

Table 1. DSC and XRD data for several substituted pentaerythritol compounds

Compound	-R	DSC data				XRD data	
		T_{tr} (°K)	ΔH_{tr} (kcal.mole ⁻¹)	$T_{m.p.}$ (°K)	ΔH_m (kcal.mole ⁻¹)	T (°K)	a (Å) (e.s.d.)
I	-COOH	394.7	6.89	492	decomposition	415	8.93 (5)
II	-CH ₃	351.3	5.14	497.0	1.23	373	8.86 (5)
III	-NO ₂	347.4	5.30	438	decomposition	355	8.89 (5)
IV	-NH ₂	407.3	7.87	446.0	0.71	—	see text

normally behaving melting points, with completely reversible transitions between phases I and II and between phase I and the melt. Compounds I and III undergo reversible transitions between phases I and II, but decompose without melting at higher temperatures.

Compounds II, III, and IV have been previously studied with DSC (Murrill & Breed, 1970). The results of the two investigations are in good agreement.

The X-ray study of IV deserves special mention. The X-ray pattern of the high-temperature phase has only one line. This was the only line observed, even though many photographs were taken of several specimens at a number of temperatures between 407.3 and 446.0°K. This line is characteristic of a crystalline material, appearing as either a sharp line or one showing evidence of preferred orientation. It has a d spacing of 4.97 Å. When the temperature was raised above 446.0°K, a broad diffuse band ($d=5.1-5.2$ Å), characteristic of a liquid, appeared.

The other compounds all show two or more unique reflections in the high-temperature phase. They were indexed and unit-cell and space-group assignments were made in the usual manner (Rudman & Post, 1968). However, no conclusions concerning the lattice parameters or space group of IV can be made on the basis of a single observation. We can only state that the high-temperature phase is crystalline and can be differentiated from the liquid phase. It is possible that the rate of molecular reorientation in this phase is so great that only nearest neighbor effects (similar to that observed for a liquid) are apparent. A study of the rate of reorientation in this phase, using nuclear magnetic resonance or neutron inelastic scattering methods, would be of interest.

Room-temperature single-crystal data for this compound (IV) have been determined by Rose & Van Camp (1955). They reported the space group as $P2_12_12_1$. A re-investigation of this phase revealed the following systematic ab-

sences: $0kl$, $k+l$ odd and $hk0$, h odd. These absences are consistent with space groups $Pnma$ (No. 62) or $Pn2_1a$ (No. 33). The lattice parameters, obtained from precession photographs, were refined from powder data using a modified version of the program *PIRUM* (Werner, 1970) on a CDC 3300 computer. These values, $a=7.816$ (5), $b=8.822$ (3) and $c=8.867$ (4) Å, are in good agreement with the results of the earlier investigation (7.80, 8.82 and 8.89 Å respectively).

In conclusion, we find that each of the compounds investigated forms a highly disordered crystalline phase just below the melting point, as does pentaerythritol itself. With the exception of IV, they form face-centered cubic phases with similar lattice constants (a for R = -CH₂OH is 8.963 Å, Nitta & Watanabé, 1938). The deviations from the spherical character of the molecules caused by the substitution of these four functional groups does not prevent the formation of a plastic-crystal phase. Even in the cases of I and III, where the introduction of a highly polar group results in decomposition rather than melting, the X-ray study indicates that crystals of phase I are plastic in nature.

References

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