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Tetrabenzo[*de,no,st,c*$_1$*d*$_1$]heptacene

By George Ferguson* and Masood Parvez

The Chemistry Department, The University of Guelph, Guelph, Ontario, Canada N1G 2W1

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Abstract. $C_{42}H_{22}$, $M_r = 526{\cdot}6$, monoclinic, $a = 24{\cdot}613\ (14)$, $b = 3{\cdot}860\ (2)$, $c = 25{\cdot}895\ (17)$ Å, $\beta = 95{\cdot}85\ (6)°$, $V = 2447{\cdot}4$ Å^3, $Z = 4$, $D_c = 1{\cdot}43$ Mg m^{-3}, $F(000) = 1096$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo $K\alpha$) $= 0{\cdot}088$ mm^{-1}. Systematic absences $h0l$, $h + l = 2n + 1$; and $0k0$, $k = 2n + 1$ determined space group $P2_1/n$ uniquely. The structure was solved by direct methods in space group Pn and then refined by full-matrix least-squares calculations in space group $P2_1/n$ to $R = 0{\cdot}079$ for 923 observed reflections ($I > 3\sigma I$). The asymmetric unit contains two independent half-molecules (I and II) at inversion centres separated by $\frac{1}{2}a$. Both molecules have the same twist conformation; the terminal pyrene moiety is twisted (4·6° in I, 4·8° in II) out of the central anthracene plane to relieve intramolecular overcrowding of the phenanthrene type.

Introduction. Crystals of $C_{42}H_{22}$ (Fig. 1) prepared by Clar (1964) and Macpherson (1962) are dark-red needles with well defined faces; a small needle crystal of dimensions 0·24 × 0·11 × 0·08 mm was mounted with the b axis 10° offset from the φ axis of a Hilger & Watts Y290 four-circle diffractometer. The unit-cell dimensions were determined from a least-squares analysis of the setting angles of eight reflections with θ(Mo $K\alpha$) in the range 10–15°. Intensities were measured by the $\theta/2\theta$ scan technique ($2° < \theta < 25°$) and graphite-monochromated Mo $K\alpha$ radiation. Thirty steps of 0·02° in θ and of 2 s duration were taken through each diffraction position and stationary crystal–stationary counting background counts of 15 s duration were measured at the beginning and end of each scan. The intensities of three reflections, measured as 'standards' after every 100 reflection measurements, did not change significantly during the course of the data collection. The crystals of this hydrocarbon, like those of many other aromatic hydrocarbons, *e.g.* β-dinaphthoperopyrene (Robertson & Trotter, 1959), dipernaphthyleneanthracene (Rossmann, 1959), circumanthracene (Clar, Kelly, Robertson & Rossmann, 1956) and β-tribenzopyrene (Roberts & Ferguson, 1977), showed a very rapid decrease in intensity with increasing scattering angle. Of the 5399 reciprocal-lattice sites surveyed, only 923 reflections had $I > 3\sigma(I)$. These were labelled observed and, after appropriate Lorentz and polarization corrections, were used in the refinement of the structure. No corrections for absorption were considered necessary.

The structure was solved by direct methods using *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Because the molecule contains arrays of regular hexagons, we anticipated some problems with E maps using a simple direct-method approach, and indeed we were not disappointed. An initial trial run with *MULTAN* 78 and Wilson (1942) scaling led to an infinite 'chicken-wire' structure. When we introduced structural information, *via* K-curve normalization, the distribution of E's appeared to be noncentrosymmetric rather than centrosymmetric and an E map, computed with the phases of the 436 reflections with $E > 1{\cdot}2$, again led to a 'chicken-wire' array of peaks. At this point we decided to try and solve the structure in the noncentrosymmetric space group Pn which would also require the asymmetric unit to contain two independent $C_{42}H_{22}$ molecules. The first E map produced by *MULTAN* 78 with K-curve scaling and Pn space-group symmetry revealed the entire structure. Inspection of the coordinates showed immediately that the centres of two molecules thus revealed were separated by exactly ($\frac{1}{2}$,0,0), implying that the correct space group, as indicated by the systematic absences, was $P2_1/n$ [non-standard setting of $P2_1/c$ with equivalent positions $\pm(x,y,z;\ \frac{1}{2} + x,\ \frac{1}{2} - y,\ \frac{1}{2} + z)$]; the asymmetric unit contains two independent half-molecules. For computational convenience we

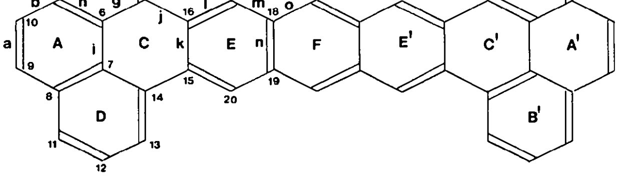

Fig. 1. Tetrabenzo[*de,no,st,c*$_1$*d*$_1$]heptacene showing the crystallographic numbering, and the bond- and ring-labelling schemes.

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* To whom correspondence should be addressed.

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Table 1. *Fractional coordinates with estimated standard deviations in parentheses and calculated coordinates for the hydrogen atoms*

The atoms are numbered according to the scheme shown in the molecular formula in Fig. 1 with a '1' placed before each atom number in molecule (I) and a '2' before each atom number in molecule (II). The H atoms have the same numbers as the C atoms to which they are bonded.

	x ($\times 10^4$)	y ($\times 10^3$)	z ($\times 10^4$)		x ($\times 10^4$)	y ($\times 10^3$)	z ($\times 10^4$)		x ($\times 10^4$)	y ($\times 10^3$)	z ($\times 10^4$)
C(11)	4924 (5)	42 (4)	6982 (5)	C(121)	4510 (5)	−164 (4)	5092 (5)	H(12)	4162	−146	6810
C(12)	4418 (5)	−70 (4)	7087 (5)	C(21)	1879 (4)	−271 (4)	5994 (6)	H(13)	3915	−151	7648
C(13)	4269 (7)	−72 (5)	7589 (6)	C(22)	1849 (6)	−209 (4)	6518 (6)	H(14)	4521	28	8353
C(14)	4624 (7)	34 (5)	8010 (7)	C(23)	2305 (5)	−250 (5)	6868 (5)	H(19)	6256	482	8530
C(15)	5130 (6)	153 (4)	7899 (6)	C(24)	2767 (6)	−390 (4)	6729 (5)	H(110)	5412	283	8664
C(16)	5288 (5)	171 (4)	7394 (5)	C(25)	2816 (5)	−487 (4)	6200 (6)	H(111)	6944	626	7918
C(17)	5813 (6)	296 (4)	7311 (5)	C(26)	2366 (5)	−408 (4)	5831 (7)	H(112)	7203	651	7078
C(18)	6183 (7)	423 (4)	7728 (6)	C(27)	2399 (4)	−508 (4)	5300 (6)	H(113)	6605	463	6383
C(19)	6013 (7)	406 (4)	8245 (6)	C(28)	2886 (6)	−649 (4)	5171 (6)	H(117)	4411	−172	6094
C(110)	5515 (7)	284 (4)	8321 (6)	C(29)	3347 (5)	−706 (4)	5527 (6)	H(120)	6035	349	5779
C(111)	6697 (7)	549 (4)	7635 (7)	C(210)	3309 (5)	−627 (4)	6026 (6)	H(121)	4188	−293	5176
C(112)	6853 (6)	565 (4)	7138 (6)	C(211)	2912 (6)	−749 (4)	4624 (6)	H(22)	1514	−136	6635
C(113)	6496 (5)	452 (4)	6724 (6)	C(212)	2495 (6)	−705 (4)	4260 (7)	H(23)	2289	−177	7216
C(114)	5978 (5)	324 (4)	6786 (5)	C(213)	1988 (5)	−565 (4)	4401 (5)	H(24)	3067	−426	6985
C(115)	5591 (5)	208 (4)	6345 (6)	C(214)	1956 (4)	−479 (4)	4918 (5)	H(29)	3677	−795	5419
C(116)	5073 (4)	61 (4)	6446 (5)	C(215)	1431 (5)	−333 (3)	5057 (5)	H(210)	3613	−667	6275
C(117)	4742 (5)	−61 (4)	6029 (6)	C(216)	1410 (5)	−218 (3)	5599 (6)	H(211)	3238	−850	4528
C(118)	4858 (6)	−32 (3)	5494 (6)	C(217)	936 (5)	−69 (4)	5719 (5)	H(212)	2532	−767	3910
C(119)	5371 (5)	115 (4)	5416 (5)	C(218)	459 (4)	−30 (4)	5362 (5)	H(213)	1688	−527	4147
C(120)	5703 (5)	238 (4)	5843 (5)	C(219)	476 (5)	−160 (4)	4847 (5)	H(217)	924	17	6062
				C(220)	982 (5)	−295 (4)	4721 (4)	H(220)	1005	−365	4372
				C(221)	−29 (5)	120 (4)	5500 (5)	H(221)	−51	195	5846

Table 2. *Mean bond lengths* (Å) *in tetrabenzoheptacene averaged over chemically equivalent bonds*

For details of the bond labelling see Fig. 1.

The largest variation between chemically equivalent bonds is in bond *c* where lengths in the range 1·383 (23) to 1·475 (22) Å were found.

Bond		Calculated (HMO)	Bond		Calculated (HMO)
a	1·34 (2)	1·36	*h*	1·41 (2)	1·40
b	1·44 (2)	1·40	*i*	1·43 (2)	1·40
c	1·42 (2)	1·39	*j*	1·48 (2)	1·42
d	1·36 (2)	1·38	*k*	1·46 (2)	1·41
e	1·40 (2)	1·38	*l*	1·36 (2)	1·38
f	1·39 (2)	1·39	*m*	1·42 (2)	1·40
g	1·42 (2)	1·40	*n*	1·42 (2)	1·41
			o	1·38 (2)	1·39

Table 3. *Mean bond angles* (°) *in tetrabenzoheptacene averaged over chemically equivalent angles*

For details of the bond labelling see Fig. 1.

Four of the chemically equivalent bond-angle sets have values which differ by 4σ to 5σ: *e.g.* angles *f–j* 117·4–123·0 (1·2)°; *c–h* 117·3–123·5 (1·3)°; *c–d* 116·3–122·7 (1·4)°; and *b–h* 117·3–124·3 (1·5)°.

Bonds		Bonds	
a–b	121 (1)	*g–i*	122 (1)
b–c	121 (1)	*g–j*	119 (1)
b–h	120 (1)	*h–i*	120 (1)
c–h	120 (1)	*j–k*	120 (1)
c–d	120 (1)	*j–l*	123 (1)
d–e	121 (2)	*k–l*	118 (1)
e–f	121 (1)	*l–m*	125 (1)
f–g	120 (1)	*m–n*	117 (1)
f–j	121 (1)	*m–o*	123 (1)
g–h	119 (1)	*n–o*	120 (1)

placed one half-molecule (I) at ($\frac{1}{2}$,0,$\frac{1}{2}$) and the other (II) at (0,0,$\frac{1}{2}$), independent inversion centres in space group $P2_1/n$.

Three cycles of full-matrix least-squares calculations with isotropic C atoms lowered R to 0·127. When the C atoms were allowed anisotropic motion R fell to 0·098 in three cycles and a difference map computed at this stage revealed the H atoms; these were allowed for (in geometrically idealized positions with C—H 0·95 Å and U_{iso} 0·06 Å^2), but not refined, in subsequent calculations. In three more rounds of calculations convergence was achieved with R = 0·079 and R_w = $(\sum w\Delta^2/\sum wF_o^2)^{1/2}$ = 0·079. Weights in the least-squares calculations were derived from the counting statistics. Scattering factors were those of Cromer & Mann (1968) for C and of Stewart, Davidson & Simpson (1965) for H. A difference synthesis calculated at the conclusion of the refinement had no significant features.

The final fractional coordinates for molecules (I) and (II) are in Table 1. Mean bond lengths and angles averaged over the two independent half-molecules are in Tables 2 and 3.* Fig. 2 is an *ORTEP* (Johnson, 1971) view of molecule (I) and Fig. 3 shows a stereoview of the arrangement of six molecules in the unit cell.

Discussion. The crystal structure (Fig. 3) is typical of the packing of many aromatic hydrocarbons, and contains almost planar molecules stacked along **b**, with only normal van der Waals distances between them.

The mean molecular dimensions (Table 2) are in accord with expected values, and show that the shortest bond is *a* (see Fig. 1) and the longest is *j* in the phenanthrene-like region. For comparison, using the Hückel molecular orbital (HMO) method (Streitweiser & Brauman, 1965), we have also calculated bond lengths (Table 2), which agree qualitatively with those determined by our diffraction study. In particular, the HMO calculations show that bond *a* has the highest double-bond character (0·77) and bond *j* the lowest (0·42), in agreement with our observations.

Relief from steric strain in the phenanthrene-like regions of the molecules is obtained mainly by small changes in the torsion angles of the C(2)–C(1)–C(16)–C(17) type (see Fig. 1) from 0° in an idealized planar structure to 4·0 and 6·2° in molecule (I), and 3·3 and 7·3° in molecule (II). These displacements result in the molecules adopting a slight twist conformation. The angle between the terminal pyrene (rings *ABCD* in Fig. 1) and the central anthracene (rings *EFE'*) moieties is 4·6° in molecule (I) and 4·8° in molecule (II), and the signs and magnitudes of the displacements of the atoms from the various mean planes show clearly that there is twisting about the *A*–*A'* axis rather than a simple folding at the *C*–*E* ring junctions. As a consequence of the inversion centres, the overall conformation of each molecule is one in which rings *B* and *D'* are twisted to one side of the central *EFE'* plane and rings *D* and *B'* to the other, rather than a propeller one.

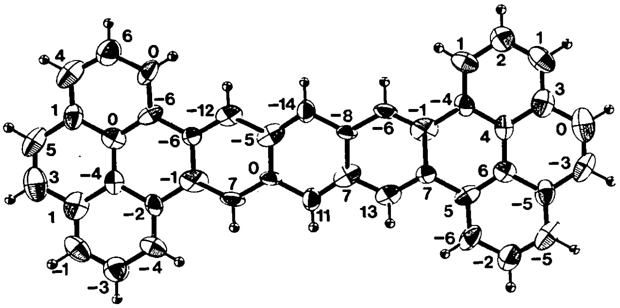

Fig. 2. View of molecule (I) with 50% probability ellipsoids for C and spheres of an arbitrary radius for H. Also shown are the displacements (Å × 10^2) of the C atoms from the molecular plane (numbers on the left side refer to I, on the right side to II). Estimated standard deviations of the displacements are 0·01–0·02 Å.

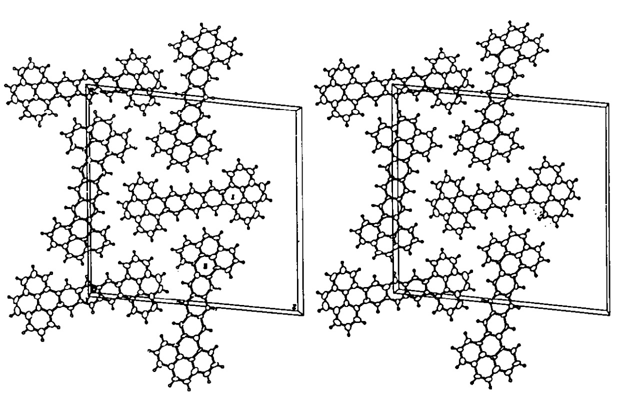

Fig. 3. Stereoview of the crystal structure.

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* Lists of structure factors, anisotropic thermal parameters, a complete list of bond lengths and angles and some mean-plane data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34424 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.