NASA CR 137,636
SN-8249-A1
AVAILABLE TO THE PUBLIC

CROSSLINKING AND DEGRADATION MECHANISMS IN MODEL SEALANT CANDIDATES

K. L. Paciorek, J. Kaufman, and R. H. Kratzer

September 1974

Annual Report No. 1
Prepared under Contract No. NAS2-7981 by

ULTRASYSTEMS, INC.
IRVINE, CALIFORNIA

for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
AMES RESEARCH CENTER

Robert W. Rosser, Technical Manager

49

NASA CR 137,636
SN-8249-A1

CROSSLINKING AND DEGRADATION MECHANISMS IN MODEL SEALANT CANDIDATES

By K. L. Paciorek, J. Kaufman, and R. H. Kratzer

September 1974

Annual Report No. 1
Prepared under Contract No. NAS2-7981 by
ULTRASYSTEMS, INC.
Irvine, California

for

AMES RESEARCH CENTER
NATIONAL AERONAUTICS & SPACE ADMINISTRATION

Robert W. Rosser, Technical Manager

FOREWORD

This Final Report describes the work performed by the Chemicals and Materials Research Department, Ultrasystems, Inc. under contract NAS2-7981, "Study of Crosslinking and Degradation Mechanisms in Model Sealant Candidates". The investigations were carried out during the period from 26 November 1973 to 16 September 1974 by R. H. Kratzer, J. Kaufman, and K. L. Paciorek, project manager, with assistance from J. H. Nakahara. This contract was administered by NASA Ames Research Center with Dr. Robert W. Rosser as technical manager.

TABLE OF CONTENTS

Page No.

1.	SUMMARY	1
2.	INTRODUCTION	4
3.	RESULTS & DISCUSSION	5
	3.1 Model Compound Synthesis	6
	3.2 Degradation Studies	17
	3.3 Conclusions and Recommendations	27
4.	EXPERIMENTAL DETAILS AND PROCEDURES	29
5.	REFERENCES	42

LIST OF FIGURES

Page No.

1 DTA of $(n\text{-}C_7F_{15})_3C_3N_3$ 8

2 DTA of $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$ 9

3 DTA curves of terephthalonitrile-bis-N-oxide -- octanonitrile system 11

4 DTA curves of terephthalonitrile-bis-N-oxide -- perfluoroalkylether nitrile system 12

5 DTA of perfluoroalkylether substituted 1,2,4-oxadiazole 14

6 DTA of 3,5-bis(perfluoroheptyl)-1,2,4-oxadiazole 16

7 DTA of the residue N_2/H_2O 235°C treatment of n-perfluoroheptyl-s-triazine 23

8 DTA of n-perfluorooctanamide 24

9 DTA of perfluorooctanyl amidine 25

10 DTA of mixture of perfluorooctylhydrazidine and terephthaloyl chloride 38

11 DTA of mixture of perfluorooctylhydrazidine hydrochloride and terephthaloyl chloride 40

LIST OF TABLES

Page No.

I Results of Degradation Studies Performed on Perfluorinated Heterocyclics 18

II Results of Degradation Studies Performed on 1,2,4-Oxadiazoles Derived from Terephthalonitrile-Bis-N-Oxide 20

1. SUMMARY

The aim of the present study was to determine on model compounds which type of a heterocyclic ring offers the optimum properties for curing a sealant based on perfluoroalkyl ether chains.

Two heterocyclic ring systems were investigated, namely triazines and 1,2,4-oxadiazoles. Only a limited effort was extended to the preparation of triazoles. Five compounds, n-perfluoroheptyl-s-triazine, a perfluoroether substituted triazine, $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$, 1,4-bis[(5-perfluoro-n-heptyl)-1,2,4-oxadiazolyl]-benzene, its perfluoroalkylether substituted analogue, and 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole were synthesized and characterized. To eliminate the effect due to a tertiary fluorine present in branched materials, the pure n-alkyl-compounds were prepared.

The main starting material, perfluoro-n-octanonitrile, was obtained from commercially available perfluoro-n-octanoic acid via a three step synthesis.

Heating the perfluoro-n-octanonitrile at 190°C in a sealed tube with 5 mol percent of silver oxide gave the perfluoro-n-heptyl triazine in 84% yield; using the same technique the perfluoroether triazine $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$, was afforded in 78% yield from the respective nitrile. 3,5-Bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was obtained in a three step reaction sequence in an overall yield of 46%. Interaction of terephthalonitrile-bis-N-oxide with perfluoro-n-octanonitrile gave 1,4-bis[(5- perfluoro-n-heptyl)-1,2,4-oxadiazolyl]-benzene, in 78% yield. In a similar manner the perfluoroalkylether substituted terephthalonitrile-bis-N-oxide derived oxadiazole was prepared in a 62% yield.

The degradation investigations were performed in sealed ampoules of ca 50 ml volume over a period of 48 hr at 235 and 325°C. The media studied were nitrogen, air, and nitrogen/water. The quantities of material employed were between 0.5-1.0 g, whereas the gas pressures used were ca 350 mm at room temperature. At the conclusion of the test both the involatile and volatile components were measured, weighed, and analyzed.

The perfluoro-n-heptyl-s-triazine was recovered quantitatively after heating in nitrogen at 235 and 325°C and in air at 235°C (no oxygen depletion occurred). In air at 325°C 98.3% of the starting material was recovered unchanged, however, 89% (5.5 mg) of the available oxygen was used up. Conducting the test at 235°C in nitrogen/water resulted in complete transformation of the triazine, mainly to the amide. No starting material was recovered. Among the condensible volatiles CO_2 and fluorinated hydrocarbons were found.

The perfluoroalkylether triazine was recovered unchanged (99.4%) from the treatment in nitrogen, air, and nitrogen/water at 235°C. At 325°C in air it underwent ca 1.5% degradation (37% of the available oxygen was depleted) the main products formed were CO_2, SiF_4, and CO; traces of nitrile and compounds such as $[R_fCO]_2O$ and R_fCOF were also detected.

The 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole exhibited excellent thermal, thermal oxidative, and hydrolytic stability under all the conditions used.

Both of the hydrogen containing oxadiazoles decomposed extensively in air and nitrogen at 325°C. No starting materials were recovered from the air studies at 325°C; all the oxygen present was depleted. The perfluoro-n-heptyl substituted oxadiazole was oxidatively somewhat less stable than the perfluoroalkylether oxadiazole. In nitrogen/water at 235°C the hydrogen-containing oxadiazoles were recovered virtually unchanged; only small quantities of carbon dioxide and fluorinated hydrocarbons were formed.

To conclude,the low thermal and oxidative stability of the 1,2,4-oxadiazoles derived from terephthalonitrile-bis-N-oxide seems to stem from the ready dissociation of these materials rather than the oxidative attack upon the CH moieties on the benzene ring. The thermal stability of the two triazines appears to be equivalent under the conditions employed; however the perfluoroalkyl triazine appears definitely oxidatively less stable than the perfluoroalkylether analogue, whereas its hydrolytic stability is the lowest of all the materials investigated. It is believed that this finding is due to the CF_2 group adjacent to the triazine ring. Based on the studies performed the 1,2,4-oxadiazole substituted by perfluoroalkyl moieties appears to offer the most stable system.

2. INTRODUCTION

Perfluoroalkylethers exhibit exceptionally good thermal stability in conjunction with low glass transistion temperatures and fuel resistance. These properties render perfluoroalkylethers very attractive as potential candidates for advanced sealants required to function under extremes of temperatures in a fuel environment. For such an application it is of utmost importance to avoid introduction of weak links via curing and/or chain extending operations. Furthermore, to develop a practical sealant system the crosslinking process should proceed readily, preferentially in a quantitative yield, at relatively moderate temperatures. Ideally, it is desired for both of these conditions to be fulfilled, however in real systems compromises have to be made.

To determine which type of an arrangement offers optimum properties for curing a perfluoroalkylether based sealant system one of the approaches is to study models. Following this avenue two variously substituted heterocyclic ring systems, namely, s-triazines and 1,2,4-oxadiazoles, were synthesized and their behavior and stability in thermal, thermal oxidative, and hydrolytic environments was investigated.

3. RESULTS & DISCUSSION

The objective of this investigation was to determine on specific model compounds the relative thermal, thermal oxidative, and hydrolytic stability of potential crosslinks useful for curing perfluoroalkylether elastomers. The perfluoroalkylethers available for the actual sealant development are composed of difunctional nitrile terminated materials, obtained from diacid fluoride precursors (ref. 1). Consequently in any crosslinking and/or chain extension process either the reaction of the nitrile or the acid fluoride group can be utilized. To date the main effort was centered on the nitrile moiety.

It is well known that perfluorinated nitriles are readily trimerized with a variety of catalysts, to mention just a few, e.g., ammonia, (ref. 2) silver oxide, (ref. 3) and tetraphenyltin (ref. 3,4). One of the most widely used reactions for the production of perfluoroalkyl and perfluoroalkylether triazines is the thermal decomposition of amidines (ref. 5,6). Another avenue to this heterocyclic ring system is the treatment of amidoylamidines with either perfluorinated acid halides (ref. 7,8) or perfluorinated acid anhydrides (ref. 9). Inasmuch as the triazine ring can be readily prepared from nitriles in a number of different ways and since it is well known to exhibit good thermal stability, (ref. 2) further investigation of this system, specifically as potential crosslink for sealant application, appeared warranted.

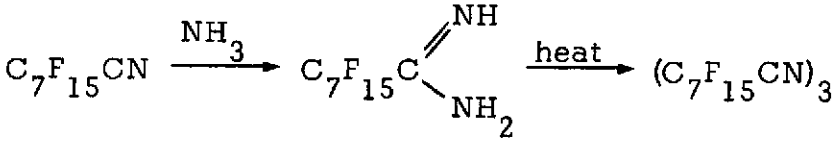
1,2,4-Oxadiazoles, in particular the members of the series formed via interaction of nitriles with terephthalonitrile-bis-N-oxide, (TPNO), offer another attractive chain extension moiety in view of their ease of formation (ref. 10-12) and the apparent elastomeric properties of products obtained in preliminary investigations (ref. 13). It has been shown by Brown and Wetzel (ref. 14) that the perfluoroalkyl substituted 1,2,4-oxadiazoles exhibit excellent thermal stability, e.g., no detectable change after 1 hr exposure to 400°C, presumably in vacuo. On the other hand

Critchley and Pippett (ref. 15) report that the decomposition temperatures of mixed phenyl-perfluoroalkyl analogues range between 200-240°C. These authors claim that the analogous 1,3,4-oxadiazoles present a significantly more thermally stable ring system with decomposition temperatures in the range of 240-300°C.

No truly extensive and reliable thermal, thermal oxidative, and hydrolytic studies were performed on any of the systems discussed above. This is in particular true for the perfluoroalkylether substituted compounds. Thus, to verify the predictions and claims the actual investigations needed to be conducted. None of the required materials was commercially available, thus all the model compounds had to be synthesized. For ease of presentation this discussion will therefore be divided into two main portions, (a) model compound synthesis, and (b) degradation studies.

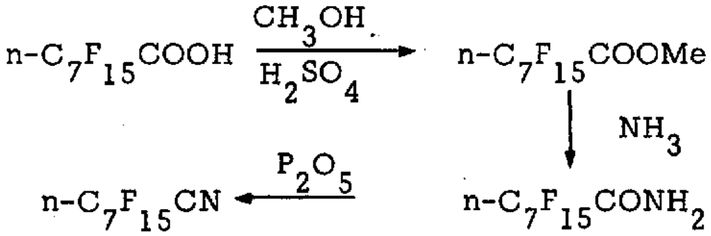
3.1 Model Compound Synthesis

As was briefly delineated above triazine rings appear to offer a very attractive crosslinking system for perfluoroalkylether based sealants. One of the triazines selected for model studies was the perfluoroheptyl substituted compound in view of its high boiling point and no detectable vapor pressure at room temperature which would permit ready separation of any volatile degradation products from the starting material. Initial synthesis was performed using the commercially available perfluorooctanonitrile via the amidine route, i.e.,



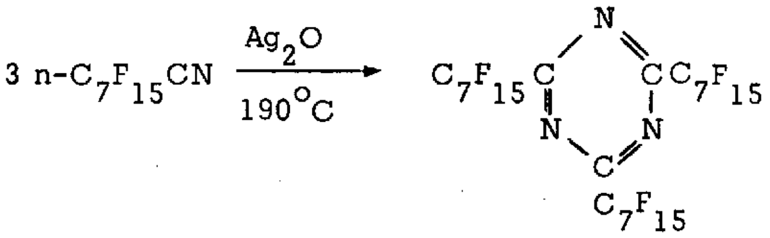
$$C_7F_{15}CN \xrightarrow{NH_3} C_7F_{15}C\begin{array}{l} /\!\!/ NH \\ \diagdown NH_2 \end{array} \xrightarrow{heat} (C_7F_{15}CN)_3$$

Based on the recovered ammonia 88% conversion took place; however, the triazine was contaminated with traces of the amidine. The product failed to solidify on cooling below room temperature, indicating that it contained both n- and branched C_7F_{15} moieties. This was confirmed by NMR spectroscopy. For the envisioned study homogeneity of the product is of utmost importance to determine whether isomerization is one of the processes which do occur under the test conditions. Pure n-isomer could be obtained only in the form of the octanoic acid. Accordingly the n-octanonitrile was synthesized in an overall yield of 75.3% following the procedure of Berry (ref. 16).



$$\begin{tikzcd}
\text{n-}C_7F_{15}COOH \arrow[r, "CH_3OH", "H_2SO_4"'] & \text{n-}C_7F_{15}COOMe \arrow[d, "NH_3"] \\
\text{n-}C_7F_{15}CN & \text{n-}C_7F_{15}CONH_2 \arrow[l, "P_2O_5"']
\end{tikzcd}$$

Since the amidine route to the triazine proved relatively tedious the perfluoro-n-heptyl-s-triazine was prepared in 84% yield following the method of Dorfman and Emerson (ref. 3) by heating perfluoro-n-octanonitrile at 190°C in a sealed tube with 5 mole percent of silver oxide.



Using the same technique the perfluoroether triazine $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$, bp 101-104°C/0.001 mm Hg was afforded in 78% yield from the respective nitrile. The perfluoroalkylethernitrile, $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$, was obtained from Dr. C. Tamborski, Air Force Materials Laboratory. The infrared spectrum of the perfluoroalkylether substituted triazine was very similar to the infrared spectra reported by Croft (ref. 17) for its higher homologues. The differential thermal analysis cu for the two triazines are presented in Figures 1 and 2.

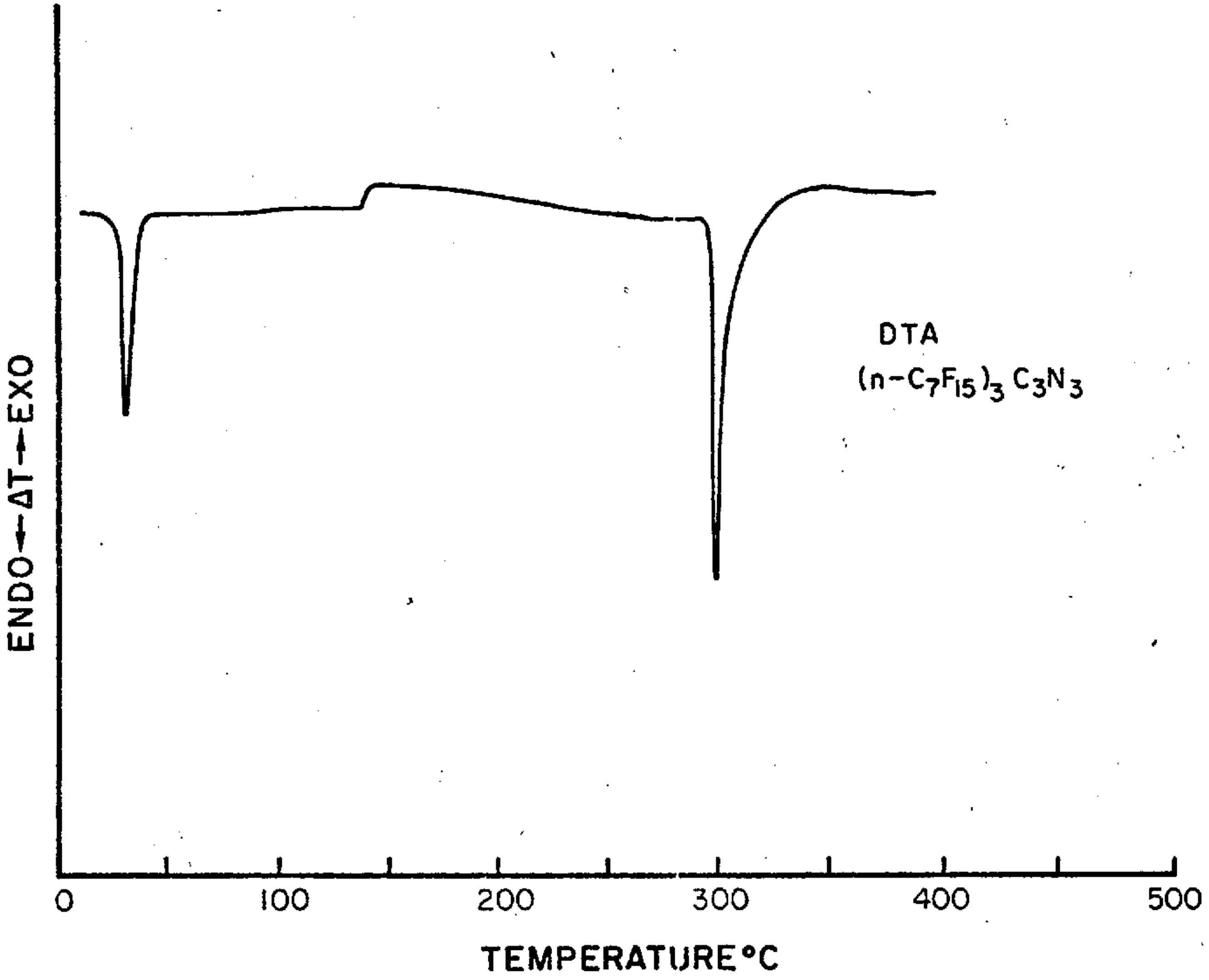


Figure 1: DTA of $(n\text{-}C_7F_{15})_3C_3N_3$

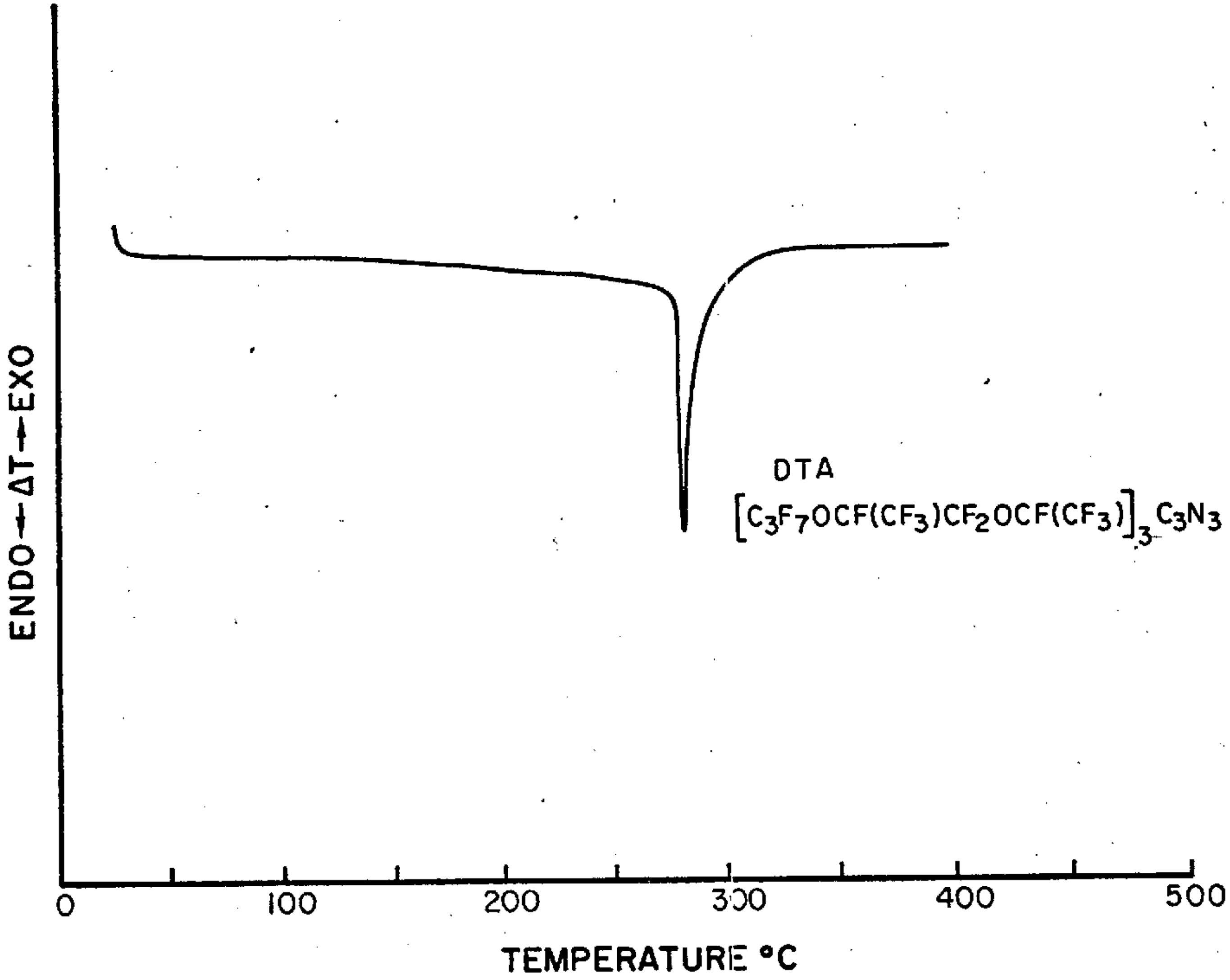
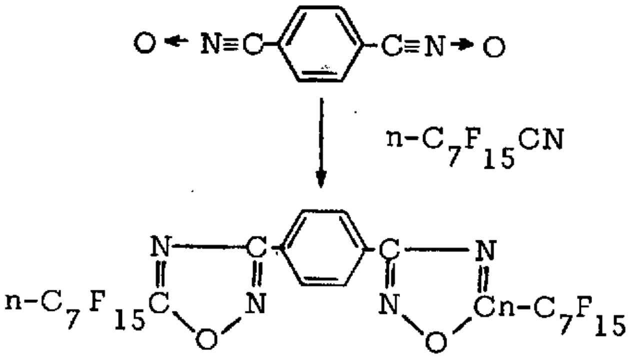


Figure 2: DTA of $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$

For the synthesis of the 1,2,4-oxadiazoles prepared under this program the same two nitriles were employed as those utilized for obtaining the above described triazines. This allowed valid comparisons to be made between the two ring systems.

To determine the optimum reaction conditions for the preparation of 1,2,4-oxadiazoles from the interaction of terephthalonitrile-bis-N-oxide and the given perfluorinated nitrile the differential thermal analysis curves of the mixtures were obtained (see Figures 3 and 4). Treatment of terephthalonitrile-bis-N-oxide (received from Hughes Aircraft Company) with an excess of perfluoro-n-octanonitrile at 50-57°C gave 1,4-bis-[(5-perfluoro-n-heptyl)-1,2,4-oxadiazolyl]-benzene, mp 127-128°C, in 78% yield. In a similar manner the perfluoroalkylether substituted terephthalonitrile-bis-N-oxide derived bis-oxadiazole was prepared. The reaction was carried out at 85-90°C; the product, bp 140-142°C/0.001 mm Hg,was obtained in 62% yield. As indicated above the optimum reaction temperature was determined from a DTA curve of the mixture of the two components (Figure 4). It should be noted that in view of the thermal instability of terephthalonitrile-bis-N-oxide and the relatively non-reactive nature of the perfluoroalkylether nitrile the range for the reaction temperature is very narrow. The two reactions can be represented as follows:



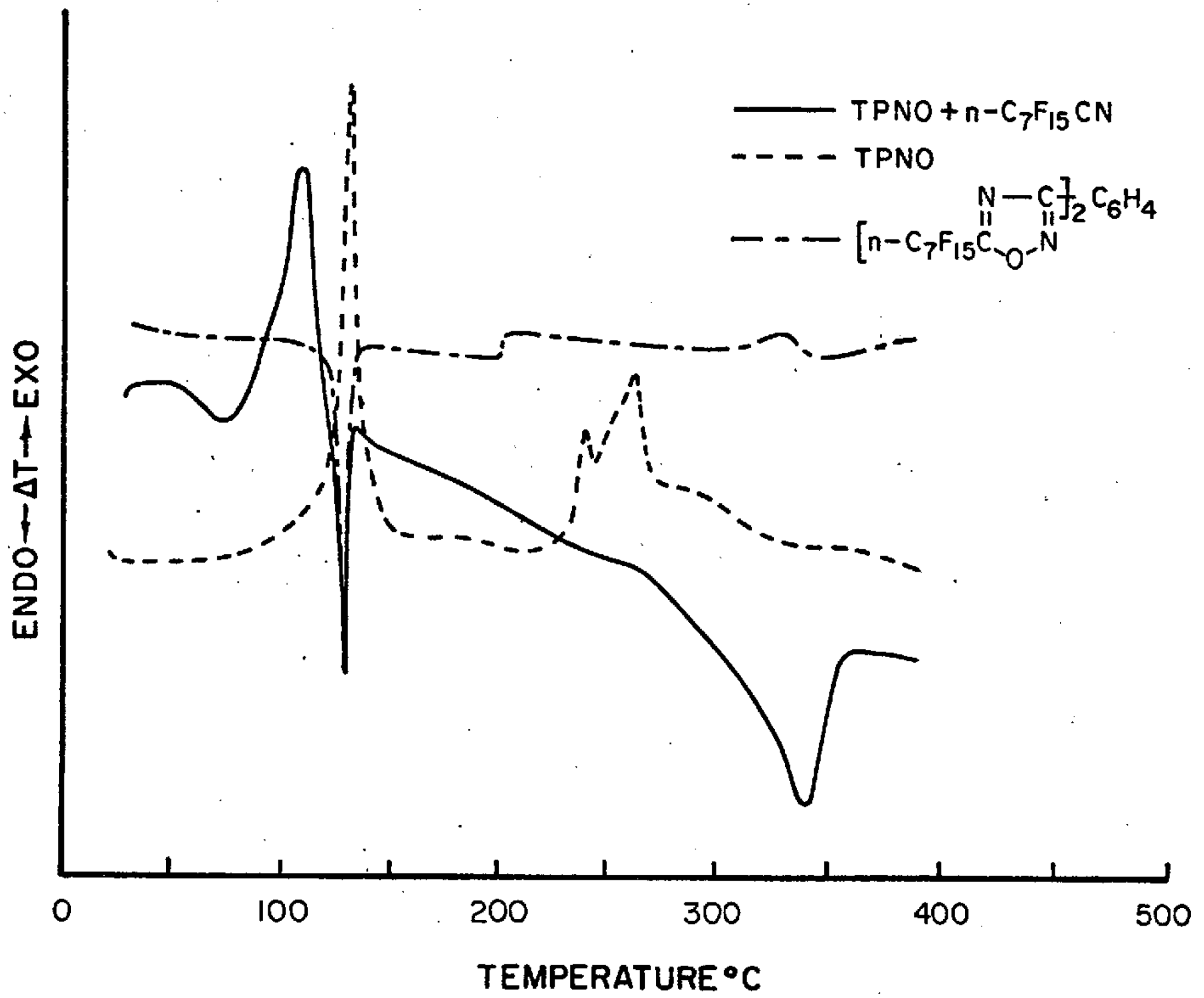


Figure 3: DTA curves of terephthalonitrile-bis-N-oxide--octanonitrile system

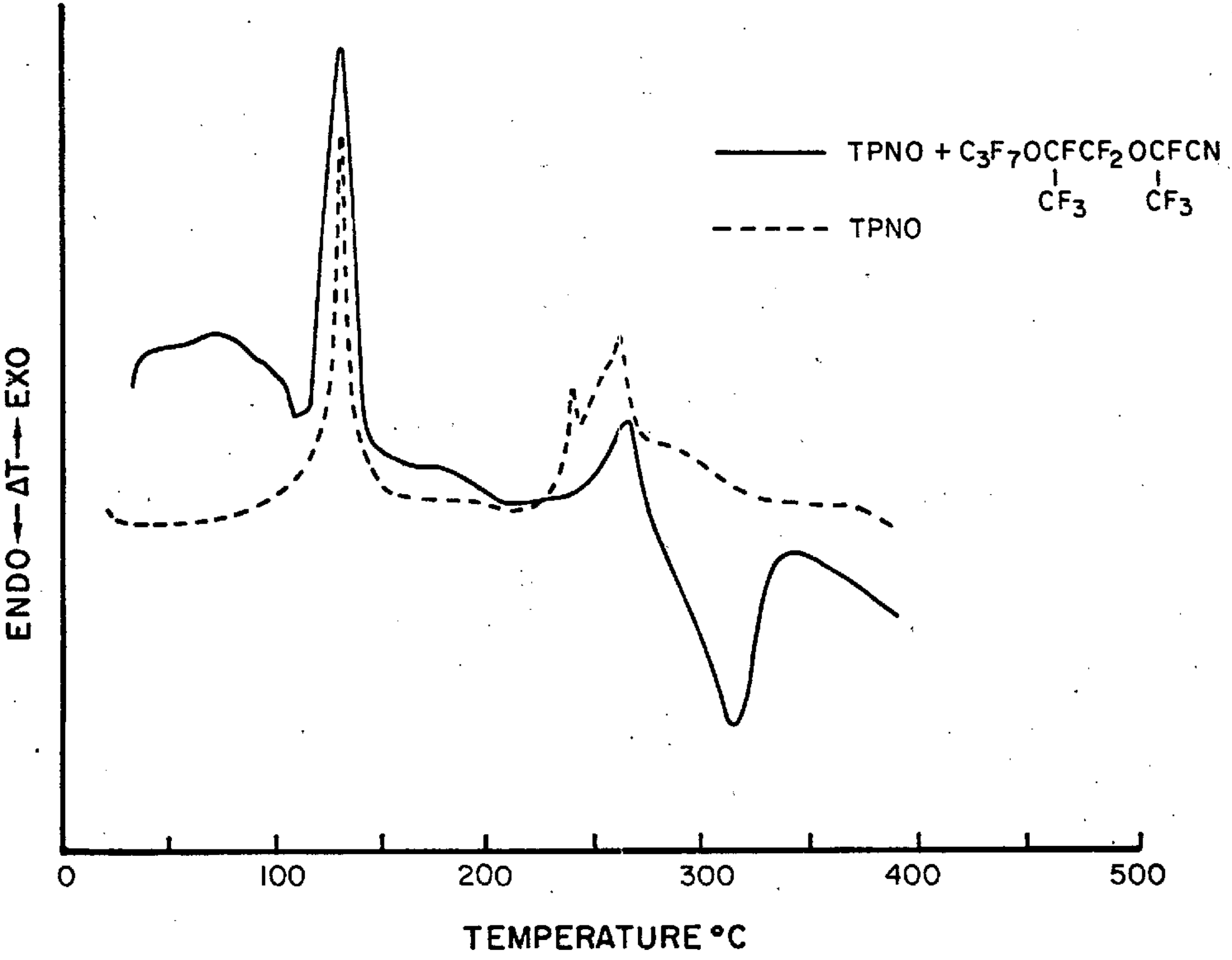
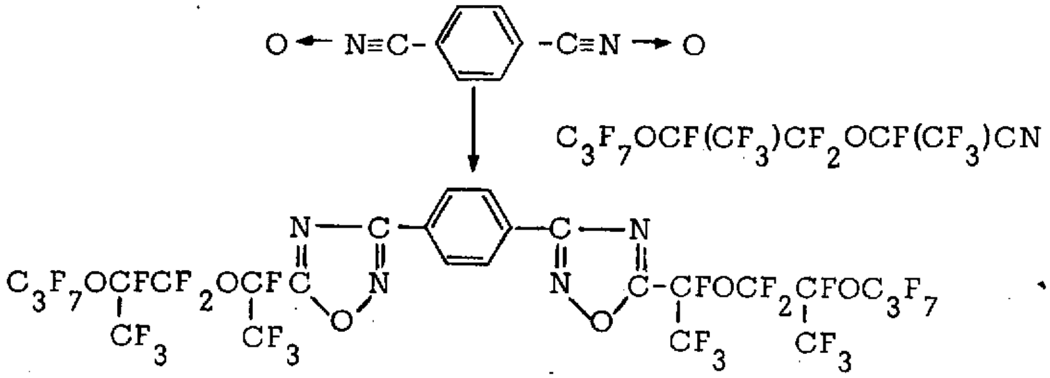


Figure 4: DTA curves of terephthalonitrile-bis-N-oxide --perfluoroalkylether nitrile system



The effective lowering of T_g by the perfluoroalkylether group as compared to a perfluoroalkyl substituent is evident in comparing the melting points of the respective triazines and oxadiazoles. This fact is particularly apparent in the case of the terephthalonitrile-bis-N-oxide derived 1,2,4-oxadiazoles where the perfluoroheptyl substituted material is a high melting solid (mp ~ 130°C), whereas the perfluoroalkylether-containing compound is a liquid at room temperature (see Figures 3 and 5).

As mentioned above, the objective of this program was to determine the relative thermal, oxidative, and hydrolytic stabilities of promising crosslinks. In order to make a valid comparison between the two chosen models, the s-triazine and the 1,2,4-oxadiazole ring systems, all other differences between the two compound classes, which may affect these stabilities, obviously have to be eliminated. However, the compounds described so far differ in one, potentially very important aspect: the two oxadiazoles have a hydrogen containing phenylene bridging group as a component, whereas the two s-triazine candidates do not contain this moiety. Accordingly, to eliminate the possible influence of the phenylene group in the oxadiazoles described above, 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole was synthesized. It was obtained as a low melting solid (mp 27-28°C) using the procedure of Brown and Wetzel (ref. 14)

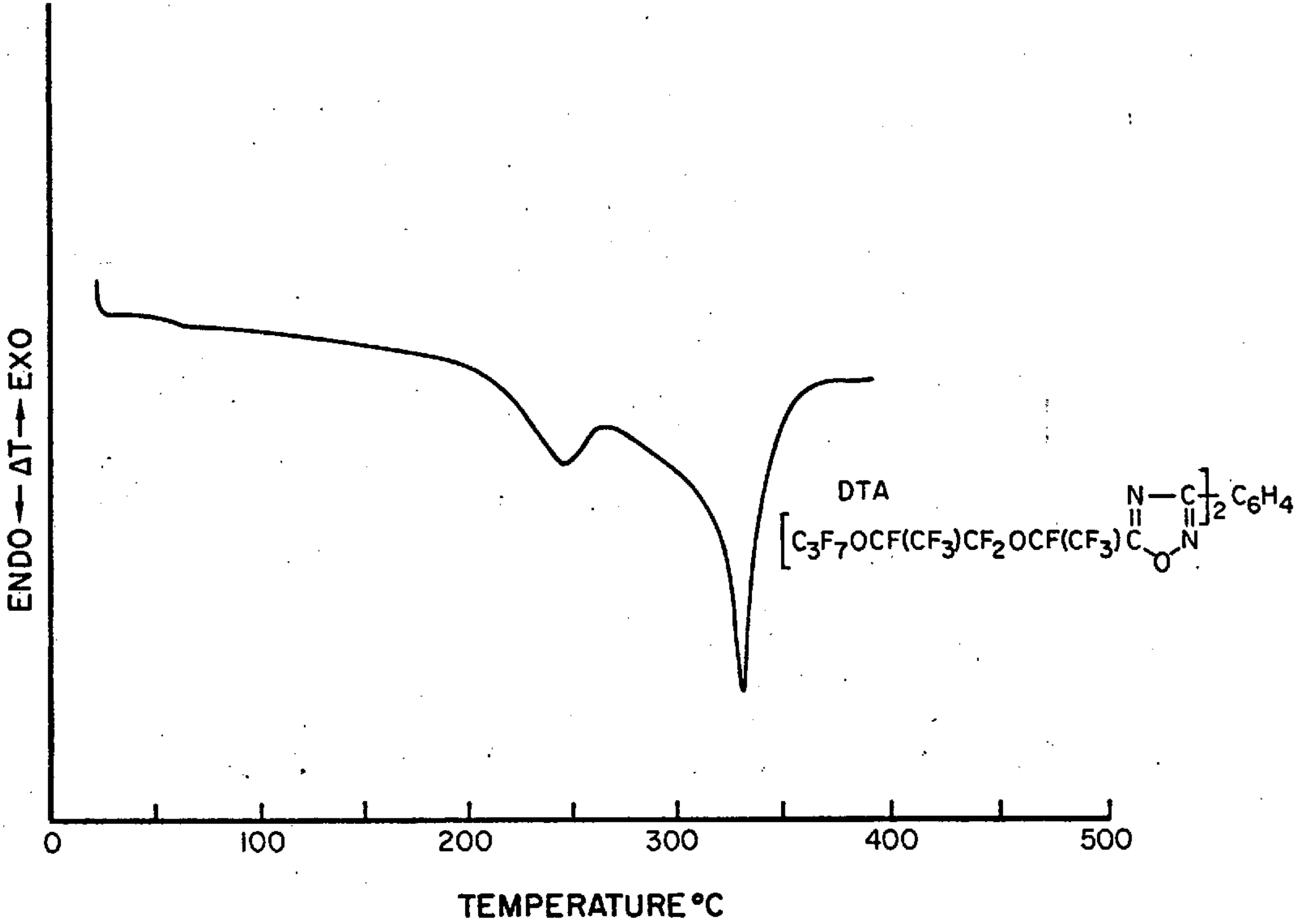
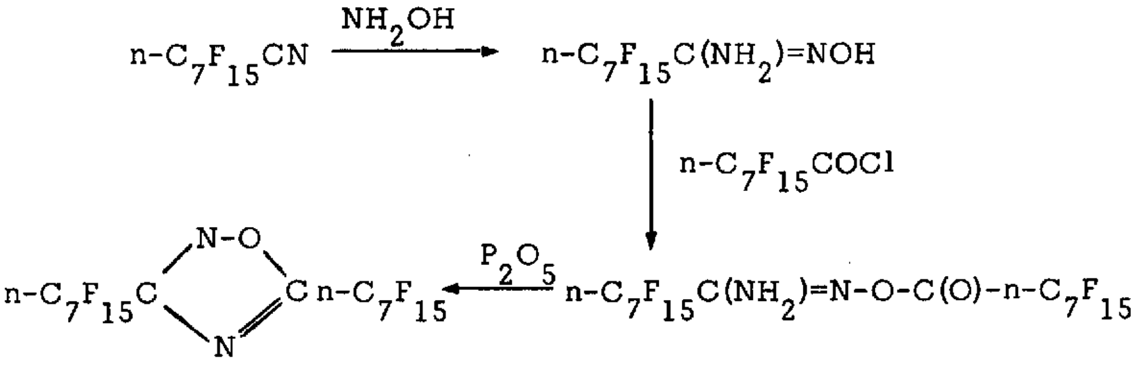
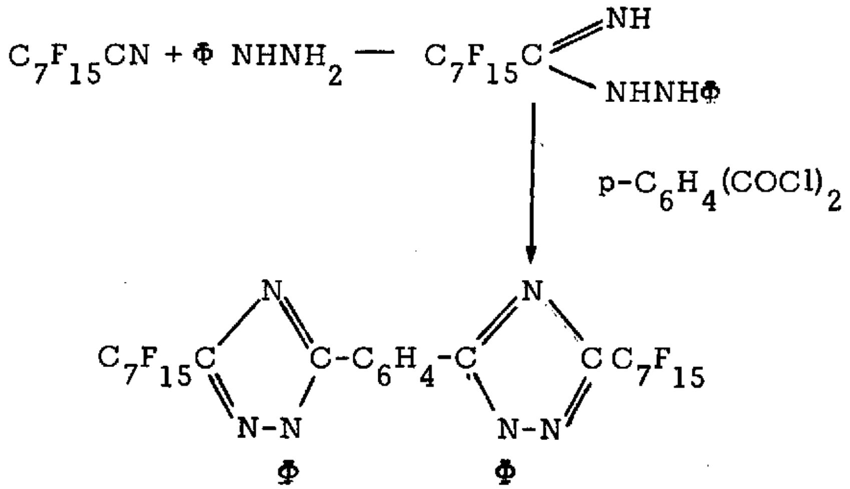


Figure 5: DTA of perfluoroalkylether substituted 1,2,4-oxadiazole



in an overall yield of 46%. The differential thermal analysis curve of this material is given in Figure 6.

A third possible ring candidate for sealant curing was the triazole system. Inasmuch as the N-H moiety in the unsubstituted triazoles constitutes a potential vulnerable site the synthesis effort was directed at preparation of a N-phenyl substituted compound. The actual model chosen was the phenylene linked bis-triazole in analogy to the terephthalonitrile-bis-N-oxide derived oxadiazoles. The following reaction sequence was initially employed:



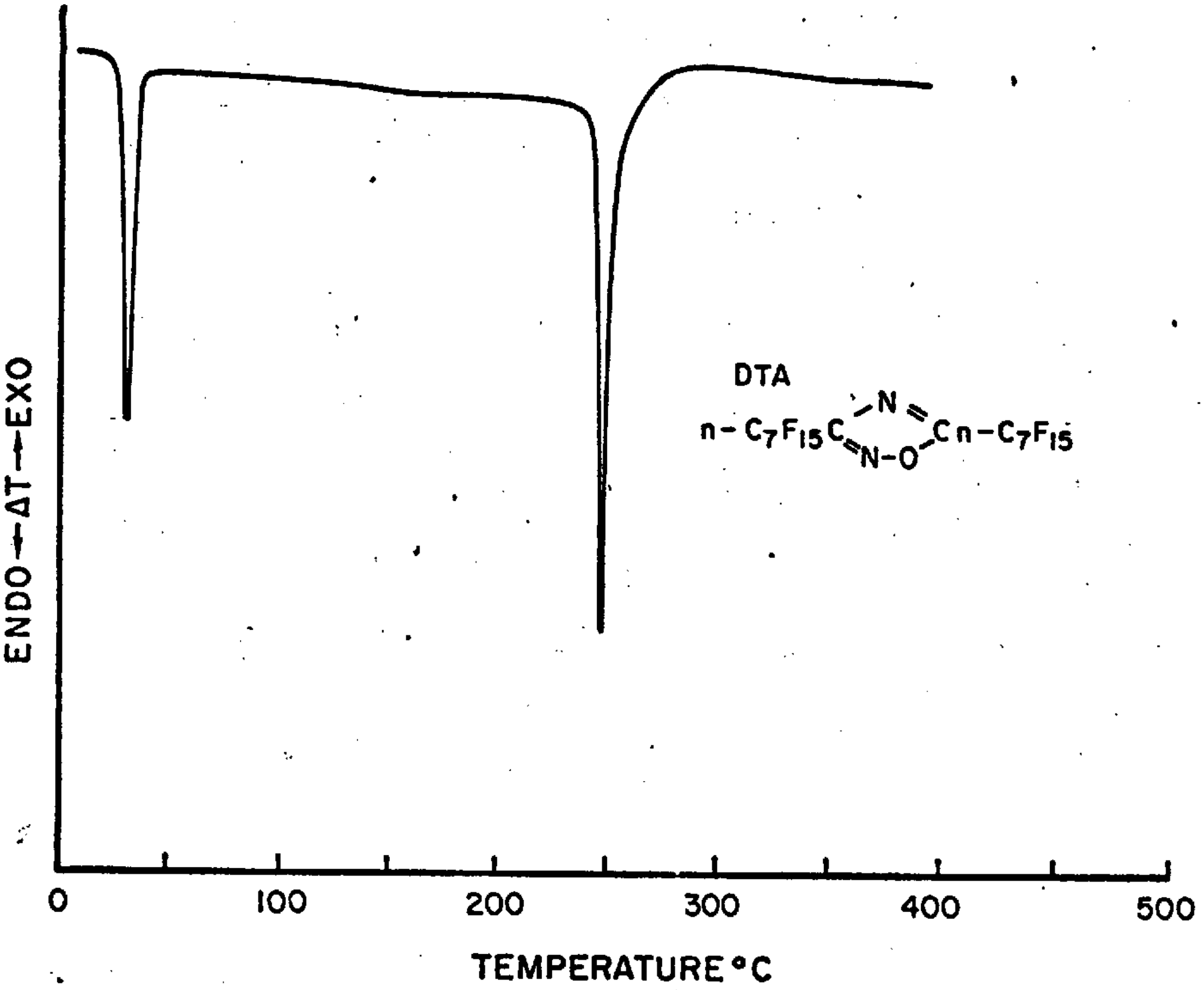


Figure 6 : DTA of 3,5-bis(perfluoroheptyl)-1,2,4-oxadiazole

The hydrazidine, $C_7F_{15}C(=NH)NHNH\Phi$ was obtained in 46.7% yield via the reaction of perfluorooctanonitrile with phenylhydrazine. Interaction of the hydrazidine $C_7F_{15}C(=NH)NHNH\Phi$ with terephthaloyl chloride in the absence of solvent at 130°C gave what appeared to be the desired triazole in trace quantities only. Conducting this reaction with the hydrazidine hydrochloride (which was prepared from the hydrazidine in a quantitative yield) again in the absence of solvent gave the triazole, mp 176-181°C in ca 22% yield. The reaction of the hydrazidine, $C_7F_{15}C(=NH)NHNH\Phi$, with terephthaloyl chloride in ether resulted in the formation of the hydrazidine hydrochloride showing that partial reaction did occur; one mol of the hydrazidine reacting with terephthaloyl chloride under hydrogen chloride evolution, the other acting as hydrogen chloride acceptor. Due to limited funds the triazole synthesis was not pursued further.

3.2 Degradation Studies

The degradation investigations were performed in sealed ampoules of ca 50 ml volume over a period of 48 hr at 235 and 325°C. The media studied were nitrogen, air, and nitrogen/water. The results of these experiments are summarized in Tables I and II. The materials tested were the five model compounds synthesized, tris-perfluoro-n-heptyl-s-triazine, the perfluoroether substituted triazine $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$, 1,4-bis-[(5-perfluoro-n-heptyl)-1,2,4-oxadiazolyl]-benzene, its perfluoroalkylether substituted analogue, and 3,5-bis(perfluoro-n-hetpyl]-1,2,4-oxadiazole.

<u>Tris-perfluoro-n-heptyl-s-triazine</u> was recovered unchanged (Table I) after heating in nitrogen at 235 and 325°C and in air at 235°C (no oxygen depletion occurred). In air at 325°C 98.3% of the starting material was recovered unchanged, however, 89% (5.5 mg) of the available oxygen was used up. Thus it could be deduced that in the presence of additional air (oxygen) more extensive decomposition would have taken place. The quantity of oxygen present in all the tests employing air was ca 0.20 mmol, which was by far insufficient for complete oxidation since the amount of sample

TABLE I

RESULTS OF DEGRADATION STUDIES PERFORMED
ON PERFLUORINATED HETEROCYCLICS[a]

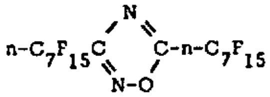
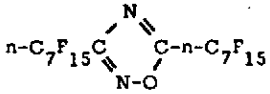
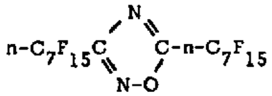
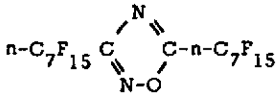
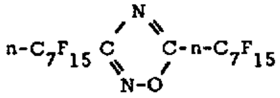
Compound	Temp °C	Atmosphere	Starting Material		Volatiles Formed									
					SiF_4		CO_2		CO		R_fCN		Other	
			Used mg	Recovered %[b]	mg	%[c]	mg	%[d]	mg	%[d]	mg	%[b]	mg	%[b]
$(n-C_7F_{15})_3C_3N_3$	235	Air	1099.3	100	0.34	0.03	1.10	0.11	-	-	-	-	-	-
$(n-C_7F_{15})_3C_3N_3$	235	N_2/H_2O[e]	1028.2	none[f]	-	-	10.77	1.18	-	-	-	-	344.7[f]	n.a.[h]
$(n-C_7F_{15})_3C_3N_3$	325	N_2	1031.7	99.8	0.25	0.02	0.72	0.08	-	-	1.6	0.16	-	-
$(n-C_7F_{15})_3C_3N_3$	325	Air	1003.6	98.3	10.35	1.04	16.02	1.79	0.15	0.03	2.1	0.21	3.0	0.30
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$	235	Air	1055.8	99.6	1.12	0.11	2.07	0.23	0.06	0.01	-	-	1.0	0.09
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$	235	N_2/H_2O[g]	999.8	99.4	-	-	0.86	0.1	-	-	-	-	99.5[g]	n.a.[h]
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$	325	N_2	1018.4	98.9	1.80	0.19	1.82	0.22	0.20	0.04	T	T	5.0	0.50
$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]_3C_3N_3$	325	Air	1019.2	98.5	6.4	0.69	8.6	1.03	0.69	0.13	T	T	0.1	T
	235	Air	777.3	99.5	-	-	0.11	0.02	-	-		-	0.3	0.04
	235	N_2	708.5	99.5	-	-	-	-	-	-	-	-	-	-
	235	N_2/H_2O[i]	716.4	99.1	-	-	0.20	0.03	-	-	-	-	64.1[i]	n.a.
	325	N_2	673.2	99.7	T	T	0.32	0.05	-	-	-	-	0.3	0.04
	325	Air	610.1	99.3	-	-	0.67	0.13	-	-	-	-	0.1	0.02

TABLE I

(Continued)

a All these degradations were performed in sealed tubes of ca 50 ml volume over a period of 48 hr under the specified conditions of atmosphere and temperature. The pressures employed were ca 350 mm at room temperature.

b Weight percent of starting material.

c Weight percent of total fluorine present.

d Weight percent of total carbon present.

e The water employed was 101.0 mg (5.606 mmol).

f The involatile residue amounted to 763.7 mg. Based on infrared analysis it consisted of pure n-$C_7F_{15}CONH_2$, which corresponds to 59.9% of the triazine employed. The 344.7 mg of unidentified volatile decomposition products contained some water and large amounts of fluorinated hydrocarbons.

g The water employed was 103.9 mg (5.767 mmol); the 99.5 mg recovered in volatiles was mainly water plus traces of fluorinated hydrocarbons.

h Not applicable.

i The water employed was 64.5 mg (3.580 mmol); the 64.1 mg recovered in volatiles was almost pure water with just traces of fluorinated hydrocarbons.

TABLE II

RESULTS OF DEGRADATION STUDIES PERFORMED ON 1,2,4-OXADIAZOLES
DERIVED FROM TEREPHTHALONITRILE-BIS-N-OXIDE [a]

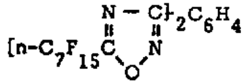
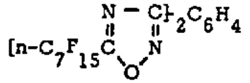
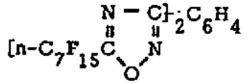
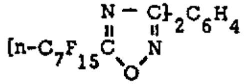
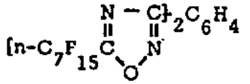
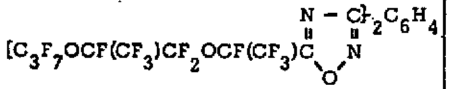
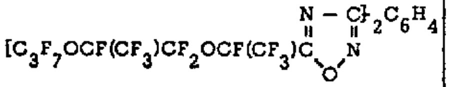
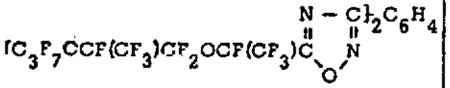
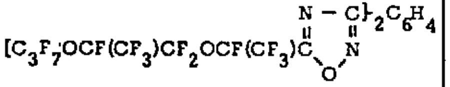
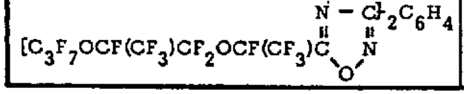
Compound	Temp °C	Atmosphere	Starting Material		Volatiles Formed									
			Used	Recovered	SiF_4		CO_2		CO		R_fCN		Other	
			mg	%[b]	mg	%[c]	mg	%[d]	mg	%[d]	mg	%[b]	mg	%[b]
	235	N_2	1008.1	98.8	0.07	0.01	1.71	0.15	-	-	7.75	0.77	0.3	0.03
	235	Air	1009.4	94.7	0.72	0.09	12.19	1.08	0.51	0.07	33.0	3.27	2.1	0.21
	235	N_2/H_2O[f]	1016.1	98.3	-	-	5.91	0.52	-	-	-	-	108	n.a.[e]
	325	N_2	1004.0	none	70.80	8.55	94.44	8.43	1.75	0.25	190.1	18.93	93.9	9.35
	325	Air	1001.5	none	263.0	31.82	170.00	15.20	7.86	1.11	?	?	255.6	25.52
	235	N_2	472.0	100	T	T	0.76	0.16	-	-	0.46	0.10	0.5	0.10
	235	Air	433.1	99.5	T	T	0.83	0.19	-	-	0.43	0.10	0.4	0.09
	235	N_2/H_2O[g]	453.8	99.1	T	T	2.48	0.53	0.07	0.02	-	-	35.8[g]	n.a.
	325	N_2	424.1	none	65.95	19.59	61.95	14.22	5.42	1.95	68.9	16.24	169.3	39.9
	325	Air	460.2	none	58.86	16.11	65.14	13.78	4.39	1.46	90.6	19.68	133.3	42.0

TABLE II
(Continued)

[a] All these degradations were performed in sealed tubes of ca 50 ml volume over a period of 48 hr under the specified conditions of atmosphere and temperature. The pressures employed were ca 350 mm at room temperature.

[b] Weight percent of starting material.

[c] Weight percent of total fluorine present.

[d] Weight percent of total carbon present.

[e] Not applicable.

[f] The water employed was 100.6 mg (5.584 mmol); the 108 mg recovered in volatiles was mainly water plus some fluorinated hydrocarbons.

[g] The water employed was 33.3 mg (1.848 mmol); the 30.8 mg recovered in volatiles was mainly water plus some fluorinated hydrocarbons.

used varied between 1 and 0.4 mmol. However, it has to be stressed that it was not the primary objective to determine the course of a complete oxidation, but rather establish whether oxidation does occur under given conditions.

Heating perfluoro-n-heptyl-s-triazine at 235°C in a water containing nitrogen atmosphere resulted in complete transformation of the triazine. No starting material was recovered. The infrared spectrum of the residue (736.7 mg) indicated pure n-$C_7F_{15}CONH_2$ which would indicate a 59.9% conversion of the triazine to the amide. However the DTA curve showed an additional endotherm at ca 85°C (compare Figures 7 and 8). Perfluoro-n-octanoic acid melts at 58.5-60°C; thus the endotherm at 85°C cannot be attributed to this material. On the other hand, the amidine melts above 90°C (see Figure 9) and it is conceivable, although not very likely, that this endotherm is due to its presence. Among the condensible volatiles CO_2 and a large fraction (344.7 mg) of unidentified products was found. The latter contained some water and large concentrations of fluorinated hydrocarbons based on great abundancies at m/e = 51 ($-CF_2H$) and m/e = 101 ($-CF_2CF_2H$) in the mass spectrum of this fraction. These hydrogen containing species must have been formed via reaction with water since water is the only potential hydrogen donor in the system.

The perfluoroalkylether triazine was recovered unchanged (~ 99.5%) from the treatment in air and nitrogen/water at 235°C. At 325°C in air it underwent ca 1.5% degradation (37% of the available oxygen was depleted). The main products formed were CO_2, SiF_4, and CO; traces of nitrile and compounds such as $[R_fCO]_2O$ and R_fCOF were also detected. The formation of SiF_4 and to a degree CO_2 observed in the majority of the experiments is most likely due to reaction of the active fluorinated species, possibly R_fCOF, with the ampoule walls. In all the decomposition studies fluorinated hydrocarbons were observed; in some instances in just trace quantities. In the fully fluorinated materials no hydrogen is present, however some hydrogen is available from the Si-OH entities in the ampoule walls.

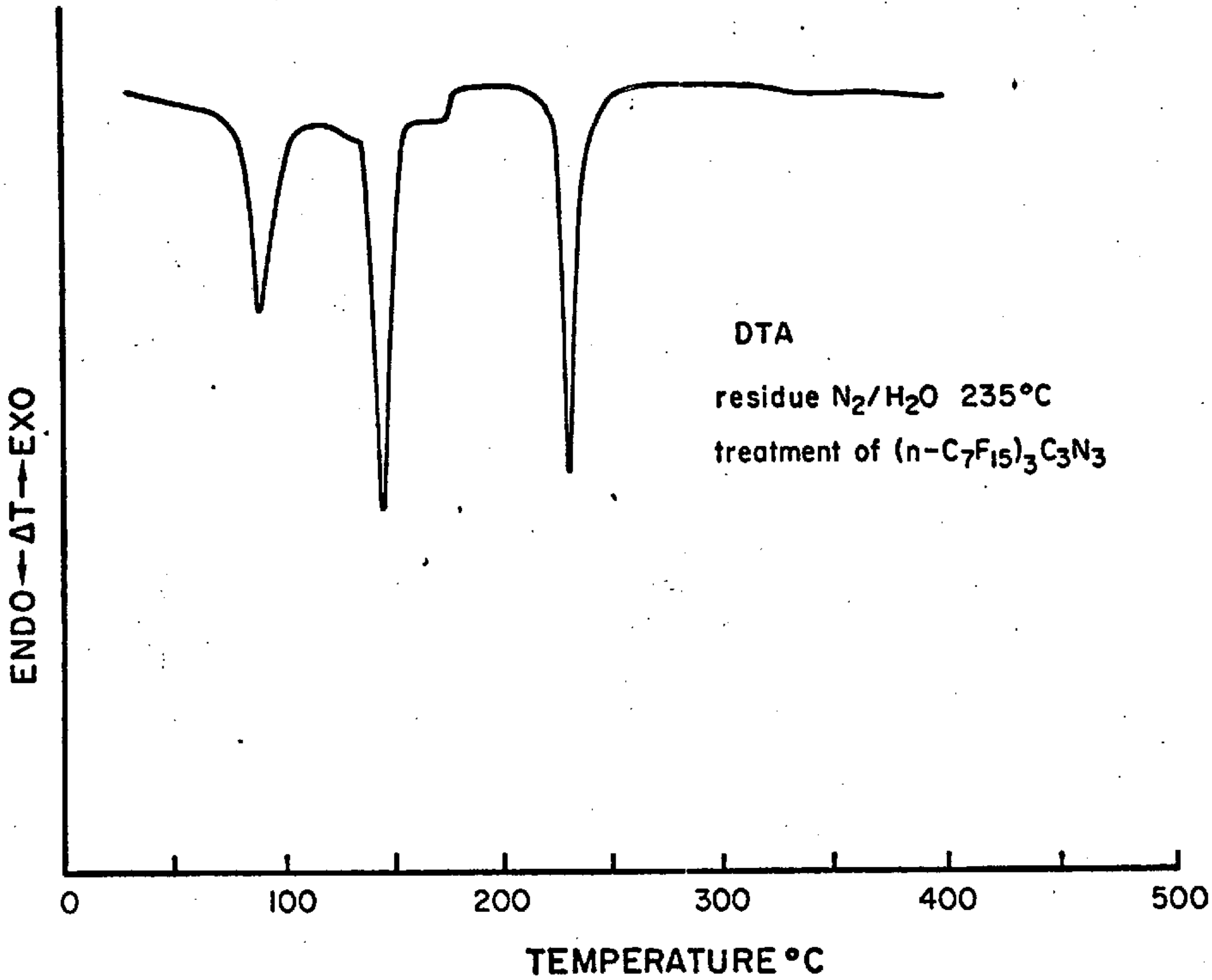


Figure 7: DTA of the residue N_2/H_2O 235°C treatment of n-perfluoroheptyl-s-triazine

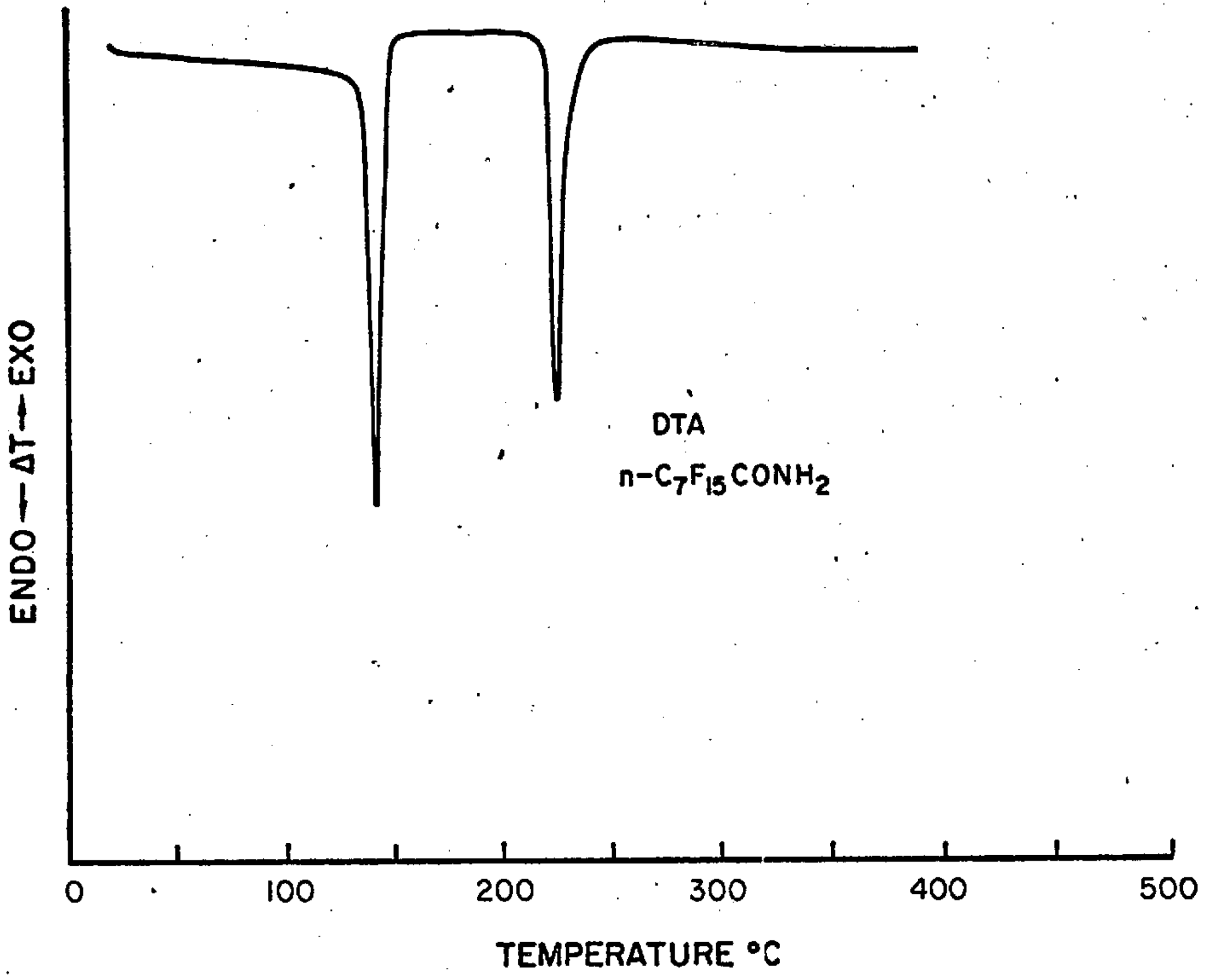


Figure 8: DTA of n-perfluorooctanamide

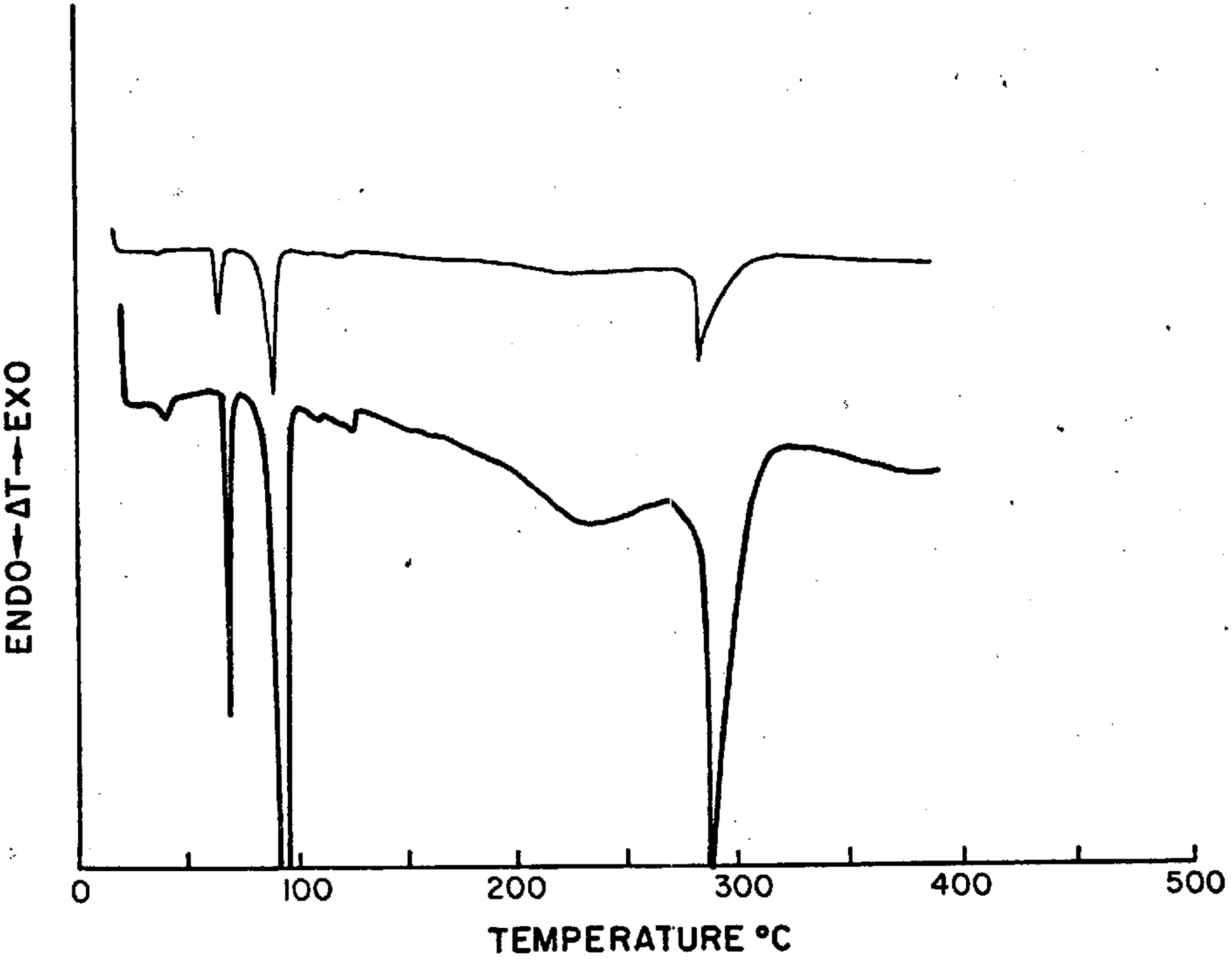


Figure 9: DTA of perfluorooctanyl amidine.

The 3,5-bis(perfluoro-n-heptyl)-1,2,4-oxadiazole exhibited excellent thermal, thermal oxidative, and hydrolytic stability as is obvious from the data given in Table I. In none of the tests conducted in air was oxygen depletion observed.

Both of the terephthalonitrile bis-N-oxide derived oxadiazoles decomposed extensively in air and nitrogen at 325°C. The data are summarized in Table II. No starting material was recovered from the air studies at 325°C; all the oxygen present was completely depleted. Inasmuch as the oxygen available was limited, after initial oxygen uptake the experiment performed in "air" was actually proceeding in nitrogen. This is in agreement with the closely comparable product composition found in the nitrogen and air tests.

The perfluoro-n-heptyl substituted oxadiazole was oxidatively (at 235°C, in air) somewhat less stable than the perfluoroalkylether based oxadiazole, i.e., 94.7 versus 99.5% of starting material recovered. Furthermore the oxygen depletion at 235°C was ca 3% for the perfluoroalkylether oxadiazole whereas in the case of the perfluoroalkyl substituted material it amounted to 51%. In nitrogen/water at 235°C the hydrogen-containing oxadiazoles were recovered virtually unchanged; only small quantities of carbon dioxide and fluorinated hydrocarbons were formed.

The infrared spectra of the terephthalonitrile-bis-N-oxide derived 1,2,4-oxadiazole residues (after all the 235°C treatments) exhibited weak absorptions at 5.72μ (from the perfluoroalkylether substituted material) and 5.80μ (from the perfluoroalkyl substituted oxadiazole). No definite assignment can be made at this time for these absorption bands. As can be seen from Table II both of the oxadiazoles afforded substantial quantities of the fluorinated nitriles on degradation. Thus it would seem that the low stability of these materials is due to dissociation. This process is very likely promoted by the electron donor effect of the aromatic ring in the presence of strongly electronegative substituents such as a perfluoroalkyl group. The infrared absorptions in the 5.70-5.80μ region mentioned above could very well be due to the amide formation from the reaction of the liberated nitrile with water. In the experiments where water was added this finding is readily explained; in the other tests water can be either formed by oxidation of CH entities or via the reaction of reactive species with ampoule walls. Inasmuch as the degree of decomposition for the perfluoroalkylether substituted oxadiazole in the presence of added water was not really different from that under purely thermal and thermal oxidative conditions one is tempted to speculate that the extent of decomposition is determined solely by thermal dissociation of the oxadiazole. In the case of 1,4-[bis-(5-perfluoro-n-heptyl)-1,2,4-oxadiazolyl]-benzene the presence of oxygen appears to accelerate this dissociation process as can be seen by comparing the results found for nitrogen and air at 235°C (see Table II).

3.3 Conclusions and Recommendations

Based on the limited investigation performed to date the bis-perfluoroalkyl substituted 1,2,4-oxadiazole appears to exhibit the best thermal, thermal oxidative, and hydrolytic stability of the systems studied. The low thermal and oxidative stability of the 1,2,4-oxadiazoles derived from terephthalonitrile oxide seems to stem from the ready dissociation of these materials rather than the oxidative attack upon the CH moieties on the benzene ring. The thermal stability of the two triazines appears to be equivalent under the conditions employed; however the perfluoroalkyl triazine appears to be definitely oxidatively less stable than the perfluoroalkylether analogue, whereas its hydrolytic stability is the worst of all the materials investigated. The hydrolytic instability of the perfluoroalkyl triazine as compared to the 1,2,4-oxadiazoles is hard to explain and it must be associated both with the triazine ring itself as well as the $-CF_2-C(=N)-N$ linkage. The hydrolytic stability of the perfluoroalkylether substituted triazine is most likely derived from the presence of the tertiary fluorine on the carbon attached to the triazine ring. It is believed that this behavior is completely independent of the ether linkage and that a perfluoroalkyl substituent attached via a $-CF(CF_3)$ group to the triazine ring will exhibit the same hydrolytic stability as the perfluoroalkylether system studied under this program.

Additonal tests will have to be conducted in the future to complete this study. Of particular importance is the determination of the hydrolytic stability of the perfluoroalkylether substituted triazine and the fully fluorinated 1,2,4-oxadiazole at 325°C as well as their stabilities in the presence of aircraft fuel. Furthermore, data on the respective stabilities of actual polymer systems will have to be developed to establish the validity of extrapolating data obtained with model compounds. The successful development of any practical system will also have to take into consideration the ease of the crosslinking and curing reaction, the physical properties of the sealant thus obtained, and the retainment of the desired properties after exposure to extremes of environments and conditions.

4. EXPERIMENTAL DETAILS AND PROCEDURES

All solvents used were reagent grade and were dried and distilled prior to use. Operations involving moisture or air sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres Model HE-93B) or under a nitrogen by-pass. The commercially available starting materials were usually purified by distillation, crystallization, or other appropriate means. This did not apply to the terephthalonitrile-bis-N-oxide received from Hughes Aircraft Company. This material was kept at -78°C and used without any purification. The perfluoroalkylether nitrile obtained from the Air Force Materials Laboratory was also employed without purification due to the relatively small sample available and the likelihood of material loss on purification.

Infrared (IR) spectra were recorded either neat (on liquids) or as double mulls (Kel-F oil No. 10 and Nujol) using a Perkin-Elmer Corporation Infrared Spectrophotometer Model 21. Thermal analyses were conducted using a duPont 951/990 Thermal Analyzer system. All the mass spectrometric analyses were obtained with a CEC Model 21-620 mass spectrometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Purification of Perfluorooctanonitrile. The perfluorooctanonitrile received from PCR, Incorporated (Product No. 18678, Lot No. 0611) was purified by fractional condensation using a high vacuum line. The material was allowed to evaporate from a warming trap (in which a small amount of a solid, colorless residue, possibly the amide, remained) and passed through traps kept at -23, -47, and -196°C. The bulk of the nitrile condensed in the -47°C trap, the -196°C trap contained a very small amount, and the -23°C trap remained empty. Based on infrared spectroscopy the condensates in the -47 and -196°C traps were identical, showing the C≡N absorption at 4.43μ. The vapor pressure of the -47°C fraction was found to be 6.2 mm Hg at 0°C and ~ 20 mm at 20°C. The melting point was lower than -47°C, yet above -78°C.

Preparation of Perfluorooctanylamidine. Into a 100 ml round bottom flask, purged with dry nitrogen, were condensed ~ 50 ml of liquid ammonia at ~ -60°C under nitrogen by-pass. To the stirred solvent were then added 10.36 g (26.223 mmol) of perfluorooctanonitrile (as received) at -40 to -39°C over a period of 20 min. Precipitation of a white solid, which soon prevented stirring, commenced as soon as the nitrile addition was started. This slurry then was kept for an additional 30 min at -40 to -34°C before the cooling bath was allowed to warm slowly to -25°C to evaporate the excess ammonia. After the bulk of ammonia had been removed the reaction flask was evacuated at room temperature to complete dryness. The colorless solid thus obtained had mp 83-84.5°C (sealed capillary) (lit. 71-73°C, (ref. 18), 86-88°C (ref. 19). A portion of this material was recrystallized from dry n-hexane, softening (?) 63°C, mp 90.5-92.5°C; its infrared spectrum exhibited characteristic absorptions at 3.0, 3.17, and 6.0μ showing the presence of NH moieties. The DTA scan (Figure 9) shows two endothermic transitions at 42°C (weak) and 69°C, melting at 93°C, a shallow reaction endotherm between ~ 130 and ~ 220°C, and a strong endotherm at 289-291°C. The endotherms at 42 and 69°C may be indicative of phase transitions, the 93°C endotherm corresponds with the observed melting point, and the endotherm at ~ 290°C with the boiling point of the triazine, $(C_7F_{15}CN)_3$. Thus the shallow and broad endotherm between ~ 130 and 220°C must be attributed to the formation of the s-triazine accompanied by liberation of ammonia.

Preparation of Tris-perfluoroheptyl-s-triazine. Inside an inert atmosphere enclosure 6.62 g (16.064 mmol) of the amidine as obtained from above described reaction were placed without further purification into a 50 ml round bottom flask, which was then attached to a high vacuum line. After reducing the pressure in the system to 300 mm Hg the flask was heated gradually from room temperature to about 160°C over a period of 2 hr, followed by heating at 155-165°C for an additional 5 hr. Ammonia evolution proceeded smoothly. Yet, despite the pressure of 300 mm Hg of nitrogen in the system sublimation of a white solid was observed at ~ 145°C. This sublimation of amidine probably is the explanation for the recovery of only 14.257 mmol of ammonia (88.8% of theory). After heating, the material left in the flask was a mobile, clear liquid which resisted crystallization even when cooled to ~ -20°C. Accordingly this product was distilled under high vacuum (0.001 mm Hg). At 69°C (bath temperature) sublimation of a white solid was observed pointing to the presence of unreacted amidine. Accordingly the contents of the flask were refluxed (without distillation) at 70-80°C under high vacuum for ~ 1 hr, which resulted in the sublimation of the remaining amidine to the cooler parts of the system. After removal of the deposited solids distillation of the liquid yielded a product bp 93-97°C/0.001 mm Hg which exhibited an infrared spectrum identical with that reported by Dorfman and Emerson (ref. 9). The material failed to solidify on cooling to 0°C; showing it to be a mixture of isomers which was confirmed by NMR spectroscopy performed by NASA Ames Research Center. The pure tris-perfluoro-n-heptyl-s-triazine is a solid at room temperature.

Preparation of Perfluoro-n-octanoic Acid Methyl Ester. Into a 500 ml round bottom flask equipped with a magnetic stirring bar and reflux condenser were placed 29.9 g of dry methanol. After cooling to 0°C, 52.9 g of concentrated sulfuric acid were added with stirring, followed by 180.3 g (0.435 mol) of perfluoro-n-octanoic acid (PCR Product No. 11026, Lot No. 4870, > 99% "n", mp 58.5-60.0°C). This slurry was then heated with stirring from 0° to 103°C over a period of 1 hr and kept at 103-105.5°C for an additional 1.5 hr. After separation of the two layers the bottom layer was washed with two 150 ml portions of distilled water and dried overnight over sodium sulfate. After decanting 168.5 g of crude ester were obtained, which on distillation at atmospheric pressure gave 162.0 g (87.4% yield) of pure ester, bp 161-162.5°C.

Preparation of Perfluoro-n-octanamide. The perfluoro-n-octanoic acid methyl ester obtained as described above (148.5 g, 0.347 mol) was placed in a 500 ml round bottom flask, mixed with 250 ml dry ether, and cooled to 0°C under a nitrogen by-pass. Then ammonia (Matheson) was passed under stirring into the solution. Within 4 min the solution became cloudy, after an additional 3 min the amount of precipitate formed prevented further stirring. The flow of ammonia was continued thereafter for further 20 min with frequent shaking of the reaction flask. Subsequently ether and excess methanol and ammonia were removed under reduced pressure at room temperature. The crude acid amide (143.1 g, 99.9% yield) thus isolated was recrystallized from a hot ~ 1:1 mixture of acetone and benzene, which produced 136.9 g (95.5% yield) of pure perfluoro-n-octanamide, mp $141-142.5^{\circ}$C.

Preparation of Perfluoro-n-octanonitrile. Inside an inert atmosphere enclosure 114.0 g (0.276 mol) of perfluoro-n-octanamide were mixed in a 2-1 round bottom flask with 120 g of phosphorus pentoxide. On top of the mixed solids were placed additional 69.3 g of P_2O_5. Then the flask contents were heated under a nitrogen by-pass to 168°C during a 30 min period at which distillation of the nitrile, accompanied by sublimation of small quantities of unreacted acid amide, commenced. Distillation of nitrile continued for 1 hr while the flask was heated at $170-212^{\circ}$C. After cooling the reaction flask was attached to the high vacuum system to collect undistilled nitrile and this fraction was distilled on the high vacuum line into a 250 ml round bottom flask, to which the original reaction distillate was added via vacuum condensation to free it from the unreacted acid amide mentioned above. The crude perfluoro-n-octanonitrile thus obtained amounted to 104.2 g. Distillation under a nitrogen by-pass at atmospheric pressure afforded 98.2 g (90.2% yield) of pure perfluoro-n-octanonitrile, bp $101-103^{\circ}$C.

Preparation of Tris-perfluoro-n-heptyl-s-triazine. In vacuo 20.23 g (51.20 mmol) of perfluoro-n-octanonitrile was condensed onto 0.619 g (2.67 mmol) of silver oxide which was previously heated in vacuo at 90° for ca 2 hr. The ampoule was sealed and heated at 193°C for 16 hr. During this period a silver mirror formed. The ampoule was cooled to -196°C and was opened to the vacuum system. A small amount of a non-condensible gas was present, possibly oxygen formed from partial decomposition of silver oxide. Subsequently the room temperature volatiles were distilled off and were fractionated using traps cooled to -78° and -196°C. In the -196°C trap only a small amount of material was found composed mainly of carbon dioxide and a small quantity of silicon tetrafluoride. The -78°C trap contained unreacted perfluoro-n-octanonitrile 1.24 g (6% yield). The room temperature involatile material on standing at room temperature solidified. Distillation in vacuo gave 16.96 g (83.8% yield) of the desired triazine, bp 115-120°C/0.001 mm Hg, mp 27-28.8°C (in capillary). The DTA curve (see Figure 1) shows the mp at 25°C and bp at 295°C at atmospheric pressure.
Anal. Calcd for $C_{24}F_{15}N_3$: C, 24.32; F, 72.14; N, 3.55. Found: C, 24.65; F, 71.44; N, 3.26.

Preparation of 1,4-Bis[(5-perfluoro-n-heptyl)-1,2,4-oxadiazolyl]-benzene. Inside an inert atmosphere enclosure 25.39 g (64.27 mmol) of perfluoro-n-octanonitrile (prepared as described above) were placed in a 50 ml round bottom flask to which was added 2.37 g (15.18 mmol) of terephthalonitrile-bis-N-oxide (TPNO) as received from Hughes Aircraft Company. This suspension was heated under a nitrogen by-pass at 52-67°C for 2.75 hr, cooled, and attached to the vacuum line to collect unreacted, perfluoro-n-octanonitrile. The amount recovered was 15.28 g (38.67 mmol) indicating that 25.60 mmol had reacted, which corresponds to 84.3% of the TPNO employed. The residue in the reaction flask was dissolved in ~ 400 ml of boiling heptane, the hot solution was filtered, and after cooling, filtering, and drying the desired bis-oxadiazole (11.14 g, 77.6% yield) mp 126.4-128.0°C was obtained. The DTA curve of this material is given in Figure 3. Anal. Calcd for: $C_{24}H_4F_{30}N_4O_2$: C, 30.33; H, 0.42; F, 59.98; N, 5.90; O, 3.37. Found: C, 30.80; H, 0.48; F, 60.29; N, 5.83.

Attempted Purification of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$. The "ether-nitrile " as received from the Air Force Materials Laboratory was purified using high vacuum technique by fractional condensation in traps kept at -23, -47, -78, and -196°C. About 60% of the sample condensed at -23°C with a vapor pressure at 0°C of 4.7 mm Hg. Approximately 40% of the sample condensed at -47°C, VP_0 = 5.5 mm Hg. Both fractions remained liquids at -78°C. This results shows that no efficient separation can be affected using high vacuum fractionation. Only a trace of material condensed at -78°C whereas a trace of an orange oil remained as residue in the distillation flask.

The unpurified material was subjected to elemental analysis. Anal. Calcd for: $C_9F_{17}NO_2$: C, 22.66; F, 67.70; N, 2.94; O, 6.71. Found: C, 23.40; F, 65.98; N, 3.12.

Trimerization of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$. The procedure adopted was basically the same as that described for the tris-perfluoro-n-heptyl-s-triazine. The ether nitrile, 10.34 g (21.68 mmol), was heated in a sealed ampoule with silver oxide, 0.249 g (1.07 mmol), at 192°C for 17 hr. A brownish solution with a silver mirror resulted; in addition some noncondensible gas, probably oxygen, was formed. Following the procedure described for the n-heptyl-s-triazine fractionation of the room temperature volatiles yielded in the -78°C trap unreacted nitrile (0.75 g, 7.2% recovery), whereas in the -196°C trap a small quantity of the ether nitrile admixed with carbon dioxide and silicon tetrafluoride was collected.

The room temperature involatile liquid on distillation gave 8.02 g (77.5% yield) of the desired triazine, bp 100-104°C/0.001 mm Hg. This material exhibited an infrared spectrum similar to that reported by T. S. Croft (ref. 17) for the higher analogues. Its DTA curve is given in Figure 2 showing a boiling point of 275°C at atmospheric pressure. A gas chromatogram of this material, using Apiezon L on Chromosorb G column, however, revealed the presence of at least four compounds, two of which (having retention times of 19.5 and 21 min, respectively) account for *ca* 95% of the total sample.
Anal. Calcd for: $C_{27}F_{51}N_3O_6$: C, 22.66; F, 67.70; N; 2.94, O, 6.71.
Found: C, 23.10; F, 68.82; N, 3.14.

Preparation of 1,4-bis([$C_3F_7OCF(CF_3)CF_2OCF(CF_3)$]-1,2,4-oxadiazolyl)-benzene. In an inert atmosphere enclosure a mixture of 0.65 g (4.16 mmol) of TPNO and 8.02 g (16.81 mmol) of $C_3F_7OCF(CF_3)CF_2OCF(CF_3)CN$ was prepared. The mixture was then stirred under nitrogen by-pass at 85-90°C for 6-1/5 hr. After cooling, the room temperature volatiles were fractionated in vacuo affording 4.49 g (9.42 mmol) of unreacted ether nitrile indicating 89%reaction based on the TPNO employed. Distillation in vacuo of the room temperature involatile residue gave 2.88 g (62% yield) of the bis-oxadiazole, bp 140-142°C/0.001 mm Hg. Based on the DTA (Figure 5) the boiling point is 325°C at atmospheric pressure.
Anal. Calcd for: $C_{26}H_4F_{34}N_4O_6$: C, 28.03; H, 0.36; F, 57.97; N, 5.03; O, 8.62, MW, 1114.26. Found: C, 28.37; H, 0.61; F, 59.21; N, 5.67; MW, 1240 (in chloroform; using Mechrolab Osmometer Model 302).

Preparation of Perfluoro-n-octylamidoxime. Under nitrogen by-pass to a stirred solution of hydroxylamine hydrochloride (2.90 g, 41.73 mmol) in dry methanol (50 ml) was added at 22-25°C sodium methoxide (0.87 g sodium in 12 ml methanol). To the resulting mixture was then introduced perfluoro-n-octanonitrile (15 g, 37.97 mmol) again at 22-25°C. After stirring for 1 hr at room temperature the solution was evaporated in vacuo. The solid residue was boiled with carbon tetrachloride and filtered hot giving 11.04 g (68% yield) of perfluoro-n-octylamidoxime, mp 133.5-135°C.

Preparation of Perfluoro-n-octanoyl Chloride. A mixture of 21.04 g (50.81 mmol) of perfluoro-n-octanoic acid and 12.23 g (60.23 mmol) of terephthaloyl chloride was heated under nitrogen by-pass at 150°C for 5-1/2 hr; this was followed by distillation at ca 40 mm Hg which gave 9.49 g (43.8% Yield) of crude perfluoro-n-octanoyl chloride. Redistillation afforded the pure product, 6.72 g (31% yield), bp 72-74°C/97 mm Hg.

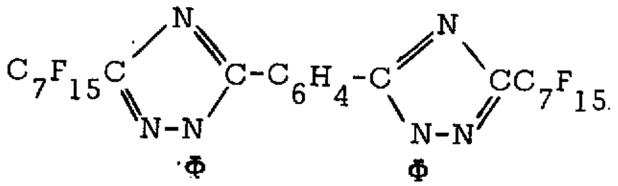
Preparation of O-perfluoro-n-octanoyl-perfluoro-n-octanylamidoxime. Under nitrogen by-pass to a stirred solution of perfluoro-n-octylamidoxime (6.72 g, 15.70 mmol) in tetrahydrofuran (25 ml) was added slowly at 0°C perfluoro-n-octanoyl chloride (6.79 g, 15.70 mmol) in tetrahydrofuran (5 ml). After completing the addition the reaction mixture was allowed to warm up to room temperature; subsequently the solvent was removed in vacuo. The solid residue was crystallized from toluene giving 10.74 g (83.0 % yield) of the desired product, mp 147-147.4°C.

Preparation of 3,5-Bis(perfluoro-n-heptyl)-1,2,4-oxadiazole. A mixture of O-perfluoro-n-octanoyl-perfluoro-n-octanylamidoxime (10.70 g, 12.98 mmol) was heated under nitrogen by-pass with phosphorus pentoxide (13.0 g, 91.59 mmol) for 6 hr at 252°C. Subsequently the oxadiazole (8.61 g, 82.3% yield) was distilled from the reaction mixture under reduced pressure; redistillation gave the pure product (8.46 g; 80.9% yield), bp 122-125°C/63-68 mm Hg. The DTA scan for this material is given in Figure 6.
Anal. Calcd for: $C_{16}F_{30}N_2O$: C, 23.84; F, 70.70; N, 3.47; O, 1.98.
Found: C, 23.86; F, 69.79; N, 3.27.

Preparation of N-phenylperfluorooctyl Hydrazidine. In the inert atmosphere enclosure to 10.04 g (25.41 mmol) of perfluorooctanonitrile (material received from PCR, Inc.: a mixture of normal and branched isomers) was added 2.79 g (25.80 mmol) of N-phenylhydrazine in tetrahydrofuran (5 ml).

The immiscible mixture was stirred overnight at room temperature. Two layers remained; no reaction occurred. The upper layer consisted of phenylhydrazine dissolved in tetrahydrofuran whereas the perfluorooctanonitrile formed the bottom layer. After heating under nitrogen by-pass at 75°C for 18 hr a homogeneous yellow solution resulted. Its infrared spectrum did not exhibit the nitrile band at 4.42μ. Removal of the room temperature volatiles in vacuo gave a yellow solid which was crystallized from heptane giving white crystals (5.97 g, 46.7% yield) of material mp 100-101.5°C. A second crystallization from heptane resulted in mp 103-104°C. The infrared spectrum indicated that the desired product was obtained.

Attempted Preparation of Triazole



(a) Via reaction of perfluorooctyl hydrazidine with terephthaloyl chloride in the absence of solvent. A mixture of perfluorooctyl hydrazine (2.50 g, 4.97 mmol) and terephthaloyl chloride (0.50 g, 2.48 mmol) was heated under nitrogen by-pass at 100°C for 1 hr and then at 120°C for an additional 1 hr. A black mass resulted. Based on the DTA scan of the mixture the process should have occurred readily around 90°C (see Figure 10). Repeated crystallizations from toluene gave a small quantity (ca 5% yield) of white crystals, mp 185-186°C, which appeared to be the desired product.

(b) Via reaction of perfluorooctyl hydrazidine with terephthaloyl chloride in ether. Perfluorooctyl hydrazidine (1.00 g, 1.987 mmol) was dissolved in ether (10 ml) to this was added under nitrogen by-pass with stirring terephthaloyl chloride (0.20 g, 0.985 mmol) in ether (10 ml) over a period

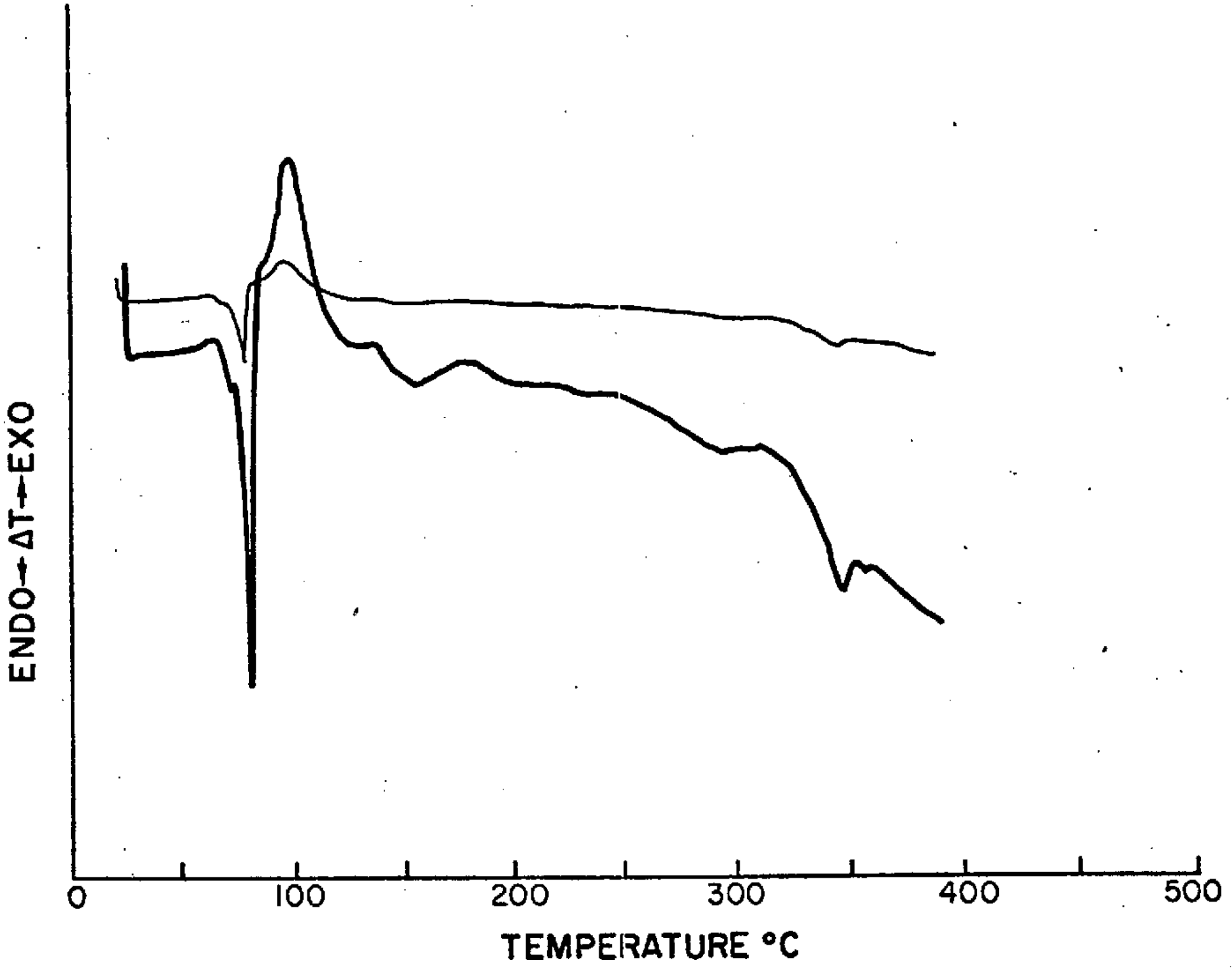


Figure 10: DTA of mixture of perfluorooctylhydrazidine and terephthaloyl chloride.

of 15 min. Subsequently the mixture containing a white precipitate was stirred at room temperature for 5 hr. Evaporation of ether in vacuo gave a solid whose infrared spectrum was almost identical with that of perfluorooctyl hydrazidine hydrochloride showing that partial reaction did occur; one mole of the hydrazidine reacting with the acid chloride with evolution of hydrogen chloride and the other acting as hydrogen chloride acceptor. To get complete reaction excess of hydrazidine appears necessary; however the resulting hydrazidine hydrochloride would have to be separated out prior to completing the cyclization at elevated temperatures.

(c) Via reaction of perfluorooctyl hydrazidine hydrochloride with terephthaloyl chloride in the absence of solvent. The perfluorooctyl hydrazidine hydrochloride was prepared by passing hydrogen chloride through an ethereal solution of the perfluorooctyl hydrazidine. Removal of ether in vacuo gave white solid which softened at 78°C and decomposed at 107°C.

In an inert atmosphere enclosure the hydrochloride (4.00 g, 7.41 mmol) was mixed with terephthaloyl chloride (0.77 g, 3.79 mmol) and then the mixture was heated under nitrogen by-pass at 130°C for 2 hr. A dark discolored solid resulted; no actual melting was observed during the heating period. Based on the DTA (see Figure 11) the reaction must take place in the vicinity of 100°C. The DTA exhibits only the melting point of the terephthaloyl chloride (at 80°C). The solid product was purified by crystallization from toluene giving ca 22% yield of material, mp 176-181°C, which based on its infrared spectrum appeared to be the desired product. The infrared spectrum was identical with that exhibited by the compound prepared in (a). No additional purification and characterizations were performed.

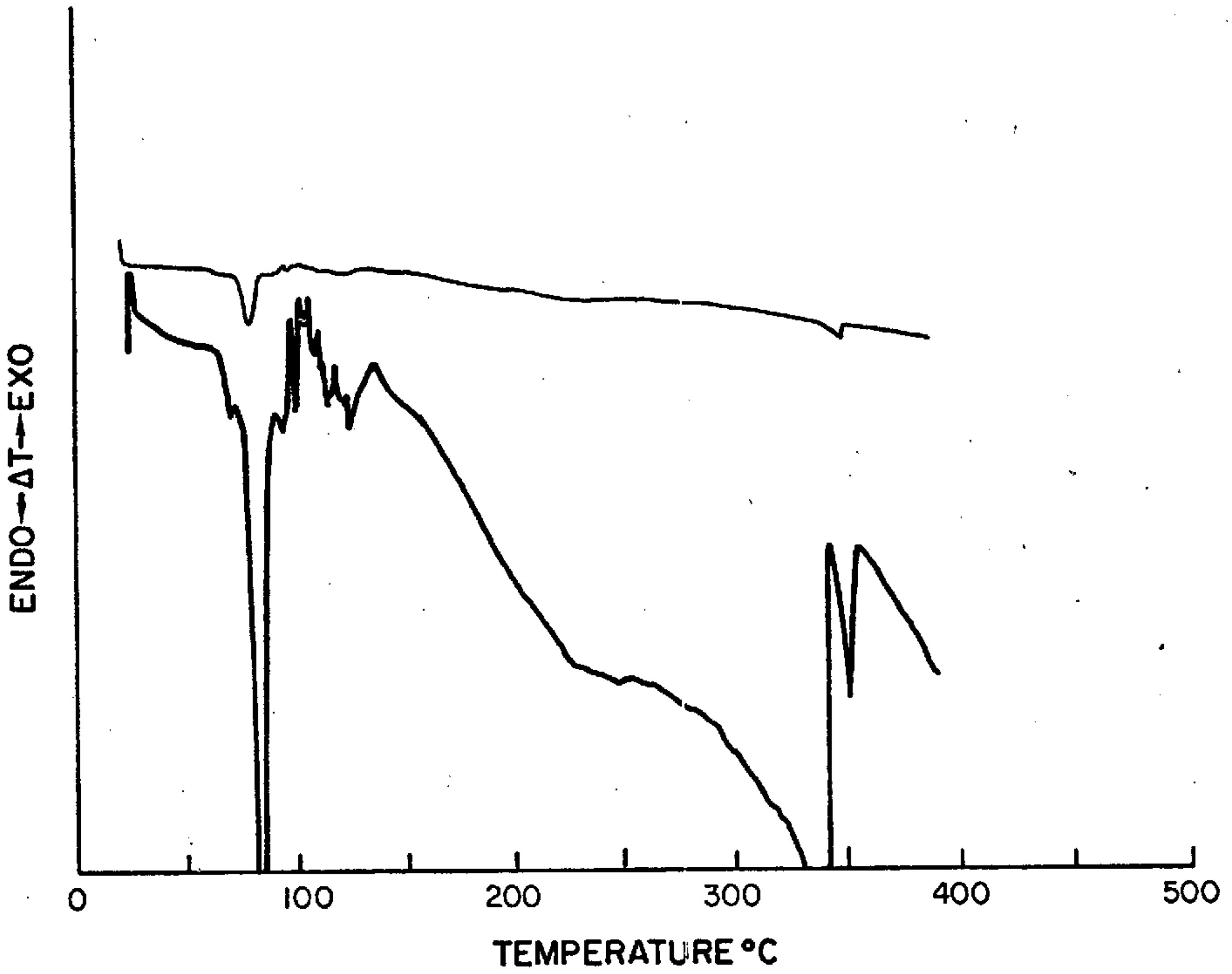


Figure 11: DTA of mixture of perfluorooctylhydrazidine hydrochloride and terephthaloyl chloride.

Degradation Studies. The degradation investigations were performed in sealed ampoules of ca 50 ml volume over a period of 48 hr at 235 and 325°C. The media studied were nitrogen, air, and nitrogen/water. The quantities of material employed were between 0.5-1.0 g, whereas the gas pressure used were ca 350 mm Hg at room temperature. In the experiments involving water, it was weighed into the ampoules. At the conclusion of an experiment the ampoules were cooled in liquid nitrogen and were opened into the vacuum system. The liquid nitrogen noncondensibles were measured and determined by mass spectrometry. The liquid nitrogen condensibles, which were volatile at room temperature, were fractionated from a warming trap through -23, -78°C into a liquid nitrogen cooled trap. Each fraction was measured, weighed and analyzed by infrared spectroscopy and mass spectrometry. The residue itself was weighed and subjected to gas chromatography, infrared spectral analyses, and differential thermal analysis.

5. REFERENCES

1) Anderson, R., and Psarras, T., Development of High Temperature Functional Fluids. AFML-TR-208 (November 1971).

2) Brown, H. C., Synthesis of Semi-Inorganic Fluorine Polymers. WADC-59-272, Part I (September 1959).

3) Dorfman, E., Emerson, W. E., and Gruber, F. J., Perfluoroalkylene Triazine Elastomeric Polymers, ML-TDR-64-249, Part III (February 1967).

4) Graham, T. L., Crosslinking and Filler Reinforcement of Perfluoroalkylene Triazine Elastomers, AFML-TR-66-402, Part II (March 1969).

5) Brown, H. C., J. Org. Chem., 22, 698 (1957).

6) Brown, H. C., J. Polymer Sci., 44, 9 (1960).

7) Brown, H. C., Shuman, P. D., and Turnbull, J., J. Org. Chem., 32, 231 (1967).

8) Dorfman, E., and Deleo, R. N., Research on Synthesis of Thermally Stable Fluorinated Polymers, ASD-TDR-63-174, Part I (December 1962).

9) Dorfman, E. and Emerson, W. E., Perfluoroalkylene Triazine Elastomeric Polymers, ML-TDR-64-249, Part II (August 1965).

10) LaRochelle, R. W., Synthesis of Nitrile Oxide Curing Agents for Perfluoroalkyl-s-Triazine Elastomers, AFML-TR-239 (May 1973).

11) Bilow, N., and Rose, K. L., High Temperatures Electrical Wire Coatings, AFML-TR-69-111, Part I (May 1969).

REFERENCES (Cont'd.)

12) Landis, A. L., and Andres, R. J., High Temperature Laminating Resins, AFML-TR-70-250 (December 1970).

13) Rosser, R., private communication.

14) Brown, H. C. and Wetzel, C. R., J. Org. Chem., 30, 3734 (1965).

15) Critchey, J. P., and Pippet, J. S., J. Fluorine Chem., 2, 137 (1972).

16) Berry, J. S., U.S. Patent 3,194,840, (July 13, 1963).

17) Croft, T. S., Exploratory Development of High Temperature Base Fluids, AFML-TR-70-251 (November 1970).

18) Groch, G. O., et al, Inorganic Polymers Program, Contract Nonr-2259(00), January 1, 1959 to January 1, 1960.

19) PCR, Incorporated, Research Chemicals for Organic Chemists, November 15, 1972.

20) Anderson, R., Psarras, T., Development of High Temperature Functional Fluids, AFML-TR-72-229, Part I, (September 1972).