

Swanson, 1974; Chowdhury *et al.*, 1977) it can reasonably be expected that the Cr–C and C–N bond lengths along [110] and $\bar{1}10$ (*i.e.* on the tetragonal basal plane) would be the same, allowing the corresponding bond lengths along [001] to be different. This entails putting constraints on the positional parameters of C(2), C(3) and N(2), N(3) such that $x[C(2)] = x[C(3)]$ and $x[N(2)] = x[N(3)]$. With such a constrained situation contributions from C and N atoms to reflexions of the type hkl : $h+k+l=2n+1$ are nil. As no other atom contributes to reflexions of the type $hk0$: $h+k=2n+1$, reflexions of this type should be systematically absent from the diffraction pattern. But our neutron powder pattern does contain diffraction peaks corresponding to these reflexions; for example, the 120 reflexion can be observed as a well-resolved and very intense peak. One is, therefore, led to rule out the possibility of the structure conforming to the above physical picture. Further confirmation of inconsistency with the above model is provided by the presence of intense non-body-centred peaks (*i.e.* reflexions for which $h+k+l=2n+1$) in the neutron data. Contributions to these reflexions can only come from deviations of the Cs atom z coordinate from $z=0.25$, the position it occupies in the cubic phase. The strong peaks corresponding to the reflexions 122, 124, 232 *etc.* observed in the neutron diffraction pattern cannot be accounted for by any small deviation of the Cs atom z coordinate.

We tried to refine our room-temperature neutron data without imposing any constraint on the positional parameters using the now well established profile refinement technique (Rietveld, 1967). The program used in this refinement was a modified version of the original Rietveld program (Hewat, 1973). The starting parameters for the least-squares refinement were either the same or very similar to those reported by Ryan & Swanson (1974) for the high-temperature cubic structure ($Fm\bar{3}m$). All our efforts to refine the structure in $P4_22_12$ failed: for no amount of distortion of the $Cr(CN)_6$ octahedron would the calculated profile reasonably agree with the observed profile. Thus, although the observed systematic absences do not

rule out the possibility of the space group $P4_22_12$, the analysis of the neutron diffraction profile completely rules out the space group for the room-temperature structure of the compound. It is now not difficult to see why Ryan & Swanson (1974) did not succeed in refining their single-crystal X-ray data in this space group.

As mentioned earlier, we have, however, succeeded in refining our neutron diffraction profile, but in a different space group ($P4/mnc$). The refinement reveals that the tetragonal distortion of the high-temperature cubic structure consists primarily of a rotation of the $Cr(CN)_6$ octahedron about the c axis and an elongation of the octahedron along the same axis. Detailed analysis of the structure will be published in a separate paper (Chowdhury *et al.*, 1977). The success of the neutron diffraction technique over the X-ray method in this particular case lies in the fact that scattering from C and N is much more sensitive for neutrons than for X-rays – the neutron scattering cross-sections of both C and N being large but different from each other.

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Triethylenediamine. III. The II \leftrightarrow I phase transition. By J. K. NIMMO and B. W. LUCAS, *Department of Physics, University of Queensland, St. Lucia, Brisbane, Queensland, Australia*

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The II \leftrightarrow I structural phase transition (at 351 K) of triethylenediamine is discussed with reference to h.c.p. \leftrightarrow f.c.c. transitions. A close relation is shown to exist between the molecular orientations in the two phases. Comparison is also made with a recent theoretical structure prediction [Reynolds, *Mol. Phys.* (1974), 28, 633–652].

Triethylenediamine (TEDA), $N(CH_2CH_2)_3N$, is a globular molecule with a structural phase transition at 351 K for atmospheric pressure (Trowbridge & Westrum, 1963). The structures of both phases have been determined by Nimmo & Lucas (1976*a, b*), and are illustrated in Fig. 1 together with the relation between their respective unit cells. Phase II may be regarded as having an approximately h.c.p. structure with $a=6.14$ (2), $c=9.46$ (2) Å at 298 K, space group $P6_3/m$, $Z=2$ ($c/a=1.54$ and the molecular shape

approximates to a spheroid), while phase I is f.c.c. with $a=8.860$ (5) Å at 354 K, effective space group $Fm\bar{3}m$, $Z=4$. The II \leftrightarrow I transition may therefore be considered in terms of h.c.p. \leftrightarrow f.c.c. transitions.

The structural changes occurring on transition can be thought to be produced as follows: by translating appropriate layers of molecules parallel to the $a_{hex} b_{hex}$ plane, the transformation from a h.c.p. to a f.c.c. arrangement is made in the usual way (the packing sequence perpendicular

to the c_{hex} axis is altered from $BCBC\dots$ to $ABCABC\dots$. As a result, each layer type (A , B or C) will contain molecules with either of the phase II orientations. To overcome this asymmetry, the molecule on each site is allowed to occupy either of these two orientations. A small rotation yields the two orientations around the $[111]_{\text{cub}}$ direction of the phase I structure. Further, the four diagonals of a face-centred cube must be threefold axes. Thus, on each site, two molecular orientations are allowed around each of the four $\langle 111 \rangle_{\text{cub}}$ directions, symmetrically equivalent to the two around $[111]_{\text{cub}}$. This produces the phase I structure. It is seen, therefore, that the structures of the two phases are simply related.

Recently, Reynolds (1974) presented a theoretical analysis of the plastic phase transformation in TEDA. At the time of publication, neither the solution to the phase II molecular conformation problem, nor a determination of the phase I structure was available (Nimmo & Lucas, 1976*a,b*). Thus Reynolds assumed a conformation for the molecule; in fact he chose the correct conformation. He approximated the crystal behaviour by using models for the orientational disordering, and predicted a structure for phase I from that of phase II. Although no precise structural description is given, his predicted structure appears to be in agreement with the experimentally determined one (Nimmo & Lucas, 1976*a,b*) both in terms of the equilibrium positions of the molecule around the f.c.c. lattice sites, and the occurrence of hindered molecular reorientations.

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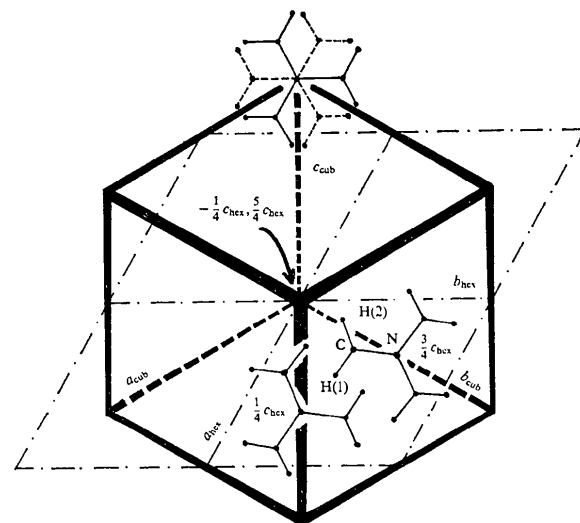


Fig. 1. The relation between the hexagonal (approximately h.c.p.) and f.c.c. unit cells appropriate to phases II and I of TEDA respectively. The cube is viewed along its $[111]_{\text{cub}}$ direction (centre of the diagram and out of the page), which is coincident with the c_{hex} axis; the cube origin is located at $-\frac{1}{4}c_{\text{hex}}$. The phase II structure is illustrated in the hexagonal unit cell at the lower right of the diagram (heights refer to the centroids of the two molecules). The two orientations of the molecule (centred on a f.c.c. lattice site) around the $[111]_{\text{cub}}$ direction for phase I are shown at the top of the diagram. There are two such orientations about each of the other $\langle 111 \rangle_{\text{cub}}$ directions, symmetrically related to those shown; the molecule on each lattice site undergoes hindered reorientations between these eight orientations.

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The crystal structure of 3 α ,5 β -dibromocholestane. By S. GORTER, *Gorlaeus Laboratories, X-ray and Electron Diffraction Section, University of Leiden, P.O. Box 75, Leiden, The Netherlands*

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Crystals of 3 α ,5 β -dibromocholestane are orthorhombic: $a=28.513(3)$, $b=7.003(1)$, $c=13.225(2)$ Å, $Z=4$, space group $P2_12_12_1$. The structure was determined by Patterson methods, using 1359 diffractometer-measured reflexions (Cu $K\alpha$ radiation). The refined structure ($R=4.74\%$) does not show unusual features in bond lengths, valency or torsion angles. However, the side chain displays an unusual conformation: it is folded about the bonds 20–22 and 23–24.

In a solution of chloroform saturated with hydrogen bromide the steroid 3 β -hydroxy-5 α ,6 β -dibromocholestane can be converted at room temperature into a mixture of mainly two compounds (Warmerdam & van der Gen, 1976): 3 α ,5 β -dibromo- and 3 β ,5 α -dibromocholestane. Due to loss of hydrogen bromide in the mass spectrometer experiments the composition of the reaction products

could not be settled beyond doubt and it was decided to carry out a diffraction analysis of the former compound.

Orthorhombic colourless needles were obtained by recrystallization from acetone: $a=28.513(3)$, $b=7.003(1)$, $c=13.225(2)$ Å at 20°C; space group $P2_12_12_1$; $D_{\text{exp}}=1.30$ g cm $^{-3}$, $Z=4$. 1359 symmetry-independent reflexion intensities larger than twice the standard deviation were meas-