A Calculation of the Molecular Orientational Disorder in Crystalline Anthrone

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In anthrone (10*H*-anthracen-9-one) crystals there may be two distinct types of molecular orientational disorder. Firstly, whole stacks of molecules along [010] may, by association with vacancies, become orientationally disordered between positions related by a twofold screw axis in the crystal. Secondly, individual molecules may become disordered between orientations related by inversion through the molecular centre of mass. Calculations with previously developed Ising-like models (with an atom–atom intermolecular potential, the data for the low-temperature unit cell and the observation of a transition temperature at 357K) reveal that at 295K both types of disorder are present. This explains previous detailed X-ray diffuse-scattering data. Parts of these data give 16 ± 1, 36 ± 9 and 25 ± 2 Å for the observed range of the order in the **a**, **b** and **c** directions. The calculations predict 16 ± 0, 37 ± 12 and 24 ± 6 Å.

1. Introduction

Measurement of the X-ray diffraction from anthrone (10*H*-anthracen-9-one), I, has shown that there is a substantial degree of crystalline disorder at room temperature (Flack, 1970*a*, *b*).

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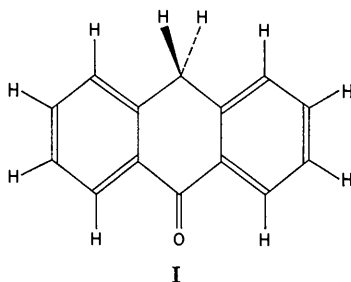
The Bragg scattering indicated space group $P2_1/a$ at room temperature and below. The intensities can be fitted well if we assume a disordering by inversion of the non-centrosymmetric anthrone molecule which gives an average centrosymmetric molecule (as this space group demands for a two-molecule unit cell).

Examination of the diffuse scattering revealed two features. Firstly, diffuse streaks in the $\{h1l\}$ and $\{h2l\}$ planes perpendicular to $(20\bar{1})$ were interpreted as being due to disorder in the stacking sequence of a layer structure in [010], or multiple twinning on $(20\bar{1})$ (Flack, 1970*b*). Secondly, layers of diffuse scattering $\{h\frac{1}{2}l\}$, $\{h\frac{3}{2}l\}$, $\{h\frac{5}{2}l\}$ were interpreted as being due to short-range order in the molecular orientations (Flack, 1970*a*). At room temperature the range of this order was found to be nine molecules in [010], three molecules in [001]; no ordering was found along [100].

To explain this disorder we need only use the experimental observation of a phase transition at 357K, to an unknown structure, which has been observed by density and electrical conductivity measurements (Pope, Geacintov & Michelson, 1966). We then use previously developed models (Reynolds, 1974*a*, *b*), which express the Helmholtz free energy of a crystal disordered in molecular orientations, in terms of a model intermolecular potential. This enables us not only to understand the microscopic origin of the disorder, but also to make a rough estimate of its magnitude.

At a given site in anthrone there may be either of two molecular orientations, related to each other through inversion. This molecular orientational disordering, 'orientational inversion disordering', should be describable in terms of a simple spin-half Ising model (Reynolds, 1974*a*), when the two spin orientations correspond to the two possible orientations of each molecule. This is because the C(9)O and the C(10)H$_2$ groups, which are exchanged in position by this inversion, are similar in size. This means that even with the inclusion of electrostatic interactions all mutual orientations of pairs of neighbouring molecules are thermally possible.

We can also expect that disorder in the *ac* plane between neighbouring stacks of molecules along [010] may be possible if there are sufficient vacancies, and geometrically and energetically similar alternative crystal structures. This allows the molecular orientations to be disordered by the interaction with vacancies as described by Reynolds (1974*b*). We can call this 'vacancy-stacking disordering'.

This type of disorder can be illustrated in two dimensions (Fig. 1). If a pure crystal of space group *A* has only a little less free energy than a crystal of space group *B*, there may be substantial disorder. The non-equilibrium vacancy concentration allows molecules of local symmetry *B* in the lattice, the vacancy preventing energetically excessive molecular overlap. This causes extra lattice enthalpy which must be counterbalanced by the extra entropy due to the disorder in the vacancy positions.

2. Ordered crystal structures

We postulate four different possible crystal space groups: α, $P2_1/a$ (unit-cell lengths $2a,b,c$); β, $P\bar{1}$ ($a\ b,c$); γ,

$P2_1/n$ $(2a,b,2c)$, a non-primitive cell actually of space group $P2_1/c$; δ, $P2_1/c$ $(a,b,2c)$. This expresses all the possible simple orientations in the ac plane of stacks of molecules along [010]. We have calculated the energy of three different types of stack in [010]. The first type is a b stack in which there is a 'ferroelec-
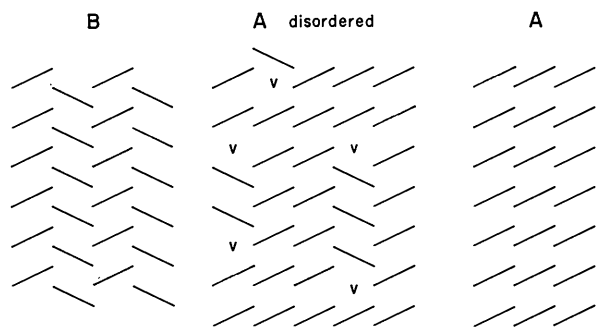

Fig. 1. Two-dimensional crystals, stacking disordering through vacancies (V).

Fig. 2. Three examples of the space groups used in the energy calculations.

tric' ordering (type a) between neighbouring molecules along [010]; that is, all the molecular electric dipoles along [010] are parallel. The second type is an 'antiferroelectric' ordering of the b stacks (type b); in which neighbouring molecular electric dipoles along [010] alternate in direction. The third type is stacks composed of 'average' molecules obtained by superimposing two inversion-related molecules at each site. We reduced the intermolecular interactions between the pair of molecules at the same site to zero, and between all other molecules to $\frac{1}{4}$ strength (type c) in order to simulate a disordered 'average' interaction. Three of the 12 simplest possible regular space groups are illustrated in Fig. 2. We calculated the crystal internal enegies by use of an atom–atom intermolecular potential (Reynolds, Kjems & White, 1974) and a carbonyl dipole moment of 3·5D (Angyal & le Fèvre, 1950). The potential parameters for oxygen were derived by extrapolation from those for carbon and nitrogen (Reynolds, 1973; Williams, 1967). In the calculations we used the room temperature α, $P2/a$, cell observed by X-ray diffraction ($2a=15\cdot60$, $b=3\cdot92$, $c=7\cdot89$ Å, $\beta=100\cdot8°$). The β, γ and δ cells were derived from the α cell by introducing or removing appropriate symmetry operations, keeping a,b,c and β constant.

For a given arrangement of types of stack along [010] in the ac plane the α,β,γ and δ lattice energies (~ -83kJ mole^{-1}) differ by less than 2kJ mole^{-1}. The energies and the energy differences are relatively insensitive to the oxygen potential parameters, so the extrapolation from carbon and nitrogen is not critical. The internal energy differences ($\Delta U_{\alpha\beta}, \Delta U_{\alpha\gamma}, \Delta U_{\alpha\delta}$) are almost independent of the arrangement of types of stacking along [010]. This means that the vacancy-stacking disorder may be calculated independently of the orientational inversion disorder. The orientational inversional disordering can then be calculated at a given vacancy-stacking disorder. This is fortunate since it removes the need for self-consistent calculations to express the coupling between the two types of disorder.

We obtain a value of 0·61 kJ mole^{-1} for $\Delta U_{\alpha\beta}$ from the lattice-energy calculation. After allowing for zero-point phonons we obtain, for the change in the Helmholtz free energy on going from α to β as a function of temperature T,

$$\Delta A_{\alpha\beta} = (0\cdot55 \pm 0\cdot2)\,(1 - T/357)\text{ kJ mole}^{-1}, \quad (1)$$

if we assume the transition at 357K is from α to β. This value for $\Delta U_{\alpha\beta}$ is only approximate since the true β structure is triclinic and not symmetry-related to the α unit cell. These assumptions, and that of constant volume, may give the estimated error. For $\Delta U_{\alpha\delta}$ we obtain a value of 0·075kJ mole^{-1}. This value was not estimated directly but calculated from the phonon frequency. An A_u symmetry translation of about 0·14 Å along [201] is sufficient to convert the estimated zero temperature α unit cell to the δ. The A_u, Brillouin zone centre, phonon with the correct eigenvector was calculated with program CRASH (Pawley, 1972) to have
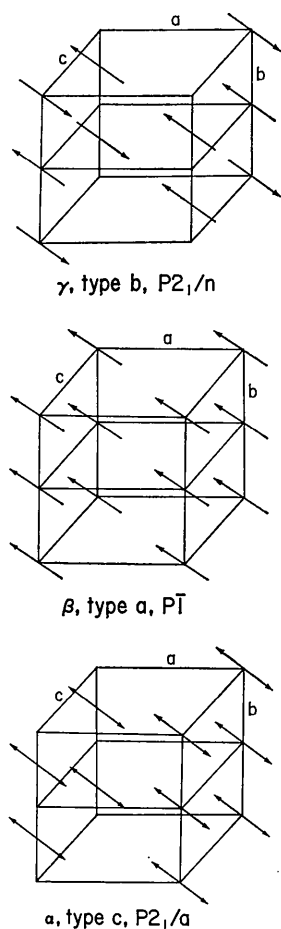
the low frequency of 7·5 cm^{-1}. This frequency and a 0·14 Å displacement gives the calculated $\Delta U_{\alpha\delta}$. After allowing for zero-point phonons we obtain

$$\Delta A_{\alpha\delta} = (0·067 \pm 0·03)(1 - T/357). \qquad (2)$$

We assume a crossing of free energies at 357K since X-ray measurements of thermal expansions (Flack, 1970a) indicate that $a=c$ for α phase around this temperature. This implies that $A_\alpha = A_\delta$. Since these energies are so close at 300K, the anharmonicity in the A_u frequency introduces a substantial uncertainty, estimated above, in $\Delta A_{\alpha\delta}$.

3. Disordered crystal structures

3.1 Vacancies

If a crystal of anthrone is grown sufficiently fast from the melt or from solution, the equilibrium vacancy concentration appropriate to the surface will be 'frozen in' as the bulk non-equilibrium value. This surface vacancy concentration is given approximately by Reynolds (1974b):

$$\varrho \simeq \tfrac{1}{96} \sum_{\substack{hkl=010,\\100,\\001}} \exp\left[-U_{hkl}/2RT\right], \qquad (3)$$

when U_{hkl} is the energy of interaction of a pair of molecules separated by hkl, and T is the growth temperature. For anthrone the significant energies are 45 kJ mole^{-1} for U_{010}, 9·2 kJ mole^{-1} for U_{100} and 9·2 kJ mole^{-1} for U_{001}. For a crystal grown from solution at 295K this gives an initial vacancy concentration of $3·3 \times 10^{-3}$.

We can write the Helmholtz free energy of the vacancies as

$$A_{vac} \simeq \frac{\varrho}{2\bar{n}_{hkl}}\left[\bar{n}_{hkl}(E_s - U_{hkl}) + U_{hkl}\right] + \frac{RT\varrho}{\bar{n}_{hkl}}\left[\ln\frac{\varrho}{2\bar{n}_{hkl}^2} - 1\right] \qquad (4)$$

where E_s is the sublimation energy and $\bar{n}_{hkl}$ the average length, in units of missing molecules, of a linear multi-vacancy along $[hkl]$. We have assumed that the average length is made up of $2\bar{n}_{hkl}$ different species, of lengths from $\bar{n}_{hkl}/2$ to $3\bar{n}_{hkl}/2$ in half-integral steps, each of concentration $\varrho/2\bar{n}^2$. If the vacancy mobility is sufficiently high to allow the vacancies to interact, but low enough to prevent the vacancies from diffusing out of the crystal (to enable ϱ to reach its low equilibrium value), then $\bar{n}_{hkl}$ will be the equilibrium value. This means that

$$\frac{dA}{d\bar{n}_{hkl}} = 0; \quad \frac{dA}{d\varrho} \neq 0. \qquad (5)$$

We assume that the molecular self-diffusion coefficient for anthrone at the melting point is 10^{-14}m^{2}s^{-1}, that molecular diffusion proceeds by vacancy diffusion, and that the activation energy is $\sim 2·3E_s$. All these assumptions appear to hold for benzene, naphthalene

and anthracene (Reynolds, 1974b, and references therein). These give

$$D = 10^{10} \exp\left[\frac{-200}{RT}\right] \quad \text{m}^2\,\text{s}^{-1}. \qquad (6)$$

At 300K, for an initial ϱ of $3·3 \times 10^{-3}$, the vacancy distribution, in $\bar{n}_{hkl}$, will be in equilibrium in about 2×10^5 s. Conversely it will take more than 2×10^{13} s for the vacancy concentration to decrease appreciably in a 10^{-4} m diameter crystal.

For [001] and [100] we obtain from (4) that $\bar{n}_{hkl} = 1$, its minimum value. However for [010] at 300K we obtain $\bar{n}_{hkl} = 2·2$. The free energy is only weakly dependent on $\bar{n}$, for $\bar{n} > 1$ in [010], so the assumption of a wide distribution in multivacancies (from 1 to 3·5 in this case) is valid.

3.2. Stacking vacancy disordering

We can express the Helmholtz free energy of this crystal, with stacking vacancy disorder, in a mean-field approximation (Reynolds, 1974b), as

$$A = A_\alpha + (1 - S_x)\frac{\Delta A_{\alpha\beta}}{2} + (1 - S_z)\frac{\Delta A_{\alpha\delta}}{2}$$

$$+ \frac{\varrho}{2}(E_s - U_{010} + U_{010}/\bar{n}) + \frac{RT\varrho}{2\bar{n}}\left[\ln\frac{\varrho}{2\bar{n}^2} - 1\right]$$

$$+ (F_x F_z)^{1/2}\frac{RT\varrho}{2\bar{n}}\left[\ln\frac{\varrho}{2\bar{n}^2} - 1\right], \qquad (7)$$

where we have assumed that the density of vacancies of half-integral length is $\varrho/2\bar{n}$. F_x is a function expressing the correlation in vacancy positions, approximated in terms of the disorder parameter S_x:

$$F_x = \left(\left[\frac{1+S_x}{2}\right]\ln\left[\frac{1+S_x}{2}\right]\right.$$

$$\left. + \left[\frac{1-S_x}{2}\right]\ln\left[\frac{1-S_x}{2}\right]\right) / \ln 2, \qquad (8)$$

where

$$S_x = \langle D\rangle_x - \langle E\rangle_x. \qquad (9)$$

$\langle E\rangle_x$ is the probability that a molecule at position 1,0,0 has the same orientation as one at 0,0,0; and $\langle D_x\rangle$ that the orientations are related by a screw axis $[\tfrac{1}{2}, b, 0]$.

Solution of the pair of equations $\delta A/\delta S_x = \delta A/\delta S_z = 0$ by successive approximation with the value of $0·75 \times 10^{-3}$ for $\varrho/2\bar{n}$ gives $S_z \simeq 0·67$ and $S_x \simeq 0·95$. We can express these figures as fractions of pure phases: $\langle\alpha\rangle = 0·81, \langle\beta\rangle = 0·025, \langle\delta\rangle = 0·165$. This type of stacking disorder produces the qualitative effects of streaks in the X-ray diffraction picture of $\{h1l\}$ and $\{h2l\}$ layers along [20$\bar{1}$], as observed.

This disorder gives an average correlation length in [010] of 667 molecules, in [100] of 40 molecules, and of 6 molecules in [001]. We must still consider the further effect of orientational inversion disordering before comparing the calculation with observations.

3.3. *Orientational inversion disordering*

We define an Ising coupling parameter $2J_{ED}^{0\frac{1}{2}1}$ as the change in the interaction energy of a pair of molecules separated in position by $(0,\frac{1}{2},1)$ in which one molecule is E and the second D (related to E in orientation by inversion through its centre of mass), when we invert one molecule through its centre of mass. These parameters can be calculated from the intermolecular potential. We obtain

$$\text{all } J_{ED}^{\frac{1}{2}(k+\frac{1}{2})l} = J_{EE}^{\frac{1}{2}kl} \simeq 0$$

$$J_{EE}^{0\bar{1}1} + J_{EE}^{001} + J_{EE}^{011} \simeq +0.84 \text{ kJ mole}^{-1}$$

$$J_{EE}^{0\bar{1}1} + J_{EE}^{00\bar{1}} + J_{EE}^{01\bar{1}} \simeq -0.84 \text{ kJ mole}^{-1}$$

$$J_{ED}^{0\frac{1}{2}1} + J_{ED}^{0\frac{1}{2}\bar{1}} \simeq 0.0$$

$$J_{EE}^{010} \simeq J_{EE}^{0\bar{1}0} \simeq 3.7 \text{ kJ mole}^{-1}.$$

90% of the values of these parameters arises from the electrostatic interaction between the carbonyl dipoles. There is a strong antiferroelectric interaction along [010], a weaker interaction along [001] in which pairs of parallel dipoles are arranged antiferroelectrically, and no interaction along [100]. For a lattice with no other type of disordering these parameters are high enough to give, with an Ising model for a spin-half rectangular system, an ordered ('antiferroelectric') crystal structure in the bc plane at room temperature (Potts, 1952; Naya, 1954). However, the finite correlation lengths due to stacking-vacancy disorder, especially of molecules along [001], lower the antiferroelectric transition temperature to below room temperature.

Correlation lengths in a six by infinite spin-half rectangular lattice cannot be calculated exactly. We define $S'_y = \langle E \rangle_y - \langle iE \rangle_y$, where $\langle iE \rangle_y$ is the probability that a molecule displaced $0,1,0$ from the reference molecule is related in orientation by inversion through the molecular centre of mass. S'_x and S'_z are defined similarly. The crudest approximation is to neglect the weak coupling along [001] and consider the system as six independent infinite one-dimensional Ising chains. Then, for independent chains $S'_x = S'_z = 0$ and $S'_y =$ tanh $(J'/RT) = 0.63$ (Stanley, 1971). We have written $J' = \frac{1}{2}J_{EE}^{010}$ to allow approximately for local shielding and relaxation effects. This gives a range of the disorder of 16 Å in **a**, 16 Å in **c**, and 21 Å in the **b** direction. An improved approximation is to consider the network as an infinite one-dimensional chain in the **b** direction, each unit of which is the exact thermodynamic average of the six interacting spins in [001]. This is a type of mean-field approximation. We find $S'_x = 0$, $S'_z = 0.34$ and $S'_y = 0.79$. The improved ranges of molecular correlation are 16 Å in **a**, 24 Å in **c**, and 37 Å in the **b** direction. Exact treatment of the coupling via 'links' in [010], and [001] etc. will further change the correlation. Since $S'_z < S'_y$ the correction to S'_y is much smaller than that for S'_z, and since S'^2_z and $S'^2_y < 1$ these changes may be small.

The errors in calculation of the energy parameters and the statistical approximations lead to reasonable maximum errors of ± 0 Å in **a**, ± 6 Å in **c** and ± 12 Å in **b**.

4. Conclusion

In melt- or solution-grown crystals of anthrone the vacancy concentration is sufficient to cause disorder in the orientations of stacks of molecules along the **b** direction. This accounts for the streaking in the $\{h1l\}$ and $\{h2l\}$ planes observed in the X-ray diffraction pattern. We can thus reject the possibility that disorder in the stacking sequence of ac layers is responsible for the streaks. Multiple twinning on $(20\bar{1})$ is too restrictive a description of the actual disorder.

This vacancy-stacking disorder has the further consequence of rendering substantial disorder in the molecular orientations of the carbonyl group (by inversion through the molecular centre of mass) thermally feasible. This orientational-inversion disordering further reduces the correlation range in translational symmetry. We calculate total disorder in the **a** direction (*i.e.* a range of $16\pm$ Å), a range of 37 ± 12 Å for the disorder in the **b** direction and a range 24 ± 6 Å for the disorder in the **c** direction. The errors quoted are estimates taking into account the large uncertainty in our calculation of such experimental quantities as $\Delta A_{\alpha\beta}$, ϱ, etc., and the gross theoretical approximations made. Short-range 'antiferroelectric' order gives layers at $\{h\frac{1}{2}l\}$, $\{h\frac{3}{2}l\}$ etc. in the X-ray diffuse scattering. The observed layers give ranges of 16 ± 1 Å in the **a** direction, 36 ± 9 Å in **b** and 25 ± 2 Å in **c**, which correspond surprisingly well with the calculation.

These two models of disorder in molecular crystals describe the situation in anthrone almost quantitively. They should be useful in predicting disorder in other systems where it may not have been suspected previously.

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