

Table 5. Selected torsion angles (°) in benzyl-P₂A sulphonate and benzyl-P₂A bromide

| | Benzyl-P ₂ A sulphonate | Benzyl-P ₂ A bromide |
|----------------------|---------------------------------------|------------------------------------|
| N(2)=C(7)-C(5)-C(4) | 32.5 (4) | 3.9 (5) |
| C(5)-N(1)-C(6)-C(8) | 74.1 (4) | 77.8 (5) |
| C(13)-C(8)-C(6)-N(1) | 61.8 (4) | 44.5 (5) |

Table 6. Short O—H...O interaction in benzyl-P₂A sulphonate (A acceptor, D donor)

| D—H | A | Transfor- mation | D—H (Å) | A—H (Å) | D...A (Å) | D—H...A (°) |
|--------------|------|---------------------|------------|------------|--------------|----------------|
| O(1)...HO(1) | O(2) | x,y,z | 0.86 (10) | 1.81 (10) | 2.666 (3) | 173.6 (4) |

ring nor signs of a less pronounced double-bond character of the C(7)=N(2) bond. Such behaviour was suggested in the closely related 2-[(hydroxyimino)methyl]-1-methylpyridinium iodide (Carlström, 1966).

The benzyl, pyridinium and oxime parts of the two molecules are individually planar. Relative orientations of these parts can best be seen from the torsion angles given in Table 5. Some torsion angles differ up to 30° between the bromide and the sulphonate, but we believe that these differences only reflect changes in the crystal packing induced by the difference in the anions of the two molecules.

The methylsulphonate anion and the 1-benzyl-2-[(hydroxyimino)methyl]pyridinium cation are linked through a hydrogen bridge (Table 6). A similar interaction could exist in the bromide since the Br...O(1) distance (3.128 Å) is shorter than the

normal van der Waals contact (3.28 Å). This could not be proved, however, because we were unable to locate a refinable H atom on O(1). In the 1-methyl analogue a short I...O distance was also noted.

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Discussion of an Order–Disorder Behaviour Near T_c in the Chloranil Displacive Transition

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Abstract

The study of the temperature variation of molecular rotations in chloranil (tetrachloro-*p*-benzoquinone) between 10 and 89 K [for $T_c = 94$ K; Baudour, Delugeard, Cailleau, Sanquer & Zeyen (1981). *Acta Cryst.* **B37**, 1553–1557] is extended above 89 K. First

it is shown that between $T_c - 5$ K and T_c a classical determination of the structure based principally on superlattice reflexions cannot be realized because the atomic displacements δ decrease continuously as T_c is approached and become of the same order as the r.m.s. thermal amplitude u . So another method is proposed based on the measurements of some main reflexions

selected for their high sensitivity to molecular rotations and exhibiting an intensity maximum at T_c . The behaviour of these main reflexions can be interpreted from two different transition mechanisms: (1) a displacive process ($\delta = 0$ at T_c) with a critical increase of molecular libration amplitude between $T_c - 5$ K and T_c ; and (2) an order-disorder process in which molecules are locked at $\delta \simeq 1.7^\circ$ without an anomalous increase of thermal motion. Arguments are advanced showing that between $T_c - 5$ K and T_c an order-disorder behaviour probably relieves the classical displacive regime.

Introduction

Structural phase transitions are usually classified into two different types: order-disorder or displacive. This classification is essentially based upon dynamical concepts. In the displacive case the phase transition is classically associated with an instability of the crystal against a particular soft mode of vibration which condenses at T_c . In the high-temperature phase each atom (or molecule or ion) oscillates about a well defined high-symmetry site. On the other hand, in the order-disorder case, above T_c , atoms override a potential barrier from one well to another: so these atoms may reside in two (or more) equilibrium positions. In this case there is no soft mode but a central peak is observed above T_c in inelastic neutron scattering, which reflects the fluctuations of clusters in which a short-range order anticipates the low-temperature long-range order.

In this classical conception one can say, from a static point of view, that a displacive transition implicates a single-minimum potential for each particle and that an order-disorder transition implicates a multiminimum potential.

However, the fact that in displacive systems a central peak is also observed (Riste, Samuelsen, Otnes & Feder, 1971) has led to controversy about its origin which can be extrinsic (defects) or intrinsic (clusters of local order), with also a possibility of interaction between these two origins. Some authors (Krumhansl & Schrieffer, 1975; Aubry, 1976; Schneider & Stoll, 1976; Bruce & Schneider, 1977) have recently suggested that real materials do not obey the above classification, which they consider over-simplified. They have developed models in which a system exhibiting a phase transition of the soft-mode displacive type behaves, in the critical region, in a fashion qualitatively similar to an order-disorder system, the spatial site separation and the barrier height being, however, much smaller than in a pure order-disorder transition. Following this conception, the effective single-particle potential always develops a double-minimum character when T_c is approached.

To try to solve the controversy, techniques giving the atomic probability density function (p.d.f.), particularly EPR and X-ray or neutron elastic diffusion, have been used. The most significant examples where a disorder model has been put forward in the high-temperature phase of a displacive transition are that of BaTiO_3 (ferroelectric transition) in the analysis of a well structured diffuse scattering (Comès, Lambert & Guinier, 1970) and that of SrTiO_3 (antiferroelectric transition) from an EPR experiment (Bruce, Müller & Berlinger, 1979) which discriminates sufficiently against the cluster-induced slow fluctuations from the fast phonon fluctuations.

To test the predictions of theoretical models, the usual X-ray or neutron diffraction techniques have also been applied, particularly to the perovskite family of compounds. In the most favourable case, that of CsPbCl_3 (Hutton, Nelmes, Meyer & Eiriksson, 1979; Sakata, Harada, Cooper & Rouse, 1980), they have only revealed a distortion of the p.d.f. from the usual harmonic Gaussian distribution. However, they have never shown a double-peaked structure, which would have established without any ambiguity the existence of disorder. It is only for well characterized order-disorder transitions not accompanied by a soft mode, such as that of *p*-terphenyl (Baudour, Cailleau & Yelon, 1977), that a double-peaked distribution has been found. The failure of diffraction techniques is due to their insensitivity to the two different time scales associated with the two components (inter-well hopping and in-well oscillations present in the local motion), and to the large thermal motion inside each well.

We have found it interesting to examine these problems of disorder in the case of a molecular crystal, chloranil, which exhibits a continuous displacive phase transition (Richardson, 1963; Chihara, Nakamura & Tachiki, 1971; Terauchi, Sakai & Chihara, 1975; Hanson, 1975; Ellenson & Kjems, 1977). But, first, we will discuss briefly, for an antiferrodistortive phase transition (*i.e.* in which the displacements are equal and opposite in adjacent cells), the information on the atomic positions which is contained in the main reflexions and in the superlattice reflexions and the conditions under which a disorder can be revealed above or below T_c . Then we will show that, for chloranil, the measurement on either side of T_c of some main reflexions selected for their very high sensitivity to molecular displacements, allows a discussion, based on physical arguments, of the different possible transition mechanisms.

Conditions of resolving a disorder

1. In the high-temperature phase

As already mentioned by several authors (Bruce & Schneider, 1977; Hutton *et al.*, 1979) the possibility of

resolving a disorder in the distribution depends on the relative magnitudes of δ , the atomic displacement from the high-temperature average position, and u , the r.m.s. thermal amplitude about each site. The disordered model is demonstrated only if the p.d.f. shows separated maxima, which requires the condition $\delta > u$ ($\delta > 1.1u$, in fact) for two Gaussian distributions separated by 2δ (Fig. 1).

If $\delta < u$ the p.d.f. is single-peaked (Fig. 1). The maximum-probability position is not confounded with an equilibrium position. The p.d.f. exhibits a distortion from the usual Gaussian distribution of the harmonic model. However, it must be noted that, inversely, such a distortion does not imply necessarily a disorder. It may also result from the anharmonicity of atomic vibrations on each site, without considering jumps between several sites. Table 1 gives estimations of δ and u for some displacive or order-disorder phase transitions.

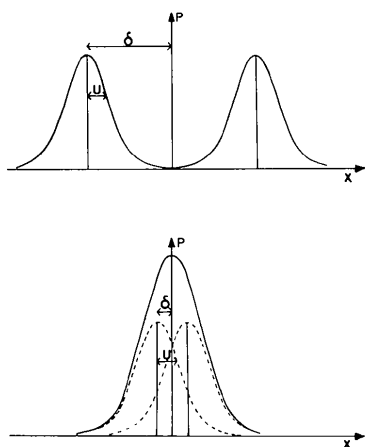


Fig. 1. The atomic probability density function shows separated maxima if $\delta > u$ for two Gaussian distributions separated by 2δ , u being the r.m.s. thermal amplitude on each site. If $\delta < u$ the p.d.f. is single-peaked and the maximum probability position at $x = 0$ is not an equilibrium position.

2. In the low-temperature phase

(a) *Main reflexions.* Main reflexions which exist above and below T_c depend only on the mean structure, the average being made on all the high-temperature (geometrically speaking) unit cells of the crystal. If the sites A and B between which each atom jumps above T_c in an order-disorder process are well defined, the fact that below T_c half the atoms are stabilized on sites A and the other half on sites B does not change the average structure. So main reflexions are insensitive to this process of fixation on a site. They do not differentiate between the long-range order more or less completely realized (Fig. 2a) in the low-temperature phase and the short-range order which generally exists in the high-temperature phase. Their constancy across the transition is schematized in Fig. 2(c) as a dashed line.

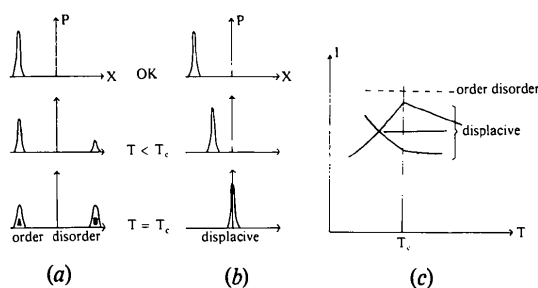


Fig. 2. (a) In an order-disorder transition the low-temperature phase p.d.f. results from a process of atomic jumps between two sites A and B . At T_c the occupancy probabilities P_A and P_B become equal. (b) In a displacive transition the p.d.f. is single-peaked and displaces its maximum towards $x = 0$, the average high-temperature phase site, as T_c is approached. (c) In an order-disorder process main reflexions have a single behaviour: they are constant across the transition (dashed line). In a displacive process main reflexions have different behaviours: they may increase, decrease or remain constant as T_c is approached. Some exhibit a well-defined intensity maximum at T_c .

Table 1. Estimations of δ (atomic displacement or molecular rotation from the high-temperature average position) and u (r.m.s. thermal amplitude) for some displacive or order-disorder phase transitions

| Compound | Nature of the transition | δ | u | Technique giving δ and u | Temperature at which δ and u are estimated | Thermal motion from diffraction technique |
|----------------------------------|-------------------------------------|---------------------------|---------------|---|---|--|
| SrTiO ₃ | Displacive and continuous | Oxygen octahedra 0.22° | 2.2° | EPR (a); neutron diffraction (b) | $\sim T_c$ (105 K) | Quasi-harmonic vibrations above T_c (c) |
| CsPbCl ₃ | Displacive and discontinuous | (a) 0.33 Å | (b) 0.40 Å | Birefringence (d); neutron diffraction (e) (f) | $\sim T_c$ (320 K) | Strongly anharmonic vibration; not resolvable disorder above T_c (e) (f) |
| <i>p</i> -Terphenyl (deuterated) | Order-disorder and quasi continuous | (d) 13° | (e) (f) 6° | Neutron diffraction (g) | $T_c + 20$ K (200 K) | Resolvable disorder above T_c (g) |
| | | (g) $\delta > u$ | (g) | | | |

References: (a) Bruce *et al.* (1979); (b) Hutton, Meyer & Nemes (1978); (c) Nemes, Meyer & Hutton (1978); (d) Mel'nikova, Aleksandrov, Anistratov & Beznosikov (1977); (e) Hutton *et al.* (1979); (f) Sakata *et al.* (1980); (g) Baudour *et al.* (1977).

On the other hand, in a displacive process, atomic positions vary as a function of temperature. Most of the main reflexions are more or less affected by these variations. However, some can be particularly sensitive to these atomic displacements. A few can even exhibit a well defined intensity maximum at T_c (Fig. 2c). These are particularly interesting, as will be illustrated with chloranil.

This difference of behaviour of main reflexions should allow, in principle, an order-disorder transition to be distinguished from a displacive one. In fact, the distinction is not so simple. Indeed if the constancy (neglecting the slow variation relative to thermal motion) of main reflexions sensitive to atomic displacements (this sensitivity being established in calculated structure factors) is an indication of an order-disorder process, inversely, the intensity variation which establishes atomic displacements is not incompatible with a process of jumps between two sites which could occur near T_c . So, the intensity maximum observed for some main reflexions at T_c implies effectively a minimum of atomic displacements δ , but this minimum is not necessarily zero.

(b) *Superlattice reflexions.* It is admitted that in antiferrodistortive structural phase transitions superlattice structure factors vary proportionally to the order parameter. So they are commonly used to study the variation with temperature of the latter. However, the order parameter has a different microscopic meaning according to the kind of transition. In the order-disorder case it is proportional to the difference $|P_A - P_B|$ between the occupancy probabilities of the two sites A ($+\delta$) and B ($-\delta$). In the displacive case it is proportional to the atomic displacement δ_e measured from the average position occupied in the high-temperature phase. So it is justified to write in a quite general way, for a superlattice structure factor:

$$F_{\text{sup}} \propto |P_A - P_B| \delta_e = \delta_m. \quad (1)$$

It is straightforward to verify that δ_m gives the centre of gravity of two masses P_A and P_B displaced respectively by $+\delta_e$ and $-\delta_e$ from the same origin.

Crystallographic experience shows that, in fact, for superlattice reflexions neither all observed structure factors, nor all calculated structure factors vary exactly in the same way as a function of temperature. So the above relation is only a rather good approximation. For example, the proportionality of F_{sup} to the molecular rotations δ has been verified with good accuracy in the case of chloranil over a wide temperature range from $T_c - 84$ K to $T_c - 5$ K (Baudour, Delugeard, Cailleau, Sanquer & Zeyen, 1981). In addition, the proportionality of F_{sup} to $P_A - P_B$ can be easily demonstrated for an order-disorder antiferrodistortive transition in which displacements are equal and opposite in adjacent cells.

From equation (1), in an order-disorder transition $F_{\text{sup}} = 0$ at T_c because $P_A = P_B$ whatever δ_e may be and in a classical displacive transition $F_{\text{sup}} = 0$ at T_c because $\delta_e = 0$ with $|P_A - P_B| = 1$.

Equation (1) implies that the order-disorder term $|P_A - P_B|$ and the displacive term δ_e are completely correlated. So the superlattice reflexions do not permit order-disorder and displacive processes to be distinguished. They give only an average position δ_m which is not a true equilibrium position if $|P_A - P_B| \neq 1$.

If $\delta > u$ (u being the r.m.s. thermal amplitude), main reflexions give true equilibrium positions, as we have seen. If a process of atomic jumps takes place below T_c (Fig. 2a), superlattice structure factors are multiplied by a factor $|P_A - P_B|$ inferior to unity, main reflexions not being affected. So in a refinement in which atomic positions are imposed from main reflexions, two different scale factors will be obtained: one for superlattice and one, larger, for main reflexions, the ratio between them being $|P_A - P_B|$.

If $\delta < u$ there is no possibility of revealing a disorder in the low-temperature phase since the disorder term $|P_A - P_B|$ is completely correlated with the positional term δ_e and δ_e cannot be obtained from main reflexions.

Fortunately, low-temperature structures are generally determined at a temperature sufficiently below T_c , so that the two conditions $\delta > u$ and $|P_A - P_B| \simeq 1$ are satisfied. In these conditions, main reflexions as well as superlattice reflexions give, in refinements, atomic positions which are at once maximum-probability positions and equilibrium positions. But when T_c is approached from below in displacive transitions, δ decreasing and u increasing, the condition $\delta < u$ is generally fulfilled near T_c . Then thermal motion masks a possible but unresolved disorder.

Conditions of the discussion of an order-disorder behaviour in chloranil

Chloranil undergoes a structural phase transition at a temperature T_c estimated at between 90 and 95 K following different authors: the lower value is given by Ellenson & Kjems (1977), the upper value by Chihara & Nakamura (1978). This transition is called displacive since it is accompanied by a soft mode (Hanson, 1975). As a result of the transition the monoclinic unit cell doubles along the c axis and the molecular displacements correspond principally to a staggered rotation about axes perpendicular to molecular planes (Terauchi *et al.*, 1975). In fact, it has been shown recently (Baudour *et al.*, 1981) that the molecular rotation has a not-negligible component about the in-plane axis passing through the two O atoms. In this study molecular displacements have been

determined within a large temperature range below T_c , between 10 and 89 K ($T_c = 94$ K). In this range the condition $\delta > u$ is always satisfied as it appears in Table 2. This implies, for reasons already mentioned, that atomic positions obtained in refinements are true equilibrium positions. The amplitudes of molecular rotations vary continuously with temperature, in agreement with a displacive process. Up to 5 K below T_c there is no indication of a disorder process: the same scale factors are obtained for main and superlattice reflexions in refinements including independent scale factors. However, an attempt (J. L. Baudour and Y. Delugeard, unpublished) to refine, with a disordered model, the X-ray diffraction data collected by van Weperen & Visser (1972) at 110 K, in the high-temperature phase, has given the same reliability factor ($R = 0.056$) as in the usual harmonic refinement. The refinement including disorder stabilizes the molecules at $\sim \pm 2^\circ$ on either side of their average position. The equivalence of the R factors expresses the aforementioned impossibility of revealing a disorder when $\delta < u$, a condition which seems fulfilled near any phase transition describable as displacive.

So we have thought, knowing the atomic positions at ($T_c - 5$ K), to use some main reflexions extremely sensitive to molecular displacements and exhibiting a maximum of intensity at T_c , to follow the variation of these displacements between $T_c - 5$ K and T_c . These main reflexions are, as we have seen, insensitive to any process of jump between two sites and depend only on $|\delta|$. So they can allow an estimate of δ at T_c to be made. Obviously they are also sensitive to any variation of the thermal motion u about each site and the problem of distinguishing between disorder and thermal motion seems to remain entire. However, from the knowledge of δ and u at $T_c - 5$ K, a discussion is possible on the respective variations of δ and u when T tends to T_c and so on the most plausible mechanism for the transition. This study is made easier in the case of chloranil for the following reasons:

– Unlike the perovskite compounds, chloranil does not exhibit a polydomain structure below T_c . So a main reflexion is not split and remains easily measurable below as well as above the transition temperature.

Table 2. A comparison between δ (displacement from the average high-temperature position) and u (r.m.s. thermal amplitude) for chlorine atoms in chloranil

The values from 10 to 89 K are from Baudour *et al.* (1981). The values at 110 K have been obtained in a refinement including disorder for the high-temperature phase (J. L. Baudour and Y. Delugeard, unpublished, see text).

| T (K) | 10 | 60 | 80 | 89 ($T_c - 5$ K) | 110 ($T_c + 16$ K) |
|--------------|------|-------|-------|-------------------|---------------------|
| δ (Å) | 0.29 | 0.23 | 0.175 | 0.134 | 0.115 |
| u | 0.02 | 0.074 | 0.092 | 0.095 | 0.131 |

– The transition is continuous, unlike that of most of the perovskites (CsPbCl_3 , for example).

– The molecular rigidity makes easier calculations of structure factors which depend only on the three Eulerian angles positioning the molecules in the unit cell. The two different possible transition mechanisms correspond to the cancellation (displacive process) or the no-cancellation (order-disorder process) at T_c of molecular rotation angles.

Experimental

The single crystal used, $5 \times 3.5 \times 1.5$ mm, was the same as that used in the study of molecular rotations as a function of temperature (Baudour *et al.*, 1981). The experiment was performed on the same D15 four-circle neutron diffractometer at the Institut Laue-Langevin, Grenoble, with the same Cu monochromator used at an incident $\lambda = 1.179$ Å. However, the cryogenic refrigeration system employing helium gas was different. Previously the cooling unit was a closed-cycle Displex Air Products cryorefrigerator. This time, it was a helium gas flow cryostat. This explains the difference observed in the determination of T_c : 94 K in the previous study, 92 K this time, although the crystal was the same. The important parameter being not T but $T_c - T$, the problem of adjusting the temperatures in the two studies was resolved by determining the differ-

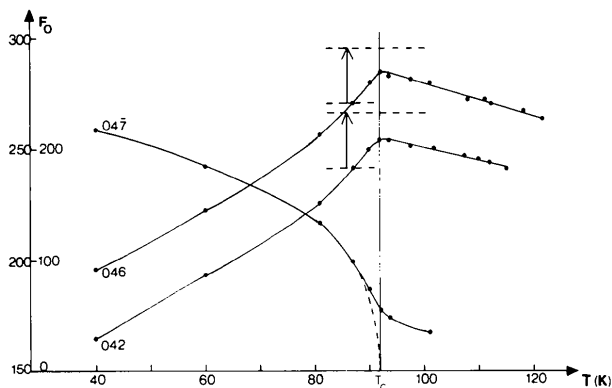


Fig. 3. Variation of observed structure factors in chloranil as a function of temperature. Main reflexions 042 and 046 exhibit a well defined maximum at T_c . The superlattice reflexion 047 apparently does not vanish at T_c but is replaced by a well structured diffuse scattering. The scale 150–300 refers to main reflexions. The scale 0–200 refers to superlattice reflexions. For convenience the observed structure factor of 042 has been multiplied by 1.5. The vertical arrows represent the variations of 042 and 046 between $T_c - 5$ K and T_c calculated in a displacive process ($\delta = 0$ at T_c) without critical increase of thermal motion in this temperature range. So this displacive model can be discarded. On the other hand, a good agreement (corresponding to the solid line through the points near the maximum at T_c) between the calculated and observed structure factor variations is obtained by considering a lock-in of molecular rotations at $\delta \simeq 1.7^\circ$ (order-disorder process).

ences in temperature from T_c , T_c being easily obtained as corresponding to the maximum of intensity for selected main reflexions. So 89 K, the estimated highest temperature at which the structure was refined in the previous study, was rather defined as $T_c - 5$ K, independently of the scale of temperatures, since T_c estimated on this scale was 94 K.

Two main reflexions (042 and 046) particularly sensitive to molecular rotations and a superlattice reflexion (047) were measured at the following temperatures: 40, 60, 80, 87, 90, 92 K (T_c) and at several temperatures above T_c up to about 120 K (Fig. 3). The temperature was controlled to within 0.1 K.

Results and discussion

The following relation, applied to a main reflexion very sensitive to molecular displacements and for the temperature range between $T_c - 5$ K and T_c , can be written:

$$\frac{F_o(T_c)}{F_o(T_c - 5 \text{ K})} = \frac{F_c(T_c)}{F_c(T_c - 5 \text{ K})}. \quad (2)$$

In this relation $F_o(T_c)$ and $F_o(T_c - 5 \text{ K})$ are observed structure factors which are easily measurable (Fig. 3). $F_c(T_c - 5 \text{ K})$ can be calculated since the structure is known at $T_c - 5 \text{ K}$. Now it is possible to test different transition mechanisms by calculating the corresponding $F_c(T_c)$. It is particularly important to control whether equation (2) is satisfied or not, by cancelling molecular rotations at T_c . However, before applying relation (2) we have taken some precautions. We have first verified that, for selected reflexions (046 and 042), the relative variation of calculated structure factors reproduced very accurately the relative variation of observed structure factors, over a large temperature range below $T_c - 5 \text{ K}$. Thus we have observed that the following more general relation is satisfied at 0.5%.

$$\frac{F_o(T_c - t_1)}{F_o(T_c - t_2)} = \frac{F_c(T_c - t_1)}{F_c(T_c - t_2)} \quad (3)$$

with t_1 and $t_2 = 34, 14,$ and 5 K , these values corresponding to temperatures at which the structure has been determined (*i.e.* 60, 80 and 89 K for $T_c = 94 \text{ K}$). So there are no secondary effects not taken into account in the intensity variation of these reflexions or, more exactly, if these effects exist (extinction, absorption, TDS) they have no influence on the ratio of structure factors.

The counting statistics are better than 0.4% of the observed structure factors.

1. Results in the high-temperature phase

We have seen that the selected reflexions, being extremely sensitive to any atomic displacements im-

plicated in the transition, are also very sensitive to any variation of the Debye–Waller factor corresponding to the same motions. Fig. 3 shows that when T_c is approached from higher temperatures, the observed structure factors increase quasi-linearly. So it appears that above T_c the Debye–Waller factor does not show any anomalous behaviour near the phase transition, contrary to what has been sometimes advanced, in relation to the softening of the mode accompanying a displacive transition (Sakata *et al.*, 1980). It is probable that the cancellation of this mode, if it does imply effectively an instability of the crystal, does not imply a large increase of thermal motion. One must remember that the Debye–Waller factor results from an integration on all modes in the Brillouin zone, and the softening concerns only a small volume of this zone which explains why it apparently has no influence on the r.m.s. amplitude.

2. Results in the low-temperature phase

Between $T_c - 5 \text{ K}$ and T_c the different possible mechanisms are as follow.

2.1. *The displacive model ($\delta = 0$ at T_c) without important thermal motion variation between $T_c - 5 \text{ K}$ and T_c .* The ratio of observed structure factors $F_o(T_c)/F_o(T_c - 5 \text{ K})$ is 1.054 ± 0.005 for reflexion 042 and 1.052 ± 0.005 for reflexion 046. The ratio of calculated structure factors $F_c(T_c)/F_c(T_c - 5 \text{ K})$ is 1.102 for 042 and 1.091 for 046. $F_c(T_c - 5 \text{ K})$ corresponds to the structure determined at $T_c - 5 \text{ K}$ and $F_c(T_c)$ is obtained by cancelling the molecular rotation angles with the same thermal parameters as those at $T_c - 5 \text{ K}$. The disagreement between the observed and calculated ratios is quite significant and means the discarding of a displacive model in which thermal motion would not increase sensibly within the small temperature range considered. The necessity for rejecting this model appears very explicitly in Fig. 3 where the maxima the observed structure factors should attain are indicated by horizontal lines.

2.2. *The displacive model ($\delta = 0$ at T_c) with an important increase of molecular libration amplitude between $T_c - 5 \text{ K}$ and T_c .* It is interesting to consider Table 3 which gives the average isotropic temperature factors for C and Cl atoms, obtained from refinements at different temperatures (Baudour *et al.*, 1981). It is

Table 3. *Equivalence of average isotropic temperature factors (\AA^2) for carbon and chlorine atoms in chloranil (from Baudour *et al.*, 1981)*

| T (K) | \bar{B}_C | \bar{B}_{Cl} |
|----------------------------|-------------|----------------|
| 60 | 0.47 | 0.43 |
| 80 | 0.65 | 0.66 |
| 89 ($T_c - 5 \text{ K}$) | 0.78 | 0.72 |

striking that the thermal motion of Cl atoms situated far from the molecular centre is very similar to that of C atoms much closer to this centre. This means that up to $T_c - 5$ K the thermal motion of the whole molecule is essentially translational. The amplitude of molecular librations is very small, in agreement with the high values of the moments of inertia.

Now for the displacive model ($\delta = 0$ at T_c) to be acceptable, it would be necessary that between $T_c - 5$ K and T_c , the r.m.s. librational amplitude increases steeply from a very small value to a value which can be estimated from equation (2) to be about 2° . This would correspond to an increase of approximately 1 for the B factor of Cl atoms. This critical variation in the librational amplitude would be related, in the classical conception, to the softening of the particular mode associated with the transition. However, as already mentioned, such an anomalous behaviour of the Debye-Waller factor has not been observed on the other side ($T > T_c$) of the curve $F_o(T)$.

Besides, the chloranil transition being continuous, the thermal-expansion effects are apparently negligible between $T_c - 5$ K and T_c . So it is hard to admit that molecules locked as regards librational motions, on a site, at $T_c - 5$ K suddenly change their equilibrium positions from $\delta \simeq 2.5^\circ$ to $\delta = 0^\circ$.

2.3. *The order-disorder model.* In this model the molecular rotations do not cancel out at T_c . A calculation of structure factors of reflexions 042 and 046 in which temperature factors at T_c are the same as those at $T_c - 5$ K shows that the ratio $F_c(T_c)/F_c(T_c - 5 \text{ K})$ is equal to the observed one $F_o(T_c)/F_o(T_c - 5 \text{ K})$ ($\simeq 1.053$) on the condition that at T_c the molecular rotations around the normal lock in at $\delta \simeq 1.7^\circ$ (Fig. 3). In this case the transition mechanism is as follows: between 10 and 87 K the amplitude of molecular rotations decreases continuously with temperature from 5.3 to 2.5° for the rotation around the normal. This first process is displacive. Between 87 K and $T_c = 92$ K molecular rotations continue to decrease but do not vanish ($\delta \simeq 1.7^\circ$ at T_c). So, near T_c an order-disorder process appears, the thermal energy becoming sufficient to destroy, progressively and completely at T_c , the antiferrodistortive long-range order. A molecule can jump from a site $+\delta$ to a site $-\delta$.

The arguments advanced against the displacive model (weak variation of the molecular potential form, no divergence of the Debye-Waller factor above T_c) are now arguments for the order-disorder model.

It must be noted that the estimation of the molecular rotation angle at T_c ($\delta = 1.7^\circ$), to satisfy equation (2), has a value compatible with that obtained ($\delta \simeq 2^\circ$) in a refinement of the high-temperature phase at 110 K, including disorder (J. L. Baudour and Y. Delugeard, unpublished). But this refinement gives the same final R as the usual harmonic refinement and is inconclusive for reasons already mentioned ($\delta < u$).

In the order-disorder model, superlattice structure factors vanish at T_c because the occupancy factors of sites $A(+\delta)$ and $B(-\delta)$ become equal. In fact, superlattice Bragg peaks characterizing the antiferrodistortive long-range order are replaced at T_c by a rather well structured diffuse scattering characterizing the short-range cluster-induced order. At T_c these diffuse scattering peaks remain easily measurable; this can give an estimation which is smaller than the real value of the limit angle δ . From Fig. 3, by taking the pseudo structure factor corresponding to TDS, proportional to δ , this proportionality being verified by a superlattice structure factor sufficiently below T_c , one finds a lower limit of δ equal to 1.4° .

In conclusion, the coherence of the results obtained from the disordered model in the refinement of the high-temperature phase, from the measurement of TDS at T_c and from some main reflexions very sensitive to molecular displacements, is a strong argument for an order-disorder behaviour in chloranil near T_c . The accurate measurement as a function of temperature of main reflexions very sensitive to molecular displacements (although, unfortunately, extremely rare) is of particular interest especially if they exhibit a maximum of intensity at T_c . Indeed, at temperatures at which superlattice reflexions vanish or are replaced by TDS, these main reflexions become, in contrast, more and more easily measurable. One must remember that a complete and quantitative discussion is possible only if the measurement of these reflexions is associated with the knowledge of the low-temperature structure near T_c , at a temperature at which molecular displacements can be again determined accurately ($\delta > u$). In these conditions the use of relation (2) allows us to discuss the different mechanisms possible for the transition. For chloranil there are serious arguments for thinking that between $T_c - 5$ K and T_c an order-disorder behaviour relieves the classical displacive regime.

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An Acetoxy Lactam Acid from 4-Amino-4-deoxymethyleneanhydrolycoctonam*

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Abstract

$C_{24}H_{35}NO_8$ is orthorhombic, $P2_12_12_1$, with $a = 12.480$ (1), $b = 21.025$ (2), $c = 9.512$ (1) Å, $U = 2495.9$ Å³, $Z = 4$, $D_m = 1.233$ (by flotation in toluene and carbon tetrachloride at 297 K), $D_c = 1.239$ Mg m⁻³, $\mu(\text{Cu } K\alpha) = 0.73$ mm⁻¹. The structure was solved by direct methods. The parameters were refined by block-diagonal least squares to a final $R = 0.048$ for 2158 observed reflexions. Intermolecular OH...O hydrogen bonds link molecules into spirals along c .

Introduction

In early structural work the diterpenoid alkaloid lycoctonine† had been converted by oxidation and pinacolic rearrangement reactions into anhydrolycoctonamic acid (Edwards & Marion, 1952). The carboxyl group was then replaced by an amino group giving an amino-keto lactam. Nitrous acid deamination of this compound gave an aldehydo lactam acid with loss of

one skeletal carbon [almost certainly C(6)] and its attached methoxy group. Because the structure of the aldehydo acid could not be rigorously assigned by spectroscopic means, and because the reactions leading to it were unusual, it was decided to carry out X-ray analysis of the acetate of the primary alcohol produced by reduction of the aldehyde group.

Experimental

Colourless prisms, m.p. 471 K, were obtained from a mixture of ether and hexane. The space group was established from precession films. The data were collected at room temperature with the Nonius CAD-4 procedures using a crystal fragment of dimensions 0.27 × 0.29 × 0.32 mm and Ni-filtered Cu radiation.

The pertinent details are: ω - 2θ scan; $1^\circ < \theta < 70^\circ$; ω scan angle = $(0.8 + 0.2 \tan \theta)^\circ$; SIGPRE (the prescan acceptance parameter) = 1.0, ITMAX (the maximum scan time) = 120 s. Two final scans were made in opposite directions with double the variable scan speed. A measurement of two standard reflexions every 100 min revealed a decrease in intensity of <5% during data collection. Three reflexions were used as orientation controls and were measured every 60 reflexions. Of 2671 measured reflexions, 2158 (81%)

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† The C(1) configuration determined in the present analysis is opposite to that found for (+)-de(oxy)methylene]lycoctonine hydroiodide monohydrate (Przybylska & Marion, 1956).