General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

REPORT

CR-102506

SPACE THERMAL CONTROL BY USE OF SOLID/SOLID-PHASE CHANGE MATERIALS

ANNUAL SUMMARY REPORT NO. 2
25 July 1969 - 24 May 1970

Contract NAS8-21452
Control DCN 1-8-28-00053

MRI Project No. 3224-C



For

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Attn: A&TS-PR-M

N70-35648 (ACCESSION NUMBER)
46 (PAGES)
CR-102506 (NASA CR OR TMX OR AD NUMBER)
1 (THRU)
18 (CODE)
(CATEGORY)
FACILITY FORM 602

SPACE THERMAL CONTROL BY USE OF SOLID/SOLID-PHASE CHANGE MATERIALS

by

E. Murrill
L. W. Breed

ANNUAL SUMMARY REPORT NO. 2
25 July 1969 - 24 May 1970

Contract NAS8-21452
Control DCN 1-8-28-00053

MRI Project No. 3224-C

For

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama 35812

Attn: A&TS-PR-M

PREFACE

This report was prepared by Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110, under Contract NAS8-21452, "Space Thermal Control by Use of Solid/Solid-Phase Change Materials." The work was administered under the direction of the Space Sciences Laboratory, George C. Marshall Space Flight Center, with Miss B. E. Richard acting as the Contracting Officer's technical representative.

This report covers work conducted from 25 July 1969 to 24 May 1970.

The work at Midwest Research Institute was designated 3224-C and was carried out by Dr. E. Murrill, Miss M. E. Whitehead and Mr. L. W. Breed, who acted as Principal Investigator, under the supervision of Dr. C. C. Chappelow, Jr., Head, Organic and Polymeric Materials Section.

Approved for:

MIDWEST RESEARCH INSTITUTE

H. M. Hubbard, Director
Physical Sciences Division

12 June 1970

TABLE OF CONTENTS

		Page
Abstract		1
I.	Introduction	2
II.	Discussion	3
	A. Supercooling and Nucleation of Compounds and Mixtures	3
	B. Volume Changes	7
	C. Additional Screening of Commercially Available Materials	7
	D. Synthesis of New Candidate Materials	9
	E. Temperatures and Heats of Transition of New Candidate Materials	12
III.	Conclusions	17
IV.	Experimental Part	18
	A. Qualitative Thermal Data	18
	B. Quantitative Standardization	18
	C. Quantitative Thermal Data	18
	D. Crystallization Studies	18
	E. Density of Trimethylolethane at 25 and 88°	21
	F. Synthesis of Candidate Substances and Their Intermediates	23
Appendix 1 - Spectral Characteristics of Synthesized Candidate Substances and Their Intermediates		31
References		39

ABSTRACT

New candidate substances for use as passive thermal control materials have been prepared and screened. Six previously unreported solid-solid transitions were found: tris(hydroxymethyl)acetic acid, 49 cal/g at 124°; monochloropentaerythritol, 36 cal/g at 61°; monofluoropentaerythritol, 33 cal/g at 68°; difluoropentaerythritol, 21 cal/g at 18°; monoaminopentaerythritol, 46 cal/g at 86°; and diaminopentaerythritol, 44 cal/g at 68°. The effectiveness of nucleating agents for the solid-solid transition on cooling of 2-amino-2-methyl-1,3-propanediol was demonstrated. Density measurements for trimethylolethane indicated about a 5% density change between the solid state and the plastic crystalline state.

I. INTRODUCTION

The solid state transitions in substances with molecular symmetry characteristics that satisfy the requirements for a stable rotor phase (plastic crystals) are potentially useful in thermal control applications. High transitional enthalpies occur in these substances when the onset of the new phase is accompanied by extensive new conformational possibilities as well as molecular reorientations.

The inherent possibilities for high enthalpies, low coefficients of thermal expansion, narrow transition ranges, and low cost of materials exhibiting the plastic crystalline materials led to the initiation of a project to determine the extent to which these materials could satisfy specific criteria for thermal control materials for manned spacecraft. The stated requirements were: transition enthalpies greater than 56 cal/g with 95% of the heat effect occurring within $\pm$ 5°* of the equilibrium temperature; a maximum of 3° supercooling below the equilibrium temperature required for the initiation of the new phase; thermal expansion not exceeding 15% between $\pm$ 50° of the equilibrium temperature; equilibrium temperatures between 0 and 100°; materials that were low in cost, nontoxic, and stable within the usable temperature range.

During the initial research period, the work, which has been reported in Annual Summary Report No. 1, Contract NAS8-21452, included the gathering of data for substances known to exhibit a plastic crystalline phase and a consideration of the theoretical definition of the mesocrystalline state and the molecular requirements for transitions with high enthalpies. On the basis of these studies, a large number of commercially available materials were selected and screened qualitatively by differential thermal analysis. As a result 33 previously unidentified substances with plastic crystalline phases were discovered.

After the existence of a solid-state transition was verified in these substances, latent heats of transition were determined for many of them by differential scanning calorimetry. Five transitions with enthalpies greater than 45 cal/g were found, although only three of the substances had transitions within the target range. With the new qualitative and quantitative data, correlations were established to aid in the selection of new candidate structures. Much of the work during the current research period involved the synthesis of compounds for screening that were not commercially available.

---

* Throughout this report, all temperatures are reported in °C unless indicated otherwise.

Also in the earlier work, some two-component systems were examined but no evidence for the formation of solid state eutectics was observed. Crystallization studies demonstrated that excessive supercooling was not an inherent property of the solid state transitions and that when supercooling did occur, the new phase could be initiated by nucleation.

This report, which is supplemental to Annual Summary Report No. 1, includes some additional determinations of transitional enthalpies of available materials, but is largely concerned with the preparation and screening of selected materials with chemical structures likely to provide high heats of transition within the desired temperature range. Work on cooling characteristics, nucleating agents, properties of mixtures, and density changes is also reported.

II. DISCUSSION

A. Supercooling and Nucleation of Compounds and Mixtures

Initial experimental work reported in Tables 40-43 of Annual Summary Report No. 1 indicated that the use of the thermal analyzer in the examination of small quantities of materials was not a reliable technique for the study of supercooling characteristics in solid-solid phase transitions. Although extensive apparent supercooling was observed by thermal analysis in many substances, very little supercooling occurred when 2.5-g. samples of the same substances were slowly cooled and the differences between the plateau temperatures and the minimum temperatures below the plateau were observed. Some new thermal analysis data summarized in Table 1 illustrate the inconsistencies. Although a transitional supercooling of 1° had been observed for pentaerythritol in the macro studies, the thermal analysis data indicated supercooling greater than 10°. The values in Table 1 can also be compared with a 2° supercooling for trimethylolethane and a 3° supercooling for 2-methyl-2-nitro-1,3-propanediol previously observed for these substances in macro studies. With the micro techniques, transitions in five substances supercooled 6 to 40°. In two fusions, one for hexadecane and the other for 2-amino-2-methyl-1,3-propanediol, the extent of supercooling was only about 1°. These results confirm that supercooling can be assessed fairly only in macro studies.

2-Amino-2-methyl-1,3-propanediol, which had consistently supercooled extensively in transition, was selected to determine the possible effectiveness of nucleating agents in initiating the new phase. In the earlier work, it had been shown that although this transition could be supercooled as much as 50°, the extent of supercooling could be reduced to 2° if the surface of the glass container in contact with the sample was scratched with a metal spatula.

TABLE 1

COMPARISON OF TRANSITION AND FUSION RANGES ON HEATING AND COOLING BY DIFFERENTIAL THERMAL ANALYSES[a/]

Substance	Heating	Cooling
Hexadecane (practical - fusion temperature)		
Quantitative Cell	17.5-22	14.5-12.5
Qualitative Cell	17.5-20.5	21.0-18.5
Trimethylolethane (unpurified)		
Qualitative Cell	83.5-85	79-78
2-Methyl-2-nitro-1,3-propanediol (recrystallized four times)		
Qualitative Cell	78-80.5	63.5-62
2-Hydroxymethyl-2-nitro-1,3-propanediol (recrystallized three times)		
Qualitative Cell	79-81	72-69.5
2,2-Bis(hydroxymethyl)propionic acid (recrystallized once)		
Qualitative Cell	153-154.5	115-113.5
Pentaerythritol (recrystallized once)		
Qualitative Cell	183-186.5	172-169.5
2-Amino-2-methyl-1,3-propanediol (sublimed twice - fusion temperatures)		
Qualitative Cell	107-109	107.5-107

a/ Heating and cooling rates 10 $\pm$ 1°C/min.

As a guide for the selection of nucleating agents, the possible range of crystal habits of various materials was considered since nucleation is favored when a nucleating agent and the new phase have surface structures that are similar.[1/] Under these circumstances a crystal of the new phase can more easily be adsorbed onto the surface and more readily form a surface that satisfies the critical radius need for nucleation. A series of nucleating agents were selected that represented various crystal habits: tetragonal-titanium dioxide, zirconyl chloride, and mercuric iodide; monoclinic-potassium

oxalate, zinc acetate, and ammonium molybdate; hexagonal-zinc and zinc oxide; rhombic-uranyl acetate; cubic-potassium iodide; and miscellaneous-carbon black.

Zinc, potassium oxalate, carbon black, and zirconyl chloride were effective (see Table 2), but no pattern that correlated effectiveness with crystal structure was apparent. The results do verify that techniques that are applicable for the initiation of a new phase in liquid-solid transitions are also effective in solid-solid transitions.

TABLE 2

MACRO STUDIES OF NUCLEATION OF 2-AMINO-2-METHYL-1,3-PROPANEDIOL[a/]

Mode of Nucleation	Minimum Temp. Before Plateau (°C)	Plateau Temp. (°C)	Cooling Rate of Bath at Plateau (°C/min)
1% Titanium dioxide; tube scratched at 26°	26	59	2
1% Mercuric iodide; tube scratched at 27°	27	63	2
1% Zinc	68	74	1
1% Ammonium molybdate; tube scratched at 34°	34	61	1
1% Uranyl acetate	30	50	1
1% Potassium iodide; tube scratched at 31°	31	59	2
1% Potassium oxalate	67	74	1
1% Carbon black	67	74	1
1% Zirconylchloride	67	74	1

a/ Transition temperature by differential thermal analysis, 76-80°.

In macro studies of crystallization of unnucleated mixtures of pentaerythritol and trimethylolethane, little or no supercooling in the transitions was observed. The transition temperatures of the mixtures occurred at intermediate temperatures between the transitions for pure pentaerythritol, 181°, and trimethylolethane, 81°. When the same cocrystallized mixtures were heated under the conditions of differential thermal analysis, transition endotherms occurred over rather broad ranges and somewhat above the transition temperature obtained on cooling. These data are summarized in Table 3. Data of this kind are consistent with the properties of phase equilibria between two solid solutions. None of the cooling or heating curves exhibited any evidence of a eutectic mixture.

TABLE 3

CRYSTALLIZATION AND FUSION CHARACTERISTICS OF MIXTURES

	Cooling Properties (macro)			Heating Properties (diff. therm. anal.)[a]	
Composition	Minimum Temp. Before Plateau (°C)	Plateau Temp. (°C)	Cooling Rate of Bath at Plateau (°C/min)	Transition Range (°C)	Fusion Range (°C)
Mixtures of pentaerythritol and trimethylolethane					
20:80	88.5	88.5	2	90-95	205-209
40:60	108	109	3	103-117	213-219
50:50	116.5	118	4	114-130	220-223
60:40	123	123	4	123-138	221-226
80:20	141	141	4	140-165	231-238
Mixtures of trimethylolethane and 2-methyl-2-nitro-1,3-propanediol					
50:50	No plateau observed			52-59	

[a] Heating rate, 15°/min.

B. Volume Changes

All consideration of the volume requirements necessary for the onset of molecular reorientation indicates a density change between 5-10%. This estimate has been verified experimentally for several substances. For example, Nitta[2] cites a volume change of 9.08% for pentaerythritol between 20° at its transition temperature and Wulff and Westrum[3] report a volume change in transition of 7.8% for succinonitrile. Additional experimental evidence was sought for one of the substances under consideration in this work in order to confirm the generalization.

Density determinations were carried out for trimethylolethane, which has a transition temperature of 81°. Between 25° and 88°, the density change was 4.8%. Because of the inherent problems in determining densities of solids and in the control of the temperature during the determinations, the error in these determinations is probably greater than the indicated number of significant figures. Nonetheless, the error is not so large that these data fail to confirm that the volume change in the transition is low.

C. Additional Screening of Commercially Available Materials

New or more highly purified samples of three materials that had been studied during the last report period, pentaerythritol, 2-amino-2-methyl-1,3-propanediol, and 2-amino-2-methyl-1-propanol, were reexamined. In addition, qualitative and quantitative data were obtained for two organosilicon substances with potentially high fusion enthalpies. These data are summarized in Table 4.

Values that had been found for the temperatures and heats of transition and fusion of pentaerythritol were somewhat lower than the values reported by Nitta.[4] When recrystallized pentaerythritol was repeatedly sublimed, the fusion temperature was increased and its range narrowed, but the values remained somewhat lower than Nitta's values. The transitional enthalpy increased somewhat, but the increase was not necessarily significant.

A new sample of 2-amino-2-methyl-1,3-propanediol, which had offered some difficulty in the initial work because of its tendency to absorb water, gave a transitional enthalpy lower than the originally reported 63.4 cal/g value. In attempts to purify the new material, the fusion temperature decreased sharply unless extremely careful precautions were taken to exclude moisture.

When a new sample of 2-amino-2-methyl-1-propanol was screened, no transition was observed; however, the broadness of the fusion range still does not preclude a transition and a very narrow mesocrystalline range.

TABLE 4

SUMMARY OF TRANSITION AND FUSION DATA FOR AVAILABLE SUBSTANCES

Compound	Transition			Fusion		
	Temp. (°C)	ΔH (cal/g)	ΔS (e.u.)	Temp. (°C)	ΔH (cal/g)	ΔS (e.u.)
Pentaerythritol (highly purified)	182-183	71.95	21.5	258	8.90	2.3
2-Amino-2-methyl-1,3-propanediol	76-78	53.25	16.0	105-107	6.72	1.9
2-Amino-2-methyl-1-propanol				14-18		
Hexamethylcyclotrisiloxane				61-63	21.59	14.4
N,N'-bis(trimethylsilyl)tetramethyl-cyclodisilazane				40-42	18.93	17.6

The absence of a solid-solid transition in this compound remains inconsistent with the properties of the other substances in the series.

The two organosilicon compounds, hexamethylcyclotrisiloxane and N,N'-bis(trimethylsilyl)tetramethylcyclodisilazane, were examined because the extent of methyl substitution in these compounds offered the possibility of many new conformation states. Since the heats of fusion for both substances were about 20 cal/g, it is probable that methyl group reorientations occur at a much lower temperature and do not contribute to the heat of fusion.

D. Synthesis of New Candidate Materials

After the results of the work described in Annual Summary Report No. 1 were obtained, structural correlations allowed the estimation of transition temperatures and enthalpies of candidate materials on the basis of chemical structure and provided a means of narrowing the field of possible structures that might be prepared for screening. As a class, functionally substituted tetrahedral compounds, particularly the derivatives of pentaerythritol, appeared to be the most promising. The preferred substituent groups were CH_2OH, CH_2NH_2, CH_2F, CH_2CN, NO_2, and CO_2H (hydroxymethyl, aminomethyl, fluoromethyl, cyanomethyl, nitro, and carboxy). On the basis of estimates of transition enthalpies and temperature made by extrapolation or interpolation of values obtained in the earlier work and a search of the literature, the compounds shown in Table 5 were selected for preparation. The choices were dictated not only by considerations of favorable transitions, but also by the accessibility of the compounds through established synthesis procedures. Research on the synthesis of candidate structures was not considered a part of the goal of the program. As nearly as possible, compounds with common intermediates and precursors were selected, and preferably compounds whose preparation had precedence in the literature.

Of the compounds in Table 5, Nos. 1, 2, 5, 6, 8, 12 and 16 were successfully prepared by the following sequences.

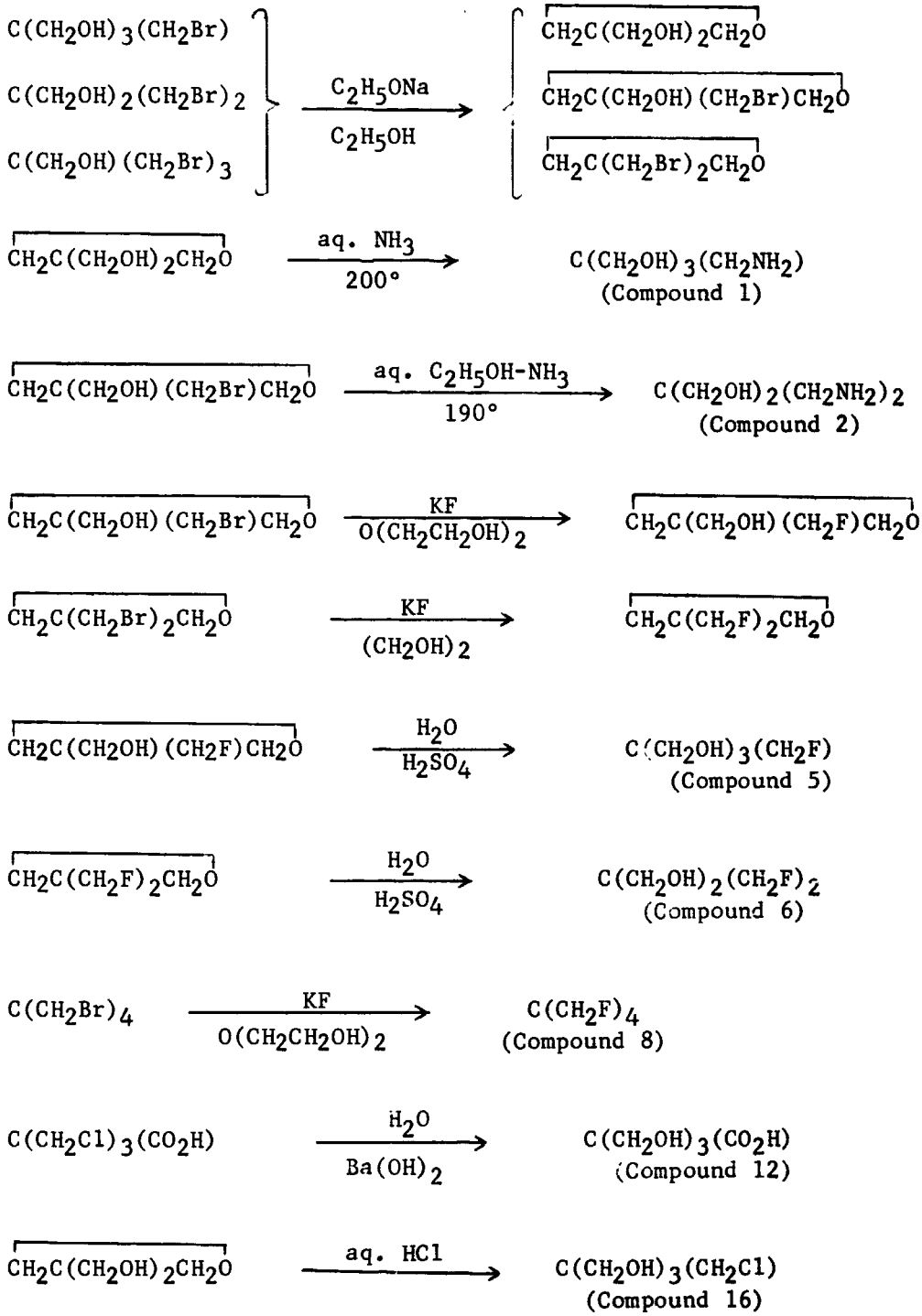
$$C(CH_2OH)_4 \xrightarrow[CH_3CO_2H]{48\%\ aq.\ HBr} C(CH_2OH)_3(CH_2Br)$$

$$C(CH_2OH)_4 \xrightarrow[CH_3CO_2H]{HBr} C(CH_2OH)_2(CH_2Br)_2 + C(CH_2OH)(CH_2Br)_3$$

TABLE 5

COMPOUNDS SELECTED FOR SYNTHESIS AND SCREENING

Compound No.	Compound Structure	Compound Name
1	$C(CH_2OH)_3(CH_2NH_2)$	Monoaminopentaerythritol
2	$C(CH_2OH)_2(CH_2NH_2)_2$	Diaminopentaerythritol
3	$C(CH_2OH)(CH_2NH_2)_3$	Triaminopentaerythritol
4	$C(CH_2NH_2)_4$	Tetraaminopentaerythritol
5	$C(CH_2OH)_3(CH_2F)$	Monofluoropentaerythritol
6	$C(CH_2OH)_2(CH_2F)_2$	Difluoropentaerythritol
7	$C(CH_2OH)(CH_2F)_3$	Trifluoropentaerythritol
8	$C(CH_2F)_4$	Tetrafluoropentaerythritol
9	$C(CH_2OH)_3(CH_2CN)$	Monocyanopentaerythritol
10	$C(CH_2OH)_2(CH_2CN)_2$	Dicyanopentaerythritol
11	$C(CH_2OH)(CH_2CN)_3$	Tricyanopentaerythritol
12	$C(CH_2OH)_3(CO_2H)$	Tris(hydroxymethyl)acetic acid
13	$C(CH_2OH)(CH_3)_2(CO_2H)$	2-Hydroxymethyl-2-methyl-1-propionic acid
14	$C(CH_2OH)(CH_3)_2(CHO)$	2-Hydroxymethyl-2-methyl-1-propanol
15	$C(CH_2F)_3(CO_2H)$	Tris(fluoromethyl)acetic acid
16	$C(CH_2OH)_3(CH_2Cl)$	Monochloropentaerythritol


C(CH2OH)3(CH2Br)
C(CH2OH)2(CH2Br)2
C(CH2OH)(CH2Br)3
C2H5ONa
C2H5OH
CH2C(CH2OH)2CH2O
CH2C(CH2OH)(CH2Br)CH2O
CH2C(CH2Br)2CH2O
CH2C(CH2OH)2CH2O
aq. NH3
200°
C(CH2OH)3(CH2NH2)
(Compound 1)
CH2C(CH2OH)(CH2Br)CH2O
aq. C2H5OH-NH3
190°
C(CH2OH)2(CH2NH2)2
(Compound 2)
CH2C(CH2OH)(CH2Br)CH2O
KF
O(CH2CH2OH)2
CH2C(CH2OH)(CH2F)CH2O
CH2C(CH2Br)2CH2O
KF
(CH2OH)2
CH2C(CH2F)2CH2O
CH2C(CH2OH)(CH2F)CH2O
H2O
H2SO4
C(CH2OH)3(CH2F)
(Compound 5)
CH2C(CH2F)2CH2O
H2O
H2SO4
C(CH2OH)2(CH2F)2
(Compound 6)
C(CH2Br)4
KF
O(CH2CH2OH)2
C(CH2F)4
(Compound 8)
C(CH2Cl)3(CO2H)
H2O
Ba(OH)2
C(CH2OH)3(CO2H)
(Compound 12)
CH2C(CH2OH)2CH2O
aq. HCl
C(CH2OH)3(CH2Cl)
(Compound 16)

Several attempts to prepare Compound 3 by the method employed for Compounds 1 and 2 failed. The sulfate of Compound 4 could be isolated, but not the free base. Although several approaches to the preparation of the fluorine-substituted derivatives were investigated, no satisfactory procedure could be found for the synthesis of Compound 7. When the procedure that was followed for the preparation of Compound 8 was followed, an unidentified by-product was isolated. Intermediates for the nitrile derivatives, the cyanomethyloxetanes, were readily prepared, but the oxetane ring could not be satisfactorily hydrolyzed, either under neutral or acidic conditions; therefore, Compounds 9, 10, and 11 could not be prepared.

Literature procedures for the synthesis of Compounds 13 and 14 were followed, but the products isolated could not be unequivocally identified as the same materials that had been previously reported. Compound 15 was not prepared because its precursor, Compound 7, was not obtained.

Structures that were considered for preparation during the literature search, but rejected, are summarized in Table 6. The compounds were rejected for a variety of reasons: possible low transitional enthalpies or the probability of transition temperatures outside the target range; the hazardous nature of some of the materials; or uncertainties concerning the methods of preparation that were not outweighed by the predicted properties of the compounds.

E. Temperatures and Heats of Transition of New Candidate Materials

Quantitative and qualitative data obtained for the newly synthesized materials are summarized in Table 7. Qualitative data verified the existence of a mesocrystalline phase in all of the tetrahedral substances that were examined. Data are also included for two intermediate oxetanes. Although one of these substances exhibited a solid state transition, its fusion entropy was too large for it to be classed as a plastic crystal, a finding consistent with the predictions based on structure. The fusion entropies for all of the tetrahedral substances were small, 3 e.u. or less, indicating that communal entropy represented the substantial portion of the entropy increment of fusion.

Of the seven tetrahedral substances prepared, five had solid state transitions within the target range, 0 to 100°. All had relatively high heats of transition, but not so high as the sought for 56 cal/g. Although not all of the substances prepared were predicted to have transitional enthalpies above 56 cal/g, the results provided values that were lower than had been expected.

TABLE 6

COMPOUNDS NOT SELECTED FOR SYNTHESIS AND SCREENING

$C(CH_2OH)_2(CN)_2$	$C(CH_2OH)_3[CH_2N(CH_3)_2]$
$C(CH_2OH)_2(CH_2SH)_2$	$C(CH_2SO_2H)_4$
$C(CH_2OH)_2(CF_3)(NO_2)$	$C(CH_2SCH_3)_4$
$C(CH_2OH)_2(NO_2)_2$	$C(CH_2SH)_4$
$C(CH_2OH)(NO_2)_3$	$C(CH_2OH)_2(CO_2H)_2$
$C(CH_2OH)_2(CH_2Cl)_2$	$C(CH_2OH)_3(CN)$
$C(CH_2OH)_3(CH_2CO_2H)$	$C(CH_2OH)(CH_2F)_2(CO_2H)$
$C(CH_3)(CH_2NO_2)_2$	$C(CH_2OH)_2[CH_2N(CH_3)_2]_2$
$C(CH_3)(CH_2OH)(NO_2)_2$	$C(CH_2OH)(CH_2F)_2(CH_2NH_2)$
$C(CH_2NHCH_3)_4$	$C(CH_2OH)_2(CH_3)(CHO)$
$C[CH_2N(CH_3)_2]_4$	$C(CH_2SO_2CH_3)_4$

TABLE 7

SUMMARY OF NEW ENTHALPY DATA FOR TRANSITIONS AND FUSIONS OF PLASTIC CRYSTALS

Compound	Transition			Fusion		
	Temp. (°C)	ΔH (cal/g)	ΔS (e.u.)	Temp. (°C)	ΔH (cal/g)	ΔS (e.u.)
Tris(hydroxymethyl)acetic acid	124-127	48.83	18.5	217-221	4.23	1.3
Monochloropentaerythritol	61-63	35.63	16.5	136-137	5.11	1.9
Monofluoropentaerythritol	68-72	33.28	13.5	203-207	10.68	3.1
Difluoropentaerythritol	18-20	21.37	10.3			
Tetrafluoropentaerythritol	-29 to -26	18.66	11.0	88-90	6.96	2.8
Monoaminopentaerythritol	86-91	45.86	17.3	200-208	7.87	2.3
Diaminopentaerythritol	68-73	44.20	16.6	159-160	9.34	2.9
3,3-Bis(hydroxymethyl)oxacyclobutane				-3 to 0	12.86	5.6
3,3-Bis(cyanomethyl)oxacyclobutane	50-58	26.90	11.3			

The prediction of transition temperature was based on the assumption that within a family of substances the addition of each functional group leads to an incremental change in the transition temperatures and fusion temperatures. Such a relationship was represented graphically in Annual Summary Report No. 1, page 15, for several families of compounds, for example, the pentaerythritol, trimethylolethane, dimethylolpropane, neopentyl alcohol, neopentane group. The correlations were not precise, but were regular enough to allow predictions of transition temperatures to be reasonably accurate. Estimates of transitional enthalpies were calculated from predicted entropies of transition, which were determined by assuming the additivity of conformation reorientations possible for each functional group in a molecular structure. A number of correlations based on this assumption can be found in the literature. Thus, in the pentaerythritol neopentyl alcohol series, the substitution of each hydroxylmethyl group for a methyl group in progressing through the series adds an equal number of statistically possible conformational states and consequently an equal entropy increment in the solid-solid transition. An exception to these rules had been observed, as might be expected, when steric crowding about the central carbon atom in the tetrahedral structure inhibited a portion of the conformation possibilities.

With these assumptions, the following estimates were made for the fluoropentaerythritol series based on a transition entropy increment for pentaerythritol of 21.5 e.u. at 182° and for tetrafluoropentaerythritol of 12.7 e.u. at -14°: monofluoropentaerythritol, 57 cal/g at 133° (19.3 e.u.); difluoropentaerythritol, 44 cal/g at 84° (17.1 e.u.); and trifluoropentaerythritol, 32 cal/g at 35° (14 9 e.u.). Since the values are qualitatively and quantitatively much lower than the experimental values reported in Table 7, it is apparent that the correlations in this series are not additive. This conclusion is particularly interesting in view of the success reported by Westrum in the calculations in which he rationalized the entropy increments of transition of pentaerythritol and tetrafluoropentaerythritol on the basis of the assumption of group additivity.[5]

One possible explanation for the disagreement is the restriction of conformational states through intramolecular hydrogen bonding in the fluoropentaerythritols; however, there was no chemical evidence of hydrogen bonding. Moreover, hydrogen bonding, particularly in difluoropentaerythritol, would probably have effected even more severe restrictions to conformational disorder than were observed. A direct explanation of the anomalous values on the basis of the available data is impossible, but two alternative explanations can be postulated, both of which are highly speculative. The similarity of the entropy increment for trimethylolethane (15.6 e.u.), monofluoropentaerythritol (13.5 e.u.), and monochloropentaerythritol (16.5 e.u.) and for dimethylolpropane (10.3 e.u.) and difluoropentaerythritol (10.3 e.u.) suggests that the contribution of the halomethyl group to the new

conformation possibilities is no greater than the contribution of the methyl group. The argument against such an explanation is, of course, the much greater entropy increment for pentaerythrityl fluoride (11.0 e.u.) than for neopentane (4.4 e.u.). Alternatively, the striking similarity between the entropy increment for pentaerythrityl fluoride (11.0 e.u.) and for difluoropentaerythritol (10.3 e.u.) suggests that the effects of new conformational states may be cancelled by loss of molecular reorientational states. Such a similarity has also been observed in the entropy increments for neopentane (4.4 e.u.) and neopentyl alcohol (4.6 e.u.).

In the aminopentaerythritol series, exact predictions could not be made since thermodynamic values had not been measured for tetraaminopentaerythritol, but by analogy with the fusion temperatures of related substances, it was assumed that the transition temperatures would be lowered as the number of aminomethyl groups was increased. On the basis of the structures, it was also assumed that the entropy increments should be as large as the entropy increment for pentaerythritol. These assumptions would lead to the prediction of high enthalpies at relatively low temperatures.

Transition temperatures for monoaminopentaerythritol and diaminopentaerythritol were drastically lower than the transition temperatures of pentaerythritol, but entropy increments of transition were not so large as the value for pentaerythritol. The consequence was that transition enthalpies were about 45 cal/g. Unfortunately, triaminopentaerythritol could not be prepared, since it now appears that this substance has the greatest probability of exhibiting a transition below 50° with an enthalpy greater than 40 cal/g.

The low values for the transitional enthalpy for tris(hydroxymethyl)-acetic acid can probably be attributed to the steric restriction of conformational disorder and the consequent decrease in the entropy increment. The difference in values for tris(hydroxymethyl)acetic acid (18.7 e.u.) and bis-(hydroxymethyl)propionic acid (21.7 e.u.) parallels the difference between 2-hydroxymethyl-2-nitro-1,3-propanediol (16.9 e.u.) and 2-methyl-2-nitro-1,3-propanediol (18.3 e.u.). In both pairs, the introduction of a group that should lead to an increase in the number of conformational possibilities actually restricts the possible orientations.

Although the cyanopentaerythritols could not be prepared, a cyano-substituted intermediate, 3,3-bis(cyanomethyl)oxacyclobutane, had a solid state transition. This transition ultimately proved not to be a plastic crystalline transformation, but its heat of transition was compared with the heat of fusion of bis(hydroxymethyl)oxacyclobutane in order to make some assessment of the heat effect that might result from cyano-group substitution. The relatively high heat of transition of the cyano derivative confirmed that the cyanopentaerythritols would probably have high enthalpies of transition if they could be prepared.

III. CONCLUSIONS

Experimental and theoretical evidence has been gathered in order to find four plastic crystalline materials that meet specified requirements for thermal control applications in spaceflight. Although four materials were not found that met all the requirements, plastic crystals as a series constitute a group of organic materials with the versatility of exhibiting as high transitional enthalpies over a broad range of temperatures as any other group of organic materials. The following plastic crystalline substances with high latent heats of transition are now known: pentaerythritol, 72 cal/g at 184°; trimethylolethane, 46 cal/g at 81°; 2-amino-2-hydroxymethyl-1,3-propanediol, 68 cal/g at 131°; 2-amino-2-methyl-1,3-propanediol, 63 cal/g at 78°; 2-hydroxymethyl-2-nitro-1,3-propanediol, 39 cal/g at 80°; 2-methyl-2-nitro-1,3-propanediol, 48 cal/g at 79°; 2,2-bis(hydroxymethyl)propionic acid, 69 cal/g at 152°; tris(hydroxymethyl)acetic acid, 49 cal/g at 124°; monoaminopentaerythritol, 46 cal/g at 86°; and diaminopentaerythritol, 44 cal/g at 68°. The chief difficulty with this series is obtaining high latent heats of transition at lower temperatures.

The data also indicate that small changes in volume occur in the solid-solid transitions and that the transitions occur over narrow temperature ranges. On cooling, many of the phase changes occur without supercooling, but when supercooling does occur, nucleating agents are effective in minimizing the problem. Mixtures of two plastic crystalline materials form solid solutions, at least in those systems that have been examined. No evidence for eutectic formation has been observed.

The existence of a plastic crystalline phase in substances can usually be predicted on the basis of its molecular symmetry. Enthalpies of transition can also be predicted, but undefined structural constraints limit the accuracy of these predictions. In nearly all of the substances prepared during the second phase of the program, transition enthalpies failed to be as large as could be predicted on the basis of the molecular structures of the substances. This failure to realize the potential heat effects must be attributed to restrictions imposed on the possible states of disorder in the plastic crystalline phase. No theoretical information is available to allow an assessment of these constraints and permit more accurate estimates of latent heats of transition.

IV. EXPERIMENTAL PART

A. Qualitative Thermal Data

All data were obtained with a DuPont Differential Thermal Analyzer with a heating rate of 15°/min in an air atmosphere. Temperature ranges in the qualitative experiments were taken as the range between the extrapolated onset of the transition and the maximum height of the endotherm. Qualitative data are included in Tables 8 and 9.

B. Quantitative Standardization

The DuPont Differential Scanning Calorimeter module was standardized for the quantitative experiments by constructing a plot of the peak temperatures versus the calibration coefficient, E , determined with standard samples of mercury, acetamide, indium, and tin.

$$E = \frac{\text{specific heat (cal/g) x heating rate (°C/min) x wt. (mg.)}}{\text{plotted area (in}^2\text{) x T scale (°C/in) x } \Delta T \text{ scale (°C/in)}}$$

The results of the calibration experiments are summarized in Table 10.

C. Quantitative Thermal Data

Quantitative determinations were carried out with a suitably standardized DuPont Differential Scanning Calorimeter with a heating rate of 10°/min in an air atmosphere in hermetically sealed pans. When transitional heats for moisture-sensitive substances were determined, the calorimeter pans were loaded in a nitrogen atmosphere. The results of the quantitative experiments are summarized in Tables 8 and 9.

D. Crystallization Studies

In the macro studies, about 2.5 g. of each substance or mixture was placed in a 150 x 15 mm. test tube and an uncalibrated 360° glass-mercury thermometer was inserted in such a way that the substance covered the bulb of the thermometer. The test sample was heated to 10-15° above its fusion temperature in an oil bath equipped with a magnetic stirrer, then allowed to cool at a rate determined by the difference in room temperature and the bath temperature. Bath temperatures and sample temperatures were recorded every 0.5 min. to determine the equilibrium temperature for phase transition (plateau temperature) on cooling. The results of these experiments are included in Tables 2 and 3.

TABLE 8

TEMPERATURES AND HEATS OF TRANSITION AND FUSION FOR AVAILABLE SUBSTANCES

Compound	Formula Weight	Transition Temp. (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Avg.	Transition ΔS (e.u.-avg.)	Fusion Temp. (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Avg.	Fusion ΔS (e.u.-avg.)
Pentaerythritol (recrystallized)									
Sublimed once		455-457				527-528			
Sublimed twice		456-457				531-532			
Sublimed three times	136.15	455-456	71.12	71.95	21.53	531	9.06	8.90	2.28
			72.70				8.47		
			72.03				9.17		
2-Amino-2-methyl-1,3-propanediol (new sample)	105.14	349-351	52.75	53.25	16.04	378-380	6.28	6.72	1.87
			52.31				6.32		
			54.70				7.55		
Sublimed once		347-350				358-360			
Sublimed twice		349-351				376-379			
2-Amino-2-methyl-1-propanol (new sample)						287-291			
Hexamethylcyclotrisiloxane	222.47					334-336	21.31	21.59	14.38
							21.86		
							21.60		
N,N'-Bis(trimethylsilyl)tetramethylcyclodisilazane	290.72					313-315	18.71	18.93	17.58
							20.13		
							17.95		

TABLE 9

ENTHALPY AND ENTROPY DATA FOR NEWLY PREPARED SUBSTANCES

Compound	Formula Weight	Transition Temp. (°K)	Transition ΔH (cal/g) Value	Transition ΔH (cal/g) Avg.	Transition ΔS (e.u. Avg.)	Fusion Temp. (°K)	Fusion ΔH (cal/g) Value	Fusion ΔH (cal/g) Avg.	Fusion ΔS (e.u. Avg.)
Tris(hydroxymethyl)acetic acid	150.13	397-400	48.56 48.96 48.98	48.83	18.46	490-494	4.10 4.32 4.26	4.23	1.30
Monochloropentaerythritol	154.60	334-336	36.57 33.97 36.65 35.35	35.63	16.49	409-410	5.38 5.05 5.06 4.96	5.11	1.93
Monofluoropentaerythritol	138.14	341-345	33.83 33.23 32.57 33.48 34.15 32.45	33.28	13.48	476-480	11.30 9.74 12.19 9.47	10.68	3.09
Difluoropentaerythritol	140.13	291-293	21.29 21.71 19.89 22.67	21.37	10.29	Sublimed			
Tetrafluoropentaerythritol[a]	144.11	244-247	18.76 19.49 17.73	18.66	11.02	361-363	7.15 6.81 6.91	6.96	2.78
Monoaminopentaerythritol	135.16	359-364	46.75 44.27 47.09 49.98 43.28 43.81	45.86	17.27	473-481	8.37 7.85 8.52 7.48 7.11	7.87	2.25
Monoaminopentaerythritol (resublimed)	135.16	359-364	45.00 43.24 44.36	44.20	16.64	473-481	7.19 6.77 7.31	7.09	2.03
Diaminopentaerythritol	134.18	341-346	44.24 43.10 43.58	43.64	17.22	432-433	9.00 9.45 9.56	9.34	2.90
3,3-Bis(hydroxymethyl)-oxacyclobutane	118.13					270-273	12.55 10.73 15.31	12.86	5.63
3,3-Bis(cyanomethyl)oxacyclobutane	136.15	323-325	27.64[b] 26.46 26.61	26.90	11.34				

a/ Reported transition, 249°K, ΔS, 12.66 e.u.; fusion, 367°K, ΔS, 3.35 e.u.[5]

b/ Estimated from overlapping peaks.

TABLE 10

QUANTITATIVE THERMAL DATA ON STANDARD SUBSTANCES REDETERMINED IN SEALED CUPS

Enthalpy (cal/g)	Peak Temp. (°C)	Substance	Number of Determination	Calibration Coefficient	Average
2.74	-31	Hg	1	154.8	155.3
			2	156.3	
			3	154.9	
63.5	89	CH_3CONH_2	1	159.0	153.4
			2	153.1	
			3	148.2	
6.79	164	In	1	159.7	155.6
			2	156.5	
			3	156.9	
			4	152.5	
			5	152.4	
14.2	242	Sn	1	163.8	163.3
			2	162.8	
			3	163.2	
			4	163.4	

In the micro studies, the usual procedures were followed with either the qualitative or quantitative cells. A heating rate of 10°/min was employed. Data from these experiments are reported in Tables 1 and 3.

E. Density of Trimethylolethane at 25 and 88°

The density of trimethylolethane was determined by the hydrostatic weighting method at 25, 73, and 88° by determining the weight of trimethylolethane, both in air and in a trimethylolethane-saturated xylene solution, by means of a Jolly balance.

1. Procedure: The Jolly balance was calibrated with weighed pieces of copper cut to various lengths to give small incremental differences in weight. A comparison of the weight of each copper strip taken on a Mettler balance with the scale deflection on the Jolly balance indicated a calibration of 0.1920 g/unit.

The apparent density of the trimethylolethane was calculated according to the following expression, in which d_s' is the apparent density of the solid (uncorrected for buoyance effects), d_L is the density of the liquid, W_o' is the apparent weight of the solid in vacuum, and W_L' is the apparent weight of the solid in the liquid:

$$d_s' = d_L W_o'/(W_o' - W_L')$$

The apparent density was corrected for buoyancy effects by the addition of a correction factor C, $d_s = d_s' + C$, in which D is the density of air:

$$C = D(1 - d_s'/d_L)$$

Calculation of d_L used the following relationship in which d_L is the density of the liquid, W_A is the true weight of the pan and wire in vacuum, W_L is the weight of the pan and wire in the liquid, and V_i is the volume of the pan and wire.

$$d_L = (W_A - W_L)/V_i$$

The true weight of the pan and wire in a vacuum was found by adding to the apparent weight the weight of an equal volume of air, $W_A = W_A' + DV_i$. The volume (V_i) was determined with water at 4°C as a secondary standard. When the density of air was assumed to be 0.0012 g/ml, V_i was 0.9958.

2. Results: The results of determining the density of xylene saturated with trimethylolethane are summarized in Table 11.

TABLE 11

DENSITY OF TRIMETHYLOLETHANE-SATURATED XYLENE

Determination No.	Temperature (°C)	Density (g/ml)
1	26	0.8630
2	25	0.8611
3	74	0.8187
4	73	0.8206
5	90	0.8091
6	90	0.8091
7	91	0.8091

The results of the density determinations are summarized in Table 12.

TABLE 12

DENSITY OF TRIMETHYLOLETHANE

Determination No.	Temperature (°C)	Density (g/ml)	Average Density (g/ml)
1	26	1.220	1.221
	25	1.213	
	25	1.234	
2	25	1.227	
	26	1.210	
	26	1.228	
	25	1.218	
3	73	1.210	1.186
4	73	1.191	
	75	1.158	
5	90	1.144	1.163
6	88	1.166	
7	88	1.179	

Trimethylolethane exhibits a transition at 81°. The change in density between 25° and 88° was about 4.8%.

F. Synthesis of Candidate Substances and Their Intermediates

1. Bromopentaerythritols:

a. Monobromopentaerythritol: The method of Wawzonek was followed.[6] After a solution of 400 g. (2.94 moles) of pentaerythritol in 3.0 liters of glacial acetic acid and 34 ml. of 48% hydrobromic acid was heated 1.5 hr., 340 ml. of 48% hydrobromic acid was added and the mixture was refluxed for 5 hr. Distillation of the acetic acid gave a viscous residue, which was heated with 1.5 liters of 98% ethanol and 100 ml. of

48% hydrobromic acid until about 1 liter of distillate was collected. A second 1.5 liters of ethanol was added and distillation was continued until an additional 1.5 liters of distillate had collected. The remaining alcohol was removed as completely as possible under reduced pressure. In two sequential steps, 1-liter portions of benzene was added to the residue and each portion was distilled out, the last traces of benzene being removed in each step under reduced pressure. After the residue was refluxed with 1-liter of dry ether, the ether was decanted and the residue was treated with a third 1-liter portion of benzene. The dry solid residue was extracted exhaustively with dry ether in a Soxhlet extractor. After the extract was cooled in an ice bath overnight, 205 g. (46%) of monobromopentaerythritol, m.p. 74-76° (differential thermal analysis) was obtained after one recrystallization from chloroform-ethyl acetate (reported m.p., 75-76°).[6]

Anal. calcd. for $C_5H_{11}BrO$: C, 30.17; H, 5.57; Br, 40.15. Found: C, 30.40; H, 5.58; Br. 40.36.

In two repetitions of the experiment, somewhat lower conversions were obtained.

b. Tribromopentaerythritol and dibromopentaerythritol: The method of Saucier was followed.[7] Anhydrous hydrogen bromide was bubbled through a boiling solution of 272 g. (2.00 moles) of pentaerythritol in 1.6 liters of glacial acetic acid for 23.5 hr. when the weight had increased to 631 g. (calcd. for tribromopentaerythritol, 486 g.). After the acetic acid was evaporated under reduced pressure, 800 ml. of toluene was added to the residue and the solution was heated to remove the toluene-water azeotrope until water no longer was collected. The residue that was obtained by evaporating the toluene was dissolved in 675 ml. of anhydrous methanol containing about 4 ml. of anhydrous hydrogen bromide and heated to allow the methyl acetate-methanol azeotrope to distill slowly. After methyl acetate distillation ceased, the methanol was evaporated, the residue was dissolved in 2.5 liters of hot toluene, and the solution was chilled. A total of 184 g. of dibromopentaerythritol precipitated and was filtered off. Evaporation of the toluene gave a residue from which an additional 54 g. of dibromopentaerythritol was separated by fractional crystallization from cyclohexane (total yield 45%). After an additional recrystallization from toluene, the dibromopentaerythritol melted at 107-110° (reported m.p. 109-110°).[7] The following fractions of tribromopentaerythritol were separated in the fractional crystallization from cyclohexane: 131 g., m.p. 61-63°; 98 g., m.p. 64-65°; 72 g., m.p. 65-68°; and 30 g., m.p. 65-66° (reported m.p. 68-69°).[7] The combined yield was 51%.

2. Oxetanes:

a. 3,3-Bis(hydroxymethyl)oxacyclobutane: A solution of sodium ethoxide in ethanol, prepared by adding 4.6 g. (0.20 g-atom) of

sodium to 250 ml. of dry ethanol, was added dropwise to 39.8 g. (0.20 mole) of monobromopentaerythritol in 100 ml. of dry ethanol while the mixture was stirred vigorously. After the addition was complete, the mixture was refluxed 2 hr., cooled, filtered, and the ethanol was evaporated. Fractional distillation gave 9.86 g. (42%) of 3,3-bis(hydroxymethyl)oxacyclobutane, m.p. 74-76°, b.p. 148-150° (0.6 mm.) [reported m.p. 84°, b.p. 128° (0.04 mm.)].[8]

Anal. calcd. for $C_5H_{10}O_3$: C, 50.80; H, 8.53. Found: C, 50.72; H, 8.50.

Two other methods for the synthesis of this compound[8,9] in which monobromopentaerythritol was treated with potassium hydroxide gave lower yields of less pure material.

b. 3-Bromomethyl-3-hydroxymethyloxacyclobutane: Issidorides's procedure was followed.[10] Sodium ethoxide in ethanol, prepared from 600 ml. of anhydrous ethyl alcohol and 8.8 g (0.38 g-atom) of sodium, was added to 100 g. (0.38 mole) of dibromopentaerythritol in 300 ml. of anhydrous ethyl alcohol. After the mixture was refluxed 2.5 hr., cooled, filtered, and the ethyl alcohol was removed, distillation of the residue gave 61.2 g. (63%) of 97-98% pure (gas-liquid chromatography) 3-bromomethyl-3-hydroxymethyloxacyclobutane, b.p. 108-110° (1.6 mm.), n_D^{20} 1.5093 [reported b.p. 141-143° (1-2 mm.); n_D^{20} 1.5101].[10]

c. 3,3-Bis(bromomethyl)oxacyclobutane: Sodium ethoxide in ethanol, prepared from 250 ml. of anhydrous ethyl alcohol and 5.0 g. (0.22 g-atom) of sodium, was added to 70.0 g. (0.22 mole) of tribromopentaerythritol in 100 ml. of anhydrous ethyl alcohol. After the mixture was refluxed for 2.5 hr., cooled, filtered, and the ethyl alcohol was removed, distillation of the residue gave 30.8 g. (59%) of 3,3-bis(bromomethyl)oxacyclobutane, b.p. 121-123° (19 mm.), n_D^{20} 1.5409 [reported b.p., 125° (23 mm.)].[11]

Anal. calcd. for $C_5H_8Br_2O$: C, 24.62; H, 3.30; Br, 65.52. Found: C, 25.24; H, 3.32; Br, 65.11.

In an experiment in which Campbell's method[11] was followed, a lower yield of a less pure material was obtained.

d. 3,3-Bis(cyanomethyl)oxacyclobutane: Campbell's method was followed.[11] To 9.00 g. (0.037 mole) of 3,3-bis(bromomethyl)oxacyclobutane in 15 ml. of 95% ethanol was added 4.07 g. (0.083 mole) of sodium cyanide and the mixture was refluxed for 24 hr. After the mixture was filtered hot and the ethanol was evaporated, 300 ml. of benzene was added, the benzene was boiled, and the insoluble portion was filtered off. The cooled filtrate, evaporated to 50 ml., gave 2.1 g. of 3,3-bis(cyanomethyl)-oxacyclobutane, m.p. 73-76° (reported m.p. 76.5°).[11] An additional 1.42 g. m.p. 72-75° (total yield, 70%) was also recovered. The compound exhibited a transition of 49-52° on differential thermal analysis.

e. 3-Cyanomethyl-3-hydroxymethyloxacyclobutane: To 10.0 g. (0.055 mole) of 3-bromomethyl-3-hydroxymethyloxacyclobutane in 15 ml. of 95% ethyl alcohol was added 2.9 g. (0.058 mole) of sodium cyanide. After the mixture was refluxed 24 hr., filtered hot, and the solvent was evaporated, distillation of the residue gave 2.58 g. (37%) of 3-cyanomethyl-3-hydroxymethyloxacyclobutane, b.p. 132-134° (1.1 mm.). G.l.c. analysis indicated 80-90% purity.

f. 3,3-Bis(fluoromethyl)oxacyclobutane: The method of Sorenson and Campbell[12] was followed. A mixture of 6.33 g. (0.11 mole) of anhydrous potassium fluoride, 10.00 g. (0.041 mole) of 3,3-bis(bromomethyl)-oxacyclobutane, and 15 ml. of anhydrous ethylene glycol was heated in a sand bath and the material boiling up to 196° was allowed to distill. To the distillate was added 40 ml. of water, and the water and entrained bis(flouromethyl)oxacyclobutane, which separated as a lower phase, were distilled. The distillate was used directly without purification in the preparation of the fluoropentaerythritol derivative.

g. 3-Fluoromethyl-3-hydroxymethyloxacyclobutane: To 10.0 g. (0.055 mole) of 3-bromomethyl-3-hydroxymethyloxacyclobutane in 5 ml. of anhydrous diethylene glycol was added 4.8 g. (0.083 mole) of anhydrous potassium fluoride. The mixture was heated with stirring at 150° for 3 hr. Slow distillation under vacuum (110 mm.) gave 7.2 g. (calcd. 6.6 g.) of impure 3-fluoromethyl-3-hydroxymethyloxacyclobutane.

Anal. calcd. for $C_5H_9FO_2$: C, 49.96; H, 7.55; F, 15.81. Found: C, 48.13; H, 8.43; F, 9.17.

3. Chloro- and Fluoropentaerythritols:

a. Monofluoropentaerythritol: A mixture of 4.0 g. (0.033 mole) of 3-fluoromethyl-3-hydroxymethyloxacyclobutane and 40 ml. of water containing one drop of sulfuric acid was refluxed 6 hr., cooled, neutralized with 10% aqueous barium hydroxide, and continuously extracted with ether for 24 hr. After the ether was distilled from the extract, the residue was extracted with eight 10-ml. portions of ethyl acetate. Evaporation of the ethyl acetate gave 3.4 g. of a residue, which upon sublimation at 140° (0.2 mm.) and recrystallization from ethyl acetate gave 0.81 g. (18%) of monofluoropentaerythritol, m.p. 204-209° (capillary), m.p. 203-207°, transition 68-72° (differential thermal analysis).

Anal. calcd. for $C_5H_{11}FO_3$: C, 43.54; H, 8.02; F, 13.74. Found: C, 43.54; H, 7.67; F, 13.52.

An attempt to prepare this compound by treating 3,3-bis(hydroxymethyl)oxacyclobutane with potassium fluoride and aqueous hydrogen fluoride was unsuccessful.

b. Difluoropentaerythritol: The distillate obtained in the preparation of 3,3-bis(fluoromethyl)oxacyclobutane was treated with a drop of sulfuric acid, refluxed 6 hr., neutralized with 10% barium hydroxide, and extracted with four 150-ml. portions of ether. When the combined ether extracts were dried over anhydrous magnesium sulfate, evaporated, and the residue was sublimed, 1.3 g. (21% overall yield) of monofluoropentaerythritol was obtained. After the crude material was sublimed, recrystallized from toluene, and resublimed at 82° (0.2 mm.), 1.04 g. (18%) of difluoropentaerythritol transition 18-20°, m.p. 131-143°, was obtained.

Anal. calcd. for $C_5H_{10}F_2O_2$: C, 42.82; H, 7.19; F, 27.09. Found: C, 42.80; H, 7.12; F, 26.97.

c. Trifluoropentaerythritol (attempted): To 15 g. (0.046 mole) of tribromopentaerythritol in 15 ml. of anhydrous diethylene glycol was added 12.1 g. (0.208 mole) of anhydrous potassium fluoride. After the mixture was heated at 145-150° for 3 hr., the pressure was reduced and 2.1 g. of a substance, which has not been identified, distilled; b.p. 131°, m.p. -15° to -25°, transition -34° to -36° (differential thermal analysis).

Anal. calcd. for $C_5H_9F_3O$: C, 42.22; H, 6.38; F, 40.07. Found: C, 48.34; H, 7.33; F, 24.90.

d. Tetrafluoropentaerythritol: After a mixture of 50 g. (0.016 mole) of tetrabromopentaerythritol and 46.4 g. (0.80 mole) of dry potassium fluoride in 50 ml. of dry diethylene glycol was heated to 210° according to a published procedure,[13] 13.0 g. of a liquid distilled. Redistillation of the liquid gave 1.8 g. (8%) of impure tetrafluoropentaerythritol, b.p. 114-115°. When the distillate was sublimed at 110 mm., 0.90 g. of pure tetrafluoropentaerythritol, m.p. 88-90°, transition -29° to -26° (differential thermal analysis), was obtained (reported b.p. 110-110.2°, m.p. 92°).[13]

Anal. calcd. for $C_5H_8F_4$: C, 41.61; H, 5.59; F, 52.67. Found: C, 38.81; H, 5.18; F, 52.44.

e. Monochloropentaerythritol: After a mixture of 4.0 g. (0.034 mole) of 3,3-bis(hydroxymethyl)oxacyclobutane and 40 ml. of 36% aqueous hydrochloric acid was refluxed 2 hr., cooled, and mixed with 100 ml. of saturated sodium chloride solution, the mixture was extracted continuously with ether for 38 hr. Evaporation of the ether and sublimation of the residue gave a solid, which upon recrystallization from ethyl acetate-chloroform afforded 3.42 g. of monochloropentaerythritol, m.p. 138-139° (reported m.p. 141°).[14] Differential thermal analysis indicated an energetic transition at 61-63° and a fusion temperature of 136-137°.

Anal. calcd for $C_5H_{11}ClO_3$: C, 38.79; H, 7.16; Cl, 22.91. Found: C, 38.73; H, 7.10; Cl, 22.96.

4. Aminopentaerythritols:

a. Monoaminopentaerythritol: An established procedure was followed for the preparation of this compound.[15] After 4.35 g. of 3,3-bis-(hydroxymethyl)oxacyclobutane in 200 ml. of an aqueous solution saturated with ammonia at 0° was heated in an autoclave for 24 hr. at 200°, the solution was evaporated and the residue was dissolved in 100 ml. of absolute alcohol. Saturation of the solution with carbon dioxide precipitated 4.23 g. (64%) of monoaminopentaerythritol carbonate. When 1.98 g. of the carbonate was heated at 180° (0.1 mm.) in a sublimator, 1.17 g. (72%) of monoaminopentaerythritol sublimed. Three additional sublimations of the product of the experiment gave 2.3 g. of monoaminopentaerythritol, m.p. (sealed capillary) 200-209° (reported m.p. 207°).[15] Differential thermal analyses showed a transition at 86-91° and a fusion temperature of 200-208°.

Anal. calcd. for $C_5H_{13}NO$: C, 44.43; H, 9.69; N, 10.36. Found: C, 44.16; H, 8.95; N, 9.84.

b. Diaminopentaerythritol: After 100 ml. of 50% aqueous ethyl alcohol saturated with ammonia at 0°C and 10.0 g. (0.055 mole) of 3-bromomethyl-3-hydroxymethyloxacyclobutane were heated in an autoclave at 190° for 22 hr., the ethyl alcohol was distilled off. The residue in 50 ml. of anhydrous ethyl alcohol was treated with dry ice until no more amine carbonate precipitated. When the 2.1 g. of amine carbonate was thermally decomposed and sublimed at 160° (0.2 mm.), reprecipitated with dry ice, and resublimed, 0.8 g. (11%) of diaminopentaerythritol was obtained, transition, 68-73°, m.p. 159-160° (differential thermal analysis).

The filtrate was concentrated to afford 4.5 g. of an oil containing the oxacyclobutane structure, assumed on the basis of the infrared band at 970 cm^{-1} (oxetane).

Anal. calcd. for $C_5H_{14}N_2O_2$: C, 44.74; H, 10.51; N, 20.87. Found: C, 44.64; H, 10.27; N, 20.69.

c. Triaminopentaerythritol (attempted): Beyaert's procedure was followed.[16] A saturated solution of ammonia in 75 ml. of 50% ethyl alcohol was prepared at 0°C and added to 10.0 g. (0.041 mole) of 3,3-bis-(bromomethyl)oxacyclobutane in 75 ml. of 50% ethyl alcohol. After the mixture was transferred to an autoclave and heated at 200° for 24 hr., it was filtered and the solvent was evaporated. Treatment of the residue with 48% hydrobromic acid precipitated 1.8 g. of a solid which was filtered off and recrystallized from water. This material, which was believed to be the

hydrobromide salt of triaminopentaerythritol, was dissolved in 15 ml. of water and treated with 0.31 g. (0.0048 mole) of potassium hydroxide in 5 ml. of water. After the water was removed, the residue was extracted six times with 10-ml. portions of hot, anhydrous ethanol and the ethanol was evaporated. An attempt to sublime the residue afforded no sublimate.

d. Tetraaminopentaerythritol (attempted): To 0.3 g. (0.0009 mole) of tetraaminopentaerythritol disulfate, reported in Annual Summary Report No. 1, p. 81, in 5 ml. of water was added 0.3 g. (0.0009 mole) of barium hydroxide in 5 ml. H_2O. The barium sulfate was filtered off and the filtrate was concentrated. The residue, mixed with 0.5 g. of tetraaminopentaerythritol monohydrate and dissolved in 15 ml. of 95% ethanol, was treated with dry ice until no more amine carbonate precipitated. Filtration gave 1.0 g. of amine carbonate of which 0.32 g. was recovered after recrystallization from a water-ethanol mixture. In a sublimation of this material, a temperature of 195° (0.2 mm.) was required to obtain about 100 mg. Tetraaminopentaerythritol should sublime at a lower temperature.

5. Cyanopentaerythritols:

a. Monocyanopentaerythritol (attempted): To 2.0 g. (0.016 mole) of 3-cyanomethyl-3-hydroxymethyloxacyclobutane in 40 ml. of water was added one drop of concentrated sulfuric acid. The mixture was refluxed 6 hr., cooled, neutralized to a pH of 7, and continuously extracted with ether for 48 hr. Evaporation of the ether extract gave 3.7 g. of a wet residue, which did not show an oxetane band in its infrared spectrum but did show a band at about 1720 cm^{-1}. The product was not identified.

b. Dicyanopentaerythritol (attempted): A mixture of 1.5 g. (0.01 mole) of 3,3-bis(cyanomethyl)oxacyclobutane and 50 ml. of water was heated in an autoclave at 150° for 24 hr. After the mixture was extracted four times with 100-ml. portions of ether, the combined ether extracts were dried over anhydrous magnesium sulfate, and the ether was evaporated. Sublimation of the residue gave 0.74 g. (50% recovery) of bis(cyanomethyl)oxacyclobutane, which was identified by infrared and differential thermal analyses.

In a second experiment, 1.4 g. (0.010 mole) of 3,3-bis(cyanomethyl)oxacyclobutane and 40 ml. of water containing a drop of sulfuric acid were refluxed 6 hr. When the mixture was cooled, neutralized with 10% barium hydroxide, extracted four times with 100-ml. portions of ether, and the ether extracts were combined, dried over magnesium sulfate, and evaporated, 0.62 g. of the oxacyclobutane was obtained. Continuous extraction of the water solution gave an additional 0.75 g. of the oxacyclobutane and 1.07 g. of an unidentified oil.

6. Hydroxy acids and aldehydes:

a. Tris(hydroxymethyl)acetic acid: The procedure described by Kutchen[12] was followed. To 12.97 g. (0.0411 mole) of barium hydroxide in 10 ml. of water was added 4.50 g. (0.0219 mole) of tris(chloromethyl)-acetic acid. The mixture was heated at 46° for 17.5 hr., acidified to a pH of 1 with 1N H_2SO_4, and filtered. After the water was evaporated and the residue extracted eight times with 50-ml. portions of ethyl alcohol, once with 50 ml. of hot pyridine, and once with 50 ml. of hot isopropyl alcohol, the combined extracts were evaporated and the residue was recrystallized from isopropyl alcohol to obtain 0.79 g. (24%) of tris(hydroxymethyl)acetic acid, m.p. 217-221°, transition 124-127° (differential thermal analysis) [reported m.p., 202-205°,[17] 210-213].[18]

Anal. calcd. for $C_5H_{10}O_5$: C, 40.00; H, 6.71. Found: C, 39.89; H, 6.65.

b. 2-Hydroxymethyl-2-methyl-1-propanal: When 50 g. (0.69 mole) of iso-butyraldehyde was condensed with 24.7 g. (1.21 moles) of formaldehyde by the method described by Wessely,[19] distillation of the product gave 39.6 g. (47%) of 2-hydroxymethyl-2-methyl-1-propanal, b.p. 79-81° (5.5 mm.). Redistillation of the 39.6 g. gave 9.47 g. of purer 2-hydroxymethyl-2-methyl-1-propanal, b.p. 86-90° (19 mm.), m.p. 81-83° [reported b.p. 78-86° (20 mm.),[20] 84-89° (17 mm.),[21] m.p. (dimer) 89-90°,[19] 93-94°,[21] 91-92°,[20] 87-89°,[22] (monomer) 23-24°].[22] The substance did not exhibit a transition on differential thermal analysis.

Anal. calcd. for $C_5H_{10}O_2$: C, 58.79; H, 9.87. Found: C, 57.78; H, 9.50.

c. 2-Hydroxymethyl-2-methyl-1-propionic acid: Wessely's procedure was followed.[19] A mixture of 5.0 g. (0.049 mole) of 2-hydroxymethol-2-methyl-1-propanal in 100 ml. of water was treated with a solution of 4.0 g. (0.025 mole) of potassium permanganate in 80 ml. of water. After the permanganate color disappeared, the mixture was filtered, made basic with 40% potassium hydroxide, and extracted with three 180-ml. portions of ether. After the remaining aqueous portion was acidified with sulfuric acid and extracted with four 180-ml. portions of ether, the combined extracts were dried over anhydrous magnesium sulfate, the ether was evaporated, and the residue was sublimed. There was obtained 1.55 g. of a material, m.p. 158-173°, transition, 70-79° (differential thermal analysis). 2-Hydroxymethyl-2-methyl-1-propionic acid melts at 123°.[19]

APPENDIX 1

SPECTRAL CHARACTERISTICS OF SYNTHESIZED CANDIDATE SUBSTANCES AND THEIR INTERMEIDATES

The data in this Appendix do not relate specifically to the studies of solid-solid phase transitions and are not necessary for the fulfillment of contract goals. These data do provide verification of the chemical structure of the compounds and intermediates synthesized as candidate thermal control materials. The n.m.r. spectra, which are summarized in Table 13, were determined with a Varian A60 n.m.r. spectrometer and include data for several reference compounds. The infrared spectra recorded in Figures 1 through 17 were determined with a Beckman Infracord spectrophotometer. Because of extremely strong absorptions found in certain regions of the spectra in Figures 4, 5, and 17, a portion of each spectrum is recorded at two film thicknesses.

TABLE 13

PROTON CHEMICAL SHIFTS IN PENTAERYTHRITOL AND OXACYCLOBUTANE DERIVATIVES

Compound	τ CH_2OH (triplet)	τ CH_2OH (doublet)	τ Ring CH_2	τ CH_2X
Pentaerythritol	5.77	6.59		
2,2,2-Trimethylolethane	5.76	6.76		9.32
2,2-Dimethylolpropane	5.69	6.85		9.22
Monobromopentaerythritol	5.52	6.60		6.48
Dibromopentaerythritol	5.07	6.57		6.49
Tribromopentaerythritol	4.66	6.55		6.47
Tetrabromopentaerythritol				6.38
3,3-Bis(hydroxymethyl)oxacyclobutane	5.22	6.41	5.67	
3-(Hydroxymethyl)-3-(bromomethyl)oxacyclobutane	4.89	6.29	5.63	6.12
3,3-Bis(bromomethyl)oxacyclobutane			5.57	6.00
3,3-Bis(cyanomethyl)oxacyclobutane			5.46	6.98

Note: Coupling constants in all CH_2OH splittings were 5 cps. All spectra were determined in D^6 dimethylsulfoxide and the chemical shifts computed on the basis of the τ 7.48 band of the D^5 dimethylsulfoxide impurity. Integrated peak areas were consistent with the structures.

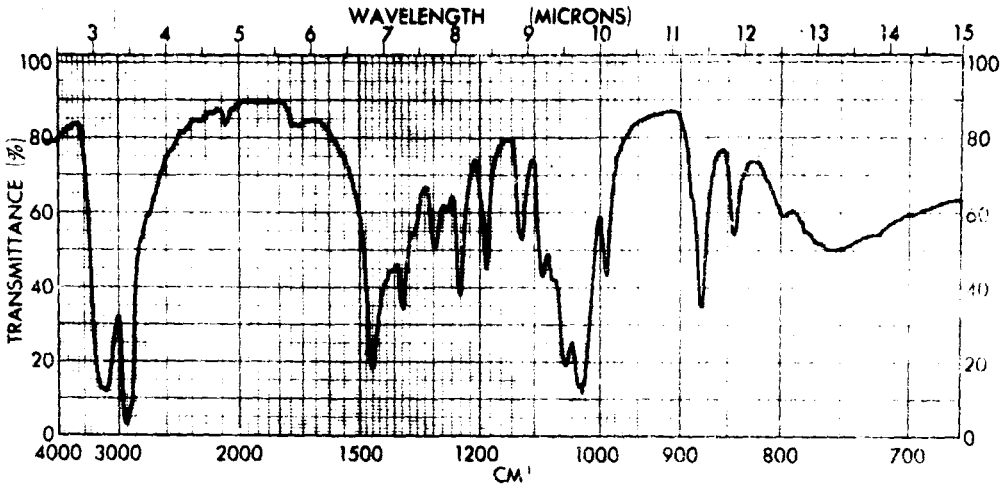


Figure 1 - Infrared Spectrum of Monobromopentaerythritol (Nujol)

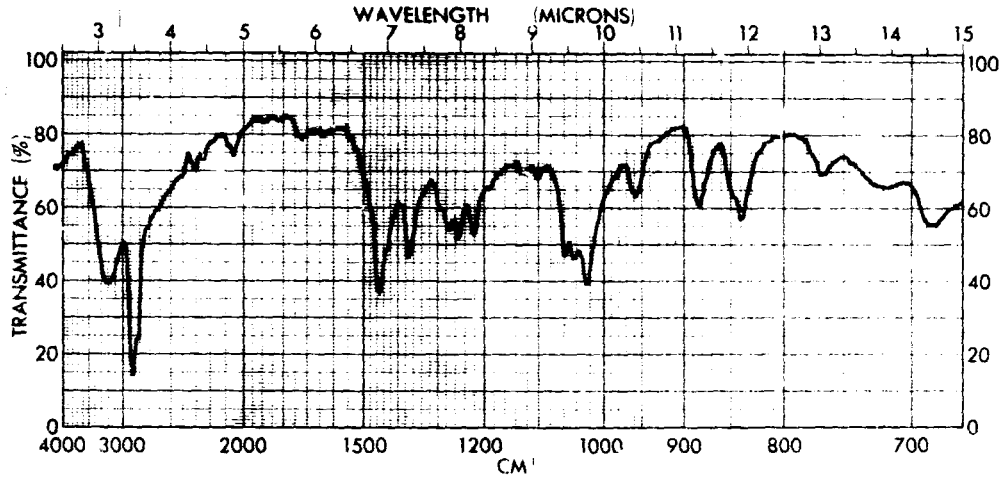


Figure 2 - Infrared Spectrum of Dibromopentaerythritol (Nujol)

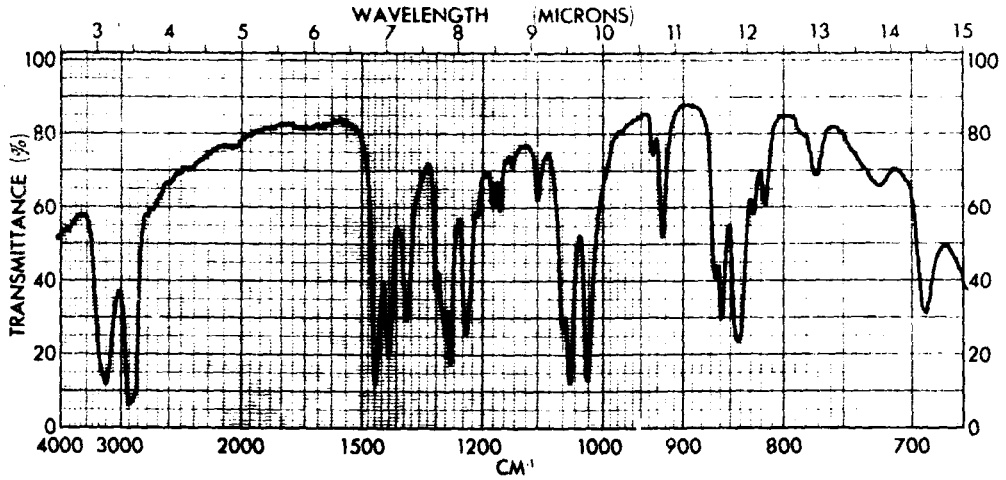


Figure 3 - Infrared Spectrum of Tribromopentaerythritol (Nujol)

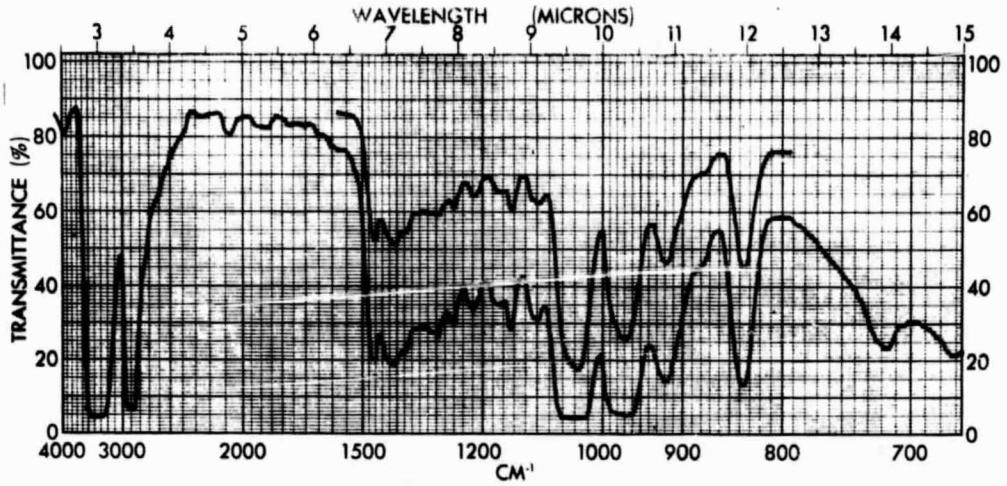


Figure 4 - Infrared Spectrum of 3,3-Bis(hydroxymethyl)-oxacyclobutane (Liquid)

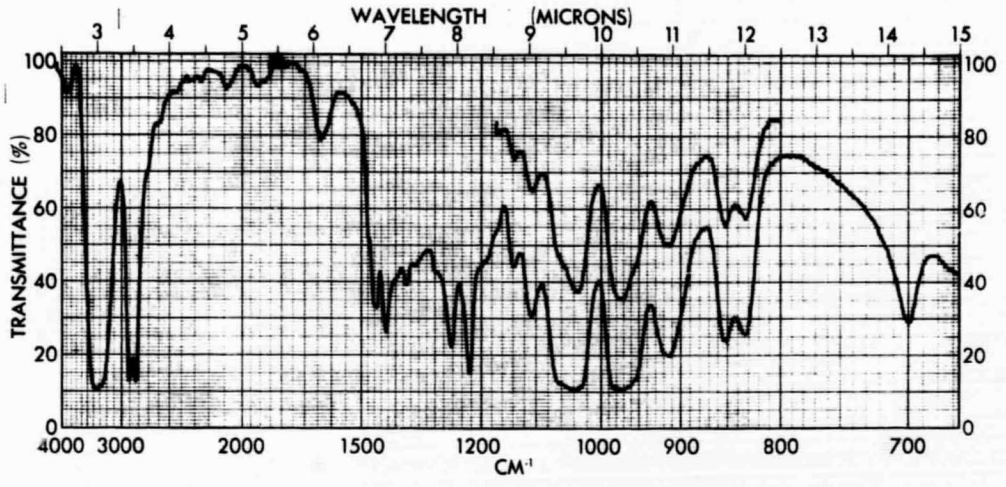


Figure 5 - Infrared Spectrum of 3-Bromomethyl-3-hydroxymethyloxacyclobutane (Liquid)

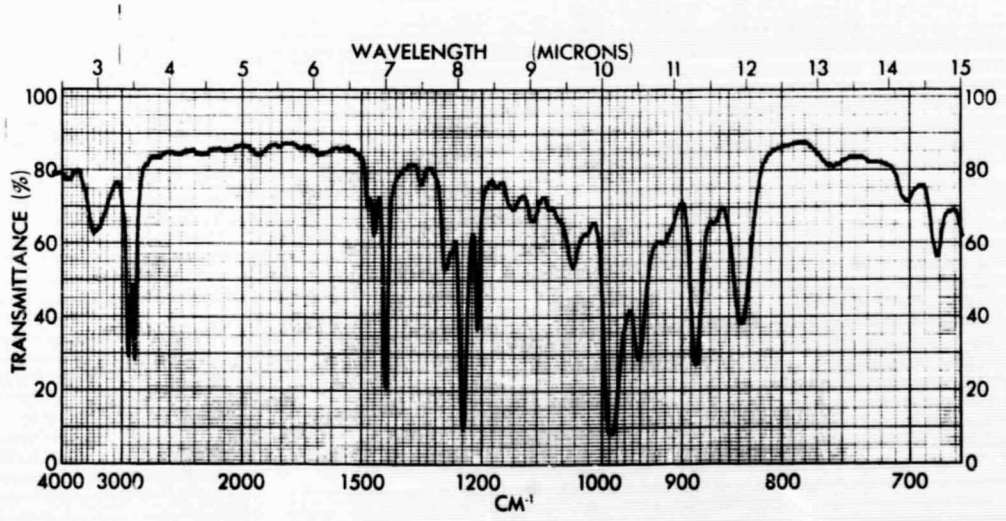


Figure 6 - Infrared Spectrum of 3,3-Bis(bromomethyl)oxacyclobutane (Liquid)

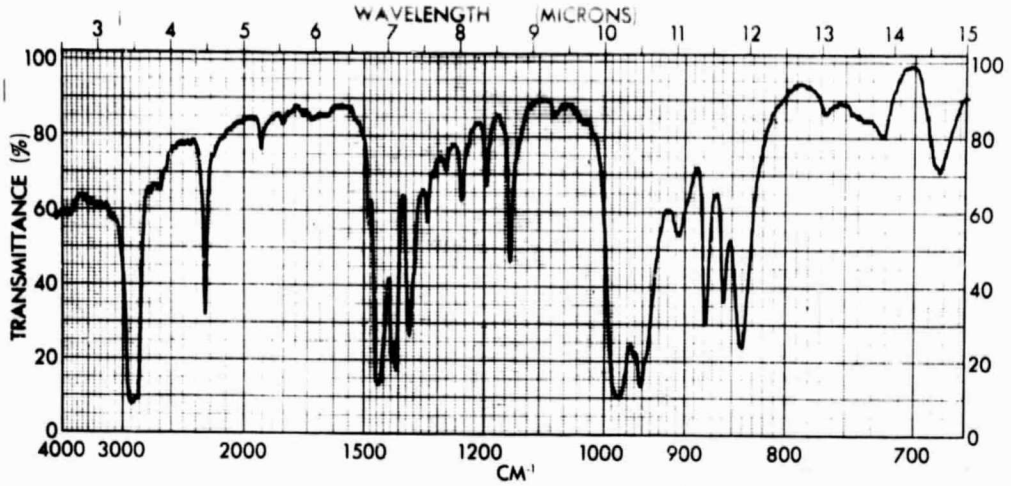


Figure 7 - Infrared Spectrum of 3,3-Bis(cyanomethyl)oxacyclobutane (Nujol)

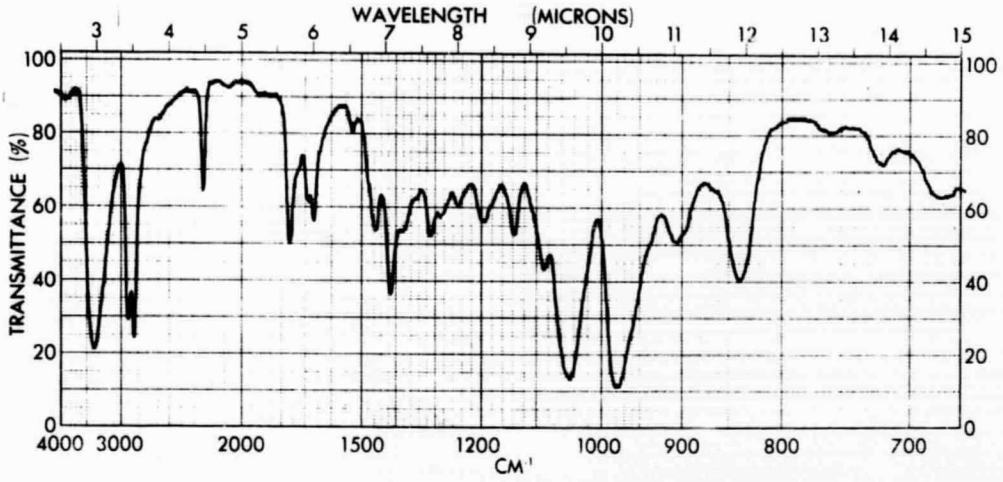


Figure 8 - Infrared Spectrum of 3-Cyanomethyl-3-hydroxymethyloxacyclobutane (Liquid)

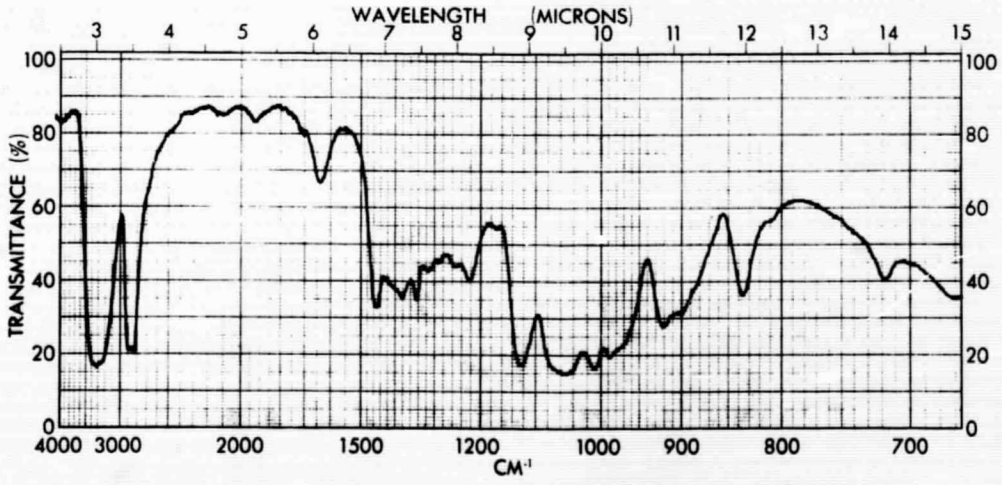


Figure 9 - Infrared Spectrum of 3-Fluoromethyl-3-hydroxymethyloxacyclobutane (Liquid)

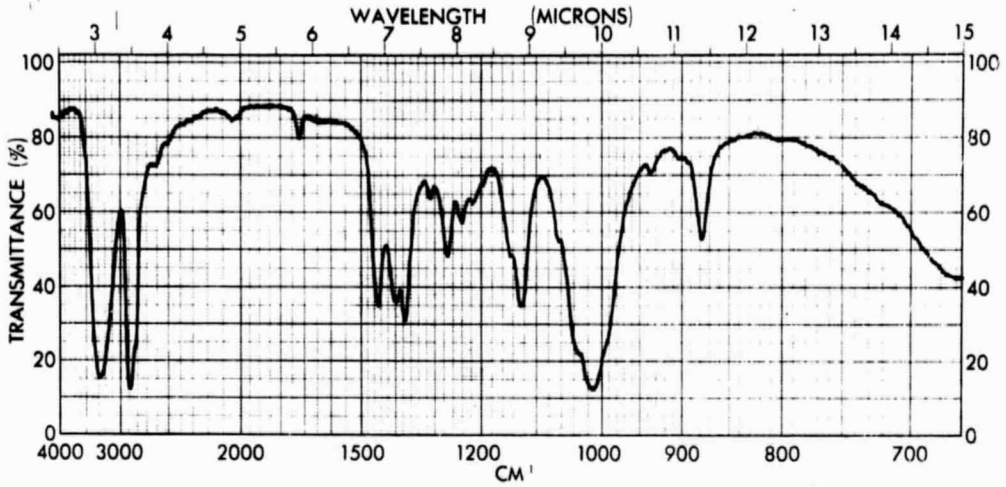


Figure 10 - Infrared Spectrum of Monofluoropentaerythritol (Nujol)

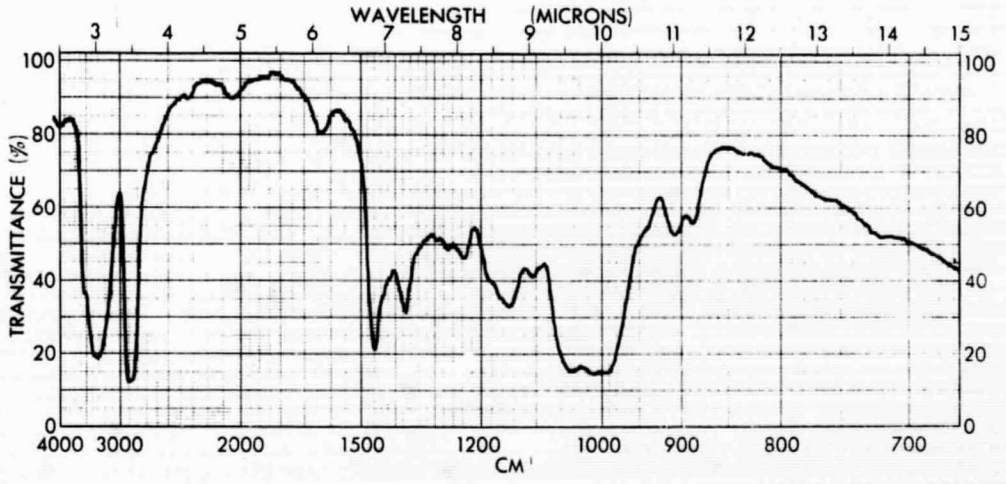


Figure 11 - Infrared Spectrum of Difluoropentaerythritol (Nujol)

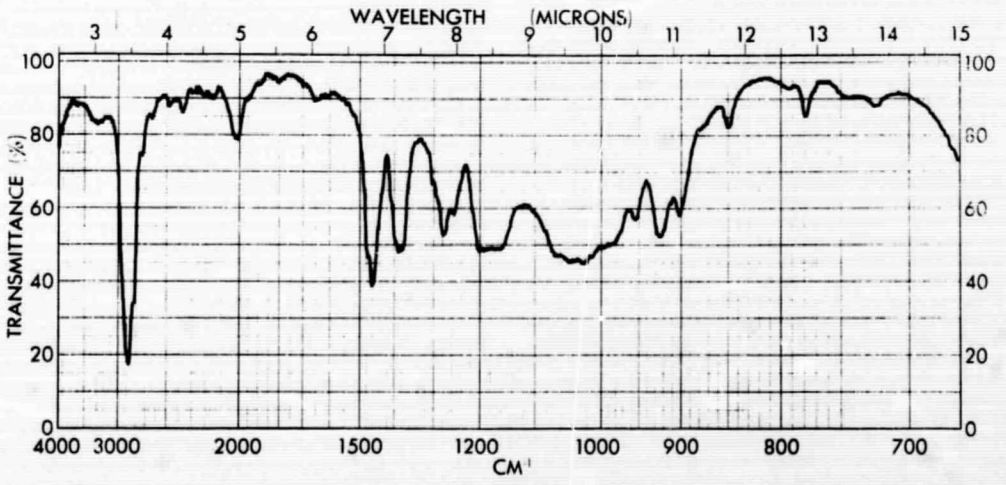


Figure 12 - Infrared Spectrum of Unpurified Tetrafluoropentaerythritol (Nujol)

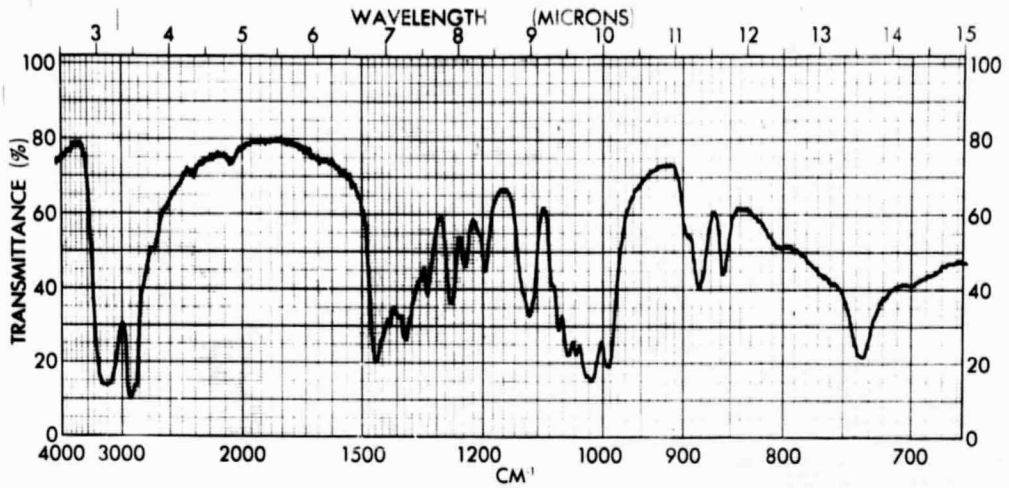


Figure 13 - Infrared Spectrum of Monochloropentaerythritol (Nujol)

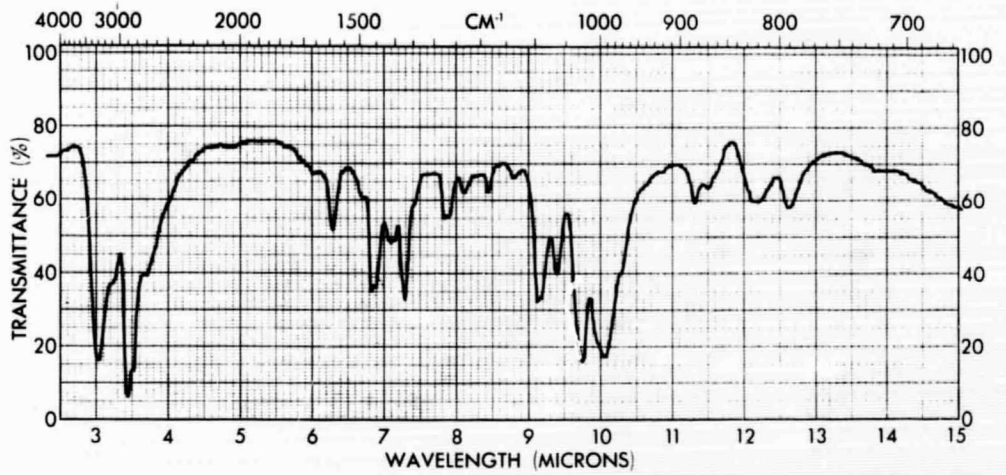


Figure 14 - Infrared Spectrum of Monoaminopentaerythritol (Nujol)

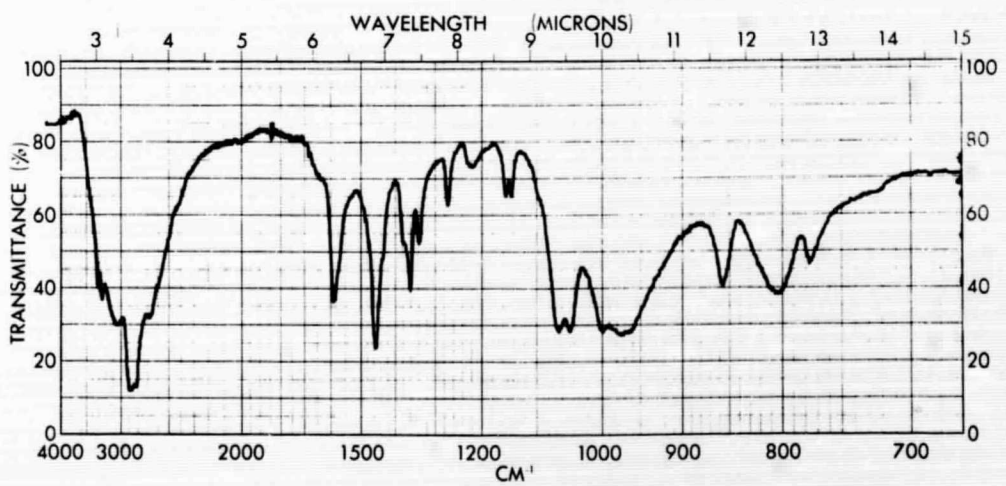


Figure 15 - Infrared Spectrum of Diaminopentaerythritol (Nujol)

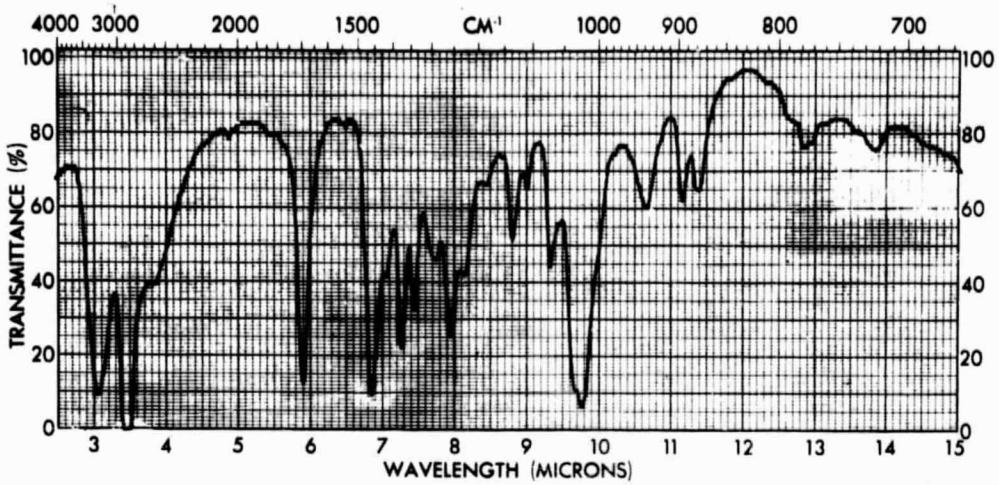


Figure 16 - Infrared Spectrum of Tris(hydroxymethyl)acetic Acid (Nujol)

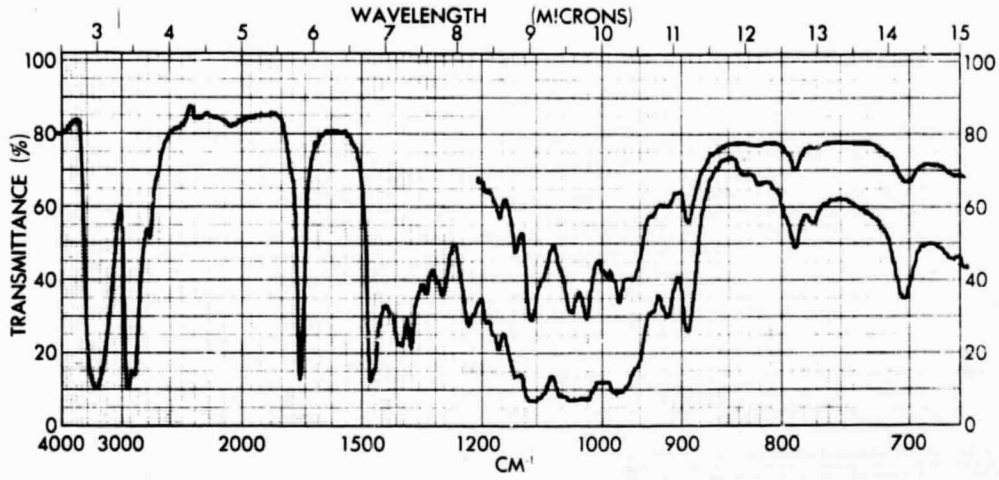


Figure 17 - Infrared Spectrum of 2-Hydroxymethyl-2-methyl-1-propanal (Smear)

REFERENCES

1. K. Jackson, "Nucleation Phenomena," D. E. Gushee, ed., American Chemical Society, Washington, D. C. (1966), Chapter 4.

2. I. Nitta, S. Seki, M. Momotani, K. Suzuki, and S. Nakagawa, Proc. Japan Acad., 26(10), 11 (1950).

3. C. A. Wulff and E. F. Westrum, Jr., J. Phys. Chem., 67, 2367 (1930).

4. I. Nitta, S. Seki, and M. Momotani, Proc. Japan Acad., 26(9), 25 (1950).

5. E. F. Westrum, Jr., Pure Appl. Chem., 2, 241 (1961).

6. S. Wawzonek, A. Matar, and C. H. Issidorides, Org. Syn., IV, 681.

7. M. Saucier, C. Sauriol, and R. L. Salvadore, Can. J. Chem., 44, 1599 (1966).

8. F. Govaert and M. Beyaert, Proc. Acad. Sci., Amsterdam, 12, 490 (1939).

9. C. H. Issidorides and A. I. Matar, J. Amer. Chem. Soc., 77, 6382 (1955).

10. C. H. Issidorides, R. C. Gulen, and N. S. Aprahamian, J. Org. Chem., 21, 997 (1956).

11. T. W. Campbell, J. Org. Chem., 22, 1029 (1957).

12. W. R. Sorenson and T. W. Campbell, Preparative Methods of Polymer Chemistry, Interscience Publishers, Inc., New York, pp. 252-253 (1961).

13. E. Gryszkiewicz-Trochimowski and O. Gryszkiewicz-Trochimowski, Bull. Soc. Chim. France, 123 (1953).

14. H. Fecht, Ber., 40, 3883 (1907).

15. F. Govaert and M. Beyaert, Proc. Acad. Sci. Amsterdam, 42, 490 (1939).

16. M. Beyaert and F. Govaert, Proc. Acad. Sci. Amsterdam, 42, 776 (1939).

17. W. Kutchen and W. Nagel, Hoppe-Seyler's Z. Physiol. Chem., 303, 230 (1956).

18. K. Heyns and H. Paulsen, Angew. Chem., 69, 600 (1957).

19. L. Wessely, Akad. Wiss. Wien. Kl. Math. Naturew., 109, 91 (1900).

20. S. Furukawa and others, Chiba Daigaku Kenkyu Hokoku, 17, 23 (1966); CA 65:13529 (1966).

21. SNAM S.p.A., Netherlands Patent 6,405,068, November 9, 1964; CA 62:16061 (1965).

22. E. Spaetch and I. Szibagyi, Chem. Ber., 76B, 949 (1943).