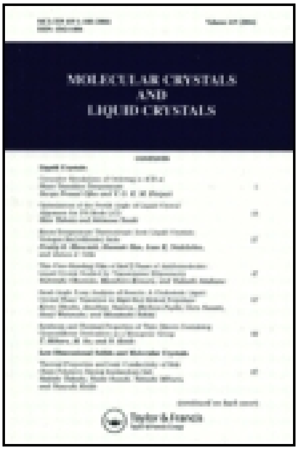

Molecular Crystals and Liquid Crystals

Phase Transitions During Crystal Growth?

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PHASE TRANSITIONS DURING CRYSTAL GROWTH?

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Three pairs of very closely related structures for three molecular solids have been determined at or above the temperature of crystal growth. In two cases the two phases are so similar that it seems surprising that they can co-exist. In the third case one of the structures seems to be a combination of a highly disordered structure that might be found in the smallest crystal nuclei and of the fully ordered structure that is seen at 130K. In all three systems it seems possible that a transition to the phase with the larger unit cell takes place sometime after crystal nucleation.

Keywords: crystal structures; phase transitions; phase relationships

INTRODUCTION

During the last several years we have come across three sets of structures that seem to suggest that phase relationships in the molecular solid state are more subtle than we had thought. In several of these systems two very closely-related phases seem to co-exist in what appear to be "single" crystals. There are hints that some of the crystals may nucleate in disordered structures that then transform during crystal growth to more ordered structures having larger unit cells. Such observations might not surprise scientists who study intermetallic compounds and complex inorganic materials, but the molecular solid state has usually been thought to be simpler because of the lower symmetry of the packing units and the shorter ranges of the intermolecular forces. There is, however, precedence in the literature [1] for "hybrid" molecular crystals.

Line drawings of the three compounds to be discussed are shown below. In all cases the crystals were studied at temperatures at or above the temperature of crystal growth. Transitions to phases having larger or

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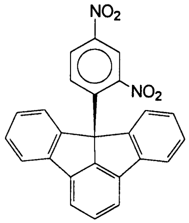
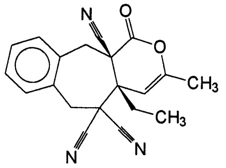
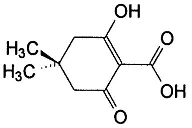


FLDNB



TRICYC



C9O4

lower-symmetry unit cells often accompany crystal cooling, but these three systems have unit cells containing several very closely related independent molecules at or above the temperature of crystal growth.

STRUCTURES

7b-(2,4-dinitrophenyl)fluoradene (FLDNB)

Crystals of FLDNB ($C_{25}H_{14}N_2O_4$) were grown from solution at 0°C and studied at room temperature [2]. There are two crystal forms, which are nearly identical and which have the same space group ($P2_1/c$). The phase found first has one molecule in the asymmetric unit ($Z' = 1$) and has large atomic displacements that indicate rotational disorder of the fluoradene ring system around its bond to the dinitrophenyl substituent. The phase found several years later has a doubled axis **a**, is 0.7% denser, and has noticeably smaller atomic displacement ellipsoids (see Fig. 1). The fluoradene ring systems of the two independent molecules in the $Z' = 2$ phase are oriented slightly differently with respect to the crystal axes [2].

Final refinements of both structures used data measured with a KappaCCD diffractometer. Data for the $Z' = 1$ structure were measured at 294 K; data for the $Z' = 2$ structure were measured at 295, 273 and 250 K. Data from the raw frames were transformed to give projections of slices hkn, and hnl, $n = 0–3$ of the reciprocal lattices of the two crystal forms; these projections show all the non-Bragg scattering as well as the diffraction maxima. The diffraction patterns of the two phases are clearly different; there is no doubt that **a** is twice as long in one as in the other. The h-odd reflections of the $Z' = 2$ phase are not exceptionally weak. There are only a few regions of the $Z' = 1$ pattern in which there are areas of intensity that correspond to half-integral h and these "spots" are more diffuse than are the Bragg peaks. Another clear difference between the two scattering patterns is the decline in average intensity with scattering angle. The

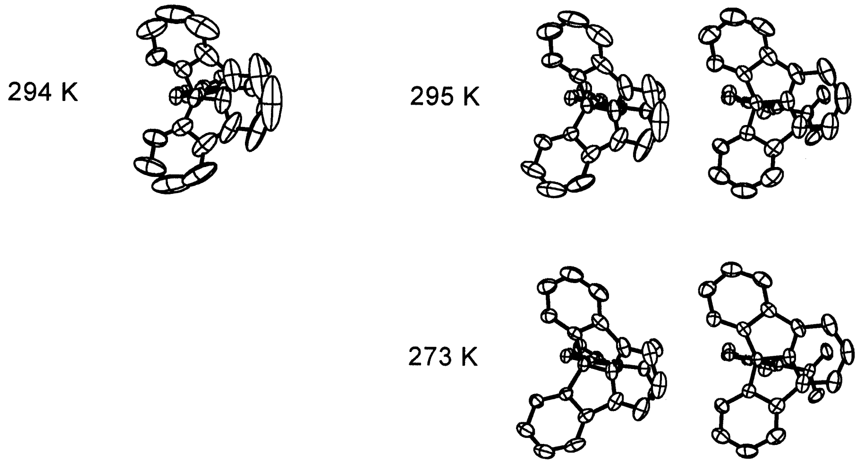


FIGURE 1 Ellipsoid plots (50% level) of the molecules of the $Z' = 1$ (left) and $Z' = 2$ (right) structures of FLDNB.

decline is substantially faster for the $Z' = 1$ form, in which the atomic displacements are larger, than for the $Z' = 2$ form.

It is tempting to suggest that a phase transition from the disordered to the ordered phase took place during the two years the crystals were left undisturbed in a laboratory drawer, but the reality may be more complicated, Re-examination of the cell constants measured years ago with a serial diffractometer shows that they are intermediate between the cell constants of the $Z' = 1$ and $Z' = 2$ forms measured with a CCD diffractometer. Furthermore, there are several indications that "single" crystals of the $Z' = 2$ form studied at 295 K are actually hybrids of the two crystal phases. Cooling from 295 to 273 K of the $Z' = 2$ crystals led to a further decrease in the unit-cell volume of 1.0%, an obvious sharpening of the diffraction pattern, and substantially smaller atomic ellipsoids for the C atoms of the fluoradene ring system (see Fig. 1). Further cooling by to 250 K (*i.e.*, by about the same amount) produced only small additional changes (*e.g.*, volume decrease of 0.2%).

(*1R**,*11S*)-1-Ethyl-14-methyl-13-oxatricyclo[10.4.0.$0^{4,9}$]-pentadeca-4,6,8,14-tetraen-12-one-2,2,11-tricarbonitrile (TRICYC)

Crystals of a TRICYC ($C_{20}H_{17}N_3O_2$) [3] were grown and studied at room temperature. Two nearly identical phases were found near 295 K, both in the space group $P2_1/c$. One of the phases has one independent molecule in the asymmetric unit ($Z' = 1$); the other has three ($Z' = 3$). The latter phase is 2.8% denser than the former and has a tripled axis **b**.

This pair of structures has many features in common with the pair described above. The structural differences between the two phases are again remarkably subtle (see Figure 2). The displacement parameters for the $Z' = 1$ phase are substantially larger than for the $Z' = 3$ phase. The diffraction patterns for the two phases are clearly different and the $k \neq 3n$ reflections of the $Z' = 3$ phase are not at all weak. The decline of the average intensity with scattering angle is substantially more rapid for crystals identified as having $Z' = 1$ than for those identified as having $Z' = 3$. Careful examination of the diffraction patterns, however, suggests that

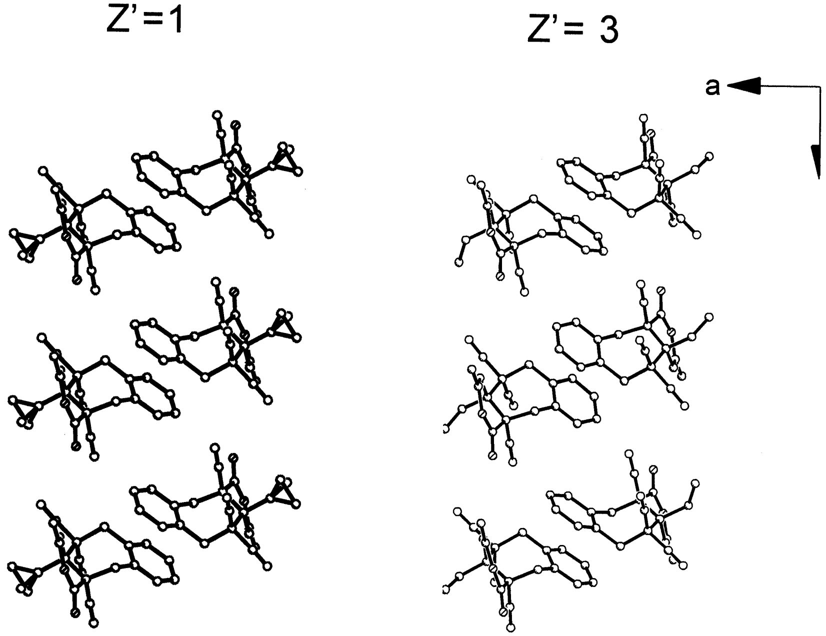


FIGURE 2 Fragments from the $P2_1/c$ structures of the $Z' = 1$ (left) and $Z' = 3$ (right) phases of TRICYC. In the $Z' = 1$ phase there are inversion centers between all pairs of adjacent molecules (5 total in the fragment shown). In the $Z' = 3$ phase two of those inversion centers have been lost. In the drawing on the left the three pairs of molecules are related by translation. In the drawing on the right the top and bottom pairs of molecules are related by inversion rather than by translation, and no symmetry operation relates either the top or bottom pair of molecules to the pair in the middle of the drawing.

most, if not all, “single” crystals of the $Z' = 1$ phase also contain at least small amounts of the $Z' = 3$ phase. It seems surprising that two such closely related phases could co-exist in a “single” crystal, but that is the conclusion that must be drawn from the diffraction patterns.

4,4′-Dimethyl-2-hydroxy-6-oxo-cyclohexene-1-carboxylic acid (C9O4)

Crystals of C9O4 ($C_9H_{12}O_4$) were grown and studied at 295 K; they were also examined at 130 K [4]. The structure at 295 K, which is modulated, is remarkably complicated. There are 5 half-molecules in the asymmetric unit (space group $Cmc2_1$). These molecules differ only in their rotations around **a** (see Fig. 3); no differences between the 5 molecules can be seen if the structure is projected down **c**. All reflections with $k \neq 5n$ are systematically weak; the reflections with $k = 5n+m$, $m = 1$ and 4 are

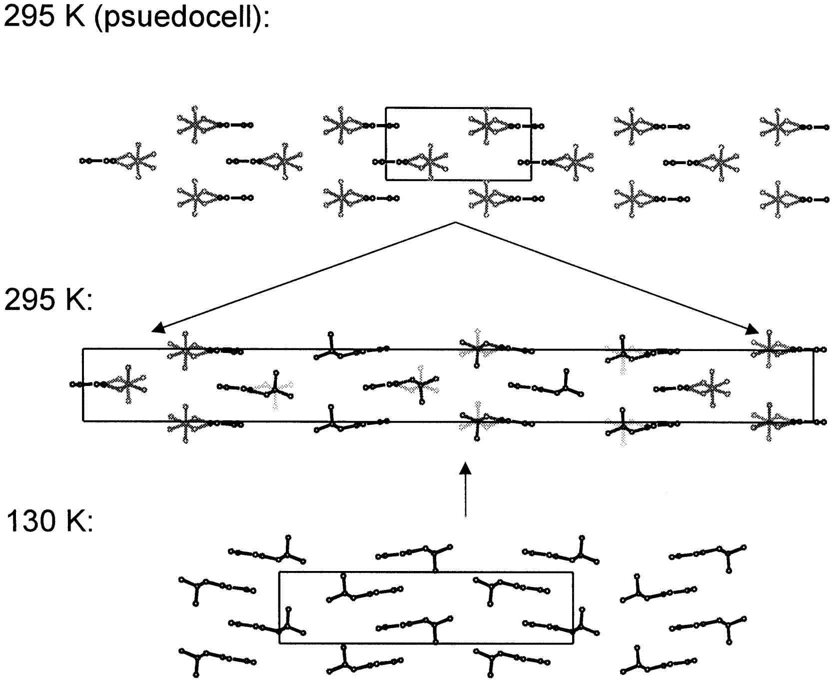


FIGURE 3 Diagrams showing relationship of the two known phases of C9O4 and of the pseudocell structure. Both orientations of the disordered molecules are shown; the gray scale codes the occupancy factors.

exceptionally weak. The structure is also disordered in a systematic, and a rather unusual, way.

The $k \neq 5n$ reflections are so weak that a satisfactory refinement can be performed [4] in a Cmcm pseudocell having $b' = b/5$. The $C(CH_3)_2$ fragment of the molecule is completely disordered above and below the plane of the four O atoms (see Fig. 3).

At 130 K the unit cell contains only two half-molecules, both of which are completely ordered.

The structure at 295 K can be understood as being a combination of the fully disordered pseudocell structure and of the ordered structure found at 130 K. Regions near $y = 0$ of the 295 K structure look very much like the pseudocell structure; regions near $y = 1/2$ of the 295 K structure look very much like the 130 K structure (see Fig. 3).

It is hard to imagine that the structural modulation seen in the 295 K structure could be established at the time of crystal nucleation. A comparison of the three structures shown in Figure 3 suggests that the crystals might nucleate in the simple, highly disordered, pseudocell structure and then transform during crystal growth to the more ordered structure with a much larger unit cell. When the crystals are cooled they undergo a transition to yet another related structure that has a smaller, simpler, and fully ordered unit cell.

CONCLUSION

Complex phase behavior has been observed for three purely molecular crystals. The key to recognizing these phenomena, and to being able to describe them, was the use of a diffractometer equipped with an area detector rather than with a point detector. The possibility of transforming the raw intensity data so that both the Bragg and the non-Bragg scattering could be viewed in projections that included reciprocal axes was also very important.

Complex phase bahavior is better known for intermetallic compounds and complex inorganic materials, than for molecular crystals. Crystals of these harder, more electron-rich substances were often studied by electron diffraction, by X-ray single-crystal photographic methods, or by powder diffraction. All these methods, which are much less used for molecular crystals, are more likely to reveal unexpected scattering than is structure determination with a serial diffractometer. In any event satellite reflections and non-Bragg scattering, which are the signs of complex phase behavior, are less likely to be seen for the softer, more electron-poor molecular crystals, which scatter X-rays relatively poorly.

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