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Stereochemical Constraints and Lattice Relaxation in Crystal Photochemistry

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The relationship of crystal structure, molecular orientation and conformations of reactants and products is central to an understanding of solid state organic photochemistry. The calculation of the properties of lattices containing foreign molecules is described, with allowance for relaxation in position and orientation coordinates. The experimentally studied cleavage of dianthracene molecules in its crystal, and the cleavage of the photoisomer of 1,2-di-(9-anthryl)-ethane, are systems in which the effect of lattice constraints can be examined. It is shown that a useful degree of rationalization of experimental results is possible, in terms of the stable conformations available to the cleaved systems, within the "cage" or cavity enveloping the reactive site.

1. INTRODUCTION

Photochemical changes in molecular solids take place within the constraints of the cage of molecules about the reaction site. A broad consequence, which has been recognized for a long time,[1] is that the stereochemical course of certain dimerizations and related reactions in crystals is topochemically determined, in the sense that the product molecule has that molecular structure which was preformed by the crystal packing of the reactant. In cases where the structure of the product does not mimic the perfectly ordered crystal of the reactant, as in the dimerization of 9–cyanoanthracene,[2] the product is believed to be preformed in disordered zones under contraints of exactly the same type. There is evidence to support this view.

We propose in this paper a more detailed approach to the problem of lattice constraints on photochemistry, by studying the relaxation of the host crystalline environment in the presence of foreign molecules or molecule fragments of various types, and analysing the energy-optimized conformations and configurations of the encapsulated objects. In the first part the computational method is described, and its application considered to some simple situations (e.g. the substitution at a lattice site of a larger or smaller molecule than the replaced host molecule) which allow it to be tested. Next the experimental facts[3] are described, and the theoretical method applied, for the photochemical cleavage of crystalline dianthracene into two anthracene molecules. Finally the experimental findings[4] are sketched for the analogous reaction in the more complex case of 1,2-di-(9-anthryl)ethane, and the application of the theory indicated. In each, the method is to calculate the local structure, including the reacting system itself, at and about the reactive site with allowance for lattice relaxation as earlier briefly described.[5]

2.1 Lattice packing calculations

At low temperature and pressure the potential energy of a crystal lattice composed of rigid bodies can be approximated by the total pairwise intermolecular potential energy V,

$$V = \frac{1}{2}\sum_i V_i = \frac{1}{2}\sum_i \left(\sum_{j \neq i} V_{ij} \right)$$

where V_{ij} is the potential energy of interaction of molecules i and j, and the sum is over all molecules of the lattice. The equilibrium structure at, and in the vicinity of, a defective site in an otherwise pure, perfect lattice of known structure can be calculated by minimizing V with respect to the position and orientation variables of the molecules constituting the defect and of its surroundings. The procedure is to optimize the positions and orientations of a set of molecules i by minimizing the energy V_i. All other molecules, $j \neq i$, are held fixed in their experimentally determined or previously optimized positions, so that the interactions V_{ij} are functions of the position and orientation variables of i alone. The calculations are done cyclically over a set of molecules which include the site of disturbance and its surroundings. Convergence to a system saddle-point is avoided, or made very unlikely, by a procedure in which the accuracy of each minimization is chosen to be fairly low initially and then gradually increased after each cycle. Iteration is terminated when V differs by less than a chosen tolerance between cycles.

The V_{ij} are approximated as the sum of atom–atom interactions[5] of the (exp -6) form with the parametrization in Williams's set IV,[6] and for consistency with the parameter set the position of all aromatic protons, unless otherwise stated, is taken to lie at 0.1027 nm from the carbon nucleus in the experimentally determined carbon–hydrogen bond. The molecules included in each calculation, namely those of which the positions and orientations are allowed to relax to accommodate the defect site, are all those for which there are atom–atom contacts of 1.0 nm or less. Both modified Newton[7] and quasi-Newton[8] schemes were used to solve the single molecule problems.

The key to a reliable and fast method for energy minimization with respect to molecular orientations is the choice of parameters to represent the displacements from the initial positions. The Euler angles, while practically the most useful for many purposes, are unsatisfactory as variational parameters in the minimization.

It has been shown[9] that the orientational potential gradients can be expressed in terms of the principal torque $\boldsymbol{\tau}$ as

$$\nabla_\alpha V_i = -\mathbf{S}^T\boldsymbol{\tau} \tag{1}$$

where ∇_α denotes the derivatives with respect to the Euler angles (ϕ, θ, ψ)[10] and:

$$\mathbf{S} = \begin{pmatrix} \sin\theta\sin\psi & \cos\psi & 0 \\ \sin\theta\cos\psi & -\sin\psi & 0 \\ \cos\theta & 0 & 1 \end{pmatrix}$$

Using Eq. (1) it can be shown[9] that steepest descent produces a rotation about an axis which may make an angle as large as $\delta = |\pi/2 - \theta|$, for $0 \leqslant \theta \leqslant \pi$, with the axis of current torque. As a consequence the minimization will be inefficient whenever θ is not close to $\pi/2$, and convergence to an artificial stationary point may occur when $\theta \approx 0$. Thus to ensure fast convergence θ must be maintained close to $\pi/2$ by the appropriate choice of body frame, *vide infra.* Maintenance of this condition is an undesirable complication in the calculation.

This problem is overcome by using as parameters for the rotation matrix the quantities χ, ξ, η and ζ[11] sometimes known as quaternion parameters. Euler's theorem that the rotation of a body about a point is equivalent to a rotation about an axis through the point enables parametrization in these four quantities. The quaternion 4–vector $\mathbf{q}$ is defined in terms of the rotation ω, and the normalized axis of the rotation $\boldsymbol{\mu}_0^T = (\xi_0, \eta_0, \zeta_0)$ may be written as in Eq. (2),

$$\mathbf{q}^T \equiv (\chi, \xi, \eta, \zeta) \equiv (\chi, \boldsymbol{\mu}^T) \equiv \left(\cos\frac{\omega}{2}, \boldsymbol{\mu}_0^T \sin\frac{\omega}{2}\right) \tag{2}$$

The four parameters satisfy by definition $\|\mathbf{q}\| = 1$, and are related to the Euler angles by the equations

$$\begin{aligned} \chi &= \cos\tfrac{1}{2}\theta\cos\tfrac{1}{2}(\phi + \psi) \\ \xi &= \sin\tfrac{1}{2}\theta\cos\tfrac{1}{2}(\phi - \psi) \\ \eta &= \sin\tfrac{1}{2}\theta\sin\tfrac{1}{2}(\phi - \psi) \\ \zeta &= \cos\tfrac{1}{2}\theta\sin\tfrac{1}{2}(\phi + \psi) \end{aligned} \tag{3}$$

Thus the rotation matrix takes the simple form:

$$\mathbf{A}(\mathbf{q}) = \begin{pmatrix} \xi^2 - \eta^2 - \zeta^2 + \chi^2 & 2(\xi\eta + \zeta\chi) & 2(\xi\zeta - \eta\chi) \\ 2(\xi\eta - \zeta\chi) & -\xi^2 + \eta^2 - \zeta^2 + \chi^2 & 2(\eta\zeta + \xi\chi) \\ 2(\xi\zeta + \eta\chi) & 2(\eta\zeta - \xi\chi) & -\xi^2 - \eta^2 + \zeta^2 + \chi^2 \end{pmatrix} \quad (4)$$

Where $\mathbf{A}(\mathbf{q})$ is defined as transforming a laboratory vector $\mathbf{x}_{\text{lab}}$ to the body frame by $\mathbf{x}_{\text{body}} = \mathbf{A}(\mathbf{q})\,\mathbf{x}_{\text{lab}}$. The simplest minimization procedure was obtained[9] by converting the constrained problem of minimizing V_i subject to $\|\mathbf{q}\| = 1$ into an unconstrained problem in seven variables by redefining $\mathbf{A}(\mathbf{q}) = \mathbf{A}(\mathbf{q}/\|\mathbf{q}\|)$ for all non-zero $\mathbf{q}$ and adding a penalty term quadratic in the displacement $(\|\mathbf{q}\| - 1)$ to the energy function.

Variation with respect to linear displacements is straightforward and not further discussed. Right-handed axes are used throughout, and crystallographic inversion symmetry has been used unless stated otherwise.

2.2 Trial applications of the method of calculation. Pure crystals

In the calculations to be described for both naphthalene and anthracene the "active" site is considered together with an environment, namely a set of molecules the positions and orientations of which are varied to minimize the energy. The sites of these molecules are listed in Table I, the central molecule being at (0, 0, 0). Sites of types 1 and 2 are translationally equivalent and non-equivalent to (0, 0, 0). The X-ray structures used are, for naphthalene, that of Cruickshank[12] and for anthracene that of Mason.[13] With the use of the method described the structure of the naphthalene crystal (room temperature) and that of anthracene (measured at 95K) are well reproduced as described elsewhere.[5] The agreement is a test of internal consistency. The poorer result is for naphthalene, in which for one pair of molecules there is a centre of mass discrepancy with the measured structure of 3×10^{-3} nm and an error of 2.5° in the orientation of one axis.

It is a general feature that calculations of structures give more reliable results than those of lattice energies: this is not unexpected, because the potentials governing the molecular packing vary steeply with the interatomic separations, and the location of the coordinates of the minima in the total energies is rather accurate. The total energies themselves are much less precise: comparisons within a single structure, such as the potential energy decrease of 7 kJ mol^{-1} and 13 kJ mol^{-1} found as the result of allowing the environ-

TABLE I

Sites of molecules in the lattice-relaxed environment

Molecule	Type in unit cell	Site coordinates *a*	*b*	*c*
1	1	0.0	0.0	1.0
2	1	0.0	0.0	−1.0
3	2	−0.5	0.5	−1.0
4	2	0.5	−0.5	1.0
5	2	−0.5	−0.5	−1.0
6	2	0.5	0.5	1.0
7	2	0.5	0.5	0.0
8	2	−0.5	−0.5	0.0
9	2	0.5	−0.5	0.0
10	2	−0.5	0.5	0.0
11	1	0.0	1.0	0.0
12	1	0.0	−1.0	0.0
13	1	1.0	0.0	1.0
14	1	−1.0	0.0	−1.0
15	1	0.0	1.0	−1.0
16	1	0.0	−1.0	1.0
17	1	1.0	0.0	0.0
18	1	−1.0	0.0	0.0
19	1	0.0	1.0	1.0
20	1	0.0	−1.0	−1.0

ment to relax from the literature structures of naphthalene and anthracene, are more reliable than comparisons between different structures.

2.3 Replacement of a host molecule by a smaller molecule

If a host molecule is replaced by a larger impurity, such as anthracene embedded in naphthalene host crystal, the impurity adopts an orientation very close to that of the host.[5] The local overcrowding in the lattice must be relieved by displacements and orientation changes of the surrounding molecules, which account for a potential energy drop of 117 kJ mol^{-1}, very much larger than in the pure crystal relaxation, as expected.

Where the substituted impurity is a smaller molecule, for example naphthalene in anthracene as host, there is a result which is at first sight unexpected, but which is typical. The trial structure is that in which the naphthalene is on the inversion centre at the vacated site, with the orientation of the displaced host. Even without relaxation of the environment, the energy minimized structure is that in which the naphthalene has moved to a position with its centre of mass on one of two inversion-related sites. Its orientation is little changed but the centre of mass in one of the two positions is moved along the three crystallographic directions **a**, **b**, and **c**′ by 0.05, 0.01 and −0.08 nm. The calculated barrier to passage from one site to the other is small (2 kJ mol^{-1}), and the result cannot therefore be insisted on strongly. The same preference for displaced impurities is found in other cases, however, there are exceptions e.g. benzene in naphthalene, which has a local energy minimum at the inversion centre as well as at two symmetry related off-centre sites.

The packing of naphthalene in the anthracene cavity is that the two rings of naphthalene more or less superimpose on the centre and end rings of the replaced anthracene, so that locally the packing is similar to the pure crystal, but at the expense of a void in the position of the third anthracene ring.

2.4 Lattice structure adjacent to a vacant site

If one molecule is removed from a lattice of naphthalene or anthracene, and the surrounding molecules allowed to relax to a minimum energy structure, the vacancy is left more or less intact. There are small changes in positions, the effect of which in both cases is to alter the cavity towards a spherical volume: the nearer neighbours retreat slightly and the more remote ones advance. The same pattern is found near a divacancy, formed by removing two neighbour molecules along the **c** axis. The result again reflects the fact that the structure responds in a way to preserve the attractive interactions by making only such small displacements as are required to relieve the repulsive stresses. The attractive terms themselves vary quickly with distance (R^{-6}), and their total contribution is much greater when the normal crystal packing is preserved than in any structure in which the vacant volume is occupied by neighbours. The results quoted in Table II, for a single vacancy in naphthalene, show that orientational displacements in the most affected neighbour molecules (9–10 of Table I) are slight. The bracketed values are direction cosines in the pure crystal lattice. No molecule is displaced more than 0.01 nm from its normal position.

TABLE II

Orientation displacements about a vacancy in naphthalene (direction cosines of principal axes in molecules 9–10)

	a	*b*	*c*′
L	−0.4249 [−0.4379]	0.1828 [0.2103]	0.8866 [0.8741]
M	0.2854 [0.3207]	−0.9024 [−0.8718]	0.3228 [0.3704]
N	0.8591 [0.8399]	0.3902 [0.4425]	0.3313 [0.3143]

3.1 Photocleavage of dianthracene in its crystal. Experimental

Ferguson and Mau[3] studied the properties of sandwich dimers produced within the crystal of dianthracene by irradiation with 254 nm radiation. The dimers show excimer emission, and of the two types of emission the one here discussed was identified as characteristic of isolated dimer sites in the ordered dianthracene lattice. The cleavage reaction was shown to be capable of photochemical reversal, leading to reformation of the dimer, at a rate with a temperature dependence giving an activation energy near to 600 cm^{-1} (7.2 kJ mol^{-1}). Moreover the excimer emission appeared only in dimers produced in an excited state by photocleavage, and not by excitation of the dimer ground state, suggesting that after excimer emission the dimer relaxed to a configuration from which the excimer structure, and photodimerization, were attainable only with thermal activation. Results for the polarization of the dimer absorption spectrum were in agreement with expectations from the dianthracene crystal structure.[14]

3.2 Photocleavage of dianthracene. Application of the theory

The room temperature crystal structure of dianthracene A_2 belongs to the space group P_{bca} with four molecules in the unit cell. For the cleaved anthracene molecules in $A + A$ the molecular geometry is taken from Mason.[13] In lattice relaxation calculations the "cage" environment included all atom–atom contacts less than 1.0 nm with the centre molecule or guest. Full details of the methods will be given elsewhere.

The molecular structure of dianthracene is shown in Figure 1.

As a preliminary, a packing calculation was made on the pure crystal of A_2 with the help of the program CRASH written by Dr. G. S. Pawley. Beginning with the experimental structure, unit cell dimensions and molecular orientations were varied, under P_{bca} symmetry, to minimize the total intermolecular potential energy. No molecular orientation changed by as much as 1°, and the small changes in unit cell dimensions of $\Delta a = -0.02$ nm, $\Delta b = -0.01$ nm and $\Delta c = +0.01$ nm are compatible with the neglected effects of zero-point motion and thermal expansion.

In seeking the conformation of the anthracene pair produced by cleavage of A_2 at a site of the dianthracene lattice we proceed as earlier described for a single guest replacing a host molecule. An A_2 molecule is removed, and replaced by two anthracenes. Using the experimental cell dimensions, a cage is constructed out of the 14 nearest neighbours. The positions and orientations

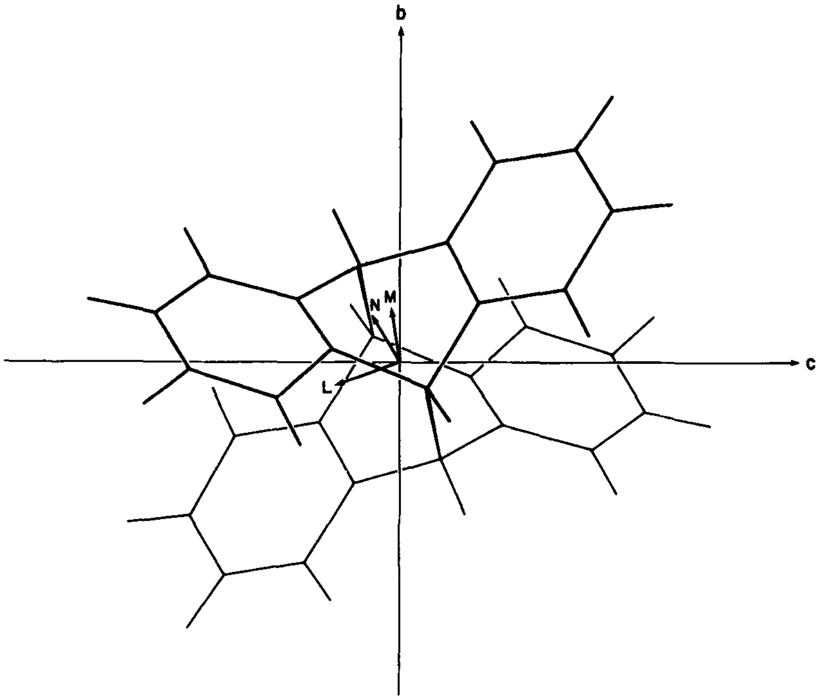

FIGURE 1 Molecular structure of dianthracene in its crystal, projected on the (*bc*) face.

of these molecules, and those of the inserted anthracene, are varied to minimize energy. The lattice of molecules outside the relaxed cage is kept fixed. The initial position of the anthracenes, which is the starting point for the variational search, is the eclipsed conformation with principal axes parallel to those of the replaced A_2. The cavity occupied by $A + A$ was first searched without relaxation for stable configurations of the molecule pair. There is one stable structure only, in which the anthracenes remain parallel, but with planes displaced away from the eclipsed position, and with centre of inversion retained with respect to the lattice site. The separation of the planes is 0.347 nm. The structure is illustrated in Figure 2. The uniqueness of the minimum energy configuration was checked by systematic search: regions of the cage were sampled by starting the minimization after placing the anthracenes in selected positions with respect to the principal axes of the replaced A_2, with and without imposing inversion symmetry. In all cases there was convergence to the same optimum configuration.

The effects of allowing lattice relaxation are very small so far as the final configuration is concerned (Figure 2). The molecular planes are separated by 0.348 nm, and the small further displacement from the eclipsed position

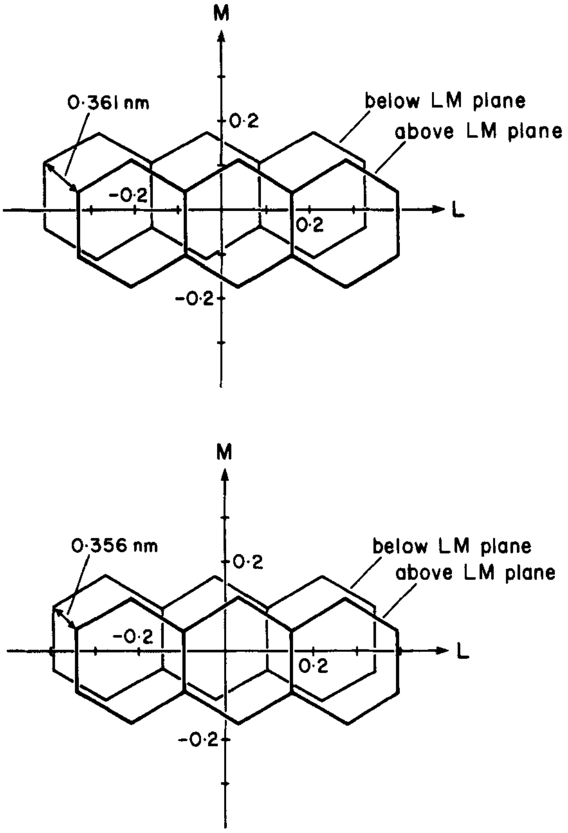

FIGURE 2 *Upper diagram.* Relative positions of anthracene molecules of a cleaved pair projected normal to the molecular planes, as calculated without lattice relaxation. *Lower diagram.* Relative positions as calculated with lattice relaxation.

leaves the carbon atoms of one molecule, in projection, lying over the centre of a carbon–carbon bond in the other, and no longer in the asymmetrical position found in the rigid cage.

The results of the calculation of total energy must be treated cautiously, as already explained. They show that the optimum relaxed crystal has a potential energy lower than that of a crystal containing A_2 by 28 kJ per mole per cleaved unit. On cleavage there is an increase in repulsion energy, but this is more than compensated by an increased dispersive stabilization. Moreover, analysis of the composition of this difference shows that the cage molecules about the cleaved pair are less stable than in the pure crystal (by 5–10 kJ mol^{-1}) while the cleaved pair is more stable (by 33–38 kJ mol^{-1}) than the A_2 from which they are derived. It is of course the case that these differences would appear in the enthalpy term of the overall reaction, and are not simply connected with the measured activation energy of 600 cm^{-1} (7.2 kJ mol^{-1}) found experimentally.

The calculated optimum packing is fully compatible with the experiments described in Section 3.1. While the initially formed excited $A + A$ pair is produced in the eclipsed structure, and is both the source of excimer emission and the starting point for the reverse reaction to the photodimer A_2, the relaxed pair is no longer eclipsed (Figure 2) and so requires an activation step before being capable of photoreaction to the dimer. The calculation also indicates that the orientation of the pair is unchanged from the parent dimer molecule, in harmony with the observed polarization of the absorption spectrum.

4.1 Cleavage of the photoisomer of 1,2-di-(9-anthryl)ethane (AEA). Experimental

We now refer to the experimental study of the molecular and crystal structure, and photoreactivity, of this compound by Anderson, Ferguson, Morita and Robertson.[4] The molecular structure of the photoisomer is shown in Figure 3. The bridging bonds in the photoisomer, which are cleaved by light, join the 9–9′ and 10–10′ atoms of the anthracene moieties. The crystal structure of the

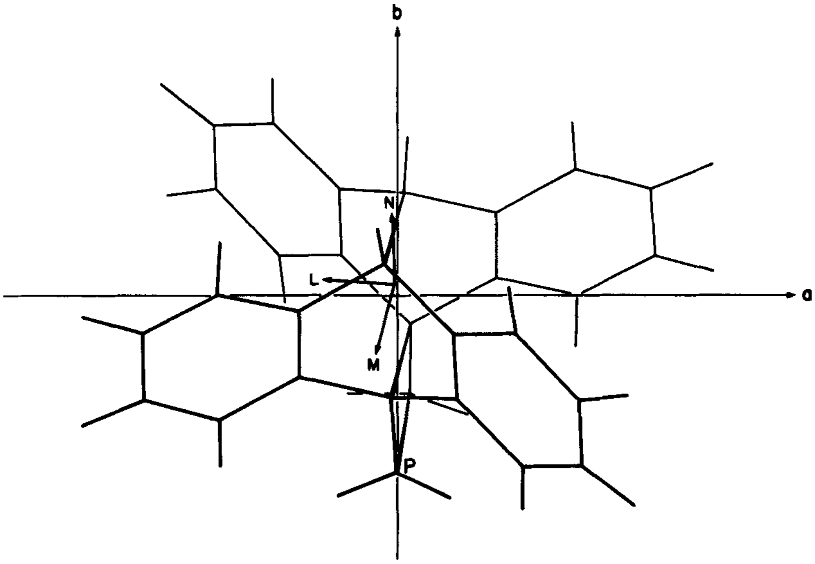

FIGURE 3 Molecular structure of the photoisomer of dianthrylethane.

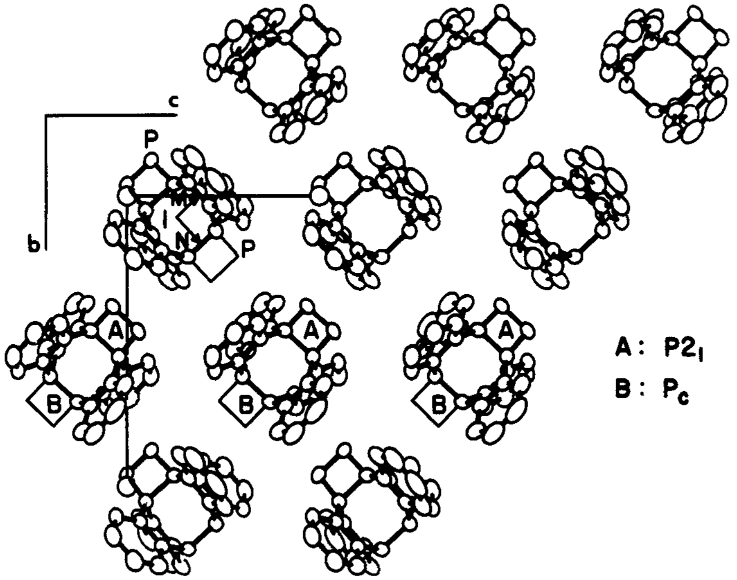

FIGURE 4 The crystal structure of dianthrylethane photoisomer, projected on the (*bc*) crystal plane. In the $P2_1$ structure the ethane bridges are as shown by *A*, in P_c as shown by *B*.

photoisomer was refined in space group $P2_1$; it was also capable of refinement fairly well in P_c, and there may be domains of each in actual crystals. The structure is indicated in projection in Figure 4. Under irradiation at the extreme long-wavelength edge of the absorption band of the crystal, nearly uniform distributions of the cleaved molecules were formed (at an average concentration of about one per thousand), embedded in the lattice of the photoisomer. The properties of the cleaved molecules were examined through their absorption spectra, fluorescence spectra, and through the photochemical reaction leading to reformation of the photoisomer.

Broadly it was found that the cleaved molecules formed are in some cases fluorescent and slowly photoisomerizable, and in others non-fluorescent and rapidly photoisomerizable. Two distinct non-fluorescent sites occur. The molecule at the site labelled P_1 is shown, by the polarization of its absorption spectrum, to retain the same orientation after cleavage as it had before. At P_2 there has been a rotation of 7–8° away from the original orientation. It was concluded that in the cleaved species the anthracene moieties were planar, and were related to one another as if by a centre of symmetry.

In the fluorescent species the spectra, including temperature dependence, were interpreted to show that the cleaved molecules occupy a single type of lattice site, but may assume two inter-convertible conformations. The appearance in the spectra of transitions which would be disallowed if the anthracene moieties were related by a (pseudo) centre of symmetry suggested that the molecular planes are not parallel, having hinged apart under the stresses of the interaction repulsions.

4.2 Dianthrylethane in the crystal of its photoisomer. Application of packing theory

The cleaved molecule in this example remains bonded through a hydrocarbon chain. The constraints on its conformation thus include bonding forces as well as cage forces of the kind already considered in 3.2. The intramolecular force system included in the calculation is shown in Figure 5. The variables are the rotation angles θ_i about the three bridging ethane bonds, the displacement angles ϕ_i from the C—C—C tetrahedral angle of the methylene groups and the bending angle ψ_i taking each anthracene out-of-plane about the 9–10 axis, as in the "butterfly" bending mode. Precise definitions are given in the Appendix. The intramolecular potential energy is the sum of

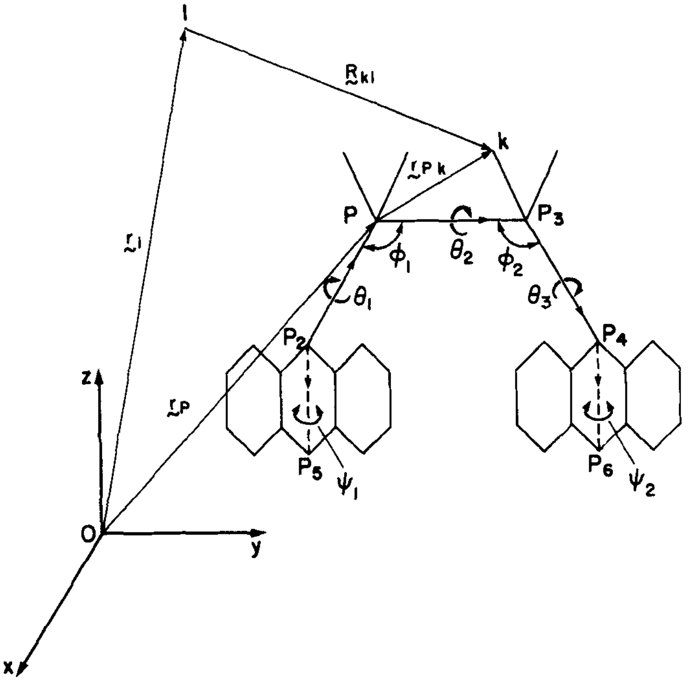

FIGURE 5 Intramolecular variables for the calculation of the minimum energy conformation of dianthrylethane.

three terms, according to Eq. (5),

$$V_{\text{intra}} = V_{NB}(\theta_i, \phi_i, \psi_i) + V_{\text{rot}}(\phi_i) + V_{\text{bend}}(\psi_i) \tag{5}$$

The intramolecular nonbonding interactions are calculated as for the intermolecular terms, namely with a (exp −6) potential with Williams's parametrization, except for atoms within an aromatic ring system or within a methylene group. Such contributions to potential energy changes are taken care of in the second and third terms of Eq. (5). The contributions by V_{rot} and V_{bend} are for all physically reasonable values of force constants overwhelmed by V_{NB}, and are unimportant for the optimum conformations, though they enter into the total energy. The optimum conformations of the free molecule, found by minimizing Eq. (5) is shown in Figure 6. The angle of torsion about the central C—C bond is 70°: other changes are small, including out-of-plane bending angles of the anthracenes of −4 to −8° depending on the particular model. This structure is grossly different from those adopted within the cage of the photoisomer, which in all cases are much closer to being eclipsed.

As explained in Section 4.1 the crystal structure of the photoisomer is refined in space group $P2_1$, and there is evidence that there may be domains

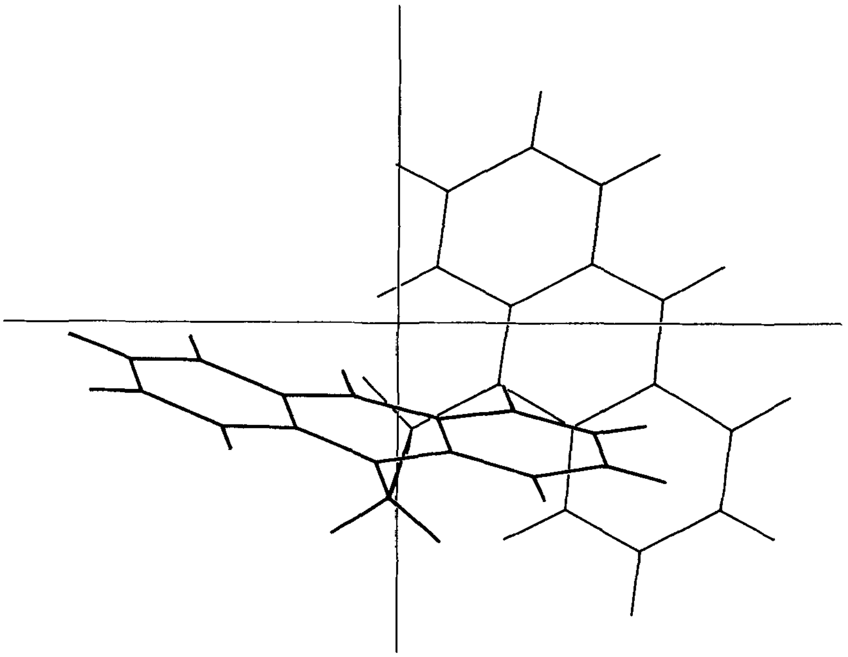

FIGURE 6 The calculated conformation of the free molecule of dianthrylethane.

also of a structure P_c. We have made calculations of the packing of AEA in both lattices and also at plausible disordered sites in each. In P_c two distinct energy minimized AEA structures exist, but in $P2_1$ there is one only.

4.3 Conformations in the ordered $P2_1$ and P_c crystal structures

In the ordered $P2_1$ structure of the photoisomer there is one conformation of AEA that is stable. The anthracene moieties are eclipsed ($\theta_1, \theta_2, \theta_3 \simeq 0°$), and the molecule has the same orientation as the parent host molecule. The structure (Figure 7) shows that the anthracenes are bent out-of-plane about the 9–10 axis, the sense of the bending being outward, to relieve the non-bonding stresses between the two ring systems. The bending angles ψ_1 and ψ_2 (Table III) are unequal and the difference can be rationalized in terms of the neighbour intermolecular contacts of the two anthracenes.

The P_c structure is compatible with two stable conformations of AEA, labelled site types *A* and *B* in Table III. Their properties were explored at three levels: (i) rigid host lattice with variation of external variables plus the rotations about the bridging ethane bonds, (ii) rigid lattice with variation of all internal and external variables, and (iii) relaxation of 20 nearest neighbour molecules, with variations included as in (ii), starting from the optimized conformation found in (ii). The latter calculation is listed in Table III. Neither molecule type is significantly displaced from the orientation or position of its parent. At site *A* dianthrylethane remains eclipsed, with the anthracene moieties bent about the 9–10 axis away from the molecule centre. At site *B* there is a 12° twist about the central ethane bridge bond (angle θ_2) and smaller twists about the other two bonds. The result is some departure from

TABLE III

Conformations of dianthrylethane in various crystal environments (Lattice relaxation included)

	Torsion angles about bridging bonds			C—C—C valence angle changes		Out-of-plane bends	
Location	θ_1(°)	θ_2	θ_3	ϕ_1	ϕ_2	ψ_1	ψ_2
Ordered $P2_1$	1	1	0	0	−3	12	20
Ordered P_c (site *A*)	1	4	3	−1	0	18	10
Ordered P_c (site *B*)	4	−12	8	−1	−1	16	14
Disordered site in P_c	0	2	1	−4	−1	20	12
Disordered in $P2_1$ (site *A*′)	−3	−2	0	−1	0	12	18
Disordered in $P2_1$ (site *B*′)	−8	14	−4	0	−1	14	18

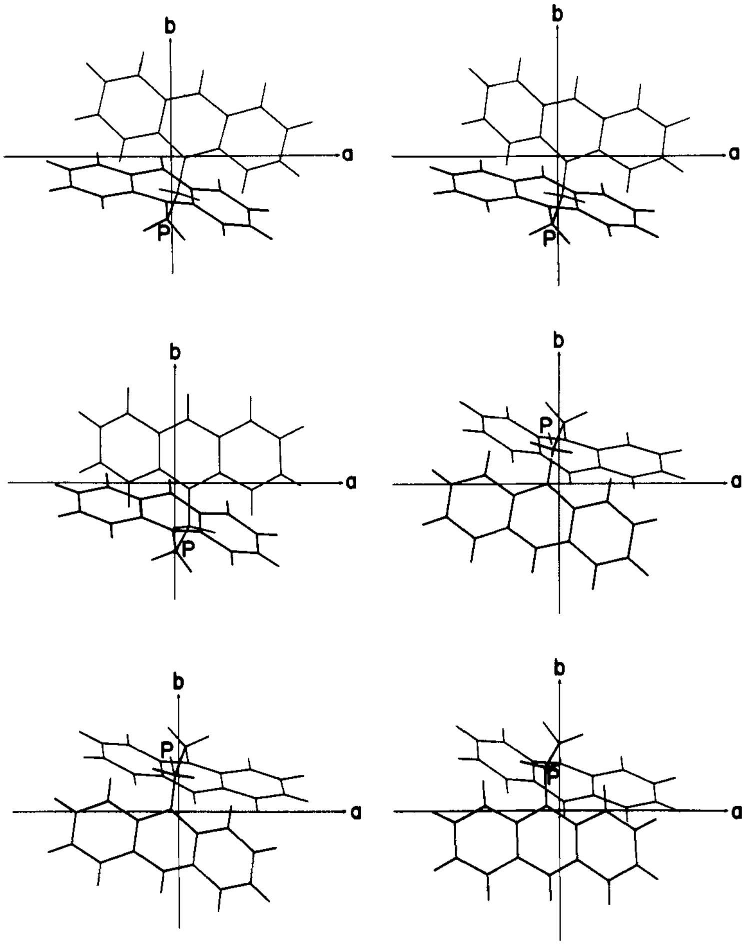

FIGURE 7 Energy minimized structures of dianthrylethane in its crystalline photoisomer. *Left hand*: P_c structure; upper: site *A*, middle: site *B*, lower: disordered site. *Right hand*: $P2_1$ structure; upper: ordered site; middle: disordered site *A'*, lower: disordered site *B'*.

eclipsing. Site *B* is more stable than *A* by about 10 kJ mol^{-1}, but we do not attach much weight to this result. The conformations are shown in Figure 7.

4.4 Disordered sites

Although X-ray analysis[4] does not show disordering at the unit cell level, the possibility exists of isolated disordered molecules in the lattice. The most plausible is a structure in which one photoisomer molecule is replaced by a molecule derived from it by inversion. Packing calculations on the photoisomer pure crystal, including the disordered molecule itself, show a very small increase in potential energy. Following that indication, the conformation was calculated of an AEA molecule notionally produced by cleavage of a disordered molecule in the P_c structure. The energy of the optimum configuration, specified in Table III, is 25 kJ mol^{-1} higher than that of the ordered lattice. It is again eclipsed and bent out-of-plane.

Calculations along similar lines may be made for disordered sites in the $P2_1$ structure of the photoisomer. The local structure in this disorder is so similar to that in the fully ordered P_c structure that similar energy minimized conformations are expected. They are listed in Table III. Evidently A' strongly resembles the eclipsed structure A of ordered P_c, and B' resembles B in its displacement from the eclipsed position.

4.5 The relation of AEA conformations to the experimental sites

We next refer to the results quoted in Section 4.1 on the fluorescent and non-fluorescent sites. The view is supported that conformations with eclipsed anthracene moieties, which partially preform the photoisomer, are photoactive and non-fluorescent; or at least that they will have relatively higher quantum yields for isomerization and low for fluorescence. The conformations with less well eclipsed structures should be less photoreactive and have higher fluorescence quantum efficiencies. Broadly, on this basis, we assign conformations B (and B') to fluorescent sites, and the other four studied to non-fluorescent sites. It should be said that there are other modes of disordering, which we have not here discussed: some have been calculated, but in all cases studied the results fall into one or other of the two categories mentioned.

The observed photoactive site P_1 (Section 4.1) is plausibly assigned to one or more of the eclipsed conformations in Table III, and inasmuch as the polarization properties are those expected for the ordered lattice, is characteristic of the $P2_1$ or P_c structure. The second, P_2, has polarization properties suggesting a rotational displacement by ~8° from the lattice position: we find no conformation so displaced, and suggest that the site may be at a dislocation or other grossly disordered location. The observed fluorescent sites are assigned to types B and B' belonging either to ordered P_c or disordered $P2_1$.

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Appendix

Definitions of internal variables chosen for 1,2-di-(9-anthryl)ethane

The molecule of 1,2-di-(9-anthryl)ethane is put into the lattice of the photodimer in an eclipsed conformation. The position of the atom labelled P in Figure 5 is illustrated in Figure 4 for the ordered and the disordered cases. The rotations about the bridging ethane bonds in θ_1, θ_2, θ_3, which in Figure 5 are labelled $\overrightarrow{P_2P}$, $\overrightarrow{PP_3}$ and $\overrightarrow{P_3P_4}$ respectively, are performed by rotating the atoms to the right of the atoms P,P_3 and P_4. A positive angle produces a right hand screw rotation with the sense of the axes as indicated.

The valence angle bend is modelled by a rotation of the anthracene moieties only. A positive rotation increases the valence angle. For the out-of-plane bends a positive angle ψ indicates that the anthracene has opened outwards.