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**The crystal structure of urea oxalic acid (2:1): a correction.** By S. HARKEMA, J. W. BATS, A. M. WEYENBERG and D. FEIL, *Chemical Physics Laboratory, Twente University of Technology Enschede, The Netherlands*

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Incorrect cell constants have been given for urea oxalic acid (2:1) in the paper by Harkema, Bats, Weyenberg & Feil [*Acta Cryst.* (1972). B28, 1646–1648]. The correct values are:  $a = 5.110$  (3),  $b = 12.400$  (3),  $c = 7.035$  (2) Å,  $\beta = 98.13$  (7)°. Corrections to the original tables of bond distances and angles are given.

In the calculation on the crystal structure of urea oxalic acid (2:1) (Harkema, Bats, Weyenberg & Feil, 1972) a wrong set of cell constants was used. The correct values for the cell constants are:  $a = 5.110$  (3),  $b = 12.400$  (3),  $c = 7.035$  (2),  $\beta = 98.13$  (7)°. The error has no appreciable effect on atomic positional parameters. The reported  $U$  values can easily be corrected for the difference in cell constants. Changes in bond angles and distances for some bonds are significant; therefore, corrections to Tables 4 and 5 in our paper are given.

Table 4. Bond distances (Å)

C(2)–C(2')	1.537 (5)	N(1)–H(4)	0.83 (2)
C(2)–O(2)	1.208 (3)	N(2)–H(2)	0.87 (4)
C(2)–O(3)	1.298 (5)	N(1)–H(5)	0.88 (3)
O(3)–H(1)	0.99 (4)	O(1)·····O(3)	2.493 (5)
C(1)–N(1)	1.329 (6)	O(2)·····N(2)	3.022 (5)
C(1)–N(2)	1.329 (4)	O(3'')·····N(2)	3.127 (3)
C(1)–O(1)	1.261 (3)	O(2'')·····N(1)	2.911 (3)
N(2)–H(3)	0.85 (2)	O(1')·····N(1)	2.954 (4)

It appears that the crystal structure of the title compound has been determined by another research group (Folting, Merritt, Schuch & Sturdivant, 1972). Comparison of

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**The formation of the plastic crystal phase in several pentaerythritol derivatives.\*** By NIRANJAN DOSHI, MOSES FURMAN and REUBEN RUDMAN, *Chemistry Department, Adelphi University, Garden City, New York 11530, U.S.A.*

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Several substituted pentaerythritol compounds [R–C(CH<sub>2</sub>OH)<sub>3</sub>, where R = COOH, CH<sub>3</sub>, NO<sub>2</sub> and NH<sub>2</sub>] have been found to undergo phase transitions to plastic crystals. With the exception of R = NH<sub>2</sub> (which has only one detectable diffraction line in the plastic state), the crystals are *f.c.c.*,  $a \approx 8.9$  Å.

Many compounds composed of tetrahedral, approximately spherical molecules undergo solid–solid phase transitions. Crystals of the highly disordered phase stable just below the melting point (phase I) are generally referred to as *plastic crystals* (Timmermans, 1961). Pentaerythritol, C(CH<sub>2</sub>OH)<sub>4</sub>, has been shown to undergo a transition at 452.7°K (Nitta & Watanabé, 1938) to just such a phase. As part of our attempts to define the sphericity of the molecular envelope that is required in order for plastic crystals to form (Rudman & Post, 1968; Rubin & Rudman, 1973), a series of substituted pentaerythritol compounds was selected for investigation.

The following compounds [RC(CH<sub>2</sub>OH)<sub>3</sub>] were studied: I tris(hydroxymethyl)acetic acid, R = –COOH; II 2-hydroxymethyl-2-methyl-1,3-propanediol, R = –CH<sub>3</sub>; III 2-hydroxymethyl-2-nitro-1,3-propanediol, R = –NO<sub>2</sub>; IV 2-amino-2-hydroxymethyl-1,3-propanediol, R = –NH<sub>2</sub>. Samples

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Table 5. Bond angles (°)

C(2')–C(2)–O(2)	121.7 (2)
C(2')–C(2)–O(3)	112.7 (3)
O(2)–C(2)–O(3)	125.7 (2)
C(2)–O(3)–H(1)	110 (3)
O(1)–C(1)–N(1)	120.0 (3)
O(1)–C(1)–N(2)	121.5 (2)
N(1)–C(1)–N(2)	118.5 (3)
C(1)–N(1)–H(5)	118 (3)
C(1)–N(2)–H(2)	119 (2)
C(1)–N(1)–H(4)	123 (3)
C(1)–N(2)–H(3)	120 (2)
H(4)–N(1)–H(5)	119 (3)
H(2)–N(2)–H(3)	119 (4)

results, which are now in excellent agreement, revealed the above mentioned error.

#### References

- HARKEMA, S., BATS, J. W., WEYENBERG, A. M. & FEIL, D. (1972). *Acta Cryst.* (1972). B28, 1646–1648.  
FOLTING, K., MERRITT, L. L., SCHUCH, A. F. & STURDIVANT, J. H. (1972). Private communication.

purified by several recrystallizations from methanol and by vacuum sublimation gave identical results.

Each compound was studied using the following methods: (a) differential scanning calorimetry (DSC) from 120°K to above the melting point utilizing techniques described elsewhere (Silver & Rudman, 1970); (b) observation through a polarizing microscope over a temperature range from room temperature to above the melting point; and (c) X-ray diffraction flat-plate powder photographs (using nickel-filtered Cu K radiation) of the high-temperature phases. The high-temperature studies were carried out using a commercially available wound-filament quartz-tube gas heater\* with compressed air.

The results of these studies (Table 1) show that as the samples are warmed, each of the compounds undergoes a solid–solid phase transition from an optically birefringent crystal to an isotropic crystal. Compounds II and IV have

\* Gas heater, Model SGH 114680, Sylvania Special Products Division, Exeter, New Hampshire 03833, USA.

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

Compound	-R	DSC data				XRD data	
		$T_{ir}$ (°K)	$\Delta H_{ir}$ (kcal.mole <sup>-1</sup> )	$T_{m.p.}$ (°K)	$\Delta H_m$ (kcal.mole <sup>-1</sup> )	$T$ (°K)	$a$ (Å) (e.s.d.)
I	-COOH	394.7	6.89	492	decomposition	415	8.93 (5)
II	-CH <sub>3</sub>	351.3	5.14	497.0	1.23	373	8.86 (5)
III	-NO <sub>2</sub>	347.4	5.30	438	decomposition	355	8.89 (5)
IV	-NH <sub>2</sub>	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 = -CH<sub>2</sub>OH 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.

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