

vice and assistance given by Dr William Parrish and the extensive calculations performed by Miss Marian Mack, both of this laboratory.

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The Crystal Structure of Acepleiadylene

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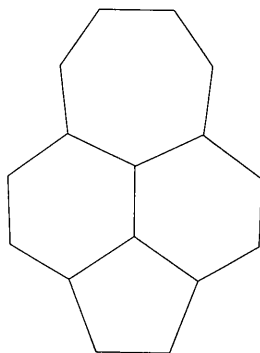
The crystal of acepleiadylene is monoclinic, probably $P2_1/a$,

$$a = 11.59, b = 11.48, c = 7.93 \text{ \AA}, \beta = 100.2^\circ, Z = 4.$$

The structure was determined by inspection of a three-dimensional Patterson synthesis, and refined with the aid of three-dimensional Fourier syntheses. The structure is disordered, the average asymmetric unit consisting of two molecules related by an approximate symmetry centre, and occupying roughly the same space. The structure is very similar to that of pyrene; the distance between adjacent parallel molecules is 3.44 \AA.

Introduction

Acepleiadylene is a non-alternant hydrocarbon first synthesized by Boekelheide & Vick in 1956. The compound has recently been the subject of theoretical and experimental investigation, including some speculation about the crystal structure (Pullman, Pullman,



Petro & Smyth, 1957). X-ray analysis was therefore undertaken with the object of discovering the nature of the packing in the crystalline state and the stereochemistry of the molecule, including bond lengths. It will be seen that this object was realized only in part.

Experimental details

The crystals of acepleiadylene available for examination were red, granular and opaque. From an examination of precession photographs it was found that the crystal was monoclinic, probably $P2_1/a$, with

$$a = 11.59 \pm 0.04, b = 11.48 \pm 0.04, c = 7.93 \pm 0.03 \text{ \AA}; \\ \beta = 100.2^\circ.$$

Also,

$$D_x \text{ (calculated density)} = 1.30 \text{ g.cm.}^{-3} (Z = 4). \\ D_o \text{ (measured density)} = 1.29 \text{ g.cm.}^{-3}. \\ \mu = 7.1 \text{ cm.}^{-1} (\text{Cu } K\alpha). \mu = 23.1 \text{ cm.}^{-1} (\text{Cr } K\alpha). \\ \text{Melting point } 161^\circ \text{C.}$$

Berthier & Pontis, 1952; Sidman, 1956*a, b*; Pitt,

Fielding & Schneider (1959) report a very small

pyroelectric effect for this crystal. However, even very long X-ray exposures have failed to reveal any reflections forbidden by the space group $P2_1/a$.

Three-dimensional intensity data were recorded on y -axis Weissenberg photographs with copper radiation for values of k up to 10. The equi-inclination technique was used for upper levels, and the correlation of the data was accomplished by means of a double-slit technique. $0k0$ reflections were recorded on a zero-level z -axis Weissenberg photograph. The more intense reflections were integrated, and measured photometrically; the rest were estimated by visual comparison with a standard wedge. Corrections were made, where necessary, for distortion of spots on upper-level photographs, and appropriate Lorentz-polarization factors were applied.

The specimen used was (very approximately) a cube of side 0.4 mm.; for this specimen it was felt that absorption corrections were unnecessary. As a precaution against extinction errors, however, a powder photograph was obtained with chromium radiation. It was found to be possible to identify, and hence to estimate the intensities of, all of the strongest reflections, and enough of the weaker ones to place the powder and single-crystal data on the same scale. On the assumption that the powder data were free of extinction errors, the two sets were then compared in a manner analogous to that described by Pincock, Taylor & Lipson (1956), and a correction to the single-crystal data was obtained. The curve is shown in Fig. 1; the effect of extinction on the strongest single-crystal reflection is to reduce its intensity to about $\frac{1}{3}$ of its true value. It is believed that the corrected data are reasonably free from error.

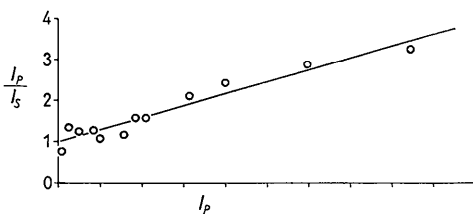


Fig. 1. Extinction correction: ratio of powder intensity to single-crystal intensity as a function of powder intensity. (Scale of abscissae is arbitrary.)

$$I_p = \text{Powder intensity.}$$

$$I_s = \text{Single-crystal intensity.}$$

1050 reflections were recorded, of a possible 2413 for the copper sphere, and 2140 with $k \leq 10$. The range of observed amplitudes is about 1 to 160.

Structure determination

It was expected that optical-transform methods would be adequate for the investigation of the structure, and this expectation seemed to be realized when inspection of the three-dimensional weighted reciprocal

lattice revealed quite clearly the orientation of the molecule in the unit cell. However, no position for this molecule could be found consistent with the observed structure amplitudes for any zone.

The data were then sharpened by the application of the function

$$\left| M(S) = \left(\frac{1}{f} \right)^2 \exp \left[\frac{-\pi^2 S^2}{p} \right] \right|$$

where $p = 7.25$ (Lipson & Cochran, 1953), and a 3-dimensional Patterson synthesis was computed. The vector density was found to be concentrated in two parallel planes, in a manner typical of a structure based on a planar molecule. (The terminology is convenient, but inexact; a plane of vector density is taken to be a distribution lying on and near, and symmetrically disposed with respect to, a mean plane.) One plane, containing the origin, seemed to consist mainly of intramolecular vectors, while the other, distant 3.4 Å from the origin, suggested intermolecular vectors. These planes made an angle of about 47° with the plane of symmetry $y = 0$, and were reflected in it to form an intersecting system.

The vector density distribution in the intramolecular plane confirmed the initial choice of orientation. Moreover, a very high peak in the intermolecular plane, assumed to be the 10 coincident C-C vectors from the naphthalene nuclei of a pair of centrosymmetrically related molecules, fixed the molecular position beyond doubt. The approximate structure thus seemed to be firmly established. However, attempts to refine it failed; it was not possible to reduce the agreement residual

$$(R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|)$$

for $h0l$ below 0.40.

After this impasse it was concluded that the space group must be wrong, or be used by the structure in

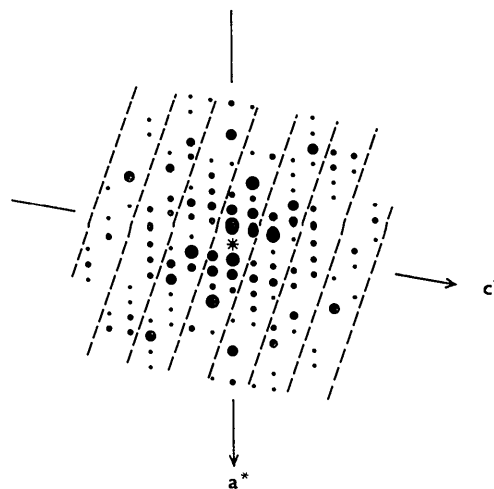


Fig. 2. $h0l$ weighted reciprocal-lattice section, showing straight fringes.

an unorthodox way. Situations of this sort are happily rare, but they are troublesome when they do occur, and it may be useful to present all the direct evidence which helped to establish the correct trial structure. There are two main features to consider.

(1) The peak in the intermolecular plane of vector density, which was assumed to fix the position of the molecule, proved on investigation to be far too high. By any method of estimation, this peak seemed to require the cooperation of all the atoms in the pair of molecules, and not just those of the naphthalene nuclei. This suggests that the pair of molecules concerned must be related by a non-crystallographic translation element instead of, or in addition to, the centre of symmetry. Such a translation element should produce in $h0l$ a set of straight, parallel fringes, and this set, with the predicted spacing, was in fact found (Fig. 2) although it had hitherto escaped notice. The significance of straight fringes has been discussed by Hanson, Taylor & Lipson (1953); the molecules are related by a non-crystallographic translation element, and if the space group possesses a centre of symmetry, the molecules must themselves be centro-symmetrical.

(2) Although the observed intensity data extended to the limit for copper radiation, and were modified by an appropriate sharpening function, the resolution in the Patterson synthesis was surprisingly poor. Peaks representing vectors between nearest-neighbour atoms were expected to lie about 1.4 Å from the origin, but were apparently completely masked by the origin peak. There appeared to be some vector density corresponding to much smaller interatomic distances, although this was difficult to demonstrate convincingly. Moreover, although the vector density distribution in the intramolecular plane left no doubt as to the orientation of the molecule, detailed correspondence between this plane and the assumed molecule was not satisfactory.

Two hypotheses can be advanced:

(a) The space group is Pa , with $0k0$ accidentally

absent for k odd. In the asymmetric unit there are two molecules, related by a fortuitous translation element.

(b) The structure is disordered, the average asymmetric unit consisting of two molecules related by a centre of symmetry, and occupying approximately the same space. The space group is $P2_1/a$, obeyed only in a statistical sense. (Such a structure has recently been reported for azulene by Robertson, Shearer, Sim & Watson, 1958.)

The second hypothesis is supported by the features discussed in (2) above, since a disordered structure will produce a more uniform distribution of vector density, and has no lower limit of effective interatomic distance. However, in view of the report of pyroelectricity, (a) was investigated first. An appropriate trial structure was assumed, and attempts were made to refine it with the aid of Fourier projections. For a projection lacking a centre, of course, such a procedure may be misleading; the Fourier synthesis tends to reproduce the assumed structure, even if it is wrong. Certainly some elegant and plausible maps were obtained, but ultimately it proved to be impossible to reduce the agreement residual for $h0l$ below about 0.30.

The second hypothesis ultimately proved to be correct. A trial structure in reasonable accord with the Patterson synthesis was adopted, and gave immediately agreement residuals of 0.24 for both $h0l$ and $hk0$.

Refinement of the trial structure in three dimensions was accomplished with two cycles of structure-factor calculation and Fourier synthesis. Because of the disorder, many of the atoms were not resolved, even in three dimensions, from their nearest neighbours. For this reason it was not practicable to refine the structure to the point usually considered desirable, and no great precision can be claimed for it.

A section of the last Fourier synthesis, evaluated in the mean plane of the composite molecule is shown in Fig. 3. (40 of the 1050 observed structure amplitudes

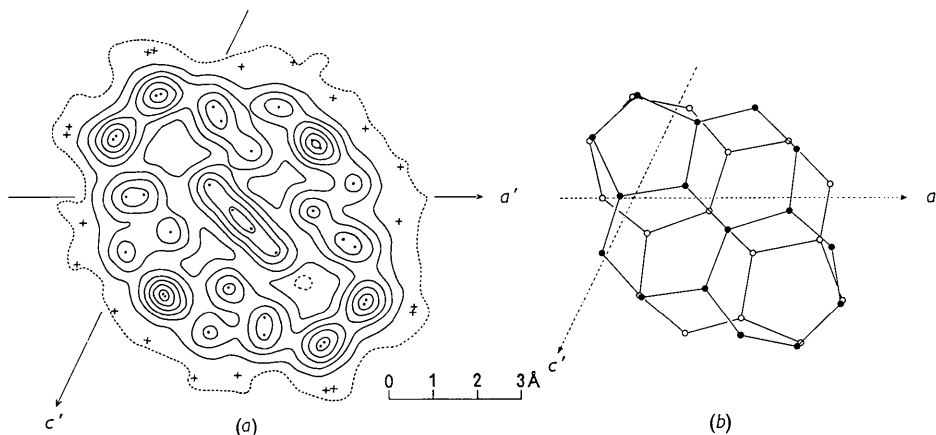


Fig. 3. (a) Electron density in the plane of the molecule. Solid contours are drawn at intervals of $1 \text{ e.}\text{\AA}^{-3}$, the lowest being at $1 \text{ e.}\text{\AA}^{-3}$. The dotted contour is at $0.3 \text{ e.}\text{\AA}^{-3}$. Carbon positions are indicated by dots and assumed hydrogen positions by crosses. (b) Interpretation of (a). a' and c' are the traces of the planes $z=0$ and $x=0$ respectively.

Table 1. Atomic positions (hydrogen positions are assumed)

Molecule (a)					Molecule (b)				
Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
C ₁	0.2988	0.0444	0.1395	4.5	C' ₁	-0.0458	-0.2692	0.0000	4.5
C ₂	0.3489	0.0454	0.3022	5.5	C' ₂	-0.0970	-0.2675	-0.1630	5.5
C ₃	0.3163	-0.0342	0.4250	5.5	C' ₃	-0.0681	-0.1920	-0.2887	5.5
C ₄	0.2333	-0.1112	0.3958	4.5	C' ₄	0.0178	-0.1152	-0.2572	4.5
C ₅	0.0750	-0.2378	0.2802	4.5	C' ₅	0.1725	0.0140	-0.1605	4.5
C ₆	-0.0093	-0.2795	0.1578	4.5	C' ₆	0.2560	0.0597	-0.0375	4.5
C ₇	-0.0947	-0.2610	-0.1750	5.5	C' ₇	0.3482	0.0493	0.2887	5.5
C ₈	-0.0614	-0.1836	-0.2930	5.5	C' ₈	0.3192	-0.0277	0.4145	5.5
C ₉	0.1047	-0.0249	-0.2552	4.5	C' ₉	0.1588	-0.1907	0.3888	4.5
C ₁₀	0.1893	0.0235	-0.1365	4.5	C' ₁₀	0.0715	-0.2395	0.2745	4.5
C ₁₁	0.2158	-0.0069	0.0308	3.5	C' ₁₁	0.0428	-0.2103	0.1000	3.5
C ₁₂	0.1525	-0.1485	0.2562	3.5	C' ₁₂	0.0988	-0.0766	-0.1286	3.5
C ₁₃	-0.0178	-0.2374	-0.0072	4.5	C' ₁₃	0.2762	0.0277	0.1188	4.5
C ₁₄	0.0380	-0.1084	-0.2150	4.5	C' ₁₄	0.2233	-0.1048	0.3460	4.5
C ₁₅	0.1486	-0.0998	0.0896	3.5	C' ₁₅	0.1106	-0.1210	0.0387	3.5
C ₁₆	0.0633	-0.1447	-0.0336	3.5	C' ₁₆	0.1984	-0.0719	0.1576	3.5
H ₁	0.3400	0.1101	0.0727	5.5	H' ₁	-0.0833	-0.3340	0.0750	5.5
H ₂	0.4200	0.1072	0.3275	5.5	H' ₂	-0.1678	-0.3284	-0.2015	5.5
H ₃	0.3664	-0.0249	0.5528	5.5	H' ₃	-0.1080	-0.1909	-0.4225	5.5
H ₄	0.2234	-0.1600	0.5075	5.5	H' ₄	0.0296	-0.0652	-0.3684	5.5
H ₅	0.0790	-0.2765	0.4053	5.5	H' ₅	0.1734	0.0562	-0.2825	5.5
H ₆	-0.0613	-0.3508	0.1925	5.5	H' ₆	0.3077	0.1282	-0.0805	5.5
H ₇	-0.1592	-0.3288	-0.1750	5.5	H' ₇	0.4194	0.1110	0.3154	5.5
H ₈	-0.1020	-0.1831	-0.4266	5.5	H' ₈	0.3533	-0.0387	0.5500	5.5
H ₉	0.0984	0.0116	-0.3821	5.5	H' ₉	0.1667	-0.2230	0.5175	5.5
H ₁₀	0.2339	0.0901	-0.1965	5.5	H' ₁₀	0.0214	-0.3081	0.3206	5.5

were omitted from the synthesis because their signs were indeterminate at this stage. The omitted terms are all small, and it has not subsequently been felt to be worthwhile to consider their effect on the electron density.) The final atomic positions were estimated from this map, and from perpendicular sections through all peaks. It is apparent from the map that individual peak electron densities decrease somewhat with distance from the centre of gravity. In the final structure-factor calculation therefore, different temperature factors have been assigned to individual atoms. Also, for this calculation, the hydrogen atoms have been assigned plausible positions, as shown in Fig. 3(a). The scattering-factor curves of McWeeny (1951) were used for all structure-factor calculations. The final positions of the atoms, and their several temperature factors, are given in Table 1. The agreement residual, for observed reflections only, is 0.18.

Reliability of the structure

The structure described is unusual, and moreover it cannot be completely refined. It is important therefore to establish its correctness by a critical examination of the individual agreement between observed and calculated structure amplitudes. It seems undesirable to publish the complete data (although these are available from the author, on request), and in Table 2(a) a summary is given instead, showing the numbers of reflections corresponding to specified categories of agreement. Values of F_o range from 0.9 to 150.5; $F_c(000)=424.0$; unobserved reflections are not considered.

The more serious discrepancies are found among the weaker reflections; only one structure amplitude ex-

Table 2

(a) Agreement summary

Category	Number of reflections
1 ($\Delta F \leq \frac{1}{2}F_T$ or $\Delta F \leq 0.1F_o$)	571
2 ($\Delta F \leq 1F_T$ or $\Delta F \leq 0.2F_o$)	303
3 ($\Delta F \leq \frac{3}{2}F_T$ or $\Delta F \leq 0.3F_o$)	113
4 ($\Delta F \leq 2F_T$ or $\Delta F \leq 0.4F_o$)	42
5 ($\Delta F \leq \frac{5}{2}F_T$ or $\Delta F \leq 0.5F_o$)	17
6 (unspecified)	4

$$\Delta F = ||F_o| - |F_c||$$

F_T = estimated minimum observable structure amplitude for the indices of the reflection concerned.

Each category includes all reflections which meet the specified conditions, and which have not been previously included. For example, a reflection in category 2 satisfies either (or both) of the conditions $\Delta F \leq F_T$ and $\Delta F \leq 0.2F_o$, but does not satisfy either of the corresponding conditions for category 1.

(b) Observed and calculated structure factors in categories 5 and 6 above

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
40 $\bar{8}$	2.2	6.6	10,3,0	5.8	10.8
12,0, $\bar{1}$	7.3	-11.8	04 $\bar{2}$	4.5	-1.0
011	3.8	-5.4	14 $\bar{2}$	4.5	8.2
216	9.6	-14.2	24 $\bar{2}$	6.9	-3.8
515	5.9	11.0	440	5.2	-2.0
11,1,3	2.7	-6.6	44 $\bar{3}$	3.1	7.2
021	5.9	-3.2	053	7.2	-4.0
124	7.8	-11.2	851	6.8	-11.6
032	4.5	-1.2	475	7.9	13.2
23 $\bar{6}$	3.2	8.4	572	7.5	-2.0
834	9.1	14.0			

ceeding 15.0 is found in category 3, and the largest in category 4 is 13.2. In order to permit a critical scrutiny of the worst disagreements, F_o and F_c for the 21 reflections not included in the first four categories are compared in Table 2(b).

The most obvious cause of disagreement is of course the incomplete refinement of the structure, with consequent inaccuracy of atomic position. The assumptions pertaining to thermal motion are suspect also; no attempt was made to allow for anisotropy, and the individual temperature factors given in Table 1 were obtained by guesswork. The structure factors are therefore certain to be in error to some extent, and the errors will be most obvious for the smaller magnitudes. It is felt that the agreement summarized in Table 2 is no worse than it should be, in these circumstances, and that the correctness of the structure is established.

Discussion of the structure

The difficulty of locating unresolved atoms has been mentioned, and there seems to be little point in attempting a quantitative estimate of the errors in the atomic positions. Bond lengths are not given because none can be measured as a distance between two resolved peaks. It is perhaps sufficient to say that the C-C bond lengths corresponding to the positions in Table 1 range from 1.27 to 1.52 Å. Obviously only very general discussion of the molecular structure is possible.

It seems likely that the molecule is quite accurately planar, since no peak in the electron-density distribution lies more than 0.04 Å from the reference plane $0.704x - 0.671y - 0.228z = 0.1485$. It is of course possible that two atoms contributing to a single peak might lie on opposite sides of this plane, and be more than 0.04 Å from it, and the resultant elongation of the peak might be concealed by anisotropic thermal motion, but this is considered to be rather unlikely.

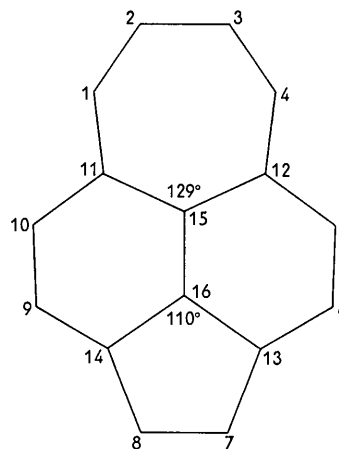


Fig. 4. The average molecule, showing the numbering system and the values of two angles.

The average bond angle for the naphthalene nucleus is of course 120°; for the 5-membered ring it is 108°, and for the 7-membered ring 128.6°. When two different ring systems share an angle, therefore, there must be some departure from regularity of at least one of them. Some distortion of the naphthalene nucleus is evident in the electron-density map of Fig. 3(a); it is shown more clearly in Fig. 4, which is a representation of the average molecule with the values of the shared angles given. These are very close to the average values for the corresponding odd-numbered rings, and thus the distortion of the naphthalene nucleus seems to be greater than might have been expected. However, it should be remembered that these angles cannot be accurately determined.

Discussion of the crystal structure is hampered by uncertainty as to the exact nature of the disorder. It seems unlikely that this is completely random, that is, that each molecule is free to choose one of two possible orientations, irrespective of the orientations

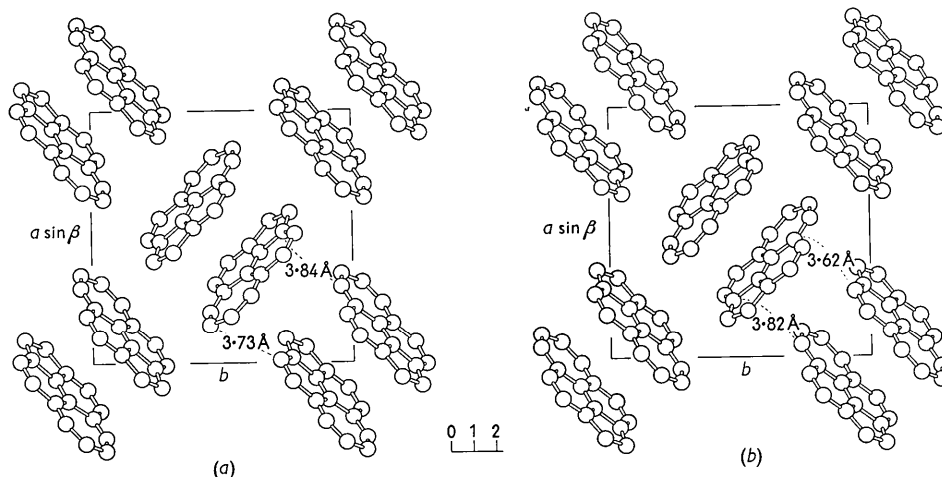


Fig. 5. The structures (a) and (b), viewed along c.

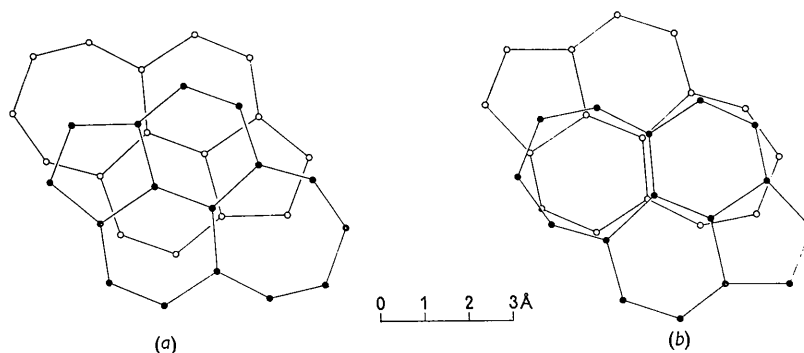


Fig. 6. Two overlapping molecules of the structures (a) and (b), viewed along the normal to the molecular plane.

of its nearest neighbours. On the other hand, there is no evidence of a finite domain size. (Diffuse regions are indeed associated with the more intense reflections, but these can be interpreted as thermal effects.) It is assumed, nevertheless, that there are small domains of order within each of which the structure is represented by either molecule (a) or (b) in Table I. These two distinct structures are illustrated in Fig. 5. Both are similar to pyrene (Robertson & White, 1947), in that centro-symmetrically related molecules partially overlap each other, as shown in Fig. 6. The relative positions (but not the interplanar distances) of these molecules differ somewhat for the two structures, and are apparently modified by proximity of other neighbouring molecules. The interplanar distance is 3.44 Å (compared with 3.53 Å for pyrene, and 3.41 Å for graphite), and this is a good value for the closest approach of carbon atoms in adjacent, overlapping molecules. The closest approach for molecules related by a c translation is 3.51 Å for (a) and 3.58 Å for (b); hydrogen atoms can play no direct part in fixing these distances. The closest approaches of adjacent, non-parallel molecules are shown in Fig. 5; no other such distance is less than 3.7 Å, and thus both structures seem plausible enough from considerations of packing. It should be mentioned, however, that a completely random structure requires no abnormally short intermolecular distances, and so cannot be ruled out on purely spatial grounds. The intermolecular distances quoted throughout are of course no more accurate than the bond lengths. However, the interplanar distance should be much more reliable.

The lengthy computations for this project were

carried out by Dr F. R. Ahmed of this laboratory using programmes of his own devising and facilities generously made available by the Commanding Officer and staff of No. 1 Army Pay Ledger Unit (IBM 650), and the staff of the Structures Laboratory, Division of Mechanical Engineering (TRANSFER, formerly FERUT). The sample of acepleiadylene was provided by Prof. V. Boekelheide, and the problem was suggested by Dr W. G. Schneider. It is a pleasure to record my indebtedness to all the above, and to Dr W. H. Barnes of this laboratory for valued advice and encouragement.

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