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ML-TDR-64-142
Part II

AD0471664

THERMALLY STABLE PERFLUORINATED POLYMERS

Henry C. Brown

TECHNICAL REPORT ML-TDR-64-142, Part II

March, 1965

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

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THERMALLY STABLE PERFLUORINATED POLYMERS

Henry C. Brown

FOREWORD

This report was prepared by the University of Florida under USAF Contract AF33(615)1368, initiated under Project No. 7340, "Non-metallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." This work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, with Dr. Christ Tamborski as Project Engineer.

The report covers work performed during the period March 1, 1964 through February 28, 1965. Personnel engaged in this work were Dr. Henry C. Brown, Principal Investigator, and Mr. John Turnbull, Mr. Gerald McNeely and Mr. H.J. Gisler, Research Assistants.

The manuscript was released by the author in April, 1965, for publication as an RTD technical report.

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
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ABSTRACT

Work on the 1,2,4-triazole polymer system, in which these heterocyclic groups are connected by perfluoroalkylene chains, has included further study and assigment of structure to the cyclic product from perfluoroglutaronitrile and hydrazine, opening of this cyclic product with polymerization to poly(N^2-imidoyl perfluoroglutarhydrazidine), and synthesis of poly-(perfluoropropylene-1,2,4-triazole) both from the poly(imidoyl hydrazidine) and directly from the original cyclic monomer. Other possible routes to this type of polymer and possible reaction mechanisms have been considered.

The preparation of 2,6-*bis*(perfluoroethyl)-4-hydroxy-1,3,5-triazine has been completed.

Further study of the 2-perfluoroalkyl-5-hydroxy-1,3,4-oxadiazoles as possible monomers for polymerization has been carried out.

The synthesis of a perfluoroalkyl-substituted heterocycle with an electron-donating group attached to a heteroatom, specifically 3,5-*bis*(perfluoroalkyl)-4-amino-1,2,4-4*H*-triazole has been completed and the structure verified.

TABLE OF CONTENTS

ILLUSTRATIONS
(Infrared Absorption Spectra in Appendix)

Figure Page

I INTRODUCTION

The objective of this research is the synthesis and study of high molecular weight polymeric materials that are stable at high temperatures and are chemically inert. In this general area, the study of heterocycles containing nitrogen, oxygen or sulfur in the ring and having perfluoroalkyl groups as substituents are of particular interest. Methods of synthesizing polymers in which the backbone sturcture consists of heterocyclic groups connected by perfluoroalkylene chains are being sought.

During the present contract period, the study of synthesis of poly(perfluoroalkylene)-1,2,4-triazoles has been continued. It appears that a suitable monomer, the cyclic 1,2-diaza-3-imino-7-amino-4,4,5,5,6,6-hexafluoro-7-cycloheptene, has been formed by the reaction of hydrazine with perfluoroglutaronitrile. This monomer can be used to make the intermediate poly(N^2-imidoyl glutarhydrazidine, which can be deaminated to a polytriazole, or can be treated to produce the poly(perfluoroalkylene-1,2,4-triazole directly in one step.

Further study has been carried out on the perfluoroalkyl-substituted-1,3,4-oxadiazoles with a functional hydroxyl group attached to the ring in an effort to form an ether-type linkage between the rings. No suitable procedure has yet been found.

2,6-*bis*(Perfluoroethyl)-4-hydroxy-1,3,5-triazine has been synthesized and appears to be susceptible to hydrolysis. In this compound, as in the oxadiazoles, an hydroxy group attached to a ring carbon appears to tautomerize to the N-H, C=O form.

An example of a perfluoroalkyl-substituted heterocycle with an electron-donating group attached to one of the ring heteroatoms has been prepared by isomerizing 3,6-*bis* (perfluoroalkyl)-1,2-dihydro-1,2,4,5-tetrazine to 3,5-*bis* (perfluoroalkyl)-4-amino-1,2,4,4*H*-triazole. The chemical and physical properties of this compound are now being studied to determine its possible usefulness as a polymer component.

II DISCUSSION

A. POLY(PERFLUOROALKYLENE)-1,2,4-TRIAZOLES AND INTERMEDIATES

Previous reports have described the synthesis of model compounds in which there were one or two perfluoroalkyl-substituted-1,2,4-triazole rings. Thermal stability of this type of structure has been shown to be quite high. Work during the present contract period has been designed to produce polymers incorporating the 1,2,4,-triazole structure, as shown in Fig. 1.

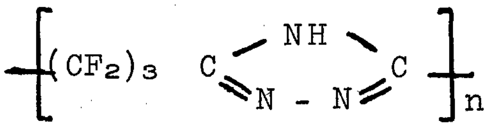


Fig. 1

1. Preparation of the cyclic monomer (I), 1,2-diaza-3-imino-7-amino-4,4,5,5,6,6-hexafluoro-7-cycloheptene

The previous technical report (ML-TDR-64-142) described the initial attempt to react perfluoroglutaronitrile with hydrazine in equimolar quantities and thus produce a monomer with cyano and hydrazidine groups on opposite ends. This type of monomer would, of course, avoid the difficulties of obtaining equimolar quantities of reactants when two unlike monomers, in this case perfluoroglutarodihydrazidine and perfluoroglutarodinitrile, were used for polymerization. It was found that one mole of perfluoroglutaronitrile reacted with one mole of hydrazine to produce a cyclic compound and a number of possible structures were listed. These structures are shown again in Fig. 2.

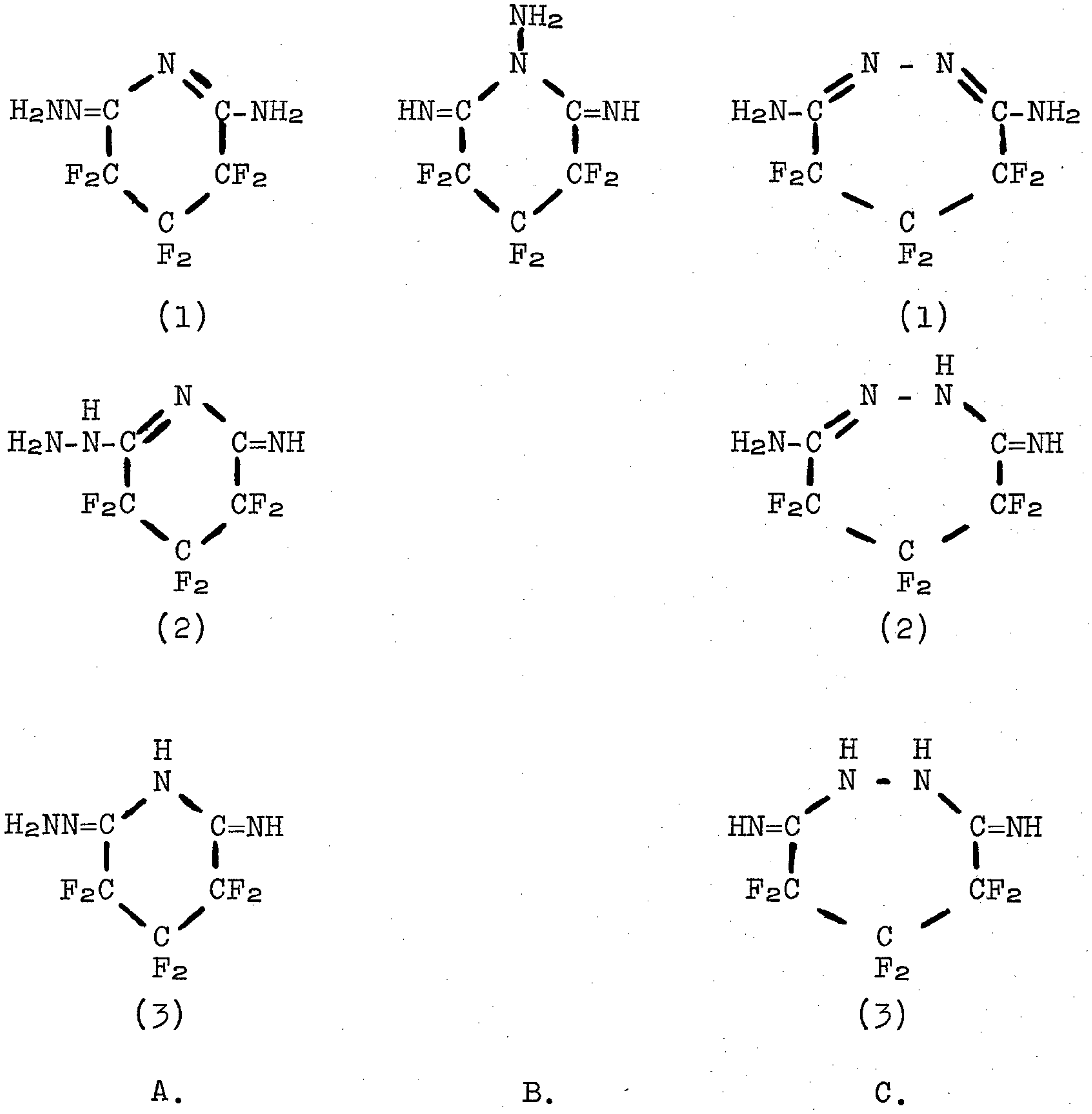


Fig. 2

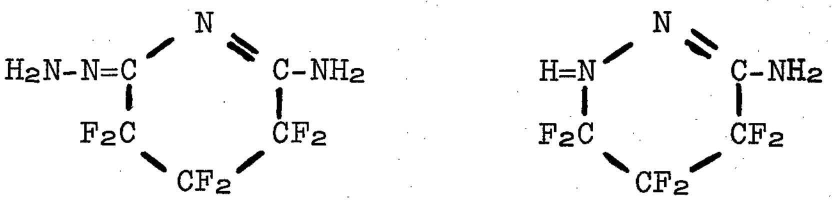
Six-membered ring structures are shown in columns A and B and seven-membered ring possibilities are shown in column C.

The nuclear magnetic resonance spectrum of the perfluoroglutaronitrile-hydrazine product (cyclic monomer I) showed that this compound contained three different types of fluorine atoms. Therefore, since the compound is cyclic, its structure is unsymmetrical with respect to the fluorine atoms. This information eliminated the structure shown in column B and also the structure C-1 and C-3, since each of these structures is symmetrical with respect to the fluorine atoms and has only two different types of fluorine.

This cyclic compound had an ultraviolet absorption maxima at 228mμ, which would seem to rule out the structure shown above with conjugated C=N bonds (A-1 and A-2); these structures contain, in addition to the conjugated system, auxochromic NH_2 groups and would probably absorb at a longer wavelength than 228mμ. This reasoning leaves structure A-3 and C-2; in order to choose between these, use was made of data obtained by further treatment of the original cyclic product I.

Heating the cyclic monomer I at 120° under reduced pressure produced a new compound which was collected as a sublimate. This new product melted at 76-77°, had an ultraviolet absorption maximum at 289mμ and did not have the same infrared spectrum as the original I. Chemical analysis showed that both compounds had identical chemical compositions. The nuclear magnetic resonance spectra showed that the sublimate had two different types of the same amount of hydrogen attached to nitrogen and that it contained three different types of fluorine atoms.

With the above information in mind, structure A-1 was assigned to this sublimate. The ultraviolet absorption maxima found for the sublimate, and attributed to structure A-1, appears reasonable if this structure is compared with that of perfluoroglutarimidine, Fig. 3, which absorbs at 254mμ. The considerable shift to lower frequencies for structure A-1 can be attributed to the fact that it has two auxochromic NH_2 groups while perfluoroglutarimidine has only one attached to the C=N conjugated system.



A-1
$\lambda_{max.}$-289mμ

Perfluoroglutarimidine
$\lambda_{max.}$-254mμ

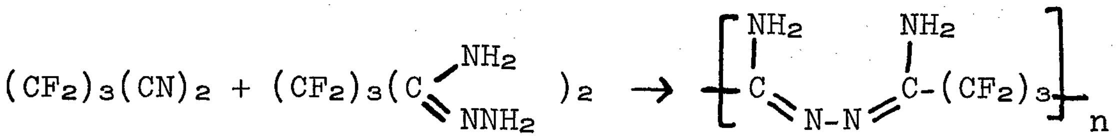
Fig. 3

Since the available infrared, ultraviolet, and nuclear magnetic resonance data could not distinguish between structures A-3 and C-2 for the original cyclic compound, consideration was given to which of these structures would be more likely to give the type of compound believed to be obtained as a sublimate under the conditions required to produce it. It would seem that conditions less drastic than heating at 120° might be required to go from structure A-3 to A-1, a simple tautomeric shift, than would be required to go from C-2 to A-1. It also appears more likely that the difference in melting points (cyclic monomer, 111°; sublimate, 77°) would result from two isomers rather than two tautomeric forms. The fact that the cyclic monomer could not be sublimed while the other product was obtained as a sublimate indicates that the sublimate is the more stable of the two structures. This might reasonably be expected in changing from a strained seven-membered ring to a six-membered ring. We are therefore assuming that structure C-2 is the correct one for the cyclic product from perfluoroglutaronitrile and hydrazine.

2. Poly(N^2-imidoyl perfluoroglutarhydrazidine)

a. From perfluoroglutaronitrile and perfluoroglutarhydrazidine

Poly(N^2-imidoyl perfluoroglutarhydrazidine) was first prepared by heating an acetonitrile solution of perfluoroglutaronitrile and perfluoroglutarhydrazidine in a sealed tube as shown in Equation 1.



$$(CF_2)_3(CN)_2 + (CF_2)_3\left(C\begin{matrix}\diagup NH_2\\ \diagdown\!\diagdown NNH_2\end{matrix}\right)_2 \rightarrow \left[\overset{\overset{\displaystyle NH_2}{|}}{C}\diagdown\!\diagdown N-N \diagup\!\diagup \overset{\overset{\displaystyle NH_2}{|}}{C}-(CF_2)_3\right]_n$$

Eq. 1

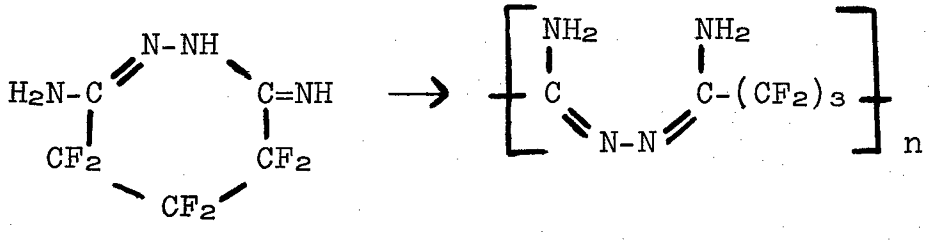
The sealed tube was used as a reaction vessel after numerous attempts to prepare the polymer from refluxing solutions of perfluoroglutaronitrile and perfluoroglutarhydrazidine in acetonitrile, carbon tetrachloride, diethyl ether, benzene, and tetrahydrofuran were unsuccessful. The use of the sealed tube as a reaction vessel limited the quantities of reactants that could be used in any given reaction to relatively small amounts, therby magnifying any small errors made in the measurement of specific quantities of reactants. These errors would result in inaccuracies in stoichiometry and may account for the low molecular weight polymeric products obtained.

The product from this reaction was an amber, brittle solid which had a melting range of 72-120° and a molecular weight of 1409.

The structure of poly(N^2-imidoyl perfluoroglutarhydrazidine) was confirmed by comparing its infrared and ultraviolet absorption spectra with the spectra of N,N'-<u>bis</u>(perfluoropropionimidoyl)perfluoroglutarhydrazidine. The infrared spectrum was obtained by casting a film from tetrahydrofuran directly on the sodium chloride plate. This spectrum showed bands characteristic of the bis-(imidoyl hydrazidine) model compound at 2.87 and 2.98μ for NH stretching, 6.05μ for C=N stretching and 6.35μ for NH deformation. The ultraviolet absorption spectra of this polymer had a maximum at 266mμ.

b. From the cyclic monomer (I)

Several unsuccessful attempts were made to open the ring of the cyclic monomer (I) to form the poly(N^2-imidoyl perfluoroglutarhydrazidine), as shown in Equation 2, by



I.

II

Eq. 2

refluxing solutions of I in tetrahydrofuran, diethyl ether, carbon tetrachloride, benzene, and acetonitrile. Heating I with a catalytic amount of triethylamine in acetonitrile in a sealed tube was also unsuccessful in producing a desired polymer structure.

The cyclic monomer (I) was successfully polymerized to structure II by heating in a sealed tube under an atmosphere of dry nitrogen at 45° and subsequently heating the tacky product at 180° under reduced pressure. The product from this procedure was a brown, brittle solid with a melting range of 180-330° and a molecular weight of 6200. This product was insoluble in benzene, carbon tetrachloride, chloroform and tetrachloroethylene and only slightly soluble in tetrahydrofuran, acetonitrile, p-dioxane and methyl ethyl ketone.

The structure of the polymer obtained from heating I was confirmed through a comparison of the spectra. The infrared spectrum had the characteristic bands at 2.83 and 2.93μ for NH stretching, 6.08μ for C=N stretching and at 6.34μ for NH deformation. The infrared spectrum also contained another band, at 3.02μ, which is probably due to associated NH stretching. The ultraviolet absorption spectrum had a maximum at 265mμ showing a small shift to higher frequencies from the maximum at 268mμ of the model compound of this structure. The shift of the ultraviolet maximum to shorter wave lengths appears to be related to the molecular weight of the polymer as shown in Table 1.

Table I

Physical Properties of Poly(N^2-imidoyl-perfluoroglutarhydrazidine

Method of Preparation	Melting Range	Molecular Weight[a]	$\lambda_{max.}$, mμ	log $\epsilon_{max.}$
Perfluoroglutaronitrile with perfluoroglutarhydrazidine	60-130°C.	1409	266	3.87
Cylic monomer heated with catalytic hydrogen chloride	65-120°C.	1136	266	4.00
Cyclic monomer heated with catalytic acetic acid in benzene	70-115°C.	1131	265	4.03
Cyclic monomer heated with catalytic hydrogen chloride in tetrahydrofuran	180-330°C.	4244	256	3.92
Cyclic monomer heated with no solvent	180-330°C.	6200	256	3.93
N,N'-bis(perfluoropropylimidoyl)-perfluoroglutarhydrazidine[b]	130-131°C.	656	268	4.24

a. Molecular weights obtained using a vapor pressure osmometer.
b. Model compound included for reference

The effect of acid catalyst on ring-opening of the cyclic monomer with subsequent polymerization into the poly(imidoyl hydrazidine) structure was also investigated. Catalytic agents used were methanol, phenol, acetic acid, and hydrogen chloride. The cyclic monomer (I) was heated at 70° for 72 hr. with catalytic amounts of each of these compounds, initially without a solvent present. The poly(imidoyl hydrazidine) structure was not obtained from heating the cyclic monomer with methanol under these conditions and only by increasing the temperature to 150° was the poly(imidoyl hydrazidine) structure obtained from the reaction of the cyclic monomer in the presence of phenol. Since these are the same conditions required to convert the cyclic monomer to the poly(imidoyl hydrazidine) structure without a catalyst, phenol is probably therefore not effective. The reactions with catalytic amounts of both hydrogen chloride and glacial acetic acid however, did result in the formation of the poly(imidoyl hydrazidine) structure although the molecular weights of these polymeric materials were low (Table 1).

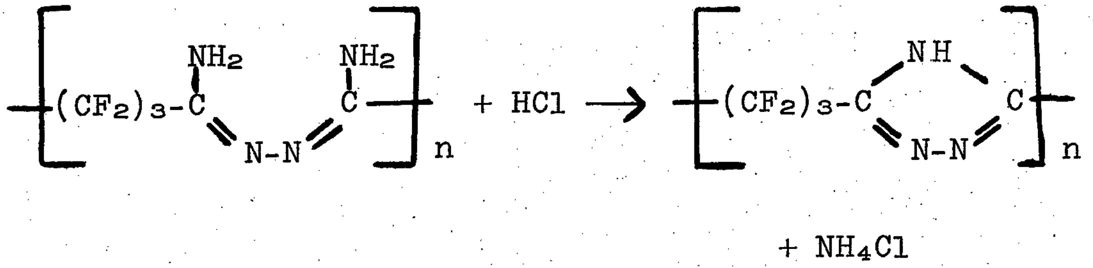
Heating the cyclic monomer with a catalytic amount of hydrogen chloride in benzene produced the poly-(imidoyl hydrazidine) structure but the low molecular weight product precipitated rapidly from the benzene solution. Since these polymers were soluble in tetrahydrofuran, a portion of the cyclic monomer was heated with a catalytic amount of hydrogen chloride in tetrahydrofuran at 90° for 160 hr. The product obtained under these conditions had the poly(imidoyl hydrazidine) structure, a melting point range of 180-330° and a molecular weight of 4244 (VPO). The cyclic monomer was also heated with a catalytic amount of glacial acetic acid in both benzene and tetrahydrofuran and, although the products obtained had the poly(imidoyl hydrazidine) structure, the molecular weights were in the range of 1200.

The results obtained from heating the cyclic monomer with acid catalysts showed that these catalysts were definitely effective in opening the ring of the monomer and aiding subsequent polymerization to the poly(imidoyl hydrazidine) structure. Hydrogen chloride was apparently the most effective catalyst when used with a solvent for the polymer formed.

The imidoyl hydrazidine structure of the polymers obtained from reactions employing catalysts was confirmed through a comparison of infrared and ultraviolet spectra. The infrared spectra of each of these materials has the characteristic bands of the bis-(imidoyl hydrazidine) model compound found at 2.88 and 2.98μ for NH stretching, 6.06μ for C=N stretching and 6.38μ for NH deformation. The ultraviolet absorption maxima range from 256mμ to 266mμ, depending upon the molecular weight of the polymer. The highest molecular weight materials had a maxima at 256mμ while the lower molecular weight materials had a maxima at 266mμ.

3. Poly(perfluoropropylene-1,2,4-triazoles)

Polymers having the poly triazole (III) structure were obtained by heating the poly(N^2-imidoyl perfluoroglutarhydrazidine) with an excess of hydrogen chloride in a sealed tube as shown in Equation 3.



Eq. 3

However, the molecular weights of these products were only about one-half as large as the molecular weights of the starting poly(N^2-imidoyl perfluoroglutarhydrazidines). This decrease in molecular weight indicated that the heating with excess hydrogen chloride resulted in some chain-breaking of the imidoyl hydrazidine polymer. The infrared spectra of the polytriazoles showed the absorption bands characteristic of the triazole model compounds with the exception that there was also absorption at 5.7 and 6.0μ .

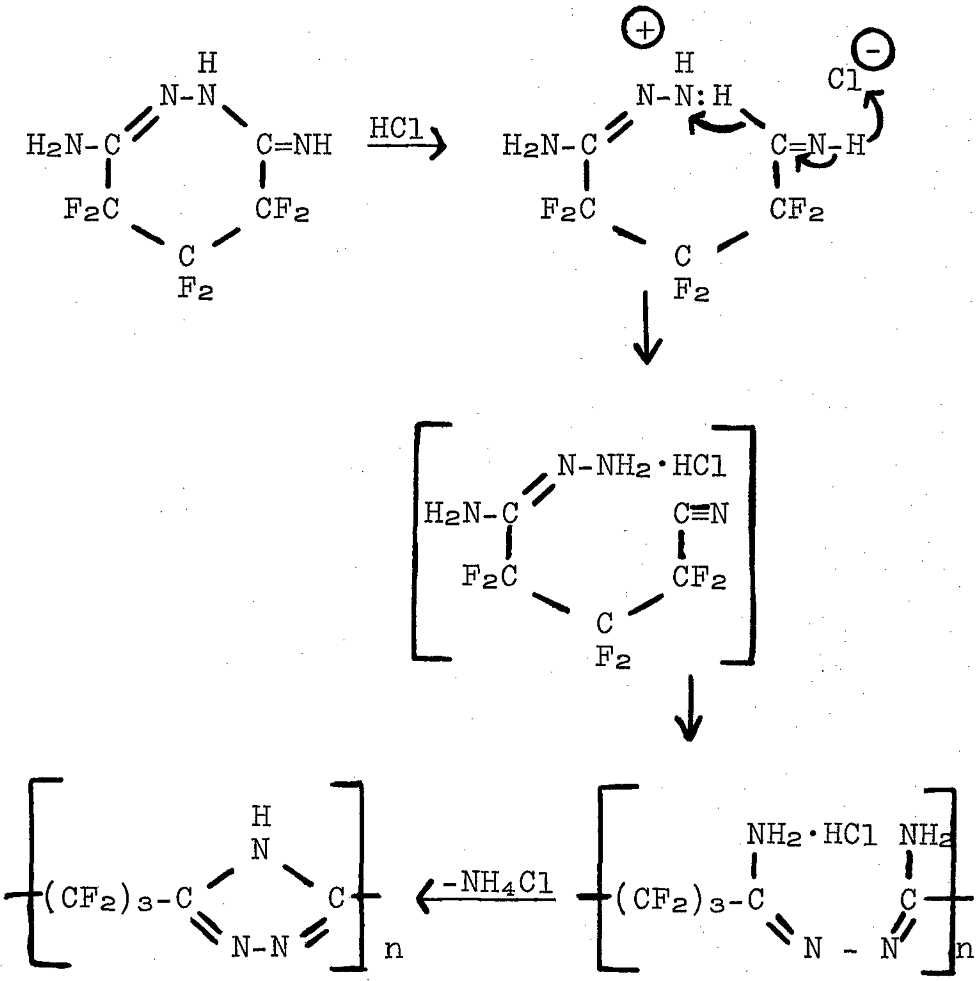
Since the synthesis of poly(perfluoropropylene-1,2,4-triazoles) from poly(imidoyl hydrazidines) requires a two-step procedure involving the reaction of a dihydrazidine with a dinitrile or opening the ring of the cyclic monomer, reaction procedures designed to proceed directly from the cyclic monomer to the polytriazole were investigated.

The cyclic monomer (I) was heated with glacial acetic acid and also with excess hydrogen chloride in sealed tubes and the desired poly(perfluoropropylene-1,2,4-triazole), III, was obtained from each reaction.

The product obtained from heating a cyclic monomer in glacial acetic acid melted at 290° and had a molecular weight of approximately 1200. This material did not show a maximum in the ultraviolet absorption spectra between 220mμ and 340mμ and its infrared spectrum exhibited the broad strong band at 3.2-3.8μ , the broad weak band at 5.5-6.0μ and the sharp strong band at 6.85 which are characteristic of the triazole model compounds.

The polymer obtained from heating the cyclic monomer with an excess of hydrogen chloride in a sealed tube was a tan solid which darkened without melting at 330°. This material was soluble in tetrahydrofuran and had a molecular weight of 3914. When this polytriazole was further heated to 220° its solubility in tetrahydrofuran decreased to the extent that only 10% of the material went into solution. The infrared spectrum of this polymer contained bands at 5.7 and 6.0μ in addition to the characteristic bands of the triazole model compound. However, after the polymer was dissolved in a 1% sodium hydroxide solution, precipitated by acidifying a solution with hydrochloric acid, and heated at 140°, the two bands at 5.7 and 6.0μ had been replaced by a single strong band at 5.4-5.8μ . Although this band was stronger than the comparable absorption found in the spectrum of the triazole model compounds, its intensity could probably be attributed to the presence of a greater amount of intermolecular association between the imino hydrogen atoms of the triazole ring and an unsaturated nitrogen atom of an adjacent molecule. The formation of such bonds along adjacent polymer chains might possibly enhance alignment of the chain in such a way that there would be a greater amount of intermolecular association.

A possible mechanism for the formation of polytriazole from heating the cyclic monomer with excess hydrogen chloride involves protonation of the cyclic monomer and subsequent ring opening as shown in Equation 4.



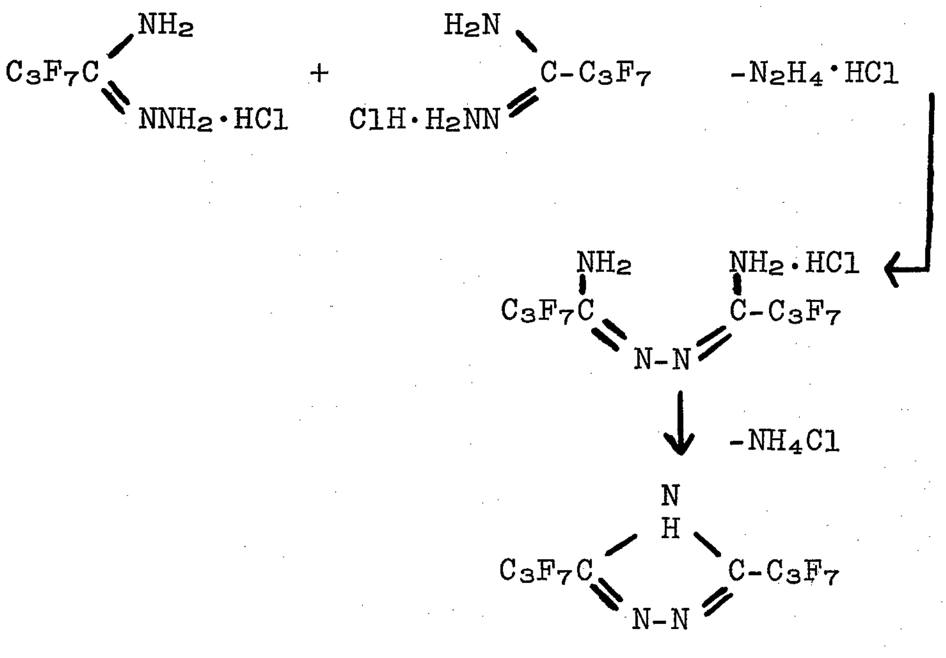
Eq. 4

Such a reaction would give an intermediate containing the cyano and hydrazidine hydrochloride structures as functional end groups, which upon heating might polymerize through addition to give the poly(imidoyl hydrazidine) hydrochloride. Ring closure with loss of ammonium chloride would then result in the polytriazole structure.

If this type of mechanism is correct, one step in the series of reactions would require the addition of a hydrazidine hydrochloride to a cyano group, or at least the addition of a hydrazidine group to a cyano group in the presence of hydrogen chloride.

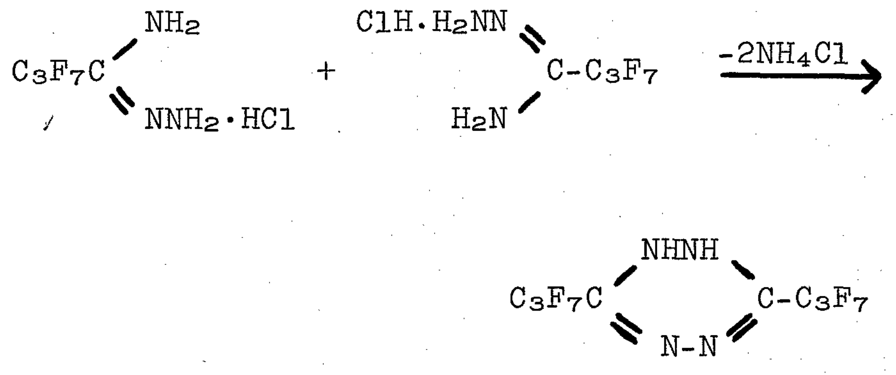
In order to find out whether such an addition can occur under these conditions, a model reaction was carried out between perfluorobutyrhydrazidine hydrochloride and perfluorobutyronitrile. After heating these reactants in a sealed tube the principal product was identified as 3,5-bis(perfluoropropyl)-1,2-dihydro-1,2,4,5-tetrazine with a minor amount of 3,5-bis(perfluoropropyl)-1,2,4-triazole.

It is possible, of course, that both products could have resulted from reactions of perfluorobutyrhydrazidine hydrochloride alone. If one mole of hydrazine hydrochloride were split out from two moles of the starting material, the imidoyl hydrazidine hydrochloride would be formed and could subsequently lose ammonium chloride to form the triazole as shown in Equation 5.



Eq. 5

If two moles of ammonium chloride were split out from two moles of the starting material, then the dihydrotetrazine could be formed as shown in Equation 6.



Eq. 6

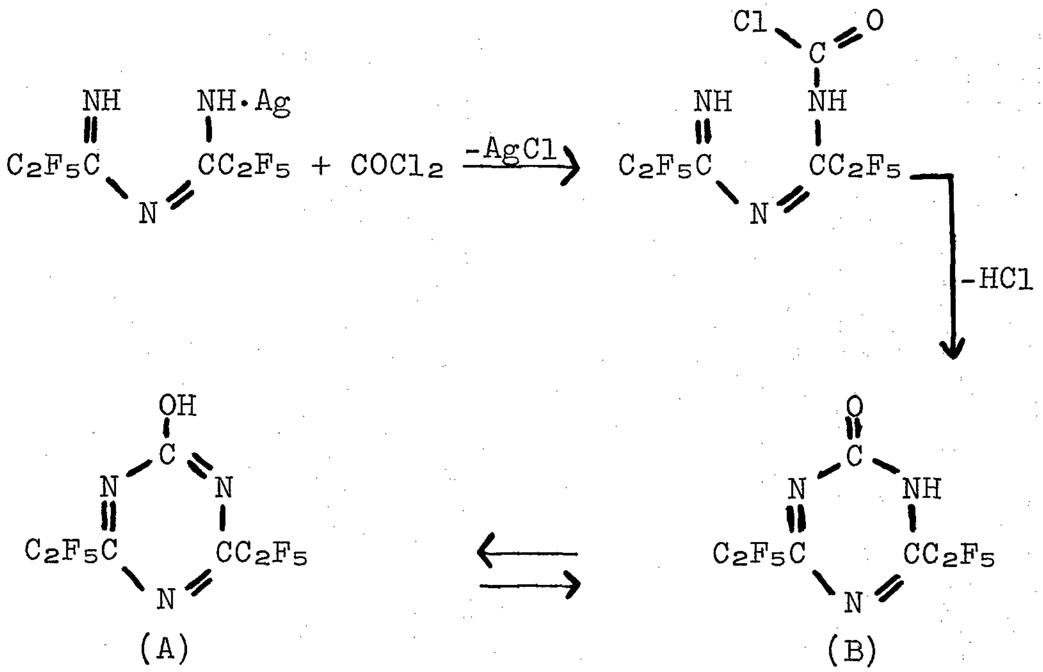
Perfluorobutyrhydrazidine hydrochloride was therefore heated under similar conditions with no perfluorobutyronitrile present; a 50% yield of the dihydrotetrazine was obtained.

The reaction between perfluorobutyronitrile and perfluorobutyrhydrazidine hydrochloride was repeated in the presence of an equimolar amount of hydrogen chloride in order to more closely duplicate the conditions of reaction between the cyclic monomer and an excess of hydrogen chloride. Under these conditions 3,5-bis(perfluoropropyl)-1,2,4-triazole was obtained in a greater yield than could have been obtained from the perfluorobutyrhydrazidine alone, indicating that the nitrile did participate in the reaction.

Another possible route to the polytriazole structure is the acylation of a dihydrazidine with a diacyl chloride. In this reaction, however, there is a possibility that hydrogen chloride produced in the acylation reaction would form an unreactive hydrochloride salt of the remaining hydrazidine groups. To determine whether the hydrazidine hydrochloride could be acylated with an acyl chloride, a reaction between perfluorobutyrhydrazidine hydrochloride and perfluoropropionyl chloride was carried out in a sealed tube. Under the conditions used, only a 22% yield of the perfluoropropyl-perfluoroethyl-substituted triazole was obtained, indicating at least that the conditions actually used were not suitable for polymer formation. Further investigation of this type of procedure, however, is planned. It is known that the acylated hydrazidine type of structure which would be produced can be dehydrated to form the 1,2,4-triazole ring.

B. 2,6-*bis*(Perfluoroethyl)-4-hydroxy-1,3,5-triazine

Since the *tris*(perfluoroalkyl) symmetrical triazines, though stable at high temperatures, are subject to hydrolytic attack, it would be interesting to learn whether alteration of one of the substituent groups would lessen this susceptibility to attack by nucleophilic reagents without decreasing the thermal stability. For this reason synthesis of the 4-hydroxy-perfluoroalkyl-substituted triazine was carried out as shown in Equation 7.



Eq. 7

In this reaction the silver salt of N'(perfluoropropionimidoyl)perfluoropropionamidine was treated with phosgene; silver chloride was precipitated rapidly on formation of the acylated product. Ring closure occurred by the elimination of hydrogen chloride from the acylated compound to give the triazine, with tautomeric structures A and B.

It should be noted that elimination of hydrogen chloride on ring closure makes possible the formation of the hydrochloride of the acylated imidoyl amidine, which has previously been described as a stable product. We might therefore expect only a 50% maximum yield of the 2,6-perfluoroalkyl-4-hydroxy-1,3,5-triazine.

This reaction was carried out by treating a diethyl ether solution of the freshly prepared silver salt of

N'(perfluoropropionimidoyl)perfluoropropionamidine with an excess of phosgene. The reaction was carried out in a flask equipped with a dry-ice-cooled reflux condenser and the excess phosgene was allowed to reflux for 2 hr. before being distilled from the reaction mixture. The reactants were originally at dry ice temperature and the first sign of formation of a white salt occurred as they were warmed to -39°.

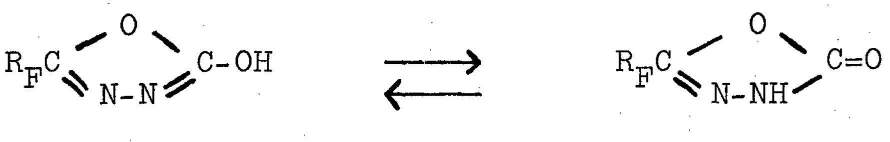
After removal of the excess phosgene and ether, the products remaining included the expected 50 yield of the 2,6-bis(perfluoroethyl)-4-hydroxy-1,3,5-triazine, a quantitative yield of silver chloride and another product, presumably the hydrochloride of the acylated imidoyl amidine.

Purification of the hydroxy triazine by chromatographic separation over neutral alumina was not successful; distillation at atmospheric pressure resulted in decomposition of the compound. Fractionation of the hydroxy triazine could be carried out at pressures less than 1 mm. Hg and the product was collected at 77°.

2,6-bis(Perfluoroethyl)-4-hydroxy-1,3,5-triazine was a clear viscous liquid soluble in diethyl ether, acetone, methyl alcohol, and benzene. It was insoluble in carbon tetrachloride and petroleum ether. The compound was soluble in dioxane but did not exhibit the typical complex formation of the tris(perfluoroalkyl)-sym.-triazines. The infrared spectra of this compound indicated the presence of a carbonyl group (C=O stretching, 5.9μ) and it apparently has, predominantly, the structure shown at B in Equation 1. This product hydrolyzed quite readily in water at room temperature.

C. 2-PERFLUOROALKYL-5-HYDROXY-1,3,4-OXADIAZOLES

We have previously described briefly (WADC Technical Report 59-272 Pt.5) the synthesis of 2-perfluoroalkyl-5-hydroxy-1,3,4-oxadiazole (A, Fig. 4) and a difunctional compound of this same type and mentioned the possibility of polymer formation by using these monomers to form a polymeric chain with ether linkages between the oxadiazole rings.



A. Fig. 4 B.

During the present a limited amount of additional study of this type of structure has been carried out.

The original preparation of the hydroxy oxadiazoles described the formation of a silver salt (or complex) as a part of the purification procedure. It has now been found that if the crude hydroxy oxadiazole, in tetrahydrofuran solution, is concentrated to a viscous oil under reduced pressure and then redissolved in benzene or toluene, crystallization of the pure compound is possible on cooling. The C_3F_7- and C_2F_5-substituted hydroxy oxadiazoles were purified in this manner.

Infrared analysis in carbon tetrachloride solution of the products obtained from these reactions showed absorption at 2.90μ (OH stretching), 3.05μ (NH stretching), a doublet at 5.40 and 5.53μ (C=O stretching) and a very weak band at 6.15μ (probably C=N). The C=O absorption at the relatively low wave length is reportedly characteristic of lactone C=O in a five-membered ring. These bands and the OH and NH absorption seem to indicate that the predominant structure is that shown at B in Fig. 4, or 2-perfluoroalkyl-1,3,4-4H-oxadiazoline-5-one.

Several approaches have been considered for the conversion of the hydroxy oxadiazoles (or oxadiazoline-ones) to the ether structure shown in Fig. 5, since the previously described 1,3-bis(5-hydroxy-1,3,4-oxadiazolyl)perfluoropropane could be used as a monomer to produce this type of polymer structure if a suitable reaction of the hydroxy group could be found. The initial attempts at dehydration of the hydroxy oxadiazole by phosphorus pentoxide, even at high temperature, were not successful.

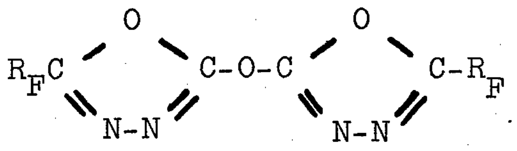
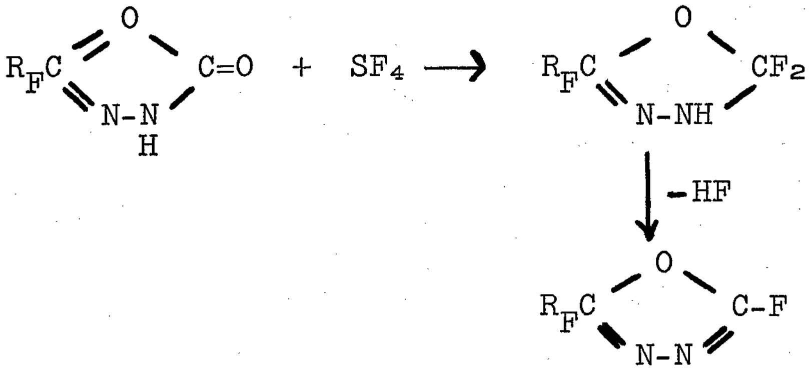


Fig. 5

Tosylates of both the C_2F_5- and C_3F_7-substituted hydroxy oxadiazoles were prepared in both acidic and basic media. The infrared analysis, however, indicated that addition of the tosyl group occurred at the nitrogen in the 4-position rather than at the oxygen attached to the 5-carbon. The infrared spectra of the tosylate also contains a doublet at 5.30 and 5.44μ , indicative of C=O in a small ring lactone group.

The perfluoroalkyl-substituted 5-hydroxy oxadiazoles can be converted to the mercury salts in good yields. Several attempts were made, therefore, to place a halogen (chlorine or fluorine) on the 5-carbon atom so that a reaction could be carried out with the metallic salts of the hydroxy oxadiazoles to form the ether linkage.

Since these compounds appeared to exist largely in the carbonyl form, several attempts were made as shown in Equation 8 to convert this carbonyl group with sulfur tetrafluoride to a difluoro group, which would almost certainly lose

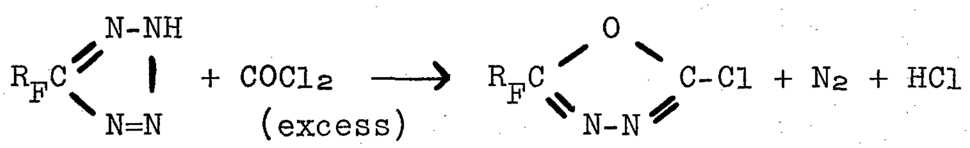


Eq. 8

hydrogen fluoride to produce the 5-fluoro compound as shown. The conditions of reaction, however, were apparently too vigorous and complete decomposition occurred in each case.

Attempts to convert the hydroxy oxadiazole to the corresponding chloro compound were made using thionyl chloride, phosphorus trichloride, and phosphorus pentachloride. Under a variety of conditions all of these attempted preparations were unsuccessful, however, and either starting material was recovered or extensive decomposition occurred.

A further attempt was made to produce a 5-chloroperfluoroalkyl-substituted oxadiazole by the reaction of 5-perfluoroalkyl tetrazole with an excess of phosgene as shown in Equation 9. Although reaction occurs readily the



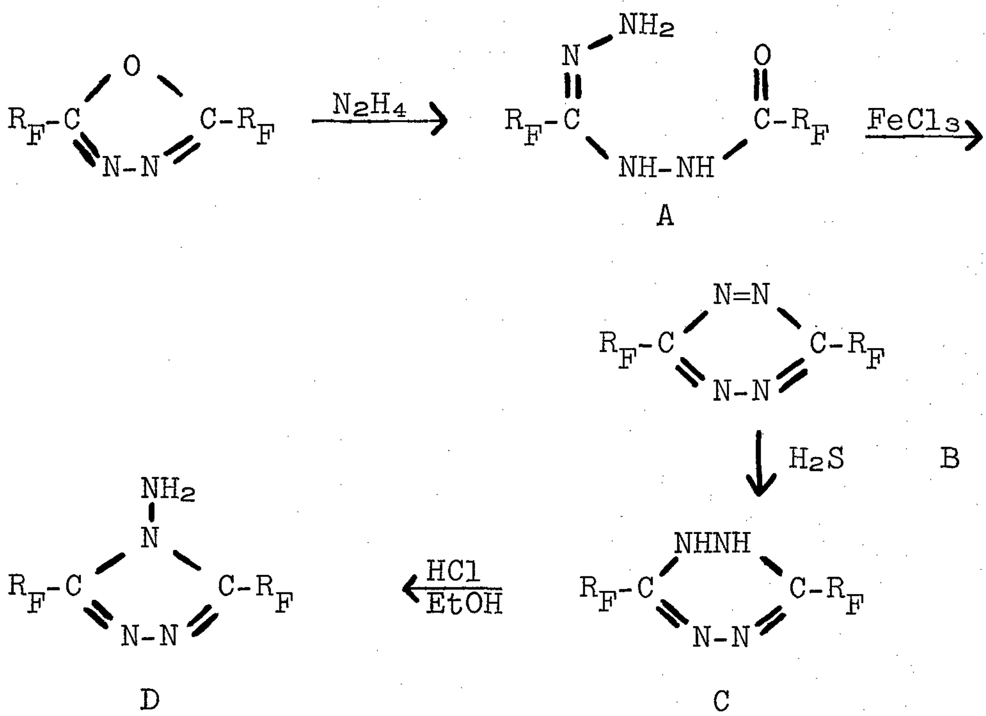
Eq. 9

desired chloro compound has not yet been isolated.

D. 3,5-BIS(PERFLUOROALKYL)-4-AMINO-1,2,4-TRIAZOLES

A 3,5-bis(perfluoroalkyl)-4-amino-1,2,4-triazole furnishes an example of an electron releasing group attached to a perfluoroalkyl-substituted heterocycle (in this case to a hetero atom rather than the carbon atom); this type of compound should be studied to determine the effect of such a group on the thermal stability and chemical reactivity of perfluoroalkyl-substituted heterocycles in general. Although we have previously reported (J. Am. Chem. Soc., 82, 4700 (1960)) the synthesis of a N-amino triazole from the reaction of perfluoroacetonitrile with hydrazine, recent work in our laboratory on another project indicates that the reported compound in this type of reaction does not have the cyclic structure.

Also in other work in our laboratory, not yet described in the literature, we synthesized the perfluoroalkyl-substituted 1,2-dihydro-1,2,4,5-tetrazines. During the present period, the isomerization of the 1,2-dihydro tetrazine to an N-amino triazole has been successfully carried out by refluxing the dihydro compound in an acidic ethyl alcohol solution. Since the preliminary work which produced the dihydro tetrazine structure is not yet available in the literature the complete synthesis from the 2,5-bis(perfluoroalkyl)-1,3,4-oxadiazole is shown in Equation 10.



Eq. 10

In this synthesis an oxadiazole ring is first opened by treatment with hydrazine to give the N^2-(α-hydrazono perfluoroalkyl)perfluoroalkyl hydrazide, A, which is then treated with anhydrous ferric chloride and undergoes a dehydration and oxidation reaction to give the 3,6-bis(perfluoroalkyl) -1,2,4,5-tetrazine, B. The perfluoroalkyl-substituted-1,2,4,5-tetrazine can be reduced to the 1,2-dihydro analog by treatment with hydrogen sulfide. The reduced compound C was then isomerized by refluxing in a mixture of hydrochloric acid and ethyl alcohol to give the 3,5-bis(perfluoroalkyl)-4-amino-1,2,4-triazole, D. The structure of the N-amino triazole was established by infrared spectra and a study of its reactions. Compound D could be acylated at the amino group; further proof was obtained by diazotization of the amino group and subsequent elimination to replace the NH_2 group with hydrogen. This reaction, unexpectedly, did not require the assistance of any reducing agent in the diazotization procedure.

Properties of the N-amino triazole have not yet been studied in detail. Thermal stability in resistance to hydrolysis will be of primary interest.

Although the above sequence of reactions to produce N-amino triazole are rather complicated for consideration for formation of a polymer containing this structure, work during the present period has also shown that the dihydrotetrazine ring can be formed from the hydrazidine hydrochloride. There is therefore a good possibility that this ring structure can be incorporated into a polymer by using a reaction of a difunctional hydrazidine hydrochloride.

E. PERFLUOROALKYL TRIAZINES

In repetition of a preparation reported by Knutson (Quarterly Progress Report No. 10, Contract AF33(616)7963) to give the bis(imidoyl amidine) structure shown in Fig. 6,

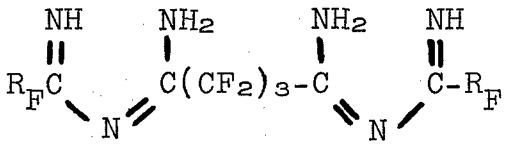


Fig. 6

a solid product was obtained, which, after recrystallization from benzene, melted at 83-97°. This product was soluble in diethyl ether, acetone, methyl alcohol and only very slightly soluble in carbon tetrachloride and insoluble in water. There was no chelate formation evident when the product was treated with cupric acetate. The ultraviolet spectrum of the product showed no absorption at wave lengths longer than 220mμ .

The lack of the typical imidoylamidine ultraviolet absorption spectrum and the resistance to chelate formation with cupric ion of this compound indicated that the product actually obtained in this reaction did not contain the imidoylamidine grouping.

To obtain more information on the character of the products from the reaction of a perfluoroalkyl dinitrile with a perfluoroalkylamidine, some additional preparations have been carried out using stoichiometric amounts of reactants rather than an excess of the perfluoroalkylamidine.

The first experiments were carried out using perfluoroadiponitrile with perfluoroalkylamidines, with the thought that the perfluoroadipo-compound would have less tendency to rearrange or cyclize and would favor the open bis-imidoylamidine structure.

A solution of 2.04×10^{-2} moles of perfluoroadiponitrile in 25 ml. of benzene was added to a stirred solution of 4.7×10^{-2} moles of perfluorobutyramidine in 100 ml. of benzene held at a temperature of 45°. Upon addition of the dinitrile, the temperature rose to 55° and was maintained between 55-60° for 1 hr. The reaction mixture was then heated at 74-80° for 1/2 hr., then allowed to cool to room temperature.

The excess solvent benzene was removed under reduced pressure to leave 8.70 g. of slightly viscous liquid having the characteristic odor of the imidoylamidine. This product was found to be soluble in methyl alcohol, carbon tetrachloride and quite soluble in diethyl ether. It was insoluble in water. When cupric ion was added, strong chelate formation was noted, similar to that occurring in the mono-imidoylamidines.

The product obtained from this reaction was allowed to stand under reduced pressure and after three days it was noted that a white solid had formed. This solid product was not soluble in benzene and was separated. The solid product was insoluble in diethyl ether and water and showed no chelate formation in the presence of cupric ion. It melted with the evolution of a gas at 138-140 C.

This reaction was repeated and again yielded a viscous liquid product. After standing for one month the product had completely solidified with no apparent weight loss.

Further repetition of this type of preparation using perfluoroadiponitrile and perfluoropropionamidine gave a product of the same type as described above; it underwent a comparable rearrangement to a non-chelate-forming structure.

These reactions indicate therefore that the open bis-imidoylamidine structure is obtained initially but that there is a strong tendency toward reorganization, even in the compound from perfluoroadiponitrile, at room temperature if allowed to stand over an extended period.

The same apparatus and preparative procedure were used to carry out a reaction between perfluorobutyramidine (7.2×10^{-2} moles in 100 ml. of benzene) and perfluoroglutaronitrile (3.6×10^{-2} moles in 20 ml. of benzene) at 50°. During the 45 min. after addition was complete, the temperature of the reaction mixture rose to 66°. The mixture was then heated for 20 min. until the temperature had reached 81°. This mixture was then set aside overnight and 19.65 g. of white solid was formed which melted at 99-103°. This product was soluble in diethyl ether, acetone and methyl alcohol. It was insoluble in water and carbon tetrachloride and formed no chelate in the presence of cupric ion. This procedure duplicates, in the product obtained, the previous reaction run using an excess of perfluorobutyramidine with perfluoroglutaronitrile.

Further study of the reaction of perfluoroglutaronitrile (1.73×10^{-2} moles) and perfluorobutyramidine (3.47×10^{-2} moles) was carried out using 100 ml. of carbon tetrachloride as a solvent. The addition of the perfluoroglutaronitrile solution to the perfluorobutyramidine solution was made at room temperature and shortly after addition was complete (10-15 min.) a 10 ml. sample of the resulting solution was removed and treated with cupric ion. Strong chelate formation was noted.

Stirring of the original mixture was continued at room temperature for 30-40 min. and solids began to appear and precipitate from the solution. The solvent carbon tetrachloride was removed under reduced pressure; remaining in the flask was 9.10 g. of white solid which, after recrystallization from benzene, melted at 99-104°. This had the same characteristics as the product obtained in the higher temperature reaction described above using benzene as the solvent and the infrared spectra were identical. This product did not react with cupric ion.

From the reaction of perfluoroglutaronitrile with perfluorobutyramidine at the lower temperature, it is evident that the open bis-imidoylamidine structure was obtained initially and it is also apparent that the reorganization or cyclization to a different structure is much more rapid than in the preparation using perfluoroadiponitrile.

III EXPERIMENTAL

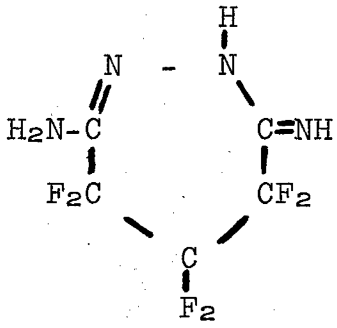
A. Poly(perfluoroalkylene)-1,2,4-triazoles and intermediates

1. Preparation of the cyclic monomer (I), 1,2-diaza-3-imino-4,4,5,5,6,6-hexafluoro-7-cycloheptene

Perfluoroglutaronitrile, 6.45 g., (0.032 mole), and 20 ml. of isopropyl alcohol were placed in a 100 ml., two-neck, round-bottom flask which was fitted with a dry-ice cooled condenser and dropping funnel containing hydrazine, 1.024 g., (0.032 mole), and 20 ml. of isopropyl alcohol. After the contents of the flask were cooled to -20°, the hydrazine solution was added slowly. After the addition was completed, the isopropyl alcohol was removed under reduced pressure and the remaining pale yellow solid was recrystallized by dissolving it in 20 ml. of diethyl ether, adding 25 ml. of petroleum ether and cooling the solution in an ice bath. 1,2-Diaza-3-imino-7-amino-4,4,5,5,6,6-hexafluoro-7-cycloheptene, 3.74 g., 50% yield, m.p. 113-114°, was obtained.

Anal. Calcd. for $C_5H_4F_6N_4$: C, 25.64; N, 23.93; F, 48.71; H, 1.72; Found: C, 25.69; N, 24.13; F, 48.39; H, 1.94.

This compound resulted from a reaction of 1:1 molar quantities of perfluoroglutaronitrile and hydrazine and has been assigned the structure



The assignment of this structure is based on the information obtained from infrared, ultraviolet, and nuclear magnetic resonance spectra. In the following preparations it will be referred to as cyclic monomer I.

2. Poly(N^2-imidoyl perfluoroglutarhydrazidine)

a. From perfluoroglutaronitrile and perfluoroglutarhydrazidine

Perfluoroglutarhydrazidine, 3.1335 g. (0.01178 mole), and 15 ml. of methyl alcohol were placed in a heavy-wall glass tube and the air removed by pumping. Perfluoroglutaronitrile, 2.3796 g. (0.01178 mole), was admitted to the reaction tube which was then sealed and allowed to stand at room temperature for 12 hr. and subsequently heated at 60° for 14 hr. The tube was opened, methyl alcohol removed under reduced pressure, and the solid product purified by dissolving it in dioxane and precipitating the pale yellow solid with water. From this reaction 0.46 g. of a polymer having the imidoyl-hydrazidine structure was obtained; melting range, 60-110°; molecular weight (VPO) 1420.

b. Ring-opening polymerization of cyclic monomer (I)

1. Effect of catalysts

a. Phenol in diethyl ether

Cyclic monomer I, 1.5 g., phenol, 0.03 g. , and 7 ml. of diethyl ether were sealed in a heavy-wall glass tube which was pumped free of air. The tube was heated at 60° for 72 hr. then cooled to room temperature and opened. Removal of the ether left a dark brown solid whose infrared spectra did not correspond to that of the previously prepared poly(N^2-imidoyl perfluoroalkyl hydrazidines).

b. Phenol

The cyclic monomer I, 1.2 g., and 0.03 g. of phenol were sealed in a heavy-wall glass tube which was then pumped free of air. The tube was heated at 70° for 72 hr. after which time a small portion of the dark brown solid product was removed and examined by infrared spectroscopy. This spectra did not resemble that of the poly(imidoyl hydrazidine). The remaining material was heated under reduced pressure at 140° for 12 hr. and 180° for 10 hr. The resulting material gave the same infrared spectra obtained previously from a sample of I heated under the same conditions without phenol; m.p. range of this product, 80-130°; molecular weight (VPO) 3162.

c. Hydrogen chloride

The cyclic monomer I, 2.0 g. (8.5×10^{-3} mole), and 1.7×10^{-4} mole of hydrogen chloride were sealed in a heavy-wall glass tube; the tube was pumped free of air and heated at 70° for 72 hr. The resulting brown solid product was dissolved in dioxane and reprecipitated with water three times to give 1.0 g. of brown polymer melting at 65-120°. The infrared spectra of this product showed the absorption maxima typical of the imidoyl-hydrazidine structure; molecular weight (VPO) 1136.

d. Hydrogen chloride in benzene

The cyclic monomer I, 1.5 g., and 1.3×10^{-4} mole of hydrogen chloride with 10 ml. of benzene were sealed in a heavy-wall glass tube, pumped free of air, and the tube was heated at 60° for 56 hr. During this heating period an amber-colored solid precipitated from the solution. The benzene was removed under reduced pressure and the remaining brown solid product dissolved in dioxane and precipitated with water three times. Total yield was 0.56 g. of amber polymer, melting range 55-170°, with the typical infrared absorption spectra of the imidoyl hydrazidine structure.

e. Hydrogen chloride in tetrahydrofuran

The cyclic monomer I, 2.0 g. (8.5×10^{-3} mole) and 1.7×10^{-4} mole of hydrogen chloride in 20 ml. of tetrahydrofuran were sealed in a glass tube. The tube was pumped free of air and heated at 100° for 144 hr. After cooling to room temperature, the tube was opened and the solution added to 50 ml. of petroleum ether. An amber solid product 1.8 g. precipitated, whose infrared spectra was the same as the spectra previously obtained from a compound known to have the imidoyl-hydrazidine structure; melting range of this polymer was 180-330°; molecular weight (VPO) 4244.

f. Acetic acid in benzene

The cyclic monomer I, 1.9 g. (8.1×10^{-3} mole), and 1.7×10^{-4} mole of glacial acetic acid with 7 ml. of benzene were sealed in a heavy-wall glass tube, pumped free of air and heated at 70° for 72 hr. During this heating period an amber solid precipitated from the solution. The tube was opened and benzene removed under reduced pressure; the remaining solid was dissolved in hot dioxane and poured into cold water to precipitate 0.15 g. of an amber, solid product melting at 70-115°. Infrared absorption spectra identified the imidoyl-hydrazidine structure; molecular weight (VPO) 1131.

g. Acetic acid in tetrahydrofuran

The cyclic monomer I, 1.1 g. (4.7×10^{-3} mole), 9.4×10^{-5} moles of glacial acetic acid and 7 ml. of tetrahydrofuran were placed in a heavy-wall glass tube which was then pumped free of air, sealed and heated at 60° for 7 days. The tetrahydrofuran solution was added to cold water to precipitate 0.5 g. of dark brown, tacky, solid material having the imidoyl-hydrazidine infrared spectra.

h. Methyl alcohol

The cyclic monomer I, 1.5 g., and 6 drops of methyl alcohol were placed in a heavy-wall glass tube. After the air was removed from the tube by pumping, dry nitrogen to a pressure of 600 mm. Hg. was admitted to the tube. The tube was then sealed and heated at 80° for 72 hr. Product resulting from this reaction was a black tar which could not be purified by dissolving in dioxane and precipitating with water. The infrared absorption spectra obtained did not appear to indicate the imidoyl-hydrazidine structure.

2. Effect of solvents

a. Methyl alcohol

The cyclic monomer I, 3.85 g., was placed in a heavy-wall glass tube with 20 ml. of methyl alcohol. After the air was removed by pumping while the tube was cooled in liquid nitrogen, the tube was sealed and heated at 75° for 72 hr. Recovered from the tube was a black tar which could not be purified and which did not have the imidoyl-hydrazidine structure.

b. Acetic acid

The cyclic monomer I, 1.5 g., and 20 ml. of glacial acetic acid were placed in a 100 ml. round-bottom flask fitted with a water-cooled condenser. The resulting solution was refluxed for 18 hr. After this period most of the acetic acid was removed by distillation and the remaining acetic acid solution poured into cold water to precipitate 1.3 g. of amber, solid polymer. This material was redissolved in dioxane and reprecipitated by addition to water to give a product melting at 65-130°. The infrared spectra of this material had an appearance characteristic of a salt. The product was further heated under reduced pressure at 150° for 5 hr.; there was no change in the infrared spectra but the melting range had changed to 290-330°.

3. Heating (I) with no catalyst or solvent

Cyclic monomer I, 2.95 g., (1.3×10^{-2} mole), was placed in a heavy-wall, Pyrex glass tube of approximately 30 ml. capacity and, after the air was removed from the tube by pumping, dry nitrogen under one atmosphere of pressure was introduced into the tube. The tube was sealed and heated at 45° for 64 hr. The tube was cooled in liquid nitrogen, opened, and the amber solid product was placed in a water-cooled sublimation apparatus and further heated under reduced pressure at 180° for 8 hr. A white solid, 0.5 g., was collected on the cold finger and the polymeric residue darkened. After being precipitated twice from dioxane-water, the polymeric material melted between 180-330°C.

3. Poly(perfluoropropylene-1,2,4-triazole)

a. From the hydrochloride of (I)

The cyclic monomer I, 1.06 g. (4.3×10^{-3} mole), dissolved in 15 ml. of diethyl ether, was placed in a heavy-wall glass tube. Hydrogen chloride was bubbled into the solution until there was no further formation of the white solid. Excess hydrogen chloride and ether were removed from the tube under reduced pressure and the tube was then sealed and heated at 100° for 10 hr. and at 120° for 12 hr. The reaction tube was opened and the amber-colored solid product was further heated under reduced pressure at 140° for 10 hr. The resulting brown product was dissolved in dioxane and precipitated with water three times to give 0.17 g. of amber polymer. This material became dark at 330° with partial softening and has a molecular weight (VPO) of 1955. The infrared spectra showed that the material had the triazole structure but there were also absorption peaks at 6.0 and 5.7 that represent functional groups other than the triazole ring.

b. From (I) with excess hydrogen chloride

Cyclic monomer I, 2.0 g., (8.5×10^{-3} mole), was placed in a heavy-wall, Pyrex glass tube of approximately 150 ml. capacity. After the air was removed from the tube by pumping, hydrogen chloride, 1.53 g., (4.25×10^{-2} mole), was condensed into the tube. The tube was sealed and heated in the following manner: 24 hr. at 90°, 24 hr. at 130°, and 24 hr. at 160°. The tube was cooled in liquid nitrogen, opened, and the tan solid product was placed in a water-cooled sublimation apparatus and heated at 210° for 8 hr. The tan solid residue was then dissolved in 1% sodium hydroxide and precipitated by neutralizing the basic solution with 1 N hydrochloride acid. A tan solid, 1.8 g., was obtained which darkened at 330° without melting.

c. From (I) with excess acetic acid

Cyclic monomer I, 5.0 g., (2.1×10^{-2} mole), and 30 ml. of glacial acetic acid were placed in a heavy-wall, Pyrex glass tube of approximately 80 ml. capacity. The tube was pumped free of air, sealed, and heated in the following manner: 125° for 40 hr., 150° for 48 hr., and 190° for 24 hr. During the 24 hr. at 190° a solid precipitated from the solution. The tube was cooled in liquid nitrogen, opened, and 1.1 g. of cream-colored solid was obtained by filtering the acetic acid solution. The filtrate was added to cold water and an additional 2.4 g. of cream-colored solid was obtained. Both solids melted at 290° and had identical infrared spectra with absorption typical of the triazole ring.

d. From poly(N^2-imidoyl perfluoroglutarhydrazidine and excess hydrogen chloride

Poly(N^2-imidoyl perfluoroglutarhydrazidine), 0.65 g., prepared from cyclic monomer I as described above, was placed in a heavy-wall, Pyrex glass tube of approximately 50 ml. capacity. After the air was removed from the tube by pumping, hydrogen chloride, 5.0 x 10^{-1} g., (1.4 x 10^{-2} mole), was condensed into the tube. The tube was sealed and heated in the following manner: 10 hr. at 90°, 24 hr. at 140° and 10 hr. at 150°. The tube was cooled in liquid nitrogen, opened, and the brown, solid product was dissolved in tetrahydrofuran, an amber polymer, .17 g., which darkened at 330° without melting was precipitated by the addition of water.

4. Reaction of perfluorobutyronitrile with perfluorobutyrhydrazidine hydrochloride

Perfluorobutyrhydrazidine hydrochloride, 2.00 g. (0.0076 mole) and 0.01 mole of perfluorobutyronitrile were placed in a heavy-wall glass tube which was pumped free of air, sealed and heated at 90° for 48 hr. The reaction tube was cooled and opened to yield 1.75 g. of a yellow solid identified as 3,6-bis(perfluoropropyl)-1,2-dihydro-1,2,4,5-tetrazine by comparison with an authentic sample. The infrared spectra of the crude product indicated that a small amount of perfluoroalkyl-substituted triazole was also present.

5. Heating of perfluorobutyrhydrazidine hydrochloride

Perfluorobutyrhydrazidine hydrochloride, 1.9 g., was placed in a heavy-wall glass tube which was pumped free of air, sealed and heated at 90° for 24 hr. The reaction tube was cooled to room temperature, opened, and the recovered yellow solid recrystallized from toluene to yield 0.76 g. (50%) of 3,6-bis(perfluoropropyl)-1,2-dihydro-1,2,4,5-tetrazine.

6. Reaction of perfluorobutyronitrile, perfluorobutyrhydrazidine hydrochloride and hydrogen chloride

Perfluorobutyrhydrazidine hydrochloride, 2.00 g. (0.0076 mole), was placed in a heavy-wall glass tube and the air removed by pumping. Perfluorobutyronitrile, 0.01 mole, and hydrogen chloride, 0.0076 mole, were condensed in the reaction tube which was then sealed and heated at 90° for 12 hr. and at 140° for 48 hr. Recovered from the tube was 0.35 g. of ammonium chloride, 0.0089 mole of gas, 1.9 g. of 3,5-bis(perfluoropropyl)-1,2,4-triazole and a very small amount of red liquid which was not identified. The yield of perfluoroalkyl-substituted triazole indicated that the perfluorobutyronitrile participated in the reaction, since the theoretical amount of triazole that could be produced from the hydrazidine hydrochloride is 1.54 g.

7. Reaction of perfluorobutyrhydrazidine hydrochloride with perfluoropropionyl chloride

Perfluorobutyrhydrazidine hydrochloride, 2.00 g. (0.0076 mole), and perfluoropropionyl chloride, 10.0 g. were placed in a heavy-wall glass tube which was pumped free of air, sealed and heated at a 120° for 12 hr. The reaction tube was cooled to room temperature and opened to yield 0.6 g. (22%) (after recrystallization from toluene) of 3-perfluoropropyl-5-perfluoroethyl-1,2,4-triazole.

B. Preparation of 2,6-perfluoroethyl 4-hydroxy-1,3,5-triazine

A freshly prepared sample, 5.80 g. (1.4×10^{-2} mole), of N'(perfluoropropionimidoyl)perfluoropropylamidine silver salt was dissolved in 50 ml. of anhydrous ethyl ether and placed in a 200 ml. flask fitted with a dry-ice cooled condenser and the flask was immersed in liquid nitrogen to freeze the contents. Air was then removed by pumping and an excess of phosgene was condensed in the reaction vessel.

Dry nitrogen was then admitted to the reaction flask and allowed to sweep over the mixture which was allowed to warm to dry-ice temperature. As the frozen reactants began to melt, stirring by a magnetic bar was initiated. The dry-ice bath was then removed from the reaction pot, and upon warming to -39°, reaction occurred to give a white solid. The excess phosgene was allowed to reflux for 2 hr. From the dry-ice cooled condenser and then the apparatus and reactants were allowed to stand over night with stirring and dry nitrogen sweep while excess phosgene distilled from the reaction flask.

After this period of standing the flask contained a finely divided white solid and a liquid solvent layer. These were separated by filtration into:

(a) A white solid (3.06 g.) which darkened upon exposure to light. No melting point was observed below 260°; however, some small amount of white solid sublimed on the walls of the capillary melting point tube. The quantitative yield of solid product was greater than that calculated for silver chloride (2.00 g.) and infrared spectra of this solid indicated that in addition to the silver chloride, there was present some acylated N'(perfluoropropionimidoyl)perfluoropropylamidine hydrochloride also.

(b) The solvent ether was removed from the liquid layer under reduced pressure to leave 3.40 g. of a product which on standing separated into a liquid layer (2.30 g.) of triazine and a solid which was apparently additional hydrochloride of the acylated imidoyl amidine.

Attempts to distill the crude triazine product recovered from the ether solution resulted in decomposition if the distillation was carried at atmospheric pressure. Chromatographic separation over neutral alumina was not effective. The crude triazine could be distilled under reduced pressure (less than 0.1 mm. Hg.) at 77°. The resulting 2,4-bis(perfluoropropyl)-4-hydroxy-1,3,5-triazine was a clear viscous liquid. This triazine was soluble in ethyl ether, acetone, methyl alcohol and benzene but was insoluble in petroleum ether and carbon tetrachloride. The triazine was soluble in dioxane but there was no complex formation as is characteristic for the tris(perfluoroalkyl) substituted triazines.

Distilled water at room temperature (28°) was added to a small portion of the triazine. After this mixture was stirred for 4 minutes, a white solid formed and was identified by its infrared spectra and melting point as perfluoropropiamide.

C. 2-Perfluoroalkyl-5-hydroxy-1,3,4-oxadiazole

1. Preparation of 2-perfluoropropyl-5-hydroxy-1,3,4-oxadiazole

A preparation of this compound similar to that described below was reported in ML-TDR-64-142.

Perfluorobutyrhydrazide, 11.0 g., was dissolved in 25 ml. of tetrahydrofuran and phosgene was bubbled through the mixture until no further reaction took place. The solution was then filtered and solvent removed under reduced pressure from the filtrate until the residue was a viscous yellow oil. This oil was redissolved in acetone and added slowly to a solution of silver nitrate; the white precipitate which formed was removed by filtration, washed with water and with acetone and dried under reduced pressure for 12 hr. at room temperature to give a white solid melting at 205° with decomposition.

The free 2-perfluoropropyl-5-hydroxy-1,3,4-oxadiazole was regenerated by making a slurry of 11.80 g. of the silver salt and 200 ml. of dry diethyl ether and passing anhydrous HCl through the slurry for 15 min. Completion of the reaction could be determined by noting the point at which the precipitated silver chloride settled rapidly to leave a clear solution; the unreacted salt of the hydroxy oxadiazole had a tendency to remain in suspension, producing a cloudy solution.

The precipitated silver chloride was removed by filtration and the filtrate evaporated to dryness. The solid product was recrystallized from benzene to give 6 g., melting point 51-52°, of pure 2-perfluoropropyl-5-hydroxy-1,3,4-oxadiazole.

A quantitative amount of silver chloride was not collected from this purification procedure; the possibility exists therefore that the product formed from silver nitrate and the hydroxyoxadiazole is not the result of 1:1 molar interaction.

2. Preparation of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole

Perfluoropropionhydrazide, 10.0 g., was dissolved in 25 ml. of tetrahydrofuran and phosgene was bubbled through the solution for 25 min. Reaction temperature remained at 0°. After the addition of the phosgene was complete, the solution was filtered and the filtrate concentrated to a viscous, yellow oil under high vacuum. This oil was then dissolved in toluene by careful heating to 45°. The toluene solution was cooled slowly to 0° and white leaflets, 7.0 g., of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole crystallized. The melting point was 43-45° and yield of 61% was obtained.

3. Tosylates of the 2-perfluoroalkyl-5-hydroxy-1,3,4-oxadiazoles

A solution of 0.55 g. of 2-perfluoropropyl-5-hydroxy-1,3,4-oxadiazole was prepared in 7 ml. of dry pyridine and 0.42 g. of p-toluene-sulfonylchloride was added. The temperature of the reaction mixture was maintained at 0°. A white precipitate formed within 20 seconds; after allowing 10 min. reaction time, the precipitate was removed by filtration and the pyridine solution was poured over a mixture of ice and hydrochloric acid. A green-white solid formed and was separated by filtration. This solid product was washed with water, dried and gave a melting point of 109-112°.

The tosylate of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole was prepared by the above procedure using 1.22 g. of perfluoroethyl-substituted hydroxy oxadiazole and 1.14 g. p-toluene-sulfonylchloride. This reaction yielded 1.53 g. of a white solid with a melting point of 85°.

An attempt was made to react 2-perfluoroalkyl-5-hydroxy-1,3,4-oxadiazole, 1.71 g., with 0.66 g. of p-toluene-sulfonylchloride in 4 ml. of acetic acid at room temperature. The reaction mixture was allowed to stand over night then poured over ice; the only solid product separated from this procedure was unreacted p-toluene-sulfonylchloride.

4. Attempted dimerization by dehydration

2-Perfluoroethyl-5-hydroxy-1,3,4-oxadiazole, 3.58 g., and phosphorus pentoxide, 5 g., were placed in a heavy-wall glass tube and sealed after removal of the air. The reaction tube was then heated 4 hr. at 150°, 12 hr. at 175°, and 6 hr. at 190°. After the reaction tube had cooled to room temperature, it was opened and the contents extracted with ether. A white solid, 3.50 g., melting point 40-44°, was recovered from the ether. The infrared spectra of this product was identical to that of the starting material.

5. Mercury salts of the 2-perfluoroalkyl-5-hydroxy-1,3,4-oxadiazoles

A solution of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole, 0.05 g., was prepared in acetone and added slowly to a saturated solution of mercuric acetate. A white precipitate appeared immediately and this precipitate was separated by filtration and dried to give a solid product melting at 185-190°.

The above procedure was repeated with 3.10 g. of 2-perfluoropropyl-5-hydroxy-1,3,4-oxadiazole and mercuric acetate and gave a mercuric salt melting at 190°. This salt was soluble in warm tetrahydrofuran, dioxane and acetone but was insoluble in hexane.

The hydroxy oxadiazole was recovered from the mercuric salt by dissolving 0.88 g. of the salt in 50 ml. of a mixture of diethyl ether and tetrahydrofuran. Hydrogen sulfide was then bubbled through the solution for 20 minutes and the mixture allowed to stand overnight. The precipitated mercuric sulfide, after it had been filtered and dried, weighed 0.382 g. The theoretical value for a mercuric salt would be 0.386 g.

6. Attempted preparations of a 5-halo-2-perfluoroalkyl-1,3,4-oxadiazole

The 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole used in the following reactions was prepared by the procedure given in the previous report[1] with the exception that diethyl ether was used as a solvent instead of tetrahydrofuran. Perfluoropropionhydrazide, 115 g. (0.646 moles) with excess phosgene gave 98.5 g. of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole (or 2-perfluoroethyl-1,3,4,4H-oxadiazoline-5-one) melting at 43.0-44.0° after recrystallization from hexane. The yield of this reaction was 74% of theoretical.

a. Reaction of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole with thionyl chloride

To a solution of 4.5 g. of thionyl chloride in 3 ml.

of benzene was added a solution of 7.7 g. (0.0378 moles) of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole in 10 ml. of benzene. The reaction mixture was refluxed 7 hr. and the solution allowed to stand overnight. The solid product, 7.0 g., was filtered and dried and identified by melting point and infrared spectra as the starting hydroxy oxadiazole.

b. Reaction of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole with sulfur tetrafluoride

The reaction of the perfluoroalkyl-substituted hydroxy oxadiazole with sulfur tetrafluoride was first attempted using acetonitrile as a solvent. 2-Perfluoroethyl-5-hydroxy-1,3,4-oxadiazole, 5.01 g. (0.246 moles), 25 ml. of acetonitrile and 9.0 g. of sulfur tetrafluoride were placed in a previously evacuated tube, sealed and allowed to stand at room temperature for three days. The tube was then opened and excess sulfur tetrafluoride allowed to escape. From the remaining mixture in the reaction tube, no product could be extracted with benzene or chloroform. There was apparently considerable decomposition of the starting materials.

An additional reaction of the perfluoroalkyl-substituted hydroxy oxadiazole with sulfur tetrafluoride was attempted using pyridine as a solvent. 2-Perfluoroethyl-5-hydroxy-1,3,4-oxadiazole, 4.46 g. (0.0218 moles) in 20 ml. of pyridine and excess sulfur tetrafluoride were sealed in a previously evacuated tube and was allowed to stand two days at room temperature. The tube was then cooled in liquid nitrogen and opened to the vacuum system. Considerable elemental nitrogen was present, and on examination of the remaining material in the tube, only decomposition products could be found.

c. Reaction of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole with phosphorus trichloride

2-Perfluoroethyl-5-hydroxy-1,3,4-oxadiazole, 1.0 g. and 1.0 g. of phosphorus trichloride in 10 ml. of chloroform were mixed and refluxed for 3 hr. There was no apparent evolution of hydrogen chloride. A 1 ml. sample of the reaction mixture was cooled to 0° and a white precipitate separated which had a melting point of 42-43°. This product was identified as unchanged starting material.

d. Reaction of 2-perfluoroethyl-5-hydroxy-1,3,4-oxadiazole with phosphorus pentachloride

2-Perfluoroethyl-5-hydroxy-1,3,4-oxadiazole, 5.6 g. (0.0274 moles), in 10 ml. of carbon tetrachloride were dropped into a solution of 6.0 g. of phosphorus pentachloride in 15 ml. of carbon tetrachloride. The solution was refluxed 1 hr. and then allowed to stand at room temperature overnight. The only products isolated from this reaction were apparently inorganic and represented decomposition.

Another reaction of the hydroxy oxadiazole, 9.7 g. (0.046 moles), was attempted using 10.0 g. of phosphorus pentachloride and 80 ml.of benzene as a solvent. The solution was stirred at room temperature for 29 hr. after which time a portion was removed and cooled to 0°C. A precipitate formed on which was identified as the starting material, perfluoroalkyl-substituted hydroxy oxadiazole. The remainder of the reaction solution was refluxed 2 1/2 hr. and evolution of hydrogen chloride was noted. However, fractionation of the reaction in mixture did not result in the separation of the desired 5-chloro-2-perfluoroethyl-1,3,4-oxadiazole.

D. Preparation of 3,5-bis(perfluoroalkyl)-4-amino-1,2,4-triazole

Preparation of some of the intermediates for formation of the perfluoroalkyl-substituted-4-amino-1,2,4-triazole are given below although this preliminary work was performed outside of this project's area; since this work has not yet appeared in the literature, description of the source of these intermediates would not otherwise be available.

1. N^2-(α-Hydrazonoperfluoropropyl)perfluoropropionhydrazide

Hydrazine (95+%), 25.6 g. (0.8 mole) was dissolved in 25 ml. of ethyl alcohol (95%) and placed in a 100 ml. flask equipped with a stirrer and cooled by an ice bath. 2,5-bis-(Perfluoroethyl)-1,3,4-oxadiazole, 31.0 g. (0.101 mole), was added slowly over a 15 min. period with stirring; the reaction mixture was allowed to stand for 1/2 hr., and 100 ml. of water was added to the solution. Adjustment of the acidity of the solution to pH-6.0 with dilute hydrochloric acid precipitated the product which was recrystallized from an acetonitrile-water solution to give 32.0 g. (93%) of N^2-(α-hydrazonoperfluoropropyl)perfluoropropionhydrazide, m.p. 177° (dec.), ultraviolet absorption maxima, 265mμ (in isopropyl alcohol) log ϵ = 4.07.

Anal. Calcd. for $C_6H_4F_{10}N_4O$: C, 21.31; H, 1.20; N, 16.57. Found: C, 21.48; H, 1.11; N, 16.73.

2. N^2-(α-Hydrazonoperfluorobutyl)perfluorobutyrhydrazide

This compound was prepared from 3,5-bis(perfluoropropyl)-1,3,4-oxadiazole by the procedure shown in the preceding preparation. N^2-(α-Hydrazonoperfluorobutyl)perfluorobutyrhydrazide was obtained in 91% yield, m.p. 171° (dec.), ultraviolet absorption maxima, 272 mμ (in isopropyl alcohol) log ϵ = 4.05.

Anal. Calcd. for $C_8H_4F_{14}N_4O$: C, 21.93; H, 0.92; F, 60.73; N, 12.79. Found: C, 22.20; H, 1.11; F, 60.45; N, 12.71.

3. N^2-(α-Hydrazonoperfluorobutyl)perfluoroacethydrazide

2-Perfluoromethyl-5-perfluoropropyl-1,3,4-oxadiazole, 30.6 g. (0.10 mole), was dropped slowly into a solution of 3.2 g. (0.10 mole) of anhydrous hydrazine in 100 ml. of 95% ethyl alcohol. Reaction temperature was maintained at 5-7° throughout the 1.5 hr. reaction by means of an ice bath. Upon completion of the addition the solution was diluted with 200 ml. of ice-cold distilled water and the pH then adjusted to ca. 6 whereupon N^2-(α-hydrazonoperfluorobutyl)perfluoracethydrazide, 24.6 g. (73%), precipitated as snow white granules, m.p. 154° (dec.).

Anal. Calcd. for $C_6H_4F_{10}N_4O$: C, 21.31; H, 1.20; N, 16.57. Found: C, 21.19; H, 1.38; N, 16.57.

4. 3,6-*bis*(Perfluoropropyl)-1,2,4,5-tetrazine

N^2-(α-Hydrazonoperfluorobutyl)perfluorobutyrhydrazide, 30.0 g. (0.068 mole) and 100 g. (0.64 mole) of anhydrous ferric chloride were mixed intimately in a 200 ml. flask which was swept by dry-nitrogen (10 ml./1 min.) into two dry-ice-cooled traps arranged in series. The reaction mixture was heated at 75° for 12 hr., at 90° for 6 hr. and at 125° for 4 hr. During this time crude product, 7.5 ml. passed into the traps. Fractionation at atmospheric pressure gave 10.0 g. (35%) of deep-red 3,6-*bis*(perfluoropropyl)-1,2,4,5-tetrazine, b.p. 150°, d^{25} 1.709, n^{25} 1.3301.

5. 3-Perfluoromethyl-6-perfluoropropyl-1,2,4,5-tetrazine

N^2-(α-Hydrazonoperfluorobutyl)perfluoroacethydrazide, 60.0 g. (.177 mole), was reacted in 12.0 g. portions with 75 g. of anhydrous ferric chloride for each portion by placing the thoroughly mixed charge in a 200 ml. flask connected to two dry-ice-cooled traps in series. The system was then swept with dry nitrogen for 10 min. The nitrogen flow rate was then adjusted to 10 ml./min. The flask and contents were then heated to 45° and maintained at this temperature for 12 hr. The total crude liquid product which collected in the traps was distilled and yielded 1.0 g. of trifluoroacetic acid, 2.4 g. of 2-perfluoromethyl-5-perfluoropropyl-1,3,4-oxadiazole, and 4.3 g. of the desired tetrazine. Infrared analysis showed the tetrazine to be still contaminated with a carbonyl containing impurity. Final purification by vapor phase chromatography (silicone SE-30 on chromosorb P, 85°, *He* flow 1.10 l./min. in a 3/8 in.by 20 ft. column) gave pure 3-perfluoromethyl-6-perfluoropropyl-S-tetrazine, 4.0 g. (7.1%) as a deep red liquid, b.p. 123°, d^{25} 1.685, n^{25} 1.3409.

Anal. Calcd. for $C_6F_{10}N_4$: C, 22.65; N, 17.62; F, 59.73. *Found*: C, 22.57; N, 18.09; F, 59.87.

6. 3-Perfluoromethyl-6-perfluoropropyl-1,2-dihydro-1,2,4,5-tetrazine

3-Perfluoromethyl-6-perfluoropropyl-s-tetrazine, 0.10 g. (3.14×10^{-4} mole), was condensed into a 70 cc. heavy-wall glass tube previously constricted for sealing. The tube and its contents were degassed; hydrogen sulfide, 1.0 g. (0.027 mole), was condensed into the tube which was then sealed and allowed to warm to room temperature. After 4 hr. the red color of the tetrazine had disappeared and a yellow solution remained. The tube was then cooled in liquid nitrogen and opened. The excess hydrogen sulfide was pumped off, the remaining yellow solid dissolved in warm toluene, and the solution filtered to remove elemental sulfur. Crystallization of the solid product from the toluene solution gave 0.09 g. (90%) of pale yellow 3-perfluoromethyl 6-perfluoropropyl-1,2-dihydro-s-tetrazine, m.p. 98.0-98.5°.

Anal. Calcd. for $C_6H_2F_{10}N_4$: C, 22.51; H, 0.63; N, 17.51. *Found*: C, 21.81; H, 0.83; N, 17.28.

7. 3,6-*bis*(Perfluoropropyl)-1,2-dihydro-1,2,4,5-tetrazine

3,6-*bis*(Perfluoropropyl)-1,2,4,5-tetrazine, 0.10 g., was condensed in a heavy-wall glass tube with 1.2 g. of hydrogen sulfide. The tube was sealed and allowed to stand at room temperature for 4 hr. The tube was opened, excess hydrogen sulfide allowed to vaporize, and the solid product dissolved in toluene. Sulfur was removed by filtration. Crystallization from the toluene solution gave 0.08 g. (80%) of pure 3,6-*bis*(perfluoropropyl)-1,2-dihydro-1,2,4,5-tetrazine, m.p. 117.5-118.0°. Ultraviolet absorption maxima, 232 mμ ($\log \epsilon_{\max.}$ 3.54).

Anal. Calcd. for $C_8H_2F_{14}N_4$: C, 22.87; H, 0.48; N, 13.34. *Found*: C, 22.90; H, 0.59; N, 13.19.

8. Isomerization of 3,6-bis(perfluoropropyl)-1,2-dihydro-1,2,4,5-tetrazine

3,6-*bis*(Perfluoropropyl)-1,2-dihydro-1,2,4,5-tetrazine, 0.12 g., was slurried in a solution of 3 ml. of ethyl alcohol and 5 ml. of concentrated hydrochloric acid at room temperature and heated slowly to reflux. After 2 hr. the yellow solution became colorless; on cooling the solution to room temperature, 0.08 g. (75%) of 3,5-*bis*(perfluoropropyl)-4-amino-1,2,4,4*H*-triazole,m.p. 104.5-105.0°, was collected.

The infrared spectra of this compound was identical to that of a sample of 3,5-*bis*(perfluoropropyl)-4-amino-1,2,4,4*H*-triazole; prepared by the method described below for 3,5-*bis* perfluoroethyl)-4-amino-1,2,4,4*H*-triazole; the melting point of a mixture showed no depression.

Anal. Calcd. for $C_8H_2F_{14}N_4$: C, 22.87; H, 0.48; F, 63.32; N, 13.34. Found: C, 23.19; H, 0.57; F, 62.68; N, 13.94.

9. 3,5-*bis*(Perfluoroethyl)-4-amino-1,2,4,4*H*-triazole

N^2-(α-Hydrazonoperfluoropropyl)perfluoropropionhydrazide, 2.10 g. (0.0062 mole), was refluxed for 3 hr. with 7 ml. of glacial acetic acid. Upon cooling and diluting the solution with 15 ml. of water, white, crystalline (plates) 3,5-*bis*(perfluoroethyl)-4-amino-1,2,4,4*H*-triazole precipitated, m.p. 96.0-96.5° (after recrystallization from toluene), yield 1.80 g. (86%).

Anal. Calcd. for $C_6H_2F_{10}N_4$: C, 22.51; H, 0.63; N, 17.51. *Found:* C, 22.27; H, 0.80; N, 17.52.

10. 3-Perfluoromethyl-5-perfluoropropyl-4-amino-1,2,4,4*H*-triazole

N^2-(α-Hydrazonoperfluorobutyl)perfluoroacethydrazidine, 0.494 g. (.00146 mole), was refluxed for 1.8 hr. in 8 ml. of glacial acetic acid to which was added 0.1 ml. of concentrated hydrochloric acid. Upon cooling the solution 15 ml. of water were added. The solution was then extracted with ether, 30 ml., in successive small portions. The extract was washed with 5% $NaHCO_3$ solution and dried over Drierite Evaporation of the ether and left a pale yellow residue which was recrystallized 3 times from toluene to give 0.068 g. (15.2%) of white crystalline 3-perfluoromethyl-5-perfluoropropyl-4-amino-1,2,4,4*H*-triazole, m.p. 90.0-90.5°C.

Anal. Calcd. for $C_6H_2F_{10}N_4$: C, 22.51; H, 0.63; N, 17.51. *Found:* C, 22.35; H, 0.77; N, 17.56.

E. Acylation of 3,5-*bis*(perfluoroalkyl)-4-amino-1,2,4,4*H*-triazoles

1. 3,5-*bis*(Perfluoroethyl)-4-amino-1,2,4,4*H*-triazole

3,5-*bis*(Perfluoroethyl)-4-amino-1,2,4,4*H*-triazole, 0.48 g. (1.5 x 10^{-3} mole), was placed in a heavy-wall glass tube and the tube pumped free of air. Acetyl chloride, 1.56 g. (2.0 x 10^{-2} mole) was condensed in the tube which was then sealed and heated at 110° for 12 hr. Removal of the excess acetyl chloride left a brown solid which was sublimed (.05 mm. Hg., 125°) and recrystallized from toluene to give 0.31 g. (57%) of white 3,5-*bis*(perfluoroethyl)-4-acetylamino-1,2,4,4*H*-triazole, m.p. 192.5-193.3°.

Anal. Calcd. for $C_8H_4F_{10}N_4$: C, 26.53; H, 1.12; N, 15.47. Found: C, 26.30; H, 1.03; N, 15.64.

2. 3,5-*bis*(Perfluoropropyl)-4-amino-1,2,4,4*H*-triazole

3,5-*bis*(Perfluoropropyl)-4-amino-1,2,4,4*H*-triazole was acylated using the procedure described in the previous preparation, with the exception that the mixture was heated at 150° for 24 hr., to give 3,5-*bis*(perfluoropropyl)-4- acetylamino-1,2,4,4*H*-triazole, m.p. 154.5-155.0°.

Anal. Calcd. for $C_{10}H_4F_{14}N_4$: C, 22.87; H, 0.48; N, 13.34. Found: C, 23.19; H, 0.57; N, 13.94.

F. Deamination of 3,5-*bis*(perfluoroalkyl)-4-amino-1,2,4-triazoles

1. 3,5-*bis*(Perfluoroethyl)-4-amino-1,2,4,4*H*-triazole

3,5-*bis*(Perfluoroethyl)-4-amino-1,2,4,4*H*-triazole, 0.10 g. (3.1 x 10^{-4}mole), was dissolved in 4 ml. of concentrated sulfuric acid, the solution cooled to 10° and a solution of 0.10 g. (1.4 x 10^{-3}mole) of sodium nitrite in 3 ml. of sulfuric acid added. Gas was evolved rapidly; after 30 min. the solution was poured over 10 g. of ice. A white solid product separated and was recrystallized from toluene to give 0.060 g. (65%) of 3,6-*bis*(perfluoroethyl)-1,2,4-triazole, m.p. 104°. Comparison of the infrared spectra of this preparation with that of an authentic sample[1], and the melting point of a mixture of the two samples established the structure.

2. 3,5-*bis*(Perfluoropropyl)-4-amino-1,2,4,4*H*-triazole

This reaction was carried out by the procedure described in the previous preparation. Reaction of 3,5-*bis* (perfluoropropyl)-4-amino-1,2,4,4*H*-triazole gave 3,5-*bis* (perfluoropropyl)-1,2,4-triazole, m.p. 109-110° (lit. -110-111°).

G. Reaction of perfluoroadiponitrile with perfluorobutyramidine

A 250 ml. three-neck round-bottom flask was fitted with a thermometer, a 25 ml. barostatic dropping funnel, magnetic stirring bar and heating mantle. Perfluorobutyramidine, 9.90 g. (4.7 x 10^{-2} mole), previously dried under vacuum, was placed in the flask and 100 ml. of benzene added. A water-cooled condenser surmounted by a drying tube was attached to the reaction flask and the benzene-perfluorobutyramidine mixture heated to 45° with stirring.

A solution of 5.26 g. (2.04 x 10^{-2} mole) of perfluoroadiponitrile in 25 ml. of benzene was prepared on the vacuum system, then added to the dropping funnel. Addition of the benzene-perfluoroadiponitrile solution to the benzene-perfluorobutyramidine solution was begun at an initial temperature of 45° which rose during addition to 55°. The temperature of the reaction flask was maintained between 55-60° for 1 hr. The solution was then heated to 74° for 15 min. and at 80° for 10 min. after which heating was discontinued.

The reaction mixture was allowed to cool to room temperature; no solid product was observed. The excess benzene was removed under reduced pressure to leave 8.7 g. of a slightly viscous liquid having the characteristic odor of the imidoylamidine.

This product was found to be soluble in methyl alcohol, carbon tetrachloride and diethyl ether. It was insoluble in water. When a solution of cupric acetate was added, strong chelate formation was noted similar to that occurring in the compounds containing only one imidoylamidine group.

The product from this reaction, presumably a bis-imidoylamidine, was allowed to stand under reduced pressure at room temperature. After three days a white solid residue appeared (3.13 g.) which was separated by filtration. This solid product cannot be redissolved in benzene and was also insoluble in diethyl ether and water. It remained soluble in methyl alcohol. The solid product showed no chelate formation in the presence of cupric ion. It melted with the evolution of gas at 138-140°.

The above reaction was repeated with 13.16 g. (6.2×10^{-2} mole) of perfluorobutyramidine in 125 ml. of benzene and 7.92 (3.1×10^{-2} mole) of perfluoroadiponitrile in 25 ml. of benzene. After removal of the solvent benzene under reduced pressure, this reaction yielded 17.42 g. of slightly viscous liquid product, identical with that obtained previously.

Upon standing at room temperature this liquid product was observed to solidify at a slow rate. After one month the liquid had completely solidified with no weight loss. Its spectral and chemical characteristics were identical with the solid product obtained in the previous reaction.

H. Reaction of perfluoroadiponitrile with perfluoropropionamidine

This reaction was carried out with the same apparatus and under the same conditions as those described above in Section G with the exception that perfluoropropionamidine was used in place of perfluorobutyramidine. The results and the behavior of the resulting product were identical with those described above.

I. Reaction of perfluoroglutaronitrile and perfluorobutyramidine

Perfluoroglutaronitrile (7.26 g., 3.6×10^{-2} mole in 20 ml. of benzene) and perfluorobutyramidine (15.26 g., 7.2×10^{-2} mole in 100 ml. of benzene) were allowed to react in the apparatus described above in Section G. The perfluoroglutaronitrile solution was added to the perfluorobutyramidine solution at a solution temperature of 50°; during the following 45 min. of stirring after addition the temperature rose to 66°. After an additional 20 min. of stirring and heating the temperature of the reaction mixture had reached 81°. The heating was then discontinued and the reaction mixture allowed to cool overnight. This procedure produced 19.65 g. of white solid product melting at 99-103°. This product was soluble in diethyl ether, acetone and methyl alcohol and insoluble in water and carbon tetrachloride. In the presence of cupric ion there was no chelate formation observed.

The reaction of perfluoroglutaronitrile and perfluorobutyramidine was also carried out using carbon tetrachloride as a solvent under somewhat different conditions than those described above.

A 250 ml. three-neck flask was fitted with a 25 ml. barostatic dropping funnel and magnetic stirring bar. Perfluorobutyramidine, 7.36 g. (3.47×10^{-2} mole) was placed in the flask and 50 ml. of carbon tetrachloride added. A water-cooled condenser was attached to the apparatus and stirring of the mixture begun. The reaction flask was protected from the atmosphere by a drying tube. A solution of 3.50 g. (1.73×10^{-2} mole) of perfluoroglutaronitrile in 50 ml. of carbon tetrachloride was prepared on the vacuum system and then placed in the dropping funnel.

The perfluoroglutaronitrile-carbon tetrachloride solution was added to the stirred perfluorobutyramidine solution at room temperature. A short time (10 to 15 min.) after addition was complete a 10 ml. sample of the reaction mixture was removed and treated with cupric ion. This procedure resulted in the formation of the typical color of the copper chelate of the imidoylamidine structure.

After the reaction mixture of perfluoroglutaronitrile, perfluorobutyramidine and carbon tetrachloride had been stirred in room temperature for 30-40 min. solids began to form in the flask. The solvent carbon tetrachloride was removed under reduced pressure and there remained in the flask 9.10 g. of white solid melting, after recrystallization from benzene, at 99-104°. This product did not form a chelate in the presence of cupric ion.

IV APPENDIX

Infrared Absorption Spectra

Fig. 1 1,2-Diaza-3-imino-7-amino-4,4,5,5,6,6-hexafluoro-7-cycloheptene

Fig. 2 N,N'-bis(Perfluorobutyrimidoyl)perfluoroglutarhydrazidine

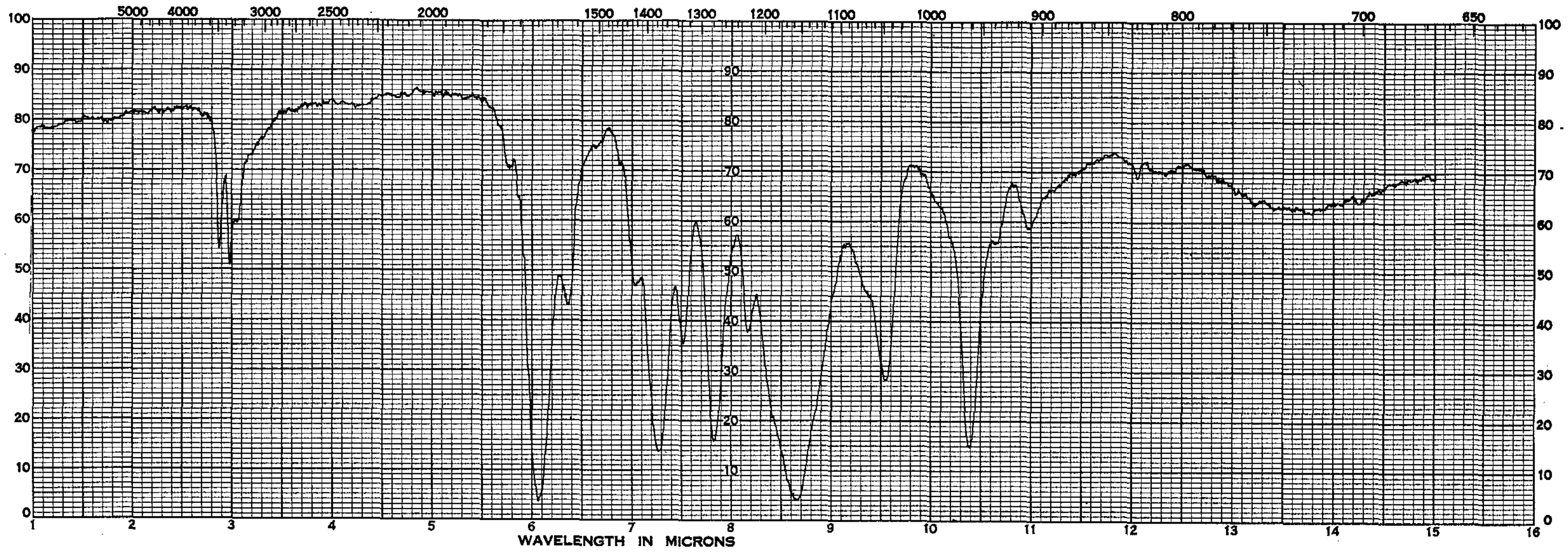


Fig. 3 Poly(N^2-imidoyl perfluoroglutarhydrazidine) (C)

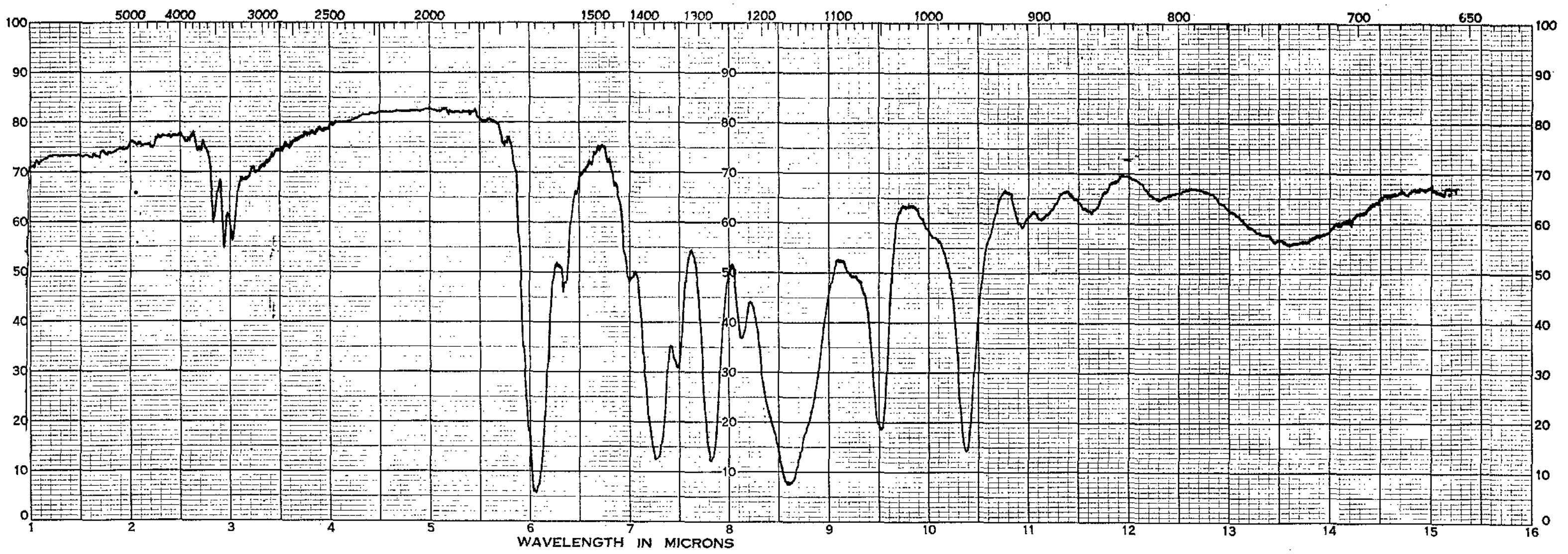


Fig. 4 Poly(N^2-imidoyl perfluoroglutarhydrazidine) (A)

Fig. 5 Poly(N^2-imidoyl perfluoroglutarhydrazidine) (B)

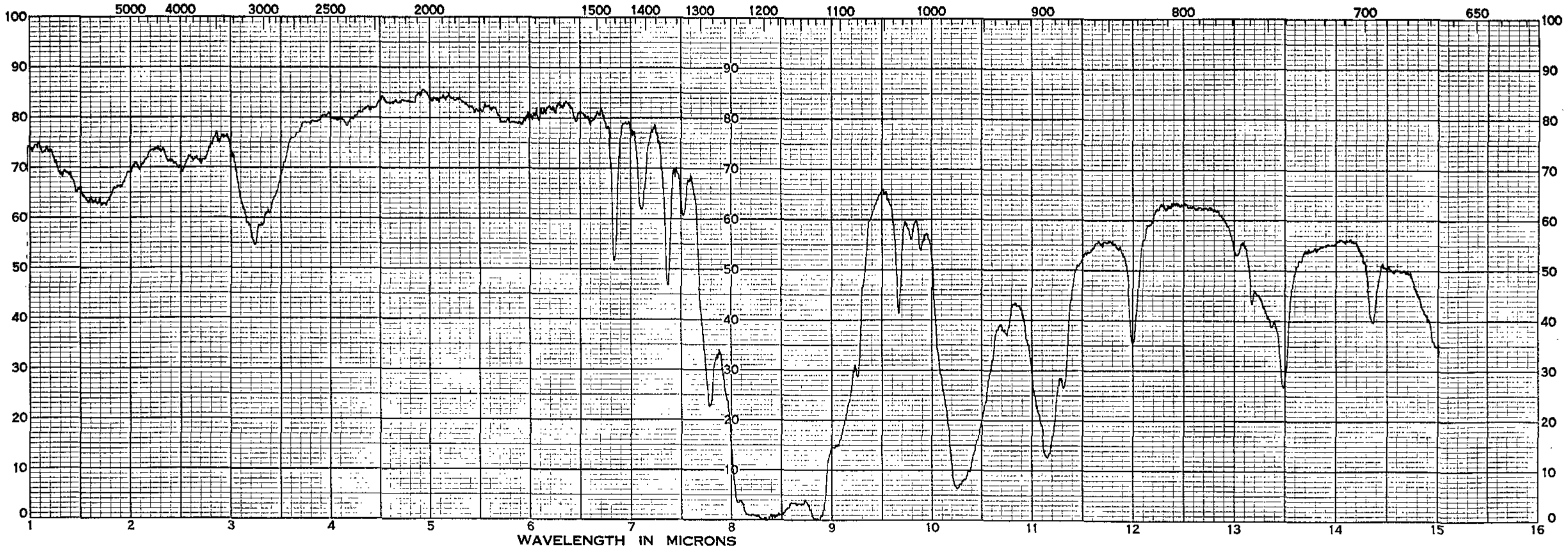


Fig. 6 1,3-*bis* [5-(3-Perfluoropropyl-1,2,4-triazolyl)]perfluoropropane

Fig. 7 Poly(perfluoropropylene-1,2,4-triazole) (A)

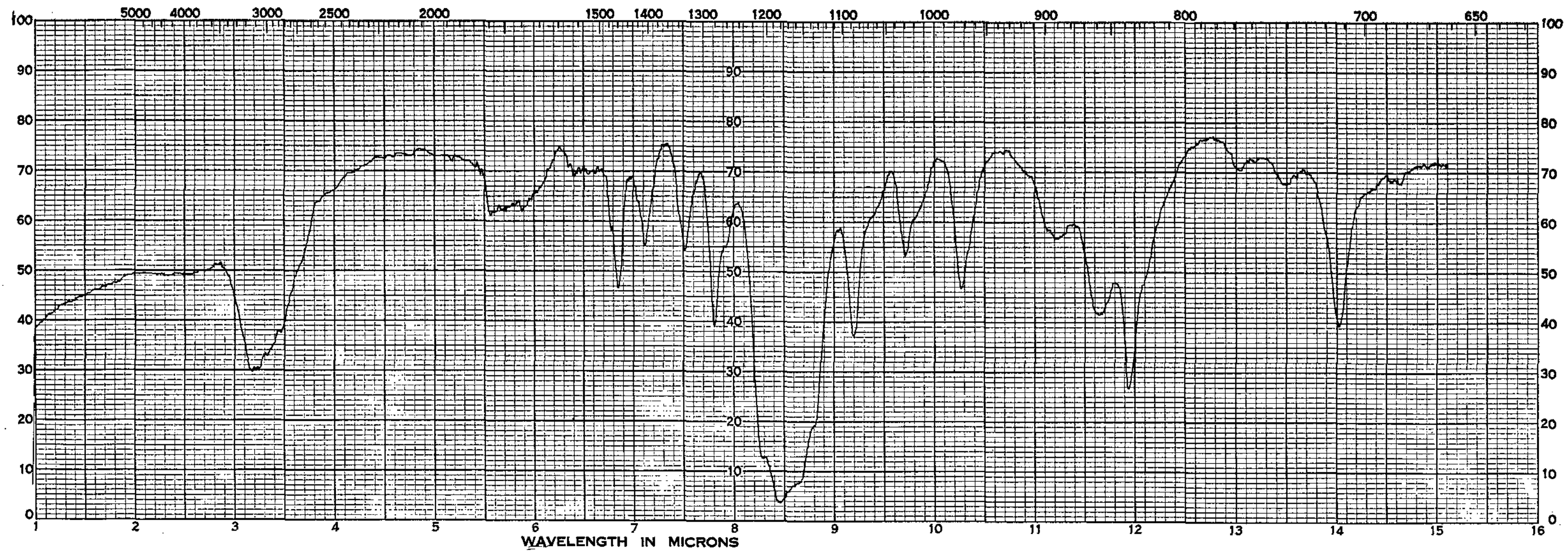


Fig. 8 Poly(perfluoropropylene-1,2,4-triazole) (B)

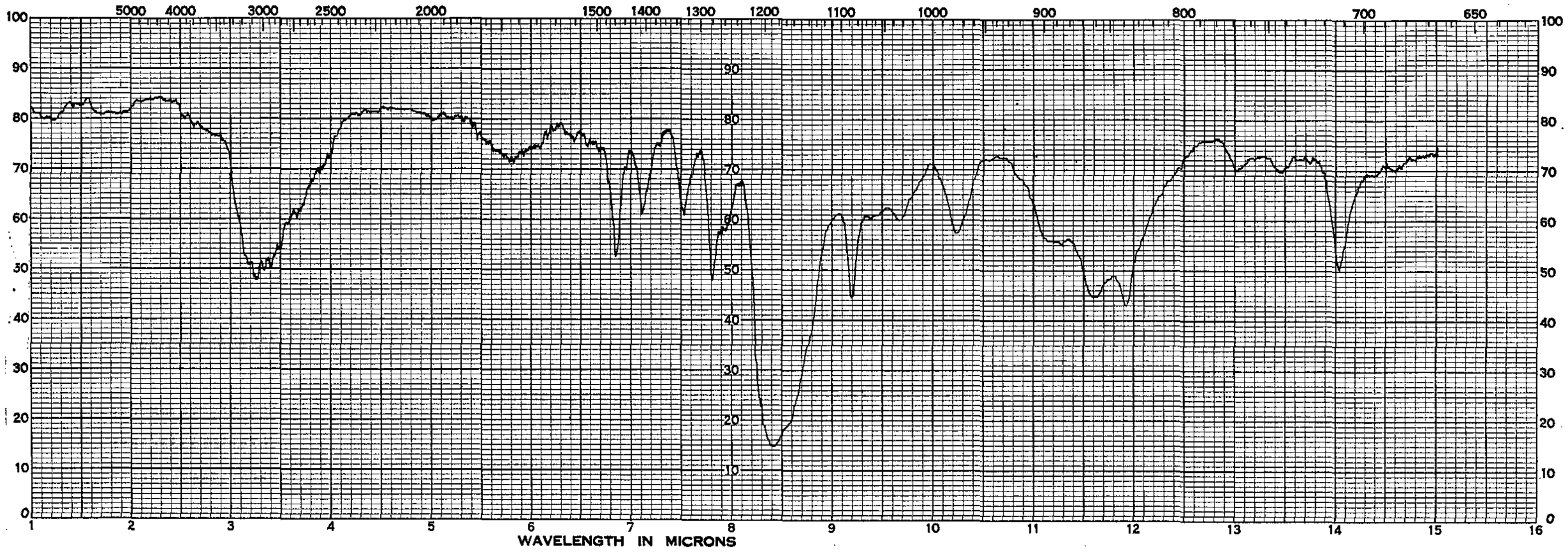


Fig. 9 Poly(perfluoropropylene-1,2,4-triazole) (C)

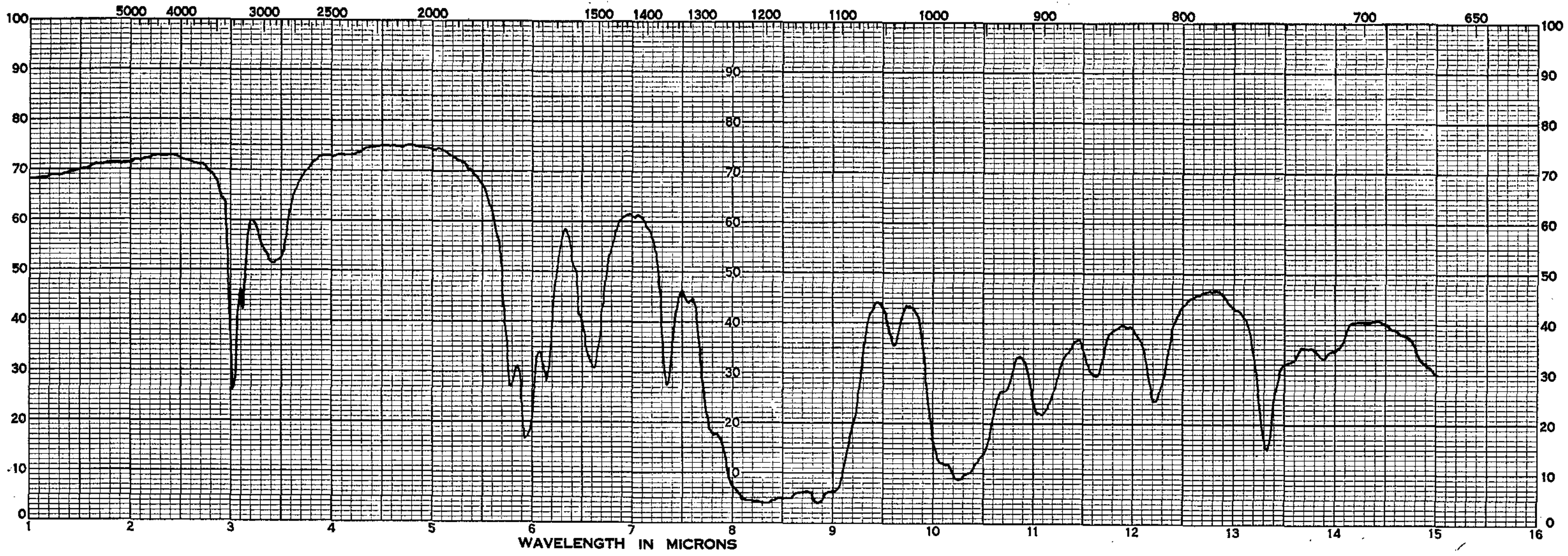


Fig. 10 N^2-(α-Hydrazonoperfluorobutyl)perfluorobutyrhydrazide

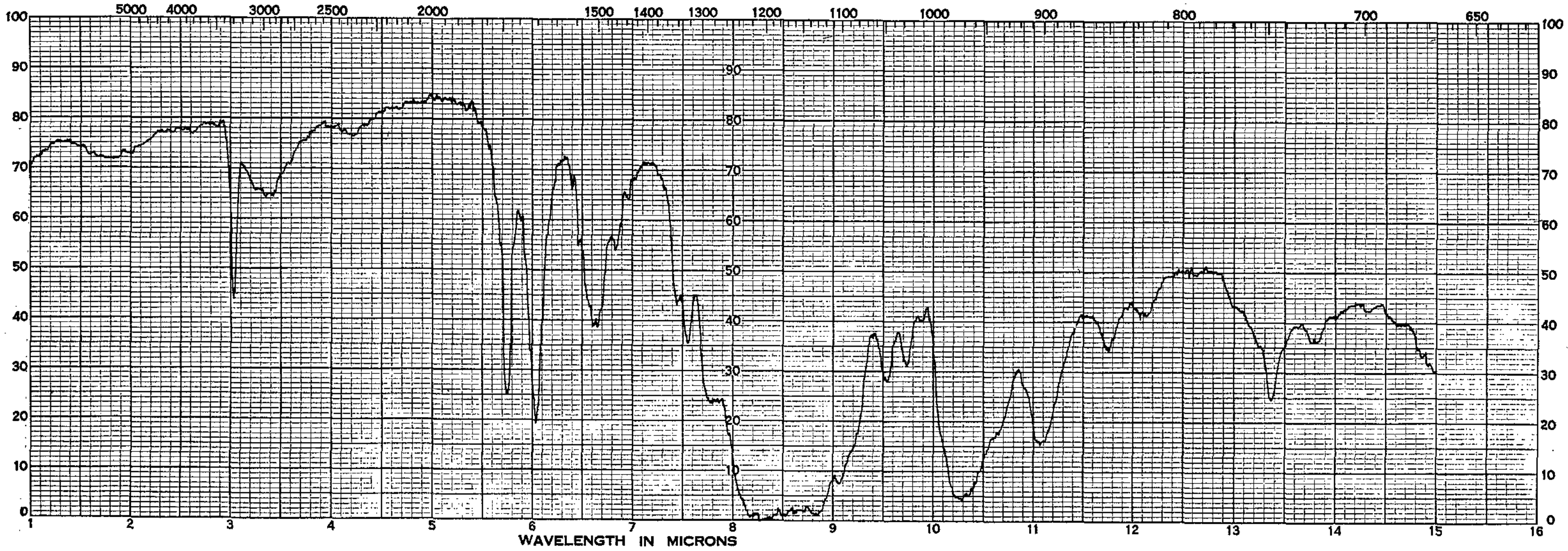


Fig. 11 N^2-(α Dimethylhydrazonoperfluoropropyl)perfluoropropionhydrazide

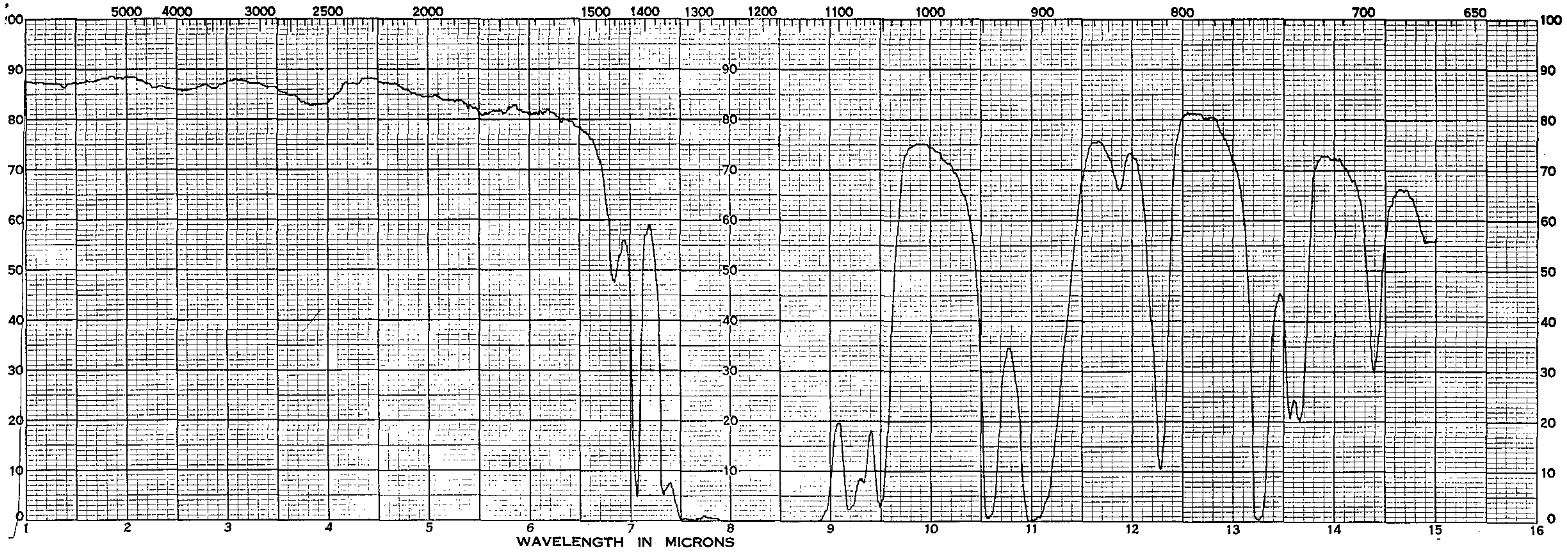
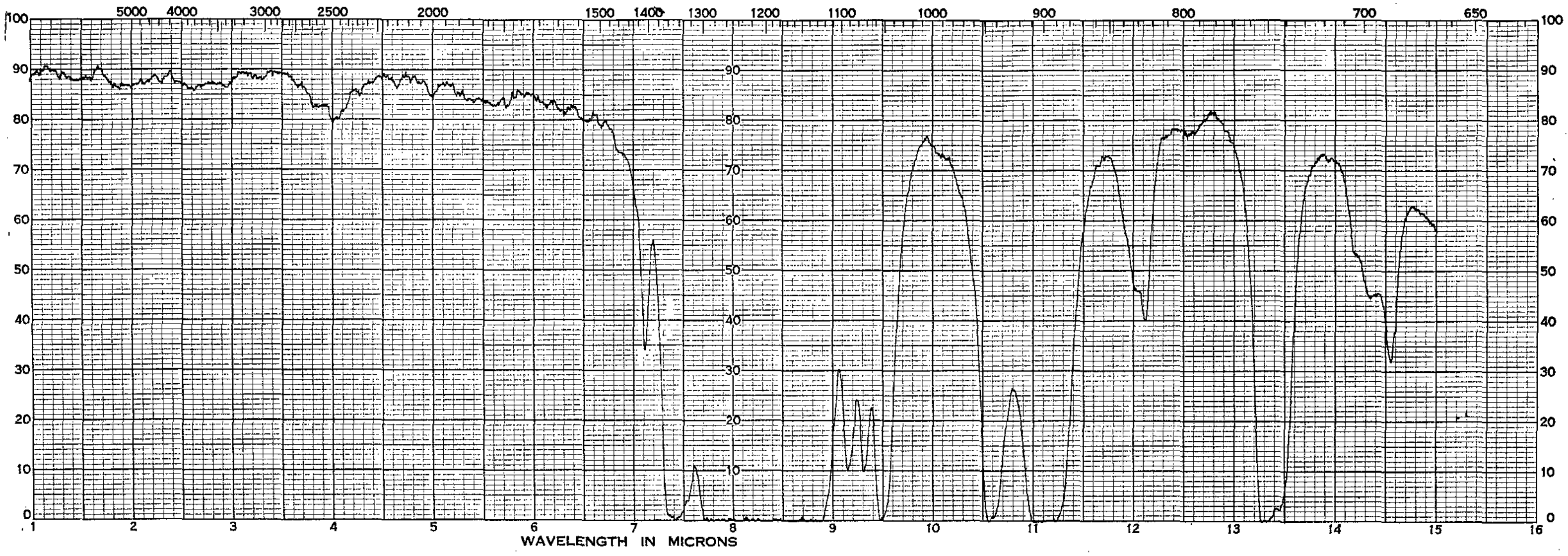


Fig. 12 3-Perfluoromethyl-6-perfluoropropyl-s-tetrazine



~~Fig.~~ 13 3,6-bis(Perfluoropropyl)-s-tetrazine

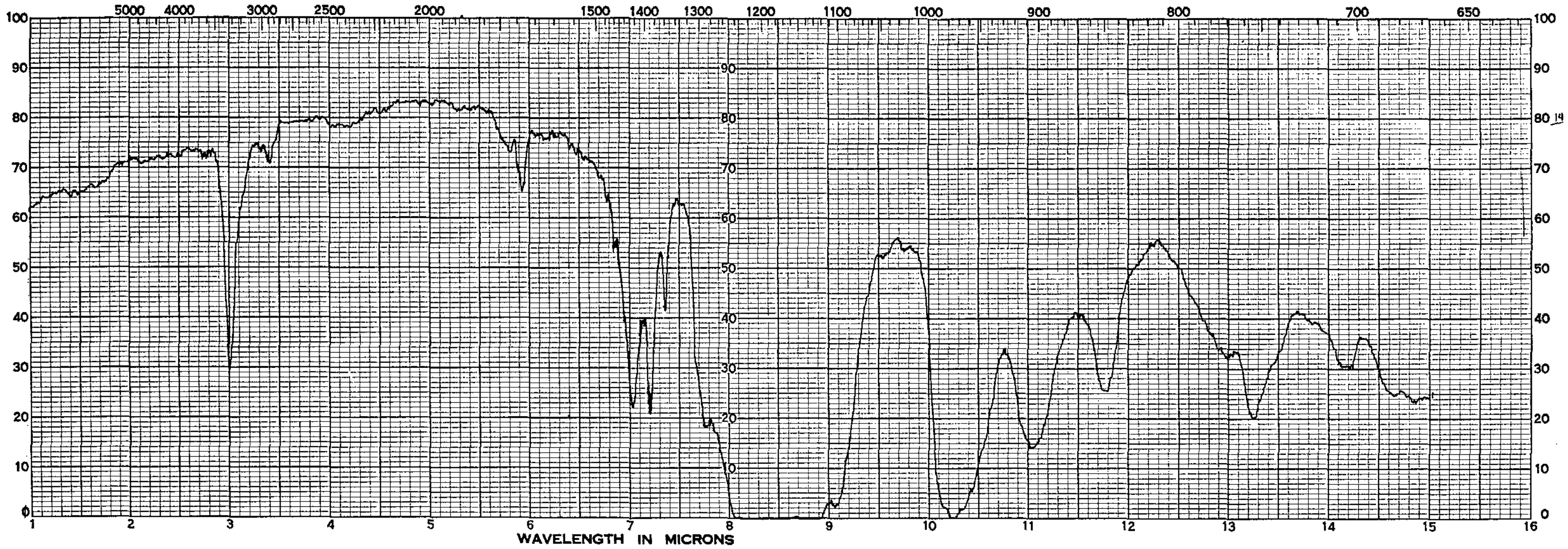


Fig. 14 3-Perfluoromethyl-6-perfluoropropyl-1,2-dihydro-s-tetrazine

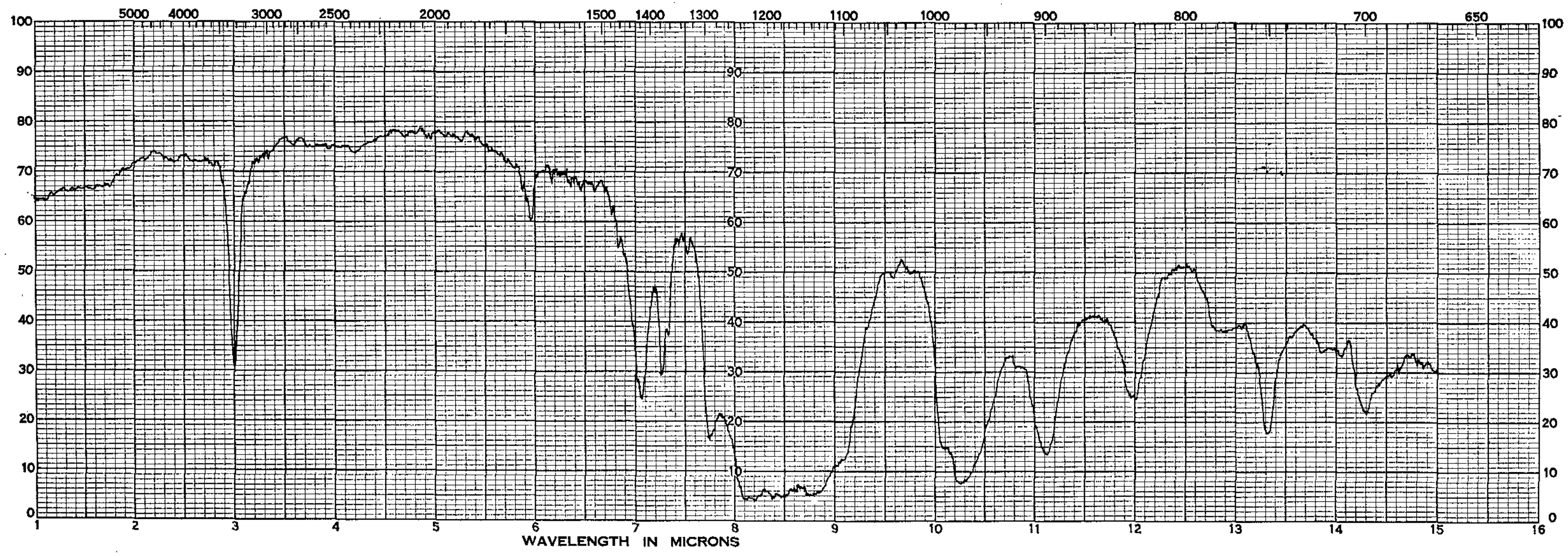


Fig. 15 3,6-bis(Perfluoropropyl)-s-tetrazine

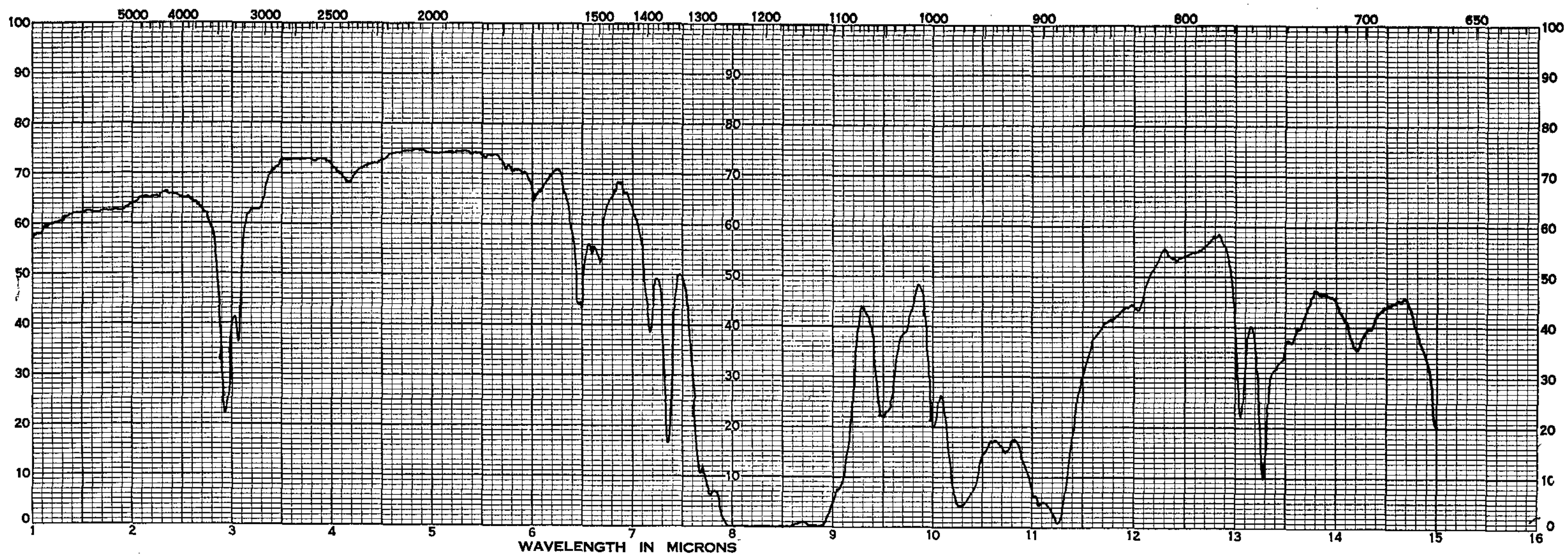


Fig. 16 3-Perfluoromethyl-5-perfluoropropyl-4-amino-1,2,4,4H-triazole

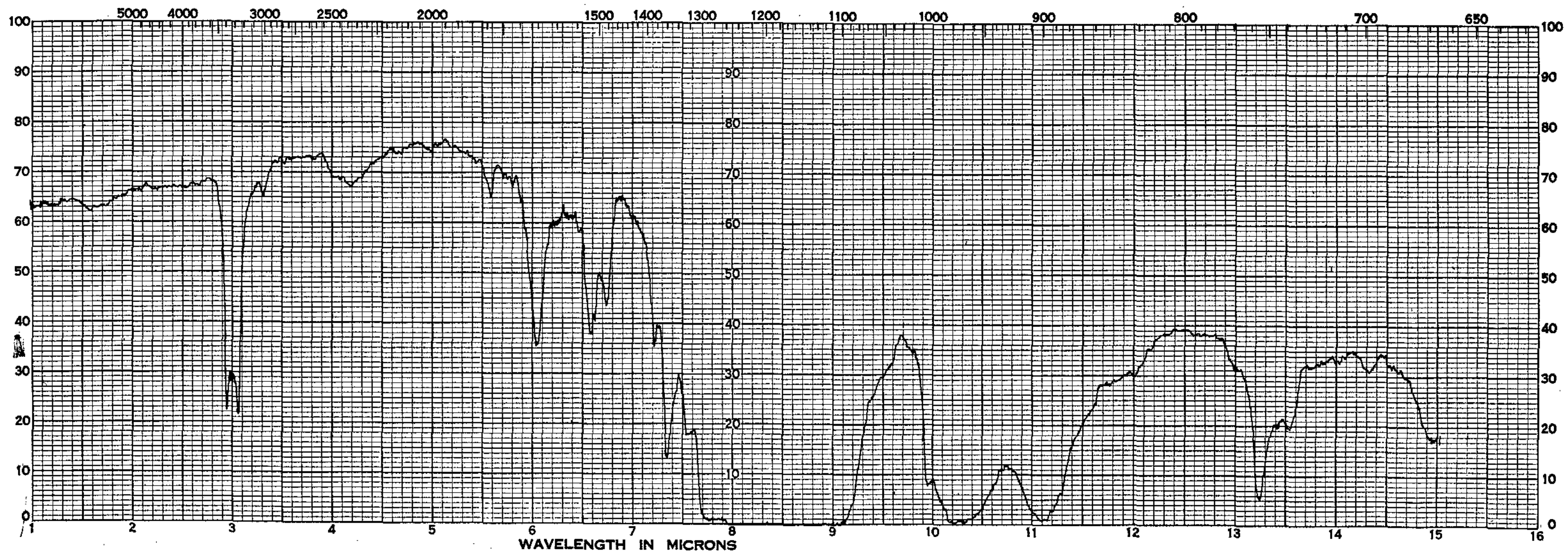


Fig. 17 3,5-bis(Perfluoropropyl)-4-amino-1,2,4,4H-triazole

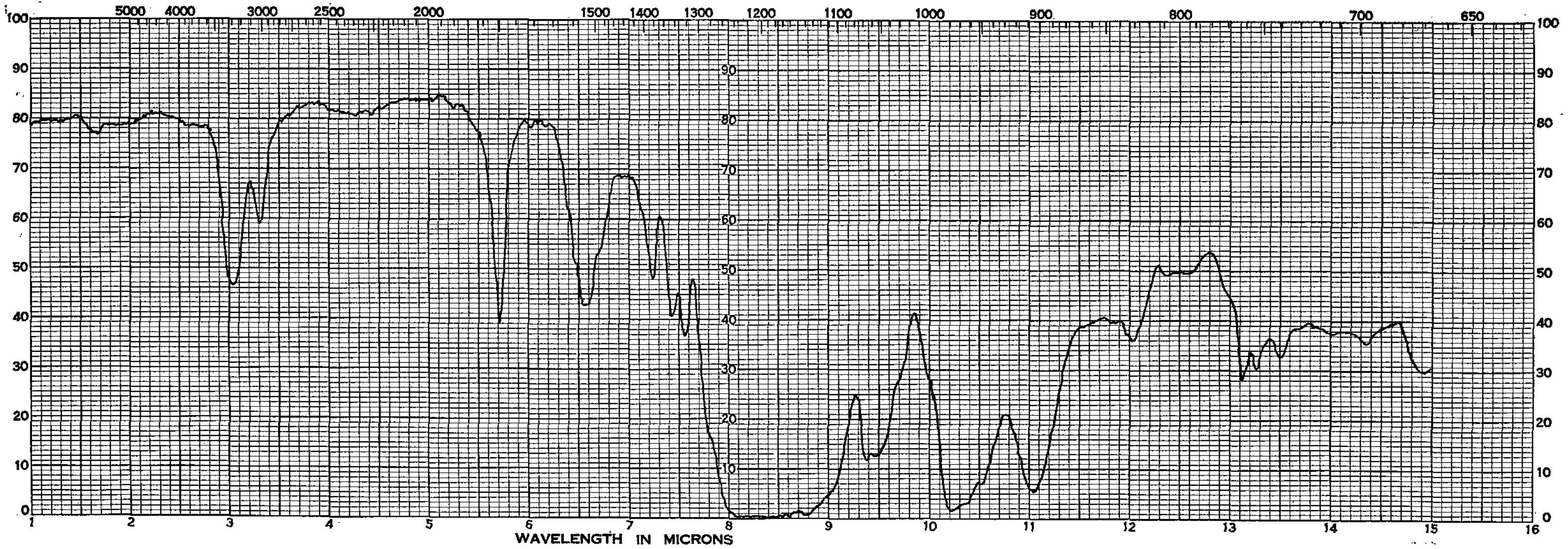


Fig. 18 3,5-bis(Perfluoroethyl)-4-acetylamino-1,2,4,4H-triazole

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1. ORIGINATING ACTIVITY *(Corporate author)* University of Florida Gainesville, Florida	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP -- --

3. REPORT TITLE

THERMALLY STABLE PERFLUORINATED POLYMERS

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
Final Summary Report - 1 March 1964 to 28 February 1965

5. AUTHOR(S) *(Last name, first name, initial)*

Brown, Henry C.

6. REPORT DATE March 1965	7a. TOTAL NO. OF PAGES 49	7b. NO. OF REFS --

8a. CONTRACT OR GRANT NO. AF 33(615)-1368	9a. ORIGINATOR'S REPORT NUMBER(S) ML-TDR-64-142, Part II
b. PROJECT NO. 7340	
c. Task No. 734004	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)* --
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13. ABSTRACT

Work on the 1,2,4-triazole polymer system, in which these heterocyclic groups are connected by perfluoroalkylene chains, has included further study and assigment of structure to the cyclic product from perfluoroglutaronitrile and hydrazine, opening of this cyclic product with polymerization to poly(N^2-imidoyl perfluoroglutarhydrazidine), and synthesis of poly(perfluoropropylene-1,2,4-triazole) both from the poly(imidoyl hydrazidine) and directly from the original cyclic monomer. Other possible routes to this type of polymer and possible reaction mechanisms have been considered.

The preparation of 2,6-*bis*(perfluoroethyl)-4-hydroxy-1,3,5-triazine has been completed.

Further study of the 2-perfluoroalkyl-5-hydroxy-1,3,4-oxadiazoles as possible monomers for polymerization has been carried out.

The synthesis of a perfluoroalkyl-substituted heterocycle with an electron-donating group attached to a heteroatom, specifically 3,5-*bis*(perfluoroalkyl)-4-amino-1,2,4,4*H*-triazole has been completed and the structure verified.

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