A Study of the Disordered Low-temperature Structure of Acenaphthylene, $C_{12}H_8$, using Semi-empirical Potential-energy Calculations

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Semi-empirical potential-energy calculations have been used to investigate the relative stability of twelve different possible ordered structures for acenaphthylene, $C_{12}H_8$, at low temperatures. The twelve structures considered represent all the different combinations of the various molecular orientations, in three crystallographically inequivalent sites, revealed by the neutron diffraction study of the structure at 80 K. Of the twelve structures investigated, ten were found to have total potential energies within *ca.* 2.5 kJ mol^{-1} of each other, thus providing strong support for the belief that the room-temperature structure is very disordered with many different molecular orientations present. The probability of the occurrence of each of the twelve structures, calculated according to a Boltzmann partition of the energy at 80 K, yields values for the site occupancies of individual molecular sites in good agreement with values obtained from the neutron diffraction experiment. Substantially the same results are obtained with the two different potentials used for comparison.

In a previous paper[1] we reported an analysis of the low-temperature crystal structure of acenaphthylene, $C_{12}H_8$, using neutron-diffraction data recorded at 80 K. Though well below the known[2] phase transition at 130 K the structure was found to be disordered. The analysis revealed quite a complex structure, with average space group $P2_1nm$ and 8 molecules per unit cell. Note that this is a non-standard space-group setting which was used to maintain consistency with the room-temperature cell (space-group *Pbam*). In the structure there were three independent (symmetry-unrelated) types of molecular site, A, B, and C (see Figure 1 and Table 1 for cell data). Site B was found to be totally ordered but sites A and C were disordered. The solution of the structure was only made possible because of the fact that the ordered site B allowed a good determination of the molecular geometry which could then be used for the molecules found in sites A and C. Use of difference-Fourier syntheses to reveal fragments of different molecular orientations in these sites, followed by the use of a powerful constrained least-squares refinement program,[3] allowed a description of the disordered structure to be made using a comparatively small number of variables, and this gave good agreement between observed and calculated intensities. Nevertheless the complexity and extent of the disorder revealed by the analysis is possibly unique amongst solved crystal structures, and some independent check on the legitimacy of the model of the disorder is desirable. In this paper we describe semi-empirical potential-energy calculations, which were carried out in order to establish whether the description of the disordered structure derived from the neutron diffraction is a valid one.

The average structure revealed by the neutron experiment showed that site B was ordered, site A contained six different molecular orientations, and site C contained two different orientations. The occurrence of the disorder may be readily understood in a qualitative way, as revealed by the drawing of the different molecular orientations occurring in site A shown in Figure 2. It is seen that the molecule presents to its environment eight protruding hydrogen atoms, which are almost identical in position for any one of the six observed molecular orientations. A similar situation applies to the two molecular orientations observed in site C (see Figure 3). Of the different orientations that were observed, 55% of the molecules in site A were found to be of the type A1 (see Figure 2) and 71% of the molecules in site C were found to be of type C1 (see Figure 3). It might therefore be supposed that the completely ordered structure consisting of molecular orientations A1, B, and C1 would represent the true low-temperature structure, which would be attained if a sufficiently low temperature were reached. However, since the Bragg diffraction experiment only allows the determination of the occupancy factors for single molecular sites and cannot provide any information concerning the joint occupancy of two or more sites, it is by no means clear that the structure consisting of entirely A1, B, and C1 molecular orientations is the most stable. In this paper we use semi-empirical potential-energy calculations to establish the relative stability of this and other possible ordered structures, in order to gain insight into the reasons for the occurrence of the disorder. We confine our attention to the twelve ordered structures which can be made up from combinations of the six different orientations for site A and the two different orientations for site C. Of the six orientations in site A only A1 and A4 have a molecular *m*-plane coincident with the space group *m*. Consequently, to carry out the calculations for the individual structures the average space-group symmetry had to be relaxed. The *n*-glide symmetry element was therefore used to relate the A and B molecules at 0*c* to those at 0.5*c*. For the C molecules constituting the molecular layers at 0.25*c* and 0.75*c* no such relaxation of symmetry was necessary and for these the full space-group symmetry was maintained. In Figure 1 we show the molecular orientations relative to the *n*-glide and 2_1 symmetry elements of the average space-group for the structure A5BC1. It is seen that the molecules depicted satisfy the *n*-glide but not the 2_1 axis. It should be noticed that if the 2_1 axis is used instead of the *n*-glide, the molecular layer at 0.5*c* would be the mirror image of the one depicted. Reference to this point is made in the discussion.

Table 1. Cell data for acenaphthylene at 80 K (after Wood *et al.*[1])[a]

Site	Average site-symmetry	Approximate centre-of-mass position	Number of disordered molecular orientations
A	*m*	0.25 0.25 0.0	6
B	*m*	0.75 0.75 0.0	1
C	1	0.75 0.25 0.25	2

[a] Space group $P2_1nm$, a = 7.584 Å, b = 7.589 Å, c = 27.851 Å; cell volume = 1 603.0 Å^3; 8 molecules per cell.

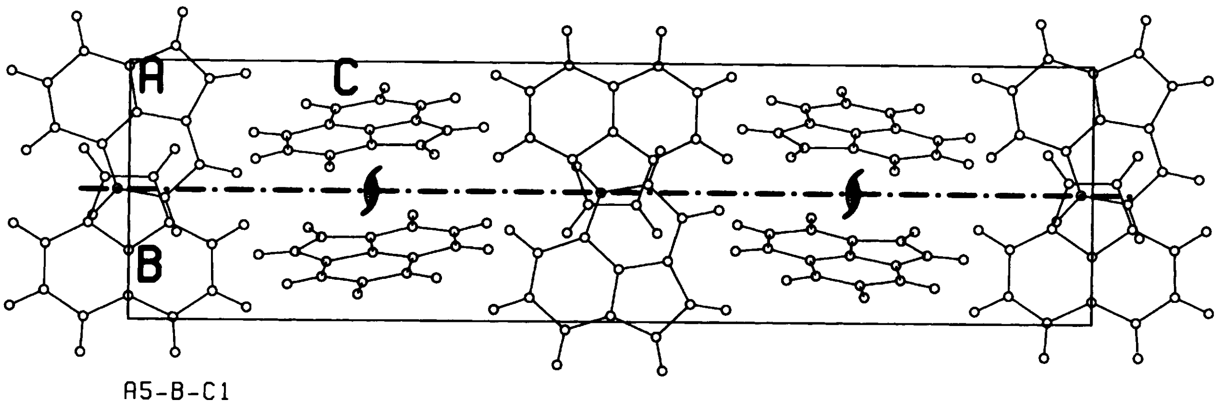

Figure 1. The unit cell of one possible ordered structure of acenaphthylene projected onto the *b–c* plane, showing the three distinct molecular sites A, B, and C, in relation to the symmetry elements of the space-group $P2_1nm$. Note that for this structure (A5BC1) the *n*-glide plane is satisfied by all molecules but the 2_1 axis is not. To obtain the full average symmetry the enantiomorphic structure (A6BC1) must be equally probable

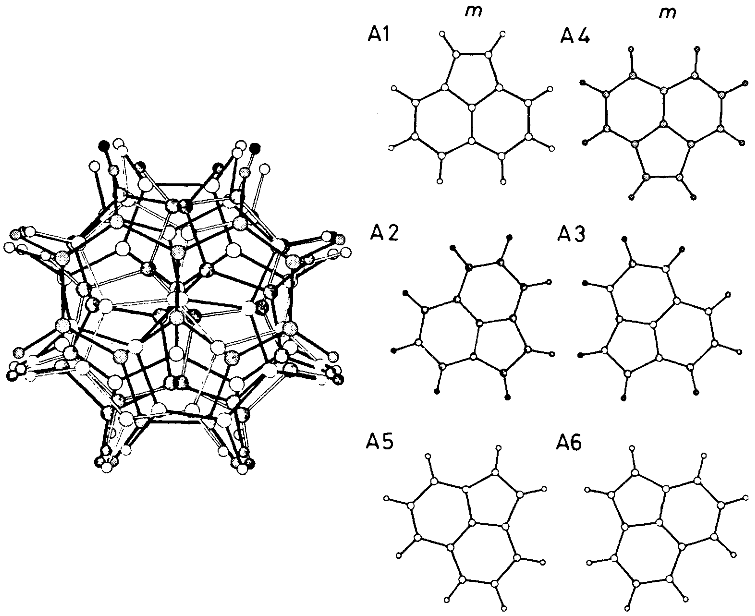

Figure 2. The overlay of the six different molecular orientations, A1— A6, observed in the disordered site A (after Wood *et al.*[1])

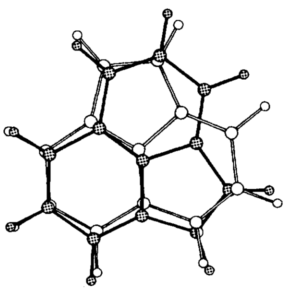

Figure 3. The overlay of the two different molecular orientations, C1 (dark bonds) and C2 (light bonds), observed in the disordered site C (after Wood *et al.*[1])

Structures derivable from combinations of the different molecular orientations when all the symmetry elements are removed are too numerous to consider.

Although a computer program[4–6] able to perform the types of calculation envisaged was available to us, this was not capable of handling a system in which three symmetry-unrelated molecular sites were present in the unit cell, as is the case for acenaphthylene. Consequently, a new program was written for the present study and the method used is briefly described in the next section.

Potential-energy Calculations

Intermolecular Potential.—Additive non-bonded atom–atom empirical potentials of the kind described by Kitaigorodskii[7] are generally accepted to provide a good approximation to the intermolecular potentials of organic materials, particularly hydrocarbons. For a review of the use of such potentials in solid-state chemistry see Ramdas and Thomas.[8] In the present work we have used a Buckingham '6-exp' interaction of the form

$$\Phi_{i,j} = -ar_{i,j}^{-6} + b\exp(-cr_{i,j}). \qquad (1)$$

For comparison we used two different sets of the empirical parameters *a*, *b*, and *c*. Parameter set I was taken from Kitaigorodskii[7] and parameter set II was set IV of Williams.[9] These values are given in Table 2. These were chosen from a set

Table 2. Potential parameters *a,b,c* of equation (1) used in the calculations. Set I was taken from Kitaigorodskii[7] and set II was set IV of Williams[9]

Parameter set I

	a/kJ Å^6 mol^{-1}	b/kJ mol^{-1}	c/Å^{-1}
C–C	1 497.9	17.6×10^4	3.58
C–H	644.3	17.6×10^4	4.12
H–H	238.5	17.6×10^4	4.86

Parameter set II

	a/kJ Å^6 mol^{-1}	b/kJ mol^{-1}	c/Å^{-1}
C–C	2 376.5	34.991×10^4	3.60
C–H	523.0	3.668×10^4	3.67
H–H	114.2	1.110×10^4	3.74

of five parameter sets tested by Markey,[10] who used each to obtain an energy-minimized structure for naphthalene. Using the criterion that the potential energy calculated at the energy-minimized structure should be as close as possible to that calculated at the observed *X*-ray crystal structure position, he concluded that the Williams set IV[9] performed the best and the Kitaigorodskii[7] the least well of the five.

Recently there has been a move towards including an additional Coulombic term of the form $q_i q_j r_{ij}^{-1}$ in equation (1). Such a term is undoubtedly of importance for organic molecules containing nitrogen or oxygen[11] and there is evidence that even for hydrocarbons, though small, the term is not negligible.[12,13] However, although the inclusion of a term of this type in the examples given in ref. (13) gives a better fit to observed crystal structures in many cases, it does not appear to be uniformly successful. In addition, it is by no means clear that the use of such a potential derived from alternant aromatic hydrocarbons should be transferable to a non-alternant hydrocarbon like acenaphthylene. The inclusion of the term represents, moreover, a considerable increase in the complexity of the calculation since there are convergence problems associated with this longer-range potential. In the absence of any direct experimental or theoretical estimation of the charge distribution on acenaphthylene, and in view of the increase in computation, it seemed inappropriate at this time to try to take account of this Coulombic term. It was considered that the use of the two dissimilar potentials chosen on the basis described above would provide a reasonable safeguard against the possibility that the results were potential dependent.

Representation of Structures.—The molecular geometry derived from the neutron-data analysis was used throughout, for all molecular sites. This molecular geometry had been constrained to be planar with 2 *mm* symmetry. Atomic positional co-ordinates relative to a local orthonormal axial system can be found in Wood *et al.*[1] Rotational matrices, ***V***, and translational vectors, ***T***, for transforming these local co-ordinates into unit-cell co-ordinates, for each of the molecular orientations A1—A6, B, and C1,C2 were also given.

For each ordered structure the initial positional parameters used were generated by applying the appropriate ***V*** and ***T*** for the A, B, and C sites to the molecular co-ordinates, together with symmetry transformations to generate the rest of the molecules in the unit cell. For sites A and B only the *n*-glide transformation was required, but for the C sites both the *m*-plane and *n*-glide were required. Subsequent relaxation of the structure preserved this symmetry, and also maintained the rigid body geometry of the molecule.

The total interaction energy, *U*, was computed as the sum of all non-bonded pair interactions (1), *i.e.*

$$U = \frac{1}{2}\sum_{h,h'}\sum_{i,i'}\sum_{j,j'}\left[\frac{a_{j,j'}}{r^6_{h,i,j,h',i',j'}} + b_{j,j'}\exp(-c_{j,j'}\, r_{h,i,j,h',i,j'})\right] \quad (2)$$

where *h,h′* go over all unit cells; *i,i′* = 1,2, . . . 8 go over all molecules in the *h*th and *h′*th cells, respectively; *j,j′* = 1,2, . . . 20 go over all atoms in the *i*th and *i′*th molecules, respectively; $r_{h,i,j,h',i',j'}$ is the distance between the *j*th atom of the *i*th molecule in the *h*th cell and the *j′*th atom of the *i′*th molecule in the *h′*th cell. Note $i \neq i'$ for $h = h'$.

The summation was taken over all pairs within a range of 12 Å. This range which required the inclusion in the calculation of three unit cells in the *a* and *b* directions but only one in the *c* direction, was considered sufficient to achieve satisfactory accuracy (see Kitaigorodskii[7] and Markey[6]). Since it could not be expected that any one of the twelve ordered structures derived directly from the experimental results would be at an energy minimum, we followed the usual procedure of allowing each structure to relax into its local minimum-energy configuration before any comparisons were made. The total interaction energy for each structure was minimized with respect to the rotations, ***V***, and translations, ***T***, of each molecule type, and also with respect to changes in the cell parameters *a*, *b*, and *c*. The rotation matrices ***V*** were parametrized using the Cayley–Klein or quaternion parameters,[4–6] but for later presentation they have been expressed in terms of the more commonly used Euler angles,[14] θ, φ, and ψ, *i.e.*

$$\boldsymbol{V} = \begin{array}{ll} \cos\psi\cos\varphi - \cos\theta\sin\varphi\sin\psi & \\ -\sin\psi\cos\varphi - \cos\theta\sin\varphi\cos\psi & \\ \sin\theta\sin\varphi & \\ \quad\cos\psi\sin\varphi + \cos\theta\cos\varphi\sin\psi & \sin\psi\sin\theta \\ \quad -\sin\psi\sin\varphi + \cos\theta\cos\varphi\cos\psi & \cos\psi\sin\theta \\ \quad -\sin\theta\cos\varphi & \cos\theta \end{array} \quad (3)$$

Each molecule type thus requires, in general, three orientational and three translational parameters, but taking into account the fact that the B molecule was constrained to strictly adhere to the *m*-symmetry of the average space group, and one *x*-co-ordinate must be fixed to define the origin of the system, a total of (at most) 17 parameters are required to define the structure. For structures containing either A1 or A4 the number of parameters was further reduced by three since the rotation matrices, ***V***, for these molecules were also restricted to conform to the *m*-symmetry.

Relaxation Process.—We used the Newton method to adjust the above 17 (at most) parameters in order to proceed toward the energy minimum. Let ***X*** be a vector whose components are the above-mentioned parameters defining the crystal structure and $\boldsymbol{X}_1$ is the initial vector obtained from the reported experimental structure. The *K*th relaxation step involves the move from $\boldsymbol{X}_K$ to $\boldsymbol{X}_{K+1}$ according to the following formula:

$$\boldsymbol{X}_{K+1} = \boldsymbol{X}_K - [\nabla^2\, U(\boldsymbol{X}_K)]^{-1}\, \nabla U(\boldsymbol{X}_K) \quad (4)$$

where $[\nabla^2\, U(\boldsymbol{X}_K)]^{-1}$ is the inverse of matrix $\nabla^2\, U(\boldsymbol{X}_K)$ which consists of second derivatives of the potential energy with respect to the parameters, and $\nabla U(\boldsymbol{X}_K)$ contains first derivatives. These derivatives are as follows:

$$\frac{\partial U}{\partial \alpha} = \sum_{h}\sum_{h'}\sum_{i}\sum_{i'}\sum_{j} f_1(r)\, \boldsymbol{X}_j \frac{\partial \boldsymbol{X}_j}{\partial \alpha} \quad (5)$$

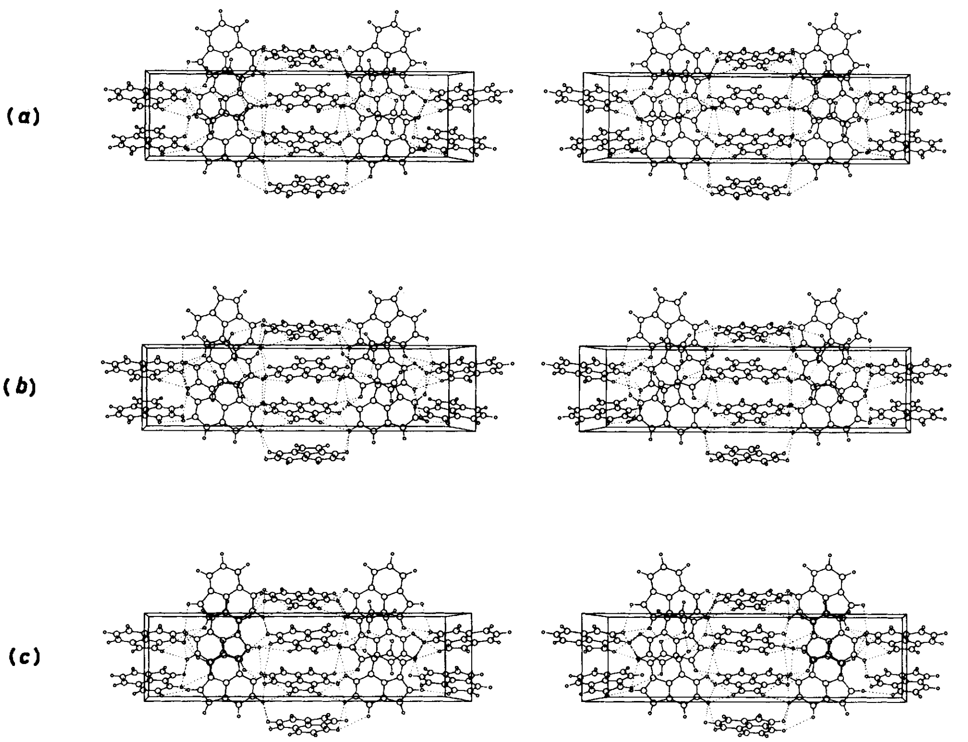

Figure 4. Stereoplots viewed down *b* of the three lowest energy structures: (*a*) A1BC1; (*b*) A1BC2; (*c*) A5BC1. All H–H contacts less than 3.0 Å are shown by dotted lines

$$\frac{\partial^2 U}{\partial\alpha\partial\beta} = \sum_h \sum_{h'} \sum_i \sum_{i'} \left[\sum_j f_1(r)\, \boldsymbol{X}_j \frac{\partial^2 \boldsymbol{X}_j}{\partial\alpha\partial\beta} + \sum_j f_1(r) \frac{\partial \boldsymbol{X}_j}{\partial\alpha} \frac{\partial \boldsymbol{X}_j}{\partial\beta} + f_2(r) \left(\sum_j \boldsymbol{X}_j \frac{\partial \boldsymbol{X}_j}{\partial\alpha} \right) \left(\sum_j \boldsymbol{X}_j \frac{\partial \boldsymbol{X}_j}{\partial\beta} \right) \right] \quad (6)$$

where,

$$f_1(r) = [6ar^{-7} - bc\exp(-cr)]/r$$

and

$$f_2(r) = [-42ar^{-8} + bc^2\exp(-cr) - f_1(r)]/r^2.$$

Here *h* and *h'* run over all molecules, and *i* and *i'* run over all atoms of molecules *h* and *h'* respectively. $\alpha,\beta = 1,2,\ldots\alpha_m$ are parameters describing the structure.

Since the algorithm used to relax the structure considers all the molecular positions and cell dimensions explicitly, it is very effective, and *ca.* 10 steps were usually sufficient to bring the system to the energy minimum.

Results and Discussion

The results of the energy minimizations using both parameter sets I and II for all twelve structures are presented in Table 3. It is noted that there are pairs of structures, *e.g.* A2BC1 and A3BC1, having the same energy. These structures are in fact enantiomorphs, related by an *m*-plane normal to *c*. For all but two of the twelve structures (A2BC2 and A3BC2) the final energies were to within *ca.* 2.5 kJ mol^{-1} of the energy of the most stable configuration (A1BC2, closely followed by A1BC1). This result was essentially the same for the two parameter sets, although the actual energies for parameter set II were generally *ca.* 6 kJ mol^{-1} lower. In Figure 4 we show, for comparison, stereoscopic projections of the two most stable structures, together with one of the less stable ones. In these figures all intermolecular H–H contacts less than 3.0 Å are indicated by dotted lines.

In Table 3 we also list, for each of the twelve structures, the percentage change in cell parameters on relaxation. These changes are, in the main, quite small, and comparable to the 1—2% accuracy found by Kitaigorodskii[7] for ordered crystals such as benzene, naphthalene, and anthracene. There are however notable exceptions, namely for some axes of the last five structures involving C2, but these are the least stable of the configurations and such changes for these structures are perhaps not surprising. It is perhaps also significant that for the two most stable structures, A1BC1 required a larger than average reduction in *b* while A1BC2 required a similar reduction in *a*, thus implying that the observed cell dimensions are a compromise between opposing preferences. It is possible that use of a Coulombic term in the potential energy (1) could affect this latter observation, since it is found[13] that cell dimensions are predicted rather more accurately when Coulombic terms are included. On the other hand there is no reason to suppose that structures differing in cell dimensions by *ca.* 5% could not form an intimate disordered mixture of the sort envisaged. For example, in binary alloy systems local size-effect distortions of *ca.* 5% of the average lattice spacing are not uncommon.[15] The changes here are seen to be somewhat smaller for parameter set II, which is in accord with Markey's[10] findings in his comparison of the two parameter sets. The percentage change in cell volume is negative for all but the two most unstable structures using parameter set I, and this is consistent with the fact that the potentials should yield the structure at 0 K.

The rotation matrices, *V*, and translation vectors ***T*** required for transformation of the positional co-ordinates in the local orthonormal axes to the crystal axes are given in a supplementary publication [SUP 56723 (9 pp)]* for each of the twelve relaxed structures, for each set of potential parameters.

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* For details of the supplementary publication scheme see 'Instructions for Authors, 1988,' *J. Chem. Soc., Perkin Trans. 2*, 1988, issue 1, section 4.0.

Table 3. Parameter set I

	Cell parameter change (%)			Volume change (%)	PE initial (kJ mol^{-1})	PE relaxed (kJ mol^{-1})	Boltzmann probability
Configuration	Δa	Δb	Δc				
A1BC1	+1.5	−5.4	+1.0	−3.23	−87.366	−89.973	0.272
A2BC1	−0.1	−2.9	+0.5	−2.49	−85.621	−89.144	0.078
A3BC1	−0.1	−2.9	+0.5	−2.49	−85.621	−89.144	0.078
A4BC1	+1.5	−5.0	+1.1	−2.49	−85.563	−89.077	0.071
A5BC1	−0.2	−2.8	+0.5	−2.47	−86.111	−89.186	0.083
A6BC1	−0.2	−2.8	+0.5	−2.47	−86.111	−89.186	0.083
A1BC2	−5.5	−0.2	+2.6	−3.20	−85.881	−89.981	0.275
A2BC2	+2.0	−5.2	+3.9	+0.47	−77.613	−84.416	0.000
A3BC2	+2.0	−5.2	+3.9	+0.47	−77.613	−84.416	0.000
A4BC2	−8.0	+3.3	+2.5	−2.80	−80.249	−88.680	0.039
A5BC2	−10.0	+5.9	+2.9	−2.08	−79.768	−87.814	0.011
A6BC2	−10.0	+5.9	+2.9	−2.08	−79.768	−87.814	0.011
Parameter set II							
A1BC1	+0.4	−4.8	+0.4	−3.99	−93.588	−95.755	0.252
A2BC1	−0.7	−2.8	+0.1	−3.40	−92.220	−95.048	0.087
A3BC1	−0.7	−2.8	+0.1	−3.40	−92.220	−95.048	0.087
A4BC1	−0.1	−3.9	+0.7	−3.37	−89.923	−94.475	0.037
A5BC1	−1.1	−2.5	−0.0	−3.63	−92.437	−95.111	0.095
A6BC1	−1.1	−2.5	−0.0	−3.63	−92.437	−95.111	0.095
A1BC2	−4.4	−1.7	+1.9	−4.29	−92.245	−95.906	0.316
A2BC2	−2.7	−1.4	+3.6	−0.63	−87.295	−90.525	0.000
A3BC2	−2.7	−1.4	+3.6	−0.63	−87.295	−90.525	0.000
A4BC2	−7.0	+1.8	+1.8	−3.62	−87.379	−93.931	0.016
A5BC2	−7.5	+2.6	+2.3	−2.89	−88.387	−93.383	0.007
A6BC2	−7.5	+2.6	+2.3	−2.89	−88.387	−93.383	0.007

In Table 4 are listed, for all twelve structures, the changes that occurred in the Eulerian angles θ, φ, and ψ, and the centre of mass displacements, as the structures were relaxed. In most cases the position of the energy minimum was found to be fairly close to the unrelaxed structure. Only for the two least stable structures (A2BC2 and A3BC2) was there any substantial molecular reorientation. The next most unstable structures (A4BC2, A5BC2, and A6BC2) suffered some moderate shifts, but the seven remaining structures generally involved only small deviations from the unrelaxed structures. The centre-of-mass displacements were calculated as the difference in fractional co-ordinates of the relaxed and unrelaxed structures multiplied by the observed cell dimension.

At room temperatures (where $kT \simeq 2.5$ kJ mol^{-1}) the existence of numerous possible structures having energy differences of less than *ca.* kT provides a ready explanation for the fact that the room-temperature crystal structure is very disordered. At 80 K (where kT is *ca.* 0.67 kJ mol^{-1}), the temperature at which the neutron data were collected, the energy differences between the structures are relatively more significant. It is interesting to consider the disorder at 80 K in terms of these different hypothetical ordered structures.

Suppose that any macroscopically small region of the structure conforms to one or other of these (and only these) different configurations. We can then compute the probability of each occurring according to a Boltzmann partition of energy, *i.e.*

$$P_i = \frac{\exp(-U_i/kT)}{\sum_{i=1}^{N} \exp(-U_i/kT)} \qquad (7)$$

Here, i runs over the twelve configurations listed in Table 3, and U_i is the potential energy of the ith configuration. These probabilities are given in the last column of Table 3, for the case of $T = 80$ K.

These probabilities may be used to derive site-occupancies for individual molecular sites for comparison with those obtained from the neutron experiment. To obtain, for example, the probability with which molecular orientation A1 occurs in the A-site we must add the probabilities for the two structures A1BC1 and A1BC2. Similarly to obtain the probability with which C1 occurs we must add the probabilities for the six structures which contain C1. The resulting site probabilities calculated in this way are shown in Table 5 in comparison with the observed site occupancies. These results show remarkably good agreement between the calculated probabilities and the experimental site occupancies, for both parameter sets I and II. It should be noted that while the structure A1BC2 is the most stable of the twelve ordered structures, the other structures involving C2 are all relatively unstable compared with the corresponding structures involving C1 and consequently the total probability of C2 is considerably less than C1.

In deciding at the outset to perform the calculations on the particular twelve structures described, we used the n-glide symmetry element of the average space group to relate the A molecules in the layer at 0c to those in the layer at 0.5c. If, alternatively, we had used the 2_1 axis the molecular layer at 0.5c would have been inverted and a different set of structures would have resulted. Of these, those containing A1 or A4 would have been identical to the corresponding structures described here, since for these the n-glide and 2_1 axis are satisfied simultaneously, but those containing A2, A3, A5, or A6 would be different. However the difference between these structures and the ones described here is only in the relative orientation of the molecular layers at 0c and 0.5c, and the interaction between these layers is very weak. This was confirmed by calculation; the difference in energy between the structures generated using the n-glide or the 2_1 axis was only *ca.* 0.003 kJ mol^{-1}. Consequently,

Table 4. Changes in the Eulerian angles and translations of the centres-of-mass of molecules in the equilibrium structures relative to the experimentally determined structures

Configuration	Type of molecule	Rotation about Euler angle/°			Centre-of-mass translation/Å		
			I	II		I	II
A1BC1	A	θ	0.2	0.3	Δ*x*	0.02	−0.01
		φ	—	—	Δ*y*	0.07	−0.14
		ψ	—	—	Δ*z*	—	—
	B	θ	−1.0	−0.8	Δ*x*	0.01	0.03
		φ	—	—	Δ*y*	−0.01	−0.11
		ψ	—	—	Δ*z*	—	—
	C	θ	−0.3	−2.1	Δ*x*	−0.12	−0.08
		φ	−3.1	−2.1	Δ*y*	−0.02	−0.01
		ψ	−0.5	0.3	Δ*z*	0.00	0.01
A2BC1 and A3BC1	A	θ	1.2	0.9	Δ*x*	0.00	0.01
		φ	1.3	1.2	Δ*y*	−0.01	−0.15
		ψ	0.2	0.0	Δ*z*	0.13	0.14
	B	θ	0.2	0.0	Δ*x*	0.00	0.01
		φ	—	—	Δ*y*	0.22	0.10
		ψ	—	—	Δ*z*	—	—
	C	θ	2.7	0.4	Δ*x*	−0.09	−0.06
		φ	−1.8	−1.1	Δ*y*	−0.00	0.00
		ψ	−1.7	−1.0	Δ*z*	−0.12	−0.10
A4BC1	A	θ	−3.9	−4.3	Δ*x*	−0.02	0.00
		φ	—	—	Δ*y*	0.22	0.03
		ψ	—	—	Δ*z*	—	—
	B	θ	−1.1	−0.7	Δ*x*	0.00	0.02
		φ	—	—	Δ*y*	0.38	0.31
		ψ	—	—	Δ*z*	—	—
	C	θ	4.9	2.5	Δ*x*	−0.00	0.04
		φ	−2.8	−1.5	Δ*y*	0.00	0.01
		ψ	−1.8	−1.0	Δ*z*	−0.02	−0.02
A5BC1 and A6BC1	A	θ	−0.7	−0.6	Δ*x*	0.00	0.02
		φ	−2.4	−2.3	Δ*y*	−0.03	−0.13
		ψ	−2.4	−2.7	Δ*z*	0.13	0.12
	B	θ	0.3	0.1	Δ*x*	0.01	0.02
		φ	—	—	Δ*y*	0.23	0.17
		ψ	—	—	Δ*z*	—	—
	C	θ	2.5	0.9	Δ*x*	−0.10	−0.07
		φ	−1.7	−0.8	Δ*y*	0.01	0.02
		ψ	−1.7	−1.2	Δ*z*	−0.13	−0.12
A1BC2	A	θ	−3.3	−2.2	Δ*x*	0.09	0.07
		φ	—	—	Δ*y*	−0.21	−0.22
		ψ	—	—	Δ*z*	—	—
	B	θ	2.8	1.8	Δ*x*	0.11	0.09
		φ	—	—	Δ*y*	−0.14	−0.24
		ψ	—	—	Δ*z*	—	—
	C	θ	1.5	1.8	Δ*x*	0.14	0.13
		φ	1.1	0.6	Δ*y*	0.03	0.03
		ψ	0.4	0.0	Δ*z*	0.03	0.03
A2BC2 and A3BC2	A	θ	0.2	0.6	Δ*x*	−0.03	0.04
		φ	0.0	2.4	Δ*y*	−0.30	0.17
		ψ	−0.5	−0.3	Δ*z*	0.16	0.22
	B	θ	−0.6	1.5	Δ*x*	−0.08	−0.02
		φ	—	—	Δ*y*	−0.38	0.12
		ψ	—	—	Δ*z*	—	—
	C	θ	11.1	0.2	Δ*x*	0.04	−0.10
		φ	−2.7	0.6	Δ*y*	−0.08	−0.03
		ψ	−23.4	−27.9	Δ*z*	−0.23	−0.12
A4BC2	A	θ	−10.1	−9.1	Δ*x*	0.14	0.12
		φ	—	—	Δ*y*	0.04	−0.01
		ψ	—	—	Δ*z*	—	—
	B	θ	5.3	4.4	Δ*x*	0.11	0.09
		φ	—	—	Δ*y*	0.08	0.12
		ψ	—	—	Δ*z*	—	—
	C	θ	0.9	0.9	Δ*x*	0.29	0.27
		φ	3.6	3.1	Δ*y*	0.06	0.07
		ψ	7.4	7.4	Δ*z*	0.04	0.04

Table 4 (*continued*)

Configuration	Type of molecule	Rotation about Euler angle/°			Centre-of-mass translation/Å		
			I	II		I	II
A5BC2 and A6BC2	A	θ	−0.4	−0.2	Δx	0.18	0.13
		φ	3.4	1.7	Δy	−0.15	−0.18
		ψ	−2.3	−2.4	Δz	0.10	0.08
	B	θ	6.5	4.1	Δx	0.16	0.12
		φ	—	—	Δy	0.01	0.02
		ψ	—	—	Δz	—	—
	C	θ	0.7	0.9	Δx	0.27	0.21
		φ	4.7	3.2	Δy	0.05	0.06
		ψ	5.2	3.3	Δz	−0.08	−0.09

Table 5. Comparison of the calculated site occupancies of the disordered structure at 80 K, derived from the Boltzmann probabilities for the 12 ordered structures given in Table 3

Molecular orientation	Parameter set I	Parameter set II	Experimental (Wood *et al.*[1])
A1	0.547	0.568	0.554
A2	0.078	0.087	0.088
A3	0.078	0.087	0.088
A4	0.110	0.053	0.082
A5	0.094	0.102	0.094
A6	0.094	0.102	0.094
C1	0.665	0.654	0.708
C2	0.335	0.346	0.292

difference in energy between the structures generated using the *n*-glide or the 2_1 axis was only *ca.* 0.003 kJ mol^{-1}. Consequently, including these additional twelve structures in the partition (7), would result in a halving of each of the probabilities in the last column of Table 3, with each of the new set of twelve receiving the other half of the probability. The site probabilities given in Table 5 would be unaffected by this further partitioning.

We realize that this picture of the disorder is overly simplistic. For a more complete description many other possible configurations should also be considered, including ones in which no symmetry is necessarily preserved on a local scale. To obtain the most complete description, a full molecular dynamics simulation could be carried out, and this would automatically explore all energetically feasible configurations. Such a simulation would, however, be an enormous task, considerably beyond our present computational capability. The fact that of the twelve configurations considered, A2BC2 and A3BC2 were of sufficiently high potential energy to contribute insignificantly to the calculated probabilities, makes it seem likely that, in any more extensive study, most other conceivable configurations would similarly contribute insignificantly, unless their local structure closely resembled those energetically favourable ones described above. It is, however, realized that the very close agreement between observed and calculated site occupancies given in Table 5 is perhaps rather fortuitous in view of the approximations made both in the specification of the disordered ensemble and in the intermolecular potential itself. Nevertheless, despite these limitations, the present results do provide substantial support for the validity of the observed neutron diffraction results.[1]

Before the neutron-data refinement was available Sanford *et al.*[16] attempted to use semi-empirical potential-energy calculations to explore the energy barriers to rotation of the molecule in its own plane, following the detection of such motions by wide-line n.m.r. experiments. As a basis for their calculation they used co-ordinates derived from an earlier structure-solution attempt, but no details of the actual molecular or crystal geometry used were recorded. Nevertheless it is clear that the structure on which these calculations were performed was essentially our A1BC1 structure. Their investigations essentially consisted of calculating the potential energy as a function of the angle of in-plane rotation, for each type of molecular site separately. With the publication of the neutron-data refinement it became clear that the low-temperature structure is much more complicated than had previously been supposed. Consequently some doubt must reside on the rather simple energy-barrier determinations that were performed. With the multiplicity of different molecular orientations that are present, it seems to us most likely that any rotational behaviour would involve correlated motion of the molecules in the different molecular sites. With a view to obtaining a better understanding of the sorts of such motions that may occur, we are currently using the results of the present study as a starting point for making lattice-dynamical calculations on the system.

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