Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1975). A**31**, 386

Orientational disorder in hexachlorobenzene crystals.

BY P. A. REYNOLDS, *Research School of Chemistry, Australian National University, PO Box* 4, *Canberra, A.C.T., Australia*

(*Received* 12 *November* 1974; *accepted* 2 *January* 1975)

Calculations show that defects should occur in hexachlorobenzene crystals [typical atom (x,y,z)] consisting of a $\frac{1}{2}$ vacancy, followed by n molecules along [010] with typical atom $(x,\frac{1}{2}-y,z)$, terminated by a $\frac{3}{2}$ vacancy. The energy of the defect is predicted as $(12\pm3)+(3\pm2)n$ kJ mol^{-1}, with $\sim10^{-5}$ of the molecules in the crystal misoriented. X-ray diffuse scattering experiments may be interpreted to indicate that this is the defect that occurs, and that it has an energy of $(12\pm2)+(2{\cdot}6\pm0{\cdot}8)n$ kJ mol^{-1}.

Introduction

Levelut & Lambert (1974) have shown that there is substantial, structured, diffuse X-ray scattering from hexachlorobenzene crystals at room temperature. This was interpreted as arising because all the hexachlorobenzene molecules adopted either of two conformations, substantially distorted from the gas-phase planar geometry, while maintaining a local $P2_1/c$ symmetry. The thermal motion found by X-ray diffraction (Brown & Strydom, 1974) correlates well with that predicted from dynamical measurements and calculations (Bates, Thomas, Bandy & Lippincott, 1971; Scherer & Evans, 1963) leaving little room for reduction in Bragg intensity due to atomic positional disorder of *all* molecules. Theoretical studies of the crystal predict that the molecule is rigid enough to prevent the crystal field from distorting the molecule noticeably from D_{6h} to C_t symmetry (Strel'tsova & Struchkov, 1961).

An alternative explanation, retaining planarity of the molecules in the crystal, is that a small fraction of the molecules (k) are orientationally disordered, an atom $\mathbf{r}_t$ being transformed to $(\mathsf{R}\,.\,\mathbf{r}_t+\mathbf{T})$ in the disordered region. This has been postulated to occur in anthrone (Reynolds, 1975*a*), *p*-dichlorobenzene (Reynolds, 1975*b*), and anthracene (Craig, Ogilvie & Reynolds, 1975) where $\mathbf{T}=(0,\frac{1}{2},0)$ and $\mathsf{R}=\begin{pmatrix}-1&0&0\\0&1&0\\0&0&-1\end{pmatrix}$.

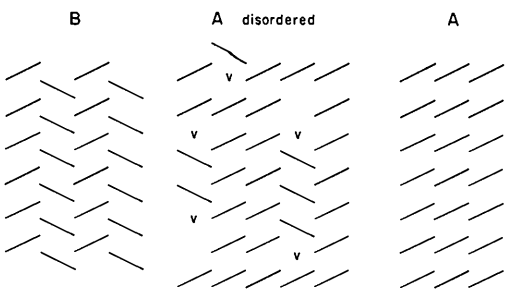

Fig. 1. Stacking-vacancy disorder in a two-dimensional crystal. *A* and *B* are two possible structures close in Gibbs free energy.

The defect is a stack of n misoriented molecules along [010], starting and terminating at a vacancy. This type of disorder for a two-dimensional crystal is illustrated in Fig. 1. The ideal ordered crystal structure *A* is the stable one, and *B* is a structure of only slightly higher Gibbs free energy. A section of the thermodynamically stable crystal, *A*, for a given concentration of monovacancies is represented by the centre panel. Some molecules, when the distance between a pair of monovacancies is small, will be in a different orientation. Their number will be given by a Boltzmann distribution, if this disorder is small enough for cooperative effects to be unimportant (Craig *et al.*, 1975). The presence of vacancies is necessary since otherwise there will be unacceptably high repulsion energies between neighbouring molecules of different orientation.

Calculation

Using three different 'atom–atom' intermolecular potentials (Reynolds, Kjems & White, 1974; Bates & Busing, 1974; Bonadeo & D'Allessio, 1973) we have searched for thermally populable orientational defects in hexachlorobenzene. Misorientation of a stack of n molecules along [010] is the only energetically feasible simple defect. If an ordered atom has coordinates $(x,y,z)=\mathbf{r}_t$, then there are only two energy minima, at $(x,y+\frac{1}{2},z)$ and $(x,\frac{1}{2}-y,z)$. The former, for all three potentials, has an energy greater than 15 kJ mol^{-1} of misoriented molecules, for $n=\infty$.

The latter has an internal energy (A) of 5·2, 3·6 and 1·0 kJ mol^{-1} for the three potentials in the order cited. We allowed the molecules in the stack, and their nearest neighbours, to relax to a minimum in the molecular orientational angles. This reduced the energies from about double the above energies, while the molecules in the defect moved, at most, 6°.

Calculation of the vacancy concentration (p), by the method of Reynolds (1975*b*), shows that the vacancies will be monovacancies, in the absence of orientational disorder; and will have a concentration in a melt-grown crystal of 1×10^{-3}, 2×10^{-3} and 1×10^{-3} for the three potentials. Where two monovacancies are separated by n molecules along [010], they will be in equilibrium with n misoriented $(x,\frac{1}{2}-y,z)$ molecules and one $\frac{1}{2}$ vacancy and one $\frac{3}{2}$ vacancy. One $\frac{1}{2}$ and one $\frac{3}{2}$ vacancy are more stable compared with

two monovacancies by approximately the energy of interaction of a pair of molecules with corresponding atoms (x,y,z) and $(x,\frac{1}{2}-y,z)$, which exist on either side of a $\frac{1}{2}$ vacancy. This energy, B, is calculated as 15·5, 9·5 and 11·5 kJ mol^{-1}. We can write the fraction

$$k \simeq \sum_{n=1}^{\infty} np^2 \Big/ \left(1+\exp\left[\frac{nA-B}{2RT}\right]\right). \qquad (1)$$

The factor 2 has been introduced to reduce the internal energy to the Helmholtz free energy, allowing for local phonon softening and lattice relaxation around the defect. We calculate $k=10^{-5}$, 2×10^{-5} and 5×10^{-5} for the three potentials.

X-ray diffuse scattering

Levelut & Lambert (1974) observed sheets of diffuse scattering in reciprocal space at integral **k** vectors with the $\mathbf{k}=0$ sheet absent. The width of these sheets gave a correlation length of five molecules at 300K in b, which varied little with temperature; and no correlation in a or c. The intensity of the diffuse scattering decreased to about $\frac{2}{3}$ of its 300K value at 100K.

We assume that the energy of the defect varies as $nA-B$ where n is the energy of a single link and B an end correction. These figures give, from equation (1), that $A=2{\cdot}6\pm0{\cdot}8$ kJ mol^{-1} and $B=12\pm2$ kJ mol^{-1}.

If we assume that the defect is a simple rotation and translation of the ordered molecules, then the apparent absence by symmetry of the $k=0$ layer implies that the defect has $\mathsf{R}=\begin{pmatrix}1&0&0\\0&\pm1&0\\0&0&1\end{pmatrix}$ and $\mathbf{T}=(0T_y0)$. We further assume that the diffuseness of the sheets in k does not markedly affect the intensity distribution in h and l. R and **T** can be determined completely by fitting the observed, qualitative, intensity variation in the diffuse sheets to the diffuse intensity which an $n=\infty$ defect would produce. This is given by, with b_t as the atomic form factors,

$$I_d(hkl)\propto k\,\frac{(1+\cos^2\pi l)}{2}\Big\{\sum_{t}^{\text{asymmetric unit}} b_t\,.\cos(hx_t+ky_t+lz_t) - b_t\cos[hx_t+k(T_y\pm y_t)+lz_t]\times\cos\pi k\Big\}^2. \qquad (2)$$

Using the positions and intensities of the Bragg spots we can estimate the surface in reciprocal space to which each position on the X-ray film corresponds. We can then integrate $I_d(hkl)$ over the appropriate path in h and l for a given k. Only $(x,[y+0{\cdot}3\pm0{\cdot}1],z)$ and $(x,[-y+0{\cdot}5\pm0{\cdot}1],z)$ give a qualitatively correct intensity distribution in the layers $\{h1l\}$, $\{h2l\}$ and $\{h3l\}$.

Discussion

The X-ray diffuse scattering experiment shows that the defect probably consists of misoriented molecules {either $(x,[0{\cdot}3\pm0{\cdot}1+y],z)$ or $(x,[0{\cdot}5\pm0{\cdot}1-y],z)$} with a misorientation energy of $2{\cdot}6\pm0{\cdot}8$ kJ mol^{-1} of misoriented molecules. This is terminated by a structure of energy 12 ± 2 kJ mol^{-1}. The nature of the termination can only be experimentally determined from a far more accurate intensity fitting. The theory predicts that $(x,\frac{1}{2}-y,z)$ is a favourable misorientation of molecules with energy 3 ± 2 kJ mol^{-1}. The end energy is 12 ± 3 kJ mol^{-1}, and consists of a $\frac{1}{2}$ vacancy at one end and a $\frac{3}{2}$ vacancy at the other. The orientation $(x,[y+0{\cdot}3\pm0{\cdot}1],z)$ for the misoriented molecules may be rejected since it has a very high energy (> 100 kJ mol^{-1}) due to much overlapping of chlorine atoms.

This agreement is sufficiently detailed to provide the first good experimental evidence of the existence of this type of defect, and suggests the validity of using 'atom–atom' potentials to predict its occurrence in other crystals.

References

BATES, J. B. & BUSING, W. R. (1974). *J. Chem. Phys.* **60**, 2414–2419.

BATES, J. B., THOMAS, D. M., BANDY, A. & LIPPINCOTT, E. R. (1971). *Spectrochim. Acta,* **27**A, 637–648.

BONADEO, H. & D'ALLESSIO, E. (1973). *Chem. Phys. Lett.* **19**, 117–119.

BROWN, G. M. & STRYDOM, O. A. W. (1974). *Acta Cryst.* B**30**, 801–804.

CRAIG, D. P., OGILVIE, J. F. & REYNOLDS, P. A. (1975). To be published.

LEVELUT, A. M. & LAMBERT, M. (1974). *Mol. Cryst.* **23**, 111–126.

REYNOLDS, P. A. (1975*a*). *Acta Cryst.* A**31**, 80–83.

REYNOLDS, P. A. (1975*b*). *Mol. Phys.* In the press.

REYNOLDS, P. A., KJEMS, J. K. & WHITE, J. W. (1974). *J. Chem. Phys.* **60**, 824–832.

SCHERER, J. R. & EVANS, J. C. (1963). *Spectrochim. Acta,* **19**, 1739–1775.

STREL'TSOVA, I. N. & STRUCHKOV, YU. T. (1961). *Zh. Strukt. Khim.* **2**, 312–326.