

Cyclophanes, XXX [1]
The Crystal Structure of
[2.4]Paracyclophane at $-95\text{ }^{\circ}\text{C}$

Peter G. Jones^{*a}, Zissis Pechlivanidis^b, and Henning Hopf^{*b}

^a Institut für Anorganische und Analytische Chemie and

^b Institut für Organische Chemie, Technische Universität, Hagenring 30, D-3300 Braunschweig, FRG

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Paracyclophanes, X-Ray

[2.4]Paracyclophane crystallizes in the orthorhombic space group *Pbca* with cell constants (at $-95\text{ }^{\circ}\text{C}$) $a = 1151.5(5)$, $b = 1832.9(7)$, $c = 1304.1(4)$ pm. The structure was refined to $R = 0.053$ for 1626 unique observed reflections. The aromatic ring systems are inclined to each other at an angle of 21° . The longer bridge is capable of more relaxation than the shorter, as is reflected in the non-bonded distances 279, 386 pm between bridgehead atoms and in the smaller displacements of the associated benzylic carbon atoms from the aromatic ring planes. The central bond length of the longer bridge (151.8 pm) is shorter than would be expected for a single bond.

The strong electronic interactions between the benzene rings of [2.2]- and [3.3]paracyclophane have fascinated many chemists, and have made these molecules the most thoroughly studied bridged aromatics to date [2–4]. The proximity of the two rings not only has a pronounced influence on the various spectra of these molecules but also is the origin of some interesting chemical effects. It has been noted [5], for example, that a carbonyl substituent at C-4 in [2.2]paracyclophane often directs an incoming electrophile into the so-called pseudogeminal position, *viz.* to a position of the unsubstituted ring exactly opposite the already substituted carbon atom.

We are interested in investigating how far these directing effects extend, and therefore decided to study the chemical behaviour of the title compound. It is known from Cram's classical papers [6] that the still higher-bridged phanes behave like conventional aromatic compounds. One would therefore expect that there should be no such directing effects in these

latter molecules. [2.4]Paracyclophane, on the other hand, might be an interesting intermediate case since formally it is a hybrid of a short- and a long-bridged phane. Since we wish to relate geometrical and chemical properties it is obviously desirable to determine the molecular parameters of the [2.4]phane.

Experimental

For the preparation of the title compound we followed the procedure given in the literature [7], *i.e.* carried out a ring expansion of [2.2]paracyclophane with diethyl fumarate and subsequently decarboxylated and reduced the initially formed [2.4]paracyclophane diester. Crystals suitable for X-ray analysis were obtained by recrystallization from ethanol. A room-temperature structure determination proved unsatisfactory because of extreme thermal motion effects, especially in the longer bridge, and was therefore repeated at $-95\text{ }^{\circ}\text{C}$.

Crystal structure determination

Crystal data: $\text{C}_{18}\text{H}_{20}$, $M_r = 236.35$, orthorhombic, space group *Pbca*, $a = 1151.5(5)$, $b = 1832.9(7)$, $c = 1304.1(4)$ pm, $U = 2.752\text{ nm}^3$, $Z = 8$, $D_x = 1.14\text{ Mg m}^{-3}$, $F(000) = 1024$, λ (MoK α) = 71.069 pm, $\mu = 0.06\text{ mm}^{-1}$, $T = -95\text{ }^{\circ}\text{C}$.

Data collection and reduction: A colourless tablet *ca.* $0.9 \times 0.5 \times 0.2$ mm was mounted on a glass fibre and transferred to a Nicolet P3 diffractometer fitted with an LT-2 low-temperature attachment. 2998 intensities were registered to a maximum 2θ of 50° (monochromated MoK α radiation). Of 2411 unique reflections ($R_{int} = 0.012$), 1626 with $F > 4\sigma(F)$ were used for all calculations (program system XLS). The orientation matrix was refined from setting angles of 44 reflections in the range $2\theta = 20\text{--}24^{\circ}$.

Structure solution and refinement: The structure was solved by routine direct methods using the room temperature data; the coordinates thus obtained were used as a starting point for the refinement of the low temperature data. After anisotropic refinement of all C atoms, the H atoms were identified in a difference Fourier synthesis; because of the moderate data/parameter ratio, they were placed in idealized positions and refined using a riding model. The final R value was 0.053, with $R_w = 0.047$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0003 F^2$. 163 parameters; S 1.6; max. Δ/σ 0.001; max. $\Delta\rho$ $0.2 \times 10^{-6}\text{ e pm}^{-3}$.

Final atomic coordinates are presented in Table I, with derived bond lengths and angles in Tables II and III. The molecule of the title compound is shown in Fig. 1, with a packing plot in Fig. 2. Further details of the structure determination (torsion angles,

* Reprint requests to Prof. Dr. P. G. Jones or Prof. Dr. H. Hopf.



Table I. Atomic coordinates ($\times 10^3$) and equivalent isotropic displacement parameters (pm^2).

Atom	x	y	z	U(eq)*
C(1)	406(3)	7920(1)	6496(2)	554(10)
C(2)	1046(2)	7951(1)	5448(2)	507(9)
C(3)	1794(2)	7296(1)	5244(2)	378(8)
C(4)	2806(2)	7166(1)	5796(2)	404(8)
C(5)	3320(2)	6489(1)	5808(2)	423(8)
C(6)	2864(2)	5910(1)	5244(2)	411(8)
C(7)	1936(2)	6061(1)	4603(2)	463(9)
C(8)	1400(2)	6740(1)	4612(2)	426(8)
C(9)	3280(2)	5141(1)	5446(2)	569(10)
C(10)	2701(2)	4834(1)	6428(2)	502(9)
C(11)	1436(2)	4619(1)	6302(2)	498(9)
C(12)	661(2)	4818(1)	7230(2)	439(8)
C(13)	423(2)	5629(1)	7233(2)	326(7)
C(14)	1124(2)	6114(1)	7762(2)	340(7)
C(15)	1051(2)	6861(1)	7584(2)	365(7)
C(16)	262(2)	7144(1)	6882(2)	377(8)
C(17)	-522(2)	6664(1)	6438(2)	401(8)
C(18)	-434(2)	5922(1)	6605(2)	373(7)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table II. Bond lengths (pm).

C(1)–C(2)	155.4(4)	C(1)–C(16)	151.8(3)
C(2)–C(3)	150.1(3)	C(3)–C(4)	139.0(3)
C(3)–C(8)	138.8(3)	C(4)–C(5)	137.6(3)
C(5)–C(6)	139.4(3)	C(6)–C(7)	138.5(4)
C(6)–C(9)	151.1(4)	C(7)–C(8)	138.8(4)
C(9)–C(10)	154.9(4)	C(10)–C(11)	151.8(4)
C(11)–C(12)	154.7(4)	C(12)–C(13)	151.0(3)
C(13)–C(14)	138.5(3)	C(13)–C(18)	139.1(3)
C(14)–C(15)	139.1(3)	C(15)–C(16)	138.9(3)
C(16)–C(17)	138.7(3)	C(17)–C(18)	138.1(3)

C(2)–C(1)–C(16)	112.2(2)	C(1)–C(2)–C(3)	113.6(2)
C(2)–C(3)–C(4)	121.7(2)	C(2)–C(3)–C(8)	120.4(2)
C(4)–C(3)–C(8)	117.2(2)	C(3)–C(4)–C(5)	121.4(2)
C(4)–C(5)–C(6)	121.3(2)	C(5)–C(6)–C(7)	117.1(2)
C(5)–C(6)–C(9)	119.9(2)	C(7)–C(6)–C(9)	122.5(2)
C(6)–C(7)–C(8)	121.2(2)	C(3)–C(8)–C(7)	121.2(2)
C(6)–C(9)–C(10)	110.3(2)	C(9)–C(10)–C(11)	114.7(2)
C(10)–C(11)–C(12)	114.1(2)	C(11)–C(12)–C(13)	109.8(2)
C(12)–C(13)–C(14)	121.8(2)	C(12)–C(13)–C(18)	120.5(2)
C(14)–C(13)–C(18)	117.3(2)	C(13)–C(14)–C(15)	120.9(2)
C(14)–C(15)–C(16)	121.1(2)	C(1)–C(16)–C(15)	119.8(2)
C(1)–C(16)–C(17)	121.7(2)	C(15)–C(16)–C(17)	117.6(2)
C(16)–C(17)–C(18)	120.7(2)	C(13)–C(18)–C(17)	121.7(2)

H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany; they may be ordered by quoting a full literature citation and the deposition number CSD 53716.

Discussion

As would be expected, the low temperature structure of the title compound (in contrast to the room temperature structure) shows acceptably low U values (see Table I). An analysis of the thermal parameters showed that the molecule cannot be treated as a rigid body, so that no libration correction could be applied; however, the bond lengths should be appreciably more reliable than those of the room temperature study.

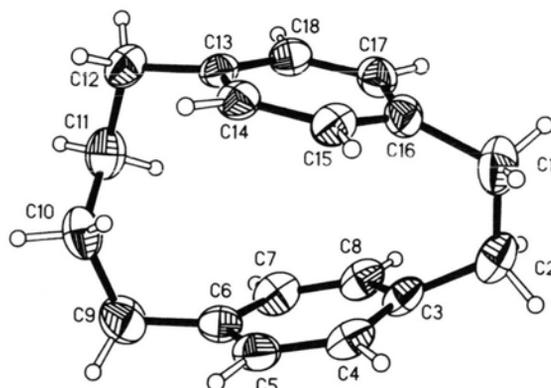


Fig. 1. Thermal ellipsoid plot (50% level) of the title compound, showing the atomic numbering scheme. H atom radii are arbitrary.

Table III. Bond angles ($^\circ$).

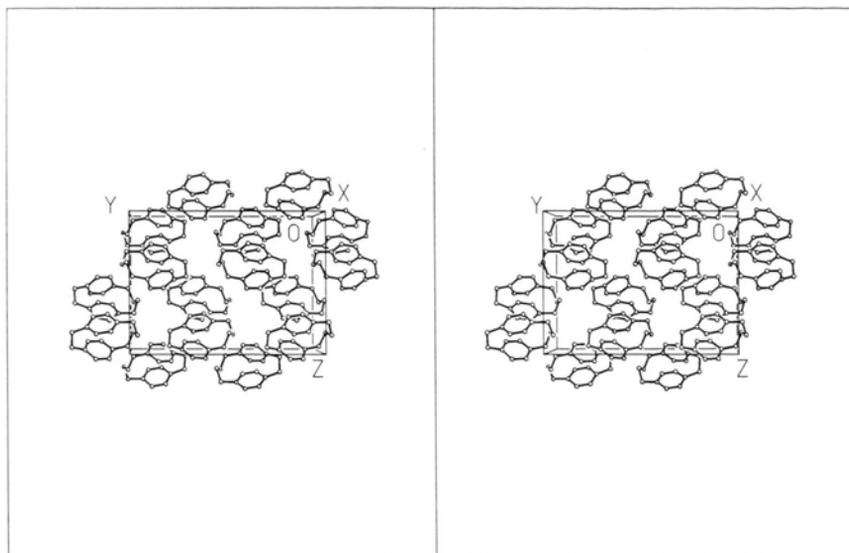


Fig. 2. Stereographic packing diagram of the title compound. Radii are arbitrary; H atoms omitted for clarity.

Crystal structures of cyclophane derivatives have been reviewed by Keehn [8]. The current structure mirrors some of the typical features of the thoroughly studied [2.2]paracyclophane system, but the unequal bridges necessarily lead to some significant differences. The rings are inclined to each other at an angle of 21° . The planes were calculated excluding the bridgehead atoms, since these are usually displaced from the rings towards the centre of the molecule; in the current structure, the displacement is 7 pm for all four such atoms C3, C6, C13, C16, and associated with these displacements are narrow ring angles of $117\text{--}118^\circ$. The displacements of the benzylic carbons are amplified to 44 pm for C1 and C2, 37 pm for C12 and 39 pm for C9.

The bridge single bond lengths are normal (154.7–155.4 pm) with the exception of C10–C11, which is noticeably shorter at 151.8 pm. Consistent with this observation, the formally sp^3 bond angles at C10 and C11 (114.7 , 114.1°) are appreciably larger than at C9 and C12 (110.3 , 109.8°). It remains to be seen whether this is typical of four-membered

bridges in cyclophanes. The corresponding angles in the shorter bridge, which might be expected to show more strain, are 112.2 and 113.6° . The torsion angles in the bridges adopt values that cannot easily be characterized under the usual categories: -23.5° about C1–C2, 74.6° about C9–C10, -140.3° about C10–C11 and 75.2° about C11–C12.

Typical of [2.2]paracyclophanes are the short non-bonded distances between corresponding atoms of the two rings. The current structure thus has a characteristic C3...C16 contact of 279 pm. In [2.2]paracyclophane the distance between the corresponding bridgehead atoms is practically identical at 278 pm [9]. The four atoms of the longer bridge, however, allow relaxation of the C6...C13 distance to 386 pm. The shortest intermolecular non-bonded distance between C atoms is 369 pm for C2...C5 (second atom at $0.5+x$, $1.5-y$, $1-z$).

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