

## Note

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### Solid-solid phase transitions determined by differential scanning calorimetry Part II. Octahedral substances

E. MURRILL AND L. W. BREED

*Midwest Research Institute, Kansas City, Missouri (U. S. A.)*

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Recently, we discussed the observation of previously unreported phases in a number of tetrahedral substances<sup>1</sup>. In the course of our work, we have also observed new plastic crystalline phases in two derivatives of ethane, which can be classified according to Aston<sup>2</sup> as being octahedral molecules. A number of ethane derivatives, like the methane derivatives previously discussed, exhibit plastic crystalline behavior and have sufficiently low fusion entropies to indicate that the acquisition of positional freedom can mostly account for the energy requirements for fusion.

Data for tetramethylsuccinic acid and tetramethylsuccinonitrile are summarized in Table I. Also reported are data obtained in this laboratory for hexachloroethane, which has been studied by others. The tetrahedral dicarboxylic acid, dimethylmalonic acid, does not exhibit a transition above  $-50^{\circ}\text{C}$ .

In many substances with solid-solid transitions, a portion of the entropy change at the transition must be attributed to conformation disorder as well as to molecular reorientational disorder, wherever conformational disorder is possible. However, the entropy at transition for 2,2,3,3-tetramethylbutane (Table II) is less than transitional entropy for neopentane (4.4 e.u.)<sup>9</sup> indicating no additional new disorder in the transition as a consequence of methyl group reorientations or rotation about the central carbon-carbon bond. The latter observation can be confirmed with molecular models.

Restriction of conformational disorder by crowding of substituent groups about the ethane nucleus is readily demonstrated by comparing the transitional entropies of various substituted ethanes in Table II. When the central ethane structure is substituted by six or five methyl groups, entropy increments of transition of 3-5 e.u. are observed, but when the extent of substitution is reduced to four, in either the symmetrical or unsymmetrical derivative, the value increases to 10-11 e.u. This value is the same as the entropy change observed for the disilane structure substituted by six methyl groups (hexamethylidisilane), in which the larger covalent radius of silicon reduces the steric barrier to conformation disorder. It is necessary to assume then, that steric factors inhibit possible reorientations about the central bond in some ethane derivatives and as a consequence effect a reduction in the entropy increments.

TABLE I  
EXPERIMENTALLY DETERMINED ENTROPIES AND TEMPERATURES OF TRANSITION AND FUSION

	Transition			Fusion		
	T (°C)	ΔH (cal/g)	ΔS (e.u.)	T (°)	ΔH (cal/g)	ΔS (e.u.)
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{NC}-\text{C}-\text{C}-\text{CN} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	71-73	31.77	12.58	168-170	12.54	3.87
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{HO}_2\text{CC}-\text{C}-\text{C}-\text{CO}_2\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	108-111	18.43	8.43	190-193	8.88	3.34
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\   \quad   \\ \text{Cl}-\text{C}-\text{C}-\text{Cl} \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$	46-48 71-72	2.63 6.37	1.95 4.38	179-184	---	---

In tetramethylsuccinonitrile and tetramethylsuccinic acid, the size of the carboxy and nitrile groups can be expected to provide a barrier to reorientation about the central bond similar to the barrier observed in 2,2,3,3-tetramethylbutane; therefore, the entropy changes in transition, insofar as they exceed the entropy of the parent hydrocarbon, can probably be attributed to the new conformational possibilities introduced by the carboxy and nitrile groups. Certain analogies between tetramethylsuccinic acid-related structures confirm this explanation. The difference in transitional entropy changes in pivalic acid (7.5 e.u.)<sup>10</sup> and tetramethylsuccinic acid is relatively small, but the difference cannot be assigned to greater molecular reorientation possibilities in the octahedral molecule in comparison with the tetrahedral molecule, since the entropy change in transition for neopentane is actually larger than the entropy change for 2,2,3,3-tetramethylbutane. Additional justification for limiting the assignment of new conformational possibilities to those related to the carboxy group can be observed in the difference in the entropy increment for tetramethylsuccinic acid and 2,2,3,3-tetramethylbutane (5.3 e.u.) being about twice the difference in pivalic acid and neopentane (3.1 e.u.).

Several related structures (Table II) have also been reported to exhibit solid state transitions, including 2,3-dichloro-2,3-dimethylbutane and 2,3-dibromo-2,3-dimethylbutane. Therefore, it was surprising when it was found that pinacol (tetramethylethylene glycol) did not exhibit a transition above  $-80^{\circ}\text{C}$ . However, comparison of the fusion temperatures reported in the literature of many other related compounds, particularly those with the structures  $\text{C}_2(\text{CH}_3)_n\text{Cl}_{6-n}$  and  $\text{CSi}(\text{CH}_3)_n\text{Cl}_{6-n}$  indicate that the solid-solid transition phenomenon is a common property of the series.

The existence of a plastic crystalline phase can usually be predicted through comparisons of fusion temperatures of substances within a homologous series or by comparison of the fusion temperature substances in which a sufficiently large substituent group is present that the *meso*-crystalline state is not stable. With the proper molecular geometry, molecular reorientation freedom will occur close to the expected fusion temperature, but the solid state remains stable to a considerably higher temperature. This effect can be illustrated in the fluorocarbon series in which tetrafluoromethane melts at  $-184^{\circ}\text{C}$  and octafluoropropane melts at  $-183^{\circ}\text{C}$ <sup>11</sup>. Hexafluoroethane melts at  $-100^{\circ}\text{C}$ , but has a transition at  $-169^{\circ}\text{C}$ , close to the range of the fusion of the higher and lower homologous.

#### EXPERIMENTAL

All qualitative data were determined with a DuPont 900 Differential Thermal Analyzer at a heating rate of  $15^{\circ}\text{C}/\text{min}$  in an air atmosphere. The quantitative data were obtained with the Differential Scanning Calorimeter module at a heating rate of  $10^{\circ}/\text{min}$  with hermetically sealed pans. The procedure and calibration were described earlier<sup>1</sup>. Tetramethylsuccinonitrile and tetramethylsuccinic acid were prepared by the method described by Bickel and Waters<sup>12</sup>. Heats of fusion could not be

TABLE II  
LITERATURE VALUES FOR TEMPERATURES AND ENTROPIES OF TRANSITION AND FUSION

	Transition			Fusion			Ref.
	T (°C)	$\Delta H$ (cal/g)	$\Delta S$ (e.u.)	T (°C)	$\Delta H$ (cal/g)	$\Delta S$ (e.u.)	
$\begin{array}{c} \text{F} \quad \text{F} \\   \quad   \\ \text{F}-\text{C}-\text{C}-\text{F} \\   \quad   \\ \text{F} \quad \text{F} \end{array}$	-169.17	6.47	8.59	-100.05	4.65	3.71	3
$\begin{array}{c} \text{Cl} \quad \text{Cl} \\   \quad   \\ \text{Cl}-\text{C}-\text{C}-\text{Cl} \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$	45 72	2.59 8.300	1.93 5.70	185	9.84	5.09	4
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	-120.7	4.18	3.134	100.82	15.78	4.82	5
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{H} \end{array}$	-151.8	5.846	4.825	-24.58	5.393	2.174	6
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\   \quad   \\ \text{H} \quad \text{H} \end{array}$	-137	18.0	11.4	-128.0	2.23	1.32	6

## NOTE

$  \begin{array}{c}  \text{CH}_3 \quad \text{H} \\    \quad   \\  \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\    \quad   \\  \text{CH}_3 \quad \text{H}  \end{array}  $	-132.27 -146.34	0.786 14.96	0.480 10.166	-98.99	1.607	0.795	6
$  \begin{array}{c}  \text{CH}_3 \quad \text{CH}_3 \\    \quad   \\  \text{CH}_3-\text{Si}-\text{Si}-\text{CH}_3 \\    \quad   \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	-51.4	15.9	10.5	14.5	4.94	2.51	7
$  \begin{array}{c}  \text{CH}_3 \quad \text{CH}_3 \\    \quad   \\  \text{Cl}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	-10 to +4			159-160°			8
$  \begin{array}{c}  \text{CH}_3 \quad \text{CH}_3 \\    \quad   \\  \text{Cl}-\text{C}-\text{C}-\text{Cl} \\    \quad   \\  \text{CH}_3 \quad \text{CH}_3  \end{array}  $	75-100			dec.			8

determined for hexachloroethane because of its (explosive) reactivity with the aluminum pans.

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