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β-Tribenzopyrene (Naphtho[1,2,3,4-rst]pentaphene)

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β-Tribenzopyrene crystallizes in the orthorhombic system, space group $Pn2_1m$ with $a = 4.0260$ (5), $b = 10.693$ (3) and $c = 19.720$ (4) Å and two molecules in the unit cell. The molecule is required to have crystallographic mirror symmetry. The structure was refined to an R of 0.046 for 331 observed reflexions. The considerable strain inherent in a planar molecular model is spread out over the ring systems and is relieved by a succession of out-of-plane bendings and angular deformations such that the C atoms in the most overcrowded region have an intramolecular separation of 3.04 Å, and the separation of the hydrogens attached to these carbons is only 1.98 Å. In achieving this, ring A remains essentially planar, whereas all the other rings are forced to adopt boat conformations.

Introduction

As part of our continuing interest in overcrowded molecular structures (Ferguson & Robertson, 1963; Roberts, Brauer, Tsay & Krüger, 1974), we have examined $C_{28}H_{16}$ (I) by X-ray diffraction.

Crystal data

$C_{28}H_{16}$, FW 352.4, orthorhombic, $a = 4.0260$ (5), $b = 10.693$ (2), $c = 19.720$ (4) Å, $V = 848.95$ Å³,

(I)
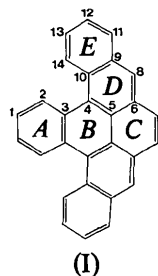
$Z = 2$, $D_x = 1.38$ g cm^{-3}, $\mu = 0.085$ cm^{-1}, $F(000) = 368$, λ(Mo $K\alpha$) = 0.71069 Å, space group $Pn2_1m$.

The systematic absences ($0kl$ when $k + l = 2n + 1$) allow the space group to be either $Pn2_1m$ (an alternative setting of $Pmn2_1$, C^7_{2v}, No. 31) or $Pnmm$ (an alternative setting of $Pmmn$, D^{13}_{2h}, No. 59). $Pn2_1m$ was chosen on chemical grounds; with $Z = 2$ this space group demands molecular symmetry m, whereas $Pnmm$ demands molecular symmetry mm which is not possible. The equivalent positions for $Pn2_1m$ are x,y,z; $x,y,\bar{z}$; $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; $x, \frac{1}{2} + y, \frac{1}{2} + z$.

An acicular, yellow crystal of dimensions $0.60 \times 0.08 \times 0.08$ mm was mounted with $\mathbf{a}^*$ parallel to the φ axis of the Hilger & Watts Y-290 four-circle diffractometer. The unit-cell dimensions were determined by least-squares refinement of θ values measured for 12 reflexions. Reflexion intensities were measured for two octants with the $\theta/2\theta$ step-scan technique and graphite-monochromated Mo $K\alpha$ radiation. Seventy steps, each of range $0.01°$ (θ) and of 2 s duration, were taken through each diffracting position. Background counts of 35 s were measured at the start and end positions of each scan. Appropriate Lorentz–polarization corrections were applied to the 1947 hkl and $\bar{h}kl$ reflexions with θ (Mo $K\alpha$) < 25°; of these, 600 had $I > 3\sigma(I)$ and were classified as 'observed'. Averaging the two equivalent forms where appropriate produced an R_{ave}† of 0.028 and resulted in 331 unique 'observed' reflexions.

Although the molecule is required, from space-group considerations, to straddle the crystallographic mirror plane it could be placed arbitrarily in the y direction. With the framework of the overcrowded hydrocarbon benzo[c]phenanthrene (Hirshfeld, Sandler & Schmidt, 1963) as a model (Fig. 1) the structure was solved in its short a-axis projection via Patterson and trial-and-error methods. It then only remained to find the correct x coordinates. This was done with a trial-and-error procedure (Stout & Jensen, 1968) to scan the $h0l$ zone for the optimum agreement between F_o and F_c. Four cycles of full-matrix least-squares refinement with the three-dimensional data on the structure thus obtained reduced R to 0.18. Relocation of one C atom followed by two further cycles of refinement gave $R = 0.14$. The refinement was concluded by allowing the C atoms to vibrate anisotropically and by fixing H atoms in geometrically expected positions (with C—H = 1.00 Å) after each cycle with an isotropic U of 0.05 Å^2. This led to final values of 0.046 and 0.058 for R and R_w‡ respectively. The weighting scheme used was $w = [\sigma^2(F)(2F_{min} + F_o + 2F_o^2/F_{max})]^{-1/2}$. Scattering factors were those of Cromer & Mann (1968) for C and of Stewart, Davidson & Simpson (1965) for H. A

† $R_{ave} = \{\Sigma [n \Sigma \omega(\bar{F} - F)^2]/\Sigma [(n - 1) \Sigma \omega F^2]\}^{1/2}$, where the inner summations are over the n equivalent reflexions averaged to give $\bar{F}$ and the outer summations are over all unique reflexions.

‡ $R_w = [\Sigma \omega(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$.

difference synthesis calculated at the conclusion of the refinement confirmed the correctness of the structure by its general flat topography. Another difference synthesis was calculated with the H atom contributions omitted from the F_c calculation; diffuse maxima of height 0.3 to 0.5 e Å^{-3} were observed at the calculated H atom positions.

To increase the ratio of observations to variables (only 2.5 for 3σ data) we repeated the last cycles of refinement using observed limits of 2σ and 1σ. This resulted in R values of 0.071 (454 reflexions) and 0.095 (631 reflexions) and no significant change in the coordinates or improvement in the standard deviations of either positional or thermal parameters. We thus concern ourselves only with conclusions based on the 3σ refinement.

The C atom coordinates with standard deviations calculated from the inverse matrix of the final refinement cycle are presented in Table 1; calculated H coordinates are in Table 2. Bond lengths and valency angles with standard deviations calculated from the full covariance matrix are listed in Table 3.*
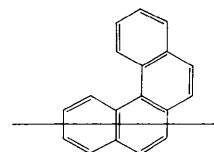
Fig. 1. The structure of benzo[c]phenanthrene used as a model for the trial-and-error solution; the molecule is shown oriented with respect to the crystallographic mirror plane.

Table 1. *Fractional coordinates* ($\times 10^3$)

	x	y	z
C(1)	161 (3)	166	465 (1)
C(2)	169 (3)	278 (1)	430 (1)
C(3)	181 (3)	395 (1)	464 (1)
C(4)	151 (3)	513 (1)	426 (1)
C(5)	22 (3)	614 (1)	463 (1)
C(6)	−92 (3)	724 (1)	429 (1)
C(7)	−237 (2)	824 (1)	466 (1)
C(8)	−67 (3)	729 (1)	360 (1)
C(9)	100 (3)	636 (1)	323 (1)
C(10)	233 (3)	526 (1)	355 (1)
C(11)	160 (3)	651 (1)	252 (1)
C(12)	341 (4)	568 (2)	217 (1)
C(13)	480 (4)	465 (1)	250 (1)
C(14)	433 (3)	444 (1)	317 (1)

Discussion

The molecule possesses crystallographic m (C_s) symmetry (Fig. 2). Of prime interest is the distortion of the molecule from planarity caused by the steric interaction of the hydrogens bonded to C(2) and C(14). The distance C(2)···C(14) is only 3·04, while H(2)···H(14) is 1·98 Å. In achieving these separations, buckling of the molecular framework occurs, but the distortions are not uniform around the ring systems as the torsional angles [Fig. 4(c)] and mean-plane data show. Thus ring A remains essentially planar (maximum deviation 0·006 Å) whereas the other rings adopt boat conformations with the greatest buckling in rings B (deviations −0·074 to +0·143 Å) and D (−0·084 to +0·063 Å).

In order to rationalize the observed conformation of the molecule it is necessary to have some idea of the bond orders in the idealized planar structure. To this end the valence bond (VB) approach with Kekulé structures (Pauling, 1960) and the Hückel molecular-orbital (HMO) method (Streitweiser & Brauman, 1965) were used to give the π bond orders (p) shown in Fig. 3(a).

Bond lengths (l) were then calculated with the relations (Cruickshank & Sparks, 1960) $l = 1·477 − (1·477 − 1·337)[1·333p/(0·33p + 1)]$ and $l = 1·46 − (p − 0·40)/0·45$ (0·12) for the VB and HMO approaches respectively [see Fig. 3(b)]. Our calculations are in excellent agreement with the predictions of Vasudevan & Laidlaw (1970).

The high π bond order at C(7)—C(7') has been demonstrated by an experiment (Clar, McAndrew & Stephen, 1970) in which a methyl group was substituted on C(7) and in which the observed methyl doublet in the NMR spectrum closely resembles the pattern observed in methyl olefins. In the present work, the observed bond lengths [Fig. 3(c)] agree qualitatively with the results of the VB and HMO treatments. In particular, C(7)—C(7'), C(1)—C(2), C(11)—C(12) and C(13)—C(14) reveal considerable double-bond character, with lengths ranging from 1·35 to 1·38 Å.

Both the HMO and VB methods show a low π bond order for the C(3)—C(4) bond (in keeping with our observed bond length, 1·48 Å). Although their accuracy is not high, the bond lengths generally reflect the predic-

Table 2. *Calculated coordinates for the hydrogen atoms (fractional, ×10³)*

	x	y	z		x	y	z
H(1)	156	85	440	H(11)	65	726	228
H(2)	166	277	380	H(12)	376	579	167
H(7)	−340	895	441	H(13)	619	405	223
H(8)	−171	800	335	H(14)	540	370	339

Table 3. *Bond lengths (Å), valency angles (°) and standard deviations*

| C(1)—C(1')	1·37 (2)	C(3')—C(3)—C(2)	118 (1)
C(1)—C(2)	1·38 (1)	C(3')—C(3)—C(4)	121 (1)
C(2)—C(3)	1·42 (1)	C(5)—C(4)—C(3)	115 (1)
C(3)—C(3')	1·41 (2)	C(10)—C(4)—C(3)	124 (1)
C(3)—C(4)	1·48 (1)	C(10)—C(4)—C(5)	122 (1)
C(4)—C(5)	1·41 (1)	C(6)—C(5)—C(4)	120 (1)
C(4)—C(10)	1·44 (1)	C(5')—C(5)—C(4)	122 (1)
C(5)—C(5')	1·44 (2)	C(5')—C(5)—C(6)	119 (1)
C(5)—C(6)	1·43 (1)	C(7)—C(6)—C(5)	120 (1)
C(6)—C(7)	1·42 (2)	C(8)—C(6)—C(5)	119 (1)
C(6)—C(8)	1·37 (1)	C(8)—C(6)—C(7)	121 (1)
C(7)—C(7')	1·35 (3)	C(7')—C(7)—C(6)	121 (1)
C(8)—C(9)	1·40 (2)	C(9)—C(8)—C(6)	122 (1)
C(9)—C(10)	1·44 (2)	C(10)—C(9)—C(8)	122 (1)
C(9)—C(11)	1·43 (1)	C(11)—C(9)—C(8)	120 (1)
C(10)—C(14)	1·40 (1)	C(11)—C(9)—C(10)	118 (1)
C(11)—C(12)	1·35 (2)	C(9)—C(10)—C(4)	115 (1)
C(12)—C(13)	1·39 (2)	C(14)—C(10)—C(4)	126 (1)
C(13)—C(15)	1·35 (2)	C(14)—C(10)—C(9)	119 (1)
		C(12)—C(11)—C(9)	121 (1)
C(1')—C(1)—C(2)	120 (1)	C(13)—C(12)—C(11)	120 (1)
C(3)—C(2)—C(1)	122 (1)	C(14)—C(13)—C(12)	122 (1)
C(4)—C(3)—C(2)	121 (1)	C(13)—C(14)—C(10)	120 (1)
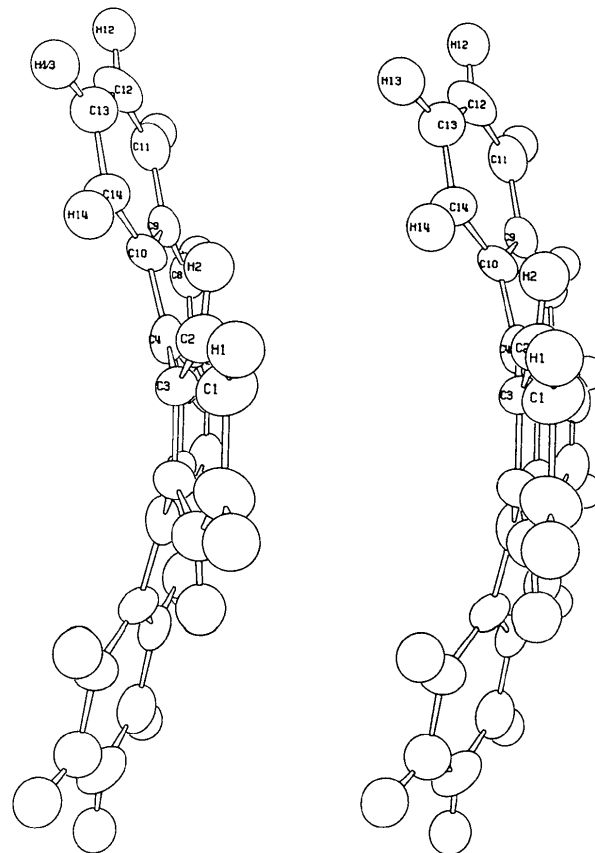
Fig. 2. A stereoscopic view of the naphtho[1,2,3,4-rst]pentaphene molecule projected parallel to the best plane of the central anthracene moiety.
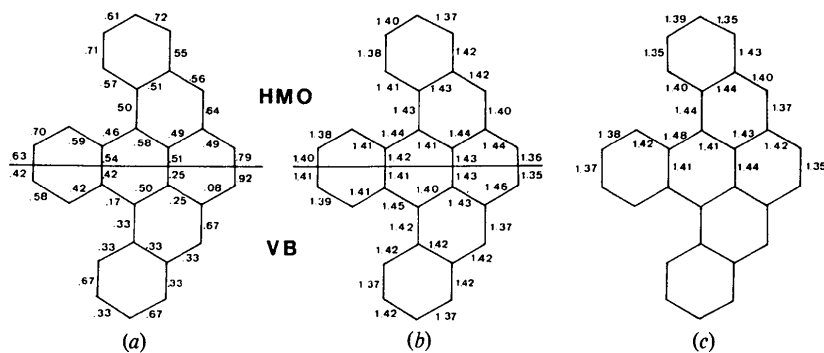
Fig. 3. HMO (above the line) VB (below the line) calculations of (a) π bond order and (b) bond lengths. For comparison the observed bond lengths are given in (c).
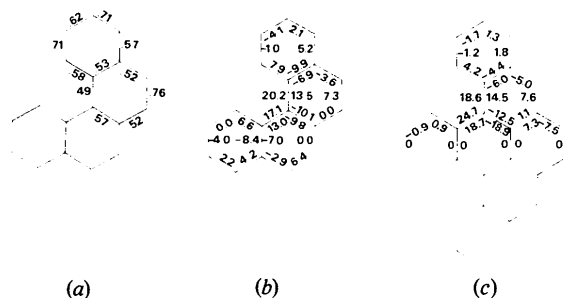

Fig. 4. (a) Bond orders and (b) torsion angles for benzo[c]phenanthrene, and (c) torsion angles in naphtho[1,2,3,4-rst]pentaphene.

tions made on theoretical grounds, indicating that relief from steric strain is not achieved by bond-length extension. Angle bending does however play a significant role, as shown, for example, by the angles C(3)—C(4)—C(10) [124(1)] and C(4)—C(10)—C(14) [126 (1)°].

It is of interest to compare this structure with that of benzo[c]phenanthrene, which also has small π bond orders [Fig. 4(a)] in those parts of the molecule which experience the most steric strain. For this purpose, torsion angles for the two structures are shown in Fig. 4(b) and (c). It is clear that these molecules experience fairly similar distortions because they have a similar pattern of π bond order in the overcrowded region, i.e. essentially the same sites are available for low-energy skeletal deformation.

The crystal structure (Fig. 5) consists of columns of molecules extended in the a direction with normal van der Waals distances between columns.
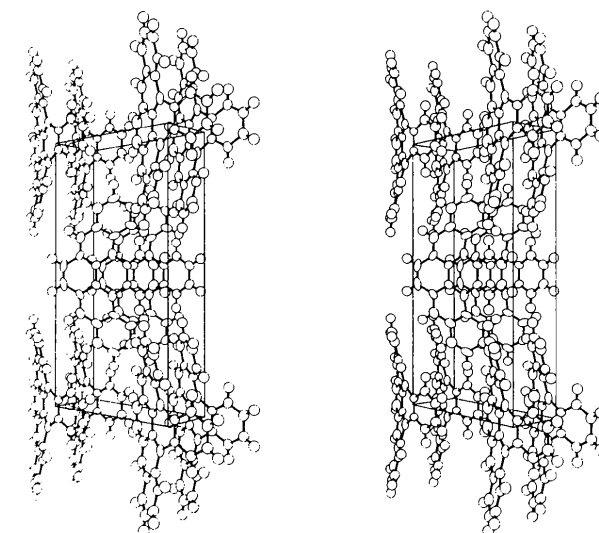
Fig. 5. Stereoscopic packing diagram in general projection.

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