Chemical Physics 114 (1987) 259–265
North-Holland, Amsterdam

CRYSTAL CONSTRAINTS AND PHOTOCHEMICAL H-TRANSFER IN THE ACRIDINE–FLUORENE MIXED CRYSTAL

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Received 17 November 1986

Calculations are reported of the packing energy of acridine as a substitutional guest molecule in crystalline fluorene as host. Acridine is treated in its ground state and, in an approximate way, in a singlet excited state. Also calculations are reported of the radical pair (acridinyl–fluorenyl) formed by photochemical H-transfer. Experiments have shown that of the two stereochemically distinct orientations available to acridine in the fluorene lattice one is strongly favoured, namely the orientation in which the acridine N is adjacent to the methylene of fluorene, and therefore able readily to form a N...H–C hydrogen bond. Packing calculations in the bulk crystal give too small an energy difference to account for this strong preference. It is suggested that conditions at the growing crystal face determine the orientation of acridine molecules as they are incorporated into the lattice. Various mechanisms are discussed.

1. Introduction

The fluorene crystalline matrix has been shown to provide a suitable host to study intermolecular photochemical H-transfer as a solid state photoreaction. The photoreactive unit is created when hydrogen acceptor guests like acridine, phenazine, and anthracene are doped into the lattice. The structure, mechanism and kinetics of this reaction system have been studied extensively [1–4]. In particular, given the known three-dimensional course of this photoreaction, it appears attractive to address here some questions of wider interest using well developed molecular packing calculations [5].

Does the local molecular packing affect the stereospecific reactivity discussed in ref. [6] for this system? Is it possible to assume a preformation of the reactive guest–host partners due to lattice constraints? What kind of changes affect the host lattice due to the presence of the disturbing guest molecule, and what kind of lattice relaxation can be expected? Can one understand the apparently selective orientation of the asymmetric acridine molecule within the fluorene lattice as implied by the kinetic results [7]?

With these questions in mind we present here the results of calculations based on an atom–atom intermolecular potential. This method has been used successfully to deal with problems of photochemical behaviour in pure and mixed molecular crystals [5]. The task is now different because an intermolecular atom transfer is involved in the reaction starting from the precursor, a pair of photoexcited guest (acridine) and fluorene host molecules, and ending with the product, an acridinyl–fluorenyl radical pair.

2. Calculation details and input parameters

The strategy and techniques for the calculation of the equilibrium packing in the neighbourhood

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(North-Holland Physics Publishing Division)

of a guest molecule have been described in detail before [5,6]. The total intermolecular potential energy of the guest molecule and its immediate environment of host molecules is minimized with respect to molecular position and orientation. The energies are sums of atom–atom potentials, here the Righini–Califano nitrogen set [8], together with a term for the effect of electronic excitation. This change of potential is taken into account by an additional term $-A/R^6$ to represent the increased interaction of the excited molecule with its neighbours; R is the centre of mass separation of the molecules on different sites. The proportionality factor can be estimated to some extent on the basis of the change of polarizability of the molecule upon excitation [9]. A range of A-values 0.12–0.22 kJ mol^{-1} nm^6 has been evaluated from anthracene and is used also here. Since the effect of excitation turned out to be small, the high end of this range has been used.

The spherical region of the crystal in which molecules were allowed to move had a radius of 1.4 nm, containing sixty-eight molecules. The calculations were started with all molecules in the positions as given by the X-ray structure and the guest placed substitutionally at one site. The molecular positions and orientations were then allowed to relax so as to minimize the sum of all atomic pair potential energies. The interaction between the molecules can be assumed to displace mainly the center of mass and the orientation of each molecule as a whole.

The resulting energies are obtained as those of

(a) the individual guest molecule alone,

(b) the pair energy of the guest and one fluorene neighbour in a specific site, and

(c) all sixty-eight molecules together.

The atomic coordinates were taken from the X-ray structure of the fluorene crystal [10]. The guest was placed substitutionally in a chosen fluorene site with the same centre of mass. The intramolecular coordinates of acridine were taken from ref. [11]. The small deviations from exact substitutional guest site as indicated by the experimental results [2] can be ignored at the present level of detail in the calculations. The acridinyl radical was created by attaching a hydrogen atom to the nitrogen atom in the geometry of a planar aromatic N–H fragment with the distance $r_{NH} =$ 0.097 nm. Similarly a hydrogen was removed from the fluorene methylene group in order to create the fluorenyl radical pair partner. As shown experimentally [1,2], the remaining hydrogen in the central fluorenyl group rearranges itself to a planar aromatic C–H fragment configuration which has been chosen for our calculations. Again small, but experimentally established, deviations from an exact planarity of the whole molecule are ignored for the moment.

Recently, refined X-ray data have become available for the fluorene lattice [12–14]. Although slightly different lattice parameters and atomic coordinates are reported, and even a slight V shape is deduced for the fluorene molecule, checks with these new parameters showed that the calculated energies do not differ by more than 1 kJ mol^{-1} per molecule. As such differences are too small to be significant at our level of calculation it was decided not to repeat all calculations already completed with earlier lattice parameters and atomic coordinates [10].

As our interest focuses mainly on a possible selective acridine–fluorene reaction geometry it is important, however, that the recent X-ray data confirm a regular lattice for fluorene with no detectable disorder with respect to the arrangement of the central CH_2 groups. Such a disorder has been identified in the very similar crystal of dibenzofuran but has been positively excluded for the fluorene lattice [13]. Hence, without additional interactions, a guest molecule like acridine with only C_{2v} symmetry should be able to occupy two orientations in the same substitutional site which are inequivalent with respect to the CH_2 group of the fluorene neighbours, in particular the reactive neighbour site.

3. Results

The results for the main ground state configurations are collected in table 1 and are now explained in more detail.

3.1. *Fluorene as "guest" in fluorene*

This configuration of the pure crystal lattice itself provides a standard test for the calculation

Table 1
Molecular packing energies in kJ mol^{-1} for various guest/host combinations

Guest/host combinations [a]:	F/F	A/F		·AH/·FH
Relative orientation [b]:		(1)	(2)	(1) [c]
(a) guest mol alone	−181.87	−181.06	−178.2	−184.9
(b) guest–host pair	−345.37	−344.11	−338.4	−345.4
(c) unit of 68 mol	−8057.3	−8054.6	−8050.6	−8055.3

[a] F fluorene, A acridine, ·FH fluorenyl, ·AH acridinyl.

[b] Relative orientations: (1) nitrogen of A close to CH_2 group of F neighbour; (2) nitrogen of A more distant to CH_2 group.

[c] Values for orientation (2) differ by less than 0.1% in case (b) and less than 0.02% in (c).

as well as a set of reference numbers (see first column in table 1). Besides the energies listed, the program gives changes in the molecular positions and orientations. The "guest", i.e. a host fluorene molecule selected for individual study, rotates by no more than 1.2° about any axis and its centre of mass is moved by 0.0014 nm. The neighbour fluorene molecules are rotated and displaced even less.

The same test has been applied in earlier calculations [5]. In each of naphthalene and anthracene the total potential energy of the environment was minimized for angle and centre of mass displacement of a target molecule and twenty neighbours. The result was compared with the X-ray structure. The largest angular deviations are, in both cases, 2.1°. The largest centre of mass displacement is in naphthalene (3×10^{-3} nm). The outcome of fluorene indicates a satisfactory application of the procedures.

3.2. *Acridine as a guest in fluorene*

When acridine is placed substitutionally into the A lattice site of the fluorene it can assume two orientations:

(1) the nitrogen is close to the translationally equivalent fluorene molecule along the crystalline *b*-axis.

(2) the nitrogen points away from this fluorene methylene group, and photoreaction cannot occur unless there is a large disturbance to the molecular packing.

The second and third column in table 1 show, however, energies for the two orientations differing by only a few kJ mol^{-1}. On the basis of the molecular packing energies, orientation (1) is favoured over (2) by no more than 4 : 1.

The centre of mass of the acridine molecule is displaced only 0.01 nm in the *ab*-plane and not at all along the crystalline *c*-axis. This result confirms the general experimental finding that all changes, including those due to the H-transfer photoreaction, are limited to the crystalline *ab*-plane. This has therefore been termed the reaction plane [2]. Changes in the orientation of the molecules are also very small.

Other guest molecules which can be easily doped into the fluorene lattice, like phenazine, dihydrophenazine and anthracene have also been investigated. The resulting energies turn out to be all very similar to those listed in table 1 for acridine, with comparably small displacements and changes of orientation. This can be considered as another sign of the "stiffness" of the fluorene lattice. When the guest molecule can be fitted into the lattice at all, it replaces a fluorene nearly substitutionally and the packing energies turn out to be very similar. In the case of dihydrophenazine, the energy minimum in the unrelaxed lattice is at −171.3 kJ mol^{-1}, with displacements from the host lattice site of 0.0024 and 0.0007 nm in the x and y directions. There are rotations of about 1.9° of both in-plane axes from those of the displaced host.

When the radical pair product is incorporated in the lattice the resulting energies are very similar (last column in table 1) as expected from the minor alteration of the overall guest molecular structure induced by just the transfer and rearrangement of hydrogen atoms.

3.3. Electronically excited guest molecules

Photoreaction occurs from the excited triplet state of the guest molecule acridine [3,4]. Molecular packing calculations involving excited guest molecules have in other cases provided considerable insight into photoreactive pathways and stereospecificity [5]; in particular the lattice response to the local excitation can be simulated in its time development by allowing an increasing number of host molecules to relax under the additional potential $-A/R^6$ switched on with the excitation of the molecule. Here, allowing only the acridine molecule to move within the lattice results in a packing energy of -253.4 kJ mol^{-1} for the guest alone and -413.9 kJ mol^{-1} for the guest–host pair as compared with the ground state values shown in the second column of table 1. Allowing both members of the guest–host pair to move lowers the energies slightly to -254.6 and -414.1 kJ mol^{-1} respectively. These energies decline slowly as more molecules are included in the relaxing set. Finally, when all sixty-eight molecules are allowed to move the energies are -272.9 and -435.8 kJ mol^{-1}. More important is the additional result that in all these calculations, displacements and reorientations away from the starting positions in the ground state turn out to be very small. As a further example, excited dihydrophenazine [15] (using $A = 0.22$ kJ mol^{-1} nm^6) is displaced by 0.02 and -0.001 nm in the x and y directions and displaced away from the host orientations by a maximum of 2.6°. One can compare this result with earlier calculations [5,9,16]. The response in orientations to excitation in those cases covers a wide range, up to about 9° change in excited 9-CNA in its own crystal. From this and other results we believe that the fluorene lattice is one of the "stiffest" of those so far studied, allowing little movement by guests away from the location on the displaced host molecule either in ground or electronically excited states.

4. Discussion

Within experimental accuracy all acridine molecules in the fluorene lattice react with the same kinetics. The key observation [3] is that the decrease in time of the acridine population is fitted satisfactorily by a single-exponential decay function. There is no evidence of a second slow decay corresponding to a non-photochemically active acridine orientation. An outstanding problem is to rationalize this observation, i.e. the fact that, of the two feasible orientations of the acridine as a substitutional guest, only one is populated. Alternatively one would have to assume that the acridine molecules can change between the two possible orientations at a rate which would have to be fast compared to the reaction rate (3×10^4 s^{-1} at 300 K). Such a rotational mobility is predicted to produce an observable nuclear relaxation rate in the host crystal which is not observed experimentally. In addition, magnetic interactions like the hyperfine splittings could be affected, a result which has not been observed experimentally. Therefore we can conclude that after the crystal is formed from melt or solution, and the cage of host molecules surrounding the guest established, there is little possibility of reorienting the acridine molecule at temperatures well below the melting point. In a lattice without vacancies the potential barrier opposing the required rotation, even allowing for molecular flexibility, is high enough to lock the molecule in its initial orientation. Reorientation is easier if there is a vacancy adjacent to the guest. It has been estimated that in the anthracene crystal vacancies are built in to the forming crystal, grown at 300 K, at a concentration of about 4.8×10^{-3}, far higher than the calculated equilibrium concentrations of 10^{-15} [17]. If we accept that the estimate applies to fluorene, we see that in a mixed crystal of 1/1000 mole per mole the concentration of vacancies adjacent to a guest is already very low, of the order 10^{-5}–10^{-6}. We conclude that guest reorientation in the formed lattice, below the melting point, may be discarded as a mechanism.

It is more promising to discuss whether the conditions at the time of crystal formation can favour the deposition of guest molecules in one of the two orientations over the other. The short-range forces that govern the packing energy are now only a part of the forces acting on a guest molecule at the growing crystal surface. Long-range forces can have an effect on the orientation of a guest as it approaches and offers itself for incorporation. The possibilities are forces between the molecular dipole moments or moments of higher order, and hydrogen bond interaction, again electrostatic in type, but localized in the methylene group of fluorene and the acridine nitrogen. The latter are discussed first.

4.1. Hydrogen bonding

An estimate can be attempted for the strength of the H-bond formed in the crystal. The bond is of the C–H...N type, of which an example has been studied in detail in solid HCN. The change in the C–H stretching frequency due to hydrogen bonding has been determined as $\Delta\nu_{\mathrm{C-H}} = 180$ cm^{-1} [18]. General empirical equations are known [19] relating the enthalpy of the hydrogen bond to the observable change in the CH-stretching frequency. From that we can conclude for a linear C–H...N bond between acridine and fluorene in solution a bond energy may be as great as 12 kJ mol^{-1}, much greater than the small energy differences in the calculated packing energies based on van der Waals interactions only.

The above H-bond energy is estimated as follows: Enthalpies for pyridine adducts of O–H acids with an O–H...N hydrogen bond follow quite well the following correlation [19]:

$$-\Delta H(\mathrm{kJ\ mol^{-1}}) = 0.0126\,\Delta\nu_{\mathrm{O-H}} + 0.43 \pm 0.9. \tag{1}$$

For the N–H...N hydrogen bond the changes $\Delta\nu_{\mathrm{s}}$ are related

$$\Delta\nu_{\mathrm{O-H}} = 1.6\,\Delta\nu_{\mathrm{N-H}}. \tag{2}$$

In the case of acridine doped in fluorene a C–H...N hydrogen bond can be formed. Such a bond, although in this case linear, has been studied extensively between HCN molecules in the gas phase as well as in solids [18]. For the crystal HCN the C–H...N bond length of 0.32 nm compares well with the situation in the fluorene lattice. The change in the C–H stretching frequency due to hydrogen bonding (reference gas phase) is determined to be

$$\Delta\nu_{\mathrm{C-H}} = 180\ \mathrm{cm^{-1}}. \tag{3}$$

Identifying this frequency change (3) with $\Delta\nu_{\mathrm{O-H}}$ or $\Delta\nu_{\mathrm{N-H}}$ in eqs. (1) and (2) we calculate a hydrogen bond strength

$$-\Delta H = 11.3 \text{ or } 17.2\ \mathrm{kJ\ mol^{-1}}. \tag{4}$$

Furthermore, a fairly strong H-bond is reported between phenol (C_6H_5OH) and acridine in CCl_4 solution [20]. The frequency change $\Delta\nu_{\mathrm{O-H}} = 520$ cm^{-1} is correlated to an enthalpy of

$$-\Delta H = 27.6\ \mathrm{kJ\ mol^{-1}}. \tag{5}$$

It may be concluded that for a linear C–H...N intermolecular H-bond between fluorene and acridine in solution an enthalpy of at least 12 kJ mol^{-1} is expected from this analysis.

In the fluorene crystal, acridine has been established to enter the lattice substitutionally in its four sites per unit cell. If there is no orientational preference only half the acridine molecules are in the situation where the aza-group is close to the fluorene methylene group of the closest neighbour along the bond from which photochemical H-abstraction can occur; even in this geometry the closest methylene C–H bond of fluorene and the potential H-bond direction from the acridine aza-group are nearly at right angles, and only weak H-bonding is expected in the lattice. No experimental evidence has been found for even a weak acridine–fluorene complex in the ground state.

In the course of crystal growth however the guest orientation allowing H-bonding will be favoured for an acridine approaching a fluorene already laid down at the growing surface. The direction of crystal growth is known to be in the crystalline *ab*-plane for fluorene, so that attractive force between the fluorene CH_2-group and the acridine aza-group can have an influence so long as acridine is mobile during the approach phase to a growing fluorene surface.

It seems possible therefore that incipient hydrogen bonding is responsible for a selective orientation of the acridine molecule within the fluorene lattice. If we suppose that the approach is by an acridine in an orientation giving a linear C–H...N bond, and compare it with an orientation allowing no bond at all, then the energy difference could be as much as the 12 kJ mol^{-1} quoted above. At 300 K the Boltzmann factor is $> 10^2$, in favour of the photochemically favoured orientation.

4.2. Electrostatic "directing" forces

Electrostatic forces between an approaching acridine and molecules of fluorene at the growing crystal face act at still longer range. The forces between dipole moments fall off as R^{-4} so that, as a generalization, one can say that they have an orienting effect on the acridine before the incipient H-bond acts, and before the influence is felt of the local van der Waals forces that will eventually determine how the acridine is packed into the structure. However at any growing face there are as many inward as outward facing fluorenes, and the effect of whole-molecule dipoles cancels out. It is perhaps possible that there the net charge on a methylene H, associated with the C–H bond dipole, could act on the nitrogen of an approaching acridine to promote a favourable packing of this acridine, but we are not able to give detailed support. We think that the energy of hydrogen bonding, acting to favour one of the two acridine orientations at the time of guest incorporation into the lattice, is the most likely hypothesis. Again we emphasize that due to the nearly perpendicular C–H...N bond geometry in the crystal lattice, this hydrogen bonding energy is expected to be negligible in the bulk crystal and hence of no importance for the intermolecular forces govern-

Table 2
Fluorene, $C_{13}H_{10}$ [a)]

$M_r = 166.22$, orthorhombic, Pnma, $a = 8.487(3)$, $b = 18.898(9)$. $c = 5.717(3)$ Å,
$V = 916.9(7)$ Å, $Z = 4$, $D_m = 1.206$, $D_x = 1.204$ g cm^3, MoKα, $\lambda = 0.71073$ Å, $\mu = 0.6$ cm^{-1}, $F(000) = 352$, $T = 295$ K,
$R = 0.039$ for 397 reflections

C and H positions by least-squares refinement				10^{-3} U_{eq}/U_{iso} (Å^2)
C(1)	0.6453(2)	0.2114(1)	0.5697(3)	5.12
C(2)	0.5746(3)	0.1631(2)	0.7186(5)	6.93
C(3)	0.5934(3)	0.0913(2)	0.6731(6)	8.16
C(4)	0.6798(3)	0.0689(2)	0.4861(6)	8.47
C(5)	0.7501(3)	0.1163(2)	0.3363(4)	7.52
C(6)	0.7322(2)	0.1879(1)	0.3785(4)	5.47
C(7)	0.7965(5)	1/4	0.2444(7)	6.63
H(2)	0.516(2)	0.1799(11)	0.857(4)	7.1(7)
H(3)	0.546(3)	0.0579(13)	0.783(4)	10.3(10)
H(4)	0.693(2)	0.0181(15)	0.450(4)	9.2(8)
H(5)	0.811(3)	0.1016(14)	0.208(5)	9.2(9)
H(71)	0.917(4)	1/4	0.247(6)	10.3(13)
H(72)	0.756(4)	1/4	0.083(6)	9.1(11)

C positions corrected for libration. H positions corrected to idealized C–H internuclear distance 1.08 Å			
C(1)	0.6451	0.2113	0.5701
C(2)	0.5740	0.1628	0.7199
C(3)	0.5930	0.0908	0.6740
C(4)	0.6799	0.0683	0.4860
C(5)	0.7505	0.1158	0.3354
C(6)	0.7326	0.1876	0.3777
C(7)	0.7972	1.4	0.2429
H(2)	0.510	0.1816	0.871
H(3)	0.541	0.0539	0.796
H(4)	0.694	0.0129	0.446
H(5)	0.820	0.0993	0.187
H(71)	0.924	1/4	0.247
H(72)	0.761	1/4	0.062

[a)] The molecule is slightly folded (dihedral angle about 1.2°) in agreement with ref. [13].

ing the photochemical reaction [1–4] from the precursor to the product state.

Acknowledgement

DS would like to thank the Australian National University for a productive and enjoyable stay as visiting fellow in 1985/86.

Appendix

The preceding (table 2) unpublished results on the crystal and molecular structure of fluorene have been provided by Professor J. Trotter [14], Department of Chemistry, University of British Columbia, Vancouver, Canada. Further details can be obtained from Professor Trotter. Atom numbering as in ref. [10].

References

[1] R. Furrer, M. Heinrich, D. Stehlik and H. Zimmermann, Chem. Phys. 36 (1979) 27;
V. Macho, J.P. Colpa and D. Stehlik, Chem. Phys. 44 (1979) 113.

[2] D. Stehlik, R. Furrer and V. Macho, J. Phys. Chem. 83 (1979) 3440.

[3] B. Prass, F. Fujara and D. Stehlik, Chem. Phys. 81 (1983) 175;
J.P. Colpa, B. Prass and D. Stehlik, Chem. Phys. Letters 107 (1984) 469.

[4] D. Stehlik and H.M. Vieth, Mol. Cryst. Liquid Cryst. 93 (9183) 83;
D. Stehlik, in: Photoreaktive Festkorper, ed. H. Sixl (Wahl, Karlsruhe, 1984) p. 1.

[5] D.P. Craig, R.N. Lindsay and C.P. Mallett, Chem. Phys. 89 (1984) 187, and references therein.

[6] D.P. Craig, B.R. Markey and A.O. Griewank, Chem. Phys. Letters 62 (1979) 223.

[7] J.P. Colpa and D. Stehlik, Chem. Phys. 81 (1983) 163.

[8] R. Righini and S. Califano, Chem. Phys. 17 (1976) 45.

[9] D.P. Craig and C.P. Mallett, Chem. Phys. 65 (1982) 129.

[10] D.M. Burns and J. Iball, Proc. Roy. Soc. A 227 (1955) 200.

[11] D.C. Philips, F.R. Ahmed and W.H. Barnes, Acta Cryst. 13 (1960) 365.

[12] V.K. Belsky, VB.E. Zavodnik and V.M. Vozzhennikow, Acta Cryst. C 40 (1984) 1210.

[13] R.E. Gerkin, A.P. Lundstedt and W.J. Reppart, Acta Cryst. C 40 (1984) 1892.

[14] J. Trotter, private communication.

[15] B. Prass, C. von Borczyskowski, P. Steidl and D. Stehlik, J. Phys. Chem., submitted for publication.

[16] K. Norris, P. Gray, D.P. Craig, C.P. Mallett and B.R. Markey, Chem. Phys. 79 (1983) 9.

[17] D.P. Craig, J.F. Ogilvie and P.A. Reynolds, J. Chem. Soc. Faraday II 72 (1976) 1603.

[18] R.E. Hoffman and D.F. Hornig, J. Chem. Phys. 17 (1979) 1163.

[19] M.D. Joesten and L.J. Schaad, Hydrogen bonding (Dekker, New York, 1974).

[20] W.R. Jones, R.N. Seel and N. Sheppard, Spectrochim. Acta A 25 (1969) 385.