

Refinement of the Crystal Structure of Orthorhombic Dibenz[*a,h*]-anthracene

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The crystal structure of the title compound has been refined from (a) three-dimensional, single-crystal X-ray diffractometer data and (b) three-dimensional photographic data. Crystals are orthorhombic, space group *Pcab*, with $a = 8.263(2)$, $b = 11.466(2)$, $c = 15.238(2)$ Å, $Z = 4$. Starting with previously reported atomic parameters the structure was refined anisotropically (a) by full-matrix least-squares to R 0.035 (715 unique reflections), and (b) by block-diagonal least-squares to R 0.067 (1 148 unique reflections). Bond-lengths for each refinement are in good agreement with each other and with those predicted by Pauling's formula for single-bond-double-bond resonance. The molecule is centrosymmetric and planar.

DIBENZ[*a,h*]ANTHRACENE was the first carcinogenic hydrocarbon to be synthesized and the orthorhombic crystal form was first described by Iball¹ and by Krishnan and Bannerjee.² Some of the crystals produced by Iball from ethyl acetate solutions were later used by Robertson and White³ in their determination of the crystal structure. The stability of these crystals is remarkable as the same batch of crystals first produced in 1935 were used in the Dundee refinement described in the present paper. They are still perfectly formed prisms with bright faces, and they are absolutely colourless. The

Space group *Pcab* (D_{2h}^{15} , No. 61). Cu- K_{α} radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_{\alpha}) = 5.66$ cm⁻¹.

Intensity Measurements.—(a) *At Dundee.* Equi-inclination Weissenberg photographs (multifilm packs) were taken about the *a* and *b* axes on a Leeds-Cox Weissenberg fitted with a device which gave integration in the direction of the camera translation. This eliminated any necessity to correct for the contraction and elongation of the spots on higher-layer photographs. Intensities were measured by recording the film densities on a photoelectric densitometer. The absorption factors of the films were measured independently and structure factors were placed on a common scale

TABLE 1
Atomic fractional co-ordinates ($\times 10^4$); (10^3 for hydrogen)

	X		Y		Z	
	P	D	P	D	P	D
C(1)	-250(3)	-240(9)	-1 433(2)	-1 431(6)	3 573(2)	3 581(5)
C(2)	546(3)	539(9)	-390(2)	-392(6)	3 361(2)	3 363(5)
C(3)	617(3)	630(8)	-28(2)	-21(6)	2 503(2)	2 505(5)
C(4)	-79(3)	-87(7)	-684(2)	-682(5)	1 821(1)	1 819(4)
C(5)	-20(2)	-19(7)	-325(2)	-320(5)	906(2)	902(4)
C(6)	768(3)	764(7)	684(2)	690(5)	621(1)	621(4)
C(7)	800(3)	796(7)	1 021(2)	1 028(5)	-256(2)	-259(4)
C(8)	1 593(3)	1 601(8)	2 080(2)	2 083(5)	-522(1)	-520(4)
C(9)	1 614(3)	1 621(8)	2 420(2)	2 431(6)	-1 362(2)	-1 366(4)
C(10)	859(3)	871(7)	1 741(2)	1 740(5)	-2 040(2)	-2 041(4)
C(11)	920(3)	933(8)	2 094(2)	2 092(6)	-2 927(2)	-2 933(4)

	X		Y		Z		B	
	P	D	P	D	P	D	P	D
H(1)	-26(3)	-31	-166(2)	169	422(1)	421	7.1(7)	6.0
H(2)	107(3)	106	10(2)	14	386(2)	387	8.7(8)	6.0
H(3)	118(3)	116	70(2)	69	234(2)	237	8.5(8)	6.0
H(6)	128(3)	133	121(2)	119	106(1)	106	6.8(7)	6.0
H(8)	220(3)	220	254(2)	259	-3(1)	-8	6.9(6)	6.0
H(9)	216(3)	217	313(2)	314	-153(1)	-154	7.4(7)	6.0
H(11)	149(3)	150	280(2)	285	-302(2)	-310	7.4(8)	6.0

P = Philadelphia, D = Dundee; Dundee hydrogen parameters were not refined.

crystals used for the Philadelphia refinement were freshly prepared from ethanol and were pale yellow. The monoclinic form was first described by Iball and Robertson⁴ and its structure was determined by Robertson and White.⁵

EXPERIMENTAL

Crystal Data.— $\text{C}_{22}\text{H}_{14}$, M 278.35. Orthorhombic, $a = 8.263(2)$, $b = 11.466(2)$, $c = 15.238(2)$ Å, $U = 1 445.5(5)$ Å³, $D_c = 1.289$, $Z = 4$, $D_m = 1.29$ g cm⁻³, $F(000) = 584$.

¹ J. Iball, *Nature*, 1936, **137**, 361.

² K. S. Krishnan and S. Banerjee, *Z. Krist.*, 1935, **91**, 170, 173.

by relating sets of common reflections. No absorption corrections were applied.

(b) *At Philadelphia.* Intensities for two octants of the reflection sphere ($h, k, \pm l$) were collected in the 2θ range 0–140° with a Syntex PI automated diffractometer with monochromatized (graphite) Cu- K_{α} radiation by a variable θ – 2θ scan and a minimum scan rate of 1° min⁻¹. From a total of 2 987 recorded intensities, 1 340 unique reflections (81.2% of those theoretically accessible) were obtained by

³ J. M. Robertson and J. G. White, *J. Chem. Soc.*, 1947, 1001.

⁴ J. Iball and J. M. Robertson, *Nature*, 1933, **132**, 750.

⁵ J. M. Robertson and J. G. White, *J. Chem. Soc.*, 1956, 925.

averaging the $\pm l$ sets. The threshold for observation was taken as $I > 3\sigma(I)$, with $\sigma(I)$ determined from counting statistics, which gave 715 observed reflections. Values for $\sigma(F)$ were derived from $\sigma(F) = (F/2)\{[\sigma^2(I)/I^2] + \delta^2\}^{1/2}$, where δ is a measured instrumental uncertainty and was here 0.014. Data were corrected for Lorentz and polarization factors and placed on an absolute scale with a Wilson plot. No absorption correction was applied.

Structure Refinement.—Both refinements began with the atomic parameters of Robertson and White³ and while the Dundee data were used with a block-diagonal least-squares computer program, the Philadelphia refinement was carried out with a full-matrix program. In the former, the final R was 0.067 for 1 148 independent structure factors and in the latter it was 0.035 for 715 independent structure factors. In the Philadelphia data a correction for extinction was applied to 11 strong reflections ($F > 50$). The weighting schemes used were (a) $w = 1/\{1 + [(|F_o| - F^*)/G^*]^2\}$, $F^* = 20$, $G^* = 20$; and (b) each reflection had a weight derived from the experimental $\sigma(F)$. In (a) scattering factors were taken from ref. 6, and in (b) those for carbon were taken from ref. 7, and for hydrogen from ref. 8.*

RESULTS AND DISCUSSION

Final positional parameters are in Table 1. Table 2 gives bond lengths from each refinement, C-C bond distances calculated from Pauling's formula for single-bond-double-bond resonance in aromatic hydrocarbons,⁹

TABLE 2
C-C Bond lengths (Å)

	(1)	(2)	(3)	(4)
(1)-(2)	1.390(9)	1.403(2)	1.407	1.407
(2)-(3)	1.376(9)	1.372(2)	1.374	1.382
(3)-(4)	1.418(8)	1.407(2)	1.411	1.407
(4)-(5)	1.458(8)	1.454(2)	1.456	1.458
(4)-(10')	1.413(8)	1.412(2)	1.415	1.407
(5)-(6)	1.392(7)	1.398(2)	1.402	1.394
(5)-(7')	1.423(7)	1.424(2)	1.429	1.423
(6)-(7)	1.395(7)	1.392(2)	1.394	1.394
(7)-(8)	1.434(7)	1.438(2)	1.442	1.458
(8)-(9)	1.348(8)	1.338(2)	1.340	1.351
(9)-(10)	1.436(8)	1.436(2)	1.441	1.458
(10)-(11)	1.416(8)	1.412(2)	1.413	1.407
(1)-(11')	1.369(9)	1.358(2)	1.362	1.382

Experimental results for (1) Dundee and (2) Philadelphia, with standard deviations in parentheses; (3) Philadelphia values corrected for thermal motion, and (4) calculated values according to ref. 9.

and bond lengths corrected for thermal motion. The thermal motion corrections are small and in no case are $> 2.5\sigma$. Bond angles are listed in Table 3. The thermal motion analysis indicates that the assumption of rigid-body molecules is valid and that the motion is largely translational. The molecule is planar, but not quite as planar as some other aromatic condensed ring hydro-

* Observed and calculated structure amplitudes, together with Tables of thermal parameters and thermal motion analysis are in Supplementary Publication No. SUP 21352 (11 pp., 1 microfiche). For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1974, Index issue.

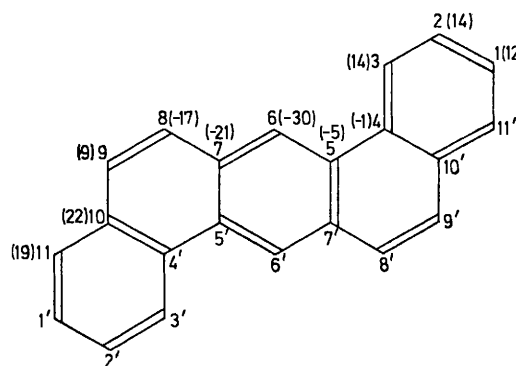
carbons. The equation of the mean plane is $-0.854 09X + 0.505 58Y + 0.122 13Z = 0$; deviations of individual atoms from this plane are given in the Figure. The

TABLE 3
C-C-C Bond angles (deg.) with standard deviations in parentheses

	D	P
(1)-(2)-(3)	121.0(6)	119.9(2)
(2)-(3)-(4)	120.8(6)	121.6(2)
(3)-(4)-(5)	122.5(5)	122.6(2)
(3)-(4)-(10')	118.2(5)	118.0(2)
(4)-(5)-(6)	123.3(5)	123.3(2)
(4)-(10')-(11')	119.3(5)	119.3(2)
(4)-(5)-(7')	118.7(5)	119.5(2)
(4)-(10')-(9')	119.8(5)	119.5(2)
(5)-(6)-(7)	122.3(5)	122.5(2)
(5)-(7)-(8')	119.9(5)	118.9(2)
(5)-(7)-(6')	119.6(5)	120.2(2)
(5)-(4)-(10')	119.4(5)	119.1(2)
(6)-(7)-(8)	121.4(5)	120.9(2)
(6)-(5)-(7')	118.1(5)	117.3(2)
(7)-(8)-(9)	121.3(5)	121.4(2)
(8)-(9)-(10)	121.0(5)	121.6(2)
(9)-(10)-(11)	120.9(5)	121.2(2)
(1)-(11')-(10')	121.3(5)	121.3(2)
(2)-(1')-(11)	119.5(6)	119.9(2)

D = Dundee; P = Philadelphia.

shortest carbon-carbon intermolecular distance is 3.615 Å between C(1) and C(6) of the molecule at $x - \frac{1}{2}, -y, \frac{1}{2} - z$.



The crystallographic numbering system used in the analysis. Values in parentheses are deviations (Å × 10³) from the mean plane

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⁶ 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

⁷ D. T. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

⁸ R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

⁹ L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., 1960, Cornell University Press, Ithaca, New York, p. 235.