Calculated Molecular Orientational Disorder in Anthracene Crystals

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Received 15*th December*, 1975

Calculations based on an atom–atom intermolecular potential suggest that there are at least three crystal structures of anthracene close in energy to the observed $P2_1/a$ phase. Bulk concentrations of misoriented molecules up to 10^{-2}-10^{-3} mole per mole at room temperature are found by crude calculations and are associated with vacancies and dislocations. The misoriented molecules form strings of 10-100 units along the [010] direction. In zones of mixed packing photodimerisation, perhaps of vibrationally excited molecules, appears to be sterically possible.

According to the principle of topochemical preformation developed by Cohen and Schmidt,[1] photochemical reactions in molecular crystals proceed with a minimum of atomic and molecular movement, and the steric relation of product and reactant follows from the structure of the host crystal. Anthracene ($P2_1/a$) is a member of a class in which the crystal structures seem not at all adapted to formation of dimers, in that nearest neighbour π–π interaction does not seem possible,[2] yet the reaction does proceed. Beginning with the discussion of 9-cyanoanthracene [3] the hypothesis has developed that lattice imperfections, such as dislocations or other forms of disorder, are necessary to provide reaction sites in such a crystal. Typically the reactions have an induction period during which the rate is very small, and there is preferential reaction on surfaces and in small regions in the interior of the crystal, rather than homogeneous or random distribution of product. Recently there has been much important work in this field.[1, 2, 4-6]

Photodimerisation may occur when a delocalised excitation is trapped so that it affects a site at which the local packing, either of the perfectly ordered or disordered crystal, brings the molecules close enough and in the proper orientations. Excitation of one or more lattice vibrations may also be needed.

We examine some types of molecular orientational stacking defects which are thermodynamically feasible, and their relation to vacancies and dislocations. After finding the internal energy of some plausible crystal structures of anthracene, we estimate the types and concentrations of vacancy in freshly grown crystals, and then discuss the orientational disorder associated with vacancies and dislocations and its relationship to photodimerisation.

ANTHRACENE CRYSTAL STRUCTURES AND MISORIENTATION ENERGY

The observed space group of crystalline anthracene at 1 atm pressure is $P2_1/a$. The structure may be built up, conceptually, from chains of molecules formed in either

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b or ***a*** directions, which are directions of strong intermolecular coupling, condensing first to (*ab*) layers and then to crystals. According to Zorkii's method,[7] 16 different structures can be generated from the ***b*** chain by having, along the ***a*** and ***c*** directions, the next stack oriented by either the identity operation or a two fold rotation, then translated by either 0 or ***b***/2. To calculate the lattice energies, we have used Williams' empirical " atom–atom " intermolecular potential functions [8] (set IV), and summed over 32 neighbouring molecules. The unit cell structure was found by allowing rigid molecules to relax to an energy minimum by variation of the Eulerian angles : the intramolecular atomic coordinates of the central molecule were taken from X-ray diffraction data on crystalline anthracene at 290 K. The unit cells used were generated by symmetry from that observed for $P2_1/a$ anthracene at 290 K. Only four structures yielded large lattice binding energies : the known $P2_1/a$ (monoclinic) structure, $P2_1/c$ and $P2_1/n$ (or $P2_1/a'$) structures (also monoclinic) and a $P\bar{1}$ structure (triclinic). The structures are illustrated schematically in fig. 1, and their calculated energies U_θ listed in table 1. The structures may be generated by simple translations in ***a*** and ***c***, and/or rotation-translation by two fold screw axes [$\frac{1}{4}$, *b*, 0] or [0, *b*, $\frac{1}{2}$] ($P2_1/a$ cell). The four crystal structures were then allowed to relax by changes in the molecular Eulerian angles and in the unit cell parameters. The energies $U_{\theta,a}$ for these minima are given in table 1, with the associated unit cell variables. The energy of the $P2_1/n$ structure reaches only a local minimum because, by correlated alteration of β and c in a change in which the direction [001] in $P2_1/n$ (fig. 1) becomes [102] of $P2_1/a$, one may be converted to the other against the small energy barrier of $\leqslant 0.5$ kJ mol^{-1}. The Eulerian angles of the molecules vary little from structure to structure, five degrees on average, and eleven degrees at most from the known angles of $P2_1/a$ at 290 K. Experimentally the temperature effect on Eulerian angles is very small.[9] The calculated energies are only slightly changed by the use of the other sets of atom–atom potential parameters tested.[10, 11] These results indicate that the $P2_1/a$ structure would be the most stable at 0 K, although our calculations really apply to phononless structures.

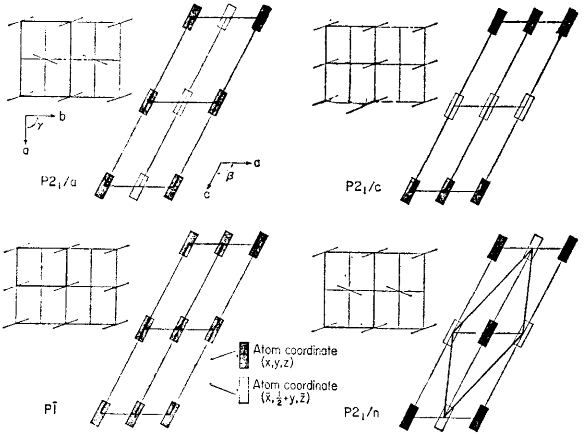

FIG. 1.—Diagram of four energetically feasible unit cells of anthracene showing relative orientations of the molecules in one *ac* plane cross-section.

From these lattice energies we next calculate the energy required to produce a particular type of disorder in the $P2_1/a$ lattice, namely, by turning a complete stack of molecules by π about the ***b*** axis and translating by ***b***/2. The energy to effect this misorientation can be assembled by combining the energies of the various fully ordered lattices in table 1. If W is the required energy, we find that

$$W \simeq 3U(P2_1/a) - U(P2_1/c) - U(P\bar{1}) - U(P2_1/n). \tag{1}$$

Eqn (1) is based on the assumption that the energy difference between phases arises solely in three separate constant interactions between nearest neighbour stacks along [100], [001] and [102]. This leads to $W = 20.8$ kJ mol^{-1} with use of the first row of table 1. We have no way of knowing what the effect of optimisation of dimensions would be in this case. We are not justified in building the misorientation energy from values for individually relaxed structures (second row of table 1), since the individual interactions between stacks are no longer constant from phase to phase. On the other hand the value 20.8 kJ mol^{-1} is too large, since relaxation must reduce the actual energy requirement per mole of misoriented molecules (J) to disorder the structure. We might reasonably guess a reduction of at least 3 kJ mol^{-1}, the amount of the stabilisation of the $P2_1/a$ structure itself. The resulting value $J \approx 18$ kJ mol^{-1} is still overestimated by the implied constraint of translational symmetry, which is no longer present, especially in situations of short misoriented stacks. The magnitude of J cannot be given accurately by the atom–atom potential method because it is the difference between large numbers (with different mixes) of distinct types of intermolecular interactions (*e.g.* amount of π–π interaction). We therefore estimate $J = 18 \pm 10$ kJ mol^{-1} for the π-rotation of complete $\boldsymbol{b}$ stacks. At this value, measurable amounts of material in other than $P2_1/a$ structure might be expected at room temperature on thermodynamic arguments. However, the kinetics of crystal growth may determine the particular form the disorder takes.

TABLE 1.—ENERGIES, UNIT CELL DIMENSIONS, ANGLES AND VOLUME OF PHASES OF CRYSTALLINE ANTHRACENE

	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/a$	$P2_1/a$*
U_θ/kJ mol^{-1}	89.08	94.05	93.63	99.20	—
$U_{\theta,a}$/kJ mol^{-1}	93.00	95.55	94.51	102.2	105
a/nm	0.435	0.430	0.846	0.809	0.839
b/nm	0.567	0.586	0.585	0.596	0.599
c/nm	1.137	2.203	2.263	1.108	1.111
α/deg	88.6	90	90	90	90
β/deg	122.9	124.4	122.7	123.0	126.0
γ/deg	91.9	90	90	90	90
V/nm^3	$\frac{1}{2} \times 0.472$	0.458	2×0.471	0.448	0.452

* Values extrapolated from experimental data to be applicable to the phononless structure at 0 K. The previous four columns contain values calculated from the atom–atom potential method.

There is evidence of a metastable phase of anthracene formed photochemically from crystalline $\Delta^{9,9'(10H,10'H)}$-bianthracene at 77 K which may be related to high pressure stable phases of anthracene.[12, 13] We expect this phase to have the $P2_1/c$ structure, because we can derive this structure on splitting bianthracene in its known crystal structure [14] with no further molecular rearrangements.

VACANCIES

CONCENTRATIONS

The equilibrium concentration of vacancies calculated from exp $(-E_v/RT)$, where E_v is the free energy to create a vacancy, is realistic only if crystal growth is slow and the vacancy mobility sufficient to permit the much larger initial kinetically controlled vacancy concentration, ρ, appropriate to a growing surface, to reduce by diffusion out of the crystal.

In a molecular crystal the vacancy energy may be expected to approach closely the lattice sublimation energy, E_s, as in crystals of Ne (~90 %) or less closely as in Kr (~70 %) and other cases where local relaxation is greater.[15] Noting that the effect in crystal Kr is already a 30 % reduction in the heat of sublimation, we take for the much larger anthracene molecule a maximum of 50 % reduction in the room temperature lattice sublimation energy of 102 kJ mol^{-1}.[16] The equilibrium vacancy concentrations for E_v = 102 and 51 kJ mol^{-1} at 300 K are 10^{-15} and $10^{-7.5}$ respectively. Vacancies in real crystals are initially governed by the kinetics of crystal growth. We estimate that, in a crystal growing from pure material at the melting temperature at a rate exceeding $\sim 10^{-7}$ m s^{-1}, or from room temperature solution at a rate exceeding $\sim 10^{-9}$ m s^{-1}, most of the vacancies at the surface will be incorporated into the crystal as the non-equilibrium concentration of vacancies in the bulk. We make a calculation of the vacancy concentration ρ, as a crude approximation, following the lines of an argument given by Reynolds.[17]

The calculation is of the rate at which vacancies are formed at a surface compared with the rate for normal molecule deposition. The relative rate, equated to the vacancy mole fraction for vacancies formed at a growing (001) face is

$$\rho(001) = D \exp\{-A_{001}/RT\} \tag{2}$$

the pre-exponential term D being a factor measuring the probability that an approaching molecule reaches a lattice site at which it may be built into the lattice " above " a vacant site, *i.e.* displaced from it by one lattice spacing in the c direction. Attachment of a molecule is taken to be possible only when the four neighbour sites in the same plane are already occupied, leading to a value of the statistical factor D of 1/30. A_{001} is the amount by which the Helmholtz energy is changed by the introduction of a vacancy adjacent to a surface molecule along c, and T is the temperature at which the crystal is formed. The presence of a vacancy next to an occupied site allows some relaxation, the effect of which on the internal energy and entropy may be approximated crudely as before by setting $A_{001} \approx \frac{1}{2}U_{001}$, where U_{001} is the interaction energy of two molecules separated by one lattice spacing along c. Contributions to the vacancies are made by growth at each of the faces such as (100), (010) and (001) in proportions that are not known. The values found from lattice energy calculations of $U_{001} \sim 4.8$, $U_{010} \sim 17.9$, $U_{100} \sim 19.7$ kJ mol^{-1} give a value for the mean of $\rho(100)$, $\rho(010)$ and $\rho(001)$ of 4.8×10^{-3} for a crystal grown at 300 K and about 8×10^{-3} at 480 K. The absolute rates of growth at the faces are certainly not equal, as the taking of a mean implies, but these vacancy concentrations fall nearly within the range of $1\text{-}7 \times 10^{-3}$ calculated from specific heat data near melting point by Baughman and Turnbull.[18] There are other sources of vacancies, such as thermal stress on cooling, which would increase the disparity from equilibrium values still further.

The initial concentrations decrease because of migration of vacancies to pre-existing defects such as dislocations or surfaces. The rate can be estimated from the vacancy mobility derived from the experimental molecular self-diffusion constant,[19] which suggests that one-tenth of the vacancies will have diffused 10^{-5} m in ~1 h at the melting point or in 10^{13} h at 300 K. Thus unless the crystal is annealed for hours near the melting point, the vacancy concentration will not decrease significantly towards the equilibrium value, even though vacancies are mobile enough to move a few nm in a period of a few hours.

NATURE OF VACANCIES

Vacancy mobility, though small in terms of the time required for diffusion to surfaces and dislocations, is sufficient even at room temperature to produce an equilibrium in the cluster size, for which vacancy migrations of only a few tens of unit cell spacings are required. We write the Helmholtz energy of a concentration, ρ, of n-fold multivacancies randomly distributed along a line, allowing a 50 % relaxation in the first enthalpy term due to local relaxation, as [17]

$$A_n^{abc} = (\rho/2)[n(E_s - U_{abc}) + U_{abc}] + RT\rho/n[\ln(\rho/n) - 1] \quad (3)$$

where U_{abc} is the interaction energy between molecules along the $[abc]$ direction. Substituting for ρ and U as found before we find that isolated monovacancies are the most stable vacancy type: condensation to produce small linear multivacancies is not favoured.

MOLECULAR ORIENTATIONAL DISORDER

THE ASSOCIATION OF DISORDER WITH VACANCIES

The most probable local disorder structures are those of table 1. As vacancies occur in the forming [010] chains some will be frozen in as single vacant sites in otherwise perfect stacking. Others, half-integral vacancies, will be initial points for stacking disorder, with the next part of the chain rotated by π, until terminated by another half vacancy.

This initial, non-equilibrium, kinetically controlled orientational disorder (and vacancy nature and concentration) is likely to relax to an equilibrium value at a rate determined by the diffusion coefficient. This is so because motion of half vacancies causes molecular reorientation. We assume that half vacancy and monovacancy mobilities are the same, which could be inaccurate, and that the strings of misoriented molecules are never larger than 10^2 nm. At the melting point this gives a time of about 1 s for attainment of molecular orientational equilibrium and 10^9 h at 300 K. Comparable times for attainment of equilibrium in vacancy concentration are, perhaps, 10^4 times longer, owing to the assumed greater distance between vacancy sinks.

We can conclude that near the melting point equilibrium values of orientational disorder are appropriate whereas for crystals at lower temperatures, non-equilibrium values dependent on crystal history apply. Initially we will discuss a situation of equilibrium in vacancy nature and molecular orientation, in a non-equilibrium vacancy concentration.

(a) EQUILIBRIUM CONTROL OF MOLECULAR ORIENTATION

Since the stacking fault junctions must be half integral vacancies, the simplest possibility is that a single vacancy dissociates into two half vacancies, which provide the origin and terminus of a misoriented stack. An alternative is that two vacancies disproportionate into a half vacancy and a three-halves vacancy and in the same sense provide origin and terminus for a misoriented stack. We thus consider that local zones of misoriented structure are associated with [010] half integral vacancies. Many of the vacancies are integral, and not associated with molecular misorientation.

The values in table 1 indicate that the energy J required to half rotate a stack of molecules is composed predominantly of two components of equal magnitude J', the changes in interactions along [100] and [102] ($P2_1/a$ cell); the change along [001] is much smaller. We define the disorder parameter S to be the probability that adjacent molecules in an [010] stack have the same orientation minus the probability that they differ by a π rotation about [010]. The fraction of misoriented molecules is $(1-S)/2$. P is the fraction of the vacancy concentration ρ which exists as monovacancies and $(1-P)$ as half vacancies. For a disorder parameter $S < \sim 0.95$, we can write the Helmholtz energy of the crystal [17]

$$A \sim \left\{\frac{\rho P E_s}{2} + PRT\rho[\ln \rho - 1]\right\} + \left\{\frac{(1-S)J}{2}\left(1 - \frac{T}{T_m+\delta}\right)\right\} + \left\{\frac{\rho(1-P)}{2}\left[E_s + \frac{U_{010}}{2}\right] + 2F(1-P)RT\rho[\ln 2(1-P)\rho - 1]\right\} \quad (4a)$$

in which

$$F \simeq -\left[\frac{1+S}{2}\ln\left(\frac{1+S}{2}\right) + \frac{1-S}{2}\ln\left(\frac{1-S}{2}\right)\right]\Big/\ln 2. \quad (4b)$$

The first term is the Helmholtz energy of monovacancies. The third term is the half vacancy Helmholtz energy estimated as the relaxed vacancy energy $E_s/2$ together with a contribution $U_{010}/4$ for the [010] bonding lost by the translation of a stack of half rotated molecules plus a non-random mixing entropy. The second term in eqn (4a) represents the energy required to misorient a fraction $(1-S)/2$ of the molecules for which we have assumed the Helmholtz energies of the pure phases to intersect at a small temperature increment δ above the melting point T_m. For misorientation to occur, half vacancies are necessarily present above and below each stack of misoriented molecules. The expression thus incorporates the balance between this extra internal energy and the extra entropy (expressed by the approximate correlation function F) gained by the half vacancies as they disorder. Solution of eqn 4 with the help of values in table 2 for J, T, δ and ρ shows that the Helmholtz energy is minimised at $S = 1$, $P = 1$ for all the sets given except the first when we obtain $P = 0$, $S \simeq 0.3$ as the Helmholtz energy minimum. There are thus no co-operative disordering effects except, possibly, very near the melting point. We can thus calculate this type of disorder on the basis of the dissociation of an individual monovacancy to a pair of half vacancies separated by m misoriented molecules (an " m-stack ").

We must also consider the alternative dissociation of two monovacancies to form one half vacancy and one three-halves vacancy. This condition is equivalent to a random distribution, of concentration ρ, of monovacancies [calculated according to eqn (2)], being replaced in part by a half vacancy and a three-halves vacancy at either end of a stack of orientationally misoriented molecules along [010] (" n-stack ").

The energy difference between an oriented stack of n molecules between two monovacancies and a misoriented stack between half and half or three-halves vacancies consists of two terms in our model. One is the difference in the vacancy energy compared with once or twice the monovacancy energy, and the other is the energy J of misorientation already discussed. For the replacement of one monovacancy by two half vacancies, the vacancy Helmholtz energy is increased by $U_{010}/2$, produced by the loss of the short range contact by one molecule and with allowance for relaxation. For the replacement of two monovacancies by half and three-halves vacancies there is no similar term, and we assume no contribution to the energy. The sole contribution is from misorientation, namely the quantity J, the internal energy per mole of misoriented molecules. The value $J = 18 \text{ kJ mol}^{-1}$ can be applied to a complete π-rotated stack, the only relaxation allowed being that for unit cell changes in a lattice without vacancies. In the presence of vacancies, as here, further relaxation is possible and J will be reduced. A value of one half the original unrelaxed value is a reasonable lower limit. In calculations we have considered values in the range 11-18 kJ mol^{-1}.

With the assumption of Boltzmann statistics we can now calculate the probability of formation of misoriented m- and n-stacks, and the average number of misoriented molecules per stack.

The probability of two designated sites being vacant, and separated by n occupied sites is $\rho^2(1-\rho)^n$. The fraction of molecules so misoriented is

$$Q_t(\tfrac{3}{2},\tfrac{1}{2}) = \rho^2 \sum_{n=0}^{\infty} n(1-\rho)^n(1+e^{n\sigma})^{-1}. \tag{5}$$

The average length of a misoriented stack is

$$\bar{L}(\tfrac{3}{2},\tfrac{1}{2}) = \frac{\sum_{n=0}^{\infty} n\rho(1-\rho)^n(1+e^{n\sigma})^{-1}}{\sum_{n=0}^{\infty} \rho(1-\rho)^n(1+e^{n\sigma})^{-1}}. \tag{6}$$

For m-stacks (terminated by two half vacancies) the misorientation energy is taken to be $m\sigma + U_{010}/2RT$, where $U_{010}/2$ is, as before, one half the nearest neighbour coupling along [010]. Also for each monovacancy there are two ways in which the m-stack may form along [010], so that the expression analogous to eqn (5) for the m-stack expressions is

$$Q_t(\tfrac{1}{2},\tfrac{1}{2}) = \frac{2\rho \exp[(-U_{010}/2RT)-\sigma)}{[1-\exp(-\sigma)]\{1-\exp(-\sigma)+2\exp[(-U_{010}/2RT)-\sigma]\}} \tag{7a}$$

$$\bar{L}(\tfrac{1}{2},\tfrac{1}{2}) = [1-(1-\rho)\exp(-\sigma)]^{-1}. \tag{7b}$$

We have neglected the interaction between stacks, which at high disorders will mutually interfere, and also the temperature dependence of U_{010}.

A range of calculated values of $\bar{L}_m$, $\bar{L}_n$, Q_t^n, Q_t^m is given in table 2 for various temperatures of the crystal, with sample values of δ, and J held at 11 and 18 kJ mol^{-1}. In eqn (6) and (7) temperature dependence appears in both σ and ρ but at the lower temperatures ρ is very small and may be neglected. We conclude, for example, that

TABLE 2.—AVERAGE FRACTION OF MISORIENTED MOLECULES $(1-S)/2$, CALCULATED FROM THE PARAMETERS GIVEN

T/K	δ/K	J/kJ mol^{-1}	ρ	Q^n/ρ^2	$\bar{L}_n$	Q^m/ρ	$\bar{L}_m$	$(1-S)/2$	Q_t^{kin}	$\bar{L}^{\text{kin}}$
480	20	11	0.01	56	10	6.1	9.5	0.07-0.3	0.14	92
480	20	11	0.0	68	11	6.1	9.5	0	0.13	∞
480	20	18	0.01	22	6.7	3.1	6.1	0.03	0.13	87
480	100	11	0.01	3.4	2.9	0.7	2.6	0.007	0.10	72
480	100	11	0.0	3.6	3.0	0.7	2.6	0	0.06	∞
480	100	18	0.01	1.3	2.0	0.3	1.9	0.003	0.07	61
450	0	11	0.01	22	6.6	2.5	5.6	0.03	0.16	86
450	0	11	0.0	24	6.9	2.5	5.6	0	0.11	∞
450	0	18	0.01	8.4	4.3	1.2	3.6	0.01	0.14	80
300	0	11	0.01	0.26	1.3	0.02	1.24	2×10^{-4}	0.02	42
300	0	11	0.0	0.26	1.3	0.02	1.24	0	7×10^{-3}	∞
300	0	18	0.01	0.07	1.08	0.004	1.07	4×10^{-5}	7×10^{-3}	34
150	0	11	0.01	10^{-3}	1.002	4×10^{-6}	1.002	4×10^{-8}	2×10^{-4}	29
150	0	11	0.0	10^{-3}	1.002	4×10^{-6}	1.002	0	10^{-6}	∞
150	0	18	0.01	0	1	4×10^{-8}	1	4×10^{-10}	3×10^{-6}	29

at 300 K an unannealed melt grown crystal would contain in the bulk an equilibrium fraction 10^{-4} misoriented molecules, to within an order of magnitude, at a small average stack length of, say, 1-4 molecules. At higher temperatures the average stack size is ~10, and the bulk fraction of misoriented molecules can increase to 10^{-2}.

(b) KINETIC CONTROL OF MOLECULAR ORIENTATION

We can construct a non-equilibrium model for the incorporation of half vacancies, and thus misoriented molecules, into the growing surface, in a similar way to that for vacancies. The initial production of a half vacancy in an ordered stack along [010], is again assumed to involve a statistical factor to ensure that all four neighbours are present on the surface, and a Boltzmann factor of $\exp[(U_{010}/2\boldsymbol{RT})+\sigma]$ which takes account of the Helmholtz energy difference between the two possible molecular orientations. To terminate a misoriented stack by incorporation of a further half vacancy we must include a Boltzmann factor $\exp[(U_{010}/2\boldsymbol{RT})-\sigma]$. We neglect any interference between half vacancy and monovacancy production, and assume that half vacancies can be produced by growth only along [010]. Growth in other directions may also give misoriented molecules. We obtain, as a rough estimate of the fraction of misoriented molecules under conditions of kinetic control

$$Q_t^{\text{kin}}(\tfrac{1}{2},\tfrac{1}{2}) = \frac{30\rho b+1-30\rho}{180\rho b+6b^2-180\rho b^2} \tag{8a}$$

where $b = \exp(\sigma)$ and for the average length of a misoriented stack

$$\bar{L}^{\text{kin}} = 29-\frac{30}{b}+\frac{1}{b\rho}. \tag{8b}$$

The calculated values, at various growth temperatures, are given in table 2.

The non-equilibrium Q_t^{kin} is substantially greater than the equilibrium value. It suggests that a crystal grown at 300 K may have up to 1 % of molecules misoriented. The much higher values near the melting point will rapidly decay to the equilibrium values, which are themselves of the order of 1 %.

MISORIENTATIONS ASSOCIATED WITH DISLOCATIONS

Typical melt grown anthracene crystals contain 10^4 etch pits mm^{-2}; these are believed to indicate the presence of dislocations with large Burgers vectors. Within the core of a dislocation substantial energy is stored. It is of the order of 50 kJ mol^{-1}, divided among some fifty molecules, per molecular translation along the dislocation, even for a unit Burgers vector dislocation. These energies are so much larger than the differences between the calculated crystal phase energies that we may expect the existence of regions between the central dislocation cavity and the radius of the core (where elastically strained $P2_1/a$ begins) in which perhaps half the molecules are misoriented relative to the external $P2_1/a$ phase. Crudely, a fraction $10^{-7\pm2}$ times the cube of the typical Burgers vector of molecules, in total, are implied to be misoriented in such a crystal. We have attempted no calculation of this fraction because the large stored energy makes the potential functions unreliable; also values of the Burgers vector are unknown, and substantial co-operative effects occur. Nevertheless, the total number of misoriented molecules at dislocation cores may be comparable to those in the bulk of the crystal.

Partial dislocation loops can be formed enclosing a plane of misoriented molecular pairs. We calculate from the pure crystal lattice energy that the planes enclosed by partial dislocations $(2h, 0, \overline{2l+1})\pm\frac{1}{2}[2l+1, 0, 2h]$ are of energies ranging from 5.5 kJ mol^{-1} of molecules in the misoriented plane, (*e.g.* $(20\bar{1})\frac{1}{2}[102]$) to 11 kJ mol^{-1}, (*e.g.* $(40\bar{1})\frac{1}{2}[104]$). The elastic strain around a large Burgers vector dislocation may encourage formation of such loops. Another family of partial dislocations, $(pqr)\pm\frac{1}{2}[2l+1, \pm 1, 2h]$, $q\neq 0$, has a very much larger ($>$400 kJ mol^{-1}) calculated energy per molecule in the plane enclosed by the dislocation loop. This is due to an extremely unfavourable interaction along [010] across the boundary. This would be reduced by substantial positional relaxation of the molecules, but probably remains several times larger than the energies for the first family of partial dislocations.

DISCUSSION AND CONCLUSIONS

The results for this model crystal indicate that for unannealed anthracene grown from the melt there may be, dispersed throughout the crystal, complex defects consisting of m misoriented molecules terminated at each end by a half vacancy, and a few terminated at one end by a three-halves vacancy: the misorientation is defined by the screw rotation $(\hat{C}_2^b+\boldsymbol{b}/2)$. The fractional concentration of such molecules is estimated to be to within an order of magnitude of 10^{-2}, a value comparable to the kinetically controlled (non-equilibrium) vacancy concentration of 10^{-2}-10^{-4}, but greater than the equilibrium vacancy concentration. Possibly as many misoriented molecules may also be associated with the region of disorganisation in a dislocation core. These misoriented molecules may be described in terms of festoons of partial dislocation loops, of which some of type $(h\,0\,l)\,\frac{1}{2}\,[\bar{l}\,0\,h]$ are of particularly small energy about the central dislocation (*e.g.* $(h\,0\,l)\,[010]$) core. Annealing the crystal near its melting point will reduce the vacancy concentration, and correspondingly the fraction of misoriented molecules in the bulk crystal, by allowing the vacancies to diffuse into crystal imperfections, or possibly to form further dislocation loops within the crystal. Preparation of the crystal by growth from solution will decrease the concentration of misoriented molecules because both vacancy and dislocation concentration decrease: this will be even more marked in vapour grown crystals.

When a molecule is misoriented, its local environment becomes $P\bar{1}$, and there will be compression within the $P2_1/a$ structure, except at the stack ends where the local density is lower. Lattice compression should lead to exciton trapping, in that it increases the dispersive stabilisation of the upper state more than the ground state. The compressed molecules should therefore absorb at longer wavelength and act as excitation traps. The misorientation is such that the orientation of pairs of molecules ($\boldsymbol{a}/2$ separated and parallel, adapted to strong electronic interactions) would facilitate dimerisation involving only molecular distortions and motion associated with lattice vibrational modes of <150 cm^{-1}. Such dimerisation has been noticed at dislocation cores [20] where we expect a large local concentration of misoriented molecules.

Misorientation is thus another way in which the stereochemical demands of dimerisation can be met, in addition to *e.g.* $(001)\frac{1}{2}[110]$ partial dislocations.[21] This secures a similar stacking fault, though not identical, and also should lead to trapping.[22] Dimerisation will not cause much local reorganisation, because the molecular volume and shape of bianthracene are similar to those of a parent pair of anthracene molecules. Further reaction, after all suitably misoriented molecules have been converted, will be slower; however, because reorientation of molecules by diffusion of half integral vacancies of partial dislocations along [010] is kinetically the most favoured process, growth of stacks of misoriented molecules along [010] will be favoured. Such strings of dimer along [010] have been observed in a partially dimerised crystal.[20]

From studies of the substituted anthracene, 1, 8-dichloro-9-methylanthracene, Thomas *et al.*[5] have concluded that dislocations are important in facilitating formation of the *trans*-dimer which the structure of the perfect crystal would not favour. Tetracene crystals prepared by low temperature sublimation show an excimeric photon emission interpreted as being due to sandwich-like pairs present in the disordered crystal.[23] In the case of 1, 8-dichloro-10-methylanthracene, electron microscopy has enabled the detection of a second phase,[6] introduced when a melt of this substance is rapidly cooled, but not extending through the entire crystal of parent monomer; this second phase is responsible for a differential enthalpic signal below the normal melting point of the stable phase. Although there was no proof of a connection between the existence of the unstable phase and the photochemical behaviour, which in this system, as in anthracene itself, defies the topochemical principle,[1] we think these phenomena are related to the presence of crystallographically defined orientational defects as considered here.

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