

Crystal Structure of Acenaphthylene, $C_{12}H_8$, at 80 K by Neutron Diffraction

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The crystal structure of acenaphthylene at 80 K has been determined using neutron ($\lambda = 1.238 \text{ \AA}$) diffraction data. Though well below the known phase transition (at 130 K) the structure was found to be disordered with space group $P2_1nm$ and $a = 7.584(6)$, $b = 7.589(7)$, and $c = 27.851(21) \text{ \AA}$. Constrained least-squares refinement led to a residual R of 0.069 using 92 variables for 950 reflections having $I_o > 3\sigma(I_o)$. The structure has three symmetry-unrelated molecular sites A—C. Site B was found to be totally ordered but sites A and C were disordered. Six different molecular orientations, related approximately by rotations in the molecular plane, were located in site A, while for site C two different orientations were found. The major molecular fragment in site A had an occupancy of 0.554(12) and that for site C an occupancy of 0.708(9).

Acenaphthylene (I), $C_{12}H_8$, has attracted considerable attention in the literature over recent years because of its photodimerization and polymerization properties and because of the fact that it undergoes an order-disorder phase transition (at 130 K) which probably involves a rotation of the molecule in its own plane.¹ Despite this interest in the compound, attempts to elucidate the detailed crystal structure by *X*-ray diffraction techniques have, to date, largely been unsuccessful.²⁻⁴ The reason for this was undoubtedly the high degree of disorder which is present in the structure at room temperatures. Welberry⁵ published a description of the low-temperature phase based on a set of *X*-ray film-data, which was limited because of experimental difficulties in maintaining a low enough temperature with the gas-flow type of cooling employed. Although the basic packing and molecular orientations were revealed in that investigation, it was concluded that the extent and quality of the data were insufficient to allow determination of precise atomic co-ordinates.

In an attempt to obtain better structural information we have collected single-crystal neutron diffraction data at 80 K. Although it had been supposed that the difficulties of the earlier *X*-ray determination⁵ had been associated with the quality and extent of the data, preliminary attempts to analyse the current data revealed that even at 80 K, *ca.* 50 °C below the transition, the low-temperature phase was not completely ordered. Since the earlier study,⁵ however, methods for handling disordered structures using constrained least-squares refinement techniques have developed considerably^{6,7} and in this paper we describe the use of these techniques in determining the low-temperature structure of acenaphthylene.

At room temperature acenaphthylene crystallizes in space group $Pba2$ or $Pbam$. The room temperature structure exhibits characteristics of marked disorder—strong diffuse scattering and a rapid decline in reflection intensity with increasing θ . In the region of 130 K the crystals undergo a reversible change involving the formation of a superlattice by a doubling of the c cell-edge. The resulting space group as shown by Welberry⁵ is $P2_1nm$ and that of the average cell (*i.e.* ignoring the superlattice reflections) is $P2_1am$. Note that these space groups are non-standard but have been used to maintain consistency with the room temperature cell.

Experimental

Crystal Data.—Orthorhombic; $P2_1nm$ (*cf.* standard orientation $Pmn2_1$); using neutron data ($\lambda = 1.238 \text{ \AA}$) at 80(1) K, $a = 7.584(6)$, $b = 7.589(7)$, $c = 27.851(21) \text{ \AA}$; $V = 1603.0 \text{ \AA}^3$; D_{exp}

(flotation at room temperature) = 1.26, D_{calc} (80 K) = 1.26 Mg m^{-3} ; $Z = 8$; $\mu(\lambda = 1.08 \text{ \AA}) = 0.180 \text{ mm}^{-1}$.

Data Collection.—Acenaphthylene crystals were grown by slow evaporation from toluene solution. The crystal selected for data collection had the (001), (00 $\bar{1}$), (110), ($\bar{1}\bar{1}0$), (1 $\bar{1}0$), and ($\bar{1}10$) faces developed, their distances from a common internal origin being 1.55, 1.55, 2.05, 2.05, 2.93, and 2.93 mm, respectively. The resulting maximum absorption weighted mean free path length, \bar{T} , in the crystal was 3.98 mm ($\mu\bar{T} = 0.72$).

The intensities of 1 078 unique reflections with $2\theta < 80^\circ$ were measured at 80(1) K on the four-circle diffractometer, 2TANA, at the Australian Atomic Energy Commission Research Reactor, HIFAR. A θ - 2θ scan was used, the scan width being 2.1° in 2θ . A standard reflection was monitored periodically. Its maximum deviation from the mean value was 4.7%. Lorentz and absorption corrections were applied to the data. Unit cell dimensions were obtained from a least-squares analysis of the 2θ values of 24 reflections with $38^\circ < 2\theta < 68^\circ$.

Structure Refinement.—The superlattice has eight molecules in the unit cell. There are three distinct, crystallographically unrelated molecular sites which we designate as A—C (see Figure 1). Sites A and B have site symmetry m while C has no

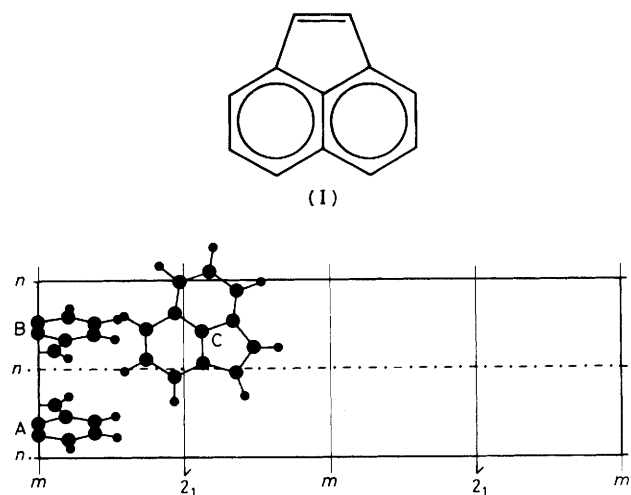


Figure 1. The asymmetric unit projected onto the a - c plane, showing the three distinct molecular sites A—C in relation to the symmetry elements of the space group $P2_1nm$

symmetry restriction. In the ideally ordered structure envisaged by Welberry⁵ sites A and B were occupied by single molecular orientations in which the molecular symmetry plane coincided with the space group *m*-plane. Initial molecular positions and orientations used for the current refinement were based on those of Welberry.⁵ The individual molecular geometries from that work were very poor and in the present work we decided to use a single refineable molecular geometry common to all three sites. The initial molecular geometry used was obtained by taking the average carbon geometry of the acenaphthylene moiety in two derivative compounds,^{8,9} and constraining the geometry to *mm*2 symmetry using the vector addition method of Craven¹⁰ with constraints applied. Hydrogen atom positions were then generated in such a way that they lay in the plane of the carbon frame, and the C–H bonds, whose lengths were set at 1.1 Å, bisected the endocyclic bond angles. This molecular geometry, defined relative to a local orthonormal axial system, was then transferred to each of the sites A–C by the appropriate axial system transformations,⁷ the initial values of which were evaluated by least-squares using RAELS83¹¹ by minimizing the distance residuals between the corresponding atoms in the reference molecule and the molecules of Welberry.⁵ In subsequent stages of the refinement both the local co-ordinates of this single molecule and the parameters of the three axial system transformations were refined. Thermal motion at each molecular site was described in terms of independent rigid-body TLX models.^{12,13} The axial systems used to describe these TLX motions were updated by RAELS83¹¹ after each cycle of refinement so that the origins coincided with the ‘centres of libration’ and the axial directions coincided with the principal axes of the *L* tensors. In the absence of site-symmetry restrictions there are 6 refineable parameters for each axial system and 15 refineable parameters for each rigid-body TLX model.

Stage I. The totally ordered model structure, in which each site contained a single molecular orientation, was refined using full-matrix least-squares with the program RAELS83¹¹ and all data. This refinement resulted in $R = 0.133$, $R_w = 0.227$, and $S = 7.70$ for 67 refineable parameters. The quantity minimized was $\sum \omega(I_o - \kappa I_c)^2$ where $\omega^{-1} = \sigma^2(I_o)$ and $\sigma(I_o)$ was obtained from counting statistics. Note that the agreement factors were derived from F_o and F_c even though the refinement was based on I_o . Neutron scattering lengths used were those of Koester *et al.*¹⁴ Of the 67 refineable parameters, 19 described the local co-ordinates of the planar (*mm*2) molecule, 11 defined the location and orientation of the molecule at the three sites A–C, and 35 were used to specify the TLX rigid-body thermal parameters (the site symmetry restrictions at sites A and B and the need to fix the origin in the *a* direction eliminated 17 parameters from the unrestricted case). The remaining two parameters were scale-factors applied to the main lattice ($l = 2n$) and superlattice ($l = 2n + 1$) reflections. The use of two different scales for the main and superlattice reflections attempts to account for incomplete ordering of the superlattice, as for example reported by Cailleau *et al.*¹⁵ for the case of biphenyl, but assumes that the unit cell in the disordered phase is simply the average of the two halves of the ideally ordered supercell. The resultant ratio of the scales for the superlattice to the main-lattice reflections was 0.84. The three molecular orientations used in this initial stage of the refinement correspond to the fragments A^I, B, and C^I in the final parameters list (see Tables 1 and 2).

Stage II. A Fourier difference map phased from the parameters of the Stage I refinement clearly indicated molecular disorder at sites A and C. At site A, all atoms of a second molecule (fragment A^{IV} in the final co-ordinates list), related to the first by a rotation of *ca.* 180° about an axis perpendicular to the plane of the molecule, were present in the map. Similarly at site C, all atoms of a second molecule (C^{II} in final co-ordinates

Table 1. Atomic co-ordinates relative to a local orthonormal axial system for the acenaphthylene molecule

	$X_L/\text{Å}$	$Y_L/\text{Å}$	$Z_L/\text{Å}$
C(1)	−0.697(6)	2.229(8)	0.0
C(2)	0.697(6)	2.229(8)	0.0
C(3)	2.393(5)	0.201(9)	0.0
C(4)	2.420(5)	−1.224(9)	0.0
C(5)	1.288(5)	−2.017(8)	0.0
C(6)	−1.288(5)	−2.017(8)	0.0
C(7)	−2.420(5)	−1.224(9)	0.0
C(8)	−2.393(5)	0.201(9)	0.0
C(9)	−1.169(5)	0.841(8)	0.0
C(10)	1.169(5)	0.841(8)	0.0
C(11)	0.0	−1.386(10)	0.0
C(12)	0.0	0.0	0.0
H(1)	−1.304(13)	3.089(12)	0.0
H(2)	1.304(13)	3.089(12)	0.0
H(3)	3.309(10)	0.792(14)	0.0
H(4)	3.402(10)	−1.705(15)	0.0
H(5)	1.367(12)	−3.090(13)	0.0
H(6)	−1.367(12)	−3.090(13)	0.0
H(7)	−3.402(10)	−1.705(15)	0.0
H(8)	−3.309(10)	0.792(14)	0.0

list), related to the first by a rotation of *ca.* 120°, were present. These two molecular orientations were included in the next stage of the refinement by specifying additional axial system transformations and molecular site-occupancy parameters, resulting in 11 additional refineable parameters. No additional TLX parameters were specified but the atoms of the new molecular fragments were included in the TLX model for each site. For this stage also, only a single scale factor for all of the data was refined. This refinement using 950 reflections with $I_o > 3\sigma(I_o)$ led to $R = 0.099$, $R_w = 0.177$, and $S = 6.02$ for 77 refineable parameters.

Most of the major peaks in the resulting Fourier difference map were in the region of site A, but further molecular fragments could not be clearly discerned. This was considered to be due to the fact that the refinement had been allowed to take up unreasonable physical parameters so as to minimize the agreement factors. In doing this the refinement had possibly reduced the peaks in the difference map which would otherwise have indicated the location of additional molecular fragments. That this had occurred was borne out by the fact that some atoms near the centre of the molecules in site A had highly anisotropic and non-positive definite temperature factors resulting from a non-positive definite T matrix in the TLX model. To overcome this problem the Stage II refinement was repeated with a constraint on the TLX model for each site to allow only an isotropic T matrix. This refinement using only 66 variables led to $R = 0.116$, $R_w = 0.214$, and $S = 7.23$, but now a difference map clearly showed further molecular fragments at site A with the molecular symmetry plane inclined at *ca.* 45 and 135° to the space group *m*-plane (fragments A^{II,III} and A^{V,VI} in the final co-ordinates list). This meant that at site A six fragments had now been located.

Stage III. The final stages of refinement were carried out with six molecular fragments at site A, a single fragment at site B, and 2 fragments at site C. For site A a TL model was used in which the T matrix was isotropic and the centre of libration was fixed at the molecular centre (at C-6 of the major fragment). For site B, a full TLX model (restricted only by the *m*-site symmetry) was used for the single fragment, and for site C a single full TLX model was used for the two fragments. An additional isotropic contribution to the thermal parameters of the hydrogen atoms, over and above that described by the TL and TLX models, was also included, since the motion for hydrogen is expected to be

Table 2. Rotation matrices, V , and translation vectors, T , transforming the local co-ordinates, $X_L(\text{\AA})$, of the acenaphthylene molecule into unit cell co-ordinates, $X_C(\text{\AA})$, at the sites A—C
$$X_C(\text{\AA}) = V X_L + T$$

Site	Occupancy	Rotation matrix*			Translation vector
					(\AA)
A ^I	0.554(12)	0.0000	0.3585	0.9335	1.5277
		0.0000	-0.9335	0.3585	1.4073
		1.0000	0.0000	0.0000	0.0000
A ^{II}	0.088(12)	-0.2569	-0.2696	-0.9281	1.4304
		0.6500	0.6624	-0.3724	1.9969
		0.7152	-0.6989	0.0051	-0.3553
A ^{III}	0.088(12)	-0.2569	-0.2696	-0.9281	1.4304
		0.6500	0.6624	-0.3724	1.9969
		-0.7152	0.6989	-0.0051	0.3553
A ^{IV}	0.082(12)	0.0000	-0.4217	-0.9067	1.5369
		0.0000	-0.9067	-0.4217	2.0660
		1.0000	0.0000	0.0000	0.0000
A ^V	0.094(12)	0.1936	0.2455	-0.9499	1.6062
		-0.6514	-0.6918	-0.3116	1.6761
		-0.7336	0.6790	0.0259	0.0769
A ^{VI}	0.094(12)	0.1936	0.2455	-0.9499	1.6062
		-0.6514	-0.6918	-0.3116	1.6761
		0.7336	-0.6790	-0.0259	-0.0769
B	1.000	0.0000	-0.3453	0.9385	5.3559
		0.0000	-0.9385	-0.3453	5.4109
		1.0000	0.0000	0.0000	0.0000
C ^I	0.708(9)	-0.7703	-0.5516	0.3200	5.4080
		0.3028	0.1252	0.9448	1.9755
		-0.5612	0.8246	0.0706	7.0188
C ^{II}	0.292(9)	0.1172	0.9390	0.3232	5.6509
		-0.0571	-0.3185	0.9462	1.8765
		0.9915	-0.1294	0.0162	6.9192

* The columns of the rotation matrices correspond to the direction cosines of the x, y, z axes of the molecule in Table 1.

greater than that for carbon because of differences in their zero-point energy. In all, the model was specified by 87 refineable parameters consisting of 19 local co-ordinates, 32 axial transformation parameters, 5 TL and 25 TLX model parameters, 4 site occupancies, 1 overall scale factor, and 1 isotropic thermal parameter for hydrogen.

This model resulted in $R = 0.072$, $R_w = 0.141$, and $S = 4.8$. All thermal parameters were positive definite and the subsequent Fourier difference map showed no evidence of further disorder at any molecular site. A further refinement was carried out after relaxing the restrictions on the TL model for site A and further slight improvement in the agreement factors resulted with the thermal parameters now remaining positive definite. Final agreement factors were $R = 0.069$, $R_w = 0.137$, and $S = 4.8$ for 92 variables and 950 reflections with $I_o > 3\sigma(I_o)$.

Throughout the refinement chemical composition was strictly maintained at each site, but there were no constraints on molecular geometry, other than the $mm2$ symmetry (which necessarily implies molecular planarity). All but two of the final shift/error ratios were less than 1.0σ with the maximum ratio being 1.4σ and the average 0.3σ . The final Fourier difference map showed no significant residual nuclear density in the region of the molecular sites. The site occupancies of the six molecular fragments at site A refined to 0.554(12), 0.088(12), 0.088(12), 0.082(12), 0.094(12), and 0.094(12). At site C the occupancies of the two fragments refined to 0.708(9) and 0.292(9). In Figure 2 we show the way in which the six fragments in site A are overlaid, and Figure 3 shows the overlay of the two fragments in site C.

The co-ordinates of the acenaphthylene atoms relative to a local orthonormal axial system are given in Table 1, and the axial system transformations that place these atoms at the sites

Table 3. Bond lengths (\AA) for the unique bonds of acenaphthylene. $mm2$ symmetry assumed

C(1)—C(2)	1.395(11)	C(11)—C(12)	1.386(10)
C(2)—C(10)	1.466(7)	C(10)—C(12)	1.441(6)
C(10)—C(3)	1.381(7)	C(2)—H(2)	1.052(13)
C(3)—C(4)	1.424(8)	C(3)—H(3)	1.090(12)
C(4)—C(5)	1.382(8)	C(4)—H(4)	1.094(11)
C(5)—C(11)	1.433(6)	C(5)—H(5)	1.077(13)

Table 4. Unique valence angles ($^\circ$) for acenaphthylene. $mm2$ symmetry assumed

C(1)—C(2)—C(10)	108.8(3)	C(12)—C(10)—C(3)	116.6(4)
C(2)—C(10)—C(12)	106.9(4)	H(2)—C(2)—C(1)	125.2(7)
C(10)—C(12)—C(9)	108.5(6)	H(2)—C(2)—C(10)	126.0(8)
C(2)—C(10)—C(3)	136.4(4)	H(3)—C(3)—C(10)	119.5(7)
C(10)—C(3)—C(4)	118.7(4)	H(3)—C(3)—C(4)	121.1(8)
C(3)—C(4)—C(5)	123.9(4)	H(4)—C(4)—C(3)	117.2(8)
C(4)—C(5)—C(11)	118.9(4)	H(4)—C(4)—C(5)	118.9(9)
C(5)—C(11)—C(12)	116.1(3)	H(5)—C(5)—C(4)	120.8(7)
C(5)—C(11)—C(6)	127.8(6)	H(5)—C(5)—C(11)	120.3(8)
C(11)—C(12)—C(10)	125.7(3)		

A—C are given in Table 2. The atomic notation and ORTEP¹⁶ thermal ellipsoid plots at the 50% probability level for the molecules at the three different molecular sites are shown in Figure 4. Individual atom position parameters and anisotropic thermal parameters are given in Supplementary Publication No. SUP 56121 (8 pp.).*

* For details of Supplementary Publications see Instructions for Authors in *J. Chem. Soc., Perkin Trans. 2*, 1985, Issue 1.

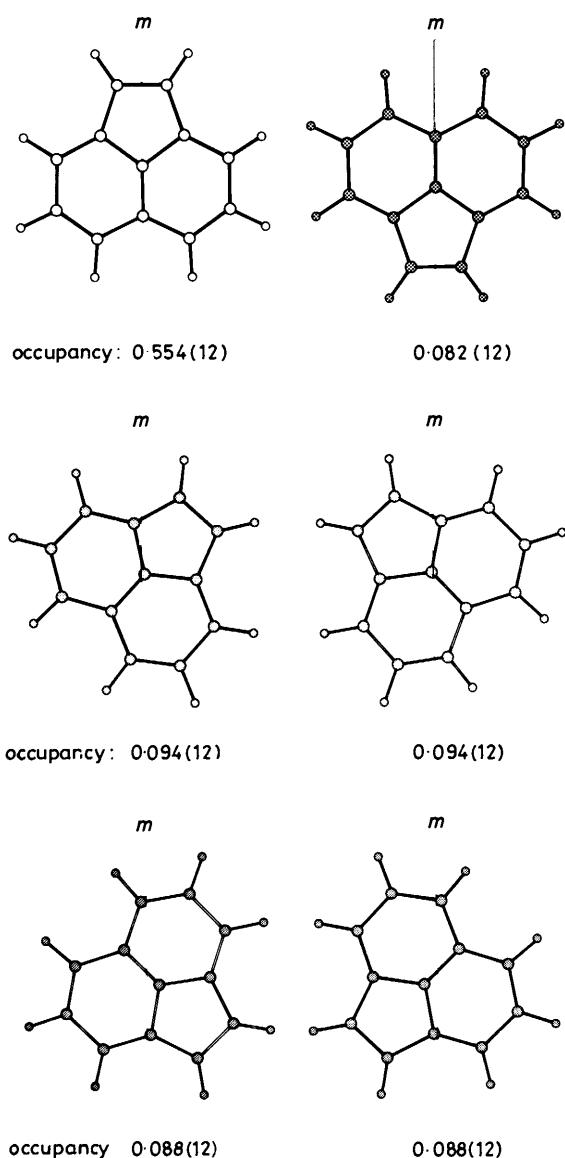
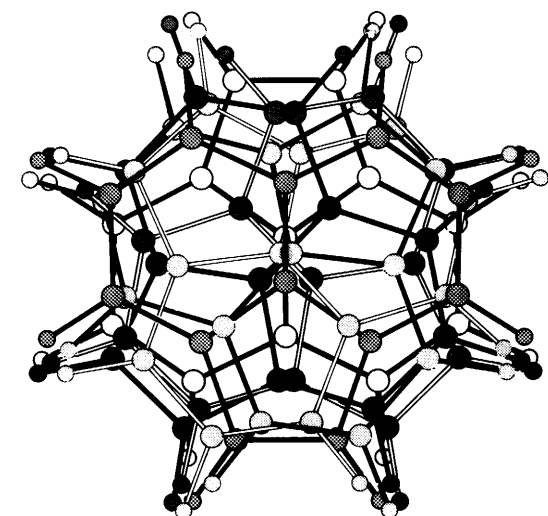


Figure 2. The overlay of the disordered molecular fragments in site A. Note the close clustering of the hydrogen positions on the periphery of the molecular shape

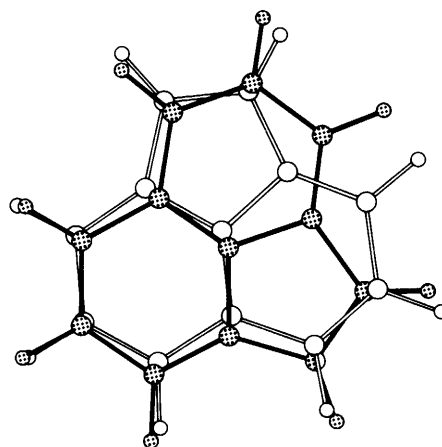


Figure 3. The overlay of the two molecular fragments in site C. The major fragment with occupancy 0.708 is represented by the solid lines

Results and Discussion

Bond lengths and angles for the single molecular species used at all sites are shown in Tables 3 and 4, respectively. The internal geometry is well determined as a consequence of the fact that site B was found to be ordered. This result demonstrates the power of constrained refinement techniques. With conventional refinement techniques a totally ordered model would give very poor geometry even for the site with no disorder, while for a disordered model involving the nine molecular fragments described here the number of refineable parameters would be far too high to allow a meaningful determination. In the present case the final refinement was carried out with only *ca.* 50% more parameters than were required for the completely ordered model used in Stage I. The derived molecular geometry is in reasonably good agreement with the geometry of the acenaphthylene moiety in the structures of the two published derivative compounds.^{8,9} The most significant differences are the C(1)–C(2) double bond and the C(12)–C(10) ring bond which are both *ca.* 4σ greater in this determination.

Table 5 lists the TLX parameters associated with each molecular site. The largest principal libration axis for each of the two disordered sites A and C corresponds approximately to the normal to the molecular plane. For the ordered site B, however, the normal to the plane corresponds to the smallest principal libration axis. It is evident from the thermal ellipsoid plots shown in Figure 4 that libration about the normal to the molecular plane in site C is still rather large, and this is also reflected in the U_{ij} values for individual atoms (particularly for the H atoms), given in Supplementary Table 2. This degree of libration is possibly indicative of there being further disorder in site C, but attempts to locate additional molecular fragments were unsuccessful. With a final *R* value as low as 0.07 any residual information in a Fourier difference map is likely to be difficult to disentangle from the inherent noise.

It is an unusual feature of this structure that site B is completely ordered with seemingly little tendency for the molecule to rotate, while in sites A and C molecular reorientation occurs with reasonable freedom. Sangford *et al.*¹ have recently reported from n.m.r. studies the occurrence of two distinct molecular motions involved in the phase transition. These could well correspond to the molecular motions which result in the disorder in sites A and C observed here, but it seems likely that site B also becomes disordered above the transition, since at room temperature the X-ray diffraction pattern indicates extremely high levels of disorder.

The overlay of the six molecular orientations occurring in site

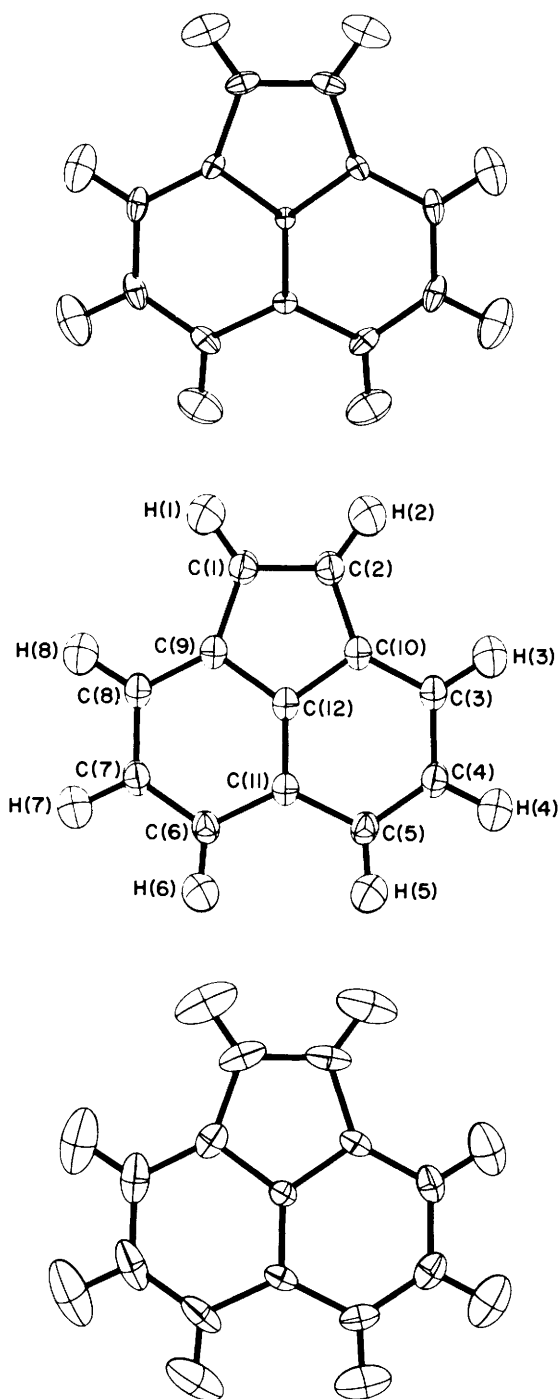


Figure 4. Thermal ellipsoid plots at the 50% probability level for the major fragments in sites A—C. Note that for sites A and C the dominant motion is a libration about an axis normal to the molecular plane

A (refer to Figure 2) shows clearly how the hydrogen positions for all of the fragments are closely clustered about eight distinct sites on the periphery of the molecular shape. This suggests a possible explanation for the disorder, since the environment of the molecule has eight more or less equally spaced 'pockets' into which these hydrogen atoms can fit. Only well below the transition does the Boltzmann partition result in one of the possible orientations becoming dominant. Since there are eight

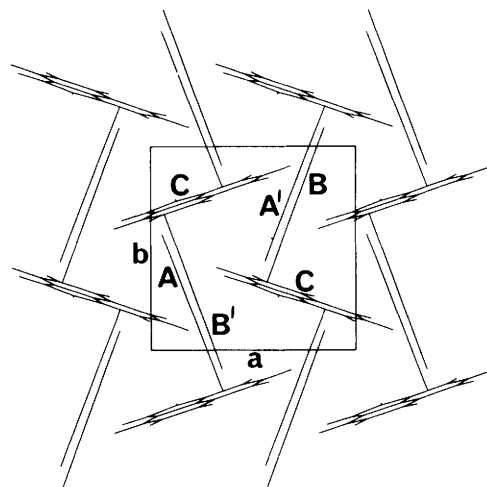


Figure 5. A projection of the structure onto the a - b plane. Molecules such as A and B form a closely packed layer at $0c$, those labelled A' and B' related to A and B by the n -glide plane form a similar layer at $0.5c$, and molecules labelled C form layers at $0.25c$ and $0.75c$

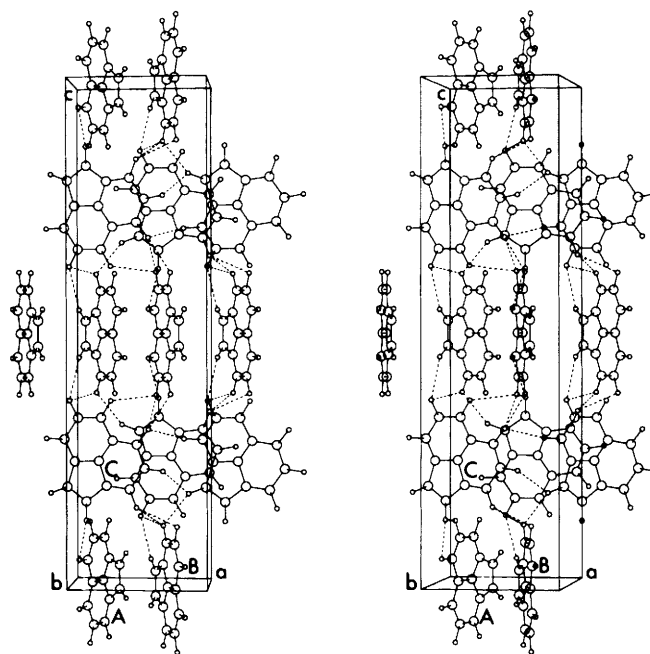


Figure 6. Stereoplots of the structure consisting of the three major molecular fragments, viewed approximately down b . All H—H contacts less than 2.75 Å are shown by dashed lines

such sites it is perhaps surprising that only six rather than eight of the possible orientations of the molecule are found to occur. The two orientations that do not occur are the ones in which the C(11)—C(12) bond lies normal to the m -plane. It may be significant that in these orientations the largest dimension of the molecule [between H(4)—H(7)] is normal to c and would perhaps be more difficult to accommodate in the closely packed layers of molecules (see below.)

The two molecular orientations in site C (see Figure 3) similarly superimpose so that the H-sites coincide closely. The coincidence is best for the H(4C^I) and the H(7C^{II}) atoms and worst for the H(8C^I) and H(3C^{II}) atoms. It is perhaps significant that the thermal ellipsoid plot for this site also reveals greater

Table 5. TLX parameters for each of the independent molecular sites in the crystal structure of acenaphthylene at 80 K*

Site	Centre of libration	Direction cosines of libration axes relative to crystal axes†			$10^4 T/\text{\AA}^2$			$10^4 L/\text{rad}^2$		
A	1.8806	0.2551	-0.9669	0.0000	149	45	0	18	0	0
	1.6764	-0.9669	-0.2551	0.0000	45	31	0	0	39	0
	0.0000	0.0000	0.0000	-1.0000	0	0	154	0	0	16
B	5.2999	0.2139	0.9769	0.0000	325	-40	0	31	0	0
	5.7368	0.9769	-0.2139	0.0000	-40	95	0	0	7	0
	0.0000	0.0000	0.0000	-1.0000	0	0	190	0	0	34
C	5.1332	-0.7109	-0.3298	-0.6212	217	-10	-15	22	0	0
	2.2078	0.0760	-0.9141	0.3983	-10	247	-7	0	71	0
	6.5503	-0.6992	0.2360	0.6749	-15	-7	153	0	0	15

* All hydrogen atoms have a superimposed isotropic thermal motion of $0.0117(16) \text{\AA}^2$.

† The direction cosines of the principal libration axes appear as column vectors. Note that the third columns of the rotation matrices in Table 2 approximate to the second columns of the axial transformations for librations.

atomic displacements for the H(1)–H(7)–H(8) side of the C' fragment.

An exhaustive description of the intermolecular contacts between all of the disordered species is hardly practical, in view of the large number of possible mutual orientations for each pair of neighbouring molecules. For the completely ordered structure consisting of the major fragment at each site the molecular packing is shown projected onto the a - b plane in Figure 5 and as a stereoplot viewed approximately down b in Figure 6. The structure is seen to consist of layers of molecules normal to the long c -axis. The layers at $0c$ and $0.5c$ are made up of A- and B-sites, while the layers at $0.25c$ and $0.75c$ consist entirely of C-sites. Figure 5 reveals the closely packed 'herring-bone' pattern for each of the layers, and also the way they superimpose. The layer at $0c$ consisting of molecules A and B is seen to be very similar to the layer at $0.5c$ which consists of the molecules labelled A' and B'. The main difference is that the molecules in the layer at $0.5c$ are rotated by 180° relative to the corresponding molecules at $0c$, e.g. B' is rotated 180° relative to A. There is also an accompanying small lateral shift in the molecular centre. These two molecular layers become identical in the room-temperature phase. As a consequence of the difference between these layers, the planes of the molecules in the C-sites are tilted so that their normals are not exactly parallel to the space-group m -plane.

Figure 6 also shows all intermolecular H–H contacts of $<2.75 \text{\AA}$. In Supplementary Table 3 these contact distances are given together with all H–C distances $<3.0 \text{\AA}$ and C–C distances $<3.7 \text{\AA}$. Only one H–H distance of 2.28\AA for the H(3B)–H(2C) contact is less than the value of 2.34\AA given by Kitaigorodskii¹⁷ for the van der Waals diameter of a H-atom.

Conclusions.—In addition to providing for the first time a reliable crystal and molecular structure determination for acenaphthylene, the present study has revealed the extent to which determination of a crystal structure containing disorder may be in error when high residual agreement factors are obtained. The initial stages of the present study used only the three major fragments of the nine that were subsequently discovered. In broadest terms it might be said that in this preliminary model a fraction, $\frac{1}{3} (0.554 + 1.0 + 0.708) = 0.754$, of the final model was specified correctly, although in fairness it should be added that the atomic sites in the other subsequently discovered molecular fragments occurred in positions approximate to those of the major fragments. Nevertheless the present findings cast doubt on the validity of structure determinations involving similar small-atom structures when the residual R -factor is in excess of 0.10. A similar conclusion has been drawn by Jeffrey *et al.*¹⁸ with regard to

carbohydrates, where it is suggested that in certain circumstances disorder may be the rule rather than the exception. In such cases it is important that derived geometry and anisotropic thermal parameters should be closely scrutinized in order to avoid erroneous or inadequate interpretation of the diffraction data. Use of constrained refinement techniques such as those described here is a powerful tool for investigating such problems.

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