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ORNL/SUB-7299/1

THE USE OF SOLID-STATE PHASE TRANSITIONS FOR THERMAL ENERGY STORAGE

Final Report for June 1, 1977—August 31, 1978

By
Amos J. Leffler
John Myers
David Weinstein

Work Performed Under Contract No. W-7405-ENG-26

Villanova University
Department of Chemistry
Villanova, Pennsylvania

U. S. DEPARTMENT OF ENERGY

Division of Energy Storage Systems

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Project Management by
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for the
DEPARTMENT OF ENERGY

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VILLANOVA, PENNSYLVANIA 19085

DEPARTMENT OF CHEMISTRY

FINAL REPORT

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Contract ORNL 7299

PERIOD: JUNE 1, 1977 to AUGUST 31, 1978

BY

Amos J. Leffler

AMOS J. LEFFLER - PRINCIPAL INVESTIGATOR

John A. Myers

JOHN MYERS - RESEARCH ASSOCIATE

David Weinstein

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ABSTRACT

A study has been carried out on the feasibility of using solid-solid phase transitions for thermal energy storage. As part of this study a literature search was made to identify the most promising types of compounds and a synthesis program was carried out to prepare certain of these substances. In addition a large number of compounds for testing were obtained from commercial sources. All of the compounds were screened for transitions using a Perkin Elmer DSC-1B differential scanning calorimeter. From this program seven compounds were found that have transition energies from 20-30 cal/g in the temperature range of 335-405 K. The most promising compound found is 5-norbornene-2,3-dicarboxylic acid anhydride having a transition of 22.6 cal/g at 366 K and an estimated cost of preparation of $0.40/lb..

A second portion of the program was devoted to an assessment of the problems that would be encountered in designing a practical heat exchanger. It was found that all of the substances tested showed a volume change at the phase transition of 4-8%. A hysteresis effect was noted in that the phase change temperatures were higher during the heating cycle than in the cooling cycle. The pellets increased irreversibly in volume during the heating phase and became structurally weaker and some of the pellet was lost by volatilization in the gas stream. The volume increase and pellet loss can be taken care of by using containers. The thermal conductivities of the substances studied are approximately the same as common organic compounds not exhibiting phase transitions. As far as can be determined all of the substances studied are relatively non-toxic.

I. Introduction

This is the final report describing the work carried out under Contract ORNL-Sub 7299-1 for the period June 1, 1977 to August 31, 1978. The aim of the project has been to find new compounds showing solid-solid transitions of high energy for thermal energy storage and to investigate the engineering problems that would be encountered in their use in a practical heat exchanger.

The first measurement of a solid state transition is probably that of Simon[1] in his classic work on the heat capacity of ammonium chloride in which he showed the existence of a lambda point at about 240 K. More important for the present work is the concept of a "plastic crystal" suggested by Timmermans[2] in 1935. He defined a plastic crystal as one in which the molecules reorient about their lattice sites and has an entropy of fusion of less than 5 entropy units. Plastic crystals show a first order phase transition at a temperature below the melting point between the rigid lattice region and the plastic crystal region and it is the energy of transition of this phase change that is of interest. In the plastic crystal region the crystal structure is of high symmetry, often being cubic, with the molecules being orientationally disordered. In the rigid lattice region the molecules can still reorient but in a restricted manner. Our aim in the present work was to find those molecules having a phase transition in the desired temperature range and at the same time having the most desirable chemical, toxicological, and economic properties.

The problem of picking substances that will show phase transitions has attracted a great deal of attention from both theoreticians and experimentalists. The theoretical understanding of the requirements for solid state phase transitions is relatively recent and still not complete. We know that molecules showing plastic phases have a relatively high degree of symmetry. Thus simple molecules such as carbon tetrachloride, furan, and succinonitrile form plastic crystals but equally symmetric molecules such as silicon tetrachloride, thiophene, and succinic anhydride do not. Similarly benzene is known to undergo reorientation about its sixfold axis of symmetry but does not show a phase transition. It is now realized that the failure of analogies of the type above is due to the failure of the mean field theory in this process. The transition between the low temperature and plastic phases is a critical process and is similar to other critical processes in that the average field of the surrounding molecules will not give the correct answer. It is necessary to calculate solutions for the field exerted by all of the neighboring molecules with known orientations. Thus we are led to the Ising lattice problem which has played such a large role in critical phenomena.

The first attempt at such calculations was made by Kitaigorodskii and co-workers[3] in the early 1960's. The approach was to assume so called non bonded interactions of the form:

$$V_{ij} = -Ar^{-6} + B\exp(-Cr) \tag{1}$$

where A, B, and C are constants for each pair of atoms and r is the distance between atoms. The total energy between two molecules will be the sum of the pairwise atomic interaction potentials. If we now set up a lattice of molecules we can calculate the interaction potential between the central molecule and the surrounding molecules as the central molecule reorients. We have a many minima surface with barriers between minima. As the temperature increases the molecules obtain sufficient energy to reorient from one well to another. The molecules also in some cases gain sufficient energy and thermal motion that they rearrange to a new lattice and a phase change results. The result of the calculations for a particular structure is a potential energy curve as a function of the angle of rotation.

We find that the calculations give two different types of potential energy curves. One type shown by benzene and many analogous compounds is a series of wells of equal depth in energy repeated every 60° degrees of angle of rotation about the hexad axis. The second type illustrated by compounds such as 1,5-difluoronaphthalene is a series of unequal potential wells[4]. This result is more interesting in that it offers more possible types of behavior. At low temperatures the molecules will be trapped in the deep wells in both cases. As the temperature increases the molecules will have sufficient energy to reorient in the equidepth well type. In the unequal type reorientation may or may not occur depending on the depth of the deepest well. If it is too great no reorientation occurs. With increasing temperature reorientation occurs to the shallow wells but of course there is still a much greater probability of finding the molecules in the deep wells. At still higher temperatures the energy of the molecules is large enough that the molecules will freely reorient in all wells with equal probability. It is at this point the phase change occurs to a structure of higher symmetry.

With this view of molecular behavior we can understand the difference between carbon tetrachloride and silicon tetrachloride. Their qualitative behavior would be the same but their quantitative behavior is different. In silicon tetrachloride the difference in energy between adjacent wells is too small to have a phase transition while it is large enough for carbon tetrachloride. In a practical sense the problem is to choose substances having the correct groups to obtain a transition in the desired temperature range. Theoretically one could make calculations based on the Kitaigorodskii approach for each molecular structure of interest. Unfortunately this would be so time consuming and expensive to be impractical. A more practical approach is to use theoretical and empirical knowledge to pick and test various materials. This is the approach that was used in the present work.

The basic reasoning used to choose structures for testing was as follows. Since most molecules showing plastic behavior have a relatively high degree of symmetry and sublime, this was made a requirement for testing. However, unless substituent groups are present in the molecule the melting point and plastic range occurs at too low a temperature to be of interest and therefore only molecules with such groups were examined. In a practical sense a melting point of about 200°C or higher was used as a screening requirement. Even if a molecule met these requirements it was not sufficient. Experimentally it was observed that molecules having the same structure except for minor differences in the substituent groups behave quite differently. Thus a particular structure having an imide group does not show plastic properties while one having an anhydride does show plastic behavior. Molecules having hydroxyl, nitrile, amino, halo, and anhydride groups seemed more likely to be plastic crystals than those with carbonyl and imide groups. It is apparent that even though the molecules are qualitatively similar it is the quantitative difference that is important.

In a practical sense, in addition to a phase transition of sufficient magnitude, there are a number of other requirements for a useful material. An obviously important factor is the toxicity of any substance especially if it is to be used in residential applications. In any practical heat exchanger thermal conductivity is important since energy must be transferred in and out at a reasonable rate. Other important considerations are cost, chemical and moisture stability, and compatibility with materials of construction. In order to assess these factors a concurrent engineering study was carried out using some of the substances found in the materials work.

II. Results

A. Literature Search: The first portion of the program was devoted to a literature search to identify the molecules that seemed most likely to show solid state transitions in the desired temperature range up to about 150°C. A basic source of information already available is the Phase Change Materials Handbook[4a] which includes a list of known substances exhibiting phase changes up to the date of publication in 1971. The report relies heavily on the work of Murrill and Breed[4b] who have studied a series of derivatives of methane which are listed in Table VI in the Appendix.

In the present search it was required that the transition temperature always be considerably below the melting point for any practical utility, hence melting points above 200°C were chosen as a practical requirement. High molecular symmetry and the functional groups described above were also required.

The literature search was made using Chemical Abstracts employing the ORBIT program of the Systems Development Corporation. The latter is a computerized form of Chemical Abstracts based on a keyword system. We have found that it is most useful for obtaining theoretical papers but much less so for finding information on specific compounds. The difficulty is that the dependence of the system on keywords means that unless these appear in the abstract, the paper will not be picked up. We therefore have found it necessary to do hand searches as well, and between the ORBIT and hand-searches our coverage is relatively complete.

For convenience the compounds were divided into three broad classes with subdivisions as listed below.

1. Two Dimensional Molecules
    a. Benzene based derivatives
    b. Naphthalene based derivatives
    c. Anthracene derivatives

  d. Heterocyclic compounds
  e. Cyclohexane derivatives
  f. Phosphazene derivatives
  g. Miscellaneous compounds

2. Cage Structures
  a. Adamantane derivatives
  b. Diamantane derivatives
  c. Oxaadamantane derivatives
  d. Azaadamantane derivatives
  e. Thiaadamantane derivatives
  f. Bicyclo compounds
  g. Camphor derivatives

3. Donor-Acceptor Coupounds

The complete listing will be found in the "First Phase Progress Report" under this contract dated June 1 to August 31, 1977.

B. Measurements of Transition Energies: Using the list of compounds of Part A as our guide, a large number of compounds were obtained for testing. Some judgement was necessary as to the particular compounds examined. For example although all known members of the diamantane class (2b) are known to exhibit solid state transitions they are not commercially available and can only be synthesized by multistep routes with low yields. Similarly a number of the compounds are available from laboratory supply houses but are far too expensive to be considered. It is well known that the cost of a chemical from a laboratory supply house does not represent the true cost but it bears a rough relation to the cost of starting materials and the number of steps in its preparation. On this basis many of the compounds that were known to be unstable, corrosive, or too moisture sensitive were eliminated. Finally toxicity was considered and substances on the "Toxic Substances List"[5] or were carcinogenic or related to carcinogenic compounds were also eliminated.

The solid state transition energies were measured using a Perkin-Elmer DSC-1B differential scanning calorimeter. Since most of the compounds tested, sublime, this method was used for purification. It might be noted that a large number of organic compounds were found to sublime even though this is not listed in the literature. Due to the sublimability of the materials being tested it was necessary to use sealed capsules for all measurements. Heating rates were kept at 20° or 40° per minute to give qualitative scans. Those showing a relatively large solid state transition were examined at slower heating rates to get quantitative transition energy values. For these measurements the instrument was calibrated with indium metal and a set of curves as a function of heating rates were obtained. The peak area of the unknown was then compared with that for the melting of indium by planimeter to obtain its value.

The results of heat capacity measurements are given in Tables I and II. In Table I are listed those materials not showing a phase transition while those that did show such a transition are shown in Table II. In Table II it is evident that a number of the materials showing transitions are not true plastic crystals since the heat of transition is relatively small compared with the heat of fusion. An example of this type is caffeine which has a solid state transition of 3.71 cal/g and a heat of fusion of 25.8 cal/g. On the other hand dl camphoric anhydride with a transition energy of 25 cal/g and a heat of fusion of 8.05 cal/g is a plastic crystal since the entropy of fusion is 2.94 e.u. In a number of cases multiple transitions were noted but their nature is not known. If they occur within a short temperature range they are still useful since a small temperature range excursion would still be satisfactory to store energy.

One of the most striking results of this work is the difficulty in predicting which compounds will show solid state transitions. Compounds that are seemingly very similar behave quite differently as shown in the examples given below in Table III. Those with Roman numeral I do not show transitions while those having

Table I

Compounds Not Showing Transition Below Melting Point

No.	Compound	Melting Point °C	Remarks
1.	1,8-Naphthalic Anhydride	275-7	Sublimes 274°C
2.	Pyromellitic Diimide	>320	-
3.	1,4,5,8-Naphthalic Dianhydride	>360	-
4.	Pyromellic Dianhydride	283	Small Subl.
5.	Tetrachlorophthalimide	333-4	Subl.
6.	p,p'-biphenyl	277-80	Subl.
7.	Tetrachlorophthalic Anhydride	256-8	
8.	Phthalimide	232-4	
9.	1,4-Dicyanobenzene	223-5	Sublimes 160
10.	Phthalazine-1,4-dione	333-4	-
11.	Adenine	>360	-
12.	Pyromellitic Dianhydride 1,5-Diamino-naphthalene Complex	262	-
13.	Chloranil-Melamine Complex	307 d.	-
14.	2-Hydroxy-1,4-naphthaquinone-Anthracene Complex	182	-
15.	1-Leucine	318-20d.	-
16.	4-Amino-1,8-naphthalimide	>360	-
17.	7-Hydroxy-4-methylcoumarin	185	Subl.

Table I (continued)

No.	Compound	Melting Point °C	Remarks
18.	dl-Isoborneol	214-5-	Sublimes
19.	Isatin	200-2	Subl.
20.	Isatoic Anhydride	251	-
21.	2-Amino-6-nitrobenzothiazole	247-50	Sublimes
22.	1-Tyrosine	322-5	Broad
23.	Phloroglucinol	218-20	Sublimes
24.	1,8-Naphthalimide	297-9	
25.	5-Aminoorctic Acid	>320	Broad 295-328°C Inconclusive
26.	1-Aminoanthraquinone	250-2 d.	
27.	2-Aminoanthraquinone	294-5	Sublimes
28.	1,5-Dihydroxynaphthalene	260-3	Broad Fusion
29.	2,3-Dihydroxyquinoxaline	>358	
30.	Inositol	225-6	
31.	5-Hydroxyisophthalic Acid	294-5	Sublimes
32.	Hydroquinone-Maleic Anhydride Diels-Alder Adduct	235	Sublimes
33.	p-Nitrobenzoic Acid	238-40	
34.	5,6-Dimethylbenzimidazole	201-3	Sublimes
35.	Isonicotinic Acid	313	Sublimes
36.	Carbazole-Anthracene Complex	211	Sublimes

Table I (continued)

No.	Compound	Melting Point °C	Remarks
37.	3,3',4,4'-benzophenone Dianhydride	226-8	
38.	Chloroxazone	190-1	Sublimes
39.	4-Amino-2,6-dimethylpyridine	183-6	Sublimes
40.	5-Nitrobenzotriazole	214-6	Sublimes
41.	5-Chloroisatoic Anhydride	272-5	Sublimes
42.	p-Hydroxybenzoic Acid	215	Sublimes
43.	2-Adamantanone	254-6	Sublimes
44.	5,7-Dichloro-8-hydroxyquinoline	180-1	Sublimes
45.	Bicyclo 2,2,2 oct-7-ene-2,3,5,6-Dianhydride	350	Anomaly near fusion
46.	Tetrabutylammonium fluoborate	160	
47.	Indole-3-carboxaldehyde	201	Sublimes
48.	6-Amino-1,3-dimethyluracil	311	Sublimes
49.	1-Tyrosine	319	-
50.	2,3-Dicyanohydroquinone	250 d.	-
51.	2,3-Diaminonaphthalene	206	
52.	N-Hydroxyphthalimide	244	Sublimes
53.	Chloranilic Acid	307	-
54.	4-Amino-2,6-dihydroxypyrimidine	>320	-
55.	4,5-Diamino-2,6-dihydroxypyrimidine Mono Hydrochloride	293	-

Table I (continued)

No.	Compound	Melting Point °C	Remarks
56.	7,7,8,8-Tetracyanoquino dimethane	297	Sublimes
57.	4-Amino-1,8-Naphthalimide	>330	-
58.	Homophthalic Acid	183	Sublimes
59.	Pyridine-2,6-dicarboxylic Acid	250 d.	Sublimes
60.	Succinic Anhydride	116	Sublimes
61.	2-Hydroxy-4-methylquinoline	310	-
62.	5-Aminoorotic Acid	>320	-
63.	3-Amino-2,5-dichlorobenzoic Acid	194-7	Sublimes
64.	2-Chlorophenothiazine	196-9	Sublimes
65.	Tetrachloro-p-xylene-α,α'-diol	225-30	Sublimes
66.	Uric Acid	>330	-
67.	N-Chlorosuccinimide	144	Sublimes
68.	dl-Camphor-3-carboxylic Acid	135	Sublimes
69.	Chloromaleic Anhydride	82	Sublimes
70.	4-Aminoquinaldine	168	Sublimes
71.	Hydroquinone	172	Sublimes
72.	dl-Isoamarine	199	Sublimes
73.	Tetrachlorohydroquinone	238	Sublimes
74.	1,5-Diaminonaphthalene	185	Sublimes

Table I (continued)

No.	Compound	Melting Point °C	Remarks
75.	N-Methylisatoic Anhydride	156	Sublimes
76.	Cyanuric Acid	>360	-
77.	Acenaphthaquinone	249	Sublimes
78.	2-Methyl-5-nitrobenzimidazole	241	-
79.	5-Methyl-s-triazolo- [1,5a] -pyrimidine-7-01	>360	-
80.	Quinalizarin	303	Sublimes
81.	6-Hydroxynicotinic Acid	327	Sublimes
82.	2,6-Diaminoanthraquinone	>327	-
83.	Melamine	363	-
84.	Hydantoin	221	Sublimes
85.	Tetramethylammonium Fluoborate	330 d.	-
86.	Pyridine-2,5-dicarboxylic Acid	256	Sublimes
87.	6-(Chloromethyl) uracil	249	-
88.	4,5-Diaminopyrimidine	200	-
89.	2,4-Diamino-6-hydroxypyrimidine Monohydrate	283	-
90.	Isonicotinic Acid	310	Sublimes
91.	2-Mercaptobenzimidazole	310	Sublimes
92.	5-Chloroisatoic Anhydride	272	Broad Fusion, Sublimes
93.	6-Chloroisatin	261	Sublimes

Table I (continued)

No.	Compound	Melting Point °C	Remarks
94.	Alizarin	287	-
95.	5-Nitrobenztriazole	214	Sublimes
96.	2,3-Diaminobenzoic Acid	253	-
97.	Tetrachlorophthalimide	333	Sublimes
98.	2,3-Dihydroxypyridine	246	Sublimes
99.	2-Methyl-5-nitroimidazole	252	Sublimes
100.	3-Methyl-2-quinoxalinol	250	Subl.
101.	Carbazole	242	Subl.
102.	1,3,5-Triphenyl-s-triazine	228	Subl.
103.	2,3-Dichloro-1,4-naphthaquinone	197	Subl.
104.	2-Hydroxy-1,4-naphthaquinone	198-9 d.	Subl.
105.	5,7-Dibromo-8-hydroxyquinoline	200	Subl.
106.	8-Hydroxyquinoline	76	Subl.
107.	N-Hydroxyphthalimide	236	Subl.
108.	Trichloromethyl-4-(3H)-quinazoline	211	Subl.
109.	2-Chloroanthraquinone	212	Subl.
110.	2,4,5,6-Tetrachloro-m-xylene	219	Subl.
111.	2-Amino-6-nitrobenzthiazole	247	Subl.
112.	1-Amino-4-hydroxyanthraquinone	191-3	Subl.

Table I (continued)

No.	Compound	Melting Point °C	Remarks
113.	5,7-Dichloroisatin	217-8	Subl.
114.	3-Hydroxypyridine N-Oxide	187	-
115.	5,7-Dichloro-8-hydroxyquinoline	180-1	Sublimes
116.	Pyromellitic Dianhydride 1,5-diamino-naphthalene Complex	262	-
117.	Hydroquinone-Maleic Anhydride Diels-Alder Adduct	235	"
118.	Carbazole-Anthracene Complex	211	-
119.	2-Hydroxy-1,4-naphthaquinone-Anthracene Complex	182	-
120.	Chloranil-Melamine Complex	307 d.	-
121.	Exo-norborneol	120	
122.	Hexachlorocyclotriphosphazene	115	
124.	dl camphoric acid methyl imide	247	
125.	5-norbornene-2,3-dicarboxylic acid imide	183-5	
126.	5-norbornene-2,3-dicarboxylic acid methyl imide	106-9	
127.	5-cyclohexane-2,3-dicarboxylic acid anhydride		
128.	dl-camphoric acid lactone	211	
129.	5,6-dihydro-p-dithiin-2,3-dicarboxylic acid imide	218	

Table II Compounds Showing Solid State Transitions

No.	Compound	Transition Temp. (K)	Heat of Transition (cal/g)	Entropy of Transition (cal/mole-K)	Fusion Temp. (K)	Heat of Fusion (cal/g)	Entropy of Fusion (cal/mole-K)
1.	Trans-2,3-dicyano-5-norbornene	335.5	27.97	12.01	369.8	3.97	1.55
2.	dl-Camphoric anhydride	375.2	25.15	12.19	498.5	8.05	2.94
3.	Bicyclo(2,2,2)-oct-5-ene-2,3-dicarboxylic acid anhydride	383.3	22.89	10.63	420.5	4.15	1.76
4.	5-Norbornene-2,3-dicarboxylic acid anhydride	365.5	22.59	10.13	432.25	3.65	1.38
5.	d-Camphoric anhydride	405.3	22.79	10.24	498.8	7.64	2.79
6.	d-Camphoric oxime	384.25	20.19	8.77	392.8	2.90	1.23
7.	2,3-Dichloro-5-norbornene-2,3,-dicarboxylic acid anhydride	398.88	18.93	11.92	457.70d	4.09	2.24
8.	2-Imidazolidone	344.0	9.07	2.27	394.3	14.20	3.10
9.	1,4,5,6,7,7-Hexachloro-5-norbornene-2,3,-dicarboxylic acid anhydride	385.4	6.85	6.59	506.0	1.73	1.27
10.	Triethanolamine borate	469.3	5.60	1.87	499.4	10.79	3.39
11.	8,8,9,9-Tetracyanoquadricyclo-(2,2,1,0,2,2,6,3,5)-nonane	430.5	4.46	2.35	467.9d	15.67	7.60
12.	Pyromellitic dianhydride	505.9	3.71	1.60	558.88	35.52	13.86
13.	Caffeine	420.8	2.05	0.95	508.83	25.81	9.94
14.	dl-Borneol	338.0	1.18	0.50	475.5	- -	- -
15.	Nicotinic acid	454.3	1.03	0.28	509.1	37.59	9.08

DSC 1B (Perkin-Elmer): All scans were run at 1.25 degrees/min. and range = 2. The calibration was done with an Indium standard. (heat of fusion = 6.8 cal/g.)

Comments

1. 2,3-trans-Dicyano-5-norbornene: The transition at 335.5 K is reversible even when cycled past fusion. However, on cooling at 1.25 deg./min. no transition peak was seen down to 315 K. On standing at room temperature (295 K) and reheating the transition reappeared at 335.5 K. After 5 cycles the transition was still present.

2. 5-Norbornene-2,3,-dicarboxylic acid anhydride: The transition was cycled approximately 35 times and no decomposition was seen. It is also reversible when cycled through fusion. On cooling at 1.25 deg./min. the transition peak appeared at 351.4 K and reheating yielded the transition again at 365.5 K.

3. d-Camphoric oxime: The transition was reversible when cycled past fusion. Hysteresis was seen on cooling at 1.25 deg./min. as the cooling peak appeared at 347 K.

4. d-Camphoric anhydride: The transition is reversible even when cycled past fusion. The sample was cycled about 8 times and still the heating peak appeared at 405.3 K. On cooling at 1.25 deg./min. yielded the transition peak at 399.4 K.

5. dl-Camphoric anhydride: Transition is reversible even through fusion. Sample was cycled about 5 times and transition still appeared at 375.2 K on heating. Hysteresis was evident on cooling and the peak appeared at 343 K when cooled at 1.25 deg./min.

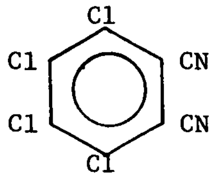
Comments (continued)

6. Bicyclo-(2,2,2)-oct-5-ene-2,3-dicarboxylic acid anhydride: The transition is reversible even when cycled past fusion. On cooling no peak appeared down to 315 K. However, on standing at room temperature (295 K) the transition reappeared at 383.3 K on heating at 1.25 deg./min.

7. 2,3-Dichloro-5-norbornene-2,3-dicarboxylic acid anhydride: The transition is reversible if not cycled through fustion. Once the fusion temperature is reached decomposition occurs and on reheating a peak appears at approximately 390 K. It is possible that a retrograde Diels-Alder reaction is occurring to yield the starting materials. Dichloromaleic anhydride melts around 385-390 K. The transition peak on cooling at 1.25 deg./min. appears at 389.8 K and reappears at 398.88 K on heating.

Table III

Examples of Closely Related Structures Behaving Differently



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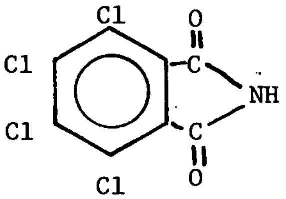

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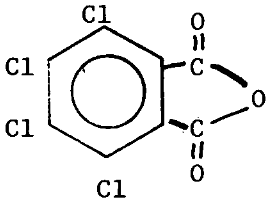

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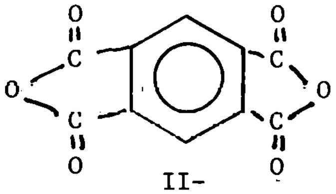

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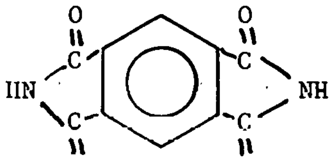

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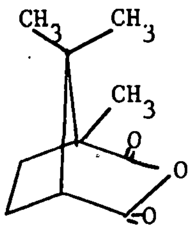

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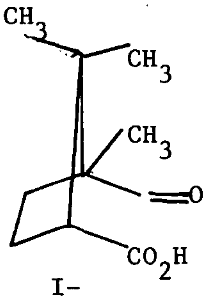

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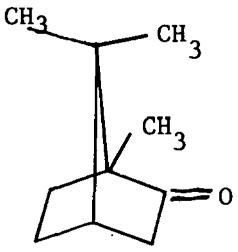

II-Camphor

Structures marked I show no transition while those marked II show solid-solid transitions.

numeral II do show transitions. Again this is similar to the difference cited in the Introduction and points out that the differences are quantitative rather than qualitative. It would be most interesting on a scientific basis to carry out a Kitaigorodskii type calculation of the intermolecular energies for some of the pairs to understand the differences.

C. Synthesis: Based on the best materials found in the phase transition energy measurements, it was attempted to synthesize compounds that were closely related. The most consistent compounds found in the present work were anhydrides and the compounds synthesized were imides, methyl imides, nitriles, alcohols and some related three dimensional molecules. The routes used were generally those described in the literature although considerable difficulty was encountered in some cases. The following general routes were used:

1. Amides - The starting anhydrides were hydrolyzed by boiling in dilute hydrochloric acid to form the acid. This was then treated with thionyl chloride or phosphorous pentachloride to form the diacid chlorides which were reacted with aqueous ammonia to form the diamide.

2. Imides - The anhydride was refluxed with concentrated aqueous ammonia and the imide separated on cooling.

3. Methyl Imides were prepared similarly to the imides by using methylamine instead of ammonia.

4. Dinitriles - The diamides described in 1. were mixed with phosphorous pentoxide and heated to form and sublime the nitriles out of the reaction mixture.

5. Dialcohols - The diacid chlorides were reduced with lithium aluminum hydride in ether or tetrahydrofuran. An attempt to reduce the anhydride with sodium borohydride and aluminum chloride as described by Brown et al led to the lactone[6].

6. Quadricyclonitriles - The nitrile was reacted with norbornadiene either by refluxing at atmospheric pressure or in a bomb.

7. Cyclophosphazenes - Ammonium chloride and phosphorous pentachloride were reacted in chlorobenzene at reflux.

8. Bicyclooctene - This compound was prepared by reaction of cyclohexadiene and maleic anhydride at 25°C.

The details of the individual preparations are given in the Experimental Section. All of the compounds prepared were tested for a solid state transition and the results are listed in Tables I and II.

D. Other Physical Properties: Since it is the aim of the program to devise a practical heat exchanger using phase change materials, it is necessary to obtain data for the design of such a heat exchanger. The information needed includes the following:

1. Heat capacity of phase change materials
2. Density
3. Thermal conductivity
4. Structural strength of the phase change material
5. Vapor pressure of the phase change material
6. Hysteresis effects in the behavior of the phase change material

The heat capacities of the materials were estimated using Kopp's rule which states that the heat capacity of a compound is the sum of the heat capacities of the substituent elements. This rule is a satisfactory approximation except of course where a phase change occurs. The latter must be measured experimentally.

The densities of compounds as a function of temperature were measured using the dilatometer apparatus shown in Figure 1. A weighed amount of the sample was placed in the lower tube and the remaining volume filled with a known weight of mercury. The apparatus was placed in an oil bath and the volume expansion measured along the calibrated scale as a function of temperature. An initial calibration

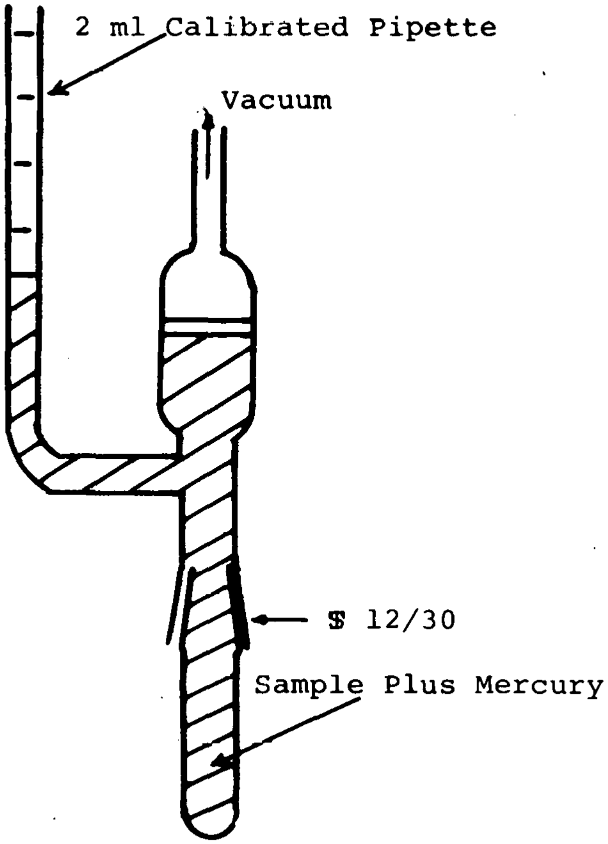

Figure 1

Dilatometer

using only mercury determined the dilatometer volume so that the volume of the sample being measured could be determined at each temperature. Temperature runs with both increasing and decreasing temperature were made in order to determine any hysteresis in the phase change.

Thermal conductivity was measured by the method of Underwood and McTaggert[7] using solid pellets of 0.5" diameter and 0.625" long.

Structural strength was noted by observation during and after the various thermal conductivity and density measurements.

Qualitative vapor pressure observations were made by noting the effect of a stream of hot air on the volume of the pellet.

Hysteresis effects were measured by noting the difference between the transition temperature of a substance starting from below and above the transition temperature.

In the present work four substances were thoroughly examined. These were dl-camphoric anhydride, d-camphoric anhydride, triethanolamine borate, and 2-imidazolidone. The results are shown in Table IV. Certain features are of interest. The volume changes at the phase change run from 4 to 8% which is well within the range expected. Thermal conductivity values are all quite normal for nonconducting solids. It might have been expected that the conductivity of the high temperature forms would be greater due to the increase in molecular motion but any increase was offset by the decrease due to volume expansion. The most significant result was the large hysteresis effect in cycling between low and high temperature. Similar effects were noted in the differential scanning calorimetry. The amount of the hysteresis is probably very much a function of the experimental conditions. It was much larger for dl-camphoric anhydride than

Table IV

	dl-Camphoric Anhydride	d-Camphoric Anhydride	Triethanolamine Borate	2-Imidazolidone
Density, g/cm^3, 25°C	1.11	1.16	1.36	1.37
Thermal Expansion, 1/°C (volumetric coefficient) Low Temperature Phase	5.2×10^{-4}	3.3×10^{-4}	1.35×10^{-4}	1.33×10^{-4}
High Temperature Phase	2.2×10^{-4}	2.2×10^{-4}		6.4×10^{-4}
Volume Change of Phase change, cm^3/g	.060	.046	>.077	.063
% Volume change, from 25°C thru phase change	11%	8.9%	>13%	9.2%
Temperature of phase change, °C				
Low to High	104	133	120 - 160?	66
High to Low	81	124	120 - 160?	61
Thermal Conductivity, cal/sec-cm-°C				
Low Temperature Phase	3.6×10^{-4}	3.1×10^{-4}	6.1×10^{-4}	6.0×10^{-4}
High Temperature Phase	2.2×10^{-4}	2.2×10^{-4}		3.4×10^{-4}
Heat Capacity, cal/g°C	.341	.341	.378	.414
Thermal Diffusity, cm^2/sec	9.5×10^{-4}	7.8×10^{-4}	11.9×10^{-4}	11.7×10^{-4}

for any of the other materials but the camphoric anhydride was the only substance that was not pressed into a pellet for the measurement. If the mechanism for the high to low temperature phase change is primarily growth around a few nuclei, then the looser form of the powder would inhibit the phase change until the temperature was low enough to cause many nuclei to form. Experimentally it was noted that the materials have little tensile strength as pellets. The increase in size of the pellets was not recovered when they cooled. Instead they became successively larger and more porous with each temperature cycle. In addition there is a very sizable weight loss due to volatilization during thermal tests. There was no evidence of corrosion of aluminum by imidazolidone; however, when imidazolidone was cycled through the phase change for three days, it was slightly darkened where it contacted copper. Finally it was clearly demonstrated that the phase transitions are stable in that as many as twenty cycles have been made through some of the phase transitions without any apparent change of temperature or energy.

III. Discussion

We can conveniently divide the discussion into chemical aspects, engineering aspects, and finally an overall assessment including economics of the concept of the use of solid state phase changes for thermal energy storage.

A. Chemical Aspects: The major effort in the present program has been devoted to finding new substances showing sizable solid state transitions at useful temperatures. Although a survey of all likely classes of compounds was made the most promising type found in the present work was the bicyclo three dimensional compounds with various functional groups. These are listed in Table II together with a number of other types. A typical example is 5-norbornene-2,3-dicarboxylic acid anhydride which has a heat of transition of 22.6 cal/g. at 365.5 K. The molecule dl-camphoric anhydride which has a similar structure was also found to show a phase change of 25.2 cal/g at 375 K. In addition to the anhydrides, trans 2,3-dicyano-5-norbornene and d-camphoric oxime were found to undergo solid state transitions. Again it should be remarked that seemingly similar compounds such as the imides of these compounds which differ only in the replacement of the ring oxygen in the anhydride with an N-H group show no transitions.

The best of the compounds found in the present work have transition energies in the 20-30 cal/g range which is significantly lower than the known series of hydroxy, amino, and carboxyl derivatives of methane. The latter series is of much lower molecular weight and hence has a larger number of interacting groups per unit weight. The philosophy in the present work was to consider larger structures with a greater number of functional groups per molecule. Unfortunately when more functional groups were added the intermolecular interaction energies were too great to permit a phase transition. Even though the interaction energy of the compounds found in the present work is lower than that of the methane derivatives, this can be compensated for only an economic basis in that the dollars per kilocalorie is nearly the same for the 5-norbornene compound due to its lower cost as compared to the methane derivatives.

B. Engineering Aspects: As a result of the physical property studies a number of important problems have been uncovered. The most important of these is the hysteresis effect that exists in the transitions when an appreciable rate of temperature change is used. The result is that on cooling the sample the transition temperature is lower than when the sample is heated. The difference between the two temperatures appears to be very dependent on experimental factors. Samples made into pellets show a much smaller difference than those used as powders. In addition the rates of heating and cooling seem to be very improtant since in some experimental work carried out on carboranes (icosahedral cage structures containing ten boron and two carbon atoms) very small hysteresis was observed when cooling rates of 1° to 2° per hour were used. When the cooling rate was 8° per hour in some of the engineering studies a hysteresis effect of about 10° was found. The importance of the hysteresis effect depends on the rate of temperature change of the storage bed. Although no design data is available for these materials it was noted that Dow Chemical Co.[8] has studied a number of solid-liquid phase change systems such as $Mg(NO_3)_2.6H_2O$,naphthalene, palmitic acid, and palmitic-stearic acid mixtures and has been able to discharge about 60% of the total stored energy without any appreciable temperature change for the output air. This suggests that with proper heat exchanger design the rate of temperature change could be minimized and thus the hysteresis effect also be minimized.

A second problem that has been found is the behavior of the phase change materials during cycling. Although it has been found that the materials can be cycled without change of transition properties there is a loss of structural strength. The volume change at the phase change is 6-7%, which is acceptable, but the unconfined pellets become irreversibly larger and more porous and this is troublesome since it weakens the material. Presumably a maximum change would be reached after a number of cycles although this has not been demonstrated. In addition the thermal conductivity decreased after cycling presumably due to the larger void volume. No temperature change of the phase change due to cycling was found suggesting that the pellet does not pick up any impurities.

All of these observations indicate that the materials as used in a heat exchanger will have to be containerized. An additional important reason for the use of containers was the observation that there is a significant loss of the material in a stream of hot air due to volatilization. The size of the container can be estimated on the basis of the maximum heat path length using the Biot number, hx/k, where h is the fluid heat transfer coefficient at the interface, x is the maximum heat path length, and k is the thermal conductivity of the solid. If the Biot number is small the solid's thermal resistance will be small. The present materials are in line with the thermal conductivity of most organic materials so that design properties are known

There are four basic geometries for enclosing a pcm and exchanging heat with a fluid: granular solids, cylindrical or bar shaped solids, thin plate solids, and massive block solids containing channels for fluid flow. The major engineering variable in all of these is the maximum heat path length, which depends on the diameter of the grains or the bar, the thickness of the plate, and the spacing of channels in a block. (A variation of the fluid channels in the block is heat channels: high conductivity inclusion which have the same function.)

Granular solids can be used either in a fixed or fluidized bed. The major advantage of a fluidized bed is that the heat transfer coefficient, h, is fairly large. This results in a high Biot number, and a situation in which the initial heat transfer rate is large but drops off quickly as the bed cools. The temperature of the exit stream from the bed also drops off as the bed cools. In a fixed bed, the bed cools first at the inlet; the temperature of the exit stream remains high through most of the cycle time. The fixed bed is more efficient, thermodynamically, in that more of the heat is recovered at the high temperature. The difference between the two is less pronounced as the ratio of latent heat to specific heat increases; there will be no difference in the thermodynamic efficiency if only latent heat is transferred. The rate of heat release is more constant with a fixed bed. For most applications, a fluidized bed should not be considered.

Choice among the four basic geometries depends on the ease of fabrication and the allowance for expansion. From the data gathered so far, it would seem that the best choice would be to confine the solid tightly enough during the phase change that there would be no residual expansion after each cycle. This will require a heavier container than one which would merely separate the solid from the heat transfer fluid. The container must also provide the structural strength. The stresses that such a container would have to withstand, and the effect of such confinement on the pcm are as yet unknown. This confinement could best be done by casting the pcm inside cylindrical tubes, taking care to avoid shrink cavities upon solidification. The tube would then be filled with the less dense, high-temperature phase. When the solid-solid phase transition occurs, the volume change should produce microvoids distributed throughout the solid. The reverse transition, to the higher volume phase, should fill these microvoids and not cause any bulk expansion. Such ideal behavior may not happen. Local expansion where there are no voids would stress the solid and the container. Extra void space, distributed through the solid, might be required; this would decrease both thermal conductivity and the volumetric heat storage capacity. If lower bulk density is desired, or if the melting point is too high for casting, the solid could be packed into the tubes to achieve the desired result. If the solid is to be relatively unconfined, it could be contained between parallel corregated plates, which would allow a limited amount of expansion.

The container problem has been studied by Dow in the work mentioned above. In their work heat transfer did not seem to be much of a problem. Standard size commercial cans and bottles were used and seemed to be satisfactory. Larger size cans are of course more desirable since the amount of container weight is smaller on this basis but the need for more heat transfer would require smaller cans at a penalty for efficiency. No thermal conductivity data for the materials used in the Dow work are available but presumably the values for the solids are of the same order of magnitude as the ones measured in the present work while the liquids do not differ greatly so that heat transfer into the storage materials will be about the same for all types of materials being discussed. Therefore the Dow work may very well be applicable to the present study although this will have to be demonstrated.

C. Economics and Other Aspects: The economics of the system is primarily dependent on the amount of thermal energy that can be stored per dollar. Costs are a function of the size and design of the storage vessel and heat exchanger plus the costs of the phase change materials. There are varying tradeoffs that are present such as a more expensive phase change material for a larger phase change energy and smaller heat exchanger and storage vessel. One of the difficulties in the discussio is the lack of hard cost data for the phase change materials. Only a few of these are available in commercial quantities and some are not even available from laboratory supply houses. Given in Table V are a list of known phase transition materials from all sources including the present work together with cost estimates, transition energies, and cost in dollars per kilocalorie of storage energy. There are a number of other materials than show relatively high energies of transition but no cost data are available. It is also evident that a controlling factor in any choice of a material is the temperature range desired. Even though pentaerithrytol is the lowest cost material it is hardly useful if a different temperature range is desired. We have observed that the energy of transition increases as the temperature of transition increases although there is no general linear relation.

Table V

Comparison of Economics of Phase Transition Materials

Compound	Transition Temp. °C	Energy Transition cal/g	Cost/Lb.[9]	Dollars/ Kilocalorie
1. Pentaerithrytol	184	72	$0.49	$0.015
2. 2-Amino-2-methyl -1,3-propanediol	78	63	1.01[1]	0.035
3. Norbornene anhydride	73	21	0.40[2]	0.042
4. Tris(hydroxymethyl)-aminomethane	86	46	1.70	0.081

1. Cost data is for 2-amino-2-ethyl-1,3-propanediol
2. Estimated based on component raw material costs times two.

Another important aspect to be considered is the toxicological properties of the materials. The materials of interest were checked in the Toxic Substances List[5] and all were found to be relatively non toxic as far as reported.

D. Future Work: The next phase of this investigation would be to construct a test apparatus where samples of phase change materials can be cycled through the phase change repeatedly.

This apparatus would include a test chamber where samples could be placed, and an air circulation loop with a heater and appropriate instrumentation for measuring and controlling the air flow rate and temperature.

Initial experimentation would be to determine the volume expansion effects, and to study different materials and methods of containing the phase change material. Simultaneous studies where possible would be made to determine heat transfer characteristics as functions of container size and type.

IV. Experimental Section

Preparation of 5-norbornene-2,3-dicarboxylic acid imide[10]: A mixture of 48 g. of 5-norbornene-2,3-dicarboxylic anhydride and 250 ml of concentrated ammonia was refluxed for five hours. On cooling the product separated out and was recrystallized from water. Yield 30 g, m. 183-5°C, lit. value 185-187°C.

Preparation of 5-norbornene-2,3-dicarboxylic acid methyl imide: The procedure used followed that described in the literature[11]. A solution of 10 g of 5-norbornene-2,3-dicarboxylic anhydride and 100 ml of 40% aqueous methyl amine was refluxed for twenty hours. At the end of this period the excess methyl amine and water were distilled off under vacuum and 30 ml. of acetyl chloride added. The white solid from the distillation went into solution with the evolution of heat. The solution was distilled for 1.5 hours and the excess acetyl chloride removed by vacuum distillation. The white product was vacuum dried and sublimed under reduced pressure to give a material m. 106-09°C.

Preparation of d-camphoric acid methyl imide[11]: This was prepared starting with d-camphoric anhydride following the same procedure as for 5-norbornene-2,3-dicarboxylic methyl imide to give a white solid, m. 247°C.

Preparation of dl-camphoric acid: The starting dl-camphoric anhydride was hydrolyzed by boiling in a dilute hydrochloric acid solution. The unreacted anhydride was filtered off and the acid recovered on cooling of the solution by filtration to give a white solid, m. 208°C.

Preparation of 5-norbornene-2,3-dicarboxylic acid dichloride[12]: A mixture of 20 g of 5-norbornene-2,3-dicarboxylic acid and 100 ml of thionyl chloride was refluxed for 24 hours until the evolution of hydrogen chloride ceased. After the addition of 20 ml of carbon tetrachloride to the mixture it was vacuum distilled to a total volume of 20 ml. An additional 40 ml of carbon tetrachloride was added and the procedure repeated twice to leave a small amount of thionyl chloride and a white solid. Next, 15 ml of diethyl ether was added and the mixture vacuum distilled to remove all of the thionyl chloride. The diacid chloride was not isolated but was used in the next step of the reaction.

In another preparation 30 g of the acid was refluxed with 50 g of phosphorous pentachloride in 450 ml of benzene[13]. The diacid went into solution immediately with a vigorous evolution of hydrogen chloride. The solution was reluxed for 24 hours until the evolution of hydrogen chloride ceased. The excess benzene and by product phosphorous oxychloride were removed by distillation, first at atmospheric pressure, and then under vacuum, leaving a liquid. About 30 ml of 30-75 petroleum ether was added and the mixture shaken and vacuum distilled. Next about 30 ml of absolute diethyl ether was added and after vacuum distillation all of the yellow color disappeared leaving the acid chloride as a white residue. This method seems superior to the thionyl chloride method described above.

Preparation of 5-norbornene-2,3-dicarboxamide: Approximately 3 g of the diacid chloride described previously was added slowly to 50 ml of concentrated ammonia with stirring. The reaction was vigorous. The white precipitate was filtered and dried overnight at 130°C to yield a solid m. 240°C.

Preparation of 5,6-dichloronorbornane-2,3-dicarboxylic acid anhydride: The procedure was similar to the literature[14]. A mixture of 2 g 5-norbornene-2,3-dicarboxylic anhydride and 4 g of iodobenzene dichloride in 20 ml of chloroform was refluxed for 0.5 hours. On cooling the produce, a white solid, separated out and was vacuum sublimed for purification, m. 171°C.

Preparation of bicyclo (2,2,2) oct-5-ene-2,3-dicarboxylic acid anhydride: A solution containing 1.33 g of 1,3-cyclohexadiene and 1 g of maleic anhydride in

15 ml of absolute ether was stirred for four hours at 25°C. A white solid precipitated, was filtered, and then sublimed in vacuum, m. 145°C.

Preparation of bicyclo(2,2,2) octene-5,7-dione-2,3-dicarboxylic acid anhydride[11]: Approximately 15 g of hydroquinone and 28 g of maleic anhydride was heated to about 200°C for 25 hours under nitrogen. On cooling a viscous dark red solution was present. The solution was mixed with 80 ml. of absolute ether, refluxed for 0.5 hour, and on cooling a brown solid precipitated. This was filtered and vacuum sublimed to give about 1 g of a light yellow solid, m. 235°C.

Reduction of dl-camphoric anhydride with sodium borohydride/aluminum chloride mixture[6]: In a 1 liter 3 neck flask equipped with stirrer, condenser, and addition funnel equipped with nitrogen inlet was placed a solution of 18 g of sodium borohydride and 18 g of dl-camphoric acid in 400 ml of diglyme. A solution of 14 g of anhydrous aluminum chloride in 70 ml of diglyme was prepared at 0°C and added dropwise to the borohydride-camphoric anhydride solution under nitrogen and the solution heated to 75°C for 1 hour. The mixture was hydrolyzed by addition to 80 ml of conc. hydrochloric acid and 700 g of ice. The resultant solution was evaporated to about 500 ml. to give a white precipitate. The solid was added to a solution of 3 g of sodium hydroxide in 250 ml of water in order to dissolve all of the borates and aluminates. The remaining material was filtered and sublimed at reduced pressure to yield a white solid m. 211°C. An infrared spectrum was run as a KBr pellet and showed a strong carbonyl band at 1670 cm^{-1} but no hydroxyl band. It is presumed to be the lactone by comparison with the infrared spectra of known lactones. Apparently the procedure does not work in this case even though it is described as a general method of reduction.

Reduction of dl-camphoric diacid chloride with lithium aluminum hydride[16]: The diacid chloride was used as the starting material. The reaction was carried out in a 3 neck flask equipped with stirrer, condenser, and addition funnel. A solution of 2.3 g. of lithium aluminum hydride in 50 ml of tetrahydrofuran was placed in the flask and 9.0 g. (0.038 moles) of the diacid chloride in 20 ml of tetrahydrofuran was added dropwise with stirring under nitrogen and refluxed for 25 hours. The solution was cooled to room temperature and the excess lithium aluminum hydride hydrolyzed by adding 20 ml. of water dropwise. Next 50 ml. of concentrated sulfuric acid was added to the mixture, the tetrahydrofuran removed by distillation, and the solution extracted five times with diethyl ether to give a yellow solution that did not crystallize on evaporation of the solvent. Instead a yellow oil was obtained which could not be crystallized. A portion was treated with acetone and on standing a white solid slowly separated. The solid could not be sublimed. It showed a strong broad band in the infrared at 3250 cm^{-1} which is that reported in the literature. No carbonyl band was observed.

<u>Preparation of 8,8,9,9-tetracyanoquadricyclo(2,2,1,$0^{2,6}$,$2^{3,5}$)nonane</u>[17]: A solution of 2 ml of norbornadiene and 1.6 g of tetracyanoethylene in 20 ml. of benzene were refluxed for 0.5 hrs to yield a dark red solution. The solution was cooled and a tan solid precipitated from the solution, was crystallized from an absolute ether-acetone mixture, and then sublimed at reduced pressure. The adduct melted at 192-4°C.

<u>Preparation of fumarodinitrile</u>[18]: Commercial diethyl fumarate was added to a solution of 6 g ammonium chloride in 60 ml of concentrated aqueous ammonia in a three neck flask equipped with stirrer, addition funnel, and condenser. The solution was stirred for one hour at room temperature and a white precipitate formed. The solid was filtered and reslurried with 200 ml of water and refiltered. Approximately 10 ml of ethanol was poured over the white solid and the solution dried under an infrared lamp for 15 hours to give about 21 g of the diamide of fumaric acid. The solid diamide and 61 g of phosphorous pentoxide were mixed in a 500 ml round bottom flask which was connected by a 17 mm glass tube to a 500 ml filter flask. The

apparatus was evacuated using a water aspirator with the glass tube extended about 15 cm. into the filter flask. The solid mixture in the round bottom flask was heated with a bunsun burner and after about 20 minutes a white solid sublimed out and was collected in the filter flask. After four hours of heating a yield of 7 g of fumarodinitrile, m. 93°C, lit. value 96°C, was obtained.

Preparation of trans-2,3-dintrile-5-norbornene[19]: A solution of 2 g of fumarodinitrile and 3 ml of cyclopentadiene in 50 ml. of absolute ethanol was refluxed for two hours and the solution evaporated to one half of its original volume at which point a white solid separated out. The solid was filtered and vacuum dried, followed by sublimation at reduced pressure to give a solid, m. 98°C.

Reaction of norbornadiene and p-benzoquinone: A mixture of 5g of p-benzoquinone and 10 ml of norbornadiene were heated for 15 hours in a bomb at 220°C. No pressure was observed at the end of the reaction. All of the volatiles from the reaction mixture were removed at 80°C by distillation leaving a black solid. The solid was sublimed in vacuum to give a black crystalline product, m. 160-3°C to a deep red liquid. An infrared spectrum showed the characteristic notricyclene peak at 830 cm^{-1}. The product is pentacyclo$(2,2,1,0^{2,6},2^{3,5},4^{8,9})$-tridecene-11-dione-10,13.

Synthesis of hexachlorocyclotriphosphazene[20]: A mixture of 15 g of phosphorous pentachloride, 30 g of ammonium chloride and 300 ml of chlorobenzene were refluxed at 130°C in a Soxhlet extractor apparatus for 24 hours with an addition 56 g of phosphorous pentachloride in the extraction thimble. This was done in order to have excess ammonium chloride in the reaction mixture since this tends to minimize the formation of linear species. The excess ammonium chloride was vacuum filtered at the end of the reaction and the chlorobenzene removed by distillation at 62°C and 74 torr. The resulting brown buttery solid was washed repeatedly with a total amount of 400 ml of 30-75° petroleum ether and the insoluble brown solid discarded. The clear yellow petroleum ether solution was distilled off at atmospheric pressure to yield white needles on cooling from the now orange solution. This is a mixture of ti, tetra, and higher cyclo species The white solid was washed with cold benzene and filtered to give the insoluble trimer and tetramer. Additional trimer and tetramer were obtained from the orange solution as before. Sublimation of the trimer-tetramer mixture yielded a white solid m. 110-15°C, lit. value 112°C for the trimer.

Table VI

Properties of Substances Showing Solid State Phase Changes

No.	Compound	Transition Temperature°C	Energy of Transition cal/g.
1.	2-methyl-2-amino-1,3-propanediol	78	63
2.	2-methyl-2-nitro-1,3-propanediol	78	48
3.	2-hydroxymethyl-1,4-butanediol	81	46
4.	2,2-bis(aminomethyl)-1,3-propanediol	68	44
5.	2-methyl-2-hydroxymethyl-1,3-propanediol	81	46
6.	2-aminomethyl-2-hydroxymethyl-1,3-propanediol	86	46
7.	2-hydroxymethyl-2-carboxy-1,3-propanediol	124	49
8.	2-amino-2-hydroxymethyl-1,3-propanediol	131	68
9.	2-methyl-2-carboxy-1,3-propanediol	152	69
10.	tetrakis(hydroxymethyl)methane (pentaerythritol)	184	72

REFERENCES

1. F. Simon, Ann. Physik 68, 241 (1922)

2. J. Timmermans, J. Phys. Chem. Solids 18, 1 (1961)

3. A. I. Kitaigorodskii and K. V. Mirskaya, Kristallografiya 9, 174 (1964)

4. A. Govezzotti and M. Simonetta, Acta Cryst. A31, 645 (1975)

4a. Phase Change Materials Handbook, D. V. Hale, M. J. Hoover, and M. J. O'Neill, Lockheed Missiles and Space Co., Contract NAS8-25183, Sept. 1971

4b. Thermal Control by Use of Solid/Solid Phase Change Materials, E. Murrill and L. W. Breed, Midwest Research Inst., Contract NAS8-21452, July 1969, May 1970

5. "Toxic Substances List", NIOSH

6. H. C. Brown and B. C. Subba Rao, J. Amer. Chem. Soc. 78, 2582 (1955)

7. N. M. Underwood and R. B. McTaggert, CEP Symposium Series No. 30, 56, 261 (1966)

8. Dow Chemical Co., Contract E (40-1)-5217 to Dept. of Energy

9. Chemical Marketing Reporter, July 17, 1978

10. W. S. Worrall, J. Amer. Chem. Soc. 82, 5707 (1967)

11. R. C. Cookson and N. S. Wariyer, J. Chem. Soc. 329 (1957)

12. P. Maurer, B. Roquefort, and D. M. Blardet, Bull. Soc. Chim. France, 426 (1973)

13. Preparative Organic Chem., Weygand, Hilgetag, 1972

14. S. Masson and A. Thuillier, Bull. Soc. Chim. France, 3508 (1971)

15. O. Diels and K. Alder, Ann. 460, 98 (1928)

16. J. Entel, C. H. Ruof, and H. C. Howard, J. Amer. Chem. Soc. 74, 441 (1952)

17. A. T. Blomquist and Y. C. Meinwald, ibid. 81, 667 (1959)

18. Organic Synthesis, Collected Vol. IV, p. 486

19. A. T. Blomquist and E. C. Winslow, J. Org. Chem. 10, 149 (1945)

20. Phosphorous Nitrogen Compounds, Allcock, Academic Press, New York, 1972

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