

## X-ray Structural Analysis of 5,6-Dihydrodibenz[*a,j*]anthracene: Evidence for the Coexistence of Ordered and Disordered Molecules\*

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The crystal and molecular structure of 5,6-dihydrodibenz[*a,j*]anthracene,  $C_{22}H_{16}$ , has been determined from three-dimensional X-ray diffractometer data. This partially hydrogenated derivative of a pentacyclic aromatic hydrocarbon crystallizes with eight molecules in a monoclinic unit cell of symmetry  $P2_1/c$  and parameters  $a = 12.1434$  (3),  $b = 8.0864$  (4),  $c = 30.6369$  (11) Å, and  $\beta = 101.130$  (1)° at 22°C. The structure was solved by direct methods and refined by the full-matrix least-squares method to  $R(F) = 8.2\%$  and  $R(F^2) = 7.2\%$  based on 3090 independent nonzero intensity data. One of the two independent molecules (*A*) is normal, whereas the crystal-disordered model for the other molecule (*B*), successfully utilized in the refinement, assumes a distribution of two partial molecules in two orientations approximately related to each other by a mirror plane through the C(8') and C(19') atoms of the middle ring. The ratio of occupancy factors for the two disordered orientations is 7:3. Each aromatic ring in both independent molecules is almost perfectly planar, and the phenanthrene moieties are approximately planar, but with an observable distortion of the rings, attributable to overcrowding of hydrogen atoms. The bond length in the electron-rich K region of the phenanthrene moiety is 1.334 (6) Å for molecule *A*. The saturated carbon atoms are about 0.35 Å above and below the plane defined by the other carbon atoms of the ring, and the adjacent and aromatic ring is twisted 21° from the plane of the center aromatic ring.

### Introduction

Polycyclic aromatic hydrocarbons are known to display a wide variety of carcinogenic activities, and a number of these compounds and their derivatives have been tested for carcinogenicity in animals (Hartwell, 1951; Schubik & Hartwell, 1957 & 1969). Recently, a series of partially hydrogenated dibenzanthracene derivatives was prepared and further investigated for tumorigenic activity on Swiss female mice (Lijinsky & Saffiotti, 1965; Lijinsky, Garcia & Saffiotti, 1970). The results of skin painting tests indicated that 5,6-dihydrodibenz[*a,j*]anthracene is significantly carcinogenic in contrast with the weak carcinogenicity of its parent, dibenz[*a,j*]anthracene. However, attempts to correlate the biological effects of chemical carcinogens with molecular structure have so far been unsuccessful, since the mechanism of carcinogenicity by formation of hydrocarbon complexes with DNA or skin protein remains a complex problem subject to considerable controversy (*e.g.* see Nagata, 1970). Nevertheless, unambiguous structural determination continues to merit attention. Crystal and molecular structures of polycyclic aromatic hydrocarbons determined by X-ray structural analyses include coronene (Robertson & White, 1945); pyrene (Robertson & White, 1947*a*); 1:2:5:6-dibenzanthracene (Robertson & White, 1947*b*; Robertson & White, 1956); 9:10-dihydroanthracene (Fer-

rier & Iball, 1954; Beckett & Mulley, 1955); 9:10-dihydro-1:2:5:6-dibenzanthracene (Iball & Young, 1958; Herbstein, 1959 & 1961); and phenanthrene (Trotter, 1963; Kay, Okaya & Cox, 1971). Apparently, no partially hydrogenated dibenzanthracene has been subjected to three-dimensional structural analysis before the present work. The present X-ray study was undertaken to provide more accurate stereochemical information (including that of all the hydrogen atoms) on the polycyclic aromatic hydrocarbon system.

### Experimental

#### *Crystal specimen*

A sample of 5,6-dihydrodibenz[*a,j*]anthracene, kindly furnished by Dr W. Lijinsky of the Eppley Institute for Research in Cancer (now at Oak Ridge National Laboratory), was recrystallized from an *n*-hexane solution. A colorless plate-like crystal of  $0.05 \times 0.15 \times 0.32$  mm dimensions was selected for the determination of cell parameters and for data collection. The crystal was mounted so that the longest dimension, corresponding to the *b* direction, was nearly parallel to the  $\varphi$  axis of the diffractometer.

#### *Unit cell and space group*

The crystal system and approximate cell parameters were determined from Weissenberg and precession photographs. Eight strong reflections in the  $2\theta$  range of 80 to 90° were centered on an Oak Ridge computer-controlled diffractometer (Busing, Ellison, Levy, King & Roseberry, 1968), using  $Cu K\alpha_1$  ( $\lambda = 1.54051 \text{ \AA}$ ) ra-

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diation, and the cell parameters were refined by the method of least squares. The density was determined by flotation in mixtures of 1,2-dichloroethane and *p*-dioxane. The observed systematic absences of  $h0l$  for  $l$  odd and  $0k0$  for  $k$  odd are uniquely characteristic of the space group  $P2_1/c$  ( $C_{2h}^2$ , No. 14) (see *International Tables for X-ray Crystallography*, 1965, pp. 98-99); this finding was later confirmed by the successful refinement of the structure. The crystallographic data are as follows:  $a = 12.1434$  (3),  $b = 8.0864$  (4),  $c = 30.6369$  (11) Å,  $\beta = 101.130$  (1)°,  $V = 2951.3$  Å<sup>3</sup>,  $F(000) = 1184$ ,  $D_{\text{obs}} = 1.23$  (2) g.cm<sup>-3</sup>,  $D_{\text{calc}} = 1.262$  g.cm<sup>-3</sup>,  $Z = 8$ ,  $\mu_{\text{Cu } K\alpha} = 5.50$  cm<sup>-1</sup>.

#### X-ray intensity data

Nickel-filtered copper  $K\alpha$  radiation was used for recording the reflection intensities. Intensities were measured for 3502 independent reflections, using the Oak Ridge computer-controlled X-ray diffractometer and the  $\theta$ - $2\theta$  step-scan technique for  $2\theta \leq 125^\circ$ . The data collection was divided into four parts with slightly different experimental conditions, as shown in Table 1. The reflections in the range  $100$ - $125^\circ$   $2\theta$  were mostly weak; they were first measured rapidly (with no filter) by the peak-top technique; then, by choice of an arbitrary cutoff, 467 'strong' reflections out of 1703 reflec-

tions tested were selected for subsequent intensity measurements.

Throughout the course of data collection, the take-off angle at the X-ray tube was  $3^\circ$ . A reference reflection was recorded after every 25 reflections as a check on the stability of the instrument and of the crystal. For each group of reflections shown in Table 1, the maximum fluctuation from the average intensity of the reference reflection during the data collection was less than 1.5% showing that the crystal was stable to X-ray exposure during data collection. Reference intensities were used to normalize the data; then Lorentz-polarization corrections were made. Absorption corrections, calculated by the method of Busing & Levy (1957), were then applied using a linear absorption coefficient of  $5.50$  cm<sup>-1</sup> for Cu  $K\alpha$  radiation. The maximum and minimum transmission factors were 0.975 and 0.919. Of 3502 independent reflections measured, 3090 had observed intensities greater than zero and were subsequently utilized as the 'observed' data.

Variances  $\sigma^2(F_o^2)$  were estimated from the empirical equation:

$$\sigma^2(F_o^2) = A^2 s^2 \{G + (t_G/t_B)^2 B + 0.0016[G - (t_G/t_B)B]^2\} / (Lp)^2,$$

where  $A$  = correction factor on the intensity for absorption,  $s$  = scale factor on the intensity,  $G$  = gross

Table 1. Experimental conditions in data collection

$2\theta$ Range	Step width in $2\theta$	Total width of scan*	Step time	Background count†
1-59°	0.05°	1.5°	2 sec	10 sec
59-90	0.05	1.6	2	30
90-100	0.05	1.6	6	90
100-125	0.05	1.6	6	108

\* The separation of the  $\alpha_1$ - $\alpha_2$  doublet was also added to these values.

† Taken at the beginning and end of each scan.

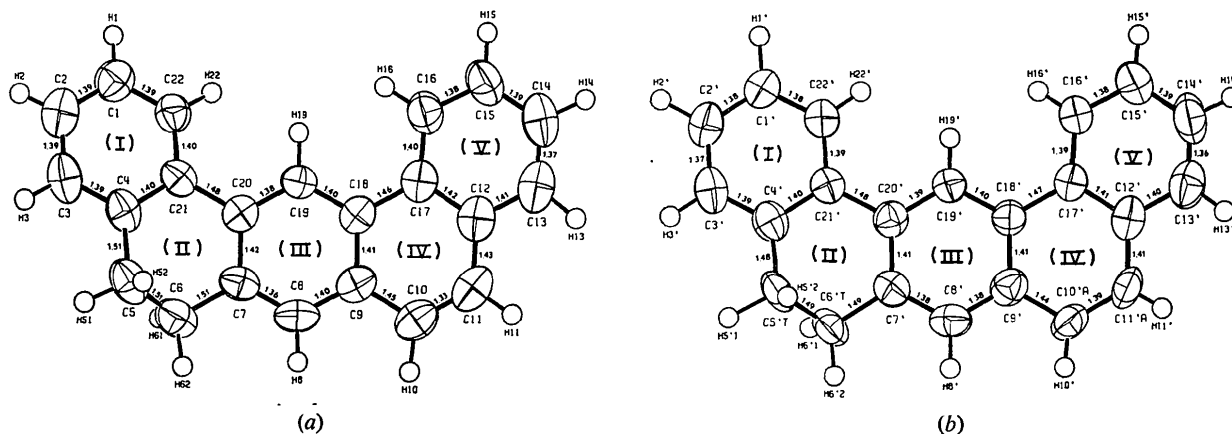


Fig. 1. Molecular configurations of  $C_{22}H_{16}$ . Part (a) shows the configuration of the normal molecule *A*, whereas (b) is that for the disordered molecule *B* with predominant occupancy factor 0.7. The hydrogen atoms are numbered according to the carbon atoms to which they are attached.

count,  $B$  = background count,  $t_G/t_B$  = ratio of the counting times of gross intensity and background, and  $L_p$  = Lorentz-polarization factor.

### Solution and refinement of the structure

The structure was solved by the application of Sayre's equation (Sayre, 1952), using Long's (1965) program. Normalized structure factors,  $E$ , were calculated with program *FAME* (Dewar & Stone, 1967). The three-dimensional  $E$  map, computed (program *FORDAPER* of A. Zalkin as modified by G. Brunton) from the 322 largest  $E$  values ( $E \geq 1.5$ ) and signs, yielded 44 peaks interpretable as the carbon atoms of two independent molecules of dibenz[*a,j*]anthracene. In the following discussion, atoms are designated by nonprimed symbols for the normal molecule *A* and by primed symbols for molecule *B*, which was found to be disordered.

This starting model was refined with all the observed intensity data by the full-matrix least-squares method (Busing, Martin & Levy, 1962), in which the function minimized was  $\sum w|F_o^2 - s^2F_c^2|^2$ , where  $s$  is the scale factor and weights  $w$  are reciprocals of the variances,

$\sigma^2(F_o^2)$ . Three cycles of refinement with all 'heavy' atoms treated isotropically resulted in an unweighted reliability index,  $R(F^2) = (\sum |F_o^2 - F_c^2| / \sum F_o^2) \times 100$ , of 16.4%. The refinement was continued with all carbon atoms assigned anisotropic temperature factors. After three cycles,  $R(F^2)$  became 14.0%. Bond-length calculations carried out at this stage with the program *ORFFE* (Busing, Martin & Levy, 1964) revealed that all carbon-

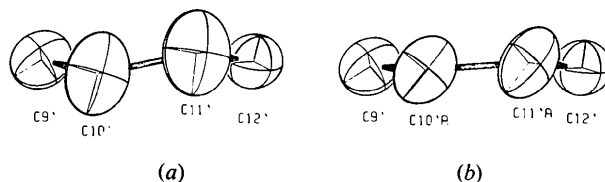


Fig. 2. Shapes of the 50%-probability thermal ellipsoids obtained before and after the breakdown of the average positions for C(10') and C(11') in ring (IV) for molecule *B*. In (a), the shapes of the ellipsoids appear to indicate qualitatively the large vibrations in the direction approximately perpendicular to the plane of ring (IV). After the breakdown, the ellipsoids for the aromatic partial-carbon atoms with higher occupancy factor seem to become almost normal as shown in (b).

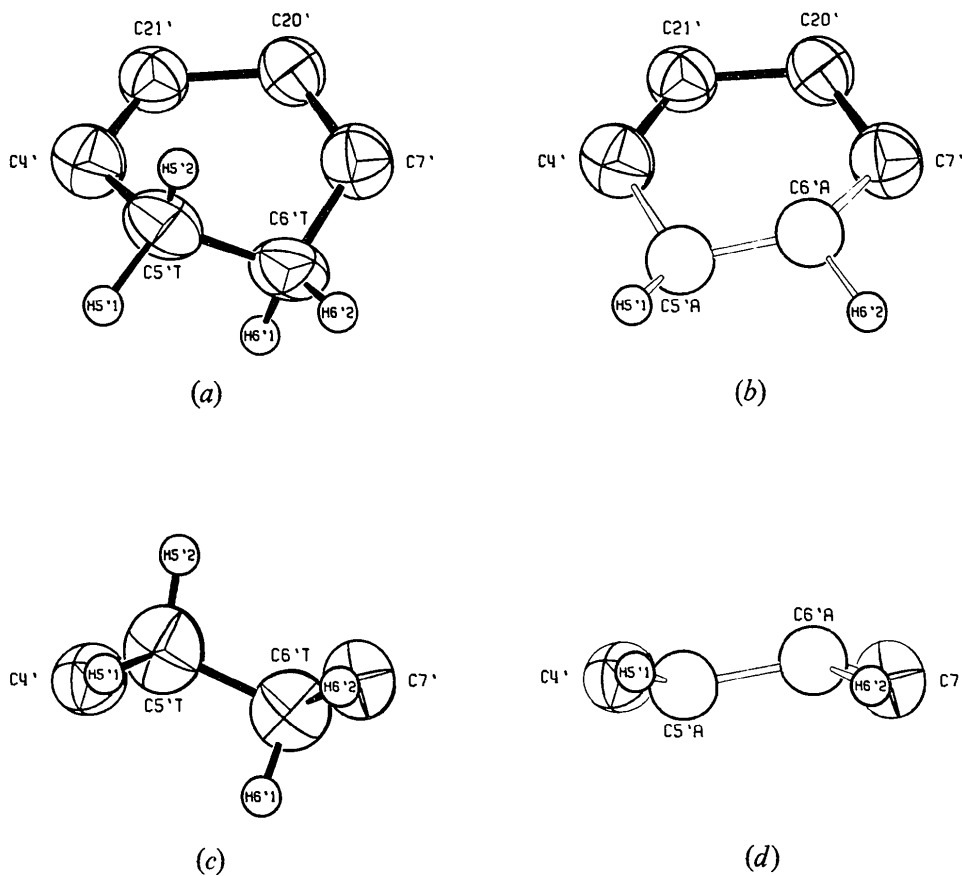


Fig. 3. Conformations of ring (II) in molecule *B*. Each of the tetrahedral [(a) and (c)] and aromatic [(b) and (d)] portions of the molecule are shown separately in the two different views. It can be visualized that H(5'-1) and H(6'-2) are shared by the two types of carbon atoms. The open bonds in (b) and (d) are those associated with the disordered atoms of the minor configuration.

carbon bond distances in both molecules were reasonable, except for an apparent distance of 1.43 Å between the presumably tetrahedral carbon atoms C(5') and C(6') in molecule *B* (for numbering scheme, see Fig. 1). This value is significantly shorter than the expected value of 1.54 Å for a carbon-carbon single bond length (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965, p. S14s).

A three-dimensional difference synthesis, phased on all carbon atoms, was calculated next, and 32 peaks were interpreted as hydrogen atoms. The refinement was carried further, with carbon atoms assigned anisotropic thermal parameters and hydrogen atoms assigned isotropic thermal parameters. After three cycles, the  $R(F^2)$  value dropped to 7.2%. Although all the C-H bond distances were reasonable, the C(5')-C(6') bond distance still persisted at an anomalously low value, 1.41 Å. At this stage, rings (I), (III), (IV), and (V) for molecule *A* [Fig. 1(a)] were nearly planar, and two tetrahedral carbon atoms, C(5) and C(6), deviated approximately 0.35 Å above and below the 'best' plane (Smith, 1962) through C(4), C(7), C(20) and C(21). For molecule *B* [Fig. 1(b)], however, atoms C(5') and C(6') were displaced 0.26 and 0.19 Å respectively in opposite directions from the best plane through the other carbon atoms of ring (II); atoms C(10') and C(11') deviated 0.19 and 0.11 Å in opposite directions from the best plane through the other carbon atoms of ring (IV). An examination of vibrational anisotropy further revealed that the  $\beta_{22}$  components of the anisotropic temperature factors for C(5') and C(6') were 0.035 (equivalent to a root-mean-square amplitude of 0.37 Å) as compared to values ranging from 0.014 to 0.019 for the other carbon atoms of the same ring; atoms C(10') and C(11') had  $\beta_{22}$  values of 0.029 and 0.032 (corresponding to r.m.s. amplitudes of 0.31 and 0.34 Å) respectively, which also were much larger than the  $\beta_{22}$  values (ranging from 0.014 to 0.107) for the other carbon atoms of the same ring.\* Assuming the compound to be pure (Lijinsky, Garcia & Saffiotti, 1970), these observed anomalies in the geometry of molecule *B* suggested that this molecule is subject to a type of disorder somewhat similar to that of dihydrothymine (Furberg & Jensen, 1968), in which two neighboring tetrahedral ring carbons were treated as disordered.

It was assumed that each of the atoms C(5'), C(6'), C(10') and C(11') occupies two alternative atomic sites

\* The anomalous thermal vibrations of atoms C(10') and C(11') were characterized further by principal-axis transformations of the vibrational ellipsoids. The vibrational anisotropy was such that the longest principal axes made angles of 34 and 19° with the normals to the planes defined by C(9'), C(10), and C(11'), and C(10'), C(11'), and C(12') respectively; the r.m.s. components of thermal displacements along the principal axes projected on the corresponding normals of the planes were 0.30 and 0.34 Å respectively, compared to values of 0.01 and 0.04 Å for corresponding atoms C(10) and C(11) in molecule *A*. Thermal ellipsoids viewed in a direction perpendicular to the normal of the best plane through C(9'), C(10'), C(11'), C(12'), C(17'), and C(18') are shown in Fig. 2(a).

with tetrahedral and aromatic geometries. For each of these atoms, the position obtained in the least-squares refinement therefore represents the *average* of two different atomic sites. Two possible atomic sites for each of the disordered carbon atoms C(5'), C(6'), C(10'), and C(11') were estimated and were designated *T* and *A* for the tetrahedral and aromatic sites respectively. These four pairs of partial-carbon atoms were then substituted for C(5'), C(6'), C(10') and C(11'). Atoms C(5'*T*), C(6'*T*), C(10'*A*), and C(11'*A*) were each assigned the same occupancy factor, *m*, while C(5'*A*), C(6'*A*), C(10'*T*), and C(11'*T*) were each assigned the occupancy factor 1-*m*. Atoms H(5'-1) and H(6'-2) are located approximately at equatorial positions with respect to the plane through C(4'), C(7'), C(20'), and C(21'); hence H(5'-1) can be considered to be 'shared' by C(5'*T*) and C(5'*A*), and H(6'-2) by C(6'*T*) and C(6'*A*) (see Fig. 3). The occupancy factors of these hydrogen atoms were taken as unity, whereas H(5'-2) and H(6'-1), considered to be associated with C(5'*T*) and C(6'*T*) respectively, were assigned the same occupancy factors as those of the partial-carbon atoms. In the same manner, the two equatorial hydrogen atoms, H(10') and H(11'), were each given an occupancy factor of unity. An attempt to locate two partial-hydrogen atoms associated with tetrahedral-carbon sites, corresponding to C(10'*T*) and C(11'*T*), was not successful.

The refinement was continued with 40 'full' and four partial-carbon atoms with occupancy factor *m* assigned\* anisotropic temperature factors, and with four other partial-carbon atoms having occupancy factors 1-*m* and 32 hydrogen atoms assigned isotropic temperature factors. Only the occupancy factor of C(5'*T*) was adjusted with the other parameters in the refinement, the occupancy factors of the other disordered atomic sites being constrained in a proper way. At the end of the refinement, the values of  $R(F^2)$  and  $R_w(F^2)$  [the latter defined as  $(\sum w|F_o^2 - s^2 F_c^2|^2 / \sum w F_o^4)^{1/2} \times 100$ ] stood at 7.2 and 10.4% respectively. The unweighted reliability index based on *F* was 8.2%. The maximum parameter shift in the last cycle for the carbon atoms was 27% of the corresponding standard deviation for C(10'*A*), whereas the maximum shift in the hydrogen parameters was 16% of the corresponding standard deviation for H(5'-2). The standard deviation of an observation of unit weight, defined  $[\sum w|F_o^2 - s^2 F_c^2|^2 / (n-p)]^{1/2}$ , where *n* is the number of observations and *p* the number of parameters fitted to the data set, was 1.020. The value of *m* was 0.70(4). A final difference map did not show any region of electron density greater than 0.25 e.Å<sup>-3</sup>. The scattering factors used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, and those of Stewart, Davidson & Simpson (1965) for hydrogen.

The final positional and thermal parameters are given in Table 2. The observed and calculated structure am-

\* Assignment was based on intermediate refinement, which showed that *m* was significantly greater than 1-*m*.

plitudes are listed in Table 3. The interatomic distances and bond angles for both molecules are given in Table 4. Figs. 1 to 5 were prepared with program ORTEP (Johnson, 1970).

### Results and discussion

#### General description of the structures

Although the molecule of 5,6-dihydrodibenz[*a,j*]anthracene almost has  $2mm$  ( $C_{2v}$ ) symmetry, the presence of two saturated carbon atoms and some molecular distortion, resulting from overcrowded hydrogen atoms, reduce the symmetry to  $1(C_1)$ . The crystal structure is composed of molecules *A* and *B* with configurations as depicted in Fig. 1, where carbon atoms are shown as 50% probability thermal ellipsoids. Fig. 1(*a*) is the configuration for the normal molecule *A*, and Fig. 1(*b*) is the configuration for the disordered molecule *B* with the predominant occupancy factor 0.7. This predominant configuration of molecule *B* has a geometry closely resembling that of molecule *A*, whereas the minor con-

figuration of molecule *B* is related to the dominant one by a pseudomirror plane passing through atoms C(8') and C(19'). An idea of the displacements of the individual partial-atom positions from ring (II) of molecule *B* may be gained by an examination of Fig. 3. Fig. 3(*a*) and (*b*) show views of the portion of the molecule in a direction approximately  $45^\circ$  from the normal to the best plane through C(4'), C(7'), C(20'), and C(21'). Fig. 3(*c*) and (*d*) are the corresponding views in a direction perpendicular to the normal.

In spite of the troublesome problem of the disorder of molecule *B*, the structure of molecule *A* seems to be well determined from the fairly accurately determined atomic parameters. The discussion is therefore centered on molecule *A* and numerical values are cited for *A*, unless otherwise stated.

The molecule can be considered to be formed by the fusion of a phenanthrene nucleus with 1,2-dihydronaphthalene along the common bond C(7)–C(20). The C(5)–C(6) bond is twisted clockwise about the direc-

Table 2. Positional and thermal parameters

The entries *X*, *Y*, and *Z* are the fractional coordinates multiplied by  $10^4$  for carbon atoms and by  $10^3$  for hydrogen atoms. The form of the anisotropic temperature factor ( $\times 10^5$ ) is  $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . For each hydrogen atom and atoms C(5'*A*), C(6'*A*), C(10'*T*) and C(11'*T*), the entry  $\beta_{11}$  is the isotropic temperature factor in  $\text{\AA}^2$ . Standard deviations of the last significant figure(s) are given here and in succeeding tables.

ATOM	MOLECULE A			MOLECULE B							ATOM	MOLECULE B			MOLECULE B						
	X	Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$	X		Y	Z	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$		
C(1)	1345(4)	5569(6)	3184(2)	967(42)	2007(87)	168(7)	100(46)	89(13)	50(20)	C(1')	6586(4)	6288(6)	5573(2)	871(38)	2989(106)	155(7)	76(52)	24(12)	209(22)		
C(2)	2494(4)	4875(6)	2849(2)	858(43)	2151(93)	216(8)	-10(51)	48(15)	116(22)	C(2')	7701(4)	6737(6)	5622(2)	873(40)	2554(101)	151(7)	249(50)	-11(13)	81(21)		
C(3)	881(4)	3931(6)	2520(2)	890(39)	1938(85)	194(7)	-29(48)	-41(14)	74(21)	C(3')	8011(3)	7794(6)	5317(2)	686(35)	2293(90)	71(7)	-6(45)	-31(2)	-96(20)		
C(4)	2010(3)	3651(5)	2525(1)	925(36)	1399(65)	135(6)	26(40)	-26(11)	25(15)	C(4')	7236(3)	8413(5)	4963(1)	755(33)	1776(74)	146(6)	-32(40)	52(11)	-61(17)		
C(5)	2389(4)	2624(6)	2169(2)	1155(45)	1964(92)	154(7)	-5(53)	-60(14)	-86(20)	C(5')	7514(9)	9663(24)	4648(4)	495(68)	2731(251)	174(13)	-192(96)	87(21)	-7(47)		
C(6)	3439(4)	3310(6)	2050(2)	1294(49)	2061(95)	124(6)	239(56)	23(13)	-52(20)	C(6')	6912(7)	9467(21)	4180(4)	601(56)	2432(216)	158(13)	-103(82)	129(20)	-17(47)		
C(7)	4341(3)	3497(5)	2462(1)	1053(40)	1493(65)	107(5)	25(41)	75(11)	-19(15)	C(7')	5681(3)	9365(5)	4174(1)	752(32)	1918(76)	143(6)	-92(43)	62(11)	55(18)		
C(8)	5443(4)	3172(5)	2464(1)	1233(46)	1650(75)	125(6)	21(46)	159(14)	-74(17)	C(8')	4923(4)	9918(5)	3810(1)	1038(40)	1877(81)	137(6)	-91(45)	122(12)	83(18)		
C(9)	6277(3)	3305(4)	2849(1)	905(36)	1386(67)	151(6)	-12(39)	127(12)	-4(16)	C(9')	3777(3)	9703(5)	3768(1)	953(37)	1550(67)	130(6)	-85(41)	25(17)	52(16)		
C(10)	7437(4)	2902(5)	2842(2)	1001(43)	1808(78)	191(8)	85(45)	160(15)	0(20)	C(10')	3007(10)	10373(21)	3393(4)	970(87)	1977(202)	120(12)	-74(95)	-21(22)	162(43)		
C(11)	8211(4)	2986(5)	3215(2)	863(41)	2041(85)	225(9)	166(48)	162(16)	90(22)	C(11')	1861(8)	10395(17)	3393(4)	820(75)	2051(180)	142(12)	-33(85)	-122(22)	179(35)		
C(12)	7951(3)	3501(5)	3630(2)	873(36)	1598(71)	177(7)	-34(41)	58(13)	91(18)	C(12')	1425(3)	9588(5)	3725(1)	797(34)	1758(74)	138(6)	128(40)	-20(11)	-54(17)		
C(13)	8785(4)	3574(6)	4018(2)	822(41)	2568(103)	235(9)	41(53)	19(16)	149(26)	C(13')	264(4)	9299(6)	3693(2)	951(43)	2725(108)	161(7)	449(55)	21(4)	-16(23)		
C(14)	8528(4)	4047(6)	4414(2)	943(45)	2568(103)	216(9)	-27(65)	-59(17)	65(25)	C(14')	-174(4)	8487(7)	1989(2)	642(39)	4181(148)	206(8)	158(63)	10(15)	-23(29)		
C(15)	7439(4)	4501(6)	4438(2)	1075(46)	2428(96)	158(7)	-74(52)	-50(14)	-80(21)	C(15')	525(4)	7652(7)	4328(2)	766(41)	4137(145)	183(8)	-187(61)	50(13)	100(28)		
C(16)	6606(4)	4447(5)	4064(2)	880(39)	2218(80)	146(6)	83(48)	-6(13)	-11(19)	C(16')	1669(3)	7789(6)	4368(2)	690(38)	3247(114)	154(7)	-117(51)	26(12)	177(23)		
C(17)	6832(3)	3929(4)	3653(1)	800(34)	1366(65)	160(6)	-82(37)	52(12)	51(16)	C(17')	2147(3)	8725(5)	4075(1)	721(31)	1631(69)	119(5)	67(37)	27(10)	-1(15)		
C(18)	5975(3)	3815(4)	3249(1)	759(33)	1366(63)	140(6)	-41(36)	78(11)	3(15)	C(18')	3363(3)	8909(4)	4112(1)	715(31)	1421(62)	121(5)	-31(35)	45(10)	20(14)		
C(19)	4842(3)	4151(4)	3243(1)	837(34)	1618(66)	104(5)	41(38)	66(11)	-10(16)	C(19')	4136(3)	8358(5)	4484(1)	676(32)	1616(68)	116(5)	15(36)	55(10)	29(15)		
C(20)	4025(3)	4006(4)	2864(1)	791(32)	1363(62)	125(5)	-18(36)	73(10)	37(15)	C(20')	5285(3)	8553(4)	4521(1)	731(31)	1427(61)	123(5)	84(36)	58(10)	10(15)		
C(21)	2827(3)	4332(4)	2462(1)	899(35)	1325(62)	106(5)	11(37)	28(11)	55(15)	C(21')	6107(3)	7940(4)	4908(1)	726(32)	1533(64)	118(5)	181(35)	61(10)	-37(15)		
C(22)	2476(3)	5305(5)	3186(1)	815(36)	1822(77)	124(5)	31(42)	42(11)	29(17)	C(22')	5801(3)	6871(5)	5205(1)	751(36)	2435(92)	148(6)	-6(45)	40(12)	103(19)		
H(1)	114(3)	623(5)	342(1)	7.3(12)						H(1')	633(3)	545(5)	582(1)	7.4(11)							
H(2)	-22(3)	509(5)	283(1)	8.4(13)						H(2')	829(3)	627(4)	590(1)	6.9(10)							
H(3)	28(3)	349(4)	228(1)	6.7(10)						H(3')	882(3)	814(4)	536(1)	5.2(9)							
H(5 <sup>a</sup> )	174(3)	255(4)	190(1)	6.6(10)						H(5 <sup>a</sup> ) <sup>†</sup>	948(4)	968(6)	468(1)	10.0(16)							
H(5 <sup>b</sup> )	250(3)	146(5)	229(1)	7.9(12)						H(5 <sup>b</sup> ) <sup>†</sup>	735(7)	1082(10)	474(3)	15.1(26)							
H(6 <sup>a</sup> )	327(3)	436(4)	193(1)	5.6(10)						H(6 <sup>a</sup> ) <sup>†</sup>	728(5)	846(7)	412(2)	7.2(20)							
H(6 <sup>b</sup> )	374(3)	249(5)	182(1)	8.7(13)						H(6 <sup>b</sup> ) <sup>†</sup>	712(4)	1038(6)	397(2)	10.4(15)							
H(8)	567(2)	277(4)	221(1)	4.2(8)						H(8')	522(2)	1042(4)	357(1)	4.5(8)							
H(10)	758(3)	264(5)	251(1)	9.3(13)						H(10')	336(3)	1094(5)	320(1)	6.8(12)							
H(11)	898(3)	268(4)	320(1)	6.5(10)						H(11')	142(3)	1079(4)	318(1)	4.7(10)							
H(13)	957(3)	312(5)	398(1)	7.2(11)						H(13')	-19(3)	1001(5)	346(1)	8.5(13)							
H(14)	161(3)	405(5)	469(1)	5.1(13)						H(14')	-98(3)	838(5)	395(1)	6.6(10)							
H(15)	723(3)	480(5)	474(1)	8.1(13)						H(15')	17(4)	696(6)	454(1)	10.9(16)							
H(16)	581(3)	475(5)	407(1)	8.2(12)						H(16')	214(3)	721(5)	459(1)	6.4(11)							
H(19)	460(3)	452(4)	352(1)	4.6(8)						H(19')	384(3)	781(4)	472(1)	5.3(9)							
H(22)	306(2)	578(4)	341(1)	4.1(8)						H(22')	503(3)	653(4)	520(1)	5.6(10)							

\* The occupancy factor *m* for C(5'*T*) was adjusted in addition to all other parameters in the least-squares program, and the occupancy factors for C(6'*T*), C(10'*A*) and C(11'*A*) were each set equal to that for C(5'*T*). A value of  $m=0.70(4)$  was obtained (see text).

† Occupancy factor was set to be  $1-m$ .

\*\* Attached to the corresponding carbon atoms of both '*T*' and '*A*' configurations. Each of their occupancy factors was assigned as unity and was not adjusted.

†† Attached to the corresponding carbon atoms, C(5'*T*) and C(6'*T*). Each of their occupancy factors was set equal to that for C(5'*T*).

Table 3. Observed and calculated structure amplitudes (x10) for 5,6-dihydrodibenz[a,j] anthracene

Table with multiple columns of numerical data representing observed and calculated structure amplitudes for various h, k, l indices. The table is organized into several sections, some labeled with 'k = 0' and 'k = 1'.



no such short contact. The remaining intermolecular  $H \cdots H$  contacts are all greater than 2.45 Å.

#### Validity of the disorder model

The validity of the hypothesis of disorder may be tested by use of Hamilton's  $R$  ratio (Hamilton, 1964 or 1965). Three models may be compared: one with no disorder, one with assumed disorder of atoms C(5'), C(6'), C(10') and C(11'), and an intermediate model with assumed disorder of only atoms C(5') and C(6'), which was also refined. The appropriate  $R$  values for the three models of increasing complexity are given in Table 6, which also lists other results appropriate for comparison. The  $R$  value ratios are:

$$\begin{aligned} R_{\text{model I}} / R_{\text{model II}} &= 10.65/10.43 = 1.021 \\ R_{\text{model II}} / R_{\text{model III}} &= 10.43/10.35 = 1.008 \\ R_{\text{model I}} / R_{\text{model III}} &= 10.65/10.35 = 1.029. \end{aligned}$$

Interpolation (Pawley, 1970) in the Hamilton tables for  $\alpha = 0.001$  gives  $\mathcal{R}_{b,n-m,\alpha}$  values of 1.005, 1.005, and 1.008 for  $\mathcal{R}_{9,2556,0.001}$ ,  $\mathcal{R}_{8,2548,0.001}$ , and  $\mathcal{R}_{17,2548,0.001}$ , corresponding to the three experimental ratios above, respectively. Hence, the hypothesis that the structure

is ordered can be rejected at the 99.9% confidence level, and likewise the rejection of model II in favor of model III.

#### Bond distances, bond angles, and consequences of crystal disorder

The final e. s. d.'s for C–C bond distances in molecule *A* and the ordered part of molecule *B* range from 0.004 to 0.006 Å, and those for C–H bond distances range from 0.03 to 0.04 Å. The e. s. d.'s for C–C–C bond angles are less than 0.5° (see Table 4).

In molecule *A*, the C–C single-bond distance of 1.510(6) Å is 0.03 Å less than the expected value of 1.54 Å. This is probably due, in part, to the presence of adjacent aromatic nuclei. The C( $sp^3$ )–C( $sp^2$ ) distances, 1.510(6) and 1.505(5) Å for C(4)–C(5) and C(6)–C(7) bonds, respectively, are compatible with the accepted average value of 1.510(5) Å (*Tables of Interatomic Distances and Configurations in Molecules and Ions*, 1965, p. S15s), and are not much different from the averaged C( $sp^3$ )–C( $sp^2$ ) distance of 1.503 Å obtained in the related structure of 9:10-dihydro-1:2:5:6-dibenzanthracene (Iball & Young, 1958). The C(10)–C(11) bond length of 1.334(6) Å is indicative of the

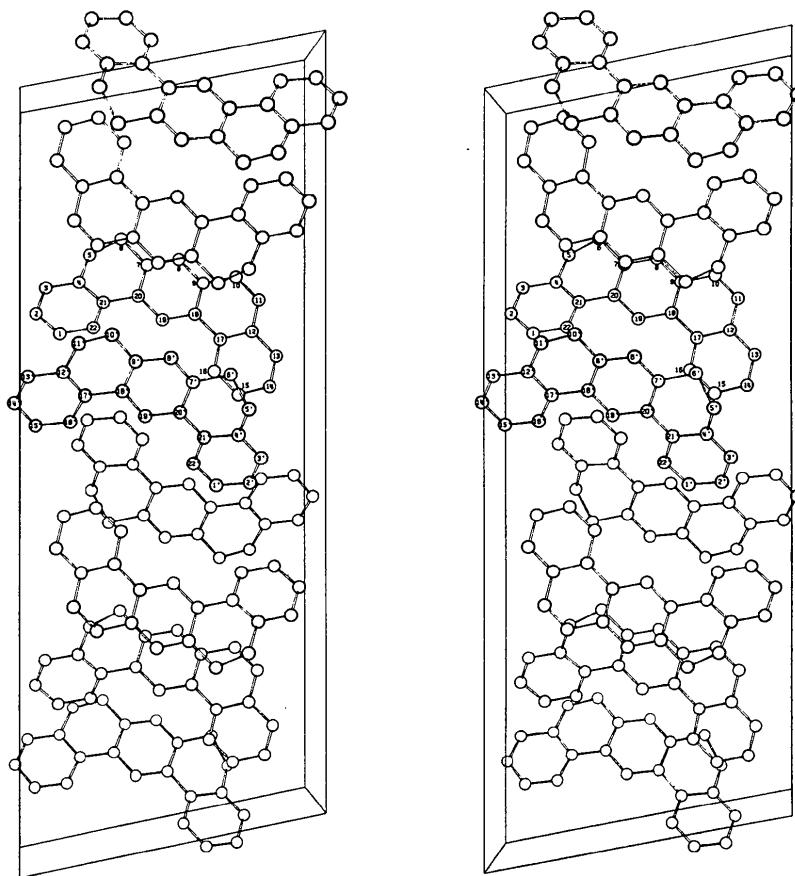


Fig. 4. Stereoscopic view of the unit cell down the  $b$  axis. As in Fig. 5, the axial systems are right-handed. For the sake of clarity, hydrogen atoms are not included. Only the orientation of molecule *B* with the larger occupancy factor (0.7) is shown. The origin of the unit cell is in the upper-left, rear corner. Only the reference molecules are labeled.



double-bond character of 1, and is in good agreement with the previous results for phenanthrene: values of 1.335 (7) and 1.352 (9) Å (both uncorrected for rigid-body motion) or 1.341 and 1.358 Å (both corrected for rigid-body motion) from X-ray and neutron studies (Kay *et al.*, 1971), and a value of 1.355 Å calculated from valence-bond theory (Trotter, 1963). Because of the apparent double-bond character of the C(10)–C(11) bond in this conjugated system, and because of the presence of overcrowded hydrogen atoms in the concave side of the molecule (Coulson & Haigh, 1963), the bond lengths involving C(9)–C(10) and C(17)–C(18) are significantly longer (by as much as 0.065 Å) than the normal value of 1.394 (5) Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965, p. S16s) for the average aromatic C–C bond distance. The 21° twist of ring (I) with respect to ring (III) about bond C(20)–C(21), somewhat relieves the steric repulsion between H(19) and H(22). The C(20)–C(21) bond distance of 1.478 (4) Å is very close to the theoretically estimated value of 1.477 Å between trigonally linked carbon atoms (Dewar & Schmeising, 1959; Cruickshank & Sparks, 1960), and is 0.03 Å shorter than the analogous distances of 1.507 (32) Å (Trotter, 1961) and 1.506 (17) Å (Hargreaves & Rizvi, 1962), both in the planar biphenyl molecule, in which the lengthening was attributed to the overcrowding of the hydrogen atoms (Hargreaves & Rizvi, 1962). The average of the C–H distances in both molecules [which range from 0.94 (3) to 1.07 (4) Å in molecule *A* and from 0.94(3) to 1.15 (4) Å in molecule *B*] is 1.00 (1) Å, and no

particularly unusual bond angles involving hydrogen were found.

The geometry of atoms C(5) and C(6) is nearly ideally tetrahedral. It is worth noting that the extra-annular C–C–C angles at C(17), C(18), C(20), and C(21) (*i. e.*, atoms on the concave side of the molecule) are invariably 2–3° larger than 120° (Table 4). Since this is true in both molecules, and since similar distortions have been observed in phenanthrene and 5,6-dihydrodibenz[*a, h*]anthracene (Wei & Einstein, 1972), it seems safe to consider the trend to be general and to attribute it to the overcrowding of the attached hydrogen atoms (see below). The exterior C–C–C angles at C(4), C(7), C(9) and C(12) are also 1–2° larger than 120° (Table 4).

In spite of the problem of disorder, the molecular parameters derived for molecule *B* are in general compatible with those obtained for the ordered molecule *A*. In the 'ordered' portion of molecule *B*, the differences from the corresponding C–C bond distances and C–C–C bond angles in molecule *A* are within three individual e. s. d.'s. However, some bond distances and angles in the disordered portion of molecule *B* differ significantly from the corresponding values in molecule *A*—particularly for the second configuration with smaller occupancy factor. These anomalies are clearly a consequence of the difficulties in treating disorder problems. Similar phenomena have also been observed in the *averaged statistical* structure of triiron dodecarbonyl (Wei & Dahl, 1969) and tetracobalt dodecarbonyl (Wei, 1969).

The atomic parameters of molecule *A* showed only

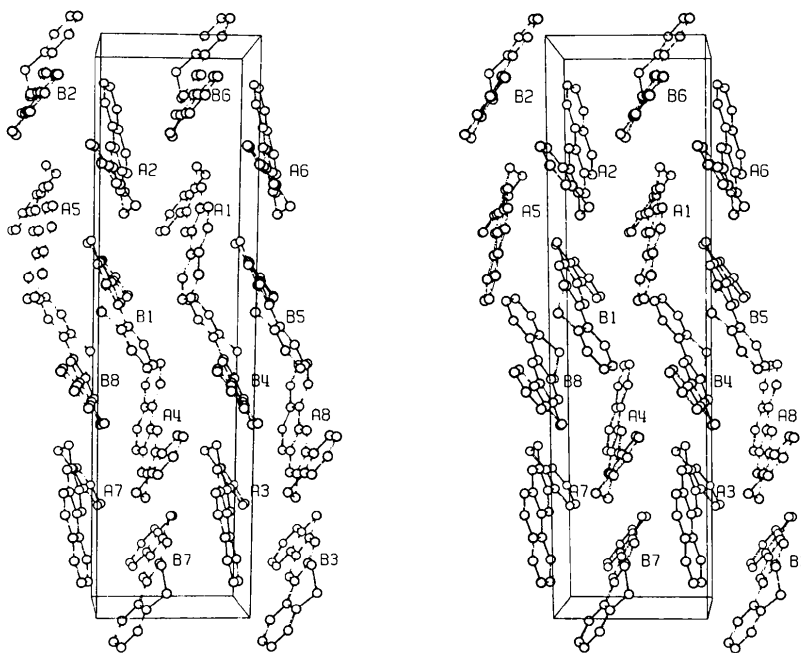


Fig. 5. Stereoscopic view of the unit cell. The origin is in the upper-right, rear corner. *A*1 and *B*1 indicate the reference molecules *A* and *B* respectively. Molecules 2, 3, and 4 are related to the basic molecules (*x, y, z*) by the following symmetry operations: 2:  $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ ; 3:  $x, \frac{1}{2}-y, \frac{1}{2}+z$ ; 4:  $1-x, 1-y, 1-z$ . Molecules 5 through 8 are those generated by translations of molecules 1, 2, 3, and 4 respectively, along the *b* axis.

very small differences among the three refined crystal models given in Table 6. These parameters may be considered as unaffected by the treatment of disorder, and therefore reliable.

*Molecular strains caused by overcrowded hydrogen atoms*

In this polycyclic aromatic hydrocarbon system, the H(16)···H(19) and H(19)···H(22) distances are 2.01 (4) and 2.11 (4) Å respectively, much shorter than the sum (2.4 Å) of their accepted van der Waals radii. A theoretical calculation of steric effects due to overcrowded hydrogen atoms in several polycyclic aromatic hydrocarbon molecules has been made by Coulson & Haigh (1963). Recently, the structure of phenanthrene has been reinvestigated by Kay *et al.* (1971); the molecular distortion caused by a pair of overcrowded hydrogen atoms in the phenanthrene molecule has been analyzed by them in terms of the distortion of molecular rings from coplanarity. The distortion of the phenanthrene moiety in the present molecule can be similarly analyzed by examining displacements of individual atoms from the best plane through atoms of the middle ring (IV). Fig. 6 gives perpendicular distances of atoms associated with the phenanthrene moiety from ring (IV). Ring (V) is twisted clockwise about the C(18) → C(17) axis,

Table 4. *Interatomic distances (Å) and bond angles (°) with standard deviations*

BOND	MOLECULE A	MOLECULE B*	C-C-C ANGLE	MOLECULE A	MOLECULE B*
C(1)-C(2)	1.385(6)	1.381(5)	RING I		
C(1)-C(22)	1.388(5)	1.378(5)	C(1)-C(2)-C(3)	120.1(5)	118.8(4)
C(2)-C(3)	1.387(6)	1.371(6)	C(2)-C(3)-C(4)	120.6(5)	121.7(4)
C(3)-C(4)	1.385(5)	1.385(5)	C(3)-C(4)-C(21)	120.1(4)	119.7(4)
C(4)-C(5)	1.510(6)	{ 1.48(1), 1.52(4) }	C(4)-C(5)-C(22)	119.4(4)	119.2(4)
C(4)-C(21)	1.401(4)	1.402(4)	C(21)-C(22)-C(1)	121.3(4)	121.0(4)
C(5)-C(6)	1.510(6)	{ 1.49(2), 1.51(5) }	C(22)-C(1)-C(2)	119.4(5)	120.6(5)
C(6)-C(7)	1.505(5)	{ 1.49(1), 1.48(3) }			
C(7)-C(8)	1.362(5)	1.377(5)	RING II		
C(7)-C(20)	1.419(5)	1.410(5)	C(21)-C(4)-C(5)	118.5(4)	{ 116.7(5), 123.7(17) }
C(8)-C(9)	1.401(5)	1.384(5)	C(4)-C(5)-C(6)	111.5(4)	{ 115.0(13), 1109.4(34) }
C(9)-C(10)	1.449(5)	{ 1.44(1), 1.58(4) }	C(5)-C(6)-C(7)	119.0(4)	{ 108.1(10), 1126.5(26) }
C(9)-C(18)	1.409(5)	1.407(5)	C(6)-C(7)-C(20)	119.1(4)	{ 120.3(5), 1115.8(12) }
C(10)-C(11)	1.334(6)	{ 1.39(2), 1.41(6) }	C(7)-C(20)-C(21)	118.7(3)	119.0(4)
C(11)-C(12)	1.427(6)	{ 1.41(1), 1.66(3) }	C(20)-C(21)-C(4)	119.2(4)	119.8(4)
C(12)-C(13)	1.406(5)	1.399(5)			
C(12)-C(17)	1.417(5)	1.410(5)	RING III		
C(13)-C(14)	1.365(6)	1.355(6)	C(19)-C(20)-C(7)	118.9(4)	118.4(4)
C(14)-C(15)	1.388(6)	1.395(6)	C(20)-C(7)-C(8)	118.8(4)	119.3(4)
C(15)-C(16)	1.376(5)	1.375(6)	C(7)-C(8)-C(9)	122.7(4)	122.5(4)
C(16)-C(17)	1.403(5)	1.386(5)	C(8)-C(9)-C(18)	119.1(4)	119.0(4)
C(17)-C(18)	1.459(5)	1.467(4)	C(9)-C(18)-C(19)	117.8(4)	118.3(4)
C(18)-C(19)	1.398(5)	1.402(4)	C(18)-C(19)-C(20)	122.7(4)	122.4(4)
C(19)-C(20)	1.379(5)	1.387(5)			
C(20)-C(21)	1.478(4)	1.480(4)	RING IV		
C(21)-C(22)	1.396(5)	1.392(5)	C(17)-C(18)-C(9)	119.6(4)	119.2(4)
			C(18)-C(9)-C(10)	119.7(4)	{ 119.9(6), 117.0(14) }
C(1)-C(11)	0.97(4)	1.10(4)	C(9)-C(10)-C(11)	120.2(5)	{ 120.1(9), 109.6(29) }
C(2)-C(12)	0.94(4)	1.07(3)	C(10)-C(11)-C(12)	122.4(4)	{ 120.4(7), 104.7(27) }
C(3)-C(13)	1.00(3)	1.01(3)	C(11)-C(12)-C(17)	119.7(4)	{ 120.7(5), 112.8(11) }
C(5)-H(5-1)	1.03(3)	{ 1.15(4), 1.09(5) }	C(12)-C(17)-C(18)	118.4(4)	118.7(4)
C(5)-H(5-2)	1.01(4)	{ 1.01(8) }			
C(6)-H(6-1)	0.94(2)	0.94(2)	RING V		
C(6)-H(6-2)	1.07(4)	{ 1.04(5), 1.12(5) }	C(15)-C(16)-C(17)	121.1(5)	122.0(5)
C(8)-H(8)	0.95(3)	0.98(3)	C(16)-C(17)-C(12)	118.1(4)	118.1(4)
C(11)-H(11)	1.07(4)	{ 0.93(4), 1.05(5) }	C(17)-C(12)-C(13)	119.2(5)	119.1(4)
C(11)-H(11)	0.98(4)	{ 0.83(3), 1.08(4) }	C(12)-C(13)-C(14)	120.9(5)	121.2(5)
C(13)-H(13)	1.05(4)	0.95(4)	C(13)-C(14)-C(15)	120.3(5)	120.3(4)
C(14)-H(14)	1.02(4)	0.96(3)	C(14)-C(15)-C(16)	120.1(5)	119.3(5)
C(15)-H(15)	1.04(4)	1.01(4)			
C(16)-H(16)	1.02(4)	0.94(3)	C(3)-C(4)-C(5)	121.4(4)	{ 123.4(5), 115.3(17) }
C(19)-H(19)	1.01(4)	0.97(3)	C(4)-C(5)-C(6)	122.4(4)	{ 120.1(5), 112.8(5) }
C(22)-H(22)	0.96(3)	0.97(3)	C(8)-C(9)-C(10)	121.4(4)	{ 120.3(6), 122.6(15) }
AVERAGES	1.00(1)	1.00(1)	C(11)-C(12)-C(13)	121.2(5)	{ 120.1(5), 116.8(12) }
C(57)···C(5A)		0.44(4)	C(16)-C(17)-C(18)	123.3(4)	123.1(4)
C(67)···C(6A)		0.52(2)	C(17)-C(18)-C(19)	122.6(4)	122.5(3)
C(10A)···C(107)		0.43(5)	C(19)-C(20)-C(21)	122.3(4)	122.7(4)
C(11A)···C(117)		0.51(3)	C(20)-C(21)-C(22)	122.3(4)	122.0(4)
H(16)···H(19)	2.01(4)	2.08(4)			
H(19)···H(22)	2.11(4)	2.12(4)			
H(5-1)···H(5-2)	1.62(5)	1.69(8)			
H(6-1)···H(6-2)	1.67(5)	1.61(7)			

\* Values in brackets are those associated with disordered atoms of the higher occupancy factor (0.7), whereas values in braces are those associated with disordered atoms of the lower occupancy factor (0.3).

Table 5. *Perpendicular distances (Å) from the least-squares planes*

The atoms marked with an asterisk are those used to define the planes. Calculations were performed with the program written by Smith (1962). All atoms used in establishing the planes were equally weighted. For constituent atoms of molecule B, the predominant configuration with the higher occupancy factor (0.7) was taken.

	(a)		(b)		(c)		(d)		(e)		
	Molecule A	Molecule B	Molecule A	Molecule B	Molecule A	Molecule B	Molecule A	Molecule B	Molecule A	Molecule B	
*C(1)	-0.002	-0.006	-0.046	-0.025	-0.001	-0.001	-0.003	-0.013	*C(12)	0.004	0.008
*C(2)	-0.005	0.004	0.045	-0.024	0.004	0.004	0.008	0.057	*C(13)	0.006	0.000
*C(3)	0.006	0.002	-0.089	-0.048	-0.004	-0.005	-0.006	-0.046	*C(14)	-0.010	-0.008
*C(4)	-0.000	-0.006	-0.089	-0.048	0.002	0.000	-0.001	0.011	*C(15)	0.003	0.008
*C(21)	-0.007	0.004	-0.350	-0.341	-0.001	-0.006	*C(17)	0.005	*C(16)	0.007	-0.000
*C(22)	0.008	0.002	0.363	0.314	-0.001	-0.007	*C(18)	-0.003	*C(17)	-0.010	-0.008
C(5)	0.010	-0.124	—	-0.05	0.007	0.138	C(10 <sup>T</sup> )	—	H(13)	-0.08	-0.03
C(20)	-0.025	0.044	—	-0.20	C(6)	0.027	C(6)	0.47	H(14)	0.03	0.03
H(1)	-0.02	-0.01	—	-0.11	C(6 <sup>T</sup> )	0.028	C(11 <sup>T</sup> )	—	H(13)	-0.08	-0.03
H(2)	0.05	-0.01	-0.11	-0.11	H(8)	—	H(10)	0.10	H(15)	-0.06	0.03
H(3)	0.03	-0.01	-1.35	-1.33	H(19)	—	H(11)	-0.02	H(16)	-0.00	0.03
H(22)	0.03	-0.01	1.28	1.21							
			0.06	0.06							

with C(15) and C(16) bent upward from ring (IV) to alleviate the steric repulsion between H(16) and H(19). On the other hand, ring (III) is bent from ring (IV) along the C(18)–C(9) bond, as evidenced by the fact that the deviations for C(20) and C(7) are approximately double those for C(19) and C(8). Although the distortions in molecule *B* appear different in detail from those in molecule *A* because of the disorder, the overall description seems to hold for both molecules of the present crystal and is in accordance with the observation of Kay *et al.* (1971).

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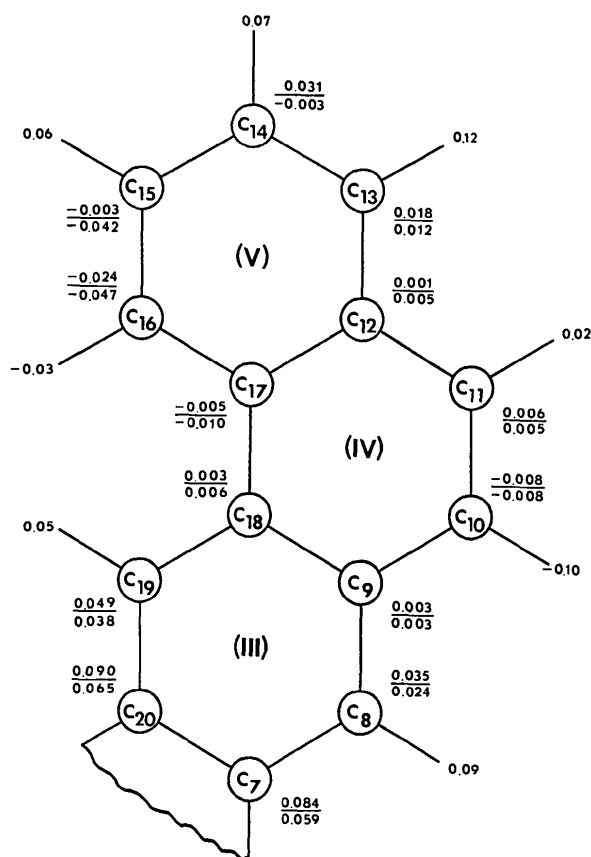


Fig. 6. Comparison of perpendicular distances from the plane of ring (IV) for the phenanthrene moiety of molecule *A* with those obtained from X-ray results for the phenanthrene molecule. Signs of the values from this work [shown above those given by Kay *et al.* (1971)] were reversed (*cf.* Table 5(*d*)) in order to facilitate the comparison.

Table 6. *Results of least-squares refinements for three models*

Letters *T* and *A* in parentheses in models II and III denote values associated with tetrahedral and aromatic carbons respectively.

Model I: no atom was considered disordered.

Model II: atoms C(5') and C(6') were treated as disordered.

Model III: atoms C(5'), C(6'), C(10'), and C(11') were treated as disordered.

	Model I	Model II	Model III
$R(F^2)$	7.27%	7.15%	7.24%
$R(F)$	8.32	8.25	8.23
$R_w(F^2)$	10.65	10.43	10.35
Error of fit function	1.040	1.026	1.020
Occupancy factor of predominant configuration	—	0.58 (4)	0.70 (4)
Number of parameters adjusted	525	534	542
Bond lengths of immediate interest			
{ C(5')–C(6')	1.414 Å	1.542 (24) ( <i>T</i> ) Å	1.489 (20) ( <i>T</i> ) Å
{ C(10')–C(11')	1.351	1.372 (33) ( <i>A</i> )	1.413 (49) ( <i>A</i> )
		1.353 (6)	1.392 (17) ( <i>A</i> )
			1.415 (56) ( <i>T</i> )
Perpendicular distances from best planes through the other four atoms of ring (II) or (IV)			
{ C(5')	–0.26 Å	–0.40 ( <i>T</i> ) Å	–0.34 ( <i>T</i> ) Å
{ C(6')	0.19	0.02 ( <i>A</i> )	0.05 ( <i>A</i> )
		0.37 ( <i>T</i> )	0.31 ( <i>T</i> )
		–0.13 ( <i>A</i> )	–0.20 ( <i>A</i> )
{ C(10')	0.19	0.19	0.10 ( <i>A</i> )
			0.51 ( <i>T</i> )
{ C(11')	–0.11	–0.11	–0.03 ( <i>A</i> )
			–0.45 ( <i>T</i> )

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