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The Crystal and Molecular Structure of [2_4]Paracyclophanetetraene

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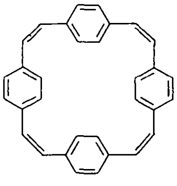
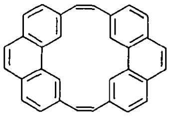
[2_4]Paracyclophanetetraene, $C_{32}H_{24}$, crystallizes in space group *Pcab* with $a = 8{\cdot}251$, $b = 22{\cdot}370$, $c = 25{\cdot}131$ Å, $Z = 8$. The structure was refined to $R = 0{\cdot}054$ for 2076 counter reflections. The molecule has an essentially planar arrangement, although the individual phenyl rings are tilted towards the main molecular plane at angles of 27–40°. The average C—C distance is 1·387 in the phenyl rings, 1·469 in the saturated and 1·312 Å in the unsaturated parts of the bridges. The aromatic character of the phenyl rings is slightly disturbed.

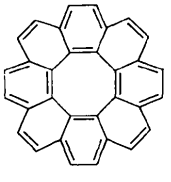
Introduction

Ring compounds in which an aromatic nucleus is part of the ring system are often called cyclophanes or phanes (Vögtle & Neumann, 1970). Smaller cyclophanes have been studied extensively (Cram & Cram, 1971; Vögtle & Neumann, 1972, 1973, 1974; Harper, 1974). Larger cyclophanes and bicyclophanes with bridging double bonds can now be prepared by Wittig reactions at low temperature (Thulin, Wennerström & Högberg, 1975; Thulin, Wennerström, Somfai & Chielarz, 1977; Högberg, Thulin & Wennerström, 1977). Some are potential starting materials for the synthesis of circulenes (Thulin & Wennerström, 1976*a*) and new types of helicenes (Thulin & Wennerström, 1976*b*), others can be regarded as annulenes (Strand, Thulin & Wennerström, 1977). Properly substituted, such cyclophanes may also function as multidentate ligands.

Some questions regarding the structure of [2_4]cyclophanetetraenes and related compounds have arisen during the synthetic work. Can [2_4]cyclophanetetraenes be planar and sustain a ring current over the perimeter, *i.e.* should they be regarded as annulenes? How large is the barrier of inversion of substituted [2_4]cyclophanetetraenes; can they exist as optically stable enantiomers? Why are photochemical ring closures of [2_4]cyclophanetetraenes, *e.g.* (I) to (II), difficult to achieve although the reaction is quite general for open-chain analogues (Mallory, Wood & Gordon, 1964)?


(I)


(II)


(III)

Parallel to the present X-ray determination, a molecular-mechanics calculation of the structures and dynamic energy barriers in [2_4]paracyclophanetetraene (I), [2_2](3,6)phenanthreneophanediene (II), and [8]circulene (III), was performed (Liljefors & Wennerström, 1977).

Experimental

Crystals of (I) (Thulin, Wennerström & Högberg, 1975) were obtained from acetic acid solution as yellow needles up to 10 mm in length. The crystal used for data collection was cut to 0·4 × 0·3 × 0·1 mm and mounted on a Syntex $P2_1$ four-circle diffractometer. The cell dimensions (Table 1) were determined from a least-squares refinement of the 2θ values from 13 reflexions centred on the diffractometer. Graphite-

Table 1. *Crystallographic data for* [2_4]*paracyclophanetetraene*

$C_{32}H_{24}$
$M_r = 408{\cdot}6$
Space group: *Pcab*
Equivalent positions:
$\pm(x,y,z)$, $\pm(\frac{1}{2}+x, \frac{1}{2}-y, z)$,
$\pm(x, \frac{1}{2}+y, \frac{1}{2}-z)$, $\pm(\frac{1}{2}-x, y, \frac{1}{2}+z)$

$a = 8{\cdot}251\ (1)$ Å
$b = 22{\cdot}370\ (4)$
$c = 25{\cdot}131\ (5)$
$V = 4640$ Å^3
$Z = 8$
$D_c = 1{\cdot}17$ g cm^{-3}
μ(Cu $K\alpha$) $= 5{\cdot}23$ cm^{-1}

monochromated Cu *Kα* radiation was used and 3600 independent reflexions were measured out to $2\theta = 115°$. The $\omega/2\theta$ scanning technique was used, and the ω scan speed was varied from 1° min^{-1} for weak reflexions up to 6° min^{-1} for strong reflexions. A standard reflexion, measured at intervals of 20 reflexions, did not show any significant variations.

The background and integrated intensity were obtained for each reflexion from a Lehmann & Larsen (1974) profile analysis (program *LELA*; Lindqvist & Ljungström, 1978). Those 2076 reflexions for which $I/\sigma(I) > 3{\cdot}0$ were regarded as observed. The intensities were corrected for Lorentz and polarization effects with a local program. No correction was performed for absorption or extinction.

Structure determination

The systematic absences uniquely indicated the space group *Pcab*. The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971). The 500 strongest reflexions, which had $E \geq 1{\cdot}15$, were used for sign determination with the Σ_2 relationship. The basis set consisted of seven reflexions: one determined by the Σ_1 formula, three for definition of origin, and three being varied in the *MULTAN* procedure. The *E* maps based on the set with the best figures of merit revealed all 32 atoms. The positions of the H atoms were obtained from geometrical calculations, and were included in the refinement. 385 parameters (atomic coordinates, anisotropic C and isotropic H temperature factors) were refined with the block-diagonal-approximation least-squares program *BLOCK* (Lindgren, 1977). The final *R* was 0·054;* the atomic coordinates are listed in Tables 2 and 3. Scattering factors due to Doyle & Turner (1968) were used for C; those for H were taken from Stewart, Davidson & Simpson (1965). The observations were given weights $w = [\sigma^2(F) + 0{\cdot}0008|F|^2]^{-1}$.

Table 2. *Atomic coordinates* ($\times 10^5$)

	x	*y*	*z*
C(1)	16352 (46)	52880 (14)	96234 (14)
C(2)	16107 (53)	47429 (16)	93010 (17)
C(3)	12812 (50)	46576 (15)	87957 (17)
C(4)	10156 (47)	50739 (15)	83599 (15)
C(5)	−648 (53)	49451 (15)	79544 (17)
C(6)	19306 (41)	56082 (13)	82916 (13)
C(7)	−2812 (50)	53013 (16)	75248 (16)
C(8)	17161 (42)	59691 (15)	78609 (13)
C(9)	5926 (45)	58363 (17)	74569 (14)
C(10)	3929 (52)	61924 (19)	69712 (14)
C(11)	4439 (52)	67731 (20)	68872 (13)
C(12)	5999 (44)	72907 (17)	72538 (12)
C(13)	11823 (48)	78241 (17)	70540 (13)
C(14)	1173 (41)	72830 (15)	77909 (11)
C(15)	13548 (47)	83133 (17)	73730 (14)
C(16)	2988 (40)	77729 (13)	81094 (11)
C(17)	9816 (39)	83087 (14)	79165 (12)
C(18)	12368 (44)	88453 (14)	82381 (14)
C(19)	13965 (42)	89220 (13)	87522 (14)
C(20)	14665 (38)	84983 (13)	92029 (12)
C(21)	7854 (44)	86587 (13)	96908 (14)
C(22)	22754 (39)	79465 (13)	91816 (11)
C(23)	8782 (46)	82917 (15)	101237 (13)
C(24)	23475 (41)	75795 (13)	96173 (10)
C(25)	16331 (41)	77364 (14)	101024 (11)
C(26)	16722 (48)	73750 (17)	105931 (12)
C(27)	17278 (49)	67989 (17)	106749 (13)
C(28)	16715 (43)	62871 (14)	103076 (12)
C(29)	24722 (53)	57592 (16)	104397 (14)
C(30)	7841 (42)	62919 (14)	98324 (11)
C(31)	7545 (42)	58060 (14)	94988 (12)
C(32)	24599 (53)	52880 (15)	101057 (16)

Discussion of the structure

Bond distances and angles, calculated with *DISTAN* (A. Zalkin, Berkeley, California), are shown in Figs. 1 and 2 and in Table 4. The values in Figs. 1 and 2 are not corrected for thermal motion. A **TLS** rigid-body-motion analysis (Schomaker & Trueblood, 1968) resulted in an overall expansion of the molecule corresponding to a lengthening of 0·004 Å of all C—C bonds. The effect is not significant for individual bonds.

Table 3. H *Atom coordinates* ($\times 10^3$) *and isotropic temperature factors*

The atoms are numbered according to the C atoms to which they are bonded.

	x	*y*	*z*	*B* (Å^2)
H(2)	189 (5)	438 (1)	954 (1)	10·6 (11)
H(3)	115 (4)	423 (1)	864 (1)	10·2 (11)
H(5)	−68 (4)	453 (1)	806 (1)	11·8 (10)
H(6)	267 (4)	574 (1)	855 (1)	5·8 (8)
H(7)	−95 (4)	531 (1)	722 (1)	11·5 (9)
H(8)	239 (3)	631 (1)	781 (1)	7·4 (7)
H(10)	8 (5)	585 (2)	671 (1)	12·8 (13)
H(11)	42 (4)	700 (1)	653 (1)	9·1 (11)
H(13)	149 (5)	779 (1)	665 (1)	12·0 (13)
H(14)	−36 (3)	692 (1)	792 (1)	6·7 (7)
H(15)	182 (3)	873 (1)	726 (1)	7·8 (8)
H(16)	−14 (3)	777 (1)	848 (1)	4·8 (7)
H(18)	133 (3)	920 (1)	802 (1)	7·7 (8)
H(19)	143 (3)	933 (1)	887 (1)	10·3 (9)
H(21)	24 (4)	904 (1)	971 (1)	7·5 (8)
H(22)	285 (3)	784 (1)	882 (1)	6·3 (6)
H(23)	35 (3)	842 (1)	1046 (1)	7·6 (8)
H(24)	295 (3)	721 (1)	959 (1)	5·0 (7)
H(26)	156 (3)	762 (1)	1091 (1)	9·4 (9)
H(27)	180 (4)	666 (1)	1111 (1)	12·9 (9)
H(29)	298 (4)	581 (1)	1084 (1)	10·8 (10)
H(30)	9 (3)	666 (1)	974 (1)	6·7 (7)
H(31)	13 (3)	581 (1)	915 (1)	6·1 (6)
H(32)	310 (4)	491 (1)	1022 (1)	11·5 (11)

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33300 (22 pp.). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

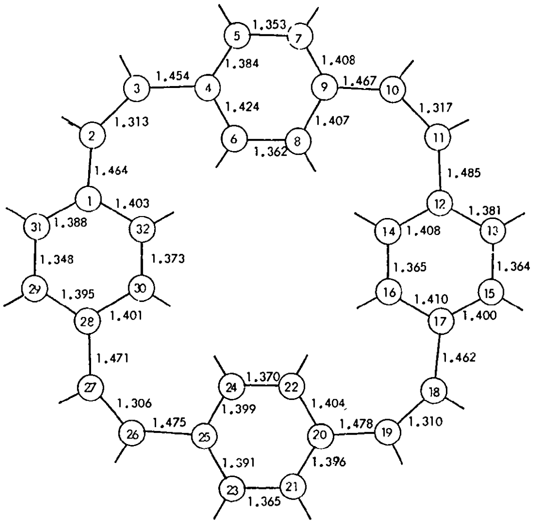

Fig. 1. Bond lengths for [2_4]paracyclophanetetraene. E.s.d.'s are 0·005 Å. The values are not corrected for thermal motion.

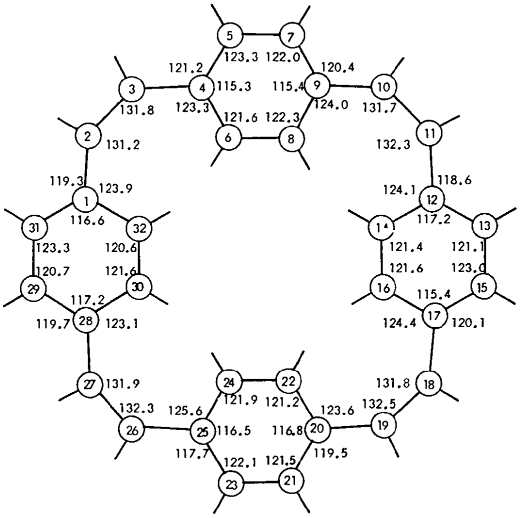

Fig. 2. Bond angles for [2_4]paracyclophanetetraene. E.s.d.'s are 0·3°. The values are not corrected for thermal motion.

Table 4. C—H *bond lengths* (Å)

C(2)–H(2)	1·02 (3)	C(18)–H(18)	0·96 (3)
C(3)–H(3)	1·03 (3)	C(19)–H(19)	0·96 (3)
C(5)–H(5)	1·08 (3)	C(21)–H(21)	0·97 (3)
C(6)–H(6)	0·93 (3)	C(22)–H(22)	1·05 (2)
C(7)–H(7)	0·94 (3)	C(23)–H(23)	0·99 (3)
C(8)–H(8)	0·96 (2)	C(24)–H(24)	0·96 (2)
C(10)–H(10)	1·03 (4)	C(26)–H(26)	0·97 (3)
C(11)–H(11)	1·02 (3)	C(27)–H(27)	1·15 (3)
C(13)–H(13)	1·04 (4)	C(29)–H(29)	1·09 (3)
C(14)–H(14)	0·96 (2)	C(30)–H(30)	1·03 (3)
C(15)–H(15)	1·04 (3)	C(31)–H(31)	1·03 (3)
C(16)–H(16)	1·00 (2)	C(32)–H(32)	1·01 (3)

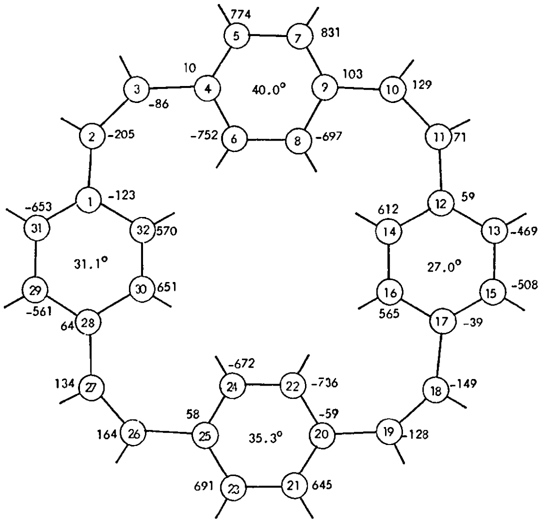

Fig. 4. Distances (Å × 10^4) from the best least-squares plane through C(1)–C(4), C(9)–C(12), C(17)–C(20) and C(25)–C(28). The angles between this plane and the best least-squares plane through each of the four phenyl rings are also indicated. The orientation of the molecule is the same as in Figs. 1 and 2.

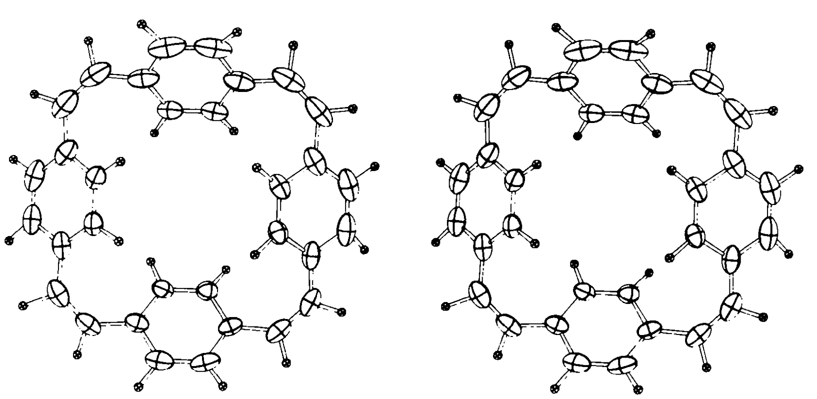

Fig. 3. Stereoscopic view of the [2_4]paracyclophanetetraene molecule. The C atoms are represented by thermal ellipsoids scaled to include 30% probability. The H atoms are represented by spheres of 0·1 Å radius. The orientation is the same as in Figs. 1 and 2.

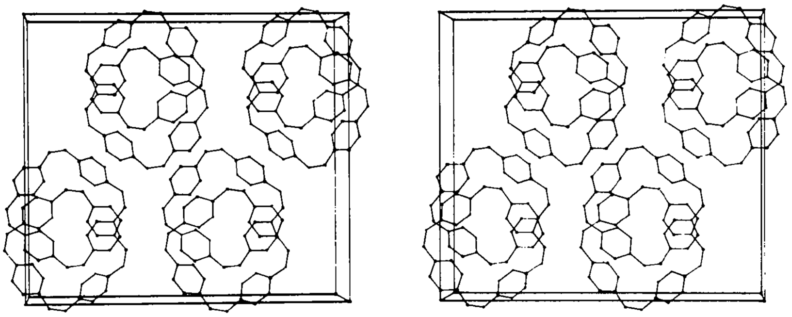

Fig. 5. The molecular packing seen along **a**.

A stereoscopic drawing of the molecule (*ORTEP*, Johnson, 1965) is shown in Fig. 3. The equation describing the best plane through the molecule (Fig. 4) is $0{\cdot}99310X - 0{\cdot}00685Y - 0{\cdot}11705Z = -1{\cdot}69449$ (Cartesian coordinates). This plane is nearly perpendicular to **a**, and the molecules are stacked on top of each other (Fig. 5) to form rods along **a**. This corresponds well to the high rate of crystal growth in this direction.

The skeleton of (I) is unexpectedly planar (Fig. 4), the largest deviation from the best plane being only 0·2 Å. The benzene rings are tilted *ca* 35° from this plane. In solution they move freely, already at −60° on the NMR time scale, *i.e.* internal and external H atoms are equivalent. The relatively planar structure requires a considerable increase in the inner bond angles at C atoms 2, 3, 10, 11, 18, 19, 26 and 27 to an average of 131·9° (Fig. 2).

The driving force for the flattening of the molecule could come from either increased resonance or from steric interactions. Resonance effects, *i.e.* delocalization of the π-electrons over the whole molecule, should be small because a completely conjugated perimeter does not fulfil the Hückel condition for aromaticity ($4n + 2$ π-electrons). Instead, in the originally expected tub form, steric interactions between the internal H and C atoms probably cause the deformation of bond angles into the actual planar structure. This assumption is supported by a molecular-mechanics calculation (Liljefors & Wennerström, 1977). The same type of steric interactions should increase the activation energy for the stilbene–dehydrophenanthrene photocyclization. The average distance between the C atoms which are bonded to each other in the dehydrophenanthrene intermediate is 3·2 Å which is the same as in *cis*-stilbene (Trætteberg & Frantsen, 1975). Along the reaction routes for the photocyclizations, these distances must decrease, which causes increased steric interactions in the cyclophane and thus prevents its photocyclization.

A consequence of the relatively planar structure is that substituted derivatives having D_2 symmetry can easily invert. Thus, stable optically active [2_4]paracyclophanetetraenes should be difficult to isolate.

The steric interaction between the inner H atoms prevents the compound from attaining a completely planar conformation. If the number of internal H atoms is reduced, *e.g.* by use of hetero-aromatic derivatives in the Wittig reaction, the steric conditions for a planar conformation are more favourable. [2_4]Thiophenophanetetraene could be planar and thus regarded as a [24]annulene. UV and NMR spectra support this assumption (Strand, Thulin & Wennerström, 1977).

The structure of (I) shows some anomalies which are not reproduced by the molecular-mechanics calculation. The bridging double bonds are very short (average 1·312 Å) as are two of the opposite bonds in the benzene rings (average 1·363 Å) (Fig. 1). All bonds have been individually determined without the use of any molecular symmetry. We have at present no explanation for these anomalies, nor is there any spectroscopic indication of unusually short double or aromatic bonds.

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The Crystal and Molecular Structure of Apterin $C_{20}H_{24}O_{10}.H_2O$ (Vaginidiol Monoglucoside), 8-[2-(Glucosyloxy)isopropyl]-9-hydroxy-8,9-dihydroangelicin

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The structure of the monohydrate of the title compound has been determined from diffractometer data. The crystals are orthorhombic, space group $P2_12_12_1$, $Z = 4$, with $a = 8{\cdot}0438$ (13), $b = 10{\cdot}0211$ (19), $c = 25{\cdot}513$ (6) Å. The structure was solved with *MULTAN* and refined by the full-matrix least-squares method to a final R value of 0·054 for 1702 observed reflections. The bonding of the sugar molecule to the aglycone is similar to the arrangement found in cellobiose. The anomeric O atom of the sugar molecule forms the glycosidic bond, and the hetero-atom of the pyranose ring is acceptor of an intramolecular hydrogen bond from the hydroxy group of the dihydrofuran ring of the aglycone. The coumarin nucleus is almost planar, the dihydrofuran ring has a half-chair conformation, but three of the ring atoms are coplanar with the coumarin moiety, and this leads to pronounced shortening of C(13)—O(7), 1·355 (5) Å. The dimensions of the coumarin moiety and the β-glucose molecule are close to normal values. All the hydroxy groups of the sugar and the water molecule are engaged in hydrogen bonds with distances from 2·718 (5) to 2·933 (5) Å.

Introduction

The coumarin nucleus is the basis of various compounds possessing important pharmacological and physiological activities (Schofield, 1922). Plant extracts containing coumarins as main constituents have been applied against gastrointestinal diseases, typhus and paralysis (Butenandt & Marten, 1932), for the therapy of leucoderma (Jois, Manjunath & Rao, 1933; Stahman, Hubner & Link, 1941), as anticoagulants (Danek, 1964; Garden, Hayes & Thomson, 1956), and recently against psoriasis. The coumarin nucleus can also exert toxic effects. Photosensitization contact dermatitis is often caused by plants containing compounds related to furanocoumarins. After exposure to the appropriate furanocoumarin in the plant, followed by exposure to ultraviolet radiation, the characteristic sunburn-like rash develops. After healing, a white atrophic area remains on the skin for months or even years. For example, contact with *Heracleum mantegazzianum* leaves produces an erythematous blush within 24 h and a blister by 48 h.

Most interest has, however, been focused on the less polar furanocoumarins. Biochemical investigation of the formation of the furanocoumarins has likewise mainly been concerned with coumarins like xanthotoxin (methoxypsoralene) and pimpinellin, *i.e.* the less polar furanocoumarins.