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A Low-temperature Phase Transition in *s*-Triazine†

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Abstract—*s*-Triazine has been counted an exception to the fairly general rule that aromatic compounds with threefold molecular symmetry occupy general positions in the crystal. It is shown that a low temperature phase of *s*-triazine exists which conforms with this rule. The transition occurs over a large temperature range below $-60°C$.

Introduction

Most phase transformations in organic structures are reconstructive, i.e. they proceed through an intermediate amorphous phase.[1, 2, 3, 4] The stress induced transformation $\beta \rightarrow \alpha$ indigo[5] and the transformation $\beta \rightleftharpoons \alpha$ 1,2:4,5-tetrachlorobenzene[6] are among the few examples of displacive organic transitions. During X-ray and neutron diffraction studies of *s*-triazine[7] we found that the rhombohedral crystals (space group $R\bar{3}c$, for the hexagonal cell $a = 9.647$ Å $c = 7.281$ Å) transform to a triply-twinned monoclinic phase on cooling below ca. $-60°C$. The transition is comparable to the transition in 1,2:4,5-tetrachlorobenzene because it is a reversible temperature induced transformation to a lower symmetric phase and therefore accompanied by twinning. The phase change in triazine is not first order: deviations from rhombohedral symmetry increase with decreasing temperature.

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‡ Visiting Scientist from the Australian AEC.

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Experimental

The transition was first observed with neutrons when a capillary enclosed crystal of approximately 1 mm^3 was cooled with a diffractometer mounted Joule-Thomson refrigerator.[8] Since camera techniques are more convenient for studying phase transitions the specimen was transferred to an X-ray precession camera and

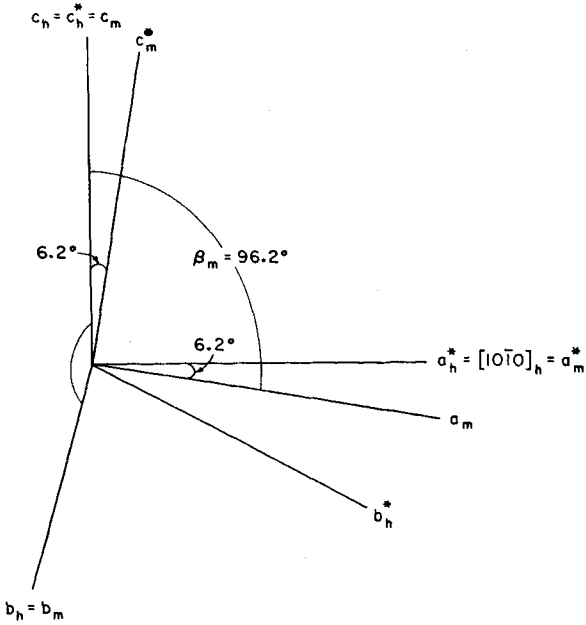

Figure 1. Relation between the hexagonal axes of the room temperature modification (subscript h) and the monoclinic axes of the low temperature form (subscript m).

cooled by a stream of cold dry nitrogen gas. A copper constantin thermocouple was mounted in the cold gas stream at 2 mm before the specimen. Precession pictures of several reciprocal lattice planes were taken at thermocouple temperatures of 0° C, −56° C, −68° C, −99° C, −129° C, −133° C and −155° C. The pictures indicate that (1) The a^*b^* plane of the hexagonal cell is, except for expansion of the reciprocal lattice, not affected by the phase change.

The a^* axis and symmetry equivalent directions expand until the phase transition is initiated and remain constant on further cooling. (2) The c^* axis in the low temperature phase remains in the hexagonal a^*c^* plane, but the a^*c^* angle becomes smaller as the tem-

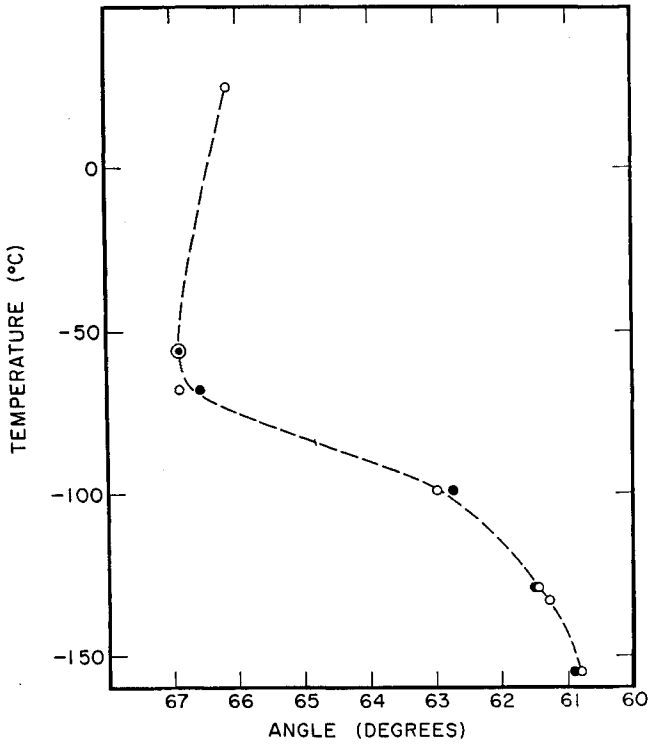

Figure 2. The variation of the angle between the reciprocal lattice axis a^* and row (ho$\bar{1}$h) as a function of the thermocouple temperature. Open circles: measured in the a^*c^* plane; full circles: measured from missetting of a^*c^* planes of the other two twin components. The second set of measurements is normalized at $-56°C$.

perature decreases. Since the hexagonal c^* axis is a three-fold axis the tilting of c^* occurs in three symmetry related directions giving rise to triple twinning. The relationship between the old and the new axes is given in Fig. 1. The low temperature phase is monoclinic if the high temperature [10$\bar{1}$0] axis (and the symmetry related

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[01$\bar{1}$0] and [1$\bar{1}$00] directions in other domains) is taken as the monoclinic a axis. (3) The variation of the β^* angle with temperature cannot be measured accurately as only one weak reflection (0006) occurs on the c^* axis. It is more convenient to measure the angle between a^* and (ho$\bar{h}$h), which can be done directly in the a^*c^* photographs and from the misalignment of the other two twins as shown by the acentricity of their (ho$\bar{h}$h) streaks in the same unscreened precession pictures. The two measurements agree well (Fig. 2). A long exposure at $-133°$ C shows that the variation in this angle is about 83% of the variation in β^*.

The Nature of the Transition

Figure 2 shows that the transition is not first order. Though the largest structural change occurs just below the initiation temperature, quite appreciable variations take place on further cooling. The change is reproducible and its magnitude is independent of the thermal history of the sample.

Structural Relation Between the Polymorphs

The room temperature structure of s-triazine was first solved by Wheatley[9] (Fig. 3). The molecules are located on the three-fold axis, adjacent molecules in the stacks, parallel to this axis being related by a center of symmetry. In a stack the interplanar distance is $c/2$, but molecules in adjacent stacks are either $c/6$ or $c/3$ apart in the c-axis direction. Obviously the direction of the stacks does not change during the transition as the a^*b^* plane and therefore the c axis remains unchanged. The observed thermal expansion of the a^* axis indicates that molecules in adjacent stacks get closer on cooling until repulsive forces prevent further approach.

A shift of the molecules parallel to the c axis direction will change the separation between molecules in neighboring stacks (Fig. 3). The interaction will be minimized when molecules in adjacent stacks alternate in height, which can be achieved by a relative

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molecular translation of $c/12$. This would increase the angle between $[1\bar{1}00]$ and [0001], which equals β^*, by

$$\text{arc tg}\left(\frac{c}{12}\Big/\frac{a\sqrt{3}}{3}\right)$$

or 6.22°. The corresponding variation in the angle between a^* and $(ho\bar{h}h)$ is $0.83 \times 6.22° = 5.2°$. The observations in Fig. 2 are

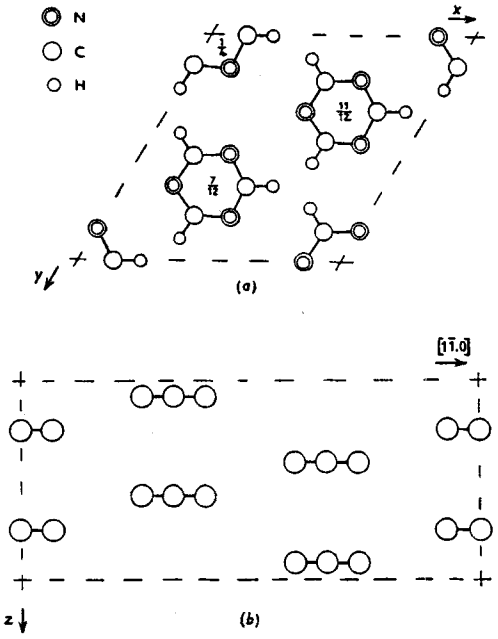

Figure 3. Triazine according to Wheatley[9] (a) projection on (0001). Beneath each molecule at a distance of $c/2$ is a second molecule related by a center of symmetry. Figures denote height above the origin in the z direction (b) stacking along $[1\bar{1}00]$.

therefore compatible with the mechanism derived from other structural considerations. It should be noted that a certain amount of rotation of the molecules out of the a^*b^* plane can not be ruled out on the basis of the present evidence.

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Conclusion

Kitaigorodskii[10] has stated that as a rule aromatic compounds with three-fold axes occupy general positions in the crystal. Triazine has been counted among the few exceptions to this rule, but the present observations show that even here the lowest energy is achieved when the three-fold axis is not retained. This suggests that other symmetric molecules located on symmetry axes such as for example cyanuric triazide,[10,11] will show phase changes on cooling. It would be of interest to investigate in detail the characteristics of these transformations.

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