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The Crystal Structures of [2.2.2.2](1,2,4,5)Cyclophane and its Birch Reduction Product*

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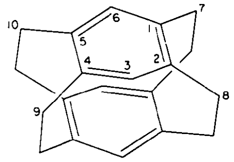
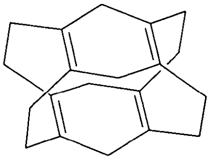
Crystals of [2.2.2.2](1,2,4,5)cyclophane (I), $C_{20}H_{20}$, are monoclinic, $P2_1/c$, $a = 8{\cdot}787\ (9)$, $b = 10{\cdot}91\ (1)$, $c = 7{\cdot}619\ (8)$ Å, $\beta = 115{\cdot}6\ (1)^\circ$ (20°C), FW 260·4, $D_m = 1{\cdot}310$, $Z = 2$, $D_x = 1{\cdot}312$ g cm^{-3}. Molecular symmetry: centre. Crystals of the Birch reduction product [(II), $C_{20}H_{24}$] of (I) are triclinic, $P\bar{1}$, $a = 7{\cdot}464\ (7)$, $b = 16{\cdot}147\ (16)$, $c = 7{\cdot}292\ (7)$ Å, $\alpha = 109{\cdot}1\ (1)$, $\beta = 69{\cdot}1\ (1)$, $\gamma = 117{\cdot}4\ (1)^\circ$ (20°C). FW 264·4, $D_m = 1{\cdot}227$, $Z = 2$, $D_x = 1{\cdot}229$ g cm^{-3}. Molecular symmetry: centre for each of two independent molecules. The crystal structures have been established by block-diagonal least-squares analysis of diffractometrically measured intensities. Final R indices are 0·033 (964 observed reflexions) for (I), and 0·068 (2316 observed reflexions) for (II). In addition to crystallographic inversion symmetry, each molecule has non-crystallographic *mm*2 symmetry. (I) is highly strained, with the aromatic six-membered rings distorted to the boat form, and the four bridging bonds stretched to 1·591 (2) Å. (II) is much less strained; the six-membered ring is boat-shaped also, but this is a stable conformation for the bond distribution, and the length of the bridging bonds is 1·519 (4) Å.

Introduction

Gray & Boekelheide (1975) have synthesized the title compound, and have predicted that, because of transannular interactions, the aromatic rings will be boat-shaped. Lindner (1976) has since calculated strain energies and geometries of this and other cyclophanes, with results which support and broaden the prediction. In addition, Boekelheide (1975) and associates have prepared compound II [the Birch reduction product of (I)]. It was expected that this compound would have a similar shape to (I), but because the boat conformation is natural to the six-membered ring (1,4-cyclohexadiene), the strain should be somewhat reduced. The crystal-structure analyses of (I) and (II) were undertaken in order to test these predictions.



(I)



(II)

Experimental

Crystals of (I) were colourless plates (100), with prominent faces (011). The specimen used for intensity measurements was a diamond-shaped plate of extreme dimensions 0·17 × 0·33 × 0·5 mm. This was mounted about the *b* axis, which corresponded to the longest dimension. The intensities of 1050 independent reflexions within the limiting sphere $2\theta = 125^\circ$ were measured with a Picker four-circle diffractometer, Ni-filtered Cu $K\alpha$ radiation, and a scintillation counter. The θ–2θ scan mode was used, with scans of 2° for $2\theta < 100^\circ$, and 3° otherwise. The scan rate was 2° min^{-1}, and background intensities were measured for 20 s at the end of each scan. 86 reflexions were considered to be unobserved, as their net intensities were less than either 50 counts or 10% of the corresponding background intensity.

Crystals of (II) were clear, colourless parallelepipeds with faces corresponding to those of the unit cell. For the specimen used in intensity measurements the interfacial distances were all about 0·4 mm. Procedures were the same as for (I), except that the limiting sphere was $2\theta = 130^\circ$, and background intensities were accumulated for 10 s. Of the 2429 reflexions scanned, 113 were considered to be unobserved. No correction was made for absorption in either case [$\mu = 6{\cdot}7$ cm^{-1} for (I), 6·3 cm^{-1} for (II)].

Structure determination

The structure of (I) was determined by inspection of the sharpened F_o^2 synthesis, and refined by block-diagonal least squares, minimizing $\Sigma\, w(\Delta F)^2$. The H atoms were assigned chemically reasonable positions and were included in the refinement. A correction for extinction was applied to the 37 most intense reflexions, with the

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Table 1. *Final atomic coordinates* ($\times 10^4$ *for* C *atoms*, $\times 10^3$ for H *atoms*); *e.s.d.'s are given in parentheses*

	x	*y*	*z*
Compound I			
C(1)	1783 (2)	−1206 (1)	1170 (2)
C(2)	1978 (2)	−240 (1)	2468 (2)
C(3)	617 (2)	56 (1)	2865 (2)
C(4)	−998 (2)	−391 (1)	1761 (2)
C(5)	−1188 (2)	−1364 (1)	466 (2)
C(6)	242 (2)	−1817 (1)	346 (2)
C(7)	2948 (2)	−1347 (1)	196 (2)
C(8)	3356 (2)	698 (1)	2905 (2)
C(9)	−2481 (2)	397 (2)	1537 (2)
C(10)	−2881 (2)	−1654 (1)	−1180 (2)
H(3)	77 (2)	77 (1)	373 (2)
H(6)	14 (2)	−247 (2)	−61 (2)
H(7, 1)	414 (2)	−121 (2)	113 (3)
H(7, 2)	286 (2)	−220 (2)	−34 (3)
H(8, 1)	447 (3)	33 (2)	312 (3)
H(8, 2)	352 (2)	117 (2)	411 (3)
H(9, 1)	−222 (2)	88 (2)	274 (3)
H(9, 2)	−342 (3)	−11 (2)	132 (3)
H(10, 1)	−279 (2)	−249 (2)	−170 (3)
H(10, 2)	−379 (2)	−165 (2)	−73 (3)
Compound II, molecule *A*			
C(1)	2815 (3)	66 (1)	3384 (3)
C(2)	2727 (3)	245 (1)	5319 (3)
C(3)	1393 (3)	−547 (2)	6469 (3)
C(4)	−577 (3)	−1189 (1)	5777 (3)
C(5)	−495 (3)	−1366 (1)	3840 (3)
C(6)	1572 (3)	−930 (1)	2446 (3)
C(7)	3795 (4)	834 (2)	2181 (4)
C(8)	3661 (4)	1244 (2)	6444 (5)
C(9)	−2617 (4)	−1459 (2)	7331 (4)
C(10)	−2416 (4)	−1842 (2)	3041 (4)
H(3, 1)	224 (4)	−91 (2)	624 (4)
H(3, 2)	100 (5)	−21 (3)	798 (5)
H(6, 1)	234 (4)	−132 (2)	203 (4)
H(6, 2)	144 (5)	−93 (2)	114 (4)
H(7, 1)	515 (7)	104 (3)	189 (6)
H(7, 2)	405 (8)	57 (4)	63 (7)
H(8, 1)	345 (8)	105 (4)	751 (7)
H(8, 2)	533 (15)	162 (7)	554 (13)
H(9, 1)	−261 (8)	−169 (4)	822 (7)
H(9, 2)	−353 (9)	−217 (4)	689 (8)
H(10, 1)	−331 (7)	−241 (3)	352 (7)
H(10, 2)	−196 (10)	−201 (5)	175 (9)
Compound II, molecule *B*			
C(1)	2399 (3)	4640 (1)	3467 (3)
C(2)	2197 (3)	4775 (1)	5424 (3)
C(3)	2664 (3)	5775 (2)	6620 (3)
C(4)	1918 (3)	6320 (1)	5940 (3)
C(5)	2107 (3)	6181 (1)	3990 (3)
C(6)	3066 (3)	5487 (2)	2588 (3)
C(7)	1667 (4)	3667 (2)	2181 (5)
C(8)	1221 (5)	3978 (2)	6528 (6)
C(9)	661 (4)	6855 (2)	7489 (4)
C(10)	1104 (4)	6556 (2)	3174 (4)
H(3, 1)	199 (4)	573 (2)	802 (4)
H(3, 2)	417 (4)	609 (2)	646 (4)
H(6, 1)	469 (5)	584 (2)	226 (4)
H(6, 2)	266 (5)	530 (2)	126 (5)
H(7, 1)	224 (13)	366 (6)	53 (11)
H(7, 2)	202 (9)	330 (4)	249 (8)
H(8, 1)	138 (13)	422 (6)	768 (12)
H(8, 2)	194 (11)	348 (5)	594 (10)
H(9, 1)	100 (9)	742 (4)	710 (8)
H(9, 2)	101 (9)	706 (4)	873 (8)
H(10, 1)	136 (7)	728 (3)	384 (7)
H(10, 2)	198 (6)	684 (3)	201 (6)

method described by Pinnock, Taylor & Lipson (1956). The largest correction was 18% of $|F_o|$. The weighting scheme used in the final stages was $w = w_1 w_2$, where $w_1 = P_1/|F_o|$ for $|F_o| > P_1$, $= 1$ otherwise, and $w_2 = \sin^2 \theta/P_2$ for $\sin 2\theta < P_2$, $= 1$ otherwise ($P_1 = 4{\cdot}0$, $P_2 = 0{\cdot}44$). With this weighting scheme there was no obvious systematic dependence of the weighted residual on either $|F_o|$ or θ. On termination of refinement R (for observed reflexions only) was 0·033.* On the final cycle the largest coordinate shift of a C atom was 14% of the corresponding e.s.d. of 0·0022 Å. The final ΔF synthesis contained no electron density outside the limits ±0·1 eÅ^{-3}.

The structure of (II) was determined routinely by symbolic addition procedures. The refinement was generally the same as for (I). Extinction effects were found to be more severe, and 85 reflexions were corrected, the largest correction being 15% of $|F_o|$. For the most intense reflexion, 001, $|F_o|$ was only 55% of $|F_c|$; correction was deemed inappropriate, and this reflexion was excluded from the refinement. The weighting scheme was the same as for (I), but with $P_1 = 1{\cdot}5$ and $P_2 = 0{\cdot}4$. The results were less satisfactory than for (I). On termination of refinement R was 0·068,* and there were apparently meaningless coordinate shifts for C atoms of as much as half of the corresponding e.s.d. of 0·002 Å. The final ΔF synthesis contained detail within the limits −0·22 to +0·33 eÅ^{-3}. Some of the residual peaks were well formed, suggesting atomic sites of low weight or occupancy, but were not explicable in terms of the proposed structure. Such anomalies have been observed in studies of similar compounds (Hanson, 1975), and have been attributed (for lack of alternative hypotheses) to the presence of small proportions of other chemical species. It need hardly be said that such a situation would be prejudicial to the reliability of the atomic parameters, particularly of those describing the thermal motion. It is fortunate that the presence of two independent molecules permits some independent evaluation of the accuracy achieved. The final atomic coordinates for both structures are given in Table 1.

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* Lists of structure factors and atomic thermal-motion parameters, and some details of the thermal-motion analysis have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32369 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The thermal motion in both structures has been analysed by the methods of Schomaker & Trueblood (1968), with the assumption that the molecules behave as rigid bodies. For (I) the analysis is quite satisfactory; the r.m.s. discrepancy between observed and calculated U_{ij}'s is 0·0012 Å^2, compared to the nominal e.s.d. of U_{ij}'s of 0·0008 Å^2. The principal r.m.s. amplitudes of translation and libration are 0·25, 0·19, 0·16 Å, and 3·7, 3·1, 2·8°. For (II) the analysis is less satisfactory, perhaps because of the difficulties mentioned above. The r.m.s. discrepancy of the U_{ij}'s is 0.0041 Å^2 for *A*, and 0·0071 Å^2 for *B*, compared to the nominal e.s.d. of 0·0012 Å^2. The principal amplitudes of translation and libration are 0·18, 0·17, 0·16 Å and 6·3, 4·9, 2·8° for *A*, and 0·19, 0·17, 0·16 Å and 7·0, 4·5, 3·1° for *B*. While the analyses do not reveal any very interesting modes of thermal motion, they do permit an estimate of the effect on the apparent atomic positions. The distances in Table 2 have been corrected with the assumption that all atoms ride on the centre of gravity of the molecule (Busing & Levy, 1964). The effect on angles is very small, and corrections to these have not been applied.

The scattering factors for C were taken from Hanson, Herman, Lea & Skillman (1964), and for H from Stewart, Davidson & Simpson (1965). The computer programs used in this work were those of Ahmed, Hall, Pippy & Huber (1966), and Gantzel & Trueblood (*MGTLS*; thermal-motion analysis).

Discussion

The analyses confirm the proposed formulations of (I) and (II). The molecules have fairly precise *mmm* symmetry, and the bond lengths and angles (Table 2) have been averaged appropriately. Except for the bridging bonds of (I), all bond lengths have typical values.

Table 2. *Interatomic distances* (Å) *and valence angles* (°)

Distances have been corrected for thermal motion, with uncorrected values given in round brackets. Values given in square brackets are those calculated by Lindner (1976). E.s.d.'s are: 0·002 to 0·003 Å (0·02 Å for H···H) and 0·14° for (I); 0·003 to 0·004 Å and 0·20° for (II). *X*(*n*′) is related to *X*(*n*) by the inversion centre.

Distances	(I)		(II*A*)			(II*B*)	
C(1)–C(2)	1·409	(1·404)	1·339	(1·327)		1·348	(1·334)
C(4)–C(5)	1·413	(1·409)	1·342	(1·331)		1·343	(1·330)
Mean	1·411	(1·406)			1·343	(1·330)	
	[1·400]						
C(2)–C(3)	1·397	(1·392)	1·515	(1·504)		1·517	(1·507)
C(3)–C(4)	1·393	(1·388)	1·518	(1·508)		1·516	(1·505)
C(5)–C(6)	1·395	(1·390)	1·513	(1·502)		1·523	(1·511)
C(6)–C(1)	1·397	(1·392)	1·518	(1·508)		1·508	(1·498)
Mean	1·395	(1·390)			1·516	(1·505)	
	[1·399]						
C(1)–C(7)	1·514	(1·509)	1·515	(1·504)		1·514	(1·503)
C(2)–C(8)	1·514	(1·509)	1·516	(1·506)		1·503	(1·493)
C(4)–C(9)	1·513	(1·508)	1·519	(1·508)		1·513	(1·501)
C(5)–C(10)	1·513	(1·509)	1·518	(1·508)		1·513	(1·501)
Mean	1·514	(1·509)			1·514	(1·503)	
	[1·540]						
C(7)–C(9′)	1·592	(1·587)	1·519	(1·509)		1·520	(1·507)
C(8)–C(10′)	1·590	(1·586)	1·518	(1·508)		1·520	(1·509)
Mean	1·591	(1·587)			1·519	(1·508)	
	[1·575]						
C–H (range)	(0·95–1·01)				(0·83–1·16)		
(mean)	(1·00)				(0·98)		
C(1)···C(4′)	2·685	(2·677)	2·809	(2·791)		2·817	(2·796)
C(2)···C(5′)	2·692	(2·684)	2·801	(2·783)		2·809	(2·787)
Mean	2·688	(2·681)			2·809	(2·789)	
	[2·615]						
C(3)···C(6′)	2·950	(2·941)	3·709	(3·686)		3·738	(3·710)
Mean	[2·885]				3·724	(3·698)	
H(3)···H(6′)	2·86	(2·85)					
	[2·873]						

Table 2 (*cont.*)

	(I)	(II*A*)		(II*B*)
Angles				
C(6)—C(1)—C(2)	118·4°	118·0°		118·4°
C(1)—C(2)—C(3)	118·2	118·8		117·7
C(3)—C(4)—C(5)	118·0	118·5		118·2
C(4)—C(5)—C(6)	118·5	118·1		117·9
Mean	118·3 [119·4]		118·2	
C(2)—C(3)—C(4)	122·4	111·7		111·8
C(5)—C(6)—C(1)	122·1	111·8		111·7
Mean	122·2 [119·9]		111·8	
C(6)—C(1)—C(7)	117·6	118·2		118·3
C(3)—C(2)—C(8)	118·5	119·1		118·3
C(3)—C(4)—C(9)	118·4	118·6		118·6
C(6)—C(5)—C(10)	117·8	118·2		118·7
Mean	118·1 [117·7]		118·5	
C(2)—C(1)—C(7)	121·4	123·0		122·6
C(1)—C(2)—C(8)	120·4	121·5		123·2
C(5)—C(4)—C(9)	121·0	121·9		122·3
C(4)—C(5)—C(10)	121·1	122·8		122·6
Mean	121·0 [120·8]		122·3	
C(1)—C(7)—C(9′)	110·8	115·4		115·5
C(2)—C(8)—C(10′)	111·4	115·0		116·3
C(4)—C(9)—C(7′)	111·6	115·0		115·2
C(5)—C(10)—C(8′)	111·3	115·0		114·3
Mean	111·3 [109·7]		115·2	

Details of some molecular planes are given in Table 3. (I) shows evidence of considerable strain. The aromatic ring is distorted to a boat form, with prow and stern atoms lying 0·13 Å from the plane of the remaining four. The attached H atoms, however, lie only 0·08 Å from this plane; they are displaced by 0·24 Å from positions of coplanarity with the three nearest C atoms. H(3) and H(6′) (the latter on the opposite ring) are thus closer together than are C(3) and C(6′). This conformation is typical of cyclophanes (Hanson, 1975); it is predicted for this molecule by the calculations of

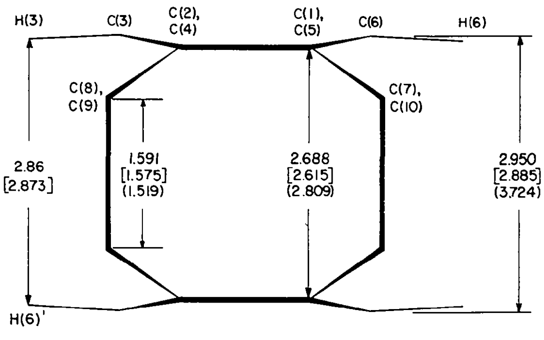

Fig. 1. A view of (I) showing some distances of interest. The first number is the observed value; the second, in square brackets, is the value calculated by Lindner (1976), and the third, in round brackets, is the corresponding value (where applicable) for compound II.

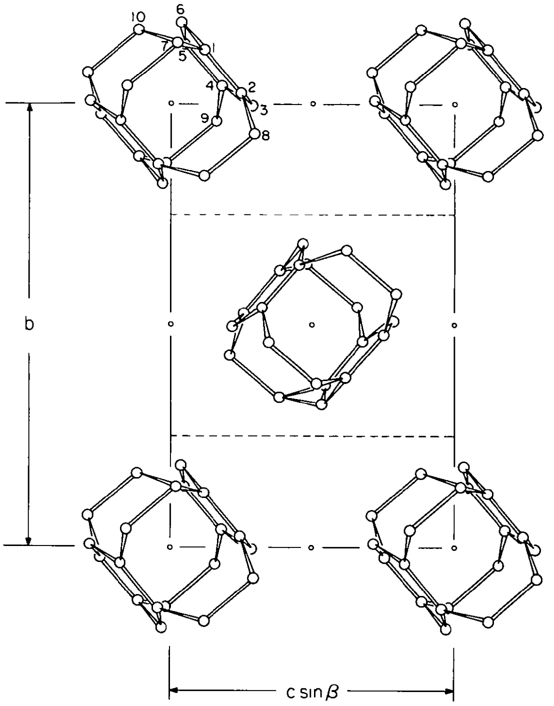

Fig. 2. The structure of (I) viewed along **a**.

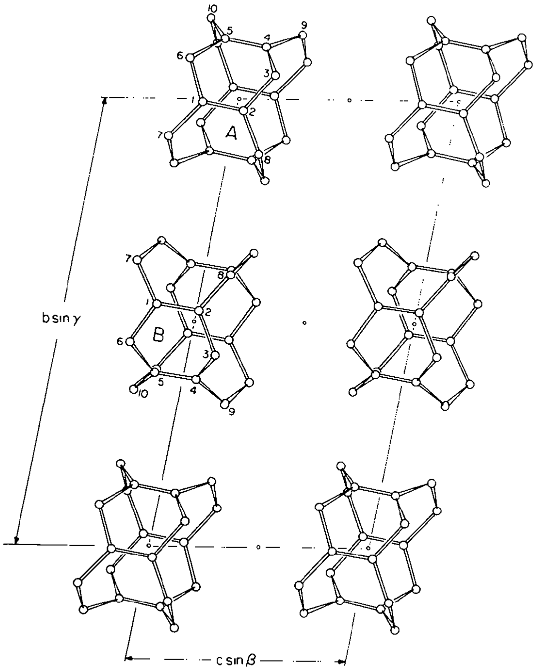

Fig. 3. The structure of (II) viewed along **a**.

Table 3. *Distances* (Å $\times 10^3$) *of some atoms from various mean planes*

Each column gives the distances for a given molecule, and a given plane. An asterisk identifies the atoms used to define the plane.

	Plane 1			Plane 2			Plane 3		
	(I)	(II*A*)	(II*B*)	(I)	(II*A*)	(II*B*)	(I)	(II*A*)	(II*B*)
C(1)	−1*	2*	2*	0*	−1*	1*			
C(2)	1*	−2*	−2*	0*	1*	−1*			
C(3)	133	439	459	0*	0*	0*	1*	−2*	0*
C(4)	−1*	2*	2*				−2*	5*	0*
C(5)	1*	−2*	−2*				2*	−5*	0*
C(6)	127	458	458	0*	0*	0*	−1*	2*	0*
C(7)	−543	−634	−630	−412	−234	−213			
C(8)	−558	−625	−636	−433	−200	−221			
C(9)	−550	−645	−654				−424	−224	−242
C(10)	−536	−654	−647				−406	−255	−229
H(3)	82								
H(6)	81								

Angle 2–3: (I), 12·25°; (II*A*), 39·64°; (II*B*), 40·44°.

Lindner (1976). The aromatic ring is defined by two planes (2 and 3, Table 3) making a dihedral angle of 12·25°. The bridging atoms lie 0·42 Å from these planes. Finally, the bridging bonds are stretched to 1·591 (2) Å. There is little indication of strain for (II). The boat form of the six-membered ring is more pronounced (dihedral angle 40·0°), but this is the natural conformation for the 1,4-cyclohexadiene nucleus. The bridging atoms lie only 0·23 Å from the adjacent dihedral planes, and the bridging bonds, 1·519 (4) Å, do not appear to be stretched. Some intramolecular distances are compared in Fig. 1. The molecular packing is illustrated in Figs. 2 and 3. There appear to be no interactions stronger than van der Waals interactions.

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