

The Crystal Structure of 8,16-Oxido-*cis*[2.2]metacyclophane-1,9-diene

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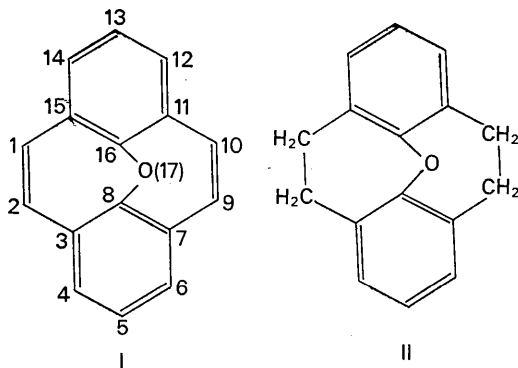
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A crystal structure analysis of 8,16-oxido-*cis*[2.2]metacyclophane-1,9-diene has been carried out at -160°C . The crystal is orthorhombic, *Pbca*, with $a=11.96$, $b=17.13$, $c=10.67$ Å, $Z=8$, formula $\text{C}_{16}\text{H}_{10}\text{O}$. The structure was determined by computer-programmed symbolic addition procedures, and was refined by block-diagonal least-squares to a conventional *R* index of 0.069. Within the limits of experimental error the molecule has *mm* symmetry. It is folded to a dihedral form so that the angle between the six-membered rings is 123.6° . Strain is inferred from the nonplanarity of these rings. The bond angle subtended by the oxygen atom is 99.7° , and the length of the double bond in the C-C bridge is 1.359 Å.

Introduction

8,16-Oxido-*cis*[2.2]metacyclophane-1,9-diene (I) is one of a series of derivatives of *cis* metacyclophane prepared by Professor Boekelheide and his associates (Hess, Bailey & Boekelheide, 1967). A strained configuration has been observed for the related compound II (Mathew & Hanson, 1968). It was expected that the substitution of double for single bonds in the C-C bridges would result in a different degree of strain in the molecule. The X-ray analysis of I was undertaken in order to determine how this difference in strain is distributed over the molecule.



Experimental

Crystal data at -160°C : orthorhombic;

$a=11.96 \pm 0.01$, $b=17.13 \pm 0.02$, $c=10.67 \pm 0.01$ Å

(λ Cu $K\alpha_1=1.54051$ Å, λ Cu $K\alpha_2=1.54433$ Å);

$V=2186$ Å³, formula $\text{C}_{16}\text{H}_{10}\text{O}$, F.W. = 218.2;

$D_m=1.30 \pm 0.01$ g.cm⁻³ (at room temperature), $Z=8$

$D_x=1.326$ g.cm⁻³, $\mu=7.6$ cm⁻¹ (Cu $K\alpha$).

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Space group *Pbca* (D_{2h}^{15}) from precession photographs. Systematic absences $0kl$ for k odd, $h0l$ for l odd, $hk0$ for h odd.

The material supplied consisted of thin colourless plates, normal to **b**, of irregular outline. No crystal of particularly suitable shape could be found; that used had the form of an equilateral triangle 0.3 mm to the side, and was 0.06 mm thick. Decomposition was found to occur over a period of several months, but no change in the measured intensities was detected during the three weeks of data collection.

The cell constants and relative intensities were measured with the General Electric XRD 5 spectrogoniometer and goniostat equipped with a scintillation counter. Copper $K\alpha$ radiation was used, with a $K\beta$ filter and a reverter (pulse height analyser). The θ - 2θ scan method was used, with precomputed settings and manual operation. The specimen was maintained at the working temperature of -160°C by immersion in a stream of cold gaseous nitrogen surrounded by an envelope of dry nitrogen at room temperature. Of the 2429 accessible reflexions (those for which $2\theta \leq 165^\circ$) significant counts were recorded for 1757. The range of observed intensities was about 1 to 5000. Absorption corrections were considered to be unnecessary and were not made.

Structure determination

The structure was determined entirely by the symbolic addition procedures of Karle & Karle (1966) with the revised programs of Ahmed & Hall (Ahmed, Hall, Pippy & Huber, 1966). A Fourier synthesis of 282 *E* values indicated unequivocally the positions of all the non-hydrogen atoms in the structure. Refinement was by block-diagonal least-squares, with the use of the program of Ahmed (Ahmed *et al.*, 1966). The quantity minimized is $\sum w(|F_o| - |F_c|)^2$. The initial weighting scheme was chosen arbitrarily, but that used in the final stages was $w = w_1 w_2$, where

Table 1(a). Parameters and e.s.d.'s for non-hydrogen atoms

$$\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \bar{z}; \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} - x, \bar{y}, \frac{1}{2} + z)$$

$$\text{T.F.} = \exp [-2\pi^2(U_{11}a^*2hz^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + U_{22}b^*k^2 + 2U_{23}b^*c^*kl + U_{33}c^*l^2)]$$

B_i are the equivalent isotropic B values in the directions of the principal axes of the thermal ellipsoids.

	x ($\times 10^5$)	y ($\times 10^5$)	z ($\times 10^5$)	U_{11} ($\text{\AA}^2 \times 10^4$)	U_{12} ($\text{\AA}^2 \times 10^4$)	U_{13} ($\text{\AA}^2 \times 10^4$)	U_{22} ($\text{\AA}^2 \times 10^4$)	U_{23} ($\text{\AA}^2 \times 10^4$)	U_{33} ($\text{\AA}^2 \times 10^4$)	B_1 (\AA^2)	B_2 (\AA^2)	B_3 (\AA^2)
C(1)	-125	12352	26033	180	24	-4	358	86	319	1.38	2.01	3.38
	26	20	34	13	13	12	16	14	17			
C(2)	4237	19119	30353	220	42	68	278	64	360	1.49	1.92	3.36
	26	19	33	14	12	13	15	14	17			
C(3)	13378	19747	39431	242	-46	92	210	26	315	1.11	1.97	2.98
	26	17	31	14	11	13	15	12	16			
C(4)	14144	25502	48651	357	-51	138	241	-53	395	1.75	1.88	4.21
	29	20	36	16	15	15	15	14	19			
C(5)	22002	24762	58152	405	-186	120	320	-92	358	1.36	2.17	5.02
	30	22	36	19	16	15	16	15	18			
C(6)	28664	18233	59364	331	-182	7	446	-8	236	1.56	1.86	4.57
	29	22	32	17	15	14	19	14	15			
C(7)	28234	12252	50276	209	-94	22	334	-1	229	1.21	1.84	3.05
	25	19	29	14	12	12	16	13	14			
C(8)	21483	13864	39905	188	-73	55	233	-28	219	0.99	1.56	2.52
	24	17	28	13	11	11	13	12	14			
C(9)	33277	4622	51676	206	-28	-18	462	118	253	1.55	1.63	4.10
	26	22	31	14	13	12	19	14	16			
C(10)	28848	-2215	47333	267	62	43	325	107	316	1.66	1.91	3.61
	28	20	33	15	13	13	18	14	17			
C(11)	18302	-2932	40385	233	47	68	230	12	241	1.25	1.75	2.56
	25	17	29	14	11	12	15	12	14			
C(12)	10831	-9180	41748	332	-9	73	218	4	321	1.71	2.01	3.16
	28	19	33	17	13	14	15	13	16			
C(13)	42	-8564	36729	315	-75	86	267	-52	280	1.63	1.75	3.43
	28	20	32	16	13	13	15	13	16			
C(84)	-3812	-1820	31308	220	-68	31	386	-67	217	1.47	1.58	3.44
	26	20	30	14	13	12	18	13	14			
C(15)	3426	4550	29735	203	-4	6	297	-34	192	1.43	1.61	2.43
	24	18	28	13	12	11	15	12	13			
C(16)	14571	3289	33144	195	-19	19	235	-36	153	1.08	1.48	2.04
	24	17	26	11	11	10	13	11	12			
O(17)	22305	8902	29688	175	-23	20	235	-15	187	1.25	1.49	1.97
	15	12	18	9	8	8	9	8	9			

$$\begin{aligned}
 w_1 &= 16/|F_o| && \text{for } |F_o| \geq 16 \\
 &= (|F_o|/16)^{1/2} && \text{for } |F_o| < 16 \\
 w_2 &= 1 && \text{for } \sin\theta \geq 0.55 \\
 &= 1.82\sin\theta && \text{for } \sin\theta < 0.55.
 \end{aligned}$$

This scheme was devised to remove strong dependence of $w(|F_o| - |F_c|)^2$ on $|F_o|$ and $\sin\theta$. The nominal minimum value of $|F_o|$ is 4.0.

The scattering factor curves of Hanson, Herman, Lea & Skillman (1964) were used throughout the analysis. Anisotropic thermal parameters were refined for the carbon and oxygen atoms. Hydrogen atoms were assumed to lie in reasonable positions, and their parameters were refined also, but with thermal motion assumed to be isotropic.

Refinement proceeded uneventfully, and appeared to be complete when the R index ($\Sigma||F_o| - |F_c||/\Sigma|F_o|$, for observed reflexions only) was 0.069. This was a slightly disappointing figure, compared with those obtained in similar analyses. Moreover, a three-dimensional difference synthesis revealed some detail inconsistent with the proposed structure. The most striking residual feature was what appeared to be a well-shaped hydrogen atom (with coordinates $x=0.0506$, $y=0.3041$, and $z=0.3594$) of peak height 0.7 e.Å³, situated 1.5 Å or more from any atom in the model. Such a hydrogen atom makes no chemical sense whatever, and cannot be accepted as part of the molecule. There are other peaks and troughs in the synthesis (within the limits -0.32 to 0.30 e.Å³) many of which cannot be reconciled with expected features (such as 'bonding electrons') of the structure. Clearly some systematic error is present. This error could perhaps have occurred during collection of the intensity data, although the

authors are unable to understand how. Alternatively the error might be in the proposed model; the true structure might, for example, be disordered, with a small proportion of lattice sites occupied by a different molecule (possibly a decomposition product) or by the same molecule in another orientation. However, the authors were unable to propose a more satisfactory model, and the refinement had to be terminated at this point. In the final cycle no parameter shift exceeded 40% of the corresponding estimated standard deviation. The final parameters are given in Tables 1(a) and 1(b).

Thermal motion

In the light of the circumstances described above, it is clear that the thermal parameters of individual atoms must be somewhat in error. It was nevertheless considered essential to determine whether the rigid-body motion of the molecule was such as to cause appreciable errors in the estimated bond lengths. An analysis was therefore carried out by the method of Cruickshank (1956) assuming arbitrarily that the centre of libration coincides with the centroid of the (equally weighted) non-hydrogen atoms. The results are reasonably consistent with rigid-body motion: the root mean square deviation between U_o and U_c is 0.0029 Å², compared with the nominal estimated standard deviation of U_i of 0.0015 Å². The greatest r.m.s. amplitude of libration about any axis is 3.5°, and the resultant errors in bond length are estimated to range from 0.002 to 0.003 Å, values considered too small to warrant any action.

Assessment of analysis

The agreement between observed and calculated structure factors (Table 2) leaves no doubt as to the essential correctness of the proposed structure. As we have

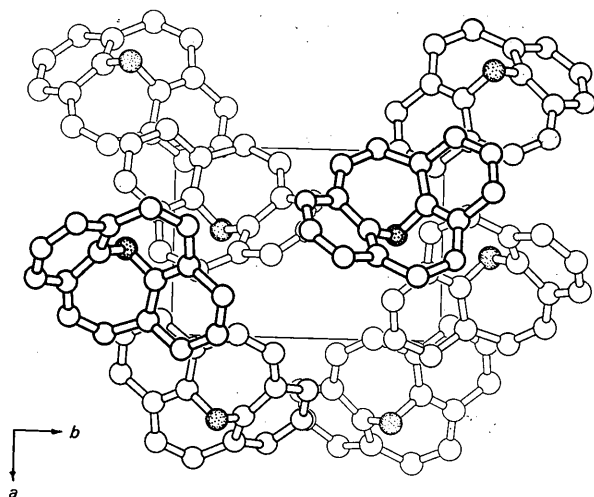


Fig. 1. A portion of the structure, viewed along c . Molecules nearest the observer are depicted in bold outline, with progressive weakening for those further away. The fraction of the unit cell indicated is $\frac{1}{2}a$ by $\frac{1}{2}b$.

Table 1(b). Parameters and *e.s.d.*'s for hydrogen atoms

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	B Å ²
H(1)	-690	1290	2097	-0.3
	30	20	33	0.6
H(2)	14	2436	2827	0.0
	30	23	35	0.7
H(4)	849	3042	4846	0.2
	33	22	37	0.7
H(5)	2276	2891	6467	1.2
	37	26	40	0.8
H(6)	3313	1749	6693	1.1
	36	26	43	0.9
H(9)	4139	435	5610	0.4
	34	23	37	0.8
H(10)	3270	-704	5053	0.6
	34	24	40	0.8
H(12)	1346	-1389	4666	0.7
	34	24	40	0.8
H(13)	-532	-1302	3735	-0.2
	30	20	33	0.6
H(14)	-1173	-147	2940	0.3
	32	22	36	0.7

Table 2. Observed and calculated structure factors

An asterisk indicates an unobserved reflexion, for which the threshold value is given. All F values have been multiplied by 10.

Table with multiple columns of numerical data representing observed and calculated structure factors for various reflections. The table is organized into several vertical sections, each with its own set of column headers (e.g., L, FO, FC). Asterisks are used to denote unobserved reflexions.

Table 3(a). Bond lengths

Revised e.s.d. = 0.008 Å.

Bond	Distance Å	Mean Å
C(1)—C(2)	1.352	1.359
C(9)—C(10)	1.366	
C(2)—C(3)	1.464	
C(7)—C(9)	1.447	1.459
C(10)—C(11)	1.468	
C(15)—C(1)	1.457	
C(3)—C(4)	1.395	1.403
C(6)—C(7)	1.411	
C(11)—C(12)	1.402	
C(14)—C(15)	1.403	1.385
C(4)—C(5)	1.388	
C(5)—C(6)	1.379	
C(12)—C(13)	1.401	1.396
C(13)—C(14)	1.371	
C(3)—C(8)	1.399	
C(7)—C(8)	1.397	1.385
C(11)—C(16)	1.390	
C(15)—C(16)	1.399	
C(8)—O(17)	1.384	1.385
C(16)—O(17)	1.385	

Mean C—H bond: 1.02 Å. Range: 0.98 to 1.08; e.s.d. 0.04 Å.

Table 3(b). Bond angles

Revised e.s.d. = 0.4°.

Angle	Value (°)	Mean (°)
C(15)—C(1)—C(2)	125.6	125.3
C(1)—C(2)—C(3)	125.2	
C(7)—C(9)—C(10)	125.3	
C(9)—C(10)—C(11)	125.2	119.5
C(2)—C(3)—C(8)	119.2	
C(8)—C(7)—C(9)	120.1	
C(10)—C(11)—C(16)	119.5	124.4
C(16)—C(15)—C(1)	119.4	
C(2)—C(3)—C(4)	124.5	
C(6)—C(7)—C(9)	124.7	115.7
C(10)—C(11)—C(12)	124.0	
C(14)—C(15)—C(1)	124.5	
C(8)—C(3)—C(4)	116.0	119.8
C(6)—C(7)—C(8)	114.9	
C(16)—C(11)—C(12)	116.0	
C(14)—C(15)—C(16)	115.9	122.3
C(3)—C(4)—C(5)	119.6	
C(5)—C(6)—C(7)	120.2	
C(11)—C(12)—C(13)	119.4	124.8
C(13)—C(14)—C(15)	119.9	
C(4)—C(5)—C(6)	122.3	
C(12)—C(13)—C(14)	122.3	117.5
C(3)—C(8)—C(7)	124.8	
C(11)—C(16)—C(15)	124.7	
C(3)—C(8)—O(17)	117.6	99.7
C(7)—C(8)—O(17)	117.4	
C(11)—C(16)—O(17)	117.8	
C(15)—C(16)—O(17)	117.4	
C(8)—O(17)—C(16)	99.7	

Range of C—C—H angles: 114 to 123°.

equivalent bond lengths are (within somewhat relaxed estimates of accuracy) equal. Bond lengths and angles are given in Table 3, and the mean values in Fig. 2.

These are consistent with the assumed distribution of bond types.

The tendency of the [2.2]metacyclophane group to be planar is checked by the mutual repulsion of C(8) and C(16). The relatively close approach of these atoms (2.12 Å) is, of course, mediated by the oxygen bridge (which also prevents a *trans* rearrangement of the phenyl groups). The dihedral shape of the molecule [Fig. 2(b)] is maintained by *compression* of the C—O—C linkage, balanced by *tension* in the C—C bridges. The resultant strain is distributed over the molecule as perturbations of the bond lengths and angles. It is, however, difficult to infer strain from the observed bond lengths. The double bond in the C—C bridge is indeed longer than the normal value of 1.337 Å (*International Tables for X-ray Crystallography*, 1962), but the difference is significant only at the 1% level.

Somewhat greater (and more obviously significant) stretching has been observed for *single* bonds in metacyclophane bridges. For example, a value of 1.573 Å is reported for *trans*-4,12-dimethyl[2.2]metacyclophane (Hanson, 1962). However, the stretching force constant for a double bond is about twice that for a single bond, so that even the small observed increase of 0.022 Å in the bond under consideration is, if real, indicative of a considerable force. There may well be some corresponding compression of the C—O bonds, but this also is difficult to demonstrate. Certainly the length of this bond is less than the 1.430 Å reported for II, but the latter value was rather drastically corrected for severe thermal motion, and is unreliable (Mathew & Hanson, 1968). The most obvious demonstration of strain is found in the deviation from normal values of some of the bond angles. For example, compression of the C—O—C linkage may be inferred from the angle at O(17), which is very much smaller than the presumably strain-free value of 111.5° reported for dimethyl ether (Sutton, 1965). It is also somewhat less than the value of 101.4° (with e.s.d. 0.4°) reported for II.

The phenyl rings are distorted to a boat shape as indicated in Fig. 2(b). This distortion is consistent with the principle that strain will be distributed as widely as possible, and not concentrated in any specific linkage of the molecule. The atoms *A*, *B*, *E* and the symmetry related atoms *B'*, *E'* are fixed in a nonplanar arrangement by the requirements of the oxygen-bridged ten-membered ring, and it is therefore impossible for the adjacent phenyl ring (*ABCDC'B'*) to be planar. If it were, then *E* would be quite far from the plane, and strain would be concentrated in the linkage *BE*. In fact the plane containing the bonds *BC* and *B'C'* (a convenient reference plane for the phenyl ring) is so oriented that *A* and *E* lie on opposite sides of it, distributing the strain more widely.

The displacements of *A* and *E* from the reference plane impose on *B* a rotation from its equilibrium orientation in a planar ring. A part of this rotation serves to twist the bond *BC*, but because of the resistance of the bond to twisting, the remainder is trans-

mitted to *C*. The rotation of *C* causes some twisting of the bond *CD* and (together with the equal and opposite rotation of *C'*) a displacement of *D* from the reference plane. The displacement is in the same direction as that of *A*, but is, of course, much smaller. The resulting asymmetrical boat distortion of the phenyl rings is characteristic of all the [2.2]metacyclophanes studied so far. An analysis of torsion angles of the aromatic bonds indicates values for *AB*, *BC*, and *CD* of 16, 5 and 5° respectively. (The torsion angle of a bond is here assumed to be the angle between two planes, each defined by the bond in question and by one of the two adjacent bonds in the ring.) Thus it appears that the strain imposed by the rotation of *B* is shared equally by the bonds *BC* and *CD*, a result which seems reasonable.

Some measures of the degree of boat distortion for various [2.2]metacyclophanes are compared in Table 4. If such distortion is interpreted as an indication of overall molecular strain, then it is clear that the present compound is much more highly strained than II, but rather less so than 4,12-dimethyl-*trans*[2.2]metacyclophane (which by this criterion is the most highly strained of all the [2.2]metacyclophanes studied so far). One more result of the extra strain is the relative flatness of the whole molecule; the angle between the mean planes of the phenyl rings is 123.6°, compared with 99.6° for II.

Table 4. Distortion of phenyl groups in some [2.2]metacyclophanes

Distances of atoms *A*, *D*, *E* from mean plane of atoms *B*, *B'*, *C*, *C'* (Fig. 2). (Mean values are given.)

Compound	ΔA (Å)	ΔD (Å)	ΔE (Å)	$\Delta D/\Delta A$
1	0.161	0.049	-0.291	0.30
2	0.095	0.018	-0.18	0.19
3	0.187	0.088	-0.435	0.47
4	0.178	0.080	-0.424	0.45
5	0.143	0.042	-0.41	0.29

1. Present compound
2. 8,16-Oxido-*cis*[2.2]metacyclophane (Mathew & Hanson, 1968)
3. 4,12-Dimethyl-*trans*[2.2]metacyclophane (Hanson, 1962)
4. 4,12-Di(bromomethyl)*trans*[2.2]metacyclophane (Mathew, 1968)
5. Di-*m*-xylylene[*trans*[2.2]metacyclophane] (Brown, 1953)

The substituents in 3 and 4 are in the same positions as the oxygen bridge in 1 and 2.

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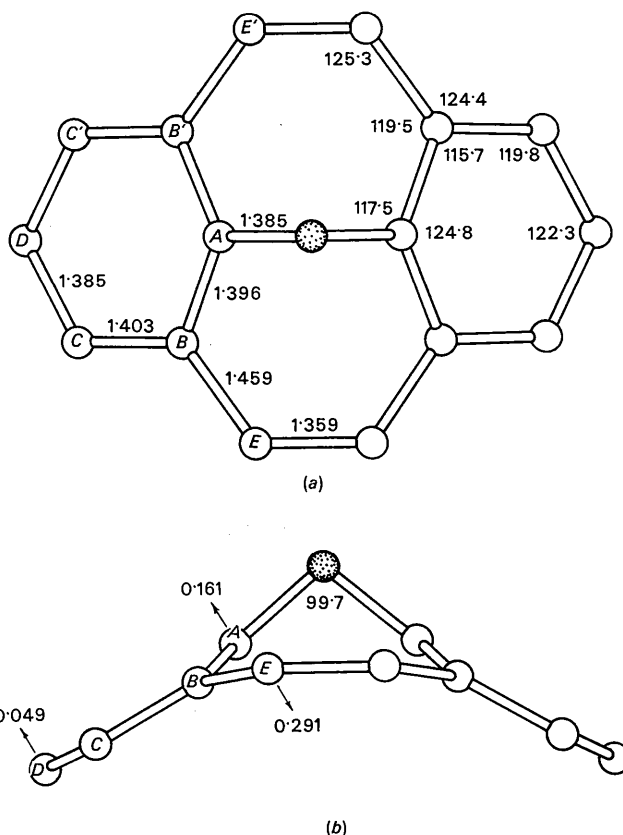


Fig. 2. Geometry of the idealized molecule, assuming *mm* symmetry. (a) Plan view, showing bond lengths and most bond angles. Mean e.s.d.'s are 0.008 Å and 0.4°. (b) Elevation. Arrows indicate the deviations (in Å) of certain atoms from the plane containing *AB* and *A'B'*.

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