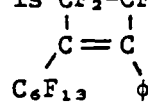
9. Reaction Between $\text{C}_6\text{F}_{13}\text{C}\equiv\text{C}\phi$ and Butadiene

The acetylene (1.0 g, 2.4 mmoles) and 1,3-butadiene (0.3 g, 5.6 mmoles) were sealed in a 20-ml polymer tube and heated at $150^\circ/3$ days. GLC of the crude mixture showed a 16:55 ratio of starting material to product. No other material was present. The product was characterized by ^1H and ^{19}F NMR and mass spectral data (m/e 474, base m/e 155).

10. Reaction Between $\text{C}_6\text{F}_{13}\text{C}\equiv\text{C}\phi$ and TFE

The acetylene (1.0 g, 2.4 mmoles), TFE (0.7 g, 7 mmole) and α -pinene (3 drops) were charged to a polymer tube which was subsequently sealed. The tube was heated in an oil bath at $170^\circ/3$ days and then cooled and vented. The crude product showed 3 components in a 9:19:2 ratio. The first is starting material while the major component is $\text{CF}_2\text{-CF}_2$ and the minor component

is probably

$$\begin{array}{c} \text{CF}_2 \quad \text{CF}_2 \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{C}_6\text{F}_{13} \quad \phi \end{array}$$


These compounds were characterized by ^{19}F NMR.

11. Preparation of α -Pyrone

Coumalic acid as purchased commercially (coumalic acid monohydrate) was pyrolyzed to give α -pyrone. However, when the commercial material was used without purification a very low yield of α -pyrone (0.3 g, from 2 g of coumalic acid) was obtained.

Some of the purchased coumalic acid was purified by sublimation to give a white solid, m.p. 209° . A portion of this material was used in the following pyrolysis.

A Vycor test tube (1 1/8" diameter x 15" length) with a ground joint at the top was packed with copper gauze. The copper gauze occupied a 12-inch length of the column extending from two inches from the bottom to one inch from the top. The bottom of the tube was charged with sublimed coumalic acid (2.0 g, 0.014 moles) and the top was fitted with an adapter leading through a 0° trap to a vacuum manifold. The tube was put into a furnace in a vertical position with the bottom 2 inch and top one inch extending beyond the furnace. The temperature of the furnace was maintained at 650-660° and a full vacuum was applied to the system. An oil bath was then used to heat the bottom of the tube to ~175° so as to cause the coumalic acid to sublime into the heated zone of the tube. After three hours, heating was discontinued and the contents of the 0°C trap were distilled to give 1.5 g (100% yield) of product boiling at 55°/0.15 mm; reported³ 110°/26 mm. (infrared, Figure 26).

B. Perfluoroalkylene Ether Polytriazines

1. Polymerization of Dinitriles to Polytriazines by NH₃ Catalysis

Pure dinitrile or mixtures of dinitriles when sealed in glass ampoules with ca 1-3% wt NH₃ and heated at 230°/1 day afforded polytriazines. The compositions and Tg's of the materials are shown in Table II. In mixed samples as Tg increases toughness and hardness increase.

2. Attempted Synthesis of Low Molecular Weight Polytriazines

A 40-ml glass ampoule was charged with 10 g of 8-EDAF dinitrile and ~0.003 g of NH₃. The ampoule was sealed and placed in a 200° oil bath.

After 168 hours there was no apparent change in viscosity of the triazine. The bath temperature was then raised to 220° for 24 hours, and a typical cheese-like gum was obtained.

The reaction was repeated several times with the samples being visibly examined at intervals as the bath temperatures were gradually increased from 200 to 220°. However, in all cases there was no apparent increase in viscosity until the cheese-like gum was obtained.

C. Polytriazines with Pendent Nitrile Groups

1. General Method

8-EDAF(G) polyimidoylamidine (33.25 g; 21.5 mmoles) dissolved in 50 g of Freon-E4 was added dropwise to a stirred mixture of 2.80 g (6.5 mmoles) of $[\text{NC}(\text{CF}_2)_3\text{CO}]_2\text{O}$ and 7.80 g (36.5 mmoles) of $(\text{CF}_3\text{CO})_2\text{O}$.

After the reaction mixture was stirred overnight at ambient temperature, 3 ml of trifluoroacetic anhydride was added and the stirring was continued overnight.

The reaction mixture was heated at 60°C under vacuum for several hours to remove the solvent. An IR spectrum of the residual viscous material (43 g) showed the absence of imidoylamidine groups and the presence of triazine groups (6.45 μ).

2. Synthesis of $[\text{NC}(\text{CF}_2)_3\text{CO}]_2\text{O}$

a. Synthesis of F-glutarimide

The reaction, $\text{CF}_2(\text{CF}_2\text{CO})_2\text{O} + \text{KOCN} \xrightarrow{\text{HCl}}$ $\text{CF}_2(\text{CF}_2\text{CO})_2\text{NH}$ was carried out twice. In the first reaction tetraglyme was used as a solvent, but due to the extreme difficulty of separating the product from this solvent the imide was obtained in only ~50% yield. The second reaction, using ethyl ether as a solvent, is described as follows.

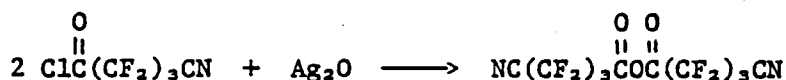
A 5-liter flask was charged with KOCN (239 g, 2.95 moles) which was then heated at 100° under full vacuum for 30 minutes to remove moisture. The flask was then cooled to ambient temperature and charged with ethyl ether (3250 ml). It was then fitted with a mechanical stirrer, a reflux condenser vented through a bubbler, and an addition funnel containing F-glutaric anhydride (650 g, 2.95 moles). The mixture was stirred while the anhydride was added during a 45 minute period; there was no gas evolved and no change in the appearance of the solution.

The addition funnel was charged with 50 ml of tetraglyme and 1.5 ml of this material was added to the stirred reaction mixture with the result that there was an immediate evolution of gas which was evolved smoothly during a 3-hr period. Since gas was still being evolved at approximately the same rate at the end of this period the reaction mixture was allowed to stir overnight with no additional tetraglyme being added. After sixteen hours there was no evolution of gas; an infrared spectrum of the reaction mixture indicated the presence of unreacted anhydride. Therefore more (~2 ml) tetraglyme was added. This again caused the immediate evolution of gas. Each time the evolution of gas slowed tetraglyme was added in 1.5-2.0 ml increments until the entire 50 ml was added. The mixture was then allowed to stir for 40 hours after which time an infrared spectrum indicated that all of the anhydride had been consumed.

The reaction flask was then fitted with a gas inlet through which anhydrous HCl was admitted; the exit gases were passed through a 0° reflux condenser. After the addition of excess HCl the flask was fitted with a distillation head and most of the ethyl ether was removed at atmospheric pressure. A full vacuum was then applied and the remainder of the ethyl ether was removed. The product was then stripped off as a water-white liquid which solidified to a white solid on cooling to ambient temperature.

The product was found to weigh 504 g representing a 76.6% yield. This imide was converted to the nitrile acid chloride in four steps using the method described earlier.¹

b. Reaction of $\text{ClC}(\text{CF}_2)_3\text{CN}$ with Ag_2O



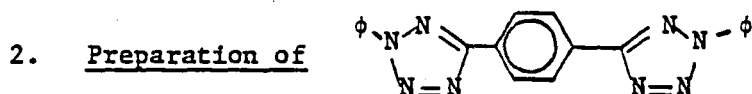
A 300-ml flask containing a stirring bar was charged with Freon-113 (100 ml), CH_3CN (0.5 ml) and $\text{ClC}(\text{CF}_2)_3\text{CN}$ (20 g, 83.5 mmoles) and fitted with a reflux condenser vented to a -183° trap and a solid addition funnel containing Ag_2O (10.4 g, 41.8 mmoles). As the reaction solution was stirred a small amount (~ 1.0 g) of Ag_2O was added. There was apparently some reaction as evidenced by a white coating which formed on the surface of the Ag_2O . However, even after heating at reflux for 2 hours most of the Ag_2O was unchanged. Another small quantity of Ag_2O was added and an immediate exothermic reaction occurred. The remainder of the Ag_2O was then added at such a rate as to maintain reflux and it appeared to be completely converted to AgCl . The product mixture was filtered and the filtrate was vacuum distilled to give 10.9 g of the proposed $(\text{NCCF}_2\text{CF}_2\text{CF}_2\overset{\text{O}}{\text{C}})_2\text{O}$. An infrared spectrum (Figure 29) of the product indicated $\sim 80\%$ purity.

D. Preparation of Bis-Tetrazole

1. Preparation of $\phi\text{NHN}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{NHN}\phi$

Terephthalaldehyde (106 g, 0.76 mole) was added in solid batches over a one hour period to a mechanically stirred solution of phenyl hydrazine

(189 g, 1.7 mole) maintained at -5° . At the completion of the addition, the reaction mixture was allowed to warm to 25° and stirred for 48 hours. The yellow precipitate that formed was filtered and washed with 200 ml of cold MeOH. It was dried at full vacuum leaving 240 g of yellow solid which was then heated with 2500 ml of absolute EtOH, filtered hot, and dried leaving 230 g of material mp $286-289^{\circ}$ (d) (infrared, Figure 27).



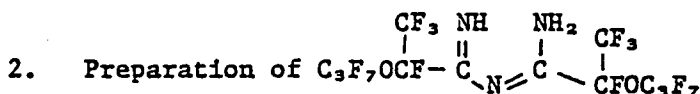
The bis-hydrazone (26.8 g, 0.1 mole) was added as a solid to a mechanically stirred solution of alkoxide prepared from ethylene glycol monomethyl ether ($\text{MeOCH}_2\text{CH}_2\text{OH}$, 300 ml) and sodium (10.3 g, 0.45 g-at). Then, phenyl azide (24.0 g, 0.22 mole) dissolved in hexane (100 ml) was added to the stirred solution. At the completion of the azide addition the mixture was heated to drive off the hexane. The mixture was heated at an internal temperature of 120° (reflux) for 8 hours, then cooled. The precipitate that settled was filtered, washed with MeOH (200 ml), then dried leaving 21 g of a yellow solid mp 198° (dec). Attempts to sublime this material ($180^{\circ}/0.1$ mm) gave decomposition. The material was treated in a Soxhlet extractor with 800 ml of C_6H_6 for four days. The C_6H_6 mixture was filtered leaving 20 g of material mp 216° (dec). A batch of this material was recrystallized twice from mixed xylenes (40 ml xylene/0.9 g of material) to yield fine yellow needles of the bis-tetrazole, mp $221-222^{\circ}$ (dec), Lit.⁷ mp $222-225^{\circ}$ (infrared Figure 28)

E. Perfluoroalkylene Ether Triazines

1. Preparation of $\text{C}_6\text{F}_5\text{OCF}_2\text{CF}_2\text{COF}^6$

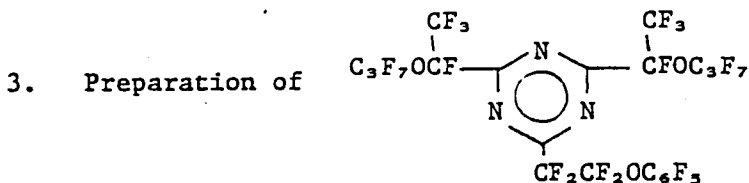
The intermediate $\text{C}_6\text{F}_5\text{OCF}_2\text{CF}_2\text{CO}_2\text{Cs}$ was prepared according to a patented procedure by reacting a tetraglyme solution of $\text{C}_6\text{F}_5\text{OCs}$ [from

C₆F₅OH (32 g, 0.17 mole) and anhydrous Cs₂CO₃ (60 g, 0.208 mole) in tetraglyme (105-ml) with TFE (30 g, 0.30 mole) and CO₂ (37.5 g, 0.85 mole) at 85°/4 hr in an autoclave. The acid salt (41.4 g) was isolated in a dry state and directly treated with SF₆ (40 psig) in a 500-ml Fischer-Porter tube using Freon E4 (60 ml) as solvent. The material was stirred overnight at 25°; then the volatiles were removed under full vacuum. Distillation afforded the acid fluoride (16.8 g, 60%) b.p. 56-57°/16 mm.



A 300ml flask was fitted with a stirring bar, a gas inlet connected to a cylinder of NH₃, a 78° reflux condenser vented to a 183° trap, and an addition funnel containing HFPO dimer nitrile, C₃F₇OCF(CF₃)CN (31.7 g, 0.102 mole). The flask was charged with ~100 ml of liquid NH₃ and the nitrile was added dropwise as the solution was vigorously stirred. At the completion of the nitrile addition the excess NH₃ was allowed to volatilize from the reaction flask. Vacuum was applied to remove the last traces of NH₃.

The addition funnel was again charged with 31.7 g of HFPO dimer nitrile and this material was added dropwise to the amidine in the reaction flask. After all of the nitrile had been added an infrared spectrum of the product indicated that it was the imidoylamidine.



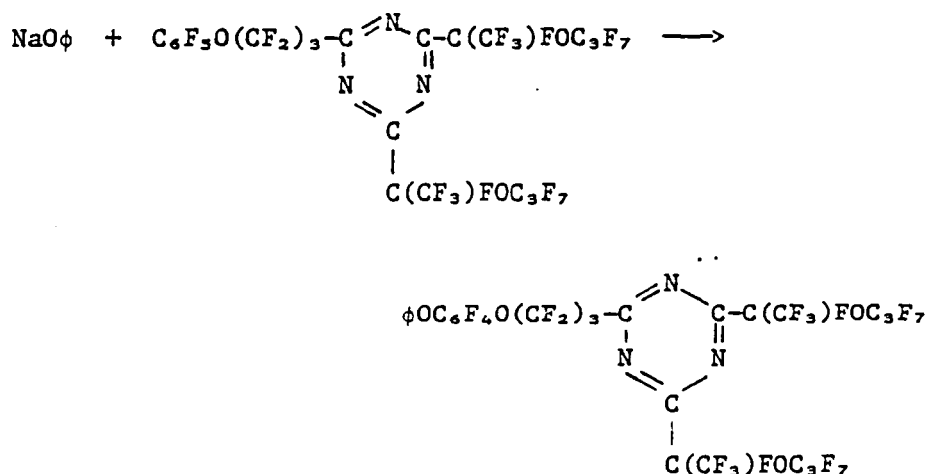
A 100-ml, 3-necked flask was fitted with a thermometer, a stirring bar, a stopcock adapter leading to a -183° trap, and an addition funnel containing C₆F₅O(CF₂)₂COF (7.0 g, 0.21 mole) dissolved in 25 ml of Freon-113. The

flask was charged with NaF (0.40 g, 0.10 mole) and HFPO dimer imidoamidine (6.40 g, 0.010 mole) dissolved in 25 ml of Freon-113. The contents of the flask were stirred as the acid fluoride was added dropwise to effect the reaction. There was no noticeable evolution of heat.

After all the acid fluoride had been added the mixture was stirred for 16 hours. An infrared spectrum indicated the presence of triazine and absence of imidoamidine. The product was then chromatographed on a column (1 cm diameter x 12 cm high) of neutral alumina and washed with 50 ml of Freon-113. The Freon was removed under vacuum to leave 13 g of a slightly viscous product which infrared indicated was the pure triazine. This material was distilled under vacuum to give 8.6 g of product which was shown by GLC to be 98-99% pure. Some solid residue (4-5 g) was left in the distillation pot.

The distillate was separated into four fractions which were shown to be identical by GLC and infrared analysis. After standing overnight one of the fractions became solid.

F. Attempted Reaction of Sodium Phenoxide with p-Fluorine of Triazine Pendent Group



A 100-ml flask was thoroughly dried and put into a dry-bag where it was charged with a stirring bar, NaOC_2H_5 (0.29 g, 2.5 mmoles), and C_6F_5 -triazine (2.46 g, 2.5 mmoles). The flask was sealed and placed on a magnetic stirrer. After less than one minute the reaction mixture became homogenous. After the mixture had been stirred for 16 hours an infrared spectrum indicated that the triazine structure was absent (see discussion). This was evidenced by the absence of the typical triazine absorption at 6.4μ as shown in the infrared spectrum of the triazine starting material.

G. Polytriazines with $-\text{CF}_2\text{I}$ Pendent Groups

General Method

A mixture of 10.16 g (30.6 mmoles) of $\text{C}_3\text{F}_7\text{OCF}(\text{CF}_3)\text{COF}$ and 3.5 g (5.4 mmoles) of $\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_3\text{OCF}(\text{CF}_3)\text{COF}$ was added slowly to a Freon E4 solution of 8-EDAF(G) polyimidoylamidine and 2 g of dry sodium fluoride.

After the mixture had been stirred overnight at ambient temperature, 10 g of HFPO-dimer acyl fluoride was added to complete the reaction and the mixture was stirred for several hours.

The reaction mixture was washed repeatedly with water to remove the acids formed. The organic layer was separated, dissolved in Freon-113 and passed over a column of neutral alumina to remove any traces of acid.

The solvent was removed under vacuum leaving 32 g of the polytriazine.

H. Cross-Linking of Polytriazines with Pendent $-\text{CF}_2\text{I}$ Groups

1. Low Temperature Curing

A small sample (1-2 g) of the above polytriazine in a Pyrex flask was placed on a rotary evaporator under vacuum and was irradiated with a u.v. lamp (Hanovia 30620 desk type lamp) for 100 hours. Under these conditions, the temperature of the sample did not exceed 40°C . Iodine along

with residual solvent was collected in a liquid oxygen trap leaving an elastomeric gum in the flask; $T_g = -61^\circ\text{C}$ (DSC).

In a separate experiment a thin film of the polytriazine on a glass support was irradiated for 50 hours. A thin film of a similar gum was obtained.

2. High Temperature Curing

A small sample (2.3 g) of the above polytriazine in a pyrex flask was placed on a rotary evaporator under vacuum and was heated with an oil bath at $200^\circ\text{--}230^\circ\text{C}$ for 60 hours.

Iodine and residual solvent were collected in a liquid oxygen trap leaving an elastomeric gum in the flask; $T_g = -60^\circ\text{C}$ (DSC).

I. Preparation of $\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{COF}$

a. Hexafluoroglutaryl fluoride (76 g, 0.31 mole) was added to a slurry of potassium fluoride (15 g, 0.25 mole) in tetraglyme (150 ml) contained in a Fischer-Porter pressure bottle. An exothermic reaction ensued and the mixture was stirred for one hour at ambient temperature.

The mixture was cooled in an ice bath and iodine monochloride (13 ml, 0.25 mole) was added and stirred for 30 minutes.

The pressure bottle was connected through copper tubing to a TFE cylinder and tetrafluoroethylene was pressured in to 60 psi. The reaction was followed by a drop in pressure and TFE was added intermittently until the reaction was complete.

After venting off the excess TFE and volatile products, the reaction mixture was filtered under pressure through a Millipore filter. Distillation of the crude reaction mixture gave 68 g of unreacted HFGF and 25 g of the product, $\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_4\text{COF}$, boiling at $138^\circ\text{--}140^\circ\text{C}$ (17.1% conversion).

b. The above iodoacyl fluoride (25 g, 0.05 mole) was added to a slurry of cesium fluoride (1.5 g) in tetraglyme (50 ml). The mixture was

cooled at -5° to 0°C and hexafluoropropylene oxide was added slowly through a vacuum manifold. The reaction was monitored by frequent sampling and GLC analysis and it was terminated when 18 g of HFPO had been added.

The crude reaction product had the following composition (GLC).

$\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_4\text{COF}$	10.8%
$\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{COF}$	44.1%
$\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}(\text{CF}_3)\text{COF}$	5.8%
HFPO-homooligomers	35.1%

Fractionation of the crude reaction mixture gave pure $\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}(\text{CF}_3)\text{COF}$ boiling at $58-60^{\circ}\text{C}/0.4$ mm (43.4% conversion).

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Infrared Spectra

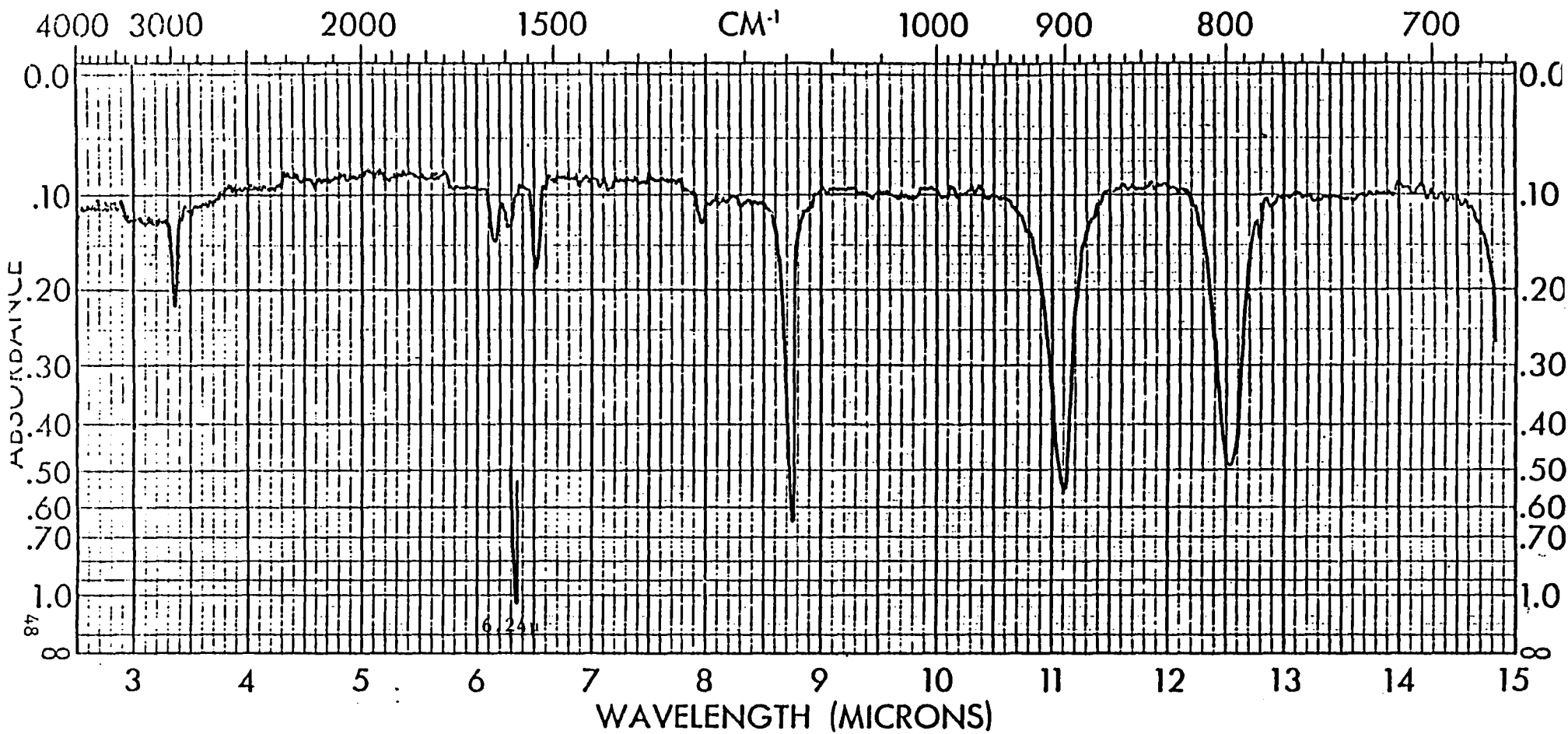


Figure 1 - Infrared Spectrum of ICH=CHCl (trans ~95%)

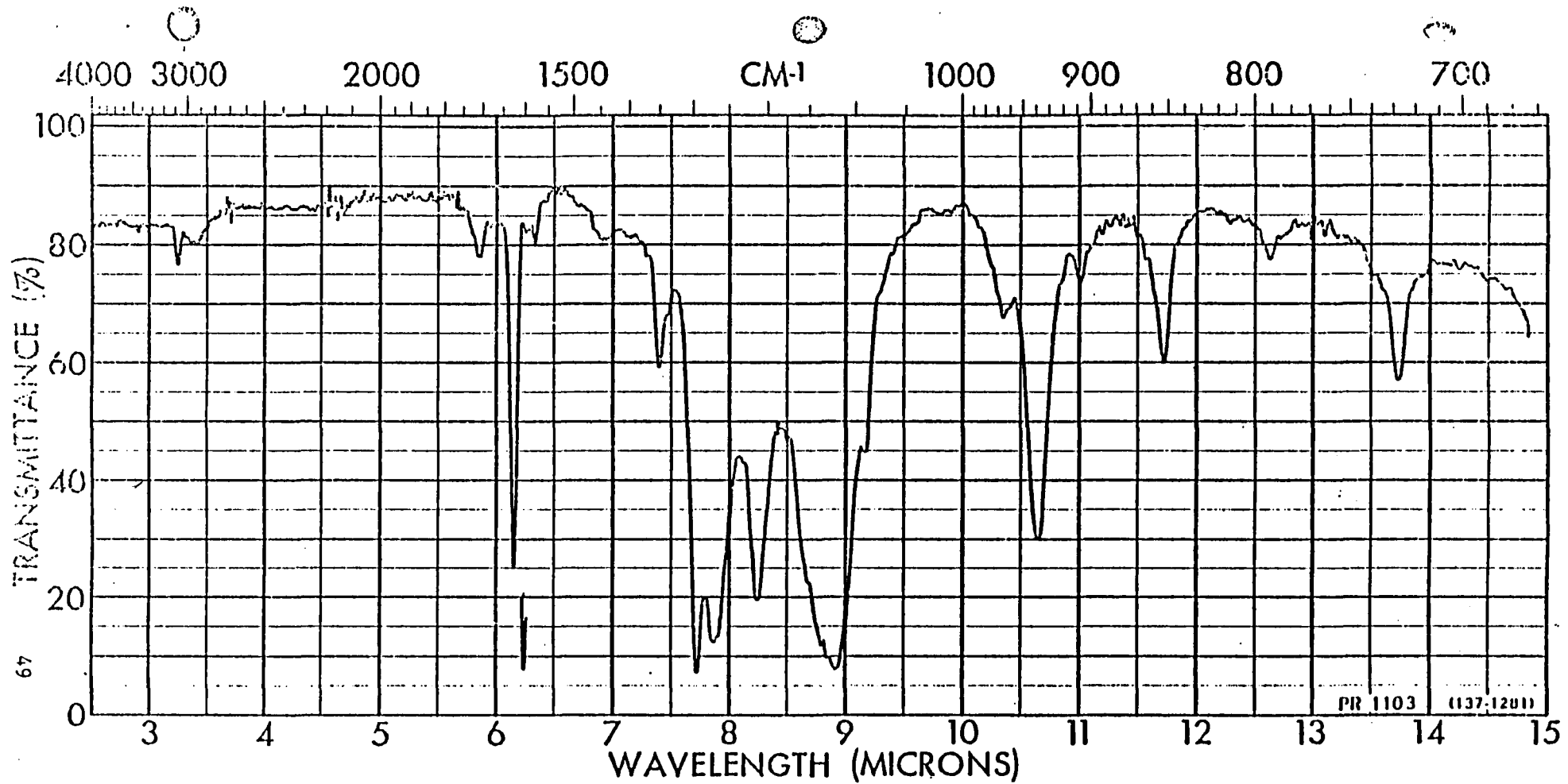


Figure 2 - Infrared Spectrum of $\text{CF}_3\text{CH}=\text{CHI}$ (trans ~95%)

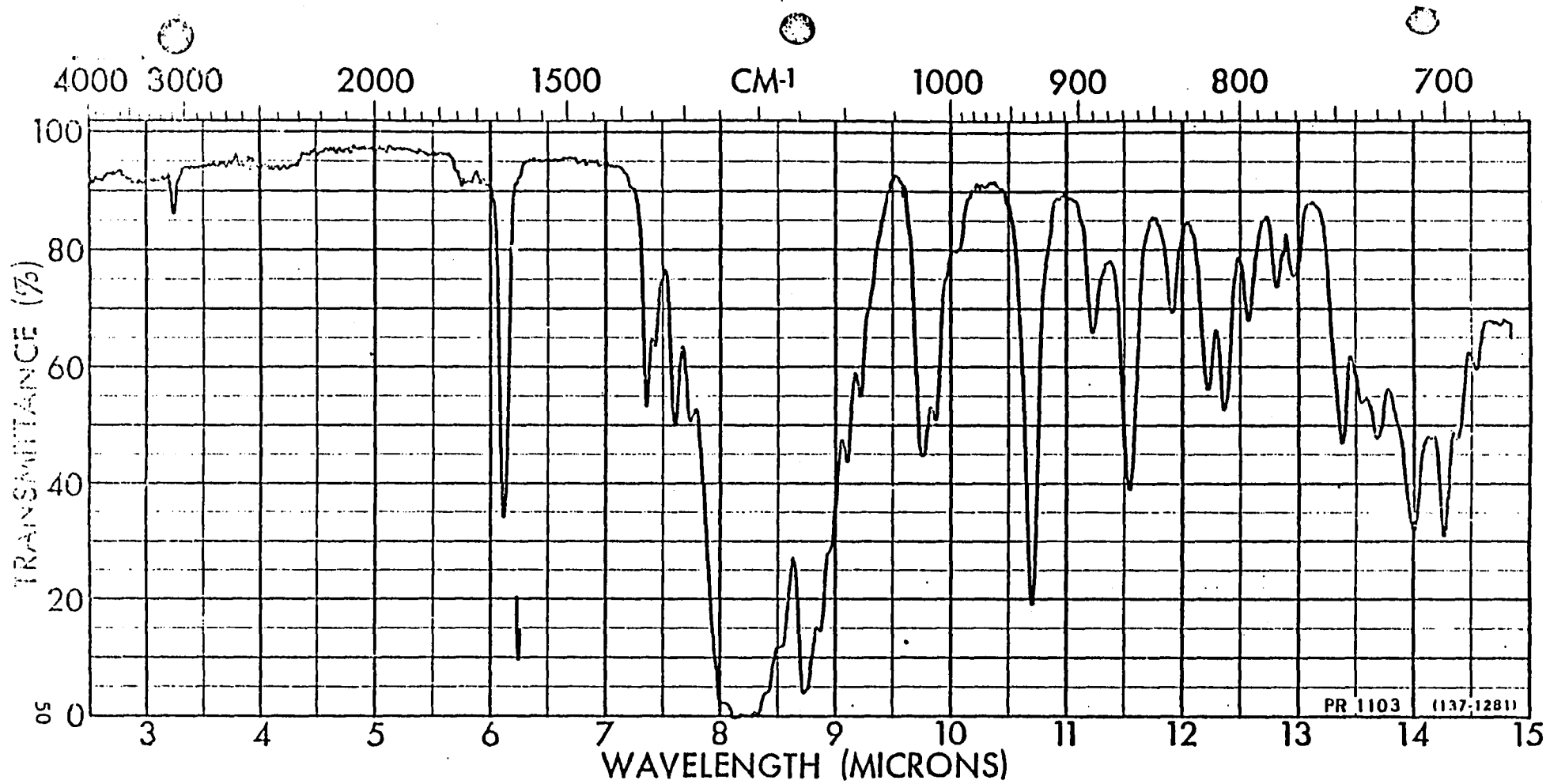


Figure 3 - Infrared Spectrum of $C_7F_{13}CH=CHCl$

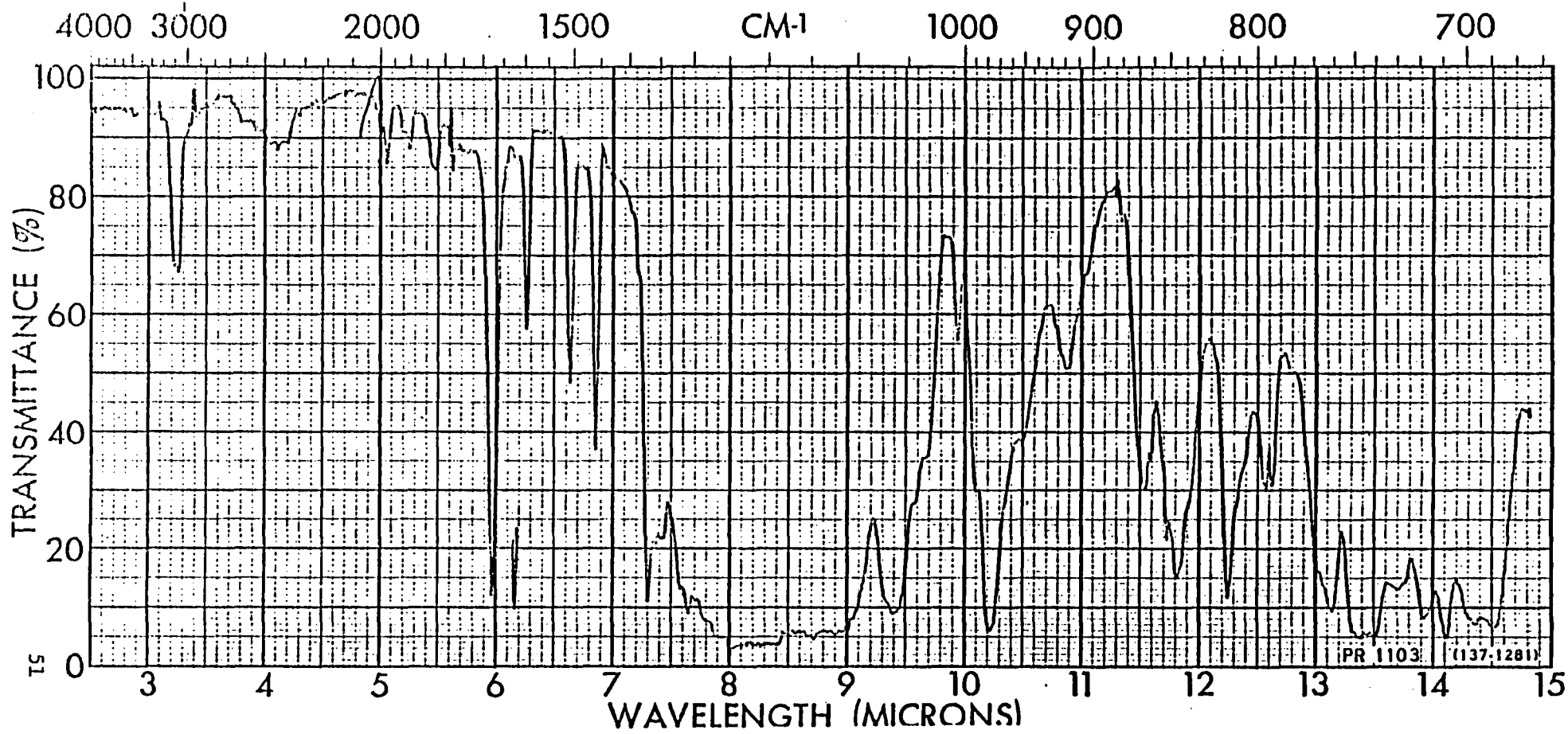


Figure 4 - Infrared Spectrum of $C_6F_{13}CH=CH\phi$

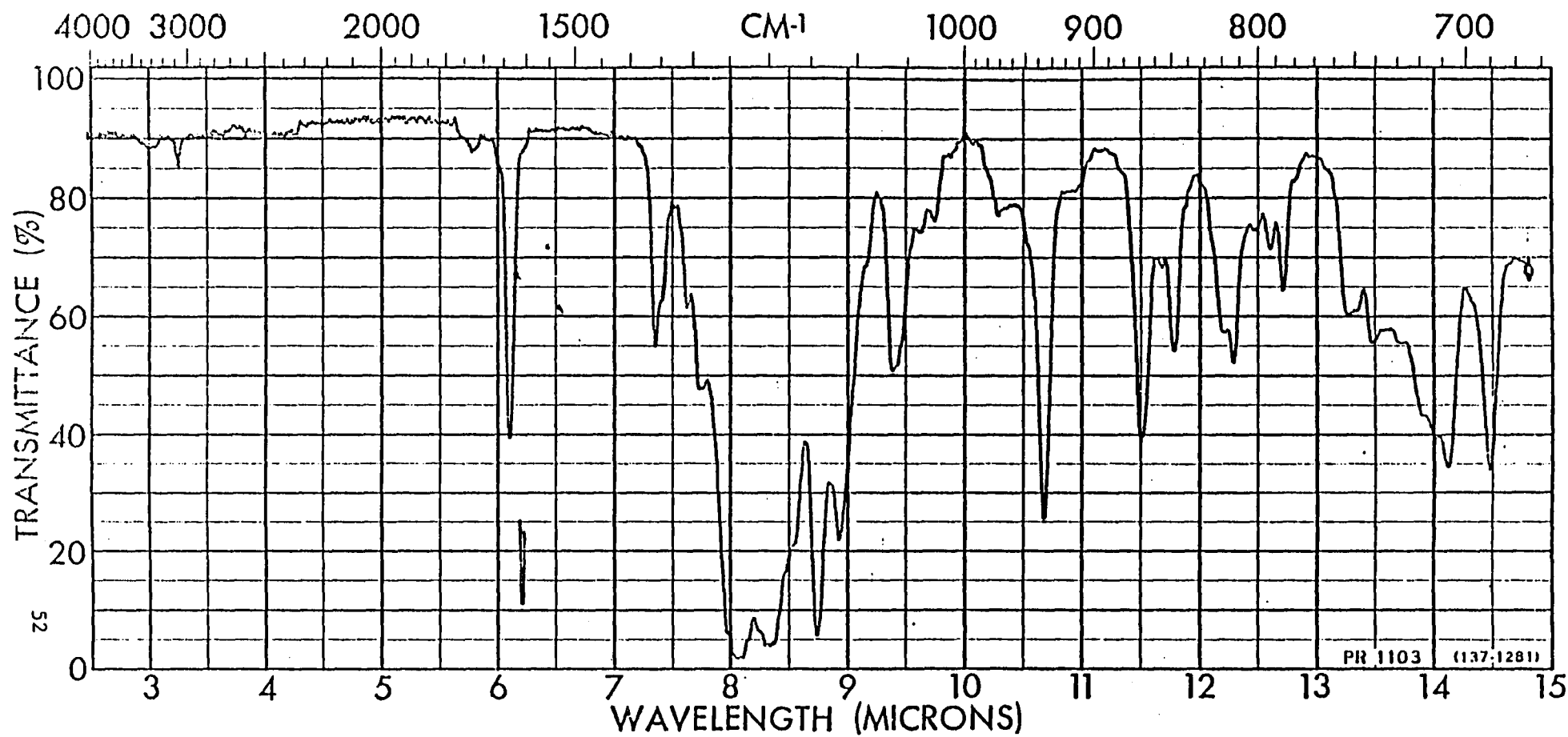


Figure 5 - Infrared Spectrum of $C_6F_{13}CH=CHCl$

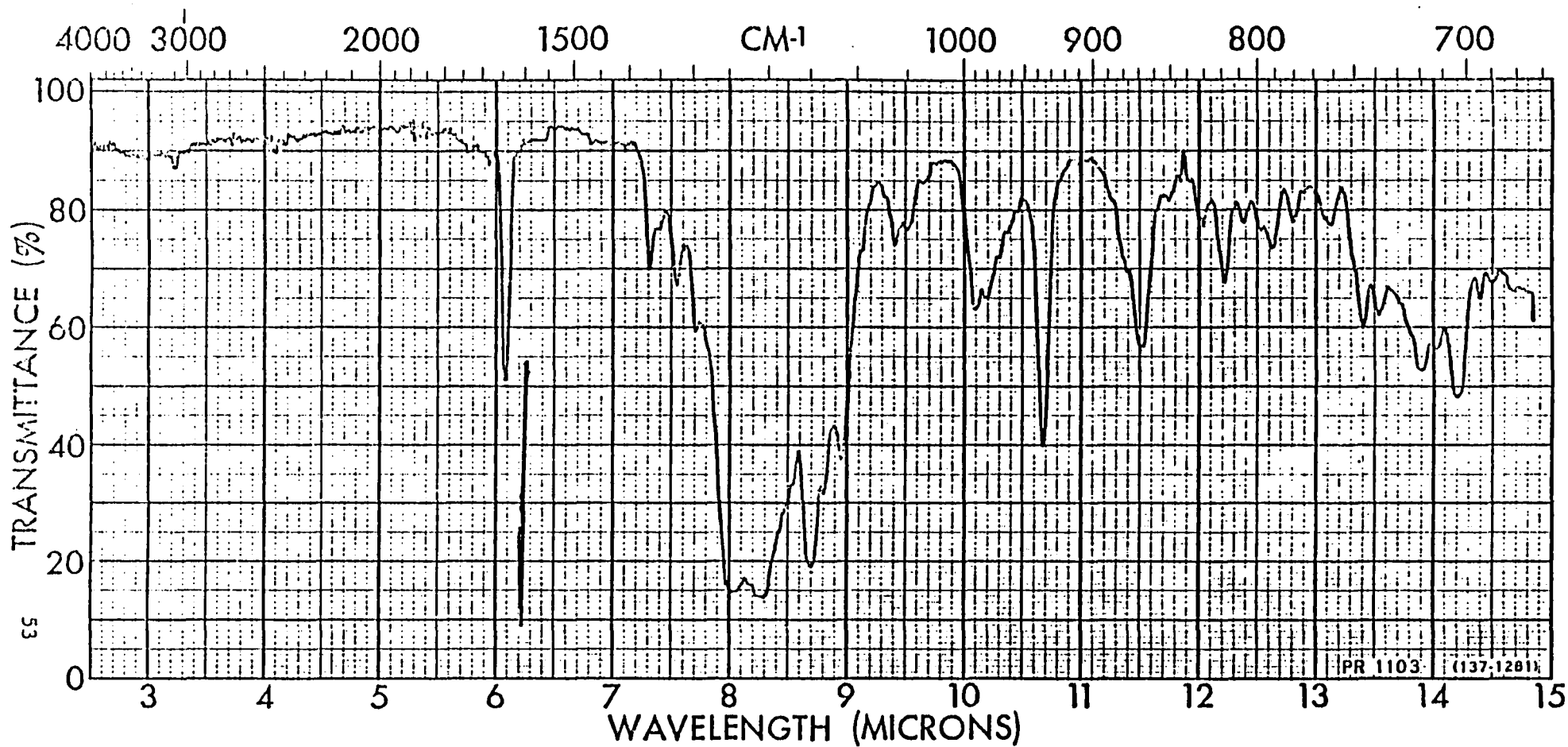


Figure 6 - Infrared Spectrum of $C_8F_{17}CH=CHCl$

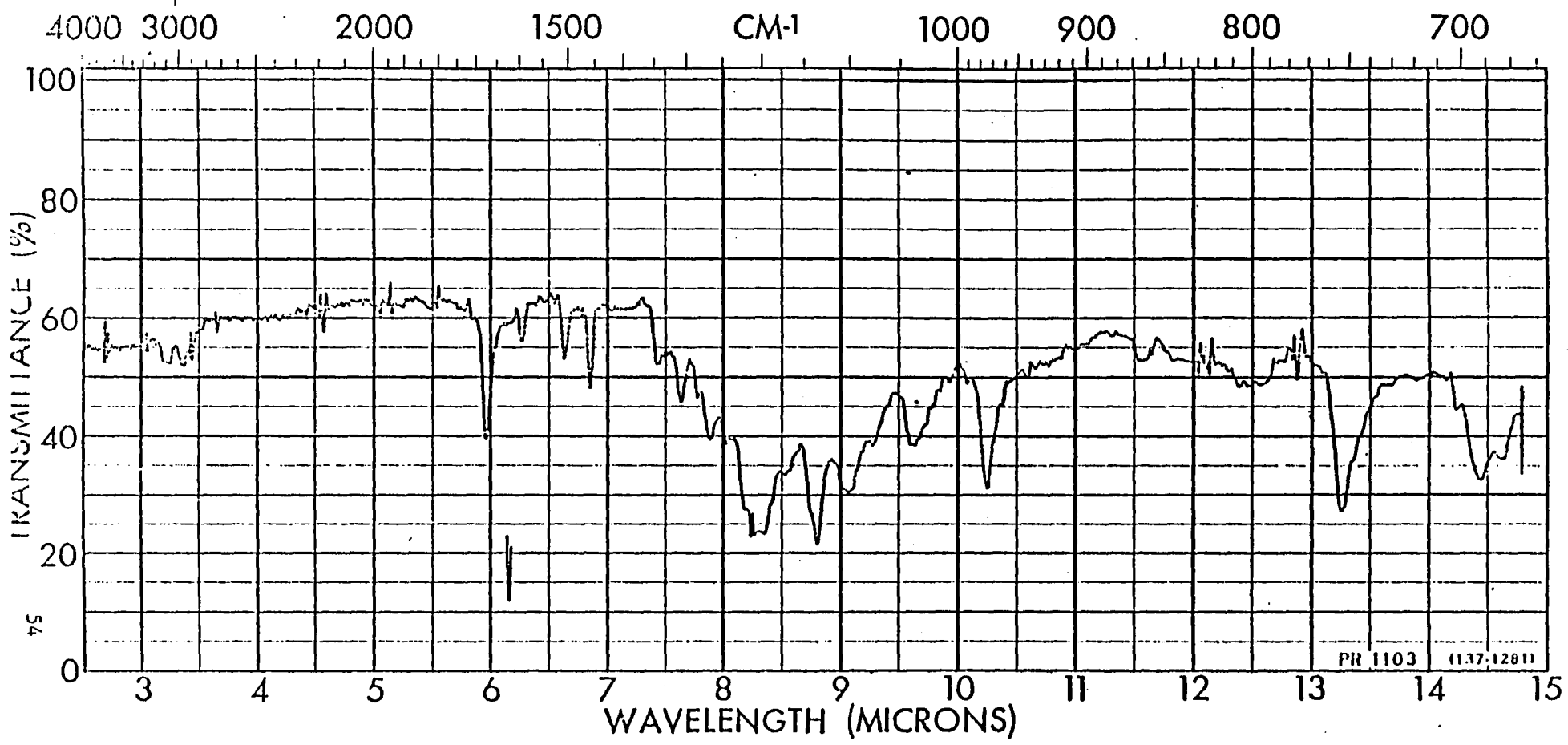


Figure 7 - $\phi\text{HC}=\text{CH}(\text{CF}_2)_6\text{CH}=\text{CH}\phi$

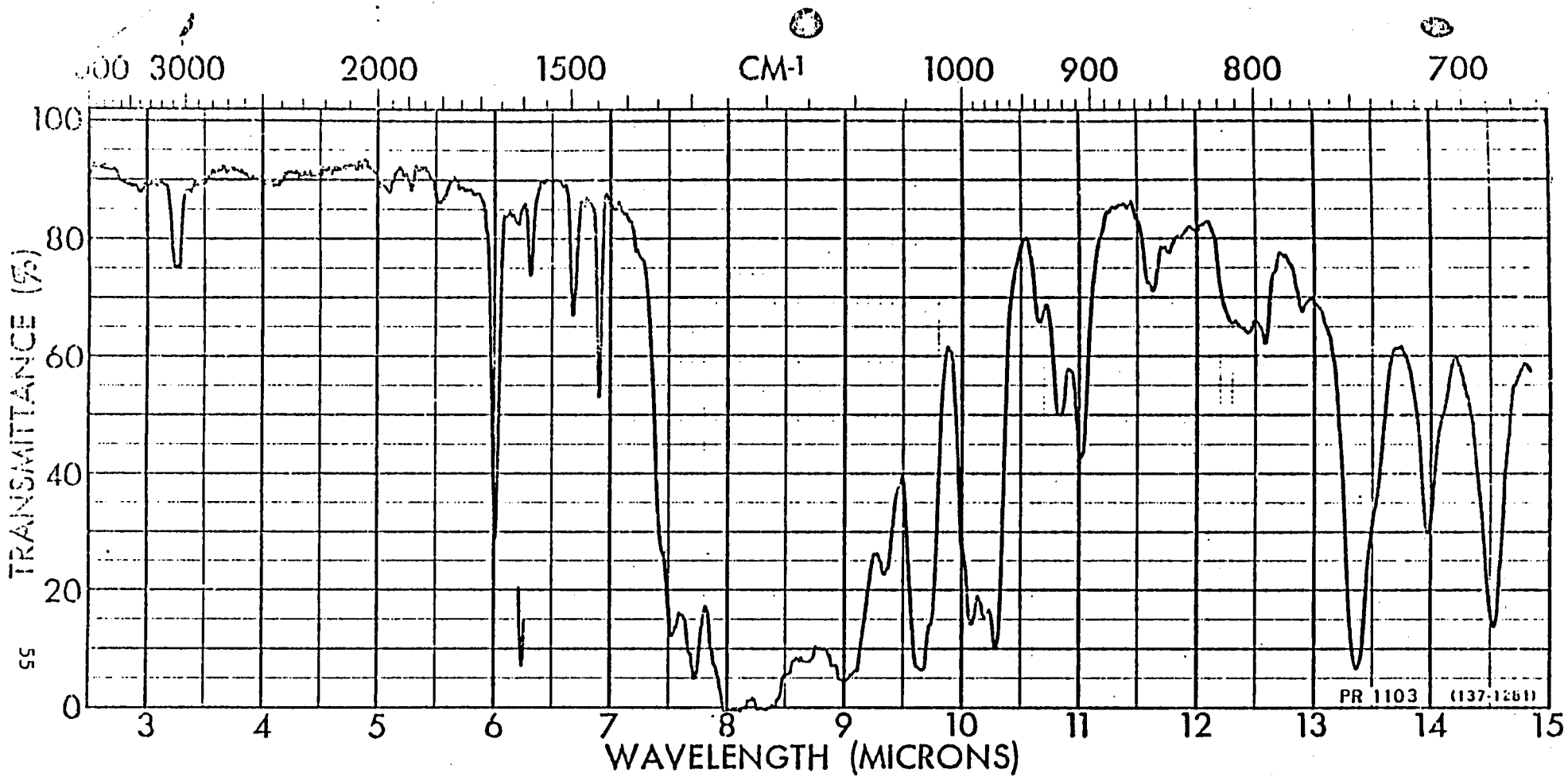


Figure 8 - Infrared Spectrum of $\text{CF}_3\text{CF}_2\text{CH}=\text{CH}\phi$

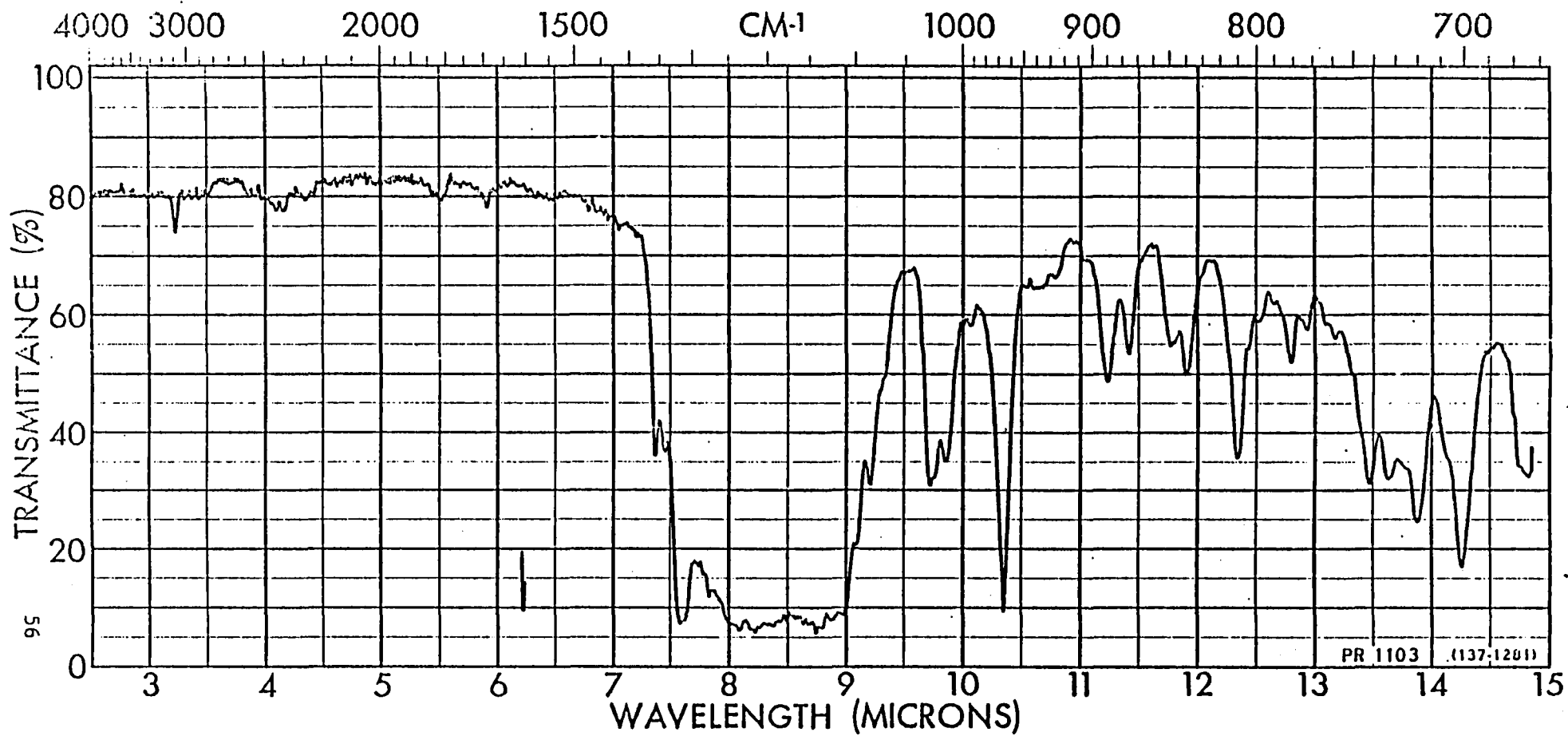


Figure 9 - Infrared Spectrum of $C_7F_{15}CH=CHCF_3$ (trans)

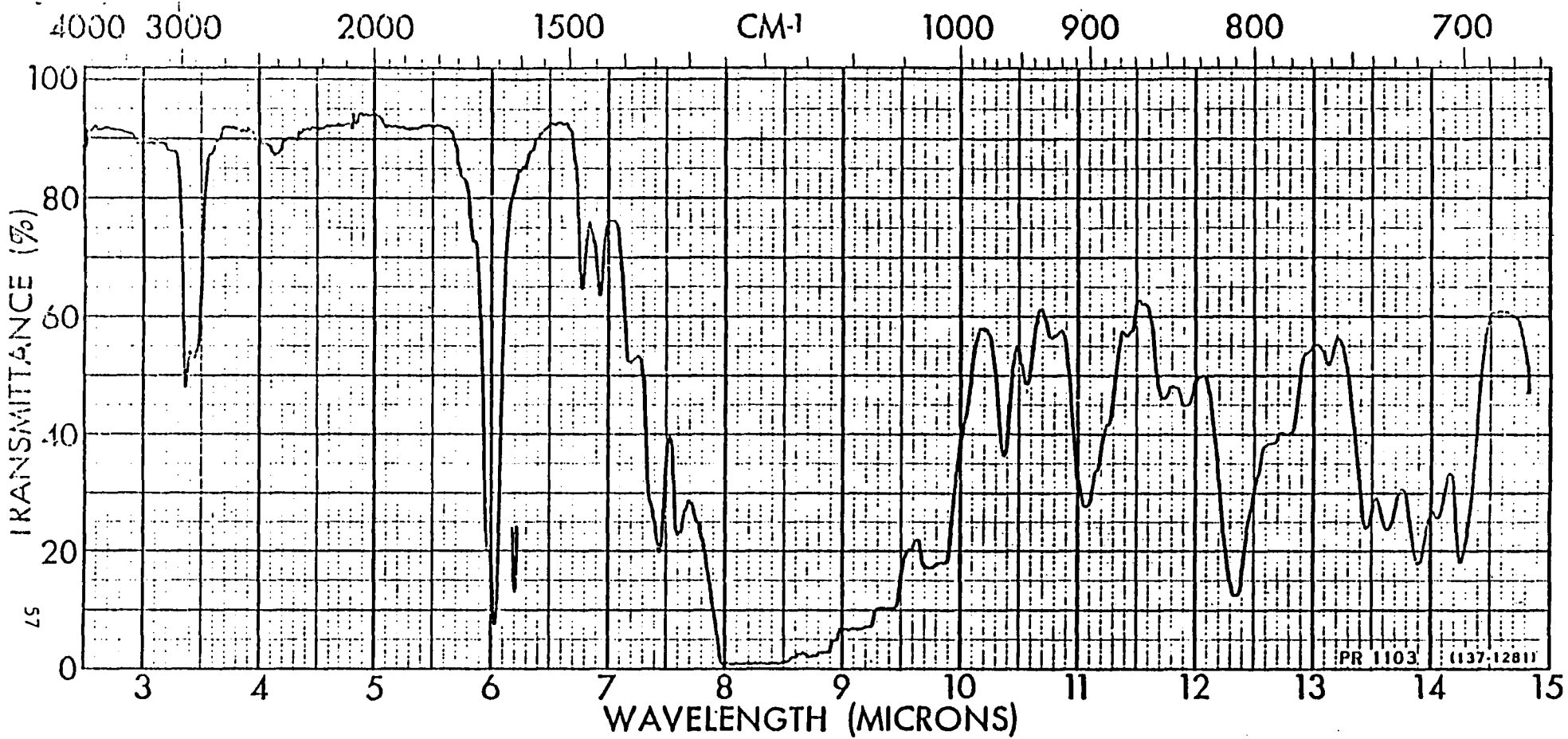


Figure 10 - Infrared Spectrum of $C_7F_{15}CH=CHOEt$ (trans)

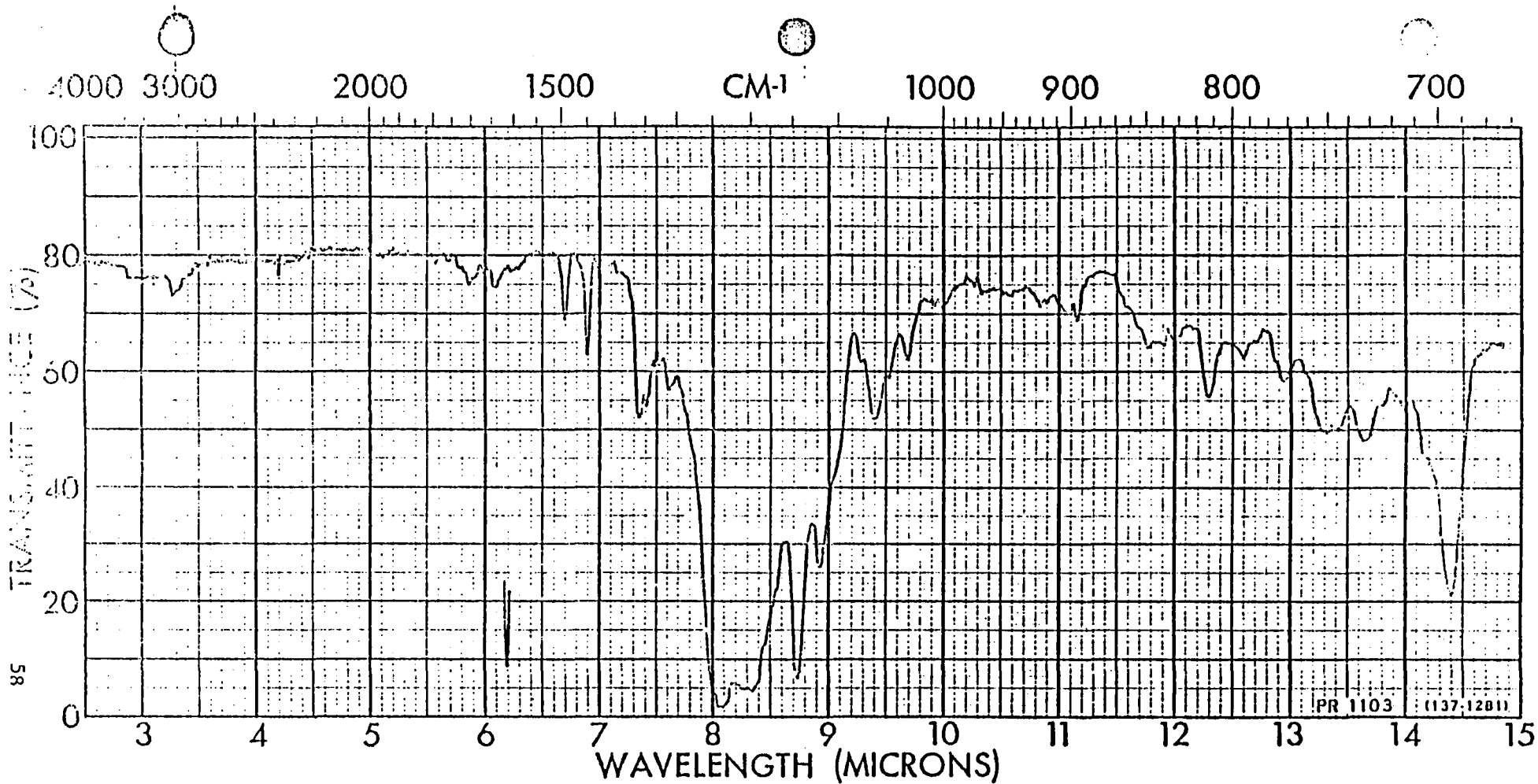


Figure 11 - Infrared Spectrum of $C_6F_{13}CHBrCHBrC_6H_5$

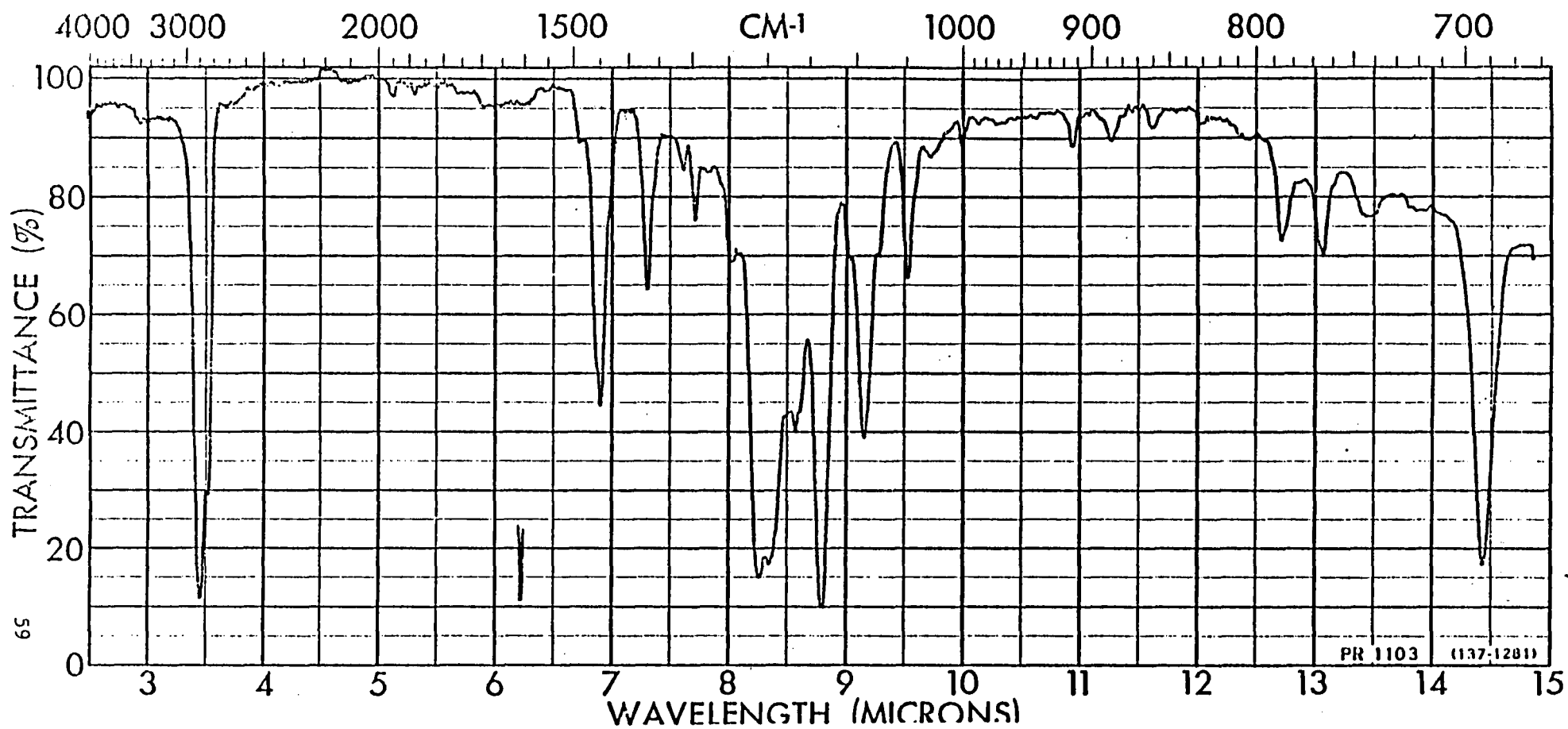


Figure 12 - Infrared Spectrum of $\phi\text{CHBrCHBr}(\text{CF}_2)_6\text{CHBrCHBr}\phi$

M.P. 225-229° (Nujol)

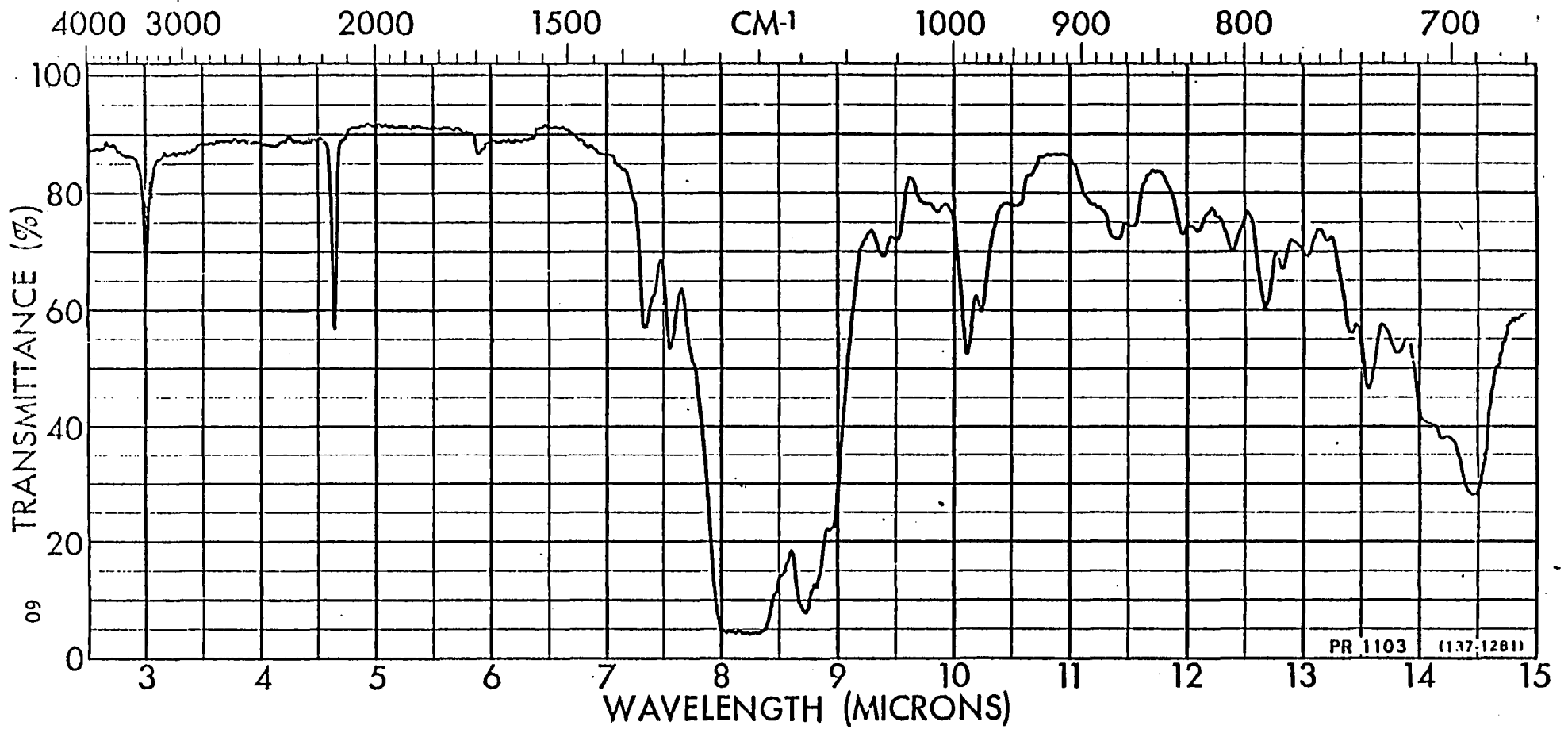


Figure 13 - Infrared Spectrum $C_8F_{17}C_2CH$

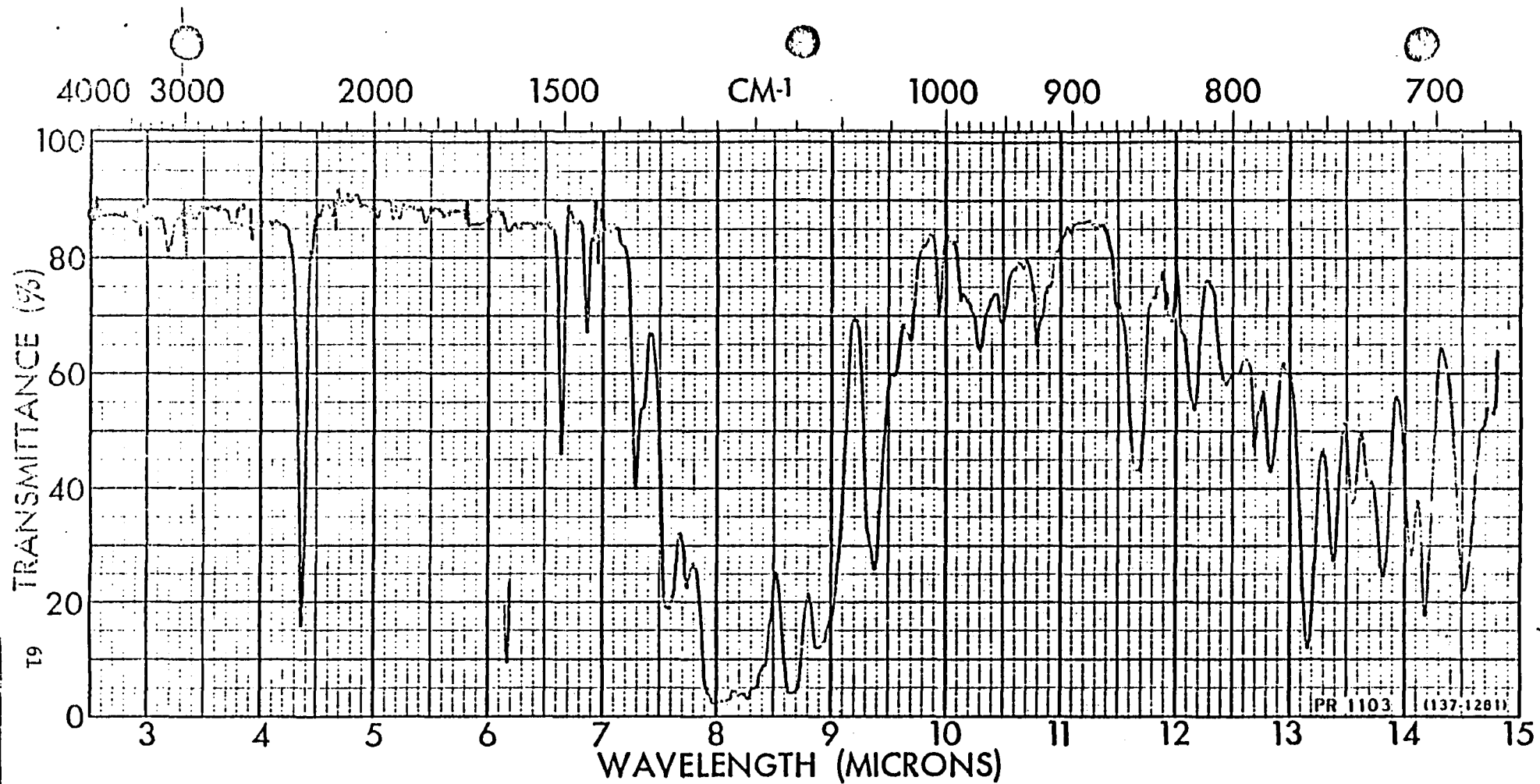


Figure 14 - Infrared Spectrum $C_6F_{13}C\equiv CC_6H_5$

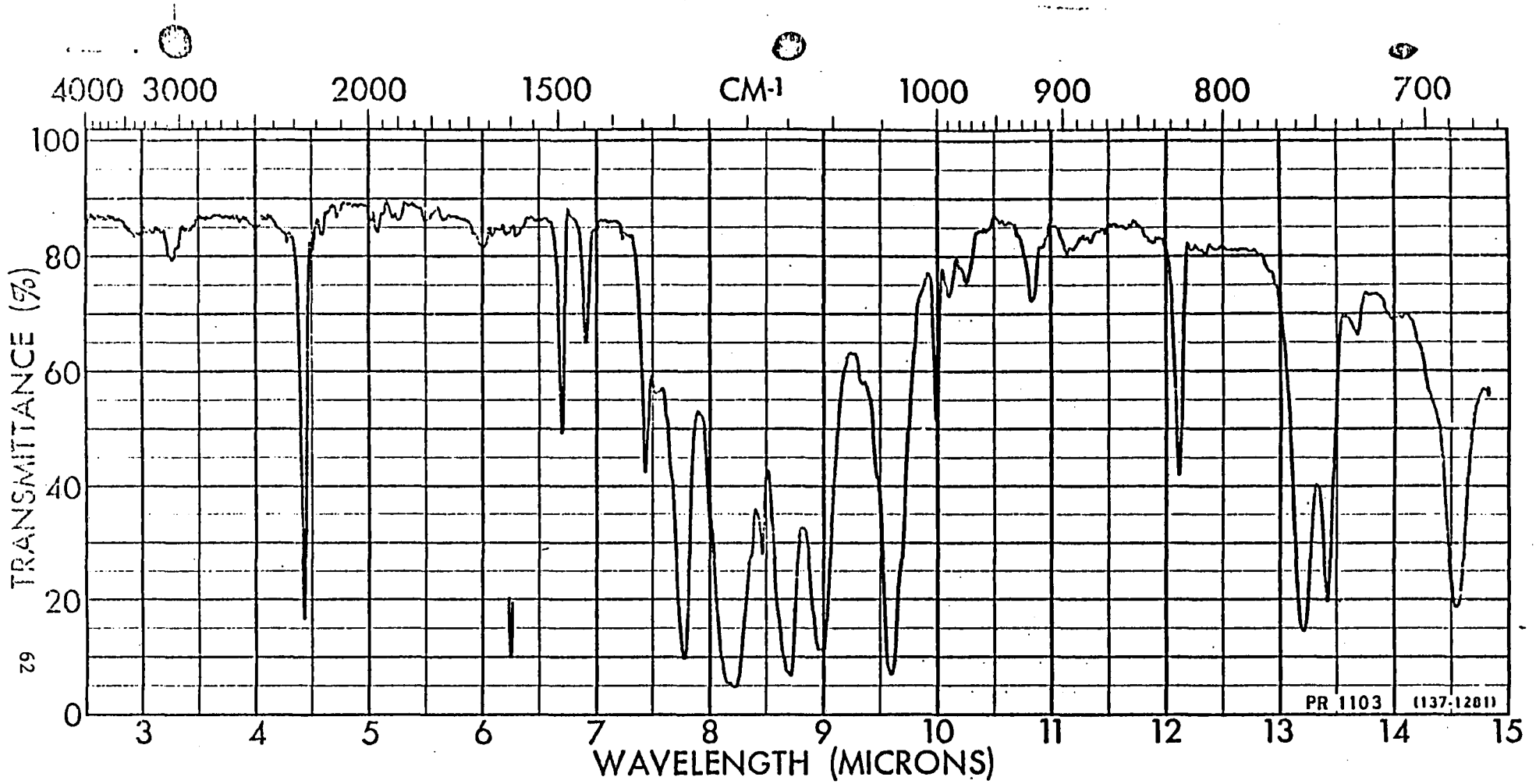


Figure 15 - Infrared Spectrum of $\text{CF}_3\text{CF}_2\text{C}\equiv\text{C}\phi$

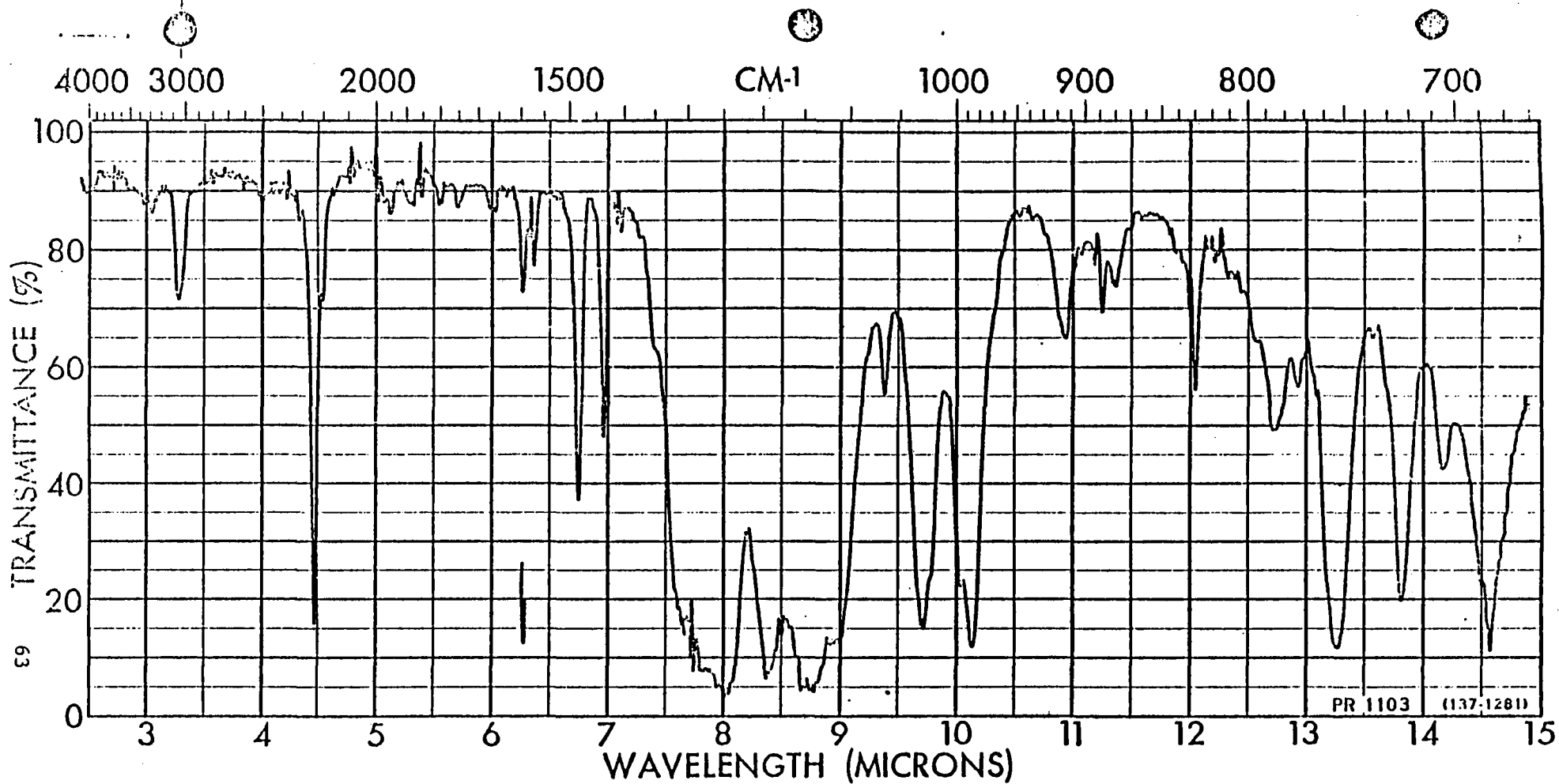


Figure 16 - Infrared Spectrum of $(CF_3)_2CFOCF_2CF_2C\equiv C\phi$

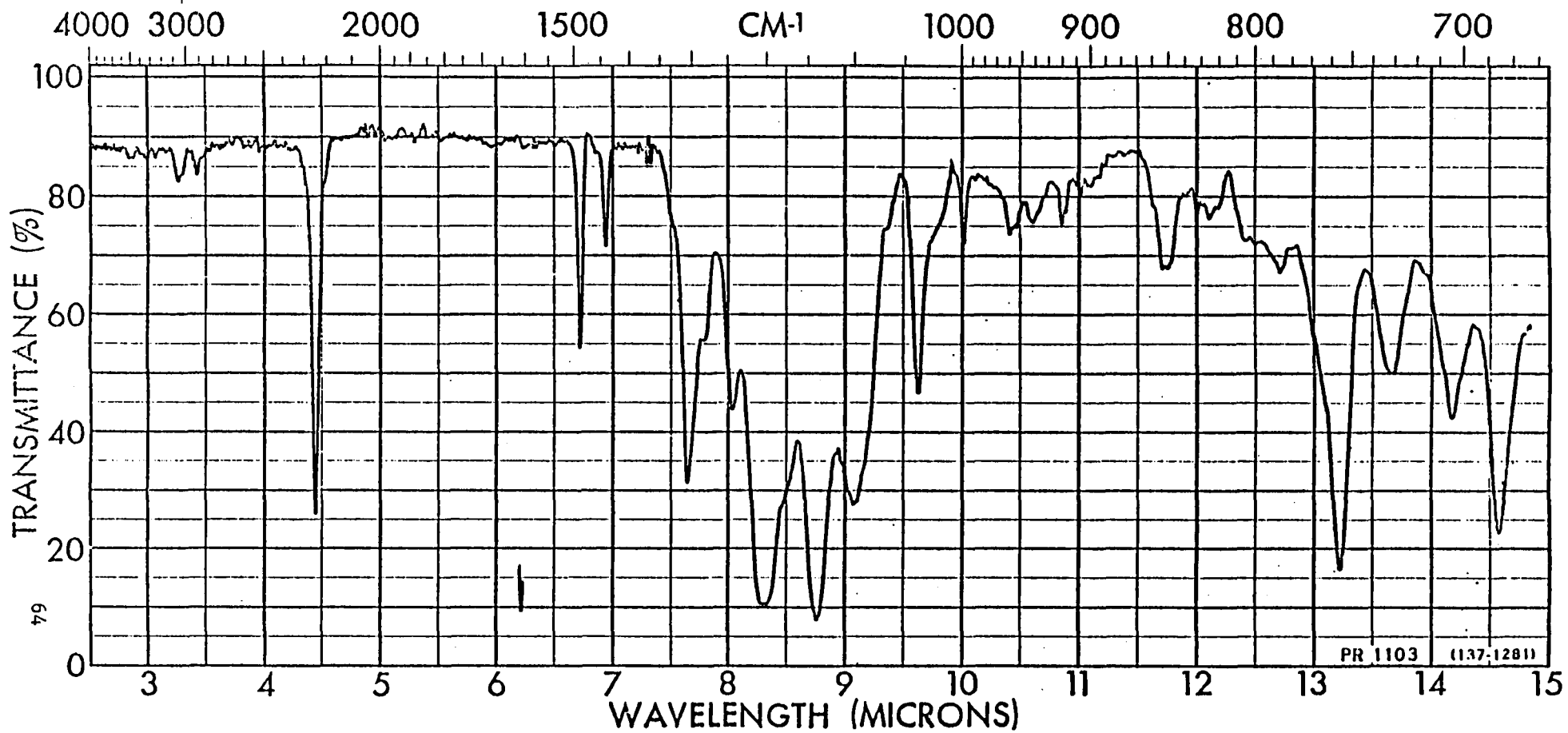


Figure 17 - Infrared Spectrum of $C_6H_5C\equiv C(CF_2)_6C\equiv CC_6H_5$

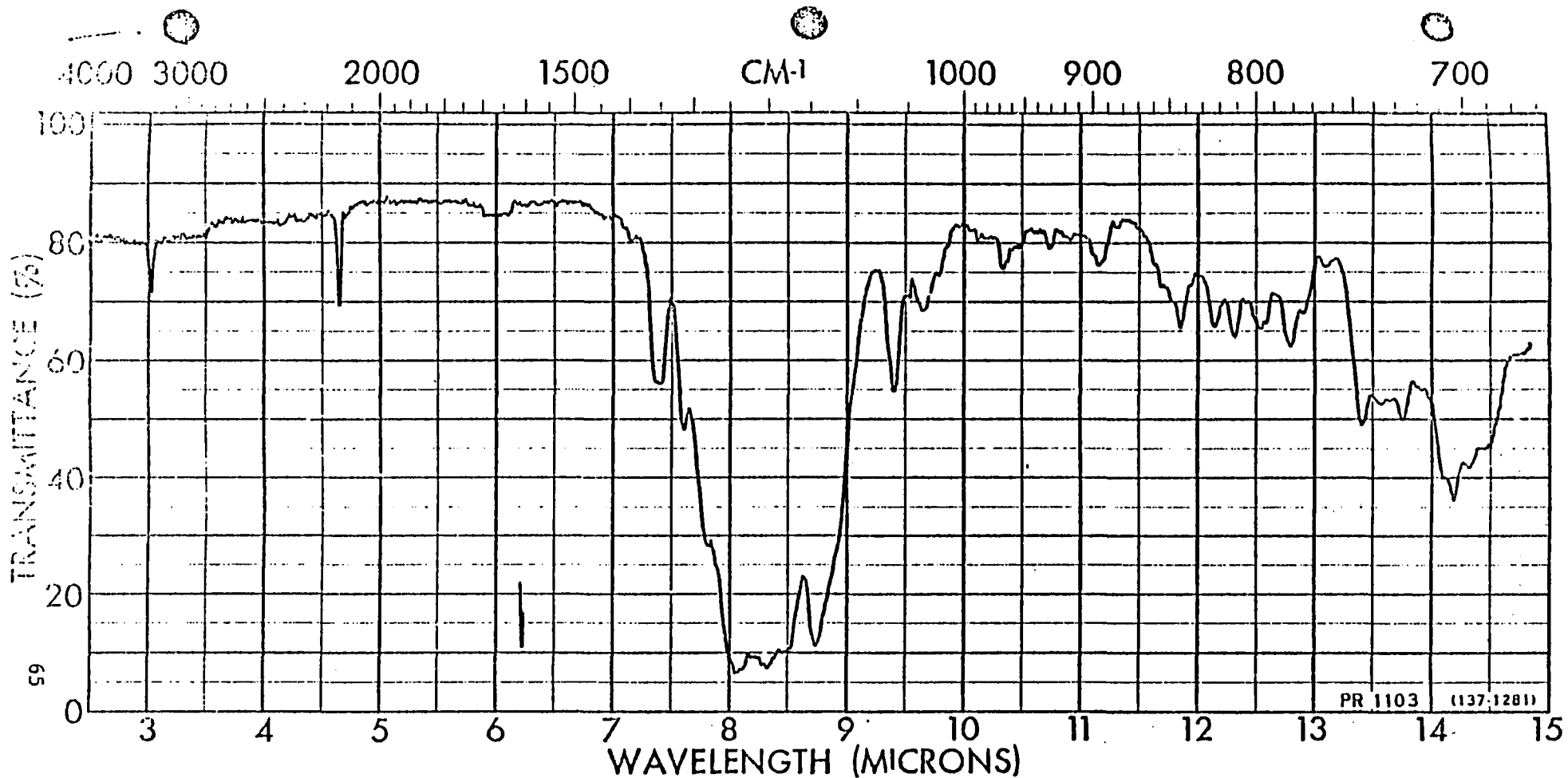


Figure 18 - Infrared Spectrum of the Mixture of $C_7F_{15}H$, $C_7F_{15}CECH$, $C_7F_{15}CECCF_3$

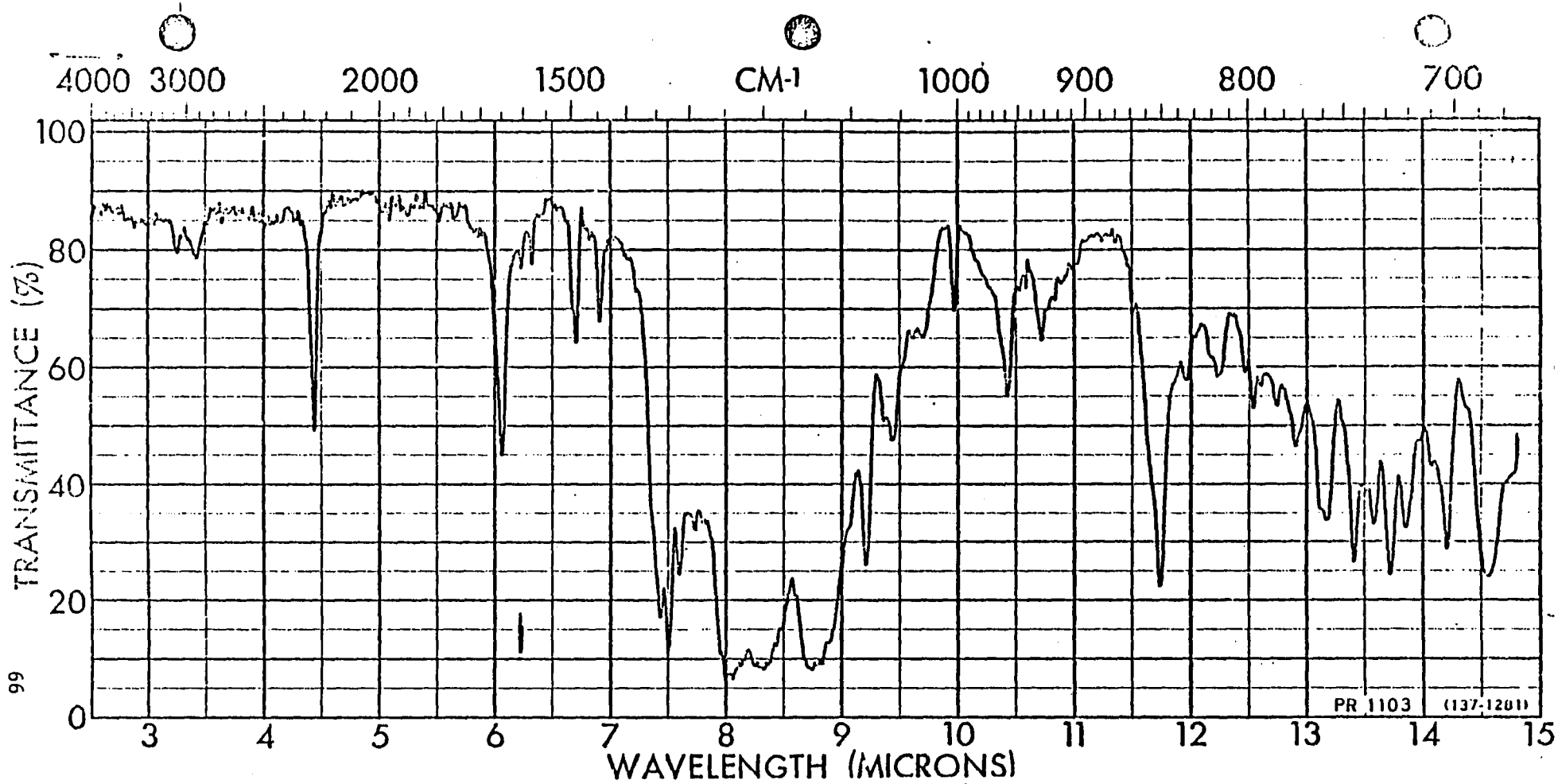
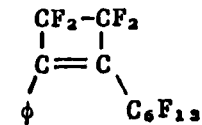
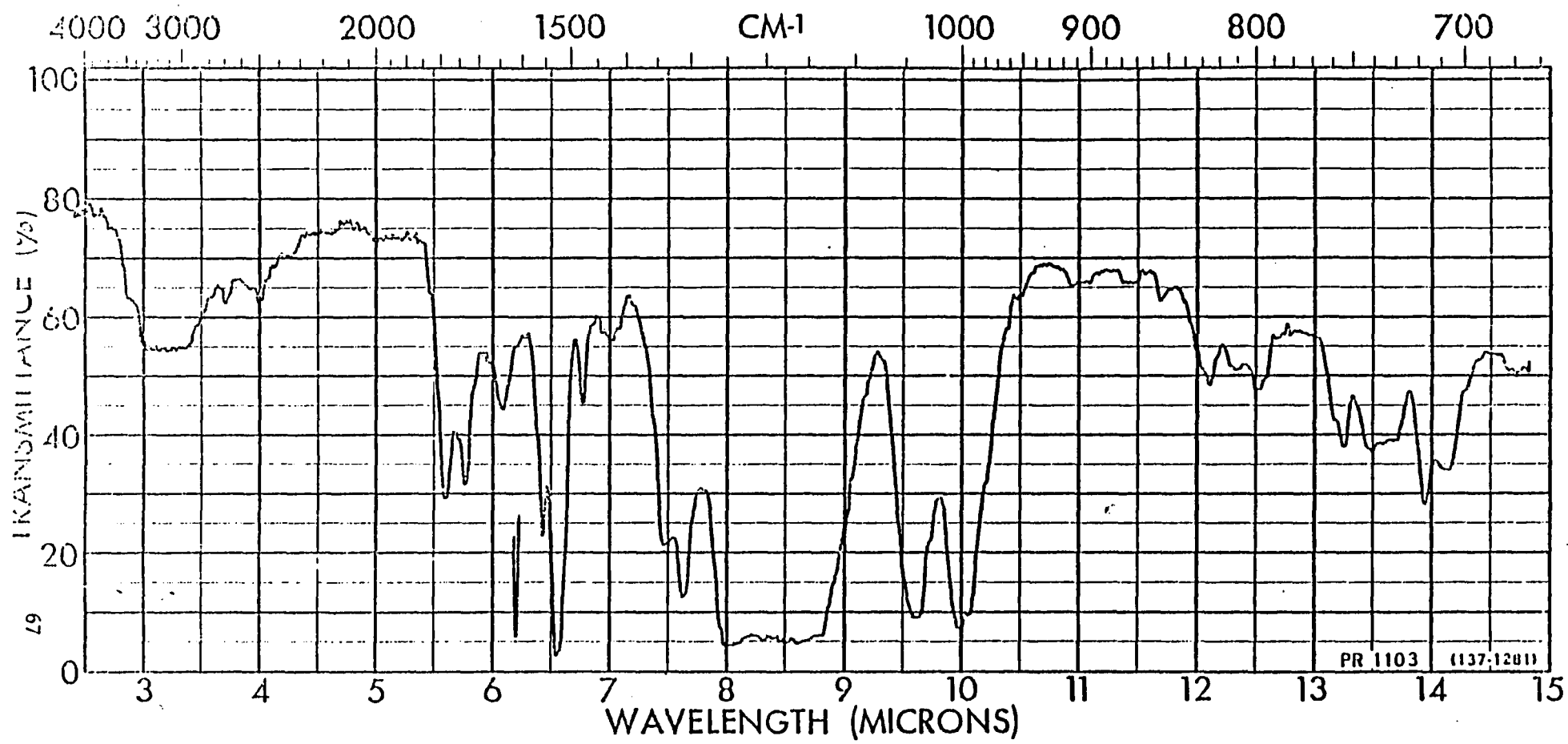


Figure 19 - Infrared Spectrum of the Mixture of $C_6F_{13}C=CC_6H_5$,





PR 1103 (137,1281)

$$\begin{array}{c}
 \text{CF}_3\text{NH} \\
 | \quad || \\
 \text{C}_3\text{F}_7\text{OCF}-\text{C}-\text{NH}_2
 \end{array}$$
 Figure 21 - Infrared Spectrum of $\text{C}_3\text{F}_7\text{OCF}-\text{C}-\text{NH}_2$

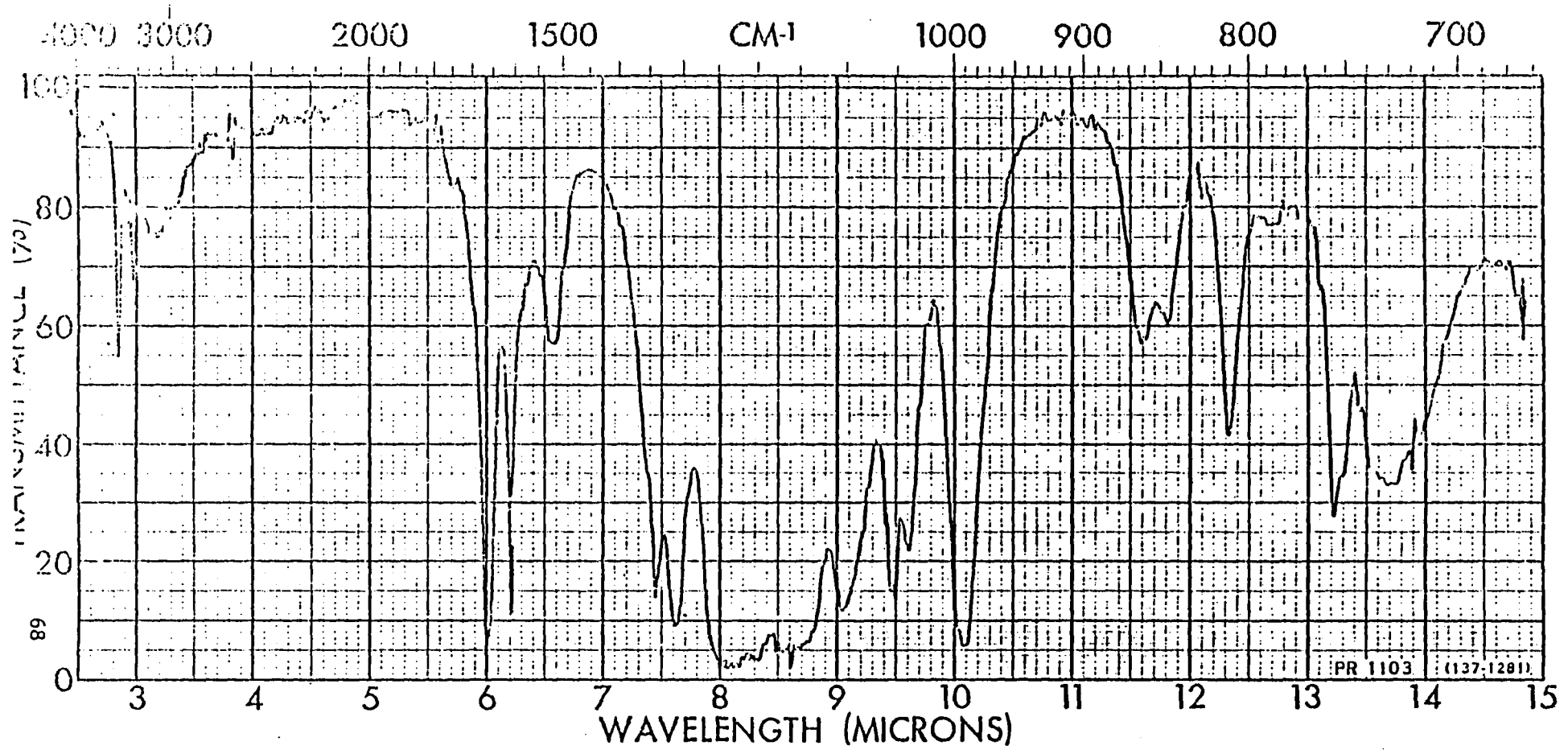
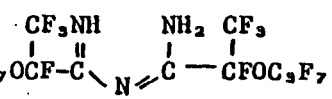


Figure 22 - Infrared Spectrum of $C_3F_7OCF-C(=O)-N=C(NH_2)CF_3$



PR 1103 (137-1291)

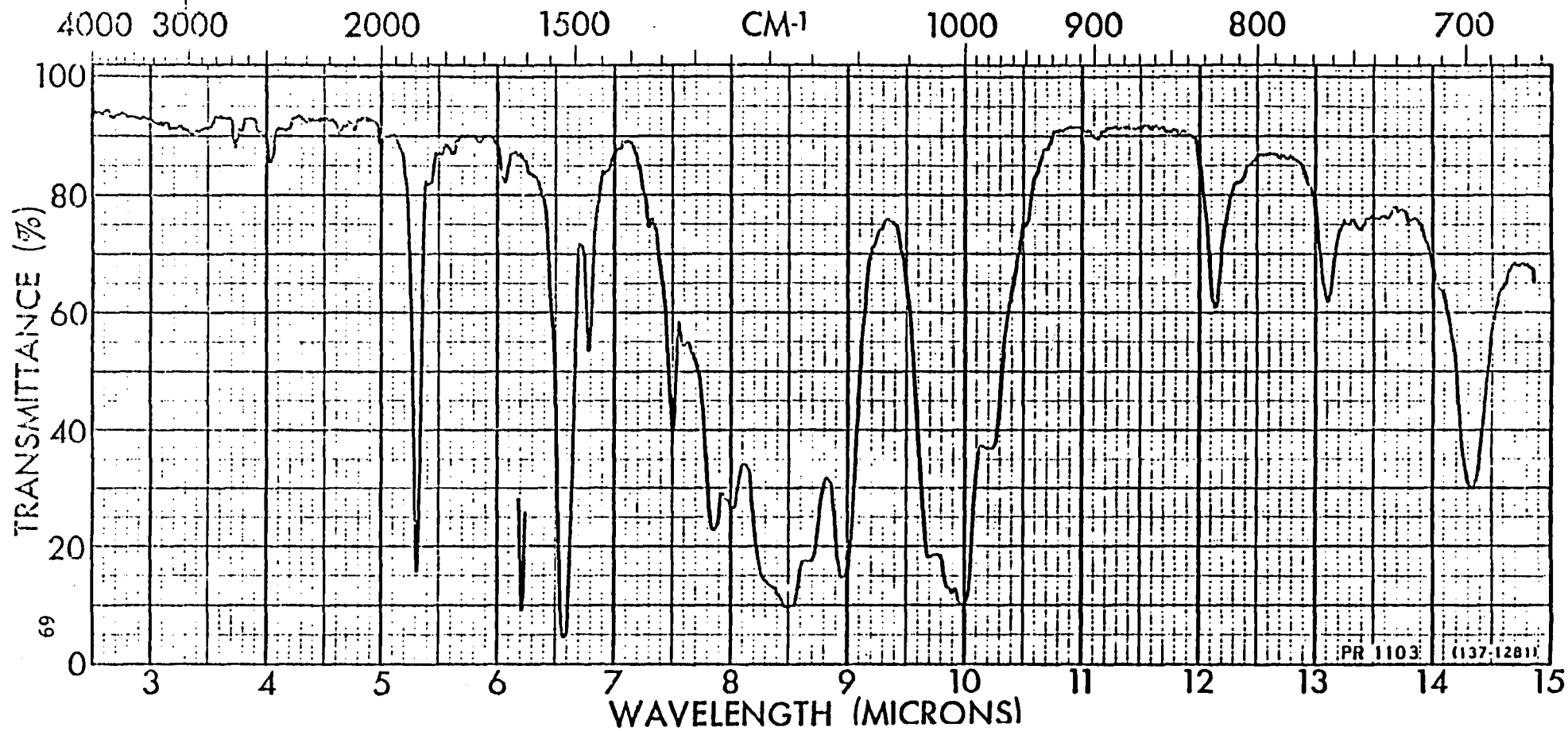
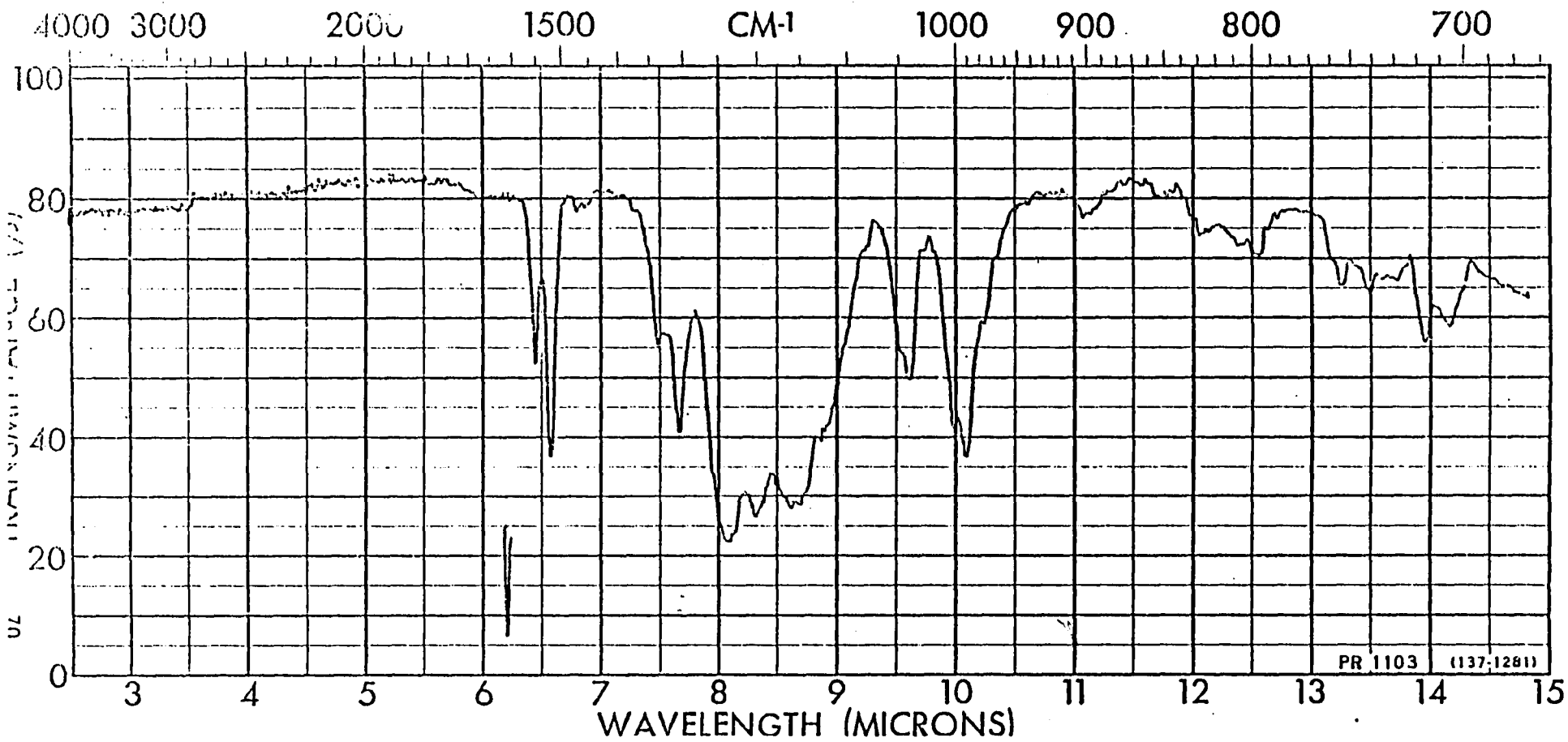
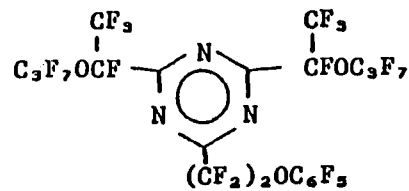


Figure 23 - Infrared Spectrum of $C_6F_5OCF_2CF_2COF$



PR 1103 (137-1281)

Figure 24 - Infrared Spectrum of



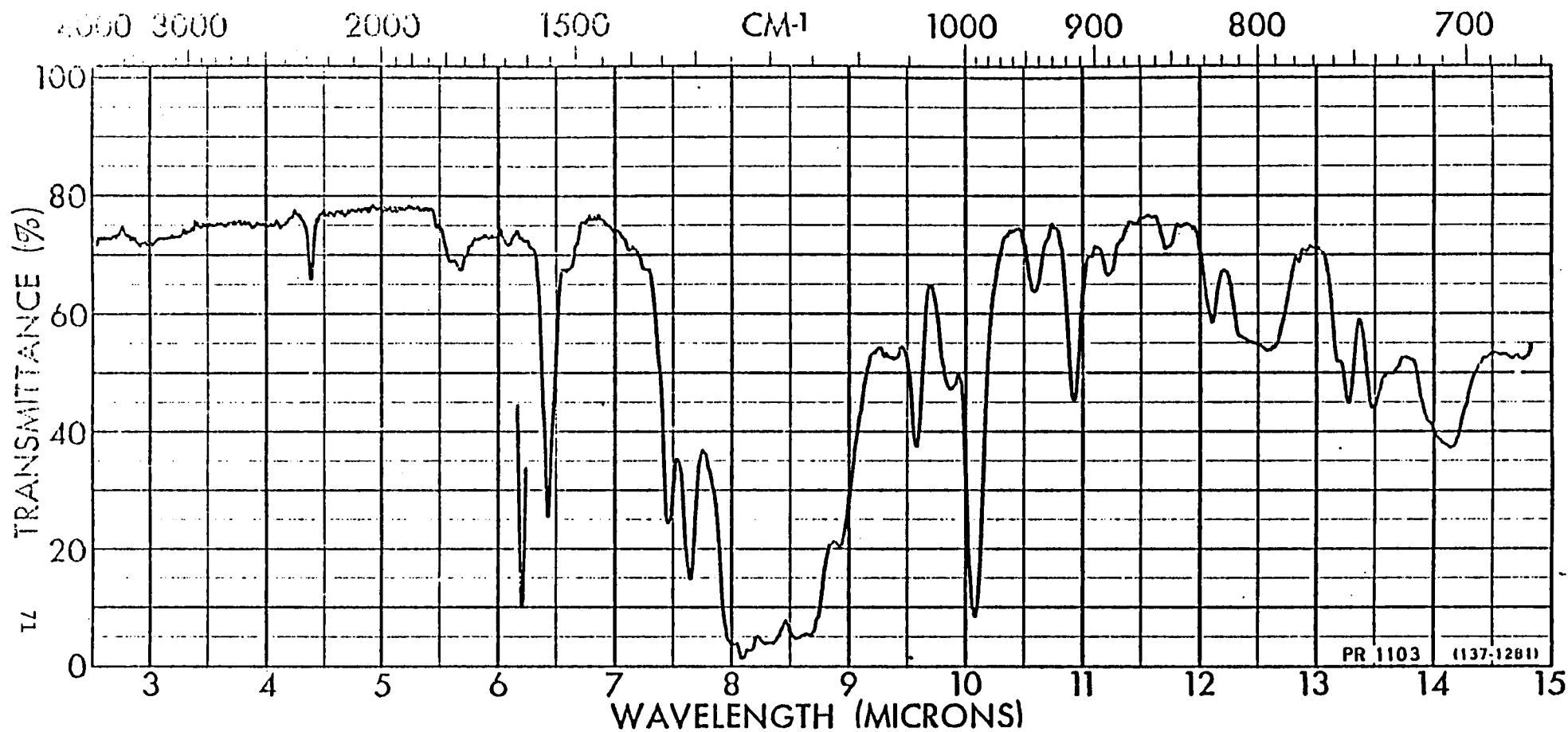
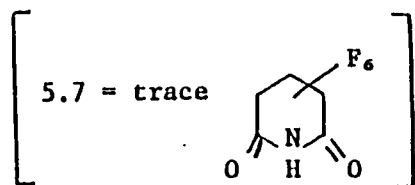
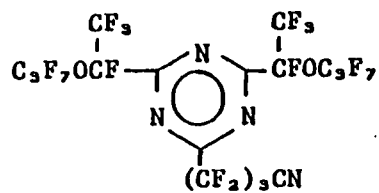


Figure 25 - Infrared Spectrum of



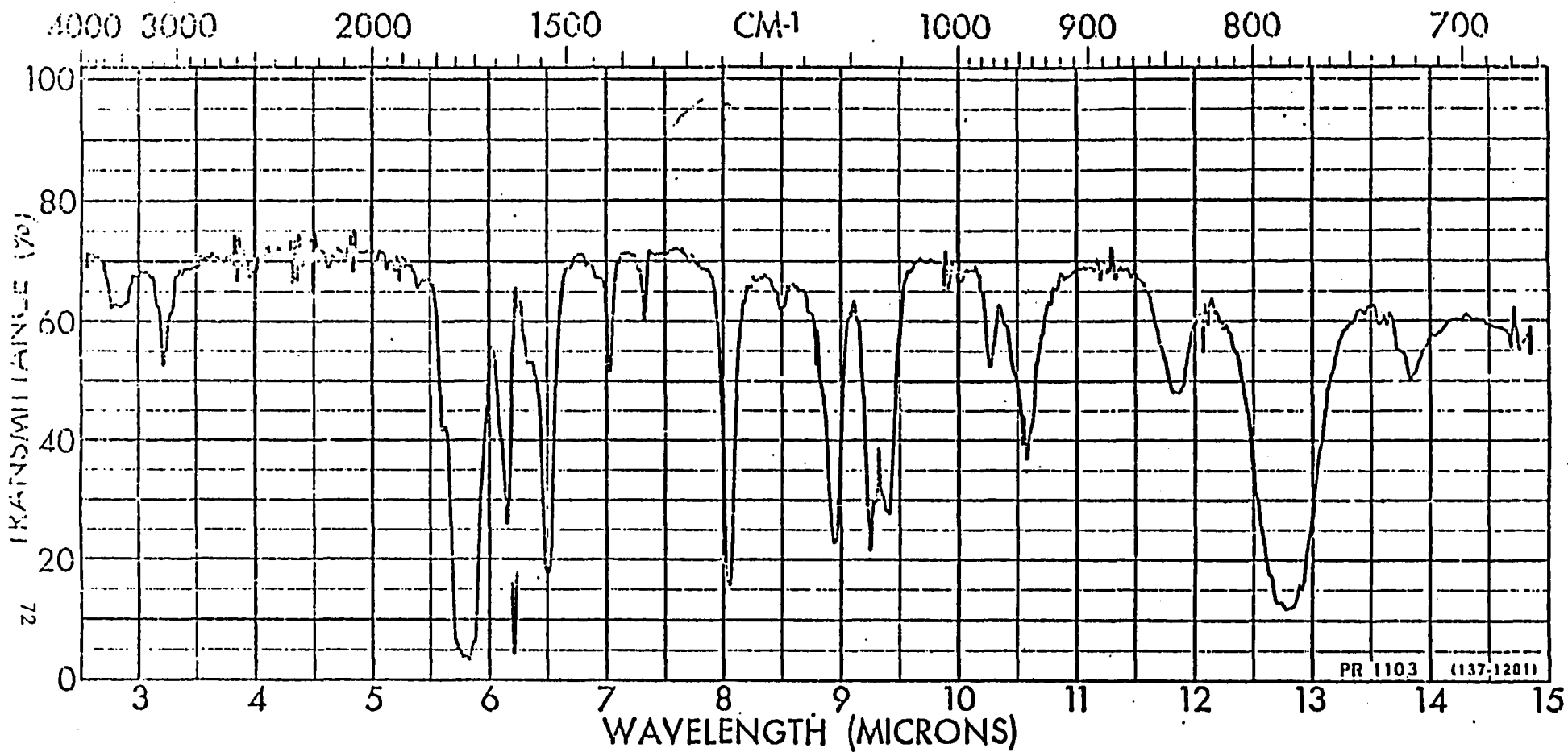
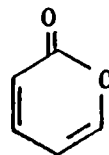


Figure 26 - Infrared Spectrum of



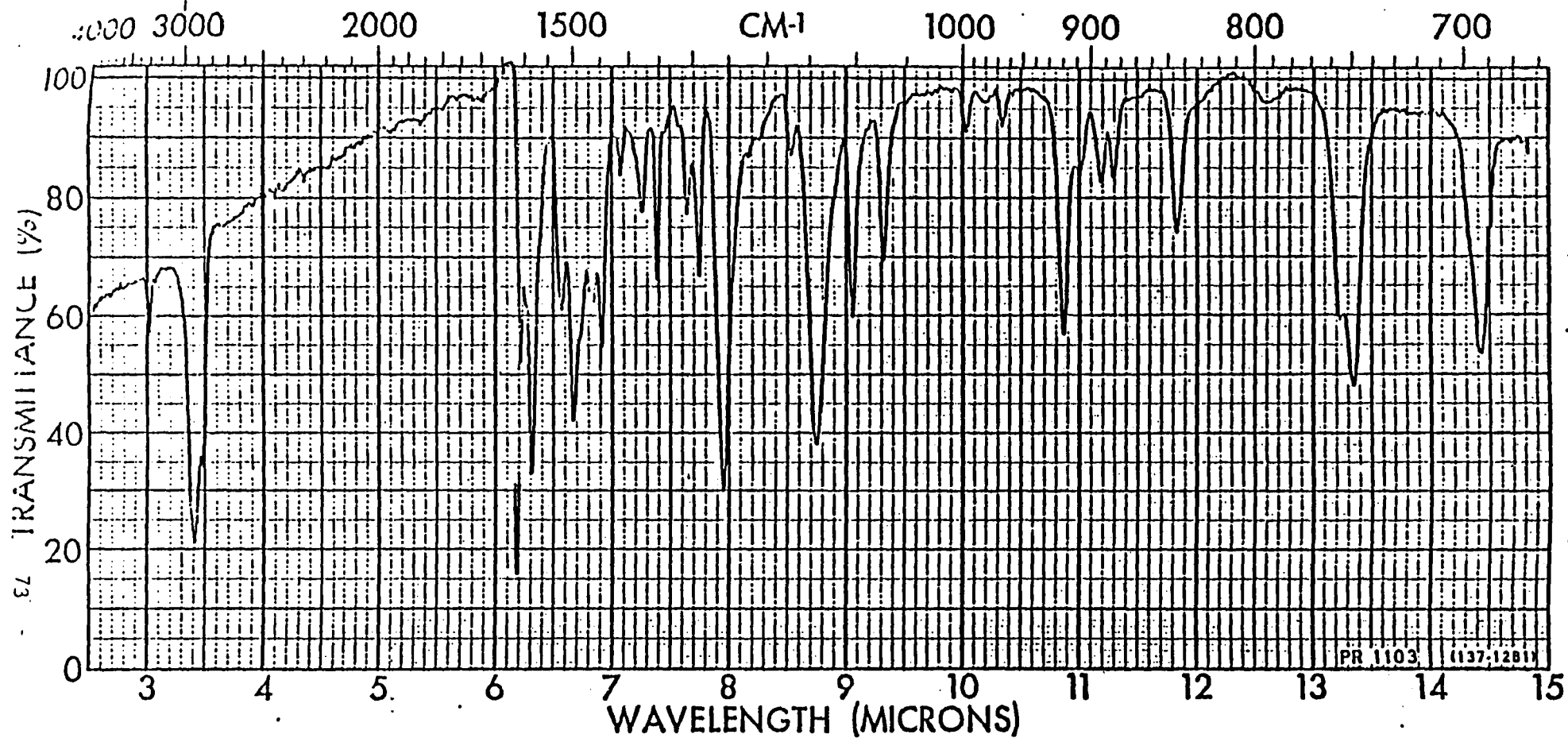


Figure 27 - Infrared Spectrum of $\phi\text{HNN}=\text{CH}-\text{C}_6\text{H}_4-\text{CH}=\text{NNH}\phi$

(Nujol)

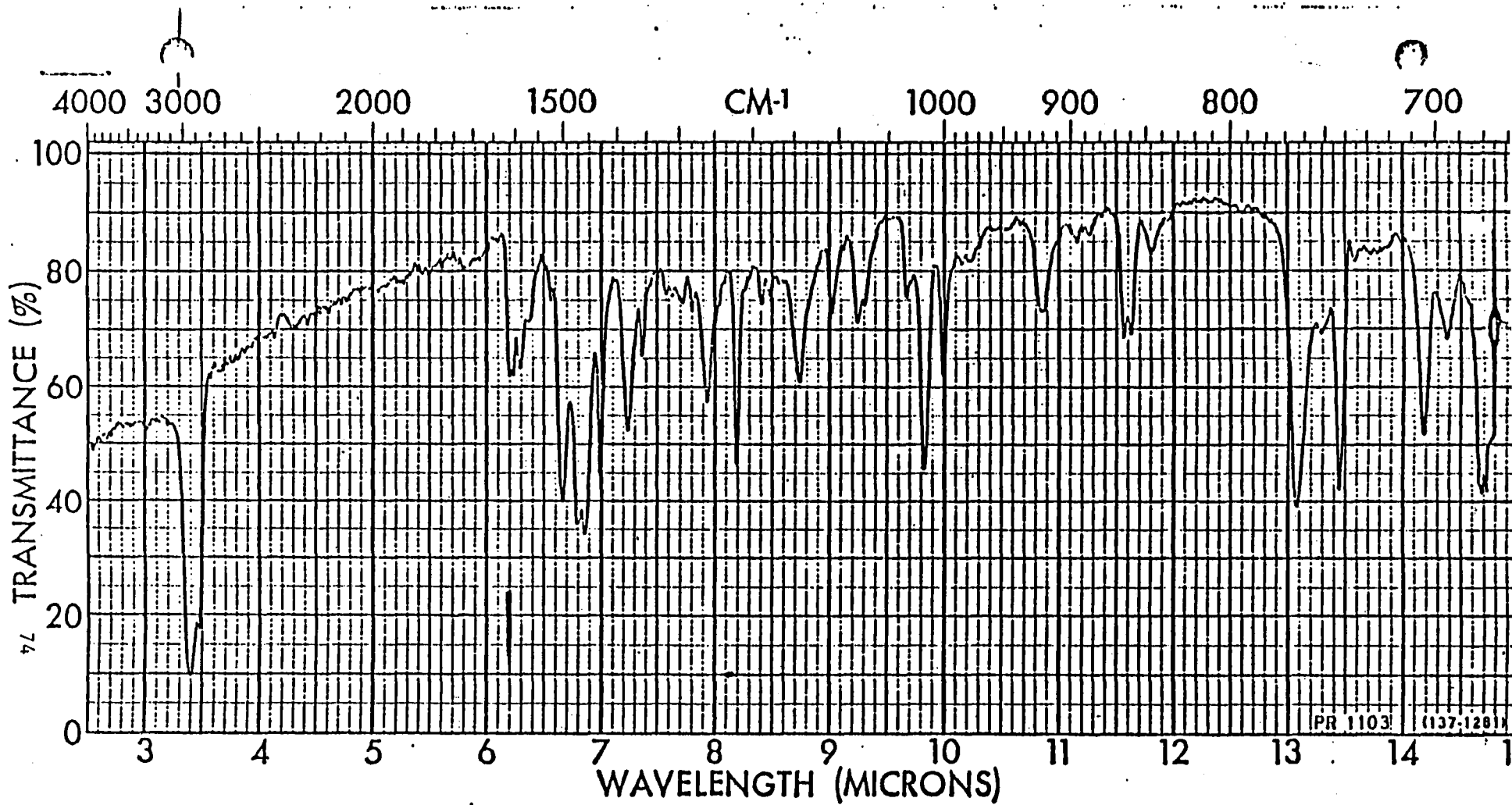
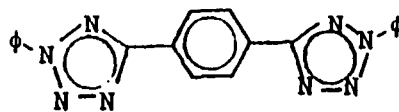


Figure 28 - Infrared Spectrum of



(Nujol Mull)

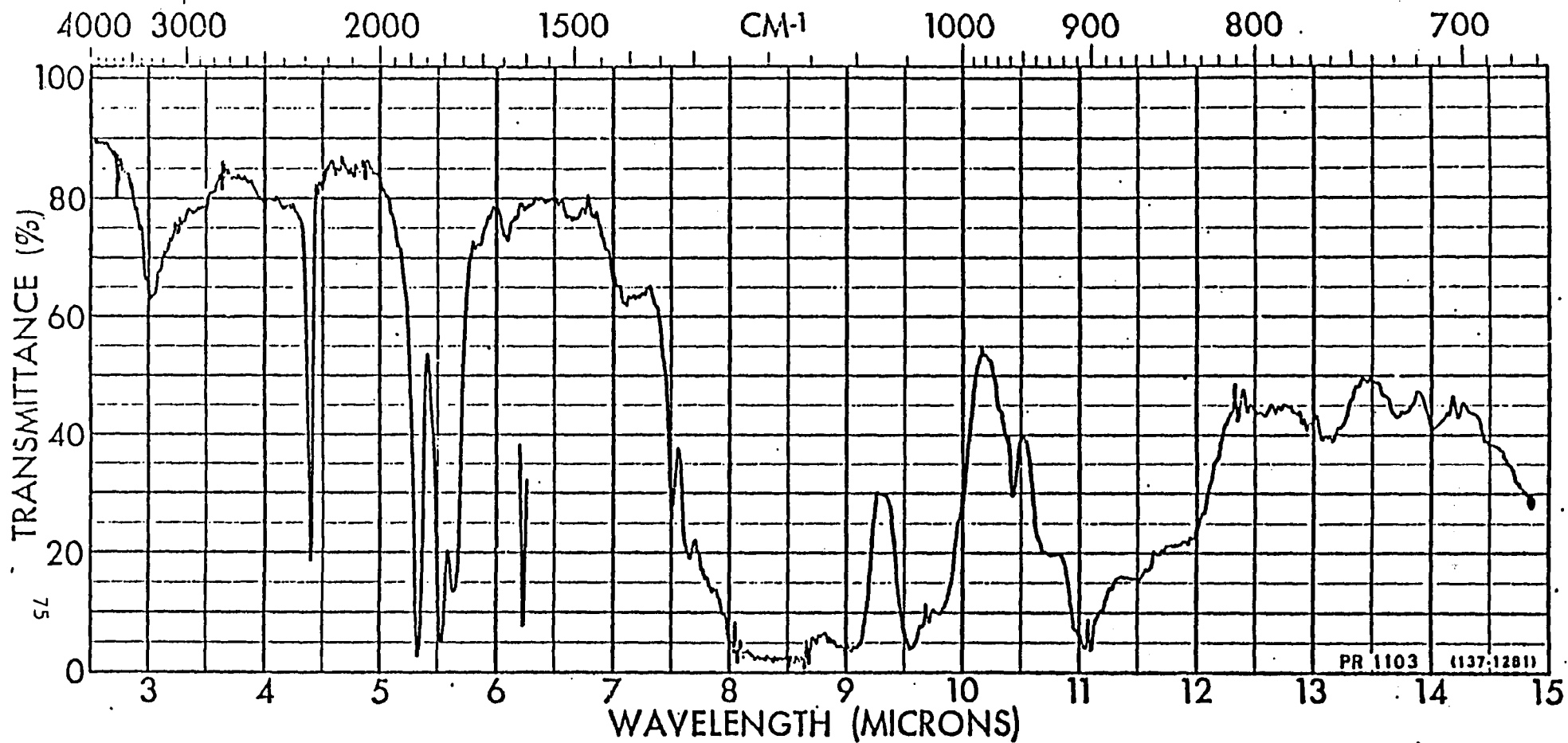


Figure 29 - Infrared Spectrum of $\text{NC}(\text{CF}_2)_3\overset{\text{O}}{\parallel}\overset{\text{O}}{\parallel}\text{COC}(\text{CF}_2)_3\text{CN}$

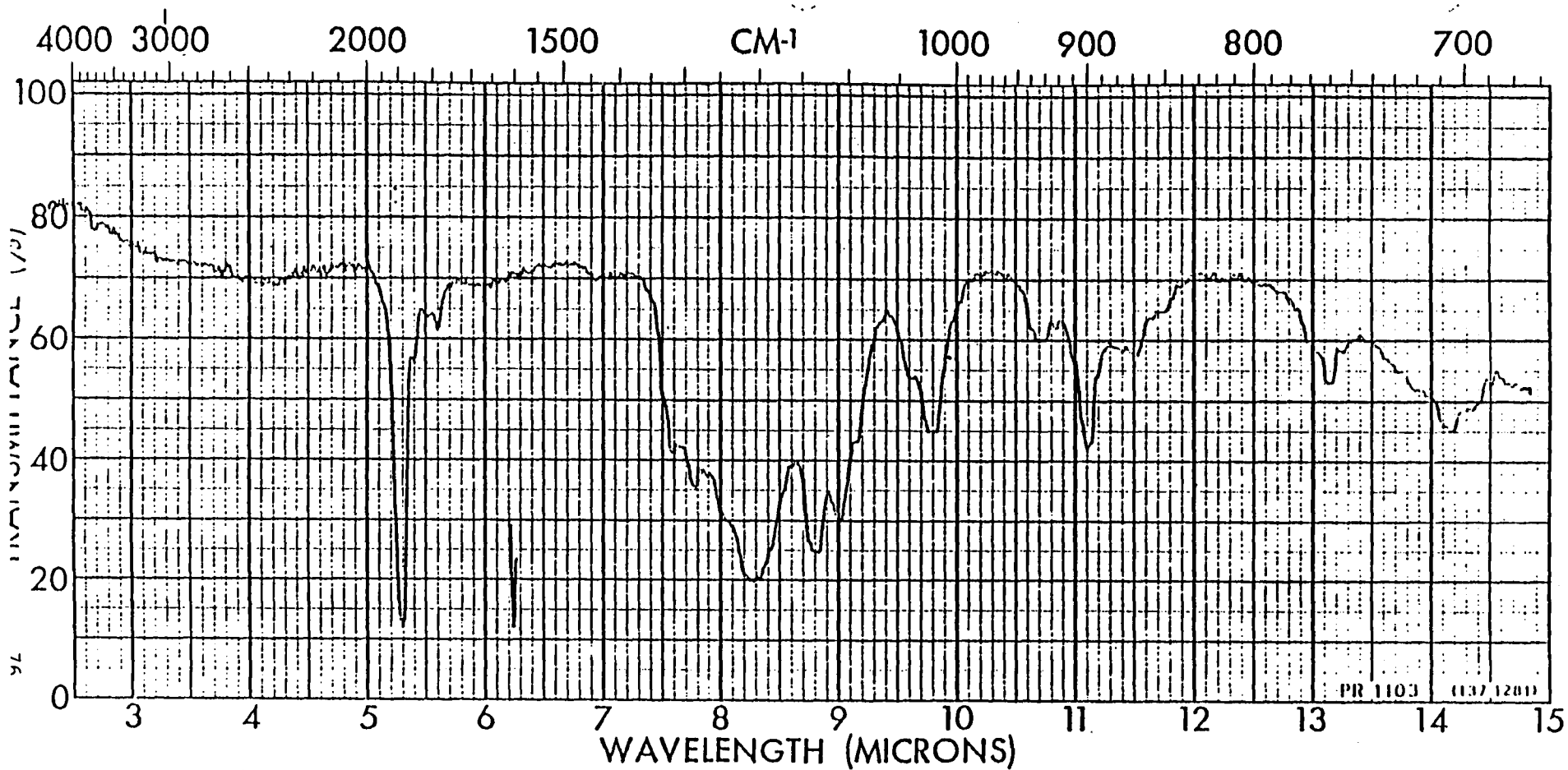


Figure 30 - Infrared Spectrum of $\text{FCO}(\text{CF}_2)_3\text{COF}$

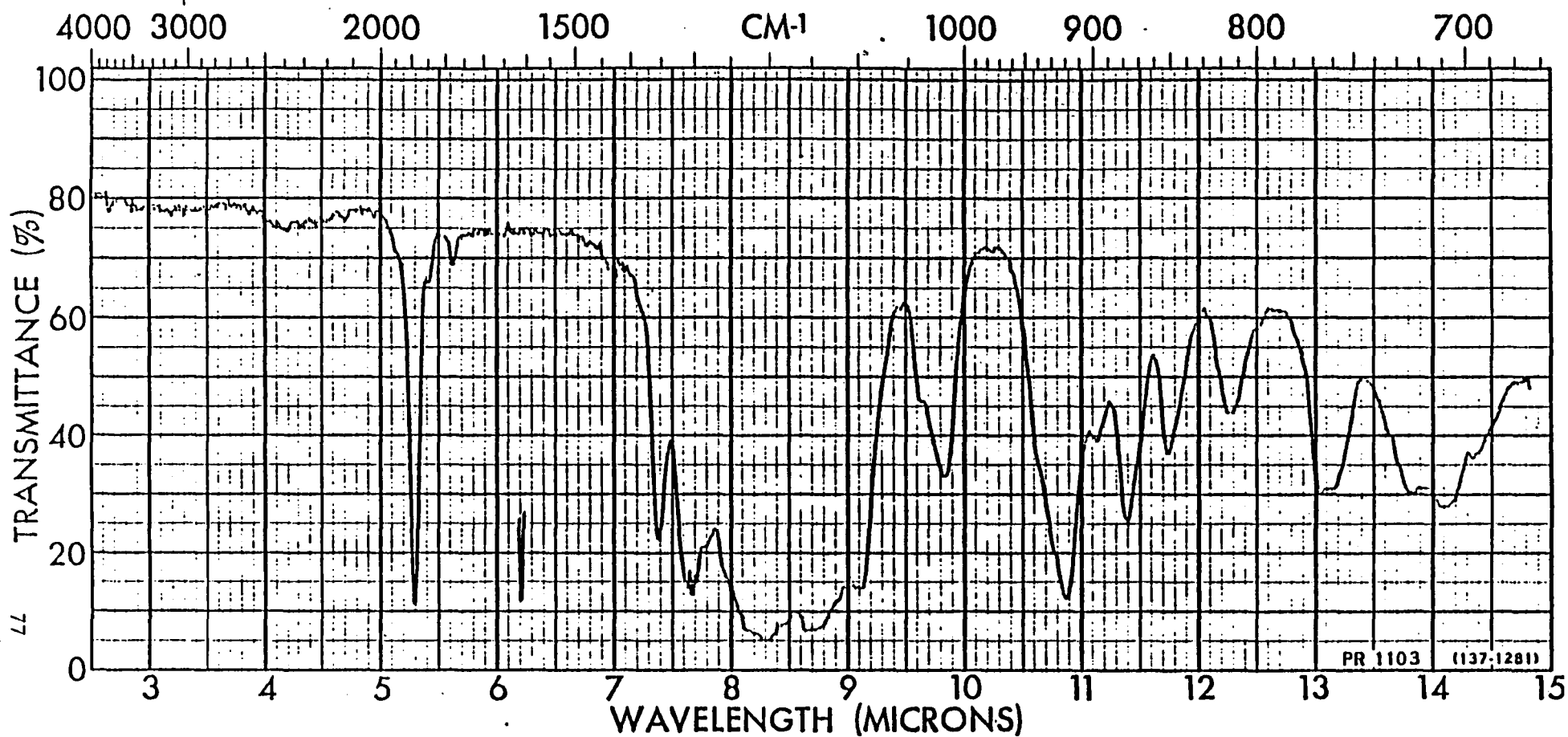


Figure 31 - Infrared Spectrum of $\text{CF}_2\text{ICF}_2\text{O}(\text{CF}_2)_4\text{COF}$

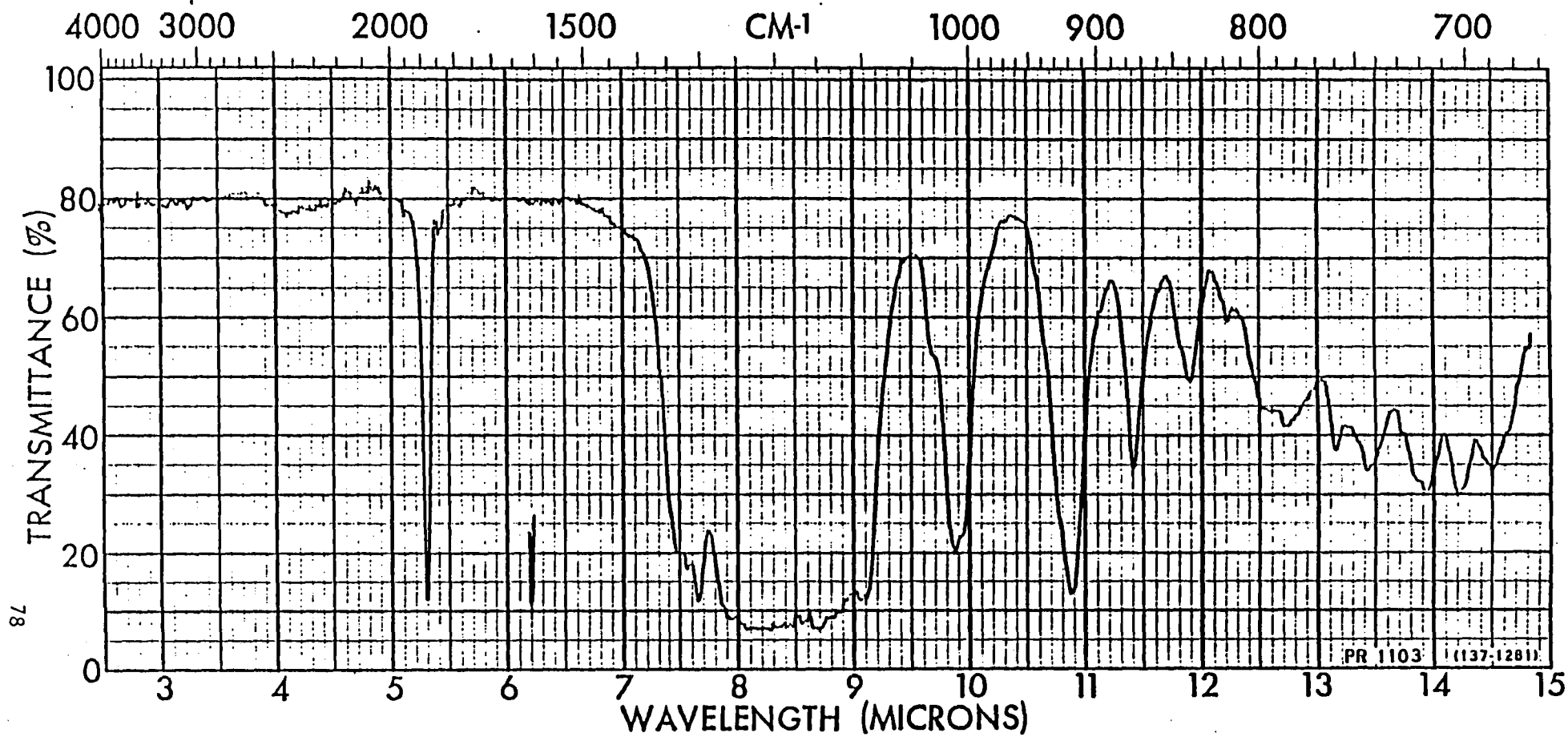


Figure 32 - Infrared Spectrum of $\text{ICF}_2\text{CF}_2\text{O}(\text{CF}_2)_5\text{OCF}-\overset{\text{CF}_3}{\underset{\text{O}}{\parallel}}\text{CF}$

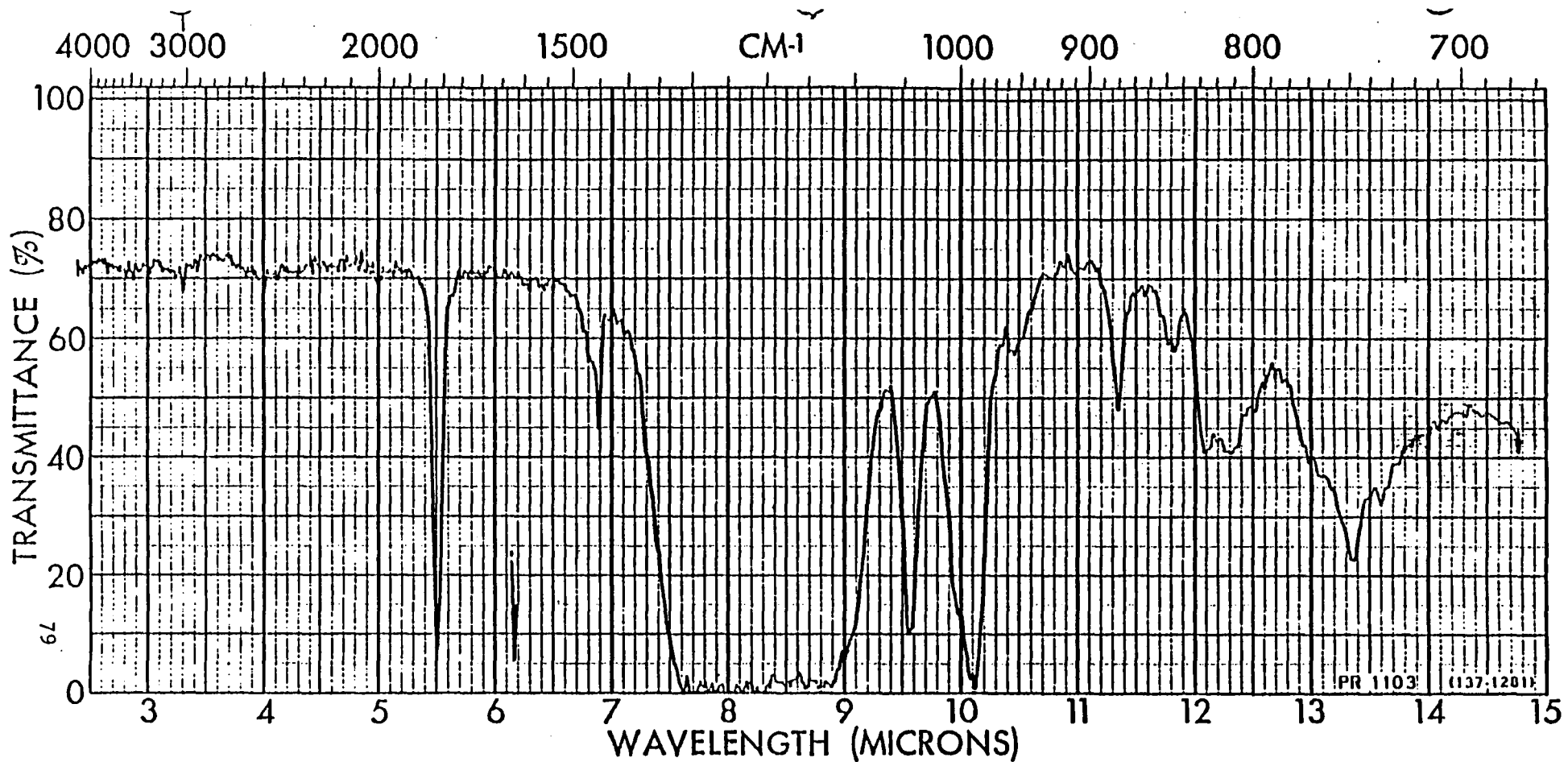


Figure 33 - Infrared Spectrum of 8-EDAF(G)-dimethylester

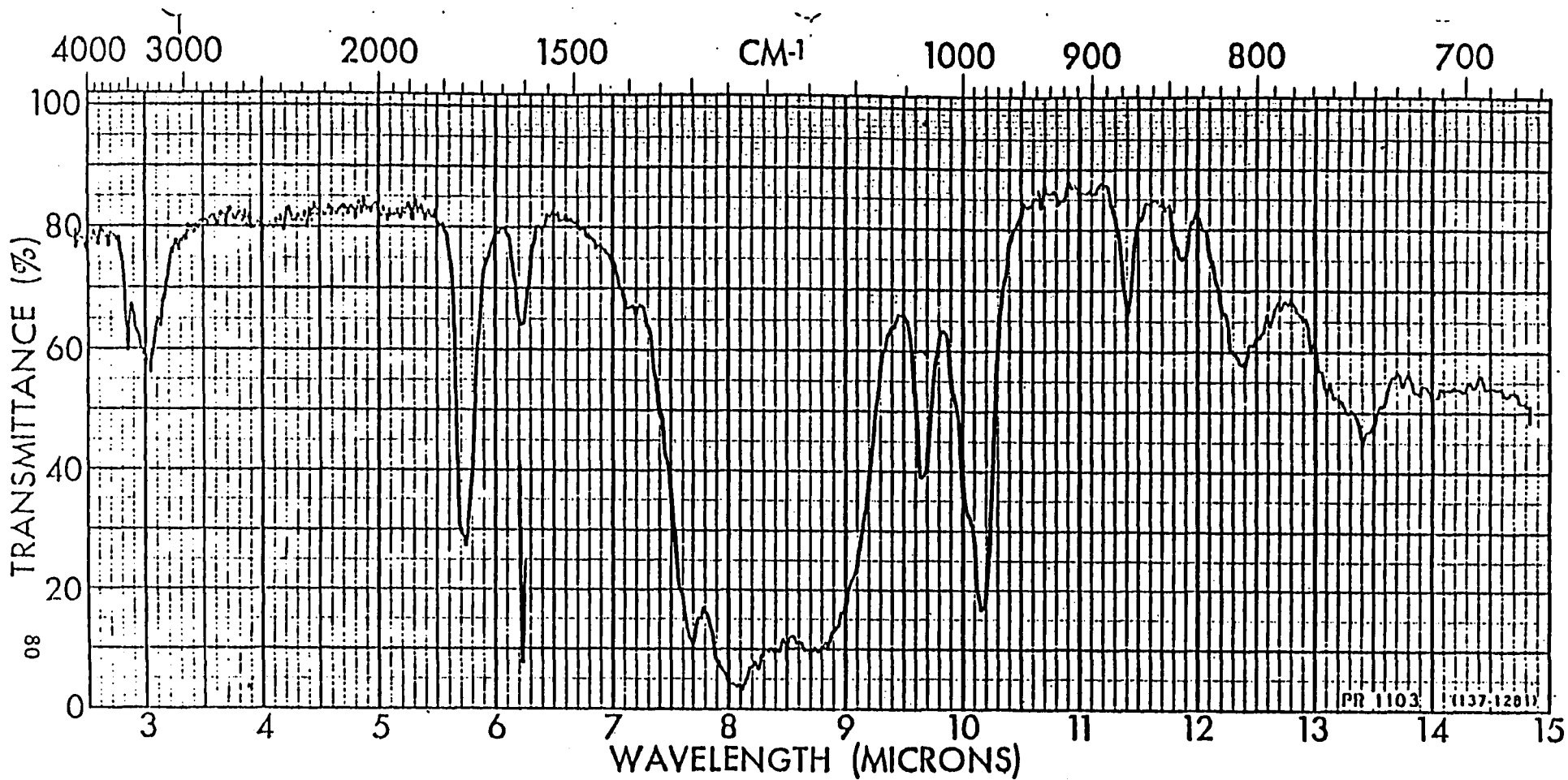


Figure 34 - Infrared Spectrum of 8-EDAF(G)-diamide

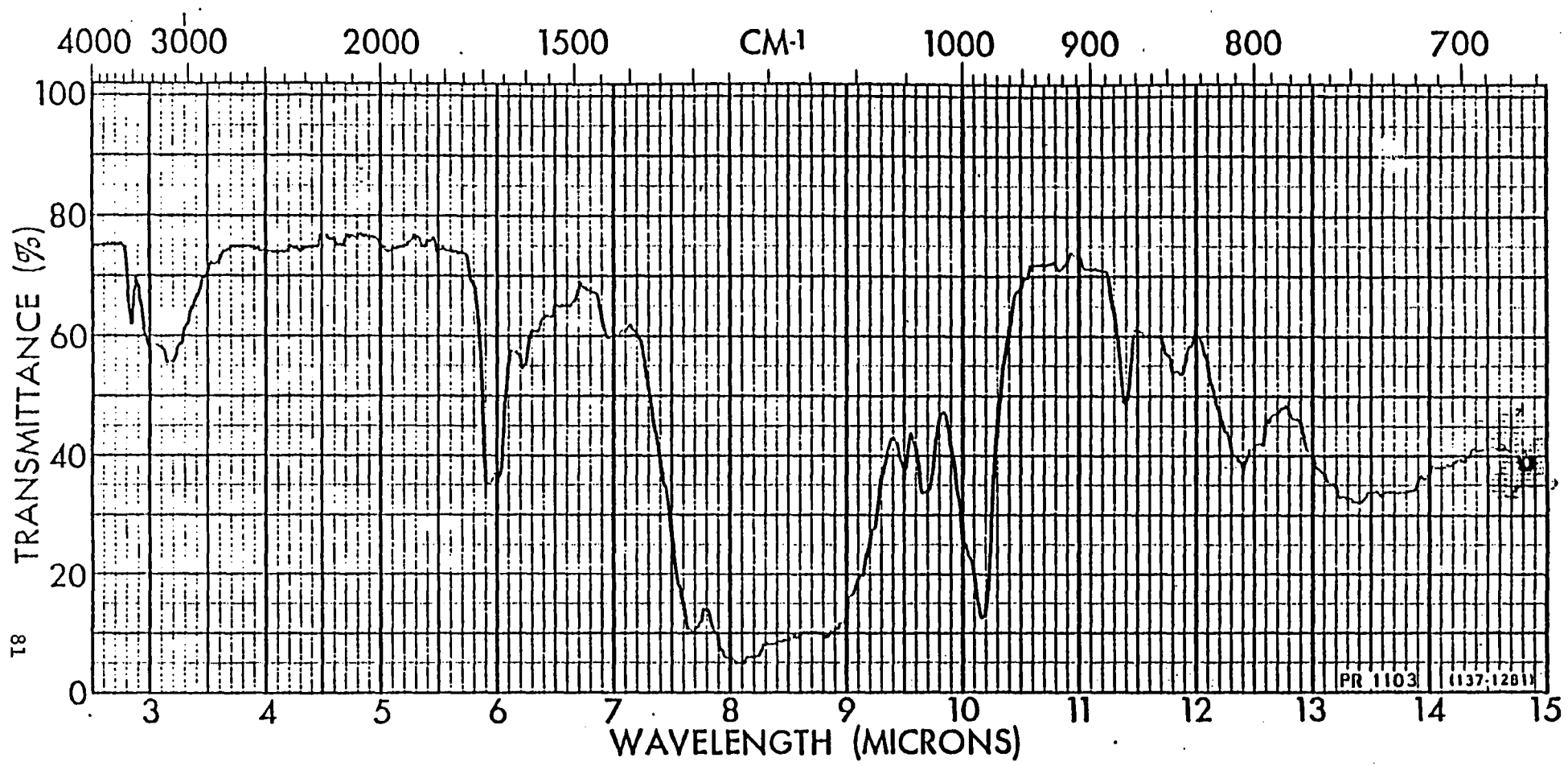


Figure 35 - Infrared Spectrum of 8-EDAF(G)-diamidine

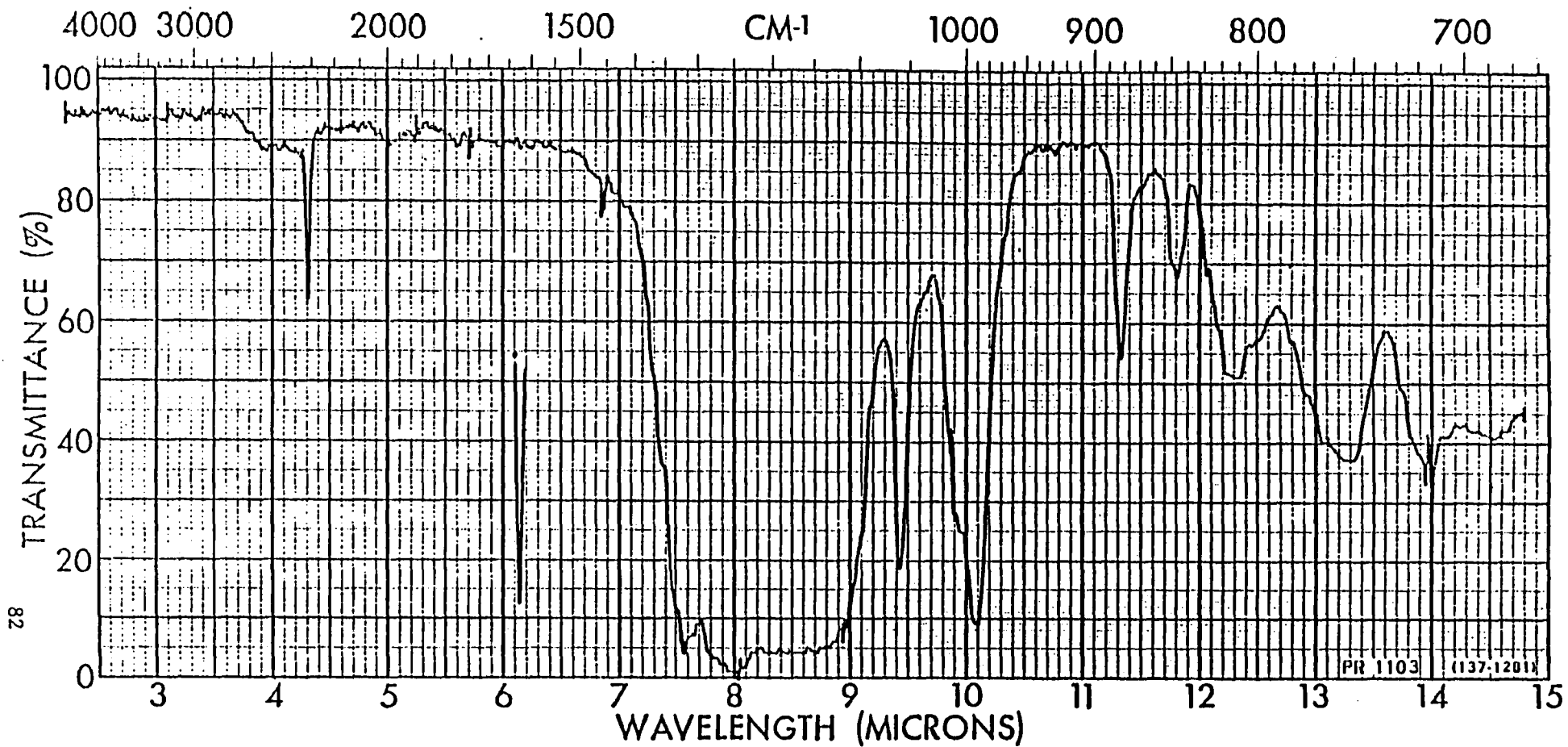


Figure 36 - Infrared Spectrum of 8-EDAF(G)-dinitrile

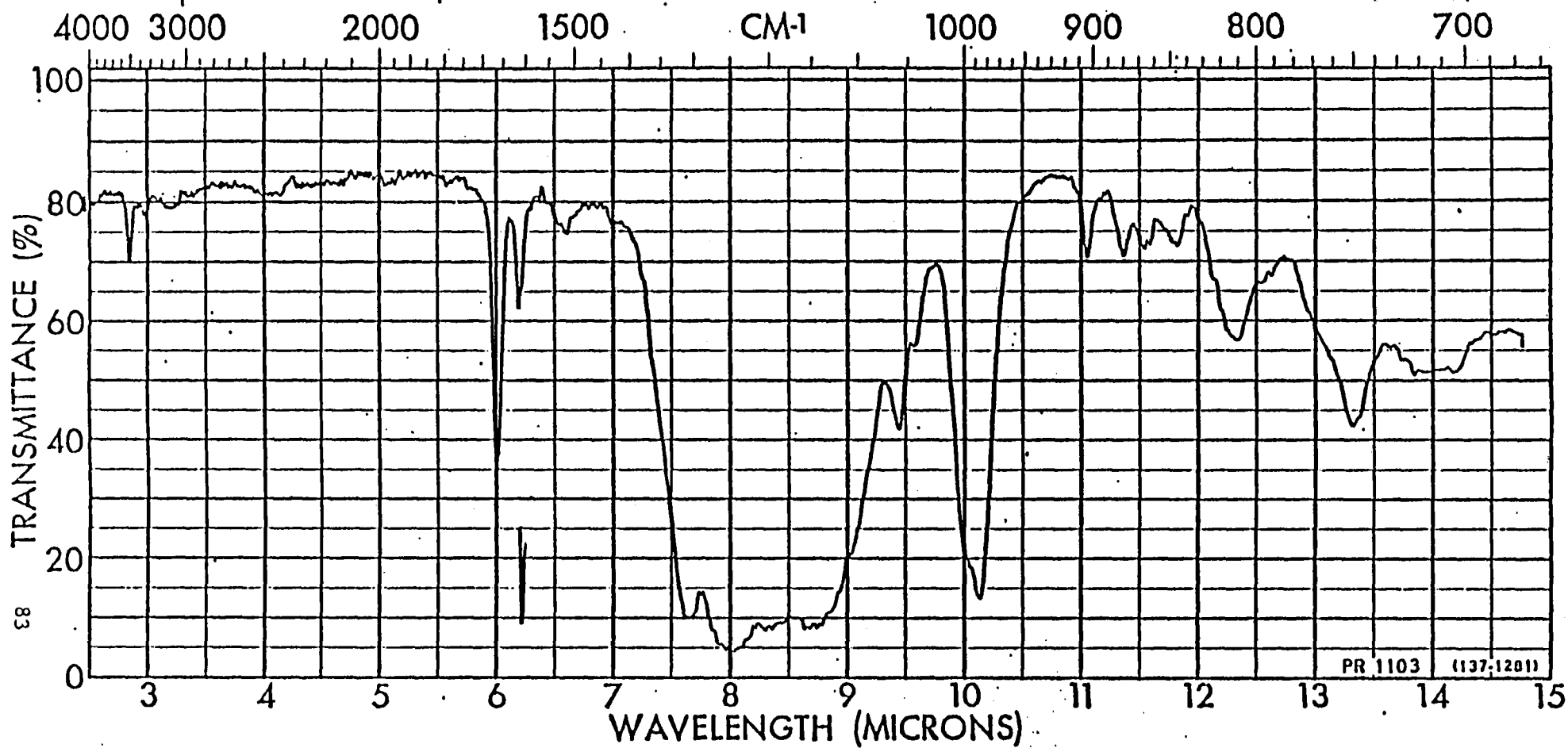


Figure 37 - Infrared Spectrum of 8-EDAF(G)-polyimidoylamidine

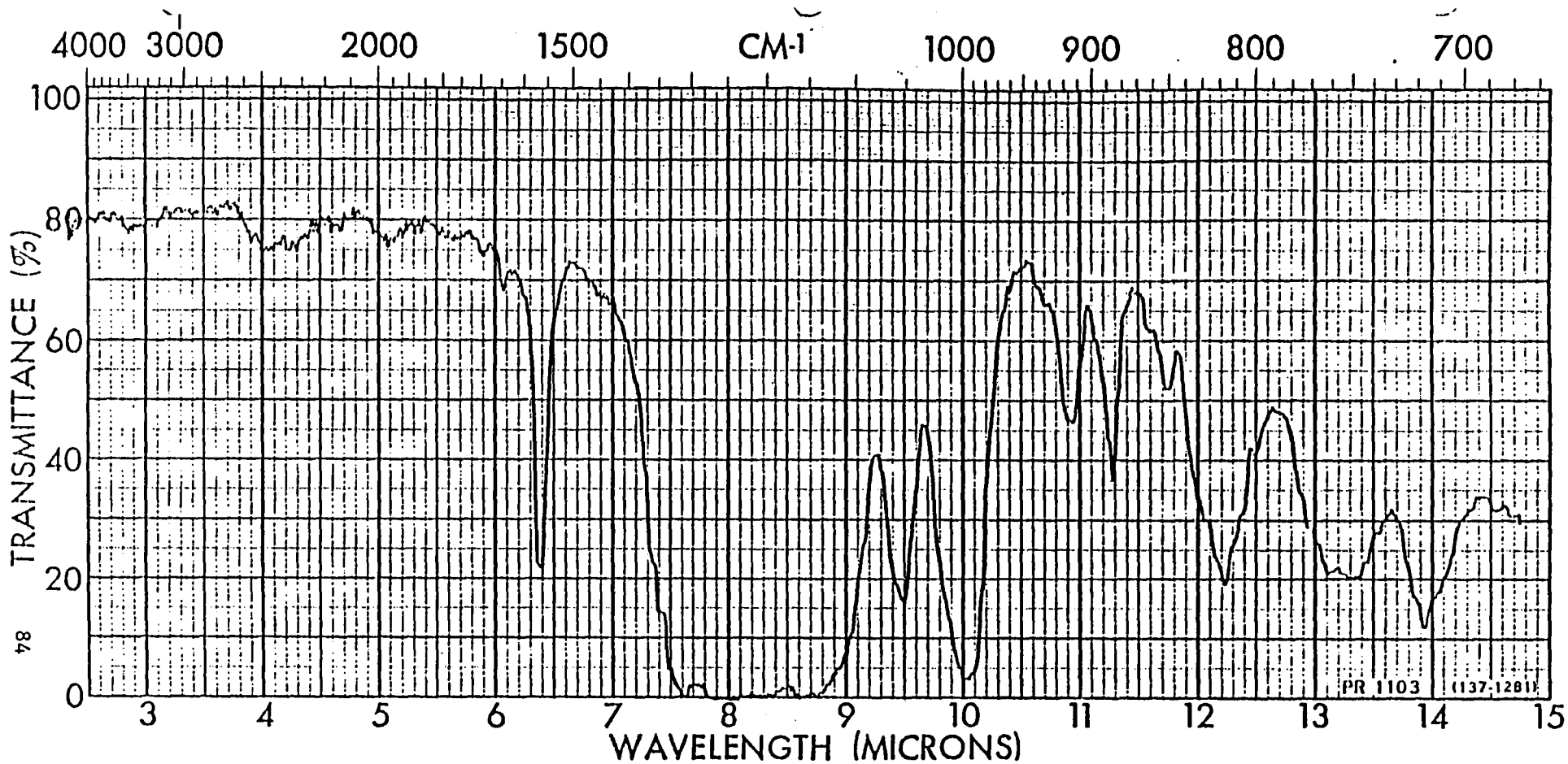


Figure 38 - Infrared Spectrum of 7-EDAF(G)-polytriazine

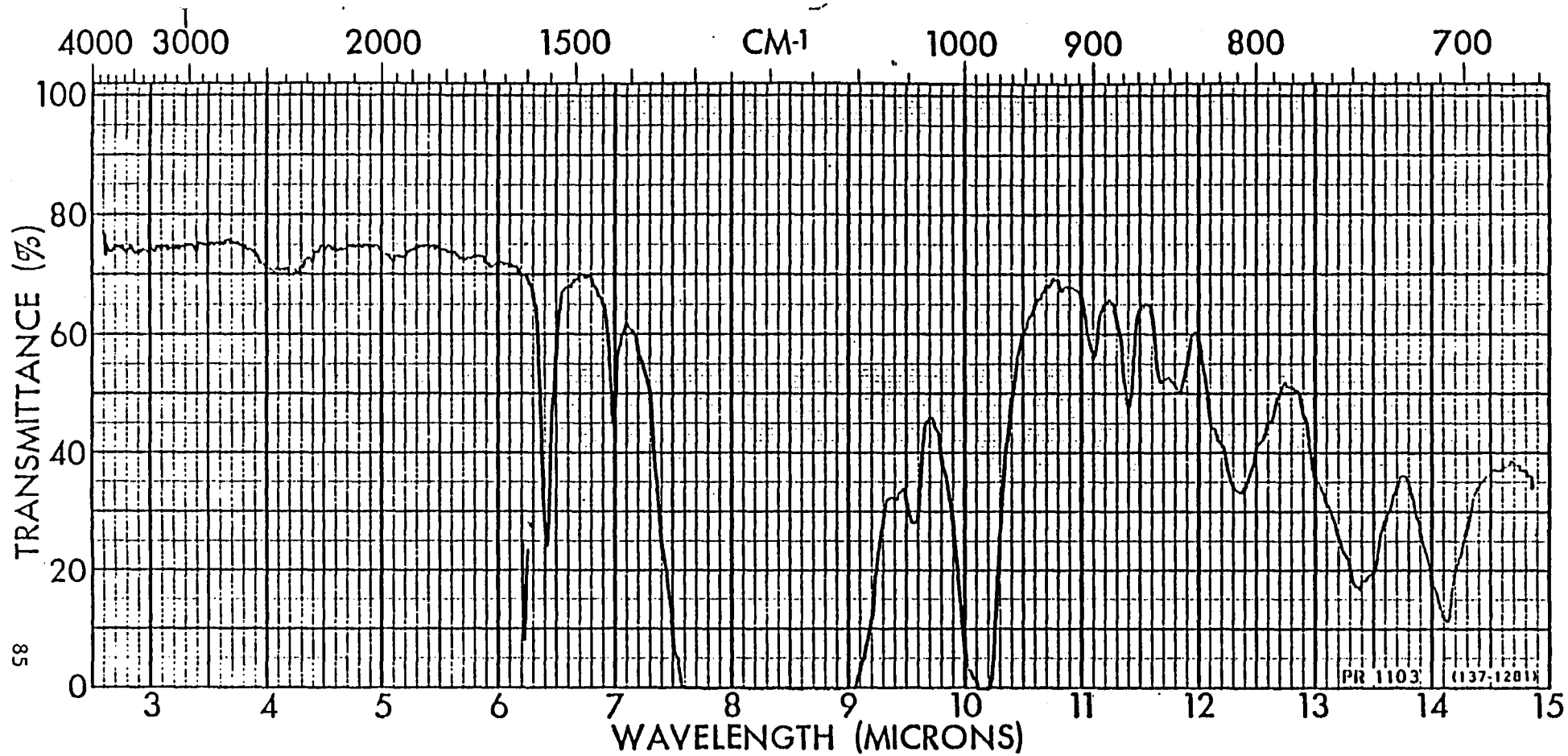


Figure 39 - Infrared Spectrum of 8-EDAF(G)-polytriazine
(15% - CN pendant groups)

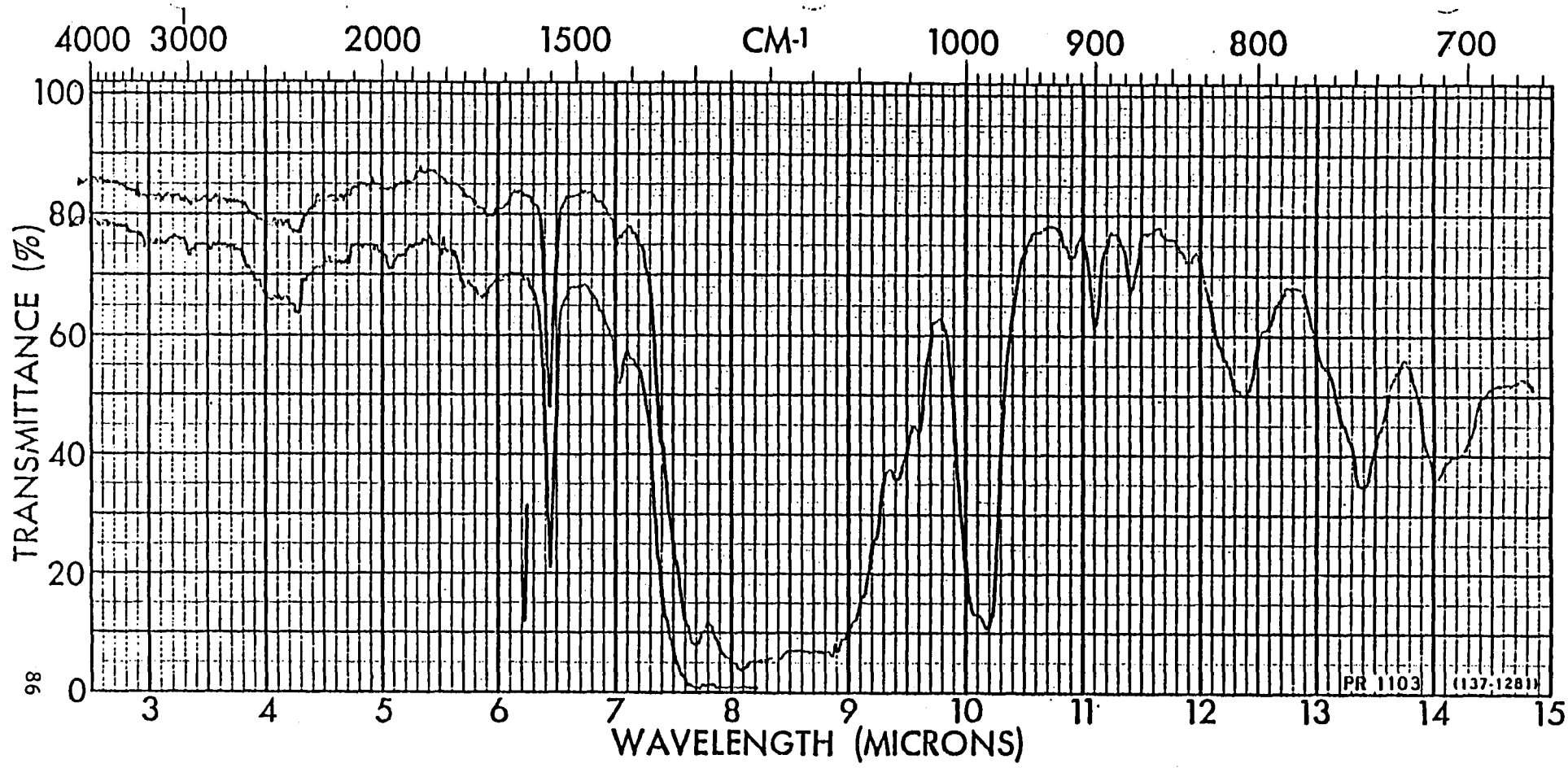


Figure 40 - Infrared Spectrum of 8-EDAF(G)-polytriazine
(15% - CF₂I pendant groups)

1. Report No. NASA CR-166409	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle Synthesis of Perfluorinated Polyethers		5. Report Date September 1982	
		6. Performing Organization Code	
7. Author(s) R. J. DePasquale, C. D. Padgett, J.R. Patton, and T. Psarras		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address PCR, Inc. Gainesville, Florida		11. Contract or Grant No. NAS2-8156	
		13. Type of Report and Period Covered Contractor Report	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546		14. Sponsoring Agency Code	
		15. Supplementary Notes Point of Contact: Bob Rosser, MS:223-6, Ames Research Center, Moffett Field, CA 94035 415-965-5244 or FTS 448-5244	
16. Abstract <p>A series of highly fluorinated acetylenes was prepared and their cyclization reactions were studied.</p> <p>A series of perfluoropolytriazines with CF₂I pendent groups were prepared. These materials can be cured thermally or photochemically to an elastomeric gum.</p> <p>Perfluoropolytriazines with -CN pendent groups were prepared. These materials can be crosslinked by reaction with terephthalonitrile oxide.</p>			
17. Key Words (Suggested by Author(s)) Polymers Elastomers Fluoropolymers Fluoroether elastomers		18. Distribution Statement Unlimited Subject Category 23	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 94	22. Price*

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