

Refined Molecular Structure of Tetrabenzo[de,hi,op,st]pentacene

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Abstract. C₃₄H₁₈, $M_r = 426.48$, monoclinic, $P2_1$, $a = 11.814$ (5), $b = 7.803$ (1), $c = 10.871$ (4) Å, $\beta = 91.41$ (4)°, $V = 1001.9$ (6) Å³, $Z = 2$, $D_x = 1.411$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.075$ mm⁻¹, $F(000) = 444$, $T = 290$ K, $R = 0.051$ for 1907 observed independent reflections. The molecule takes a skewed roof structure owing to the presence of two fjord-like overcrowding sites, which causes the distortion to a boat form in the center ring.

Introduction. The nonacyclic condensed aromatic hydrocarbon tetrabenzo[de,hi,op,st]pentacene (TBPA) consists of two perylene molecules sharing one benzene ring. It includes two fjord-like overcrowding sites in symmetry-related positions. TBPA has a lower ionization potential than other nonacyclic aromatics owing to its unusual electronic structure (Sato, Inokuchi, Seki, Aoki & Iwashima, 1982), and reacts with singlet O₂ to form an O₂ adduct, which reproduces TBPA by UV photolysis and/or thermal decomposition (Inokuchi, 1985). The crystal structure of TBPA reported by Rossmann (1959) was not reliable owing to the poor quality of the X-ray data ($R = 0.19$, large temperature factors and limited numbers of reflections). The present paper reports a refined crystal structure of TBPA; this study was carried out to elucidate the electronic character and reactivity of TBPA in relation to its characteristic molecular structure.

Experimental. The title compound was prepared by the literature method (Clar, Kelly & Wright, 1954). The sample contains impurities which could not be removed by recrystallization or vacuum sublimation methods. Separation of TBPA and a by-product from the crude products was successfully performed by gel-permeation chromatography (JAI LC-908). The structure of the by-product was confirmed by X-ray crystal analysis to be benzo[7,8]fluoreno[1,9-ab]perylene (BFP), which is an isomer of TBPA. The

X-ray crystal analysis of BFP will be reported elsewhere. The large temperature factor (7.0 Å²) in the earlier work of Rossmann (1959) is presumably ascribable to contamination by this isomer. The sample for X-ray analysis was obtained by slow evaporation from CHCl₃ solution; deep-blue colored crystal with dimensions 0.7 × 0.5 × 0.1 mm. Data collection: Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation; cell parameters refined with 20 reflections ($20 < 2\theta < 25^\circ$), systematic absence of $0k0$ for $k = 2n$, ω - 2θ scan, $-16 < h < 16$, $0 < k < 11$, $0 < l < 15$, scan speed 4° min⁻¹. Three standard reflections (04 $\bar{1}$, 34 $\bar{2}$ and $\bar{1}4\bar{1}$) showed no significant variations throughout the data collection; 2491 reflections ($4 < 2\theta < 55^\circ$) measured, 1907 independent reflections [$F_o > 3\sigma(F_o)$] were used for analysis ($R_{\text{int}} = 0.029$). Data corrected for Lorentz and polarization effects, no absorption correction applied ($\mu r < 1$). Structure solved by direct methods using SAPI85 (Fan, Qian, Yao, Zheng & Hao, 1988), full-matrix least-squares refinement (on F), scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV), all the H atoms were located on a difference Fourier map. Final refinement with anisotropic thermal factors for C atoms and with isotropic thermal factors for H atoms; 378 parameters; $R = 0.051$ and $wR = 0.045$; $w = 1/(a|F_o|^2 + b|F_o| + c)$, $a = 0.0024$, $b = -0.062$, $c = 0.447$; $S = 0.55$; maximum and minimum heights in the final difference Fourier syntheses 0.29, -0.32 e Å⁻³; maximum shift/e.s.d. = 0.23 [z of C(13)]. Calculations carried out on a FACOM A-70 computer with UNICSIII (Sakurai & Kobayashi, 1979).

Discussion. Fractional coordinates with equivalent isotropic thermal parameters of the C atoms are given in Table 1. § An ORTEP (Johnson, 1965)

§ Lists of structure factors, anisotropic thermal parameters, bond lengths and angles involving H atoms, and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54742 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0534]

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Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}
C(1)	7488 (3)	3962	12859 (3)	3.8 (4)
C(2)	8161 (4)	4100 (8)	13935 (4)	4.6 (4)
C(3)	9170 (4)	3300 (8)	14031 (4)	4.8 (4)
C(4)	10694 (4)	1628 (8)	13065 (5)	4.9 (4)
C(5)	11106 (4)	856 (8)	12065 (5)	4.8 (4)
C(6)	10485 (3)	818 (8)	10961 (4)	4.3 (4)
C(7)	9226 (4)	1041 (8)	8610 (4)	4.3 (4)
C(8)	8605 (4)	1082 (8)	7510 (4)	4.5 (4)
C(9)	7523 (4)	1687 (8)	7457 (4)	3.9 (4)
C(10)	5795 (4)	4072 (8)	6365 (3)	4.1 (4)
C(11)	5197 (5)	4541 (9)	5292 (4)	5.3 (4)
C(12)	4065 (4)	4379 (8)	5226 (4)	5.4 (4)
C(13)	2256 (4)	3775 (8)	6244 (5)	5.2 (4)
C(14)	1695 (4)	3367 (8)	7259 (5)	5.0 (4)
C(15)	2277 (4)	3091 (8)	8372 (4)	4.3 (4)
C(16)	3540 (3)	3027 (8)	10732 (4)	3.9 (4)
C(17)	4137 (3)	2804 (8)	11845 (4)	4.0 (4)
C(18)	5270 (3)	2684 (7)	11869 (4)	3.6 (4)
C(19)	9615 (3)	2391 (7)	13026 (4)	3.9 (4)
C(20)	9415 (3)	1527 (7)	10861 (4)	3.5 (4)
C(21)	8772 (3)	1576 (7)	9688 (4)	3.5 (4)
C(22)	6999 (3)	2290 (7)	8526 (4)	3.4 (4)
C(23)	5865 (3)	2892 (7)	8510 (3)	3.1 (4)
C(24)	5253 (3)	3458 (7)	7382 (3)	3.4 (4)
C(25)	3441 (4)	3863 (7)	6250 (4)	4.2 (4)
C(26)	3445 (3)	3165 (7)	8461 (3)	3.3 (4)
C(27)	4077 (3)	3040 (7)	9635 (3)	3.3 (4)
C(28)	5908 (3)	2790 (7)	10779 (3)	3.0 (4)
C(29)	7104 (3)	2675 (7)	10779 (3)	3.1 (4)
C(30)	7828 (3)	2978 (7)	11888 (3)	3.2 (4)
C(31)	8945 (3)	2282 (7)	11924 (4)	3.3 (4)
C(32)	7623 (3)	2196 (7)	9677 (3)	2.9 (4)
C(33)	4050 (3)	3463 (7)	7369 (3)	3.5 (4)
C(34)	5292 (3)	2921 (7)	9626 (3)	3.0 (4)

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

C(1)—C(2)	1.402 (8)	C(16)—C(27)	1.364 (8)
C(1)—C(30)	1.374 (7)	C(17)—C(18)	1.341 (8)
C(2)—C(3)	1.348 (9)	C(18)—C(28)	1.423 (8)
C(3)—C(19)	1.414 (9)	C(19)—C(31)	1.422 (8)
C(4)—C(5)	1.345 (9)	C(20)—C(21)	1.469 (8)
C(4)—C(19)	1.407 (8)	C(20)—C(31)	1.422 (8)
C(5)—C(6)	1.391 (9)	C(21)—C(32)	1.440 (8)
C(6)—C(20)	1.382 (8)	C(22)—C(23)	1.420 (8)
C(7)—C(8)	1.388 (9)	C(22)—C(32)	1.438 (8)
C(7)—C(21)	1.365 (8)	C(23)—C(24)	1.476 (8)
C(8)—C(9)	1.362 (9)	C(23)—C(34)	1.403 (8)
C(9)—C(22)	1.410 (8)	C(24)—C(33)	1.421 (8)
C(10)—C(11)	1.397 (9)	C(25)—C(33)	1.433 (8)
C(10)—C(24)	1.377 (8)	C(26)—C(27)	1.467 (8)
C(11)—C(12)	1.344 (9)	C(26)—C(33)	1.420 (8)
C(12)—C(25)	1.408 (9)	C(27)—C(34)	1.439 (8)
C(13)—C(14)	1.340 (9)	C(28)—C(29)	1.416 (8)
C(13)—C(25)	1.402 (9)	C(28)—C(34)	1.437 (8)
C(14)—C(15)	1.393 (9)	C(29)—C(30)	1.480 (8)
C(15)—C(26)	1.382 (8)	C(29)—C(32)	1.410 (8)
C(16)—C(17)	1.397 (9)	C(30)—C(31)	1.427 (8)
C(2)—C(1)—C(30)	120.9 (5)	C(10)—C(24)—C(23)	122.9 (5)
C(1)—C(2)—C(3)	120.7 (6)	C(10)—C(24)—C(33)	118.4 (5)
C(2)—C(3)—C(19)	121.2 (6)	C(23)—C(24)—C(33)	118.6 (5)
C(5)—C(4)—C(19)	120.8 (6)	C(12)—C(25)—C(13)	123.5 (5)
C(4)—C(5)—C(6)	120.9 (6)	C(12)—C(25)—C(33)	118.2 (5)
C(5)—C(6)—C(20)	121.4 (6)	C(13)—C(25)—C(33)	118.3 (5)
C(8)—C(7)—C(21)	121.5 (6)	C(15)—C(26)—C(27)	123.0 (5)
C(7)—C(8)—C(9)	121.3 (6)	C(15)—C(26)—C(33)	118.1 (5)
C(8)—C(9)—C(22)	120.7 (5)	C(27)—C(32)—C(33)	118.9 (5)
C(11)—C(10)—C(24)	121.7 (6)	C(16)—C(27)—C(26)	121.6 (5)
C(10)—C(11)—C(12)	120.1 (6)	C(16)—C(27)—C(34)	119.5 (5)
C(11)—C(12)—C(25)	121.6 (6)	C(26)—C(27)—C(34)	119.0 (5)
C(14)—C(13)—C(25)	121.5 (6)	C(18)—C(28)—C(29)	123.1 (5)
C(13)—C(14)—C(15)	120.5 (6)	C(18)—C(28)—C(34)	117.6 (5)
C(14)—C(15)—C(26)	121.7 (6)	C(29)—C(28)—C(34)	119.2 (5)
C(17)—C(16)—C(27)	121.5 (6)	C(28)—C(29)—C(30)	123.1 (5)
C(16)—C(17)—C(18)	120.5 (6)	C(28)—C(29)—C(32)	118.2 (5)
C(17)—C(18)—C(28)	121.9 (5)	C(30)—C(29)—C(32)	118.7 (5)
C(3)—C(19)—C(4)	122.9 (5)	C(1)—C(30)—C(29)	122.8 (5)
C(3)—C(19)—C(31)	118.1 (5)	C(1)—C(30)—C(31)	118.6 (5)
C(4)—C(19)—C(31)	119.0 (5)	C(29)—C(30)—C(31)	118.5 (5)
C(6)—C(20)—C(21)	122.1 (5)	C(19)—C(31)—C(20)	119.3 (5)
C(6)—C(20)—C(31)	118.5 (5)	C(19)—C(31)—C(30)	119.7 (5)
C(21)—C(20)—C(31)	119.4 (5)	C(20)—C(31)—C(30)	121.0 (5)
C(7)—C(21)—C(20)	122.1 (5)	C(21)—C(32)—C(22)	119.2 (5)
C(7)—C(21)—C(32)	119.0 (5)	C(21)—C(32)—C(29)	120.8 (5)
C(20)—C(21)—C(32)	118.9 (5)	C(22)—C(32)—C(29)	120.1 (5)
C(9)—C(22)—C(23)	122.2 (5)	C(24)—C(33)—C(25)	119.3 (5)
C(9)—C(22)—C(32)	118.3 (5)	C(24)—C(33)—C(26)	121.0 (5)
C(23)—C(22)—C(32)	119.4 (5)	C(25)—C(33)—C(26)	119.5 (5)
C(22)—C(23)—C(24)	123.5 (5)	C(23)—C(34)—C(27)	120.6 (5)
C(22)—C(23)—C(34)	118.0 (5)	C(23)—C(34)—C(28)	120.6 (5)
C(24)—C(23)—C(34)	118.5 (5)	C(27)—C(34)—C(28)	118.8 (5)

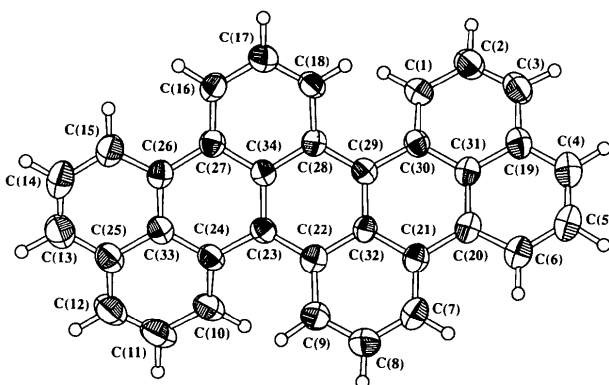


Fig. 1. ORTEP (Johnson, 1965) drawing showing the thermal ellipsoids at the 50% probability level, with the numbering scheme.

drawing of the molecule with the atom-numbering scheme is shown in Fig. 1. Bond lengths and angles are listed in Table 2.

The molecule is largely distorted from a planar structure as shown in Fig. 2(a). It twists to a propeller form with a pseudo-twofold rotational axis, which is the normal to the plane defined by C(22), C(32), C(28) and C(34), to avoid the steric hindrance between H atoms at overcrowding sites. The bond lengths and their alternations in TBPA are almost

the same as those in perylene (Camermer & Trotter, 1964). The dihedral angles are 36.9 (4) and 38.1 (5) $^\circ$ between the pairs of planes [C(1), C(28), C(30)] and [C(18), C(28), C(30)], [C(9), C(22), C(24)] and [C(10), C(22), C(24)]. The non-bonded distances C(1)⋯C(18) and C(9)⋯C(10) are 2.980 (7) and 2.987 (9) \AA , H(C1)⋯H(C18) and H(C9)⋯H(C10) are 2.16 (6) and 2.05 (6) \AA , respectively. The angles C(28)—C(29)—C(30) and C(22)—C(23)—C(24) are 123.1 (5) and 123.5 (5) $^\circ$, respectively. The results show that the steric hindrance in TBPA is released not by angle expansion but mainly by molecular twisting. This type of distortion is observed in other noncyclic aromatics, *e.g.* tetrabenz[a,cd,j,lm]perylene, which also has two fjord-like overcrowding sites (Kohno, Konno, Saito & Inokuchi, 1975).

As a result of the molecular distortion, the central benzene ring [C(28), C(29), C(32), C(22), C(23) and

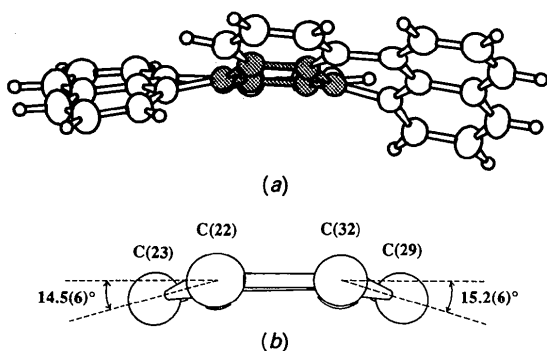


Fig. 2. (a) ORTEP (Johnson, 1965) drawing projected along the C(22)···C(34) and C(32)···C(28) direction. (b) View of the shaded central ring in (a).

C(34)] is deformed to a boat form as shown in Fig. 2(b). The flip angles of C(23) and C(29) against the least-squares plane involving C(22), C(32), C(28) and C(34) are 14.5 (6) and 15.2 (6)°, respectively, and they are larger than that in the case of [2.2]paracyclophane (12.6°), where two benzene rings are connected by two ethano bridges at *para* positions (Hope, Bernstein & Trueblood, 1972). This deformation also affects the reactivity of TBPA towards electrophiles, *e.g.* singlet O₂. Judging from the HOMO coefficients calculated by the Hückel MO method, positions C(23) and C(29) are the most reactive sites for electrophiles. The boat-shaped

deformation of the central benzene ring may introduce a facial selectivity towards electrophiles. Thus the reaction of singlet O₂ with TBPA at these positions should occur from the inner side to give the *endo*-peroxide stereoselectively.

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Studies on Nonlinear Optical Materials: Structure of Diphenylmethyl (*Z*)-1-(1-Methylthio-2-nitrovinyl)tetrahydropyrrole-2-carboxylate

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Abstract. C₂₁H₂₂N₂O₄S, *M_r* = 398.5, orthorhombic, *P*2₁2₁2₁, *a* = 9.799 (1), *b* = 11.853 (1), *c* = 17.316 (2) Å, *V* = 2011.4 Å³, *Z* = 4, *D_m* = 1.320, *D_x* = 1.314 Mg m⁻³, Cu *Kα*, λ = 1.5418 Å, μ = 1.63 mm⁻¹, *F*(000) = 840.0, *T* = 293 K, *R* = 0.055 for 1735 significant reflections. In the 1-methylthio-2-nitrovinyl moiety the C=C bond, 1.368 (7) Å, is significantly longer than in ethylene, 1.336 (2) Å. The second harmonic generation (SHG) efficiency of this

compound is only 0.25 of the urea standard. The correlation between the molecular packing and SHG is discussed.

Introduction. Nonlinear optical organic materials are gaining widespread recognition and are under intensive investigation owing to their potential applications in the field of optical signal processing (Chemla & Zyss, 1987). Organic crystals exhibiting second harmonic generation (SHG) are currently being developed (Nicoud, 1988). On the molecular level, this is made possible by the molecules bearing donor

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