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The Crystal Structure of [2.2.2](1,3,5)Cyclophane-1,9,17-triene

BY A. W. HANSON AND M. RÖHRL*

Biochemistry Laboratory, National Research Council of Canada, Ottawa, Canada K1A 0R6

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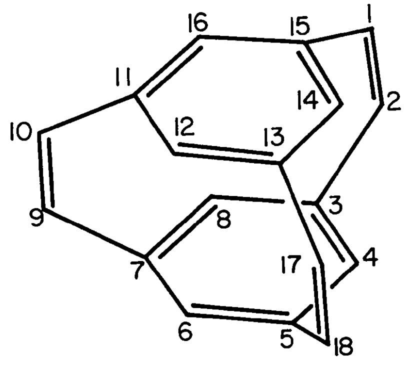
Crystals of the title compound, $C_{18}H_{12}$, are triclinic $P\overline{1}$, with $a=7{\cdot}332\,(5)$, $b=11{\cdot}663\,(10)$, $c=7{\cdot}224\,(5)$ Å, $\alpha=87{\cdot}73\,(5)$, $\beta=100{\cdot}24\,(5)$, $\gamma=105{\cdot}52\,(5)°$, $Z=2$. 1708 of a possible 1988 independent reflexions in the range $\sin\theta/\lambda \leq 0{\cdot}59$ were observed and measured diffractometrically. The crystal structure was determined by symbolic addition procedures, and refined by block-diagonal least-squares methods to a final R index of 0·043. The molecule has non-crystallographic $\overline{6}m2$ symmetry. The distance between the phenyl ring planes is 2·809 Å; each ring is chair-shaped, with the atoms lying 0·024 Å above or below the mean plane. The mean length of the bridging double bonds is 1·340 (4) Å.

Introduction

The title compound (I) is one of a number of cyclophanes prepared by Professor Boekelheide and his associates. Many of these compounds are highly strained and (I) appears to be more so than most (Boekelheide & Hollins, 1970). The crystal structure analysis was undertaken in order to study the distribution of strain.



(I)

* National Research Council of Canada postdoctorate fellow. Present address: Süddeutsche Kalkstickstoffwerke AG, 8223 Trostberg, West Germany.

Experimental details

Crystal data: F.W. 228·3, $V=586$ Å^3, $D_m=1{\cdot}29$ (by flotation), $D_x=1{\cdot}29$ g.cm^{-3}, $Z=2$, $\mu=5{\cdot}3$ cm^{-1} (Cu $K\alpha$). The wavelength assumed for Cu $K\alpha_1$ was 1·54050 Å.

The crystal system was deduced from precession and Weissenberg photographs. The space group $P\overline{1}$ is consistent with the structure analysis.

The crystals supplied were well formed and transparent. Most were of tabular habit, but some were approximately equidimensional. The specimen used for unit-cell and intensity measurements was of dimensions $0{\cdot}3\times0{\cdot}2\times0{\cdot}2$ mm. All measurements were carried out with a four-circle diffractometer and scintillation counter, using nickel-filtered Cu $K\alpha$ radiation with pulse-height discrimination. The intensities were measured in the θ–2θ scan mode (scans of 2° for $2\theta<100°$, 3° otherwise), with background counts recorded at the beginning and end of each scan. Reflexions were considered to be unobserved if their net counts were less than 4 (deca-)counts or 0·1 times the corresponding background count. It was observed that on exposure to air and X-rays the transparent crystal became opaque. No accompanying systematic changes were observed in the intensity of a standard reflexion, which was monitored during the measurement of intensity data. However, many months later the specimen was found to have lost virtually all diffracting power. (The remainder of the material, stored in a refrigerator, showed no signs of deterioration.) In the range explored ($2\theta < 130°$), 1708 of a possible 1988 reflexions were observed. Absorption corrections were considered to be unnecessary, and were not applied.

Structure determination

The approximate structure was readily deduced by symbolic addition procedures, using the program of Ahmed, Hall, Pippy & Huber (1966). The structure was then refined by block-diagonal least-squares methods, using the program of Ahmed *et al.* (1966). This program minimizes $\sum w\Delta f^2$. The weighting scheme, chosen to ensure reasonable constancy of $w\Delta f^2$ with F_o and $\sin^2\theta$, was $w = w_1 w_2$, where

$$
\begin{aligned}
w_1 &= F_o/4 \text{ for } F_o \le 4\\
&= 4/F_o \text{ for } F_o > 4\\
w_2 &= 4{\cdot}05 \sin^2\theta \text{ for } \sin^2\theta < 0{\cdot}2466\\
&= 1 \qquad \text{for } \sin^2\theta \ge 0{\cdot}2466.
\end{aligned}
$$

(The nominal threshold value of F_o is 0·6.)

The scattering factor curve used for carbon was that of Hanson, Herman, Lea & Skillman (1964), and for hydrogen, that of Stewart, Davidson & Simpson (1965). The temperature factors of the carbon atoms were allowed to vary anisotropically, while those of the hydrogen atoms (initially located in a difference Fourier synthesis) were assumed to be isotropic. During the refinement it became apparent that the strongest reflexions were suffering slightly from extinction and these were corrected by using the empirical method of Pinnock, Taylor & Lipson (1956). The structure amplitudes of 17 reflexions were thereby increased by amounts not exceeding 10%. In addition, some 31 weak reflexions, for which the calculated structure amplitudes were persistently below the estimated threshold, were arbitrarily assigned zero weight. The final parameters are given in Table 1. In the final cycle no parameter shift exceeded 28% of the corresponding e.s.d.

Assessment of analysis

The agreement between observed and calculated structure amplitudes (Table 2) is satisfactory, and there can be no doubt about the correctness of the proposed structure. The final R index ($R = \sum|\Delta F|/\sum|F_o|$) is 0·043, for observed reflexions only. The final difference map is satisfactorily featureless, with the residual electron density lying between the limits $\pm 0{\cdot}2$ e.Å^{-3}. The

Table 1. *Final atomic parameters with their e.s.d.'s*

Quantities given are: fractional coordinates ($\times 10^5$) for carbon, ($\times 10^3$) for hydrogen atoms [equivalent positions $\pm(x,y,z)$]; U_{ij} ($\times 10^4$) Å^2 for carbon atoms $\{T.F. = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \ldots + 2U_{12}a^*b^*hk + \ldots)]\}$; r.m.s. displacements D_i along principal axes of vibration ellipsoids, in Å ($\times 10^2$); isotropic Debye–Waller factors for hydrogen atoms, in Å^2.

	X	Y	Z	U11	U12	U13	U22	U23	U33
C(1)	5854(25)	34501(17)	13350(31)	570(10)	314(9)	182(9)	757(12)	311(10)	1029(14)
C(2)	17855(28)	36171(19)	876(30)	690(11)	276(10)	162(10)	896(13)	445(11)	869(13)
C(3)	34511(24)	30724(17)	4955(23)	577(9)	-190(9)	253(8)	887(12)	292(8)	552(9)
C(4)	50123(23)	36195(15)	18505(25)	530(9)	110(8)	309(8)	691(10)	197(8)	741(11)
C(5)	60742(20)	29551(15)	30130(24)	369(7)	83(7)	210(7)	670(10)	62(8)	712(10)
C(6)	56623(20)	17399(15)	26560(22)	411(8)	226(7)	157(7)	752(10)	-11(8)	600(9)
C(7)	40976(21)	11617(16)	13282(21)	494(8)	252(8)	161(7)	815(10)	-88(7)	479(8)
C(8)	30751(23)	18548(17)	1886(21)	548(9)	182(9)	171(7)	971(13)	56(8)	420(8)
C(9)	30450(23)	-887(15)	17349(23)	593(9)	242(8)	-20(7)	654(10)	-190(7)	593(9)
C(10)	18487(22)	-2488(13)	29646(23)	535(8)	114(7)	-18(7)	488(8)	-40(7)	599(9)
C(11)	16348(20)	8257(13)	38708(20)	430(7)	76(6)	168(6)	498(8)	74(6)	487(7)
C(12)	30958(21)	13822(13)	52955(20)	552(8)	145(7)	147(6)	538(8)	55(6)	433(7)
C(13)	36031(23)	26077(14)	55551(21)	612(9)	130(7)	192(7)	557(8)	-47(6)	472(8)
C(14)	24680(24)	32581(14)	44849(25)	626(9)	177(7)	330(8)	496(8)	9(7)	765(10)
C(15)	9869(21)	27279(14)	30411(24)	444(8)	222(7)	252(7)	613(9)	123(7)	734(10)
C(16)	5231(20)	15007(14)	28184(21)	384(7)	125(6)	167(6)	625(9)	74(7)	570(9)
C(17)	56846(26)	32093(15)	62288(25)	707(11)	100(8)	10(8)	594(10)	-136(8)	648(10)
C(18)	68853(24)	33760(15)	49977(28)	493(9)	47(7)	22(8)	603(10)	-69(8)	849(12)

ATOM	D1	D2	D3
C(1)	35	25	21
C(2)	37	26	21
C(3)	32	25	18
C(4)	30	26	18
C(5)	27	26	18
C(6)	27	25	18
C(7)	29	23	18
C(8)	31	24	19
C(9)	30	23	21
C(10)	27	23	21
C(11)	24	23	18
C(12)	24	23	20
C(13)	26	24	19
C(14)	30	23	20
C(15)	29	23	18
C(16)	26	23	18
C(17)	28	27	22
C(18)	30	26	21

	X	Y	Z	B
H(1)	-50(3)	381(2)	107(3)	7.7(0.5)
H(2)	158(3)	406(2)	-101(3)	7.4(0.5)
H(4)	515(3)	444(2)	220(3)	5.5(0.4)
H(6)	628(2)	127(1)	358(2)	4.4(0.3)
H(8)	192(2)	145(2)	-60(2)	5.0(0.4)
H(9)	318(3)	-79(2)	112(3)	5.8(0.4)
H(10)	113(2)	-107(1)	324(2)	5.0(0.4)
H(12)	397(2)	94(1)	589(2)	4.5(0.3)
H(14)	288(2)	411(1)	449(2)	5.0(0.4)
H(16)	-38(2)	113(1)	170(2)	4.3(0.3)
H(17)	616(3)	347(2)	751(3)	6.4(0.4)
H(18)	828(3)	374(2)	542(3)	6.3(0.4)

thermal motion of the molecule is appreciable. Rigid-body libration seems a plausible mode of motion, and is reasonably consistent with the appearance of the thermal ellipsoid plot (Fig. 1). A rigid-body analysis was therefore undertaken, using the procedure of Schomaker & Trueblood (1968). The results, summarized in Table 3, are consistent with rigid-body motion. However, the unique centre of libration lies not at the centroid of the molecule, but about 0·7 Å from it. There is no obvious reason why the unique centre should, or should not, occupy this position. Appropriate corrections, ranging from 0·003 to 0·006 Å, have been applied to the bond lengths.

The non-crystallographic symmetry ($\bar{6}m2$) of the molecule permits independent evaluation of the accuracy of the analysis. Thus there are 3, 6 and 12 measures of the double, single, and aromatic C–C distances respectively. If each bond length is compared with its mean value, the standard deviation is found to be 0·0035 Å. The nominal e.s.d. (ranging from 0·0021 to 0·0027 Å) for distances is therefore seen to be slightly underestimated. If the value of 0·0035 Å is accepted,

Table 2. *Observed and calculated structure amplitudes* (× 10)

An asterisk denotes the threshold value of an unobserved reflexion. A minus sign preceding $10F_o$ means that the reflexion was omitted from the refinement.

L	FO	FC
[illegible]	[illegible]	[illegible]

Table 3. *Rigid-body thermal parameters*

$$\mathbf{T}(\sigma\mathbf{T}) = \begin{bmatrix} 331\,(6) & -15\,(5) & 76\,(5) \\ & 513\,(6) & 60\,(5) \\ & & 431\,(6) \end{bmatrix} \times 10^{-4}\text{Å}^2$$

$$\mathbf{L}(\sigma\mathbf{L}) = \begin{bmatrix} 190\,(5) & 19\,(4) & 52\,(4) \\ & 204\,(6) & 4\,(4) \\ & & 132\,(5) \end{bmatrix} \times 10^{-1}(°)^2$$

Centroid: 0·3307, 0·2223, 0·2886
Centre of libration: 0·3104, 0·1702, 0·3381 } (fractional coordinates)

Principal axes of **T**:

Eigenvalue	Direction cosines		
0·055 Å^2	0·122	0·848	0·515
0·044	0·526	−0·495	0·692
0·028	0·842	0·186	−0·506

Principal axes of **L**:

Eigenvalue	Direction cosines		
23·2(°)^2	0·735	0·548	0·400
19·3	0·443	−0·834	0·328
10·2	0·514	−0·064	−0·856

R.m.s. discrepancy between observed and calculated U_{ij} = 0·0017 Å^2

All directions referred to the orthogonal axes for which $x'\|\mathbf{a}$, $y'\|\mathbf{a}\times\mathbf{c}^*$, $z'\|\mathbf{c}^*$

Table 4. *Intramolecular distances and angles*

E.s.d.'s for individual values are: C–C, 0·0035; C–H, 0·02 Å; C–C–C, 0·2; C–C–H, 1·5°.

	Distance (uncorrected)	Distance (corrected for thermal motion)	Mean(σ)
C(1)—C(2)	1·342 Å	1·347 Å	1·340 (4) Å
C(9)—C(10)	1·330	1·335	
C(17)–C(18)	1·333	1·337	
C(1)—C(15)	1·496	1·499	
C(2)—C(3)	1·501	1·505	
C(5)—C(18)	1·499	1·503	1·502 (1)
C(7)—C(9)	1·501	1·504	
C(10)–C(11)	1·493	1·498	
C(13)–C(17)	1·499	1·502	
C(3)—C(4)	1·391	1·397	
C(4)—C(5)	1·397	1·402	
C(5)—C(6)	1·392	1·398	
C(6)—C(7)	1·392	1·398	
C(7)—C(8)	1·395	1·401	
C(8)—C(3)	1·391	1·397	1·397 (1)
C(11)–C(12)	1·385	1·389	
C(12)–C(13)	1·389	1·393	
C(13)–C(14)	1·389	1·394	
C(14)–C(15)	1·392	1·397	
C(15)–C(16)	1·389	1·394	
C(16)–C(11)	1·392	1·398	
C(3)—C(15)	2·746	2·760	
C(5)—C(13)	2·748	2·760	2·759
C(7)—C(11)	2·744	2·758	
C(4)—C(14)	2·839	2·852	
C(6)—C(12)	2·854	2·868	2·859
C(8)—C(16)	2·841	2·856	
C——H	0·94 to 0·99		0·97

	Angle	Mean
C(1)—C(15)–C(14)	118·2°	
C(1)—C(15)–C(16)	117·6	
C(2)—C(3)—C(4)	117·9	
C(2)—C(3)—C(8)	117·6	
C(9)—C(7)—C(6)	117·8	
C(9)—C(7)—C(8)	118·0	117·9°
C(10)–C(11)–C(12)	117·6	
C(10)–C(11)–C(16)	118·1	
C(17)–C(13)–C(12)	117·4	
C(17)–C(13)–C(14)	118·5	
C(18)–C(5)—C(4)	118·3	
C(18)–C(5)—C(6)	117·4	
C(3)—C(4)—C(5)	121·3	
C(5)—C(6)—C(7)	121·6	
C(7)—C(8)—C(3)	121·5	121·4
C(11)–C(12)–C(13)	121·5	
C(13)–C(14)–C(15)	121·4	
C(15)—C(16)–C(11)	121·1	
C(4)—C(5)—C(6)	118·3	
C(6)—C(7)—C(8)	118·1	
C(8)—C(3)—C(4)	118·5	118·4
C(12)–C(13)–C(14)	118·3	
C(14)–C(15)–C(16)	118·4	
C(16)–C(11)–C(12)	118·6	
C(1)—C(2)—C(3)	118·0	
C(2)—C(1)—C(15)	117·9	
C(7)—C(9)—C(10)	118·2	118·1
C(9)—C(10)–C(11)	118·2	
C(5)—C(18)–C(17)	118·0	
C(13)–C(17)–C(18)	118·3	
C–C–H (Aromatic)	116 to 120°	118·3
C=C–H	118 to 121	119·4
C–C–H	121 to 124	122·5

differences between extreme values for a given bond type are not significant. This is true both before and after the corrections for thermal motion.

Discussion

Details of the molecular structure are summarized in Tables 4 and 5, and in Fig. 1 and 2. The molecule has fairly exact $\bar{6}m2$ symmetry, the phenyl rings eclipsing each other with a mean interplanar spacing of 2·809 Å. The bond distances are all close to their normal values, but strain is evident in the angles. The observed conformation is the result of a compromise between conflicting structural desiderata, chief among which must be the need to preserve a reasonable distance between the phenyl rings. One consequence is that the single bonds of the bridges are severely bent out of the ring planes; the average angle between a single bond and the plane of the three nearest phenyl-ring atoms is 24·2°. The phenyl rings themselves are puckered, or chair-shaped, with successive atoms lying 0·024 Å above and below the mean plane. [Alternative descriptions of the ring deformation are: opposite atoms lie 0·073 Å above and below the plane of the remaining four; the dihedral angle between planes defining the back and the seat of the chair is 6·1 (3)°; the torsion angles of the aromatic bonds, defined by the ring atoms only, are ±7·0 (4)°.]

The rather short intramolecular inter-ring contacts, shown in Fig. 2, are maintained by tension in the bridging double bonds. However, there is no indication that these bonds are in any way stretched, since the mean length of 1·340 (4) Å does not differ significantly from the nominal value of 1·337 (6) Å (*International Tables for X-ray Crystallography*, 1962). This result is typical of the diolefins of [2·2]cyclophanes, for which no significantly stretched double bonds have yet been observed (Hanson & Röhrl, 1972). In contrast, comparable stresses in [2·2]cyclophanes are frequently observed to stretch the sp^3–sp^3 single bonds to 1·57–1·59 Å (Hanson, 1962; Hanson & Huml, 1971; Hope, Bernstein & Trueblood, 1972).

As illustrated in Fig. 2, the phenyl-ring hydrogen atoms are displaced from positions of coplanarity with the three nearest carbon atoms. The displacements range from 0·22 to 0·24 Å, and are all towards the other phenyl ring. Corresponding (but generally smaller) displacements have been observed for other cyclophanes; as explained elsewhere, the phenomenon can

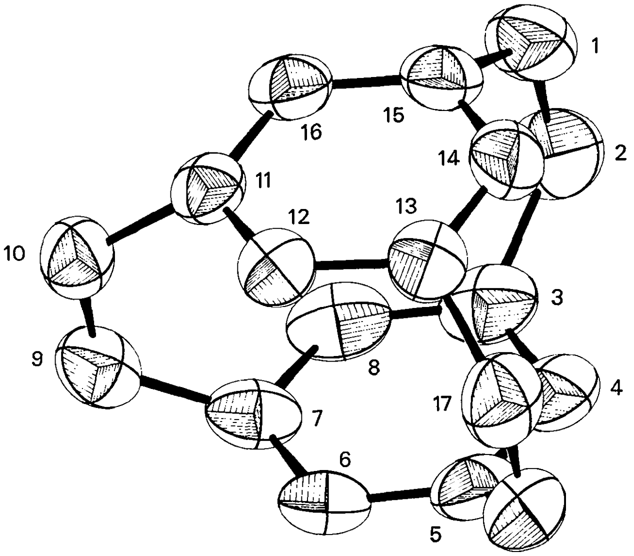


Fig. 1. The thermal ellipsoids of 50% probability.

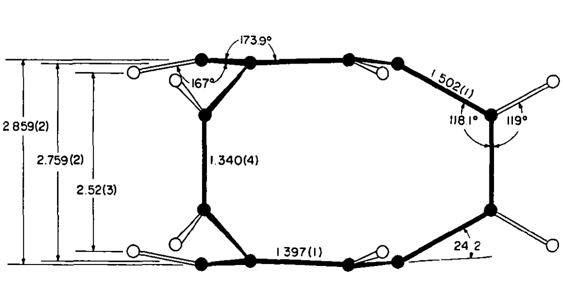


Fig. 2. An idealized molecule viewed normal to one of the mirror planes. Carbon atoms are shown as solid, and hydrogen atoms as open circles.

Table 5. *Distances* ($\times 10^3$ Å) *of atoms from various mean planes of the phenyl rings*

Each line gives the distances of the atoms from a specific plane. Bold type identifies the atoms used to define the plane.

C(3)	C(4)	C(5)	C(6)	C(7)	C(8)
−20	**20**	**−24**	**28**	**−28**	**24**
2	67	**−2**	**2**	−80	**−2**
3	**−3**	−75	**3**	**−3**	72
−68	**−1**	**1**	79	**−1**	**1**
C(11)	C(12)	C(13)	C(14)	C(15)	C(16)
24	**−25**	**25**	**−24**	**23**	**−23**
74	**0**	**0**	−73	**0**	**0**
0	**0**	76	**0**	**0**	−72
0	−74	**0**	**0**	73	**0**

be rationalized in terms of the resistance to twisting of the aromatic bonds (Hanson & Röhrl, 1972).

Intermolecular contacts are normal, the shortest (between hydrogen atoms) being 2·56 Å.

Computer programs used in this work are those of Ahmed, Hall, Pippy & Huber (1966), Gantzel & Trueblood (*MGTLS*, thermal motion analysis) and C. K. Johnson (*ORTEP*, thermal ellipsoid plot). The problem was suggested, and the specimen material supplied, by Professor V. Boekelheide.

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