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The Crystal Structure of Tetrabenzo[a,cd,j,lm]perylene

BY Y. KOHNO, M. KONNO, Y. SAITO AND H. INOKUCHI

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

The crystals of tetrabenzo[a,cd,j,lm]perylene (4,5-11,12-dibenzoperopyrene) are orthorhombic with the space group *Pcab* and the lattice constants $a = 19.997$ (4), $b = 26.635$ (4), $c = 7.656$ (2) Å and $Z = 8$. The structure was solved by the direct method and refined by a block-diagonal least-squares program to give an R value of 0·056 on the basis of the 1439 observed reflexions collected by diffractometry. In spite of its being a polycyclic aromatic hydrocarbon, the molecule is largely distorted from a planar structure owing to the intramolecular repulsion between the hydrogen atoms. It has an approximate twofold axis of rotation and assumes a propeller-like shape. The distances between the overcrowded carbon atoms are 2·97 and 2·94 Å respectively. Although the two [a,b]naphthalene rings of each benz[de]anthracene skeleton make an angle of 30·5°, the molecule retains the aromatic character.

Introduction

Tetrabenzo[a, cd, j, lm]perylene (hereinafter TBP) was prepared by the condensation of benzanthrone with copper powder, zinc chloride and sodium chloride (Aoki, 1964). This molecule is reasonably expected to show a non-planar distortion owing to intramolecular overcrowding, such as occurs in diperinaphthylene-anthracene (Rossmann, 1959) and dinaphthopero-pyrene (Robertson & Trotter, 1959). Harnik, Herbstein, Schmidt & Hirshfeld (1954) classified the overcrowded aromatic compounds into four groups. These higher condensed polycyclic aromatic hydrocarbons mostly have a tendency to form crystals which are not suitable for X-ray work and which sometimes exhibit structural disorder. Accordingly no quantitative information on intramolecular repulsion was available.

Accurately determined bond lengths and angles of polycyclic aromatic hydrocarbons may be discussed in comparison with theoretical calculations. On the other hand, a series of these compounds exhibits high photoconductivity, which is directly related to their intramolecular electronic states and to molecular arrangements in crystals. Recently TBP was found to show high photoconduction (Kohno, Kamura & Inokuchi, 1975). The detailed crystal structure of TBP is reported in the present paper.

Experimental

The crystals of TBP were kindly supplied by Professor Aoki of Toho University. Small, orange-red needles elongated along the c axis were grown by sublimation in a glass tube under helium atmosphere. The space group and the approximate cell dimensions were determined by oscillation and Weissenberg photographs with Cu $K\alpha$ radiation. The unit-cell dimensions were later refined by the least-squares method on the basis of 20 high-order reflexions measured on a diffractometer (Mo $K\alpha$, $\lambda = 0.7107$ Å).

Crystal data

C$_{34}$H$_{18}$, $M = 426.14$, m.p. 331 °C. Space group: *Pcab*, $Z = 8$; $a = 19.997$ (4), $b = 26.635$ (4), $c = 7.656$ (2) Å. $U = 4078$ Å^3; $D_x = 1.388$, $D_m = 1.37$ g cm^{-3}; $F(000) = 1776$; μ(Mo) = 0·86 cm^{-1}.

The crystal used for X-ray work was approximately $0.15 \times 0.15 \times 0.30$ mm in dimensions. All the accessible reflexions with 2θ less than 55° were measured on an automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated by a graphite plate, the ω–2θ scan technique being employed. Three standard reflexions were measured every fifty reflexions and background intensities were obtained at each end of the scan. Data were recorded for 2518 independent reflexions and those reflexions with $I < 3\sigma(I)$ were

rejected as 'unobserved', leaving 1439 independent reflexions. They were corrected for Lorentz and polarization factors, but no absorption correction was applied.

Structure determination and refinement

Approximate absolute scale and temperature factors were obtained by Wilson's (1942) method. The phases were determined by the symbolic addition procedure (Karle & Karle, 1963). The program *SIGMA* written by Ashida (UNICS, 1967) was used to list the $\sum_2$ relationships for 323 reflexions with E values greater than 1·5 and to calculate the associated probabilities. The signs of 277 reflexions were determined with probabilities larger than 0·99. All the carbon atoms were easily located in an E map computed from the signed E values. These positions conformed to the expected model of the carbon skeleton. Atomic positions and thermal parameters of the carbon atoms were refined by the least-squares method with a block-diagonal program *HBLS* written by Ashida (UNICS, 1967). With the introduction of anisotropic temperature factors for the carbon atoms, further cycles of least-squares refinement reduced R to 0·083.

At this stage, a difference synthesis revealed all the hydrogen atoms in plausible positions. Further refinement cycles with anisotropic temperature factors for carbon atoms and with isotropic ones for hydrogen atoms reduced R to 0·056. At the final stage of the refinement, all the parameter shifts were less than one third of the corresponding standard deviations. Unit weight was given to all the reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962) for the carbon atoms and for the hydrogen atoms the values given by Stewart, Davidson & Simpson (1965) were used. Table 1 lists the observed and calculated structure factors.* The atomic parameters and their standard deviations are listed in Tables 2 and 3.

A comparison of the signs obtained by the symbolic addition procedure with those from the final structure-factor calculations revealed that only four out of 277 signs used for the E map had been incorrect.

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* Table 1 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31032 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters of the carbon atoms* ($\times 10^4$)

The values of β_{ij} refer to the expression $\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\right]$. Here and elsewhere in this paper the estimated standard deviations in last figures are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	2812 (3)	982 (2)	2646 (8)	19 (2)	13 (1)	116 (10)	4 (1)	6 (4)	3 (3)
C(2)	3262 (3)	599 (2)	2072 (8)	21 (2)	14 (1)	187 (14)	3 (1)	11 (4)	5 (3)
C(3)	3025 (4)	131 (3)	1582 (9)	38 (2)	13 (1)	208 (14)	10 (1)	24 (4)	3 (3)
C(4)	2345 (3)	1 (2)	1648 (8)	25 (2)	11 (1)	178 (12)	1 (1)	−1 (5)	2 (3)
C(5)	2120 (1)	−482 (2)	1097 (10)	46 (3)	11 (1)	243 (17)	3 (2)	−2 (6)	−7 (4)
C(6)	1464 (4)	−587 (3)	1185 (10)	41 (3)	15 (1)	261 (18)	−6 (2)	6 (6)	−10 (4)
C(7)	991 (4)	−237 (3)	1737 (10)	36 (3)	15 (1)	238 (16)	−6 (2)	−0 (6)	0 (4)
C(8)	1198 (3)	243 (2)	2298 (8)	27 (2)	12 (1)	150 (12)	−3 (1)	−2 (4)	1 (3)
C(9)	734 (3)	607 (2)	3036 (8)	23 (2)	14 (1)	135 (12)	−2 (1)	−5 (4)	5 (3)
C(10)	58 (4)	484 (3)	3435 (10)	31 (2)	18 (1)	228 (16)	−6 (2)	−6 (5)	−3 (4)
C(11)	−355 (3)	817 (3)	4251 (10)	28 (2)	21 (2)	247 (17)	−1 (2)	14 (6)	14 (4)
C(12)	−118 (3)	1274 (3)	4796 (9)	24 (2)	20 (1)	190 (15)	4 (1)	3 (5)	10 (4)
C(13)	528 (3)	1421 (2)	4384 (8)	16 (2)	16 (1)	144 (12)	2 (1)	3 (4)	8 (3)
C(14)	950 (3)	1095 (2)	3452 (7)	21 (2)	13 (1)	93 (10)	−2 (1)	−11 (4)	7 (3)
C(15)	1640 (3)	1242 (2)	3014 (7)	22 (2)	10 (1)	95 (10)	−1 (1)	−6 (4)	4 (3)
C(16)	2116 (2)	867 (2)	2653 (7)	22 (1)	11 (1)	86 (90)	0 (1)	−2 (4)	6 (3)
C(17)	1886 (4)	366 (2)	2221 (8)	24 (2)	10 (1)	137 (11)	−1 (1)	−0 (4)	7 (3)
C(18)	1842 (3)	1747 (2)	2881 (7)	19 (2)	8 (1)	118 (10)	3 (1)	−11 (4)	−3 (3)
C(19)	1375 (3)	2151 (2)	2524 (9)	24 (2)	13 (1)	184 (13)	4 (1)	−3 (5)	−1 (3)
C(20)	1586 (3)	2631 (2)	2254 (9)	33 (2)	12 (1)	190 (14)	1 (1)	−10 (5)	1 (3)
C(21)	2270 (3)	2762 (2)	2337 (9)	36 (3)	10 (1)	157 (13)	−1 (1)	5 (5)	−2 (4)
C(22)	2481 (4)	3257 (2)	2060 (10)	44 (3)	11 (1)	249 (17)	−0 (2)	7 (6)	7 (4)
C(23)	3140 (4)	3378 (3)	2164 (10)	49 (3)	13 (1)	245 (15)	−9 (1)	16 (5)	0 (4)
C(24)	3619 (3)	3016 (2)	2474 (10)	33 (2)	15 (2)	201 (15)	−9 (1)	9 (5)	−2 (4)
C(25)	3438 (3)	2510 (2)	2733 (8)	29 (2)	13 (1)	128 (11)	−4 (1)	4 (4)	−1 (3)
C(26)	3918 (3)	2125 (2)	3190 (7)	22 (2)	17 (1)	106 (11)	−3 (1)	8 (4)	−0 (3)
C(27)	4596 (3)	2240 (3)	3571 (9)	27 (2)	23 (2)	187 (15)	−10 (2)	3 (5)	0 (4)
C(28)	5024 (3)	1886 (3)	4185 (9)	21 (2)	34 (2)	164 (14)	−7 (2)	−1 (5)	5 (5)
C(29)	4804 (3)	1407 (3)	4506 (9)	22 (2)	27 (2)	198 (16)	6 (2)	6 (5)	13 (4)
C(30)	4156 (3)	1269 (3)	4115 (8)	16 (2)	23 (1)	160 (13)	1 (1)	9 (4)	−3 (4)
C(31)	3711 (3)	1624 (2)	3388 (7)	20 (2)	16 (1)	107 (11)	−1 (1)	11 (4)	2 (3)
C(32)	3016 (3)	1482 (2)	2977 (7)	17 (2)	11 (1)	107 (10)	−0 (1)	1 (3)	3 (3)
C(33)	2531 (3)	1869 (2)	2870 (7)	24 (2)	10 (1)	78 (9)	1 (1)	−1 (4)	−4 (2)
C(34)	2749 (3)	2387 (2)	2678 (7)	30 (2)	11 (1)	93 (10)	−2 (1)	6 (4)	−6 (3)

Table 3. *Positional parameters for hydrogen atoms* ($\times 10^3$)

	x	y	z
H(C2)	375 (3)	70 (2)	203 (8)
H(C3)	336 (3)	−13 (2)	108 (8)
H(C5)	254 (3)	−69 (2)	57 (8)
H(C6)	124 (3)	−93 (2)	62 (8)
H(C7)	42 (4)	−34 (2)	190 (11)
H(C10)	−8 (3)	22 (2)	302 (7
H(C11)	−84 (3)	67 (3)	461 (10)
H(C12)	−45 (3)	156 (2)	523 (8)
H(C13)	74 (2)	180 (2)	461 (6)
H(C19)	82 (3)	204 (2)	231 (9)
H(C20)	121 (4)	292 (3)	148 (12)
H(C22)	215 (3)	351 (2)	183 (8)
H(C23)	329 (3)	370 (2)	176 (8)
H(C24)	412 (3)	310 (2)	253 (8)
H(C27)	475 (3)	259 (2)	354 (7)
H(C28)	548 (3)	204 (2)	462 (9)
H(C29)	508 (2)	114 (2)	507 (6)
H(C30)	398 (2)	88 (1)	424 (5)

Description of the structure and discussion

Fig. 1 illustrates the structure viewed along the c axis. The average plane of molecules is nearly parallel to (001). Fig. 2 is a projection of the structure along the a axis. As seen from Fig. 2 the molecule is largely distorted from a planar structure. It has an approximate twofold axis of rotation through the centre of the molecule and is propeller-shaped. Moreover, it is dissymmetric and the two enantiomeric molecules

exist in the crystal. In crystals of flat polycyclic aromatic hydrocarbons like coronene (Robertson & White, 1945), molecules are intimately stacked face-to-face by van der Waals forces. In the case of TBP, the two enantiomeric molecules are alternately piled up to form a column along the c axis. The overlapping between the adjacent molecular planes is not as complete as that observed in the structures of other flat polycyclic aromatic hydrocarbons. Table 4 lists some relevant intermolecular distances less than 3·5 Å. The closest approach between the molecules in the column occurs between C(30)$\cdots$C(14), C(30)$\cdots$C(15) and C(26)$\cdots$C(19), the distances being 3·360, 3·383 and 3·370 Å respectively. The molecular columns parallel to the c axis are packed laterally by weak van der Waals forces and no interatomic distance less than 3·5 Å was observed between the columns.

The bond lengths and angles in the molecule are shown in Figs. 3 and 4, together with their estimated

Table 4. *Intermolecular* C-C *distances less than* 3·5 Å

C(13^i)$\cdots$C(31^{ii})	3·465 (8) Å	C(29^i)$\cdots$C(14^{ii})	3·478 (9) Å
C(14^i)$\cdots$C(2^{ii})	3·451 (8)	C(30^i)$\cdots$C(9^{ii})	3·489 (9)
C(17^i)$\cdots$C(3^{ii})	3·402 (9)	C(30^i)$\cdots$C(14^{ii})	3·360 (8)
C(25^i)$\cdots$C(20^{ii})	3·477 (9)	C(30^i)$\cdots$C(15^{ii})	3·383 (8)
C(26^i)$\cdots$C(19^{ii})	3·370 (9)	C(31^i)$\cdots$C(19^{ii})	3·468 (9)

Key to symmetry operations

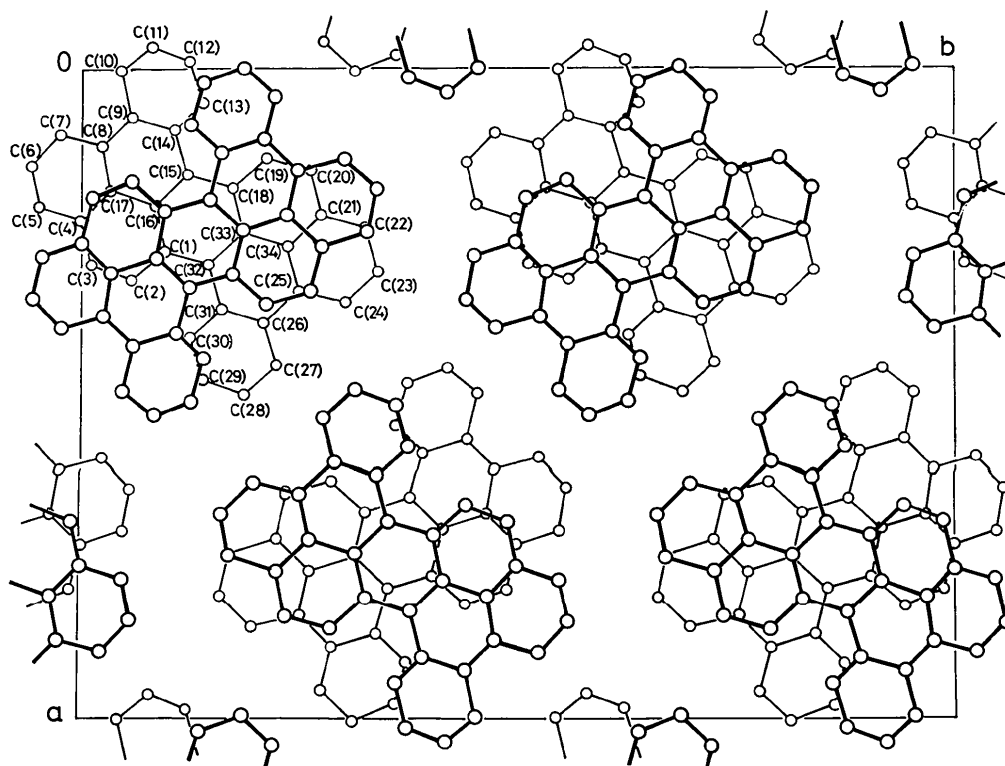|			
(i)	x,	y,	z
(ii)	$\frac{1}{2}-x$,	y,	$\frac{1}{2}+z$

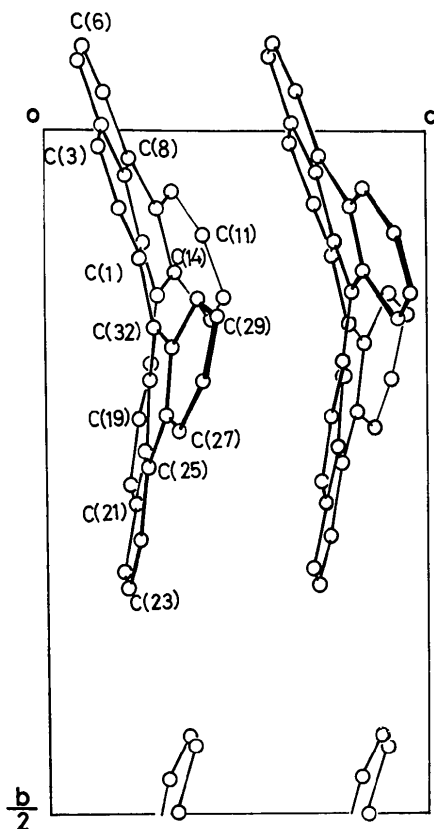Fig. 1. The structure viewed along the c axis.

Fig. 2. The structure viewed along the *a* axis. To show the non-planar distortion clearly, the molecules positioned higher up the *a* axis are not drawn.
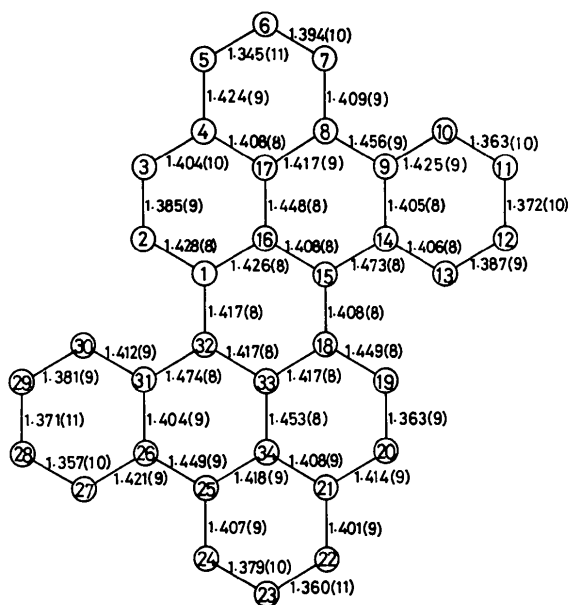
standard deviations. The average C–C bond length is 1·409 Å, slightly shorter than the bond of 1·43 Å in diperinaphthyleneanthracene and 1·431 Å in dinaphthoperopyrene. The varieties of bond lengths are meaningful in view of their estimated standard deviations. The bond lengths C(5)–C(6), C(8)–C(17) and C(14)–C(15) increase in that order (1·348 → 1·418 → 1·474 Å), corresponding to the sequence observed in dinaphthoperopyrene (1·387 → 1·423 → 1·472 Å). C(1)–C(32) and C(15)–C(18) are a little too short considering that they may lose some double-bond character owing to the molecular distortions.

As mentioned earlier, the molecule is largely distorted. If the molecule were strictly planar, the distances between C(2)···C(30) and C(13)···C(19) would become as short as 2·4 Å and H(2)···H(30) and H(13)···H(19) would be 0·55 Å. Thus the buckling of the molecular framework relieves such short contacts. Actually the non-bonded distances C(2)···C(30) and C(13)···C(19) are 2·971 and 2·944 Å, respectively. They may be compared with 3·0 Å in 3,4-benzophenanthrene (Herbstein & Schmidt, 1954a), 2·97 Å in diperinaphthyleneanthracene and 2·95 Å in dinaphthoperopyrene. The distances H(2)···H(30) and H(13)···H(19) are 1·82 and 1·87 Å, respectively, both being only slightly shorter than the sum of the van der Waals radii. The bond angles C–C–C range from 117·1° to 123·0° and the three bonds around each carbon atom are nearly coplanar. These observations suggest that the molecule of TBP still retains the aromatic character in spite of the non-planar structure.
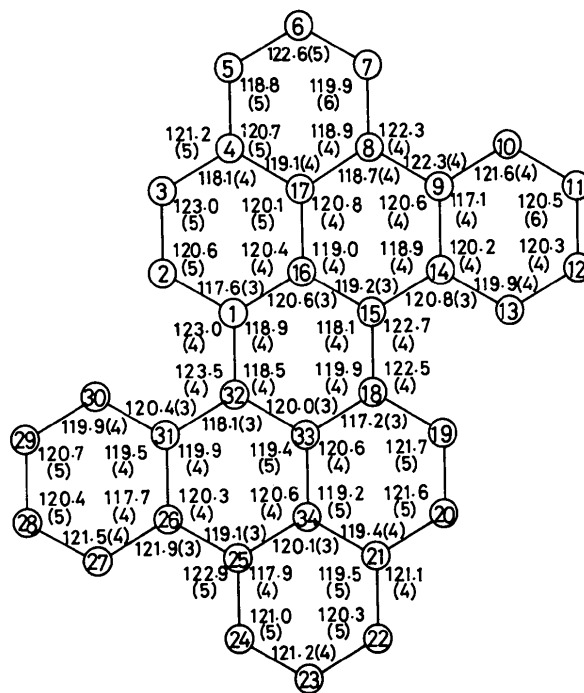

Fig. 3. Bond distances (Å) with their estimated standard deviations.

Fig. 4. Bond angles (°) with their estimated standard deviations.

Broadly speaking, the molecule of TBP consists of two nearly planar benz[de]anthracene skeletons connected to the central ring. Fig. 5 shows deviations of atoms from the mean planes through each benz[de]-anthracene moiety. Plane A is composed of C(1), C(2)$\cdots$C(8), C(16) and C(17) and B is composed of C(18), C(19)$\cdots$C(25), C(33) and C(34). The equations of the mean planes are:

Plane A:
$$-0 \cdot 1079x + 0 \cdot 3194y - 0 \cdot 9415z + 1 \cdot 6773 = 0$$
Plane B:
$$0 \cdot 0792x - 0 \cdot 1688y - 0 \cdot 9825z + 2 \cdot 6391 = 0$$

where x, y and z are coordinates in Å referred to the crystal axes a, b and c, respectively. The deviations of the carbon atoms from the mean planes show that [a,b]naphthalene moieties have a good planar structure and the atoms C(11), C(12), C(28) and C(29) largely deviate from each plane. These two planes make an angle of 30·5°, which is surprisingly large for a polycyclic aromatic hydrocarbon. The absorption spectra of TBP in benzene solution show a maximum at 445 nm, which lies at a rather shorter wavelength region for a condensed aromatic molecule of the composition $C_{34}H_{18}$. It would be interesting to see how the non-planarity of the molecule affects the π-electron conjugation. The π-electronic states of the following molecules, all having the same composition $C_{34}H_{18}$, were calculated by the modified Pariser–Parr–Pople method adopting configuration interactions: TBP, violanthrene A, violanthrene B and diperinaphthyleneanthracene. It turned out that the electronic state of the molecule of TBP is not greatly affected by non-planarity. Accordingly it may be concluded that the short wavelength of the absorption maximum will be ascribed to the characteristic molecular geometry.

There exist a number of overcrowded molecules; however, the crystals of known structure are still small in number. The crystal structures of tetrabenzonaphthalene (Herbstein & Schmidt, 1954b) and 3,4-5,6-dibenzophenanthrene (McIntosh, Robertson & Vand, 1954) have been reported, although the atomic parameters are not accurate enough to warrant a detailed discussion of the molecular geometries. More structural data are needed to enable us to discuss the mechanism of relief from overcrowding in polycyclic aromatic hydrocarbons.
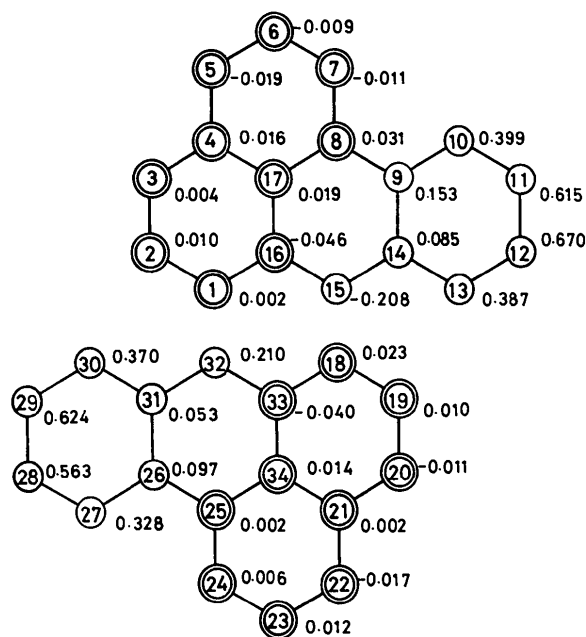
Fig. 5. The two least-squares planes with atomic displacements from each mean plane in Å. The upper is plane A through C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8), C(16) and C(17). The lower is plane B through C(18), C(19), C(20), C(21), C(22), C(23), C(24), C(25), C(33) and C(34).

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