Conformation of Condensed Polycyclic Aromatic Hydrocarbons. II. The Molecular and Crystal Structure of Violanthrene B (Dibenzo[*a*, *rst*]naphtho[8,1,2-*cde*]pentaphene)[1]

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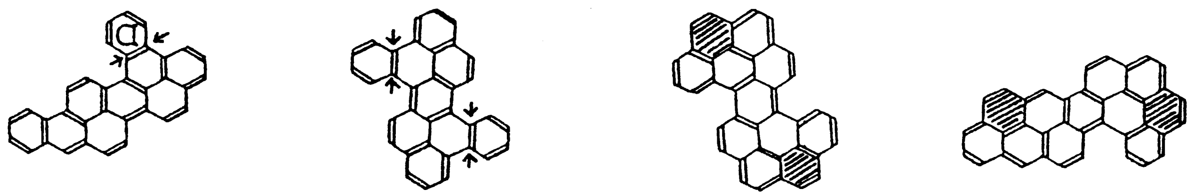
(Received April 7, 1985)

The title compound, $C_{34}H_{18}$, has been obtained by reducing violanthrone B, a byproduct in the synthesis of violanthrone. Its structure has been determined by on X-ray analysis. The space group is $P2_1/c$, with unit-cell dimensions a=25.78(1), b=3.807(5), c=19.975(8) Å, β=96.55(3)°, and Z=4. The structure was solved by the direct method and refined by a block-diagonal least-squares method to an R value of 0.076 on the basis of 1242 independent reflections. The molecules are largely distorted from a planar structure owing to a steric repulsion between the intramolecular overcrowded hydrogen atoms. Also, they are stacked face-to-face to form a column structure along the b-axis.

The title hydrocarbon, violanthrene B, was obtained by reducing violanthrone B, a byproduct in the synthesis of violanthrone. Although its structure has been assumed to be I, a confirmation by X-ray analysis is still necessary to elucidate the reaction mechanism.[2–7] Futhermore, it is very interesting to examine the molecular deformations of such overcrowded hydrocarbons as I to IV, which have very short H···H contacts. The structure of II,[8] III,[9] and IV[10] have already been reported.



I II*1) III*2) IV*3)

*1) Tetrabenzo[*a,cd,j,lm*]perylene (TBP)
*2) Diphenanthro[5,4,3-*abcd* : 5′,4′,3′-*jklm*]perylene (DPP)
*3) Anthra[2,1,9,8-*hijkl*]benzo[*de*]naphtho[2,1,8,7-*stuv*]pentacene (1,11-BisoVEB)

Scheme

Experimental

The title compound was prepared by a previously reported conventional method.[11] The crystals used for X-ray work were grown from an *o*-dichlorobenzene solution. Crystal data are as follows: $C_{34}H_{18}$; M.W. 426.5; monoclinic; a=25.78(1), b=3.807(5), c=19.975(8) Å, β=96.55(3)°, and U=1948(3) Å^3; D_x=1.455 g cm^{-3}; Z=4; space group $P2_1/c$; μ(Cu $K\alpha$)=6.44 cm^{-1}. The intensity data were collected on a Rigaku automated four-circle diffractometer with the $\omega/2\theta$ scan technique, the scanning rate being 2°(2θ) min^{-1}. The dimensions of the crystal used for the data collection were 0.05×0.2×0.5 mm. A total of 2984 independent reflections were measured up to 2θ=125°, using graphite monochromated Cu $K\alpha$ radiation, of which 1242 reflections were ($|F_o|>3\sigma(|F_o|)$). Corrections for Lorentz and polarization factors were made, but not for absorption.

Structure Determination

Systematic absences of $h0l$, $l=2n+1$, and $0k0$, $k=2n+1$ indicated the space group to be $P2_1/c$. The structure was solved by a direct method using the MULTAN 78 program.[12] Two disordered molecules with equal occupancies appeared on E-maps as shown in Fig. 1. The disordered structure was refined to R=0.162 by full-matrix least-squares with the SHELX 76 program,[13] but a further refinement based on this model was impossible. A new ordered model with a space group of Pc was constructed from the $P2_1/c$ structure by removing the crystallographic center of symmetry. The refinement was carried out by least-squares. The R value converged to 0.16. Another ordered model ($P2_1/c$) was constructed by

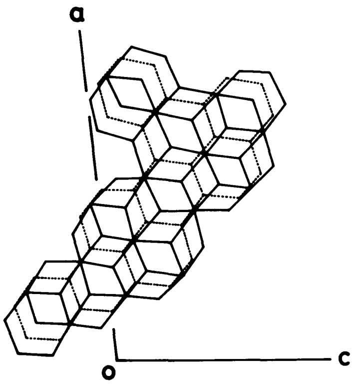


Fig. 1. The false disorderd structure (solid lines) found on the E-map and the true ordered one (dotted lines).

Table 1 Final Atomic Coordinates with Their Estimated Standard Deviations, Multiplied by 10^4 and 10 for B_{eq}

Atom	x	y	z	$B_{eq}/Å^{2}$ [a]
C(1)	1241(3)	2138(27)	−1452(5)	34(3)
C(2)	800(4)	2115(31)	−1900(5)	40(3)
C(3)	323(4)	849(29)	−1731(5)	43(3)
C(4)	291(4)	−558(29)	−1099(5)	42(3)
C(5)	746(4)	−517(27)	−613(5)	37(3)
C(6)	719(3)	−1932(29)	43(5)	39(3)
C(7)	1150(4)	−1843(26)	523(5)	34(3)
C(8)	1117(4)	−3256(28)	1205(5)	38(3)
C(9)	1540(4)	−3209(28)	1671(5)	38(3)
C(10)	2036(3)	−1904(26)	1537(5)	33(3)
C(11)	2474(3)	−1644(27)	2020(5)	33(3)
C(12)	2422(4)	−2480(29)	2739(5)	40(3)
C(13)	2838(4)	−1973(30)	3211(5)	38(3)
C(14)	3318(4)	−696(28)	3062(5)	38(3)
C(15)	3725(4)	12(32)	3570(5)	44(3)
C(16)	4183(4)	1410(35)	3408(5)	49(3)
C(17)	4275(4)	2043(32)	2732(5)	41(3)
C(18)	3878(3)	1253(29)	2218(5)	37(3)
C(19)	3977(3)	1447(27)	1499(5)	34(3)
C(20)	4474(4)	2186(33)	1328(5)	42(3)
C(21)	4586(4)	1827(32)	665(5)	43(3)
C(22)	4190(4)	617(30)	188(5)	39(3)
C(23)	3689(3)	41(30)	337(4)	35(3)
C(24)	3556(3)	700(25)	998(5)	30(3)
C(25)	3031(3)	176(26)	1166(5)	33(3)
C(26)	2578(3)	444(24)	699(5)	30(2)
C(27)	2592(3)	2116(26)	38(4)	32(3)
C(28)	2167(3)	2199(27)	−412(4)	32(3)
C(29)	1684(3)	778(24)	−288(5)	30(3)
C(30)	1227(3)	729(26)	−786(5)	31(3)
C(31)	1642(3)	−621(24)	366(5)	29(3)
C(32)	2089(3)	−671(23)	860(5)	27(2)
C(33)	2964(3)	−570(26)	1854(4)	30(3)
C(34)	3398(4)	−29(27)	2371(5)	33(3)

a) The equivalent isotropic temperature factors were computed using the following expression: $B_{eq}=1/3 \sum_{i,j} a_i a_j a_i^* a_j^*$.

averaging two positions of the corresponding atoms of the disordered molecules as shown with dotted lines in Fig. 1; however, no peaks were found at the atomic positions. This model ($P2_1/c$) coincides to the Pc model if a slight difference between two crystallographically independent molecules is neglected and the origin in the Pc model is shifted so that the molecules are related by a center of symmetry. Six cycles of refinement on this model brought the value of R to 0.076, where the thermal parameters for the carbon atoms were assumed to be anisotropic and the unit weight was applied to F_o. No peaks higher than 0.3 eÅ^{-3} were found on the final defference map. The final R was 0.076 with a maximum Δ/δ of 0.5. The atomic-scattering factors were taken from the International Tables for X-ray Crystallography.[14] The final atomic parameters and their estimated standard deviations are listed in Table 1. Lists of the observed and calculated structure factors, parameters of the hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms are kept in the office of the Chemical Society (Document No. 8632). Computations were performed on the M-280H computer at the Computer Center of the University of Tokyo.

Results and Discussion

The present study has established the structure of I. Figure 2 illustrates the crystal structure viewed along the b axis. The numbering scheme is indicated in Fig. 3, together with the deviations of the atoms from the mean plane of the molecule. The bond lengths and angles are listed in Tables 2 and 3, respectively. The mean bond length of the outer bonds is slightly shorter than that of the inner lengths and the three bonds around each carbon atom are nearly coplanar. These facts have also been found for some polycyclic

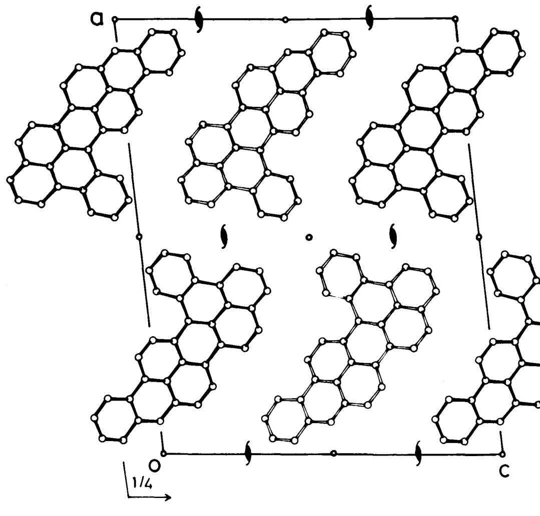


Fig. 2. A projection of the crystal structure along the b axis.

aromatic hydrocarbons.[8,9,10] Figure 4 shows a perspective drawing of the molecule. This molecule is greatly distorted from a planar conformation because of the repulsion betwen the crowded hydrogen atoms, known as an 1,7 interaction. The steric repulsion between H(23) and H(27) is mainly released by the enlargement of the C(24)–C(25)–C(26) angle and the twisting of the C(23)–C(24) and C(27)–C(26) bonds around the line C(24)···C(26) as defined in ref. 10. The angle of C(24)–C(25)–C(26) (α), the twisting angle of C(23)–C(24)···C(27)–C(26) (β) and the nonbonded C···C distances (C(24)···C(26))

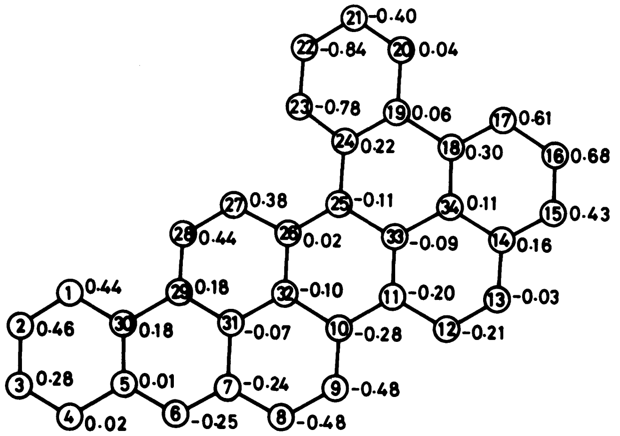


Fig. 3. The numbering scheme and displacements (l/Å) of atoms from the mean plane.

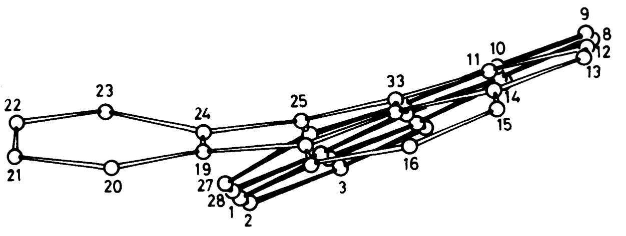


Fig. 4. A perspective drawing of the molecule.

Table 2. Bond Lengths (l/Å) with Their Estimated Standard Deviations

C(1)–C(2)	1.37(2)	C(16)–C(17)	1.42(2)
C(1)–C(30)	1.44(1)	C(17)–C(18)	1.40(2)
C(2)–C(3)	1.40(2)	C(18)–C(19)	1.48(2)
C(3)–C(4)	1.38(2)	C(18)–C(34)	1.39(2)
C(4)–C(5)	1.44(2)	C(19)–C(20)	1.39(2)
C(5)–C(6)	1.43(2)	C(19)–C(24)	1.42(1)
C(5)–C(30)	1.40(1)	C(20)–C(21)	1.39(2)
C(6)–C(7)	1.39(2)	C(21)–C(22)	1.40(2)
C(7)–C(8)	1.48(1)	C(22)–C(23)	1.37(2)
C(7)–C(31)	1.42(1)	C(23)–C(24)	1.42(2)
C(8)–C(9)	1.36(2)	C(24)–C(25)	1.44(1)
C(9)–C(10)	1.42(1)	C(25)–C(26)	1.42(1)
C(10)–C(11)	1.41(1)	C(25)–C(33)	1.43(1)
C(10)–C(32)	1.45(1)	C(26)–C(27)	1.47(1)
C(11)–C(12)	1.49(2)	C(26)–C(32)	1.40(1)
C(11)–C(33)	1.40(1)	C(27)–C(28)	1.34(1)
C(12)–C(13)	1.37(2)	C(28)–C(29)	1.40(1)
C(13)–C(14)	1.39(2)	C(29)–C(30)	1.46(1)
C(14)–C(15)	1.41(2)	C(29)–C(31)	1.43(1)
C(14)–C(34)	1.44(2)	C(31)–C(32)	1.43(1)
C(15)–C(16)	1.37(2)	C(33)–C(34)	1.45(1)

Table 3. Bond Angles (ϕ/°) with Their Estimated Standard Deviations

C(2)–C(1)–C(30)	120(1)	C(19)–C(20)–C(21)	121(1)
C(1)–C(2)–C(3)	122(1)	C(20)–C(21)–C(22)	118(1)
C(2)–C(3)–C(4)	120(1)	C(21)–C(22)–C(23)	122(1)
C(3)–C(4)–C(5)	119(1)	C(22)–C(23)–C(24)	120(1)
C(4)–C(5)–C(6)	119(1)	C(23)–C(24)–C(25)	122(1)
C(4)–C(5)–C(30)	121(1)	C(23)–C(24)–C(19)	116(1)
C(6)–C(5)–C(30)	120(1)	C(25)–C(24)–C(19)	122(1)
C(5)–C(6)–C(7)	120(1)	C(24)–C(25)–C(26)	124(1)
C(6)–C(7)–C(8)	120(1)	C(24)–C(25)–C(33)	118(1)
C(6)–C(7)–C(31)	122(1)	C(26)–C(25)–C(33)	118(1)
C(8)–C(7)–C(31)	118(1)	C(25)–C(26)–C(27)	121(1)
C(7)–C(8)–C(9)	120(1)	C(25)–C(26)–C(32)	121(1)
C(8)–C(9)–C(10)	123(1)	C(27)–C(26)–C(32)	117(1)
C(9)–C(10)–C(11)	124(1)	C(26)–C(27)–C(28)	121(1)
C(9)–C(10)–C(32)	119(1)	C(27)–C(28)–C(29)	123(1)
C(11)–C(10)–C(32)	117(1)	C(28)–C(29)–C(30)	123(1)
C(10)–C(11)–C(12)	119(1)	C(28)–C(29)–C(31)	118(1)
C(10)–C(11)–C(33)	122(1)	C(30)–C(29)–C(31)	119(1)
C(12)–C(11)–C(33)	119(1)	C(29)–C(30)–C(1)	121(1)
C(11)–C(12)–C(13)	119(1)	C(29)–C(30)–C(5)	120(1)
C(12)–C(13)–C(14)	123(1)	C(1)–C(30)–C(5)	118(1)
C(13)–C(14)–C(15)	121(1)	C(7)–C(31)–C(29)	119(1)
C(13)–C(14)–C(34)	120(1)	C(7)–C(31)–C(32)	121(1)
C(15)–C(14)–C(34)	119(1)	C(29)–C(31)–C(32)	120(1)
C(14)–C(15)–C(16)	120(1)	C(10)–C(32)–C(26)	120(1)
C(15)–C(16)–C(17)	122(1)	C(10)–C(32)–C(31)	119(1)
C(16)–C(17)–C(18)	118(1)	C(26)–C(32)–C(31)	121(1)
C(17)–C(18)–C(19)	120(1)	C(11)–C(33)–C(25)	120(1)
C(17)–C(18)–C(34)	120(1)	C(11)–C(33)–C(34)	121(1)
C(19)–C(18)–C(34)	119(1)	C(25)–C(33)–C(34)	119(1)
C(18)–C(19)–C(20)	121(1)	C(14)–C(34)–C(18)	120(1)
C(18)–C(19)–C(24)	118(1)	C(14)–C(34)–C(33)	118(1)
C(20)–C(19)–C(24)	121(1)	C(18)–C(34)–C(33)	122(1)

Table 4. Comparison of Steric Hindrance

Molecule		α/°	β/°	d(C···C)/Å
1. Benz[c]phenanthrene[15) (BPT)		124.6	31.4	3.03
2. VEB (This molecule)		124	37.3	2.93
3. 1,11-BisoVEB[a)]	A)	128.7	30.1	2.94
	B)	120.9	37.6	2.96
4. TBP	1	123.5	41.0	2.971
	2	122.7	41.5	2.944
5. DPP[a,b)]	A)	119	39	3.01
	B)	121	30	2.87

a) A and B indicate the crystallographically independent molecules. b) A and B molecules occupy the same site in a ratio of 2:1.

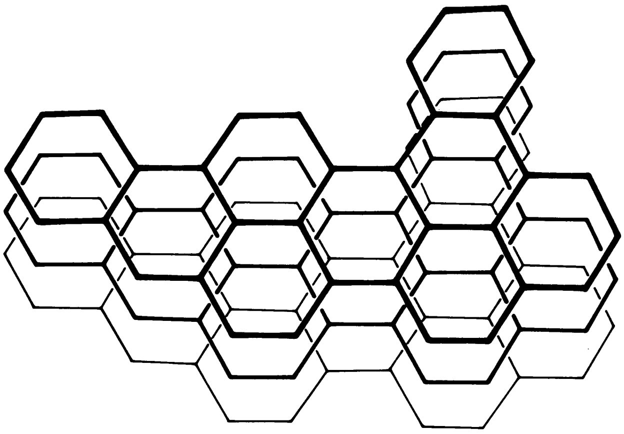


Fig. 5. Overlapping mode of the molecules.

are listed together with those of several related molecules in Table 4. Similar values were observed for the nonbonded C···C distances of the molecules. Although α in VEB is similar to that of the BPT, β resembles that of B molecules of 1,11-BisoVEB. In BPT, the expansions of the two C–C–C angles neighbouring the referred C–C–C angle also, somewhat, contributes to the relief of such a repulsion. Their angles are both 124° in BPT, whereas they are 121 and 122° in VEB. The twisting of C(23)–C(24) against the mean plane of the molecule is larger than that of C(26)–C(27) since terminal rings with C(23)–C(24) are easily bent at the bond of C(19)–C(24). The ring makes an angle of 21° to the mean molecular plane. Such bent rings are found in TBP(II),[8] where two benzene rings are bent at the bonds indicated by arrows in the scheme. On the other hand, additional (shaded) benzene rings prevent such bending in the cases of DPP (III) and 1,11-BisoVEB(IV).[9,10] The molecules are stacked face-to-face to make column structures along the *b*-axis. Figure 5 shows the overlapping mode of the molecules. The interplanar spacing (3.69 Å) is larger than the usual value. There is no unusual short contact between the molecules.

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