

398. *The Structure of Overcrowded Aromatic Compounds. Part VI.¹ The Crystal Structure of Benzo[*c*]phenanthrene and of 1,12-Dimethylbenzo[*c*]phenanthrene.*

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The crystal structure of benzo[*c*]phenanthrene has been redetermined by a full three-dimensional *X*-ray analysis at room temperature, and that of its 1,12-dimethyl derivative has been established by a partial three-dimensional analysis near 80°K. The studies have revealed the principal thermal motions of these molecules, including an appreciable internal vibration in benzophenanthrene, as well as their molecular dimensions. Bond lengths are nearly equal in the two molecules and agree well with the mobile bond orders given by published molecular-orbital calculations; thus any influence of the overcrowding on bond lengths is small. The orientation of the methyl groups in the dimethylbenzophenanthrene is such as to minimise the intramolecular repulsions at the hydrogen atoms.

AVAILABLE information about overcrowded aromatic compounds permits the following deductions. (a) Many such compounds are deformed from planarity to a configuration that is, to a good approximation, predictable. Coulson and his collaborators² have used a simple model for predicting molecular configurations of such compounds in agreement with the limited crystallographic data now available. It is almost certain that this model could be improved if sufficiently precise structural information were provided for testing its predictions. (b) Overcrowded compounds do not differ fundamentally in their behaviour from other aromatic compounds. In fact, any effects on chemical reactivity,³ ultraviolet spectra,⁴ proton resonance,⁵ etc., are usually small enough to require quite detailed investigation before they can be definitely established as due to the overcrowding. Such investigations would also be substantially aided by accurate structural information. In this context we have completely redetermined the crystal structure of benzo[*c*]phenanthrene from full three-dimensional *X*-ray data at room temperature, and we have also established, to about the same degree of precision, the structure of 1,12-dimethylbenzo[*c*]phenanthrene from partial three-dimensional data at the temperature of boiling nitrogen.

BENZO[*c*]PHENANTHRENE

Structure Determination.—Crystals are orthorhombic, with four molecules in a unit cell of space group $P2_12_12_1$. Cell dimensions, remeasured from high-angle Cu- K_α reflections on Weissenberg photographs, are: $a = 14.666 \text{ \AA}$, $b = 14.157 \text{ \AA}$, $c = 5.785 \text{ \AA}$, $d(\text{calc.}) = 1.262$. *X*-Ray diffraction spectra were recorded on equi-inclination Weissenberg photographs, with nickel-filtered copper radiation, of crystals cut to nearly cubic shape, with about 0.5 mm. edges. The photographs comprised levels 0—11 about [100], 0—3 about [010], and 0—4 about [001]. The intensities of the K_α spots were estimated by eye and corrected for Lorentz and polarisation factors but not for absorption. A common intensity scale for all photographs was established by least-squares analysis of all reflections appearing on two or on three different photographs. The method used was equivalent to that recently described by Rollett and Sparks.⁶ In all, 1377 independent reflections were observed (see Table A) and 175 more were assigned upper limits based on an estimated observational threshold. Of the former, eight were discarded because of obvious extinction. The remaining 1544 spectra—1369 observed

¹ Part V, Cahana, Schmidt, and Shah, *J. Org. Chem.*, 1959, **24**, 557.

² Coulson and Senent, *J.*, 1955, 1813, 1819; Ali and Coulson, *J.*, 1959, 1558.

³ Szwarc and Leavitt, *J. Amer. Chem. Soc.*, 1956, **78**, 3590; Pullman and Effinger, *Bull. Soc. chim. France*, 1958, **25**, 482.

⁴ Badger and Walker, *J.*, 1954, 3238; Jaffé and Orchin, *J.*, 1960, 1078; Cromartie and Murrell, *J.*, 1961, 2063.

⁵ Reid, *J. Mol. Spectroscopy*, 1957, **1**, 18.

⁶ Rollett and Sparks, *Acta Cryst.*, 1960, **13**, 273.

TABLE A.

Structure factors of benzo[c]phenanthrene.

(* indicates reflection discarded because of extinction.)

Table with 12 columns of structure factor data (h k l, 100Fo, 100A, 100B, 100Fc) and corresponding numerical values for reflections. The table is organized into three groups of columns, each with a header row for the reflection indices and intensity scales. The data includes various reflections such as 2 0 0, 4 0 0, 6 0 0, etc., with associated intensity values and signs.

TABLE A. (Continued.)

Table with 12 columns: h k l, 100A, 100B, 100C, h k l, 100A, 100B, 100C, h k l, 100A, 100B, 100C, h k l, 100A, 100B, 100C. The table contains numerical data for various crystallographic reflections, including intensity values and phase indicators.

TABLE A. (Continued.)

h	k	l	$100F_o$	$100A$	$100B$	$100F_c$	h	k	l	$100F_o$	$100A$	$100B$	$100F_c$	h	k	l	$100F_o$	$100A$	$100B$	$100F_c$	h	k	l	$100F_o$	$100A$	$100B$	$100F_c$
1			205	210	77	224	1			119	39	113	120	3			530	-480	155	504	0	4	7	202	266	0	266
3			175	-185	-52	192	2			197	-172	-2	172	4			124	20	-116	118	1			236	-222	155	271
1	0	7	<104	0	-40	40	3			197	-24	-237	238	5			282	304	-162	344	2			115	108	-19	110
2			204	0	-219	219	4			230	-69	-282	281	0	3	7	243	0	249	249	3			362	304	-49	307
3			116	0	30	30	5			112	-84	86	121	1			693	-96	-746	750	4			403	-363	240	435
4			208	0	-237	237	6			125	160	-11	160	2			226	195	71	171	0	5	7	544	0	-689	689
5			108	0	44	44	7	0	2	7	248	-254	0	254	3		603	-40	640	641	1			215	255	19	260
6			<75	0	97	97	1			315	296	-96	311	4			109	20	-135	136	2			196	-154	108	188
0	1	7	284	0	301	301	2			303	77	268	279	5			393	60	-461	465	3			253	-225	-123	456

F_o and 175 threshold F_c —were subjected to a least-squares refinement procedure that used only the diagonal matrix elements in the normal equations. The discrepancy function minimised was

$$r = \sum w(k^2 F_o^2 - |F_c|^2) / \sum w k^4 F_o^4,$$

in which both summations included all the observed reflections as well as those unobserved reflections having $|F_c| > kF_o$, the latter with F_c substituted for F_o . The weighting factors w varied approximately as F_o^{-3} but were modified in accordance with the number of observations for each reflection and their estimated reliability. The parameters adjusted by the least-squares procedure comprised: the scale factor k^2 , 3 positional co-ordinates for each atom in the molecule (asymmetric unit) ($3 \times 30 = 90$), 6 anisotropic thermal parameters for each carbon atom ($6 \times 18 = 108$), and 1 isotropic thermal parameter for each hydrogen atom ($1 \times 12 = 12$) (total 211). Scattering-factor tables were taken from Viervoll and Ögrim's results⁷ for hydrogen and from those of Berghuis *et al.*⁸ for carbon. The approximate structure

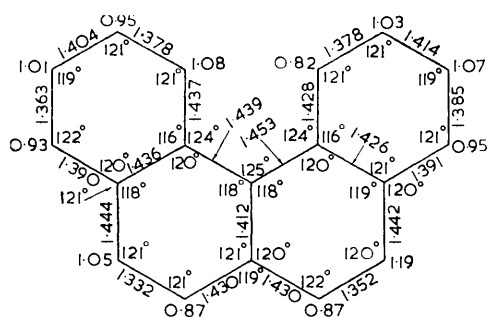


FIG. 1. Observed bond lengths, in Å, and angles, for benzo[*c*]phenanthrene. C-H bond lengths indicated next to respective carbon atoms. Dimensions are uncorrected for librational oscillations.

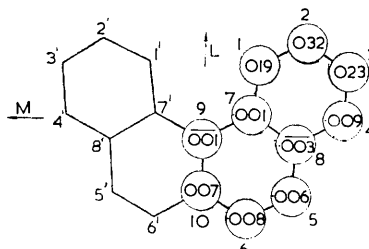


FIG. 2. Normal components S^2_{NN} , in Å², of residual atomic vibrations in benzo[*c*]phenanthrene, averaged in accordance with molecular two-fold symmetry, after subtraction of estimated rigid-body motion. Small figures show numbering of atoms, chosen to emphasise molecular symmetry and to facilitate comparison with 1,12-dimethylbenzo[*c*]phenanthrene. Arrows indicate molecular axes.

described by Herbstein and Schmidt⁹ was taken as the initial model for refinement. Twenty-seven cycles were undertaken on a WEIZAC computer and damping factors were applied to the calculated shifts on each cycle in a less-than-completely successful attempt to achieve the maximum rate of convergence. On the final cycle the maximum calculated co-ordinate shift was less than 0.002 Å for carbon and about 0.05 Å for hydrogen. The maximum cumulative shift, after moderate damping (applied shifts $\frac{1}{2}$ to $\frac{3}{4}$ of those calculated), on the last four cycles was also less than 0.002 Å for carbon and less than 0.05 Å for hydrogen. Final discrepancy factors are listed in Table 1.

Standard deviations of all final parameters, except k^2 , were estimated (or underestimated) from the diagonal approximation

$$\sigma^2(u_i) = \sum w(k^2 F_o^2 - |F_c|^2) / (n - s) A_{ii}, \quad (1)$$

⁷ Viervoll and Ögrim, *Acta Cryst.*, 1949, **2**, 277.

⁸ Berghuis, Haanappel, Potters, Loopstra, MacGillavry, and Veenendaal, *Acta Cryst.*, 1955, **8**, 478.

⁹ Herbstein and Schmidt, *J.*, 1954, 3302.

TABLE 1.

Discrepancy indices for structure determinations of benzo[*c*]phenanthrene (BP) and its 1,12-dimethyl derivative (DMBP).

	BP (room temp.)	DMBP (low temp.)
$r = \sum w(k^2 F_o^2 - F_c ^2) / \sum w k^4 F_o^4$	0.046	0.044
$R = \sum k F_o - F_c / \sum k F_o$		
All observed reflections	0.111	0.112
Excluding extinction errors	0.090	0.104
Including unobserved with $ F_c > k F_t$	0.091	0.104
E. S. D. carbon co-ordinates (average)	0.0043 Å	0.0037 Å

TABLE 2.

Atomic co-ordinates of benzo[*c*]phenanthrene.

Atom	Referred to crystal axes			Referred to molecular axes		
	x/a	y/b	z/c	L (Å)	M (Å)	N (Å)
C-1	0.3694	0.1425	0.1510	1.647	1.466	0.395
C-2	0.4141	0.0814	0.0043	2.250	2.703	0.328
C-3	0.3727	0.0502	0.2027	1.531	3.838	0.113
C-4	0.2838	0.0775	0.2479	0.183	3.697	0.394
C-5	0.1407	0.1543	0.1352	1.887	2.384	0.429
C-6	0.0926	0.2046	0.0215	2.522	1.212	0.208
C-7	0.2806	0.1776	0.0977	0.287	1.281	0.003
C-8	0.2365	0.1368	0.0980	0.453	2.463	0.291
C-9	0.2313	0.2444	0.2417	0.389	0.005	0.011
C-10	0.1359	0.2507	0.2120	1.802	0.003	0.014
C-1'	0.3687	0.3264	0.4188	1.655	1.467	0.363
C-2'	0.4048	0.3829	0.5898	2.248	2.710	0.309
C-3'	0.3484	0.4222	0.7607	1.512	3.836	0.096
C-4'	0.2565	0.4088	0.7481	0.181	3.705	0.358
C-5'	0.1192	0.3496	0.5473	1.900	2.373	0.408
C-6'	0.0815	0.3043	0.3697	2.530	1.216	0.219
C-7'	0.2730	0.3052	0.4108	0.279	1.280	0.003
C-8'	0.2169	0.3545	0.5748	0.466	2.477	0.280
H-1	0.3930	0.1650	0.2671	2.05	0.78	0.59
H-2	0.4742	0.0544	0.0689	3.19	2.74	0.74
H-3	0.4203	0.0005	0.2739	2.22	4.65	0.00
H-4	0.2587	0.0473	0.3794	0.25	4.52	0.57
H-5	0.0919	0.1172	0.2716	2.66	3.48	0.51
H-6	0.0339	0.2078	0.0046	3.39	1.21	0.19
H-1'	0.4221	0.3056	0.2994	2.37	0.74	0.74
H-2'	0.4664	0.4029	0.5825	3.12	2.84	0.66
H-3'	0.3751	0.4596	0.8934	1.96	4.74	0.20
H-4'	0.2179	0.4470	0.8363	0.35	4.47	0.41
H-5'	0.0679	0.3954	0.6078	2.64	3.11	0.29
H-6'	0.0230	0.2991	0.3426	3.39	1.09	0.28

where $n = 1369 + 23 = 1392$ is the number of reflections, observed plus threshold, included in the summations on the final cycle, $s = 211$ is the number of parameters u_i adjusted, and $A_{ii} = \sum w(\partial |F_c| / \partial u_i)^2$ is the diagonal element in the normal equation corresponding to the parameter u_i .

The estimated standard deviations in the positional co-ordinates of the carbon atoms were, as average, about 0.0043 Å, with a maximum of 0.0064 Å; corresponding figures for hydrogen are 0.054 Å and 0.085 Å. With the anisotropic thermal vibrations of the carbon atoms specified by the symmetric matrices U^r giving the mean-square displacements of the atoms in any direction from their mean positions,¹⁰ the standard deviations of the matrix elements U^r_{ij} were estimated to average about 0.0020 Å². For the hydrogen atoms, only the mean square displacements $\overline{u^2}$ were determined; the estimated standard deviations of these quantities averaged 0.017 Å². The relative standard deviation of the scale factor k^2 was estimated to be $\sigma(k^2)/k^2 = 0.011$.

The final positional co-ordinates are listed in Table 2, the vibration parameters in Table 3. Fig. 1 shows the experimental molecular dimensions, without correction for curvilinear thermal

¹⁰ Cruickshank, *Acta Cryst.*, 1956, **9**, 747.

TABLE 3a.

Observed and calculated (rigid-body) components of atomic vibration tensors U' , in \AA^2 , for benzo[*c*]phenanthrene.

Atom	$10^4 U_{11}$	$10^4 U_{22}$	$10^4 U_{33}$	$10^4 U_{12}$	$10^4 U_{23}$	$10^4 U_{13}$
C-1 (exp)	412	345	401	46	25	41
(RB)	383	328	374	27	40	6
C-2 (exp)	497	417	573	78	105	56
(RB)	540	398	438	24	13	68
C-3 (exp)	774	457	444	112	78	109
(RB)	820	501	442	17	67	40
C-4 (exp)	841	451	402	105	37	42
(RB)	821	529	427	81	48	106
C-5 (exp)	668	534	600	157	204	342
(RB)	561	555	594	169	146	238
C-6 (exp)	432	589	647	62	241	177
(RB)	401	547	713	118	249	163
C-7 (exp)	396	327	340	52	105	36
(RB)	382	345	379	57	54	40
C-8 (exp)	568	400	356	167	125	107
(RB)	551	448	431	103	45	125
C-9 (exp)	359	357	403	6	136	21
(RB)	339	342	438	32	90	9
C-10 (exp)	345	476	599	19	191	52
(RB)	340	441	611	27	189	17
C-1' (exp)	437	360	537	36	86	8
(RB)	444	314	453	59	27	40
C-2' (exp)	632	424	676	37	139	145
(RB)	665	368	560	102	27	114
C-3' (exp)	1058	446	666	55	177	147
(RB)	964	441	599	40	152	57
C-4' (exp)	837	476	545	147	79	82
(RB)	912	462	601	79	99	106
C-5' (exp)	527	491	723	136	161	260
(RB)	566	509	739	147	135	213
C-6' (exp)	388	541	779	113	239	102
(RB)	398	525	793	76	248	116
C-7' (exp)	403	328	394	4	64	23
(RB)	417	324	442	7	40	23
C-8' (exp)	526	361	506	108	107	127
(RB)	599	404	557	72	17	116

TABLE 3b.

Experimental mean square displacements $\overline{u^2}$ of hydrogen atoms, in \AA^2 , for benzo[*c*]phenanthrene.

H atom	1	2	3	4	5	6	1'	2'	3'	4'	5'	6'
$10^3 \overline{u^2}$	30	59	69	57	56	113	18	61	108	27	60	92

vibrations (see below). Equivalent C-C bonds, related by the (non-crystallographic) molecular two-fold symmetry axis, differ in measured length by 0.012 \AA RMS (root mean square), 0.023 \AA maximum. Assuming equivalent bonds to be, in fact, precisely equal in length, we may deduce from the apparent differences an RMS co-ordinate error of about 0.006 \AA . This value is, as one would expect, slightly higher than the estimate given by the diagonal least-squares formula (1).

The present bond lengths differ considerably from those reported by Herbstein and Schmidt,⁹ though not much more, on the average, than would be expected from their estimate of 0.05 \AA for the standard error in their experimental co-ordinates. The new results do not support their speculations regarding the localisation of charge at positions 3 and 5 (see Fig. 2 for numbering of atoms). The bond angles at these positions show no tendency to tetrahedral hybridisation, nor do the bond lengths show the anomalies that, in the earlier work, were interpreted as favouring such hybridisation. It is true that, in

the present structure, the C-H bonds at positions 5 and 5' deviate by 11° and 9°, respectively, from the planes of the adjacent C-C bonds. But we would not place too much reliance on the experimental hydrogen positions, whose uncertainty may greatly exceed that implied by equation (1). An observed out-of-plane deviation of 12° in the C-H bond at position 4' would, in particular, be difficult to explain except as due to experimental error.

Table 4 lists some of the shorter intermolecular approach distances together with the significant non-bonded intramolecular contacts. There is no sign of the abnormally close intermolecular contact along [001] found by Herbstein and Schmidt.⁹

We conclude that despite the deformation due to intramolecular repulsion the bonding in the molecule is normal.

Molecular Symmetry.—For convenience in the examination of the molecular configuration, Table 2 lists the atomic co-ordinates relative to a set of orthogonal molecular axes, whose origin is at the molecular centre of mass. The *L* axis is taken along the molecular two-fold symmetry axis, fitted to the midpoints of the lines joining symmetry-

TABLE 4.

Closest interatomic contacts, in Å, between reference molecule of benzo[*c*]phenanthrene centred near ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$), and neighbouring molecules related to it by indicated symmetry elements. The first-designated atom of each pair belongs to the reference molecule.

Intramolecular contacts:	C ₍₁₎ -C _(1') 3.030;	C ₍₁₎ -H _(1') 2.58;	C _(1') -H ₍₁₎ 2.47;	H ₍₁₎ -H _(1') 2.04.
<i>c</i> -axis translation:	C _(5') -C ₍₅₎ 3.335;	C _(5') -C ₍₆₎ 3.449;	C _(8') -C ₍₅₎ 3.478;	C _(8') -C ₍₈₎ 3.628;
	C _(6') -C ₍₅₎ 3.670.			
2 ₁ axis at ($x\frac{1}{4}0$):	C ₍₂₎ -C _(6') 3.650;	H _(1') -H ₍₆₎ 2.41;	H _(2') -H ₍₅₎ 2.59.	
2 ₁ axis at ($x\frac{1}{4}\frac{1}{2}$):	H ₍₂₎ -H _(5') 2.43.			
2 ₁ axis at ($\frac{1}{2}y\frac{1}{4}$):	H _(2') -H ₍₃₎ 2.43;	H _(2') -H ₍₂₎ 2.47.		
2 ₁ axis at ($\frac{1}{4}0z$):	C ₍₈₎ -C ₍₄₎ 3.660;	C ₍₄₎ -H ₍₄₎ 2.84;	C ₍₈₎ -H ₍₄₎ 2.90.	
2 ₁ axis at ($\frac{1}{4}\frac{1}{2}z$):	C _(3') -C _(5') 3.662;	H _(3') -C _(5') 2.84;	H _(3') -H _(5') 2.54.	

related atoms; *N* is normal to a reference molecular plane, chosen to pass approximately through the atoms C-7, C-9, and C-7'. The direction cosines of the molecular axes are given in Table 5. The *L* axis is seen to be inclined 8° to the crystallographic *a* axis. Furthermore, the molecular centre of mass has fractional co-ordinates (0.2577, 0.2429, 0.2480), which differ but slightly from ($\frac{1}{4}\frac{1}{4}\frac{1}{4}$). Thus the departure of the observed structure from the higher symmetry of space group $B22_12$ consists of an 8° rotation of the molecule together with a displacement of about 0.1 Å.

TABLE 5.

Direction cosines of benzo[*c*]phenanthrene molecular axes, *L, M, N* with respect to crystal axes.

	<i>a</i>	<i>b</i>	<i>c</i>
<i>L</i>	0.9903	0.0658	0.1221
<i>M</i>	0.0404	0.7053	0.7077
<i>N</i>	0.1327	0.7058	0.6958

The symmetry of the molecule itself is measured by the approach to self-coincidence attained when the molecule is rotated 180° about *L*. The RMS displacements between carbon atoms that should coincide under this operation are 0.010 Å along *L*, 0.007 Å along *M*, and 0.021 Å along *N*. The in-plane asymmetry is insignificant and accords with the RMS co-ordinate error deduced above from the internal consistency of the bond lengths, but the out-of-plane asymmetry appears to be real and may be attributed to intermolecular forces. Comparison of the *N* co-ordinates of symmetry-related carbon atoms shows that the departures from symmetry are systematic and imply a difference in the degree of out-of-plane deformation in the two halves of the molecule. Since the crystal contact distances

appear to be entirely normal, we conclude that the molecular skeleton must be fairly flexible with regard to out-of-plane deformation. It is not possible, however, to identify unambiguously the specific intermolecular interactions responsible for the slight molecular asymmetry.

Thermal Vibrations.—The observed anisotropic vibrations of the carbon atoms may be supposed to arise primarily from rigid-body oscillations of the whole molecule. Cruickshank¹¹ has shown how these rigid-body motions may be deduced from the atomic anisotropies, but his method presupposes that the axes of libration intersect in a known point, such as a centre of symmetry. In the present situation, even making the reasonable assumption that the principal libration axes intersect in a common point, we cannot locate this point *a priori*. Consequently we must determine its three co-ordinates from the experimental data along with the six components of translational vibration and the six components of libration. Unfortunately, the required equations are non-linear. For example, in place of Cruickshank's equation 2·3a

$$U_{11} = T_{11} + z^2\omega_{22} + y^2\omega_{33} - 2yz\omega_{23}$$

in which the known centre of libration is chosen as the origin of the co-ordinate system, we have the inhomogeneous equation

$$U_{11} = T_{11} + (z - z_0)^2\omega_{22} + (y - y_0)^2\omega_{33} - 2(y - y_0)(z - z_0)\omega_{23}$$

in which y_0 and z_0 are two components of the unknown libration centre. Accordingly it became necessary to use a linear approximation and to approach the final solution by successive iterations. Thus the above expression was replaced by its differential

$$dU_{11} = dT_{11} + (z - z_0)^2d\omega_{22} + (y - y_0)^2d\omega_{33} - 2(y - y_0)(z - z_0)d\omega_{23} \\ + 2[(z - z_0)\omega_{23} - (y - y_0)\omega_{33}]dy_0 + 2[(y - y_0)\omega_{23} - (z - z_0)\omega_{22}]dz_0$$

Similarly, corresponding to Cruickshank's equation 2·3b, we have

$$dU_{12} = dT_{12} - (x - x_0)(y - y_0)d\omega_{33} - (z - z_0)^2d\omega_{12} + (x - x_0)(z - z_0)d\omega_{23} \\ + (y - y_0)(z - z_0)d\omega_{13} + [(y - y_0)\omega_{33} - (z - z_0)\omega_{23}]dx_0 \\ + [(x - x_0)\omega_{33} - (z - z_0)\omega_{13}]dy_0 + [2(z - z_0)\omega_{12} - (x - x_0)\omega_{23} \\ - (y - y_0)\omega_{13}]dz_0.$$

These and similar expressions for the other atomic tensor components U_{ij} comprise the observational equations, six for each carbon atom, from which must be determined the fifteen parameters of the molecular motion. Inasmuch as the estimated standard deviations of the individual parameters U_{ij} nowhere exceeded their average value by a factor greater than two, all 108 observational equations were weighted equally. The entire operation, including the derivation of the normal equations, their solution, and substitution in the original expressions for U_{ij} for each atom, was performed iteratively on the WEIZAC computer by means of a programme written for this purpose. Virtually complete convergence was attained within fifteen cycles, which required altogether less than 0·5 hr. of computing time.

Table 6 shows the magnitudes and direction cosines of the principal axes of the ellipsoids of molecular translational and librational vibrations, derived as indicated above, together with the co-ordinates of the centre of libration relative to the molecular centre of mass. The indicated translational motion is nearly isotropic, with maximum and minimum amplitudes of 0·20 and 0·16 Å, respectively. The maximum libration amplitude is close to 3·6°, about an axis roughly normal to the mean molecular plane. This axis intersects the mean plane about 0·2 Å off the two-fold symmetry axis and about 1·1 Å from

¹¹ Cruickshank, *Acta Cryst.*, 1956, **9**, 754.

the centre of mass towards the overcrowded region of the molecule. The second largest principal amplitude is 2.6° , about an axis nearly parallel to the molecular symmetry axis. This axis is, surprisingly, more than 0.7 \AA from the mean molecular plane.

The validity of this analysis of the molecular motion may be tested by comparison of the calculated atomic vibration components $U_{ij}^r(\text{RB})$, corresponding to the derived rigid-body vibrations, with the experimental values $U_{ij}^r(\text{exp})$. Such a comparison

TABLE 6.

Principal components of rigid-body vibrations of benzo[*c*]phenanthrene and their direction cosines; also co-ordinates of libration centre with respect to molecular centre of mass, in \AA .

	Rel. to crystal axes			Rel. to mol. axes		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>L</i>	<i>M</i>	<i>N</i>
$T_1^2 = 0.0402 \text{ \AA}$	0.4344	0.5333	0.7259	0.3766	0.9074	0.1863
$T_2^2 = 0.0334$	0.7941	0.1537	0.5881	0.8683	0.2758	0.4123
$T_3^2 = 0.0262$	0.4252	0.8318	0.3567	0.3228	0.3170	0.8518
$\omega_1^2 = 0.00386 \text{ rad}^2$	0.0894	0.8209	0.5641	0.2115	0.1834	0.9600
$\omega_2^2 = 0.00208$	0.9955	0.0909	0.0256	0.9768	0.0058	0.2141
$\omega_3^2 = 0.00048$	0.0303	0.5638	0.8253	0.0337	0.9830	0.1803
Libration centre:	x_0	y_0	z_0	L_0	M_0	N_0
	1.145	0.826	0.397	1.236	0.348	0.707

(Table 3) reveals an RMS discrepancy of 0.0054 \AA^2 , which corresponds to nearly three times the average estimated standard deviation (0.0020 \AA^2) assigned to the observed $U_{ij}^r(\text{exp})$. This is a serious discrepancy, for which the most likely explanations seem to be: (a) neglect of the off-diagonal matrix coefficients in the estimation of the standard deviations; (b) systematic errors in the intensities, *e.g.*, absorption; (c) internal vibrations; and (d) bonding anisotropy.

With regard to (a) it appears that the largest errors arise through the neglect of the interactions among the three "diagonal" vibration components U_{ii}^r of each atom and of those between each of these components and the scale factor. Approximate sample calculations suggest that the first of these is unlikely to cause an error of as much as 10% in the standard deviations; the second can be shown, by statistical arguments, to lead to an underestimate of about 5% on the average. We cannot, however, exclude the possibility of some unexpectedly large off-diagonal coefficients, especially, as a Referee has pointed out, in view of the slowness of convergence of the least-squares refinement.

Effect (b) can be appraised only with regard to identifiable types of systematic errors. The absorption error, for example, should be fairly unimportant because of the cubic shape of the crystals and the virtually complete exploration of the sphere in reciprocal space accessible to Cu- K_α radiation. In these conditions any absorption error must be nearly isotropic; it might lead to an incorrect description of the rigid-body translational vibrations but would cause scarcely any discrepancy between $U^r(\text{exp})$ and $U^r(\text{RB})$. It is difficult to imagine any other kind of important error that would systematically but unequally affect the thermal parameters of different atoms in the molecule.

The non-crystallographic molecular symmetry permits an empirical test for effects (c) and (d). These are both molecular phenomena that should conform to the molecular symmetry. Accordingly, we can gauge their combined effect by comparing the symmetric tensors $\Delta U^r = U^r(\text{exp}) - U^r(\text{RB})$ of symmetry-related atoms in the molecule. To do this we form, for the eight pairs of off-axis carbon atoms, the sums and differences

$$2S_{ij}^r = \Delta U_{ij}^r + \Delta' U_{ij}^r,$$

and

$$2D_{ij}^r = \Delta U_{ij}^r - \Delta' U_{ij}^r,$$

where $\Delta' U^r$ is the symmetric tensor obtained by 180° rotation, about the *L* axis, of the

tensor ΔU^r of atom r ' symmetrically related to atom r . We expect that any symmetric contribution to the tensors ΔU^r , arising from effects (c) or (d), will be accentuated in the tensors S^r but will contribute nothing to D^r . Indeed, it was found that the RMS value of $2S^r_{ij}$ was 0.0110 \AA^2 , while that of $2D^r_{ij}$ was only 0.0057 \AA^2 . From the latter figure we deduce a value of $[108/2(108 - 15)]^{1/2} \times 0.0057 \text{ \AA}^2 = 0.0043 \text{ \AA}^2$ for the RMS random error in the components $U^r_{ij}(\text{exp})$, since fifteen parameters of rigid-body motion were fitted to the 108 components $U^r_{ij}(\text{exp})$. The disparity between this value and the least-squares estimate of 0.0020 \AA^2 is still rather large to be ascribed to effects (a) and (b), but no more plausible explanation can be offered.

From the components of the tensors S^r , referred to molecular axes (Table 7), we can seek to infer the nature of the symmetric component of the discrepancies ΔU^r_{ij} . The largest components of S^r occur in the direction N normal to the mean molecular plane.

TABLE 7.

Symmetric part of discrepancies between benzo[*c*]phenanthrene observed and calculated (rigid-body) atomic vibration tensors, in \AA^2 , referred to molecular axes, L, M, N .

Atom	$10^4 S_{LL}$	$10^4 S_{MM}$	$10^4 S_{NN}$	$10^4 S_{LM}$	$10^4 S_{MN}$	$10^4 S_{LN}$
C-1	23	48	123	20	7	1
C-2	36	31	192	50	48	65
C-3	24	19	34	22	29	134
C-4	21	16	95	30	5	81
C-5	26	31	47	45	11	70
C-6	1	16	15	3	35	11
C-7	2	12	60	0	19	0
C-8	25	31	142	36	10	30
C-9	22	33	55	—	30	—
C-10	4	15	18	—	20	—

The variations from atom to atom in the magnitude of this component S^r_{NN} strongly suggest an internal out-of-plane molecular vibration. While the X-ray data give no information about the relative phases of the separate atomic oscillations, it seems likely that the observed vibration is a symmetric mode that alternately increases and decreases the non-planar deformation of the molecule. This explanation of the symmetric part of ΔU^r is far more probable than, for example, bonding effects and accords with the apparent flexibility of the molecule deduced from the slight asymmetry of the molecular deformation. It is also supported by the observation that no such discrepancy of comparable magnitude occurs in dimethylbenzophenanthrene (see below); this must be due to the lower temperature of the measurements and, perhaps, also to the greater rigidity of the more strained molecule.

The negative values of several of the tensor components S^r_{NN} arise, no doubt, because the rigid-body vibrations have been overestimated to account for a part of the atomic motion that we now attribute to internal vibrations. Thus the magnitudes indicated in Table 6, especially for T_3 and ω_2 , are probably too large, the latter so much so, perhaps, that this libration cannot be regarded as definitely established.

If it is assumed, as a reasonable estimate, that the spurious contribution to the apparent rigid-body vibrations, due to the internal vibration, consists of a translational vibration of 0.005 \AA^2 along N and a librational oscillation of 0.001 rad^2 about L , we must subtract these motions from the molecular translation and libration tensors indicated in Table 6 and add the corresponding amounts to the tensors S^r in Table 7. The corrected values of the normal components S^r_{NN} are shown in Fig. 2. These figures conform to a pattern indicative of a flapping motion with three nodes that coincide approximately with the junctions of the four aromatic rings. Such a vibration would be expected to appear in the far infrared region of the molecular spectrum.

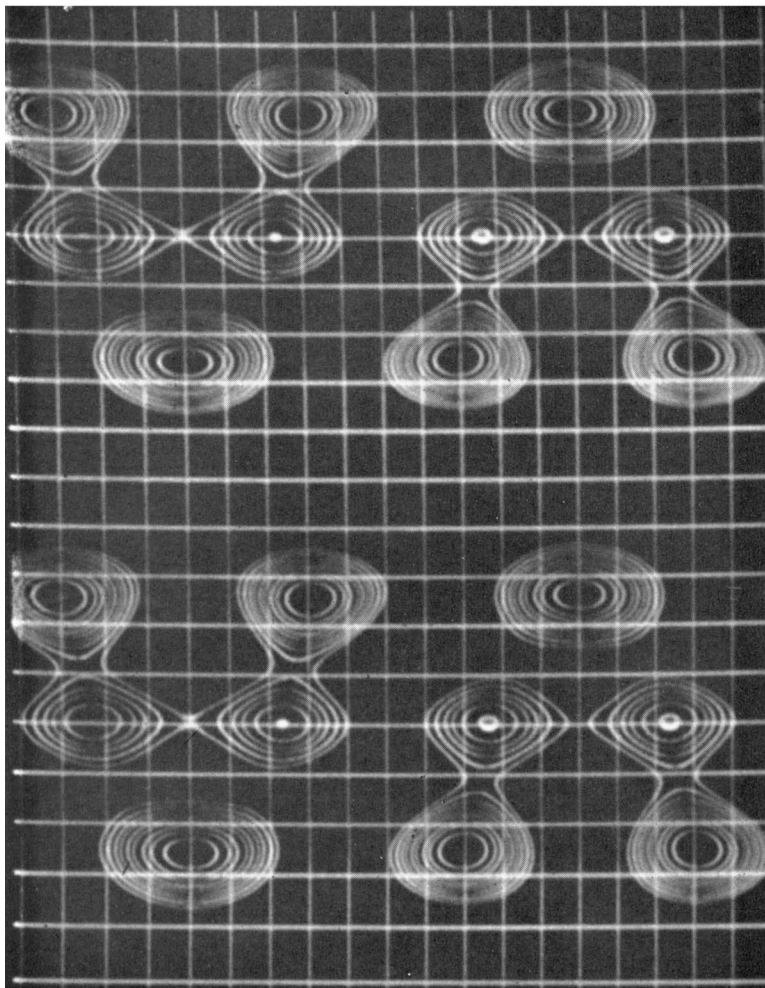


FIG. 3. X-RAC synthesis of projected $\rho(x, y)$ based on nine strong low-order $hk0$ reflections.

[To face p. 2118.]

The uncertainty about the internal vibration concerns the out-of-plane motions only and does not invalidate the results of the rigid-body analysis with regard to motion in the molecular plane. Thus the libration amplitude ω_1 is probably correct as given in Table 6 and, in particular, the displacement of the libration axis from the molecular centre of mass is a real effect attributable to the greater thickness of the molecule at its overcrowded end, which accordingly encounters greater resistance to motion in the molecular plane.

The observed librational motion results in an apparent inward displacement of the atomic centres towards the libration axes, by approximately $^{12} d\omega^2/2$, where d is the distance of the atom from the libration axis and ω^2 is the mean square libration amplitude in radians². To correct for this effect we must increase all bond lengths shown in Fig. 1 uniformly by about 0.003 Å. Bond angles and out-of-plane deformation are practically unaffected.

The molecular dimensions are conveniently considered together with those of the dimethyl derivative (see below).

DIMETHYLBENZOPHENANTHRENE

Structure Determination.—Four molecules of 1,12-dimethylbenzo[*c*]phenanthrene occupy a unit cell having, near 80°K, $a = 15.420$ Å, $b = 12.165$ Å, $c = 7.234$ Å, $d(\text{calc.}) = 1.254$. The space group is *Pbna*, requiring a molecular two-fold symmetry axis parallel to a . Solution of the structure was accomplished on X-RAC, with the use of zonal room-temperature intensity data. Nine of the strongest low-order $hk0$ reflections were selected as likely to lead to a recognisable electron-density projection along [001]. The signs of two of these—200 and 230—were fixed arbitrarily; this choice merely fixed the origin of the projection at one of the four non-equivalent positions, two at inversion centres and two on screw axes parallel to c , satisfying the requirement that all $hk0$ structure factors should be real. The signs of the remaining seven Fourier coefficients were permuted by Woolfson's method,¹³ to give sixteen Fourier maps, which were computed and photographed on the X-RAC instrument. Of these, one was chosen that displayed peaks with a fair correspondence to the expected molecular shape. The next step was to test the effect on this chosen map of reversing, one at a time, the signs of the seven Fourier coefficients. Seven new maps were prepared, each differing from the original map by one sign reversal. Four of these were definitely poorer, confirming the former signs of these four terms. The other three maps were more or less comparable in quality with the original one; thus the signs of three terms, out of the full list of nine, remained unknown. Giving these three terms all possible sign combinations resulted in a total of eight possibilities, which could readily be computed and examined individually. Of the resulting eight maps, one, having two signs reversed with respect to the original map, was undoubtedly the best of the set. This map (Fig. 3) gave a clearly recognisable picture of the molecular outline. All signs used in its computation were, in fact, correct, as confirmed eventually by the final structure-factor calculations.

A molecular model fitted to this projection led to calculated structure factors in encouraging agreement with F_o for most low-order $hk0$ reflections. Refinement proceeded gradually, by successive difference syntheses, leading to an improved model that permitted the estimation of z co-ordinates for calculation of $h0l$ structure factors. The two projections, along [001] and [010], were then refined together by difference syntheses. The structure finally obtained was clearly correct but insufficiently precise to provide useful information about the molecular dimensions. At this stage further refinement was abandoned in favour of a low-temperature structure determination.

A needle-shaped crystal of nearly 0.5 mm. square cross-section was photographed by the equi-inclination Weissenberg method while being cooled in a stream of boiling nitrogen.¹⁴ Levels $hk0$ and $hk5$ were photographed with nickel-filtered copper radiation and levels $hk0$, $hk7$, and $hk8$ with zirconium-filtered molybdenum radiation. Intensity photographs about other axes were unsuccessful because of the repeated failure of crystals that had been suitably

¹² Cruickshank, *Acta Cryst.*, 1956, **9**, 757; 1961, **14**, 896.

¹³ Woolfson, *Acta Cryst.*, 1954, **7**, 65.

¹⁴ Hirshfeld and Schmidt, *Acta Cryst.*, 1956, **9**, 233.

TABLE B. (Continued.)

<i>h k l</i>	$100F'_0$	$100F'_c$	<i>h k l</i>	$100F'_0$	$100F'_c$	<i>h k l</i>	$100F'_0$	$100F'_c$	<i>h k l</i>	$100F'_0$	$100F'_c$	<i>h k l</i>	$100F'_0$	$100F'_c$
3	504	-496	9	701	-947	7	2123	1625	0 6 8	1240	-938	10 1	2661	2431
4	819	815	0 14 7	1757	1593	9	1595	-1256	2	529	-721	11	1240	1204
12	936	1160	7	1522	-1479	11	1062	-1256	3	1240	1160	12	885	-1296
13	936	-1078	8	936	974	2 4 8	1595	-1239	4	2305	1961	14	885	620
14	936	-740	9	701	603	3	707	832	5	2123	-1576	4 8 8	1062	-730
0 12 7	619	890	10	1405	-1402	4	707	817	7	1417	-1381	6	2123	1673
1	1640	-1467	2 15 7	936	867	6	1773	-1522	8	707	-720	10	1773	-1497
7	1170	896	7	701	387	8	885	1170	9	1062	1024	14	1417	1516
8	584	650	9	701	1075	1 5 8	1417	1077	11	2305	2120	1 9 8	707	-978
9	504	-500	10 0 8	707	169	2	1595	-1239	12	1240	1368	2	770	-894
11	936	-952	10 1 8	707	069	3	2433	1974	13	1240	-1339	3	1595	1150
1 13 7	1757	-1512	10 2 8	1062	1223	6	805	-805	2 7 8	1595	1513	9	1240	-1397
7	1522	1500	5 3 8	1950	-1137	10	1950	-1422	5	1417	1260	9 10 8	885	-105
8	701	-692	6	605	-779	12	3371	3060	8	2123	-1876			

shaped to survive the thermal stresses attendant on fairly rapid cooling. Thus, while an $h0l$ photograph of a crystal that had split on cooling permitted the measurement of the c axial length, it was useless for intensity estimation, with the result that the relative intensity scales of the several level photographs could not be established experimentally.

Intensities were estimated for 512 observed reflections (Table B), plus upper limits for 130 unobserved reflections. Of the former, two were eliminated because of severe extinction. This left 640 input data for the least-squares refinement of the following parameters: a separate scale factor k_i^2 for each level ($1 \times 4 = 4$), 3 positional co-ordinates for each general-position atom in the asymmetric unit ($3 \times 17 = 51$), 1 x co-ordinate each for the two atoms on the symmetry axis ($1 \times 2 = 2$), 6 anisotropic thermal parameters for each general-position carbon atom ($6 \times 9 = 54$), 4 anisotropic thermal parameters for each special-position carbon atom ($4 \times 2 = 8$), and 1 isotropic thermal parameter for each hydrogen atom ($1 \times 8 = 8$) (total 127).

The initial model was based on the room-temperature atomic co-ordinates together with a single, estimated, isotropic thermal parameter for all atoms. This was refined, at first by adjustment of the positional co-ordinates alone, later with variable anisotropic thermal parameters as listed above. The electron-density and difference-density projections along [001], calculated with one isotropic thermal parameter, have been published previously.¹⁴ The final refinement procedure was identical with that followed for benzo[*c*]phenanthrene. However, the absence of a common, experimentally determined scale for the four reciprocal-lattice levels led to an unfortunate indeterminacy in the absolute values of the thermal parameters U_{33} . Convergence was hastened, at an advanced stage in the refinement, by the arbitrary expedient of setting the average value of U_{33} over all the carbon atoms in the molecule equal to the corresponding combined average of U_{11} and U_{22} . This restriction was relaxed for subsequent refinement cycles.

On the final cycle the maximum calculated co-ordinate shift was 0.001 Å for carbon, 0.006 Å for hydrogen. The maximum cumulative shift over the last six cycles, with damping factors one-half, was under 0.002 Å for carbon, 0.025 Å for hydrogen. The discrepancy factors are summarised in Table 1.

Standard deviations were estimated in the same manner as for benzo[*c*]phenanthrene. The number of reflections n was 521, comprising 510 observed and 11 unobserved reflections having $|F_c| > kF_t$ on the final cycle. The estimated standard deviations of the carbon co-ordinates were, on the average, 0.0037 Å, with a maximum of 0.0056 Å. For hydrogen the corresponding figures are 0.060 Å and 0.160 Å. For all atoms the standard deviations were somewhat anisotropic, being largest in the z direction; this anisotropy reflects the non-uniform sampling of the reciprocal-lattice points. The estimated standard deviations of the thermal vibration components U'_{ij} of the carbon atoms averaged 0.0015 Å². For the hydrogen atoms the estimated standard deviations of the mean-square thermal displacements \bar{u}^2 had an average value of 0.012 Å². This is larger than the average value of u^2 itself; accordingly these experimental thermal parameters are barely meaningful. Yet the fact that four of the five exocyclic hydrogen atoms have negative thermal parameters is at least consistent with other indications, both theoretical¹⁵ and experimental,¹⁶ that charge clouds in bonded hydrogen tend to be more concentrated than in the isolated atom.

¹⁵ Coulson, "Valence," Oxford Univ. Press, 2nd edn., 1961, p. 86.

¹⁶ McDonald, *Acta Cryst.*, 1956, **9**, 162; Hirshfeld and Schmidt, ref. 14.

Final atomic co-ordinates are listed in Table 8, vibrational parameters in Table 9. The bond lengths and angles are indicated in Fig. 4. Their significance is considered further below.

Intermolecular contacts (Table 10) show no abnormality.

The problem of fitting a rigid-body molecular motion to the observed atomic vibrations is considerably simpler than for benzo[*c*]phenanthrene because of the crystallographic

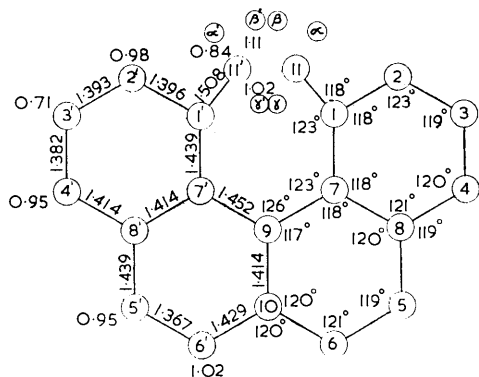


FIG. 4. Observed bond lengths, in Å, and angles for 1,12-dimethylbenzo[*c*]phenanthrene. C-H bond lengths indicated next to respective carbon atoms. Figures inside circles show numbering of atoms.

two-fold symmetry axis passing through the molecule. Rather than fifteen independent parameters, only nine need be determined: four translation components, four libration components, and one co-ordinate of the libration centre. However, when the rigid-body motion was derived from the observed vibrations of all the carbon atoms, it was found that the agreement between $U_{ij}(\text{RB})$ and $U_{ij}(\text{exp})$ was much poorer for the methyl carbon atom than for the other atoms. It was, therefore, suspected that the methyl groups might be undergoing some separate motion of their own, most plausibly a rotation coupled to a flapping motion relative to the molecular skeleton. Accordingly, the rigid-body motion was redetermined from the thermal parameters of the ring carbon atoms alone. This procedure did not materially alter the overall nature of the molecular motion, but it produced somewhat better agreement for the ring atoms (Table 9). The RMS discrepancy between $U_{ij}(\text{exp})$ and $U_{ij}(\text{RB})$ for the ring atoms alone was 0.0022 Å². This is greater than the estimated standard deviation of $U_{ij}(\text{exp})$ but the margin is much

TABLE 8.

Atomic co-ordinates of 1,12-dimethylbenzo[*c*]phenanthrene, referred to crystal axes and to molecular axes: $L \parallel a$, M , having direction cosines (0, 0.65071, 0.75933), and N (0, 0.75933, 0.65071).

Atom	x/a	y/b	z/c	L (Å)	M (Å)	N (Å)
C-1	0.3532	0.1300	0.1041	1.323	1.522	0.618
C-2	0.3898	0.0686	0.2173	1.887	2.794	0.512
C-3	0.3487	0.0539	0.4170	1.254	3.843	0.151
C-4	0.2652	0.0926	0.4410	0.034	3.668	0.622
C-5	0.1324	0.1720	0.3096	2.082	2.318	0.737
C-6	0.0893	0.2116	0.1584	2.746	1.174	0.391
C-7	0.2703	0.1809	0.1356	0.045	1.292	0.000
C-8	0.2242	0.1520	0.2974	0.666	2.409	0.495
C-9	0.2273	0.2500	0.0000	0.618	—	—
C-10	0.1356	0.2500	0.0000	2.032	—	—
C-11	0.3959	0.1258	0.0833	1.981	0.526	1.539
H-2	0.4438	0.0282	0.2253	2.72	2.99	0.99
H-3	0.3699	0.0211	0.4846	1.58	4.47	0.17
H-4	0.2364	0.0729	0.5527	0.48	4.44	0.97
H-5	0.1076	0.1515	0.4240	2.46	3.11	1.09
H-6	0.0235	0.2177	0.1613	3.76	1.14	0.46
H- α	0.3511	0.1260	0.1490	1.29	0.16	1.85
H- β	0.4435	0.0570	0.0891	2.72	1.04	2.20
H- γ	0.4464	0.1798	0.0749	2.76	0.14	1.00

TABLE 9a.

Observed and calculated (rigid-body) components of atomic vibration tensors U^r , in \AA^2 , for 1,12-dimethylbenzo[*c*]phenanthrene.

Atom	$10^4 U_{11}$	$10^4 U_{22}$	$10^4 U_{33}$	$10^4 U_{12}$	$10^4 U_{23}$	$10^4 U_{13}$
C-1 (exp)	110	78	91	6	28	39
(RB)	102	90	115	4	6	12
C-2 (exp)	188	91	139	25	23	74
(RB)	178	103	141	17	0	45
C-3 (exp)	321	124	146	7	20	89
(RB)	301	126	130	12	21	30
C-4 (exp)	246	148	109	61	5	18
(RB)	299	132	125	17	15	42
C-5 (exp)	161	116	237	64	65	103
(RB)	175	121	215	42	47	104
C-6 (exp)	124	119	283	19	75	108
(RB)	103	111	270	27	79	65
C-7 (exp)	110	84	127	25	0	14
(RB)	102	91	110	5	8	13
C-8 (exp)	155	119	118	38	38	32
(RB)	175	110	134	21	9	52
C 9 (exp)	90	111	118	—	41	—
(RB)	78	89	126	—	19	—
C-10 (exp)	108	90	193	—	35	—
(RB)	78	99	207	—	54	—
C-11 (exp)	120	175	119	36	17	24
(RB)	75	91	133	2	22	1

TABLE 9b.

Experimental mean-square displacements \bar{u}^2 of hydrogen atoms, in \AA^2 , for 1,12-dimethylbenzo[*c*]phenanthrene.

H atom	2	3	4	5	6	α	β	γ
$10^3 \bar{u}^2$	9	33	17	17	8	3	30	50

TABLE 10.

Closest interatomic contacts, in \AA , between reference molecule of 1,12-dimethylbenzo[*c*]phenanthrene, centred near $(\frac{1}{4}, 0)$, and neighbouring molecules related to it by indicated symmetry elements. The first-designated atom of each pair belongs to the reference molecule.

Intramolecular contacts:	$C_{(1)}-C_{(11')} 3.047$;	$C_{11}-C_{(11')} 3.254$;	$C_{(1)}-C_{(1')} 3.285$;	$C_{(7)}-H_{(\alpha)} 2.66$;
	$C_{(1)}-H_{(\gamma')} 2.73$;	$C_{(11)}-H_{(\gamma')} 2.74$;	$C_{(1)}-H_{(\alpha)} 2.99$;	$H_{(\gamma)}-H_{(\gamma')} 2.02$.
<i>c</i> -axis translation:	$C_{(5)}-C_{(5)} 3.345$;	$C_{(4')} - C_{(8)} 3.692$;	$H_{(5)}-C_{(5)} 2.91$;	$H_{(5')} - H_{(5)} 2.64$.
2_1 axis at $(\frac{1}{4}, 0)$:	$C_{(1)}-C_{(4)} 3.473$;	$C_{(11)}-C_{(4)} 3.641$;	$C_{(7)}-C_{(4)} 3.655$;	$C_{(1)}-H_{(4)} 2.85$;
	$C_{(2)}-H_{(4)} 2.95$;	$H_{(\beta)}-H_{(5)} 2.66$.		
<i>a</i> -glide at $(xy\frac{1}{4})$:	$C_{(2')} - C_{(6')} 3.599$;	$C_{(2')} - H_{(6')} 2.82$;	$H_{(\gamma)} - H_{(6')} 2.57$.	
Centre at $(\frac{1}{2}, 0)$:	$H_{(2)} - H_{(\beta)} 2.25$;	$H_{(\beta)} - H_{(\beta)} 2.58$.		

TABLE 11.

Principal components of 1,12-dimethylbenzo[*c*]phenanthrene rigid-body vibrations and their direction cosines with respect to crystal axes and molecular axes.

	<i>a</i> , <i>L</i>	<i>b</i>	<i>c</i>	<i>M</i>	<i>N</i>
$T_1^2 = 0.0105 \text{\AA}^2$	0	0.4210	0.9071	0.9627	0.2706
$T_2^2 = 0.0083$	0	0.9071	0.4210	0.2706	0.9627
$T_3^2 = 0.0078$	1.0000	0	0	0	0
$\omega_1^2 = 0.00164 \text{ rad}^2$	0	0.9259	0.3778	0.3156	0.9489
$\omega_2^2 = 0.00043$	1.0000	0	0	0	0
$\omega_3^2 = 0.00009$	0	0.3778	0.9259	0.9489	0.3156

Libration centre: $x_0 = L_0 = 0.723 \text{\AA}$.

smaller than in benzo[*c*]phenanthrene and is readily attributable to the effects (*a*) and (*b*) enumerated above.

The principal components of the molecular vibrations are indicated in Table 11. As

for the parent molecule, the translational motion is nearly isotropic. This result is not well established, however, but rests partly on the arbitrary assignment of relative scale factors to the several reciprocal-lattice levels (see above). The greatest libration component has an amplitude of 2.3° , about an axis normal to the mean molecular plane. This libration axis does not pass through the molecular centre of mass but, as in our earlier case, is displaced towards the overcrowded region, by 0.72 \AA . The libration amplitude about the symmetry axis is 1.2° , which is barely significant. The third component yields a small negative value of ω^2 , whose magnitude is much less than the estimated standard deviation.

Correction of the atomic positions for the apparent displacement due to the molecular libration results in a uniformly negligible increase of 0.001 \AA in all C-C bond lengths.

Methyl Groups.—The methyl-hydrogen atoms have, in general, higher thermal parameters than the exocyclic hydrogen atoms. Some rotational freedom for the methyl group may thus be indicated. Nevertheless, the positions determined for these hydrogen atoms seem sufficiently reliable to establish the approximate mean orientation of the methyl group. The bond lengths and angles within this group are highly variable but do not appear to depart significantly or systematically from tetrahedral symmetry. Assuming a perfectly symmetric methyl group, with tetrahedral bond angles and C-H bond lengths of 1.09 \AA , we can calculate the shorter non-bonded contact distances to these hydrogen atoms as functions of the azimuthal orientation of the group about the exocyclic C-C bond. These calculated distances are indicated in Fig. 5. The observed orientation, averaged from the experimental positions of the three hydrogen atoms, allows maximum clearance between the hydrogen atoms and neighbouring carbon atoms. This orientation is evidently maintained by a balance of opposing interatomic repulsions, especially those between H- γ and C-1' and between H- α and C-7' (see Fig. 4 for numbering of atoms). That the observed orientation nearly minimises the distance between H- γ and H- γ' merely emphasises the difference in van der Waals radius between carbon and hydrogen.

It is evident that any appreciable rotation of the methyl group must enhance the repulsive interactions between the two halves of the molecule. We thus expect that a flapping motion, probably involving the whole molecular skeleton, but most pronounced at the methyl groups themselves, will accompany such a methyl rotation. The excess vibrational motion observed for the methyl-carbon atom (see above) may arise in this manner.

Bond Lengths.—Comparison of the bond lengths in the two compounds (Figs. 1 and 4) shows the expected close similarity. Comparing the averages of symmetry-related bond lengths in benzophenanthrene, corrected for libration, with the corresponding values for its dimethyl derivative, one finds a difference of 0.013 \AA RMS, 0.023 \AA maximum. While some of these differences may, perhaps, be real they are evidently minor; they do not preclude our treating the two molecules as essentially similar. This means that neither hyperconjugation with the methyl group nor the extra strain consequent on substitution in the overcrowded positions produces a major change in bond lengths. The exocyclic bond length to the methyl-carbon atom (1.508 \AA), which is normal for an sp^2 - sp^3 bond,¹⁷ likewise indicates no hyperconjugation.

Accordingly we have plotted (Fig. 6) the average bond lengths for the two molecules against the mobile bond orders calculated¹⁸ for benzo[*c*]phenanthrene. This plot shows a fairly smooth relation of the usual sort between bond order and bond length, implying again that the bond lengths are scarcely affected by the overcrowding. This result is in line with two conclusions of apparently general validity for aromatic compounds: (a) molecular deformation due to interatomic repulsions does not greatly alter the bonding in an aromatic molecule; and (b) bond lengths are very insensitive indicators of subtle electronic effects,¹⁹ at least in alternant systems.

¹⁷ Somayajulu, *J. Chem. Phys.*, 1959, **31**, 919.

¹⁸ Berthier, Coulson, Greenwood, and Pullman, *Compt. rend.*, 1948, **226**, 1906.

¹⁹ Hirshfeld and Schmidt, *J. Chem. Phys.*, 1957, **26**, 923.

One may, nevertheless, be tempted to argue from the data of Fig. 6 that the 1,2- and 1,7-bonds in the overcrowded region are significantly longer than would be predicted in the absence of intramolecular repulsion. Such a supposition would accord with the fact that both these bonds appear somewhat longer in the dimethyl compound than in its parent. This effect, if real, may, perhaps, be a direct consequence of the interatomic repulsion on the electron distribution at atom C-1 rather than a result of the molecular non-planarity. This surmise is based on the observation that other C-C bonds that are bent or twisted to about the same extent as are the bonds to C-1, or more so,²⁰ show no such lengthening.

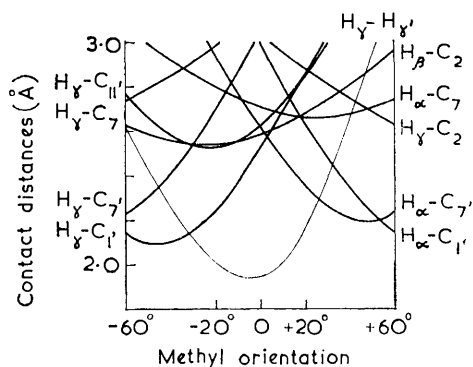


FIG. 5. Dependence on methyl-group orientation of intramolecular contacts of methyl hydrogen atoms; perfect tetrahedral symmetry assumed. Azimuth angle 0 corresponds to observed orientation.

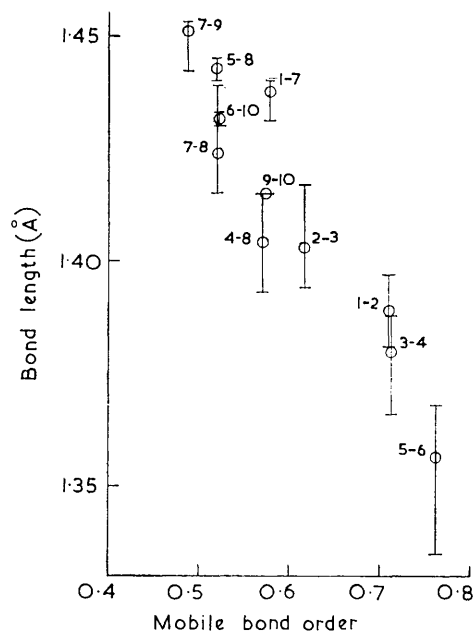


FIG. 6. Mean experimental bond lengths of benzo[*c*]phenanthrene (average) and its 1,12-dimethyl derivative, corrected for libration, plotted against calculated¹⁸ (molecular orbital) mobile bond orders for the former. Vertical lines show ranges of measured values. Numbers identify carbon atoms forming each bond.

The bond angles are likewise similar in the two compounds. The effect of the overcrowding is clearly seen in the angles at atoms C-7 and C-9 and, in the dimethyl derivative, at atom C-1 as well. It is not surprising that the departures from the usual valency angles for trigonal carbon should be nearly equal in the two molecules. While the overcrowding forces are greater in the dimethyl derivative they are more steeply inclined to the mean molecular plane, owing to the greater out-of-plane deformation, so that their in-plane components are likely to be about the same as in the parent hydrocarbon.

The out-of-plane deformations of the two molecules form the subject of Part VII²⁰ of this series.

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REHOVOTH, ISRAEL. [Received, May 24th, 1962.]

²⁰ Hirshfeld, following paper.