

The Crystal and Molecular Structure of 2,7-Dibromo-4,5-bis-(2-pyridyl)phenanthrene-3,6-diol

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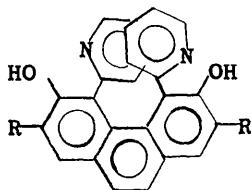
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The crystal structure of 2,7-dibromo-4,5-bis-(2-pyridyl)phenanthrene-3,6-diol has been determined from single-crystal X-ray intensity data collected with an automated diffractometer. The crystals are monoclinic, space group $I2/a$, with four molecules in a unit cell of dimensions $a = 13.860$ (1), $b = 10.869$ (1), $c = 12.923$ (1) Å, $\beta = 94.02$ (1)°. The structure was solved by the heavy-atom technique and refined by full-matrix least squares. Hydrogen atoms were located and refined. The final value of the discrepancy factor is $R = 0.028$. As a result of intramolecular overcrowding the molecule is severely distorted from a planar configuration. However, the bending is distributed over the entire molecule so that the trigonal symmetry of the bonds about any particular carbon atom is not greatly disturbed. The overcrowding has caused some bonds to be lengthened and there is a nonbonded intramolecular contact of 2.8 Å.

Introduction

In the course of his studies of inverse electron demand in Diels–Alder reactions, Fields has synthesized a number of novel overcrowded polynuclear aromatic compounds (Fields, 1969; Fields, Regan, & Dignan, 1968). Among these compounds are the 2,7-disubstituted-4,5-bis-(2-pyridyl)phenanthrene-3,6-diols:



It is evident that these molecules are severely overcrowded and that the steric repulsions of the pyridyl groups must cause the normally planar phenanthrene moiety to be considerably distorted. With molecular models one can manipulate the twists of the pyridyl groups and the distortions of the phenanthrene nucleus to obtain some feeling for the molecular shape. However, we believed a complete crystal structure analysis was necessary to define unambiguously the stereochemistry of these compounds. This report describes the three-dimensional X-ray crystal structure determination of the bromine-substituted compound ($R = \text{Br}$).

Crystal data

$\text{C}_{24}\text{H}_{14}\text{N}_2\text{O}_2\text{Br}_2$, M.W. 522.21, m.p. 290°C (decomp.).
2,7-Dibromo-4,5-bis-(2-pyridyl)phenanthrene-3,6-diol.
Yellow, long square prismatic (a) crystals.
Monoclinic ($\text{Cu } K\alpha_1 = 1.5405$ Å)

$$a = 13.860 \pm 0.001 \text{ \AA} \quad b = 10.869 \pm 0.001 \text{ \AA}$$

$$c = 12.923 \pm 0.001 \text{ \AA} \quad \beta = 94.02 \pm 0.01^\circ$$

Volume of unit cell, 1942.1 ± 0.3 Å³.

Density, calculated ($Z = 4$) 1.786 g.cm^{-3}
measured (floatation) 1.82 g.cm^{-3} .

Linear absorption coefficient, $\mu = 62 \text{ cm}^{-1}$ ($\text{Cu } K\alpha$).

Total number of electrons per unit cell, $F(000) = 1032$.

Absent spectra: hkl for $h+k+l$ odd, $h0l$ for h odd.

Space group, $I2/a$ (C_{2h}^6).

General positions: $(0, 0, 0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z; \frac{1}{2} + x, -y, z)$

Experimental

Samples of 2,7-unsubstituted ($R = \text{H}$), 2,7-dimethyl ($R = \text{CH}_3$), and 2,7-dibromo ($R = \text{Br}$) derivatives were supplied to us by Dr D. L. Fields of our Laboratories. Suitable crystals of the unsubstituted compound were not readily obtained and precession photographs of the dimethyl derivative clearly showed the crystals to be disordered. Good crystals of the dibromo compound were obtained by slowly cooling to room temperature a hot, saturated solution of the material in dimethylformamide. Space group extinctions and preliminary lattice dimensions were obtained from precession photographs.

A small square prismatic crystal $0.08 \times 0.08 \times 0.18$ mm, attached to a thin glass rod with Canada balsam, was chosen for intensity-data collection on an automatic Picker four-circle goniostat. Narrow source, open-counter ω scans (Furnas, 1957) through several reflections showed the mosaicity of the crystal to be approximately 0.15°. Twenty-nine reflections at moderately high Bragg angles ($\text{Cu } K\alpha_1$ radiation) were accurately centered through very narrow vertical and horizontal slits at a take-off angle of 0.5°. These observations were used as input to the computer program PICK2 (Ibers & Hamilton, 1966) which refined the cell and orientation parameters by the method of least squares and generated the cards to control the automated goniostat.

Intensity data were collected with Ni-filtered Cu radiation at a take-off angle of 2.5°. A scintillation de-

tector was used and the pulse-height analyzer was set for an approximately 90 per cent window. All 1659 unique reflections for $2\theta < 130^\circ$ were measured by the θ - 2θ scan technique (Furnas, 1957) at a 2θ scan rate of $1.0^\circ \cdot \text{min}^{-1}$. The scan range varied from 1.1° at low 2θ to 2.2° at high 2θ . Stationary-crystal stationary-counter background counts were taken for 40 sec at each end of the scan. For count rates above 13,000 c.p.s. brass attenuators ($\sim 68\%$ attenuation) were automatically inserted in the diffracted beam by the Picker system. To check electronic and crystal stability during the period of data collection, the intensity of the $63\bar{1}$ reflection was measured every 50th reflection. A small ($\sim 2\%$) systematic decrease was observed in the intensity of this standard reflection over the period of data collection.

The reduction of the intensity data to structure amplitudes was accomplished with the computer program *DACOR* (Smith, 1966). The background for a reflection was approximated by a straight line between the two measured background points. The intensities, corrected for background, were scaled by the standard intensities to correct for the slight systematic decrease noted in these intensities. Lorentz and polarization corrections were made but absorption was neglected. We estimate the maximum error in $|F_o|$ caused by absorption to be $\pm 25\%$, but most reflections have far smaller errors. Absorption errors are known to affect thermal parameters much more than positional parameters (Srivastava & Lingafelter, 1966) and for our crystal, which is elongated along **a**, should cause B_{11} to be systematically larger than B_{22} and B_{33} . The final parameters shown in Table 4 show this to be the case; the average value of B_{11} is 3.83 \AA^2 , of B_{22} is 2.75 \AA^2 , and of B_{33} is

2.73 \AA^2 . Standard deviations $\sigma(I)$ were based on counting statistics and the estimated error of scaling and were corrected to $\sigma(F)$. Of the 1659 measured reflections, 195 were less than $2\sigma(I)$ and were considered unobserved. The intensities of these unobserved reflections were then set equal to $2\sigma(I)$ and corrected to structure amplitudes, F_{lim} .

Determination and refinement of the structure

Scale and overall temperature factors, determined from a least-squares fit of a Wilson (1942) plot, were applied to the structure factors to place them on an absolute scale and to correct them for thermal motion. The computer program *ESORT* (Smith, 1966) was then used to compute (Hauptman & Karle, 1953) the normalized structure factor magnitudes, $|E_H|$, and the statistical averages and distribution shown in Table 1. Unobserved reflections were included in the Wilson plot and the statistical averages as $E_{\text{lim}}^2/3$ (Hamilton, 1955).

Table 1. *Statistical averages and distributions of normalized structure amplitudes*

	Experimental	Theoretical	
		Centric	Acentric
$\langle E \rangle$	0.809	0.798	0.886
$\langle E^2 - 1 \rangle$	0.941	0.968	0.736
$\langle E^2 \rangle$	0.998	1.000	1.000
$ E > 3.0$	0.2%	0.3%	0.01%
> 2.5	1.2	1.2	0.2
> 2.0	4.2	4.6	1.8
> 1.8	6.7	7.2	3.9

The data in Table 1 strongly indicate that the probable space group is the centric one, $I2/a$, rather than

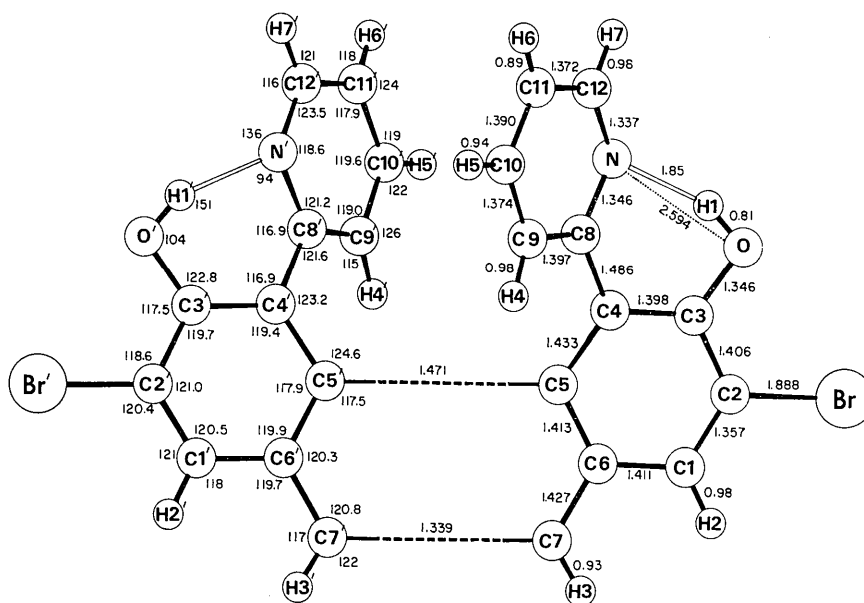


Fig. 1. Atomic labeling and interatomic distances and angles. For clarity, the C(5)-C(5') and C(7)-C(7') bonds are not drawn to scale.

the acentric group *Ia*. Since there are only four molecules per unit cell, the molecules must possess special crystallographic symmetry or be statistically disordered. No evidence of disorder was found on the precession photographs. The molecules cannot contain an inversion center and therefore must lie on the twofold axes. The distribution of the vectors in a three-dimensional sharpened Patterson map (coefficients E^2-1) verified the centric space group and the twofold molecular symmetry. Coordinates for the bromine atom were readily obtained from the Patterson map. Two cycles of isotropic least-squares refinement of the scale factor and the bromine parameters resulted in an agreement index $R_1 = \sum ||F_o| - |F_c^*|| / \sum |F_o| = 0.50$. A three-dimensional electron density map, phased by the bromine atom, clearly revealed the positions of the other fourteen non-hydrogen atoms.

The structure was refined by full-matrix least-squares with the use of all observed reflections plus those unobserved reflections for which $|F_c^*| > F_{lim}$. The quantity minimized was $\sum w(|F_o| - |F_c^*|)^2$, where

$$F_c^* = KF_c \left\{ 1 + g \left[\frac{1 + \cos^4 2\theta}{(1 + \cos^2 2\theta) \sin 2\theta} \right] F_c^2 \right\}^{-1/2}$$

$$= KF_c / G,$$

in which K is the scale factor, g is the extinction parameter (Zachariasen, 1963; Larson, 1967), and F_c is the usual calculated structure factor. The weights were defined as

$$w = [\sigma^2(F_o) + (rF_o)^2 + s(F_c - F_c^*)^2]^{-1},$$

where r and s were chosen to make the averages of

$\sum w(F_o - F_c^*)^2$ constant for groups of increasing F_o values (Cruickshank, 1965).

Three cycles of refinement with isotropic temperature factors, $g = s = 0$, $r = 0.04$, and carbon scattering factors for all atoms except bromine and oxygen yielded $R_1 = 0.16$ and enabled us to identify the nitrogen atom by its low temperature factor. Then, two cycles with anisotropic temperature factors, $g = s = 0$, and $r = 0.04$ reduced R_1 to 0.046. A difference electron-density map clearly showed the seven hydrogen atoms, as well as a considerable negative region around the bromine atom due to the neglect of anomalous scattering effects. Refinement was resumed with isotropic temperature factors for the hydrogen atoms and both the real ($\Delta f' = -0.96$) and imaginary ($\Delta f'' = 1.46$) parts of the anomalous scattering factors applied to bromine. Two cycles in which the hydrogen parameters were not varied, $g = s = 0$, and $r = 0.04$ resulted in $R_1 = 0.034$.

Up to this point g had been held equal to zero but it was obvious that the largest structure factors were affected by extinction. The 26 largest structure amplitudes were used in four cycles of refinement in which only g was allowed to vary and $r = s = 0$. These were followed by three cycles in which only the scale factor and the hydrogen parameters were varied, $r = 0.02$, and $s = 0.01$. The refinement was concluded with two cycles in which all parameters except g were varied, $r = 0.02$, and $s = 0$. For the last cycle of refinement thirteen of the 164 parameters shifted more than 0.1σ and the maximum shift was 0.28σ . The final agreement indices for the 1464 observed reflections plus the 35 unobserved reflections with $|F_c^*| > F_{lim}$ are $R_1 = 0.028$ and $R_2 = (\sum w(|F_o| - |F_c^*|)^2 / \sum w F_o^2)^{1/2} = 0.039$. The standard deviation of an observation of unit weight is 1.40. Of the 35 re-

Table 2. Final atomic parameters with their estimated standard deviations (in parentheses)

Thermal parameters are defined by the expression:

$$T_i = \exp \left[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^{*}b^{*} + 2B_{13}hla^{*}c^{*} + 2B_{23}klb^{*}c^{*}) \right].$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
Br	0.48900 (3)	0.29935 (3)	0.34986 (3)	4.93 (2)	4.91 (2)	3.58 (2)	0.64 (1)	-1.24 (1)	1.13 (1)
O	0.38666 (16)	0.51661 (19)	0.25626 (16)	4.65 (10)	2.88 (9)	3.17 (9)	0.29 (8)	-1.44 (7)	-0.30 (7)
N	0.27296 (16)	0.64121 (19)	0.12728 (16)	3.32 (9)	2.21 (9)	2.35 (9)	-0.08 (7)	-0.09 (7)	-0.10 (7)
C(1)	0.37395 (22)	0.19715 (25)	0.18206 (23)	4.07 (13)	2.68 (12)	3.21 (12)	0.56 (10)	0.28 (10)	0.93 (9)
C(2)	0.39937 (21)	0.30270 (25)	0.23298 (21)	3.64 (12)	3.41 (13)	2.45 (11)	0.44 (10)	-0.08 (9)	0.73 (9)
C(3)	0.35931 (19)	0.41633 (24)	0.20063 (19)	3.18 (11)	2.72 (11)	2.28 (10)	0.05 (9)	0.08 (8)	0.18 (8)
C(4)	0.29136 (18)	0.42083 (22)	0.11552 (18)	2.88 (11)	2.14 (10)	2.09 (9)	-0.06 (8)	0.06 (8)	0.13 (8)
C(5)	0.27576 (19)	0.31389 (22)	0.05172 (19)	3.04 (11)	1.96 (10)	2.48 (10)	0.03 (8)	0.35 (9)	0.18 (8)
C(6)	0.31157 (22)	0.20016 (23)	0.09098 (22)	4.24 (13)	2.18 (11)	2.97 (11)	0.14 (9)	0.36 (10)	0.48 (8)
C(7)	0.28224 (26)	0.08774 (27)	0.04107 (25)	6.08 (18)	1.80 (11)	4.39 (14)	0.28 (11)	0.24 (12)	0.56 (10)
C(8)	0.22972 (18)	0.53257 (22)	0.10489 (17)	3.05 (10)	2.16 (9)	1.62 (8)	-0.03 (8)	0.07 (8)	-0.08 (7)
C(9)	0.12986 (18)	0.52464 (25)	0.08254 (19)	2.82 (10)	2.80 (11)	2.25 (10)	-0.16 (9)	0.32 (8)	-0.31 (8)
C(10)	0.07601 (21)	0.63089 (30)	0.07744 (21)	3.03 (12)	4.25 (15)	2.75 (11)	0.58 (10)	0.06 (9)	-0.49 (10)
C(11)	0.12149 (22)	0.74357 (29)	0.09556 (21)	4.19 (14)	3.05 (12)	2.86 (11)	1.21 (11)	-0.15 (10)	-0.41 (10)
C(12)	0.21898 (22)	0.74325 (25)	0.12257 (20)	4.33 (13)	2.08 (10)	2.53 (11)	0.16 (10)	-0.10 (9)	-0.22 (9)
H(1)	0.3651 (24)	0.5736 (32)	0.2212 (27)	1.71 (72)					
H(2)	0.4024 (24)	0.1183 (35)	0.2035 (26)	2.42 (73)					
H(3)	0.3062 (22)	0.0152 (31)	0.0705 (25)	1.83 (67)					
H(4)	0.1042 (21)	0.4409 (29)	0.0760 (23)	1.19 (59)					
H(5)	0.0086 (25)	0.6298 (33)	0.0612 (26)	2.47 (73)					
H(6)	0.0904 (22)	0.8154 (29)	0.0937 (25)	1.31 (64)					
H(7)	0.2544 (23)	0.8208 (27)	0.1342 (25)	1.37 (63)					

Table 3 (cont.)

1-13 56 74	10-8 85 60	4-3 478 481	11-0 112 130	4 0 567 580	2 5 178 175	***** 4-10 *****	***** 4-11 *****
4 0 209 201	10-10 524 46	4 5 326 324	11-8 56 55	0 2 205 287	2-5 158 157	0 0 688 708	0 1 256 256
4 2 588 410	11 2 456 410	4 9 438 417	12 2 908 117	0 2 614 3	2 7 103 108	0 2 261 265	0 1 118 127
-2 124 136	11-1 136 131	4 7 410 418	12-1 255 255	0 4 240 243	2 7 216 205	0 4 282 282	0 3 221 218
4-4 513 508	11 0 567 518	4 7 410 418	12-2 276 276	0 4 240 243	2 7 216 205	0 4 282 282	0 7 139 152
4-4 365 368	11-3 460 310	4 0 291 294	12-3 118 127	0 6 327 316	2-0 608 54	0 0 358 303	0 7 83 100
4-6 16 104	11-5 171 176	4 11 128 134	12-4 243 243	0 6 162 171	1 0 619 17	0 8 8	1 7 301 285
4 8 6 21	11 7 445 450	-4-11 190 373	12 5 74 74	0 8 186 186	5 2 1024 1021	1-1 310 374	1 2 112 121
4 10 508 18	11-9 256 251	5 2 402 401	13 0 91 90	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
-4-10 508 12	12 0 718 727	5 2 402 401	13-2 152 142	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
12 0 71 71	12 2 508 55	5 5 353 361	13-3 72 74	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
-4-12 240 243	12 4 228 234	5 6 356 358	***** 4-8 *****	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 1 813 851	12 4 228 234	5 6 293 296	0 0 112 123	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 1 817 903	12 4 167 175	5 8 383 389	0 2 179 173	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 3 79 78	12 6 89 92	5 8 272 301	0 4 326 324	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 5 811 808	12 6 107 104	5 10 323 313	0 8 618 74	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 5 863 853	13 1 389 377	5-10 323 313	0 8 526 509	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 7 836 841	13-1 100 103	5-12 183 182	0 8 618 74	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 7 684 53	13 3 125 100	6 1 609 32	0 10 357 351	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 8 501 505	13 5 246 236	6 0 473 474	0 11 400 481	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 9 430 409	13-5 140 128	6 3 488 488	1-1 627 635	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 11 482 482	14 0 83 40	6 5 468 462	1 3 639 43	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
5 11 167 147	14 2 88 53	6 5 304 315	1 3 309 312	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6 0 508 73	14 2 54 56	6 5 176 170	1 5 263 236	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6 2 95 88	14 4 514 56	6 7 182 170	1 7 104 157	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6 2 99 182	***** 4-7 *****	6 7 308 312	1 7 103 98	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6 4 348 346	0 1 792 766	6 9 401 416	1 7 88 82	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6 6 828 85	0 3 492 711	6 11 75 71	1 11 205 134	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6 8 156 140	0 5 159 161	7 0 160 189	1 11 246 256	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6 10 181 177	0 5 582 582	7 2 282 300	1 12 140 141	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6-10 808 50	0 5 516 516	7 2 182 180	1 12 207 206	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
6-12 75 76	0 11 574 14	7 2 618 9	1 13 219 217	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 1 75 102	1 2 563 667	7 6 83 86	1 13 257 265	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 3 138 138	1 2 563 667	7 6 83 86	1 14 224 241	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 3 521 507	1 4 336 330	7 8 58 57	1 14 257 265	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 5 528 528	1 4 336 330	7 8 58 57	1 15 276 276	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 5 613 607	1 6 176 170	7-10 74 67	1 15 276 276	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 7 89 89	1 6 455 455	8 1 118 108	1 16 288 288	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 7 103 103	0 287 276	8 1 511 515	1 16 312 312	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 7 89 89	1 6 455 455	8 3 380 382	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 11 883 868	1-10 225 216	8 5 293 292	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
7 11 112 126	1-12 152 153	8 7 190 115	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 0 316 327	2 1 108 319	8 7 475 457	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 2 237 240	2 1 108 319	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 2 108 115	2 1 817 838	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 2 215 212	2 1 817 838	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 6 135 130	2 5 162 169	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 8 638 627	2 7 427 430	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 8 258 253	2 7 427 430	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 8 167 176	2 7 427 430	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 10 323 320	2 9 318 324	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
8 10 98 123	2 9 318 324	8 9 440 450	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 1 873 870	2 11 110 102	8 9 308 308	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 1 246 244	2-11 116 111	9 8 76 92	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 3 80 56	1 0 111 94	9 8 76 92	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 3 768 782	1 2 621 621	10 1 588 10	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 5 430 429	1 2 503 503	10 1 588 10	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 5 326 320	1 4 326 326	10 3 312 307	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 7 216 217	1 4 326 326	10 3 312 307	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 7 167 154	1 6 237 234	10 5 386 359	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 8 178 208	1 6 237 234	10 5 386 359	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9 8 261 264	1 8 326 327	10 7 72 78	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
9-11 88 92	3 8 167 169	10 7 138 141	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 0 163 158	1 9 178 181	10 7 138 141	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 2 160 156	3-10 109 129	11 0 107 140	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 2 203 198	1 12 267 263	11 0 107 140	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 4 838 859	3-12 278 279	11 0 233 237	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 4 604 599	1 12 267 263	11 0 233 237	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 6 608 598	4 1 718 706	11 4 142 146	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 6 18 89	4 7 906 981	11 6 538 14	1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105
10 8 85 83			1 17 336 336	1 1 385 385	1 4 176 176	1 7 357 356	2 1 108 105

Description and discussion of the structure

Fig. 1 shows the atomic labeling and the interatomic distances and angles, uncorrected for thermal motion. Estimated standard deviations for the distances and angles were calculated from the coordinate standard deviations obtained in the least-squares process. The e.s.d.'s are less than 0.005 Å for heavy-atom separations [except 0.007 Å for C(5)-C(5') and C(7)-C(7')] and 0.04 Å for distances involving hydrogen atoms. The e.s.d.'s for the angles (Darlow, 1960) are 0.3° for heavy-heavy-heavy, 2° for hydrogen-heavy-heavy, and 4° for heavy-hydrogen-heavy.

Figs. 2 and 3, stereoscopic views (Johnson, 1965) perpendicular and parallel, respectively, to the molecular symmetry axis, show the molecular geometry of

this overcrowded molecule. The distortion is distributed over the entire framework of the molecule such that the trigonal symmetry of the bonds about any particular carbon atom is not greatly disturbed. No major segment of the molecule is truly planar, yet all rings are approximately planar. The equations of least-squares planes for various parts of the molecule and the deviations of the atoms from these planes are given in Table 4. The largest atomic displacements from the mean plane of the phenanthrene moiety (*A*, Table 4) are 0.34 and 0.17 Å. When one considers the individual rings of the phenanthrene part, one finds the central ring (*B*, Table 4) is planar to 0.07 Å and the outer rings (*C*, Table 4) are planar to 0.10 Å. The angles between the plane normals are 9° for the central and outer rings and 18° for the two outer rings. Fig. 4(a), a view along

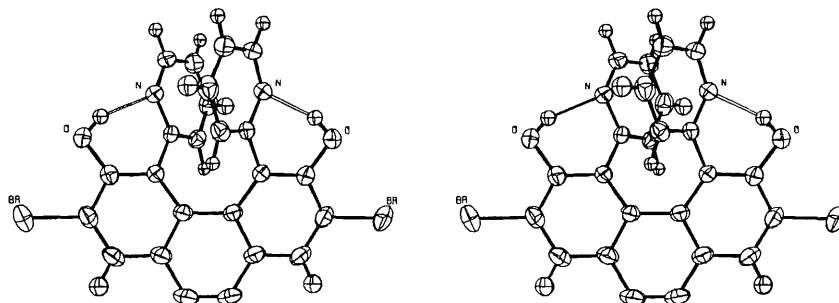


Fig. 2. Stereoscopic view of the molecule showing the 50% probability thermal ellipsoids.

the C(5)–C(5') bond, shows the approximately 20° deviation from planarity about this bond.

The most planar section of the molecule is the pyridyl group (*D*, Table 4) with a maximum atomic displacement from the plane of 0.025 Å. However, the displacements are systematic and the pyridyl group is slightly bent at C(8) and C(11) into two planes (*E*, *F*, Table 4) whose normals make an angle of 3.3°. As is evident from Fig. 3 the pyridyl group and the end ring of the

phenanthrene are far from coplanar. The normals to these two planes (*D*, *B*, Table 4) make an angle of 43° with each other. This is composed of a 40° rotation of the pyridyl group about the C(4)–C(8) bond and a 17° bend of the C(4)–C(8) bond out of the plane of the end ring. The distribution of bonds about the C(4)–C(8) bond is shown in Fig. 4(b).

Skancke (1965) has published a semi-empirical molecular orbital study of phenanthrene within the Pariser–

Table 4. Equations of least-squares planes and distances (Å) of atoms from these planes

X, *Y* and *Z* are expressed in Å units relative to the Cartesian axial system defined by the *a*, *b* and *c** axes. The planes were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) as modified by Blow (1960).

Plane <i>A</i>	0.8650 <i>X</i>	–0.5018 <i>Z</i>	=	2.9970		
<i>B</i>	0.8194 <i>X</i> +0.1540 <i>Y</i>	–0.5521 <i>Z</i>	=	3.1788		
<i>C</i>	0.8437 <i>X</i>	–0.5368 <i>Z</i>	=	2.9234		
<i>D</i>	0.2273 <i>X</i> +0.0961 <i>Y</i>	–0.9691 <i>Z</i>	=	–0.0764		
<i>E</i>	0.2041 <i>X</i> +0.0804 <i>Y</i>	–0.9757 <i>Z</i>	=	–0.2251		
<i>F</i>	0.2512 <i>X</i> +0.1135 <i>Y</i>	–0.9613 <i>Z</i>	=	0.1337		

Plane <i>A</i>		Plane <i>B</i>		Plane <i>C</i>	
C(1)	–0.166	C(1')	0.166	C(1)	0.033
C(2)	–0.101	C(2')	0.101	C(2)	–0.033
C(3)	0.145	C(3')	–0.145	C(3)	–0.022
C(4)	0.342	C(4')	–0.342	C(4)	0.073
C(5)	0.066	C(5')	–0.066	C(5)	–0.072
C(6)	–0.078	C(6')	0.078	C(6)	0.020
C(7)	–0.089	C(7')	0.089	*C(5')	–0.300
*Br	–0.328			*C(7)	0.149
*O	0.220			*C(8)	0.503
*C(8)	1.004			*O	–0.063
*H(2)	–0.351			*Br	–0.126
*H(3)	–0.163			*H(2)	0.010

Plane <i>D</i>		Plane <i>E</i>		Plane <i>F</i>	
N	0.010	*C(4)	0.033	N	–0.001
C(8)	–0.025	*C(5)	–0.616	C(8)	0.001
C(9)	0.015	*H(4)	0.100	C(10)	–0.001
C(10)	0.008	*H(5)	0.015	C(11)	0.001
C(11)	–0.023	*H(6)	–0.023	*C(9)	0.076
C(12)	0.014	*H(7)	–0.032	*C(10)	0.068
*C(3)	0.905			*C(4)	0.058

* Not included in the calculation of the plane.

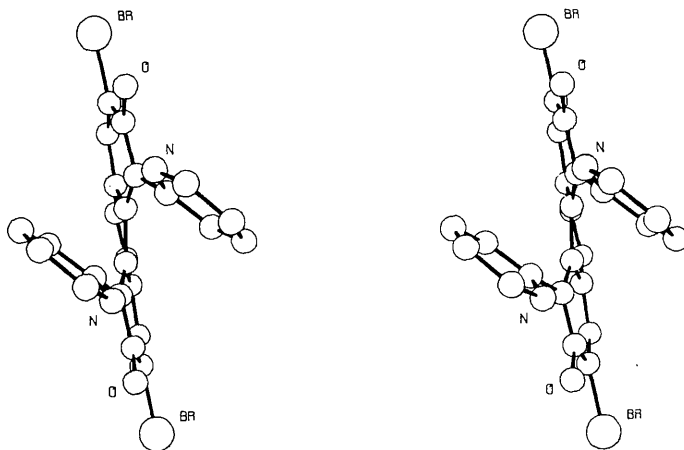


Fig. 3. Stereoscopic view of the molecule along the twofold symmetry axis.

Parr-Pople approximation. Table 5 is a comparison of the phenanthrene bond lengths observed in our structure with the distances calculated by Skancke and with those observed by Trotter (1963) in the structure determination of phenanthrene itself. The agreement of our distances with the predicted values is better than 0.03 Å for all bonds, but the differences are systematic in the

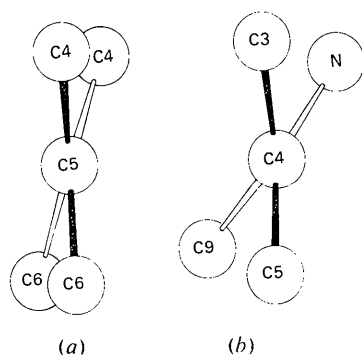


Fig. 4. Newman diagrams looking along the C(5)-C(5') and C(4)-C(8) bonds.

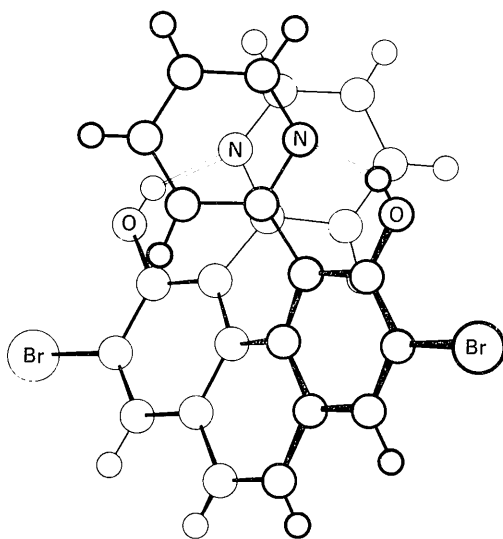


Fig. 5. Projection of the molecule normal to one of the pyridyl rings.

direction expected from the overcrowding. The bonds in the portion of the molecule overcrowded by bulky substituents, especially C(5)-C(5'), are lengthened and the bonds in the uncrowded portion of the molecule, especially C(7)-C(7'), are shortened from Skancke's calculated values. The C(5)-C(5') bond (1.471 Å) is close to the 1.488 Å expected for a formal sp^2-sp^2 single bond and the C(7)-C(7') bond (1.339 Å) is equivalent to the value 1.338 Å expected for a double bond (Dewar & Schmeising, 1960). The overcrowding and consequent distortion has apparently considerably altered the conjugation of the central ring of the phenanthrene moiety.

The C-O separation (1.346 Å) compares well with the value 1.34 Å tabulated by Lide (1962), who concluded that delocalization contributes significantly to the shortening of aromatic C-O single bonds compared with aliphatic C-O bonds. The C-Br bond (1.888 Å) compares favourably with the average distance of 1.891 Å found recently in 2,4,6-tribromoaniline (Christensen & Strømme, 1969). This is 0.05 Å shorter than the bond lengths found in aliphatic bromides (Sutton, 1965) and can be accounted for by the difference in radius between tetrahedral and trigonal carbon atoms. Thus the bromine atom does not appreciably enter into conjugation with the aromatic system, in agreement with the findings of Bersohn (1954). Likewise the C(4)-C(8) bond (1.486 Å) is a normal single bond (Dewar & Schmeising, 1960), indicating that the pyridyl group also does not enter into conjugation appreciably with the phenanthrene. In the pyridyl ring average values of the distances C-C and C-N and the angles C-N-C, N-C-C, and C-C-C are 1.383, 1.342 Å, 118.6, 122.4 and 118.8° respectively. These agree very well with the values 1.388, 1.342 Å, 118.9, 122.1, and 118.9° found for 1,2-di-2-pyridylethenediol-1,2 (Ashida, Hirokawa & Okaya, 1965) and 1.383, 1.346 Å, 117.0, 123.5, and 118.7° for 2-(2',4'-dinitrobenzyl)pyridine (Seff & Trueblood, 1968). Systematic variations of as much as 0.025 Å in the pyridyl C-C distances and in the pyridyl angles are also remarkably alike in the three compounds. The pyridyl ring is bonded to the hydroxyl group by a strong intramolecular O-H...N hydrogen bond with dimensions very similar to the O-H...N hydrogen bond found in 1,2-di-2-pyridylethenediol-1,2 (Ashida, Hirokawa & Okaya, 1965).

Table 5. Comparison of phenanthrene bond lengths (Å)

Bond		Skancke	This work		Trotter
			Obs.	$10^3 \Delta$	
C(1)-C(2)	E-F	1.376	1.357	-19	1.381
C(2)-C(3)	D-E	1.400	1.406	6	1.398
C(3)-C(4)	C-D	1.380	1.398	18	1.383
C(4)-C(5)	B-C	1.421	1.433	12	1.405
C(5)-C(6)	B-G	1.404	1.413	9	1.404
C(6)-C(1)	F-G	1.428	1.411	-17	1.457
C(6)-C(7)	G-H	1.431	1.427	-4	1.390
C(5)-C(5')	A-B	1.443	1.471	28	1.448
C(7)-C(7')	H-I	1.372	1.339	-23	1.372
Av. σ			0.004		0.014

The six C-H distances average 0.95 Å and O-H is 0.81 Å, both more than 0.1 Å shorter than accepted values but both agreeing with typical X-ray results.

Fig. 5 shows that the pyridyl rings are partially shifted past each other. The closest contact between the rings, C(8)···C(8'), is extremely short at 2.807 Å. The two pyridyl rings are not parallel but are inclined 11° to each other so the other contacts such as C(12)···C(12') (3.340 Å) are more usual.

The molecular geometry in our compound is strikingly similar to that found in 3,4,5,6-dibenzophenanthrene, whose approximate structure has been determined (McIntosh, Robertson & Vand, 1954). The two compounds contain a similar combination of fused rings and overlapping atoms and exhibit very nearly the same molecular distortions. These distortions are in accord with the conclusions of Coulson & Senent (1955) and of Ferguson & Robertson (1963), who said that relief from overcrowding is usually obtained by distortions that are well spaced over the rigid framework of the molecule and that it is relatively easy to build up large displacements in these molecules by a series of quite small distortions at each carbon atom.

The molecular packing in the crystal is shown schematically in Fig. 6. There are no unusually short intermolecular contacts.

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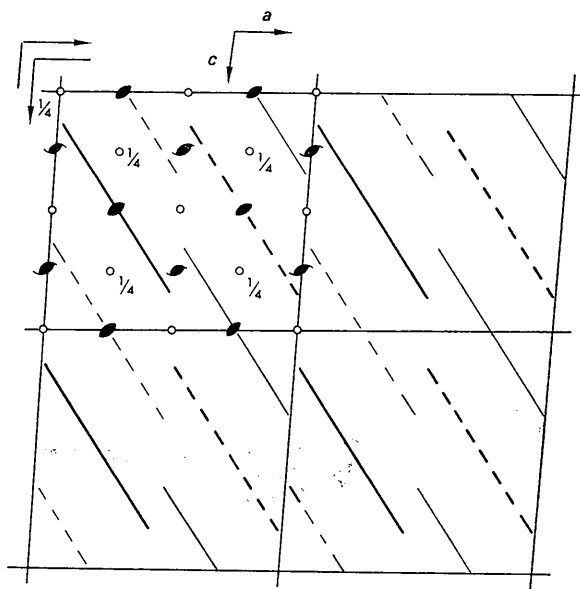


Fig. 6. [010] view of four unit-cells schematically showing the packing of the molecules. The lines represent intramolecular Br-Br vectors. Molecules with pyridyl groups oriented up or down are represented by solid or dashed lines respectively. The thick lines represent molecules located with $0 < y < 1$, the thin lines those with $-\frac{1}{2} < y < \frac{1}{2}$.