

tional 5 hr before being allowed to warm to room temperature. The flocculent white precipitate was collected, washed successively with aqueous bicarbonate and chloroform, and was dried. This gave 3.95 g (90%) of a white powder: mp $>340^\circ$; ir (KBr) 3900 and 3860 (CH), 1570 and 1500 ($-C=C-$), 1300 and 1100 ($-SO_2-$), and 1255 cm^{-1} (N^+-O^-); nmr (F_3CCO_2D plus $CDCl_3$) an AB_2 pattern at τ 1.52 and 1.74 (3 H, $J = 10$ Hz, pyridine- H), a singlet at 2.40 (4 H, para-bridged benzene- H), and a singlet at 5.10 (8 H, $-CH_2SO_2-$); mass spectrum (70 eV) m/e (rel intensity) 353 (1), 337 (4.5), 321 (3), 273 (3), 241 (2), 225 (3), 209 (100), 194 (18), 156 (16), 139 (5), 104 (50), 83 (86), 78 (41), 65 (16), 47 (23), 28 (27).

[2.2](2,6)Pyridinoparacyclophane (5). The pyrolysis of **10** was carried out using the same apparatus as described previously.³ With the first oven set at 450° and the second at $650-680^\circ$ and with a nitrogen sweep at 2.8 mm pressure a 145-mg sample of **10** was pyrolyzed to give 57 mg (66%) of a white crystalline solid. On re-sublimation this yielded white crystals: mp $80.5-81.5^\circ$; ir ($CDCl_3$) 3005, 2915, and 2850 (CH) and 1605 and 1565 cm^{-1} ($-C=C-$); nmr ($CDCl_3$) an AB_2 pattern at τ 2.74 and 3.22 (3 H, $J = 8$ Hz, pyridine- H), a singlet at 3.36 (4 H, para-bridged benzene- H), a triplet at 7.06 (4 H, $J = 6$ Hz, $ArCH_2$), and a triplet at 7.35 (4 H, $J = 6$ Hz, $ArCH_2-$); mass spectrum (70 eV) m/e (rel intensity) 209 (100), 208 (100), 194 (43), 180 (9), 168 (6), 156 (39), 143 (7), 130 (9), 115 (20), and 104 (30).

When a 20-mg sample of [2.2](2,6)pyridinoparacyclophane-1,9-diene (**4**) in 10 ml of ethyl acetate was subjected to hydrogenation over a 5% palladium-on-charcoal catalyst at room temperature and atmospheric pressure, a sample of **5**, identical in all respects with that described above, was obtained in 32% yield. Apparently the low yield of **5** is due to competitive hydrogenation of the benzene ring.

The fluoroborate salt **12** was prepared by mixing a solution of

54 mg of **5** in 5 ml of ether with commercial boron trifluoride etherate. The resulting precipitate was collected, washed with ether, and dried. Sublimation at 10^{-3} mm gave 34 mg of white crystals: mp $179-183^\circ$; ir (KBr) 3450–2500 (N^+-H) and 1580 and 1560 cm^{-1} ($-C=C-$); uv (CH_3CN) 257 nm (ϵ 4340); nmr (CD_3-COCD_3) an AB_2 pattern at τ 1.72 and 2.23 (3 H, $J = 6$ Hz, pyridine- H), a broad singlet at 3.05 (5 H, $-N^+H$ and para-bridged benzene- H), and an $AA'BB'$ multiplet at 6.80 and 6.98 (8 H, $Ar-CH_2$). This nmr spectrum was temperature dependent ($T_c -5.6^\circ$) and at lower temperatures the para-bridged benzene proton singlet separated into two signals at τ 2.35 and 3.74 ($\Delta\nu = 139$ Hz). The nmr spectrum of **12** in deuteriomethanol showed coalescence at 21° with the separate signals at lower temperatures occurring at τ 2.50 and 3.85 ($\Delta\nu = 135$ Hz).

[2.2](2,6)Pyridinoparacyclophane *N*-Oxide (**14**). To a solution of 20 mg of **5** in 10 ml of chloroform there was added 22.4 mg of *m*-chloroperbenzoic acid (85% pure) and the resulting mixture was stirred at room temperature for 10 min. The solution had become slightly yellow and was now washed successively with aqueous sodium bicarbonate and water, and then dried. Concentration of the solution followed by sublimation of the residual solid at 5×10^{-3} mm gave 14.5 mg (65%) of white crystals: mp $165-167^\circ$; ir (KBr) 2950 and 2880 ($-CH$), 1595 and 1570 ($Ar-C=C-$), and 1380 and 1230 cm^{-1} (N^+O^-); nmr ($CDCl_3$) a narrow multiplet at τ 2.64 (2 H, para-bridged benzene ArH), an AB_2 multiplet at 3.17 (3 H, pyridine- H), a narrow multiplet at 3.86 (2 H, para-bridged benzene ArH), multiplets at 6.19 and 6.68 (4 H, $-CH_2-$ adjacent to the pyridine ring), and a multiplet at 7.48 (4 H, $-CH_2-$ adjacent to the benzene ring); mass spectrum (70 eV, inlet temp, 100°) m/e (rel intensity) 225 (100), 207 (91), 196 (30), 182 (13), 168 (7), 156 (10), 143 (5), 130 (5), 118 (18), 106 (9), 78 (21), 65 (29), 51 (17), 39 (30), 27 (47).

The Crystal and Molecular Structure of [2.2](2,6)Pyridinoparacyclophane-1,9-diene

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Abstract: Crystals of [2.2](2,6)pyridinoparacyclophane-1,9-diene are orthorhombic, space group *Fdd2*, with unit cell dimensions $a = 13.85$ (4), $b = 17.38$ (6), and $c = 8.84$ (2) Å. The molecule lies on a crystallographic twofold symmetry axis and its azimuthal orientation was determined by calculating the minimum residual for a set of projection data. Atomic parameters were refined by block diagonal least squares to a final *R* value of 0.056 for the reflections with $I > 2\sigma(I)$. In contrast to the related molecule, [2.2]metaparacyclophane-1,9-diene, in which the two aromatic rings are inclined to each other at 41° , the two rings in [2.2](2,6)pyridinoparacyclophane-1,9-diene are perpendicular. The para-bridged ring exhibits severe boat distortion, comparable to that observed for the para-bridged ring in [2.2]metaparacyclophane-1,9-diene.

One of a series of compounds described by Boekelheide and his associates in the accompanying reports¹ is [2.2](2,6)pyridinoparacyclophane-1,9-diene in which a group (represented by X in Figure 1) is positioned near the "cavity" of the π -electron cloud of a para-bridged benzene ring. An earlier X-ray study of [2.2]metaparacyclophane-1,9-diene ($X = CH$) showed severe distortion of the para-bridged ring, and that the rings were inclined at 41° to each other.² The present study was undertaken to determine the conformation of the molecule with a "smaller" group near the cavity, *i.e.*, $X = N$.

Nuclear magnetic resonance studies of [2.2]meta-

paracyclophane-1,9-diene show the spectrum to be temperature dependent with coalescence at -96° , indicating a barrier to conformational flipping of 8.3 kcal/mol. On the other hand, at the lowest temperatures feasible for determining the nmr spectrum of [2.2](2,6)pyridinoparacyclophane-1,9-diene, the protons of the para-bridged ring appear as a singlet, indicating either possible *2mm* symmetry, or rapid flipping of the molecules between two conformations related by this apparent symmetry.^{1a,c} The crystallographic analysis reported here shows that the rings of [2.2](2,6)pyridinoparacyclophane-1,9-diene are perpendicular and that the molecule has twofold symmetry.

Experimental Section

Crystal samples, supplied by Dr. V. Boekelheide and Mr. K. S. Szeto, were typically well developed rectangular prisms with prominent (010) and (100) faces.

(1) (a) V. Boekelheide, P. H. Anderson, and T. A. Hylton, *J. Amer. Chem. Soc.*, **96**, 1558 (1974); (b) S. Sherrod, R. S. da Costa, R. A. Barnes, and V. Boekelheide, *ibid.*, **96**, 1565 (1974); (c) V. Boekelheide, K. Galuszko, and K. S. Szeto, *ibid.*, **96**, 1578 (1974).

(2) A. W. Hanson, *Acta Crystallogr., Sect. B*, **27**, 197 (1971).

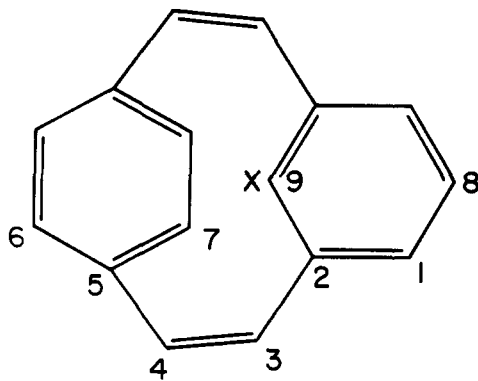


Figure 1. Schematic structure with atomic numbering.

Table I. Crystallographic Data

Unit cell dimensions	$a = 13.85 \pm 0.04 \text{ \AA}$ $b = 17.38 \pm 0.06 \text{ \AA}$ $c = 8.84 \pm 0.02 \text{ \AA}$ $V_c = 2130 \text{ \AA}^3$
Systematic absences	$hkl (h + k = 2n, k + l = 2n)$ $OkI (k + l = 4n)$ $hOl (l + h = 4n)$
Density calcd ($n = 8$)	1.28 g cm^{-3}
Density obsd	1.27 g cm^{-3}

Table III. Atomic Parameters^a

Atom	x	y	z	B or B_{11}	B_{22}	B_{33}	B_{23}		
C(1)	0796 (6)	0250 (4)	-4916 (7)	156 (6)	054 (2)	145 (8)	063 (7)	151 (12)	083 (6)
C(2)	0785 (4)	0244 (2)	-3326 (6)	087 (3)	031 (1)	127 (5)	032 (4)	078 (6)	014 (3)
C(3)	1626 (3)	0514 (3)	-2420 (10)	060 (2)	035 (2)	343 (14)	040 (8)	143 (10)	-013 (3)
C(4)	1707 (3)	0557 (3)	-0930 (9)	050 (2)	035 (2)	301 (13)	-034 (7)	-015 (8)	-020 (3)
C(5)	0922 (3)	0292 (2)	0013 (6)	060 (2)	035 (1)	146 (6)	-037 (5)	-077 (6)	002 (3)
C(6)	0786 (3)	-0485 (2)	0262 (5)	064 (2)	033 (1)	111 (4)	015 (4)	-036 (6)	020 (3)
C(7)	0134 (3)	0782 (2)	0266 (6)	077 (3)	029 (1)	119 (4)	-031 (4)	-039 (6)	016 (3)
C(8)	0 (0)	0 (0)	-5673 (9)	222 (14)	079 (7)	092 (10)	-020 (19)	-024 (22)	146 (18)
N	0 (0)	0 (0)	-2581 (5)	067 (2)	028 (2)	083 (7)	-002 (8)	011 (8)	-006 (4)
H(1)	135 (9)	033 (9)	-531 (20)					6.9 (38)	
H(3)	228 (16)	085 (17)	-191 (33)					15.8 (85)	
H(4)	229 (3)	070 (3)	-043 (6)					2.4 (09)	
H(6)	133 (3)	-082 (2)	033 (6)					1.9 (08)	
H(7)	022 (3)	129 (3)	033 (6)					1.3 (08)	
H(8)	0 (0)	0 (0)	-679 (48)					31.6 (180)	

^a Fractional coordinates: non-hydrogen $\times 10^4$, hydrogen $\times 10^3$. The anisotropic thermal parameters, $B_{ij} \times 10^4$, are the coefficients in the expression $\exp[-\sum B_{ij}h_ih_j]$; the isotropic thermal parameters, B , are in \AA^2 . Estimated standard deviations in the last figure are in parentheses. Hydrogens are numbered according to the carbon to which they are bonded.

Three-dimensional data were collected for a crystal of approximate dimensions $0.1 \times 0.1 \times 0.25$ mm using a card controlled Enraf-Nonius three circle diffractometer. Filtered Mo $K\alpha$ radiation ($\lambda 0.7107 \text{ \AA}$) was used and data were recorded to the limit of Cu $K\alpha$ radiation ($\sin \theta/\lambda = 0.66$). Corrections for the maximum and minimum absorption effects differed by only 4% and, therefore, no corrections for absorption were applied.

The θ - 2θ scan method was used with a 30-sec background count on each side of the peak and a scan time of around 60 sec. Of 681 possible reflections, 525 had a peak count which exceed the normalized background count by at least two times the variance of the peak count. In preliminary tests, a crystal exposed to the air was observed to deteriorate during exposure to X-rays. The crystal used for the final data collection was sealed in a thin-walled glass capillary, and, as judged by measurements of standard reflections, remained quite stable.

Structure Determination and Refinement

Systematic absences (Table I), shown by Weissenberg and Buerger precession photographs, uniquely determined the space group as orthorhombic, $Fdd2$. The unit cell parameters and density measurements

(Table I) indicated eight molecules per unit cell, thereby requiring the molecule to lie on a twofold axis of symmetry. It was therefore immediately apparent that the pyridine ring must straddle the z axis and be perpendicular to the para-bridged ring. With the structure and orientation of the molecule so restricted, it remained only to determine the azimuthal angle δ between the pyridine ring and the xz plane, and the sense of the molecule along the z axis.

To determine δ , a series of trial-and-error calculations were made in which $(hk0)$ structure factors were calculated, and the R index for this projection determined as a function of δ . The R index was found to be very sensitive to δ , having a sharp minimum of 0.21 for a preliminary set of photographically measured intensities.

Refinement of the structure was by block diagonal least squares. At first, the benzene to pyridine direction was assumed as positive along z , but the initial structure factor calculation gave an R value of about 0.45, and refinement was unsatisfactory. On reflection of the molecule in the xy plane, a few cycles of refinement lowered R to about 0.18. Three additional cycles with anisotropic thermal factors decreased R to about 0.09. At this point, a difference map in the region of

the benzene ring clearly showed the four expected hydrogen atoms. All other expected hydrogen atoms were then placed at chemically reasonable positions, and included in refinement with isotropic temperature factors. The final R value for reflections with $I > 2\sigma(I)$ was 0.056. The structure factors are available elsewhere³ and the final atomic parameters are given in Table III. The atom numbering (Figure 1) used in the X-ray study was chosen for convenience, and is not intended to follow chemical convention.

Atomic scattering factors were taken from the International Tables for X-ray Crystallography.⁴ The weighting scheme used in the least-squares refinement was similar to that described by Stout and Jensen for diffractometer data.⁵

(3) See paragraph at end of paper regarding supplementary material.

(4) "International Tables for X-ray Crystallography," Vol. III, C. H. MacGillavry and G. D. Rieck, Ed. Kynoch Press, Birmingham, England, 1962, p 202.

(5) G. H. Stout and L. H. Jensen, "X-ray Structure Determination, A Practical Guide," Macmillan, New York, N. Y., 1968, p 456.

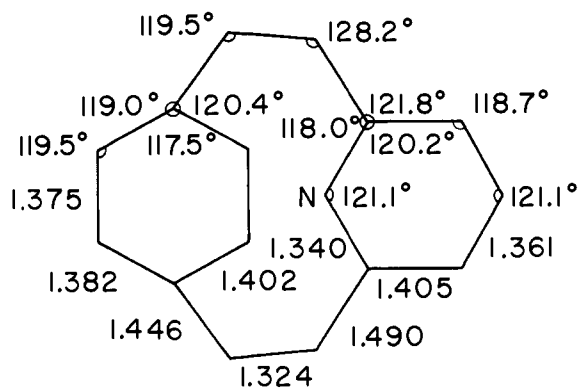


Figure 2. Bond lengths and angles.

Discussion

As was discussed above, the molecule lies on a crystallographic diad axis. In addition, the pyridine ring is not significantly aplanar, and, within the experimental accuracy, the molecule has symmetry $2mm$. This is the most important finding of the X-ray study, and as discussed in the accompanying paper^{1c} was the main motivation for the crystallographic analysis. The fact that the nmr spectrum of the title compound does not change with temperature is consistent with a perpendicular orientation of the pyridine and benzene rings in solution, but does not rule out the possibility that in the ground state the rings are inclined, and the barrier to conformational flipping is so low that the nmr spectrum would only show evidence of asymmetry at temperatures below the lowest experimentally accessible. The present study demonstrates that, at least in the crystal, the two rings are in fact perpendicular. It could be argued that the conformation of the molecule in the crystal need not be the same as that in solution, but we believe this to be unlikely. Kitaigorodskii⁶ has pointed out that a symmetrical molecule will only express its symmetry as part of the crystallographic symmetry if it can do so without lowering the packing density, and it is well known that symmetrical molecules often do not express their symmetry crystallographically. Conversely, one would not expect a molecule which in solution is intrinsically asymmetric to have symmetry imposed upon it by the crystallization process.

The intramolecular bond lengths and angles are given in Table IV and Figure 2. Some of the bond lengths show apparent departures of up to about 0.03 Å from their expected values, but in no case can these be considered as significant, especially since the standard deviations estimated from the block-diagonal refinement are likely to be underestimates of the true values. The strained bonds C(2)–C(3) and C(4)–C(5) differ by 0.044 Å, possibly reflecting their different environments. In [2.2]metaparacyclophane-1,9-diene,² where the rings are tilted and the geometry around the two bonds more similar, the bond lengths are essentially equal (1.486 Å, 1.484 Å). The third bridging bond, C(3)–C(4) (1.324 Å), is not significantly different from the corresponding bond (1.346 Å) observed in [2.2]metaparacyclophane-1,9-diene.²

In spite of the fact that in [2.2]metaparacyclophane-

(6) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York, N. Y., 1961.

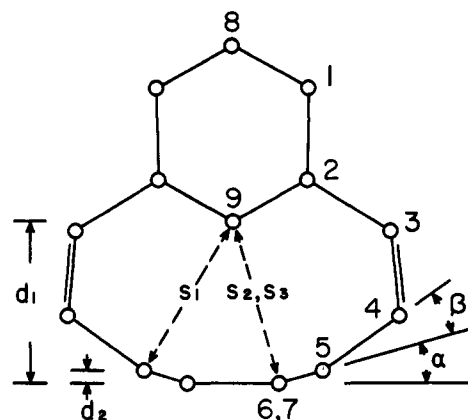


Figure 3. Intraatomic distances and strain parameters.

Table IV. Bond Lengths (Å) and Angles (deg)

C(1)–C(2)	1.405 (8)	C(8)–C(1)–C(2)	118.7 (6)
C(1)–C(8)	1.361 (9)	C(1)–C(2)–N	120.2 (5)
C(2)–C(3)	1.490 (8)	C(1)–C(2)–C(3)	121.8 (5)
C(2)–N	1.340 (6)	C(3)–C(2)–N	118.0 (4)
C(3)–C(4)	1.324 (12)	C(2)–C(3)–C(4)	128.2 (6)
C(4)–C(5)	1.446 (8)	C(3)–C(4)–C(5)	119.5 (6)
C(5)–C(6)	1.382 (6)	C(4)–C(5)–C(6)	120.4 (4)
C(5)–C(7)	1.402 (6)	C(4)–C(5)–C(7)	119.0 (4)
C(6)–C(7)	1.375 (6)	C(6)–C(5)–C(7)	117.5 (4)
		C(5)–C(6)–N–C(7)	119.6 (4)
		C(5)–C(7)–N–C(6)	119.5 (4)
C(1)–H(1)	0.86 (13)	C(1)–C(8)–N–C(1)	121.1 (5)
C(3)–H(3)	1.17 (26)	C(2)–N–C(2)	121.1 (3)
C(4)–H(4)	0.95 (5)		
C(6)–H(6)	0.95 (4)		
C(7)–H(7)	0.89 (5)		
C(8)–H(8)	0.99 (43)		

Table V. Intramolecular Parameters

Parameter ^a	[2.2]Paracyclophane-1,9-diene ⁷	[2.2]Metaparacyclophane-1,9-diene ²	[2.2](2,6)Pyridinoparacyclophane-1,9-diene (this work)
α	14°	18.4°	18.2°
β	15°	18.0°	17.1°
d_1^b	C(5)–C(5') 2.80 Å C(6)–C(6') 3.14	C 2.71 Å H 2.16 Å	N 2.51 Å
d_2	0.172 Å	0.235 Å	0.222 Å
S_1		C 2.84 Å H 2.41 Å	N 2.67 Å
S_2		C 3.17 Å H 2.37 Å	N 2.86 Å
S_3		C 2.91 Å H 2.82 Å	N 2.87 Å

^a See Figure 3. ^b The primes are used to indicate corresponding atoms in the two para-bridged rings of paracyclophane. C(5') corresponds to C(2) in Figure 3.

1,9-diene the two aromatic rings are inclined at 41°, and in [2.2](2,6)pyridinoparacyclophane-1,9-diene they are orthogonal, the corresponding bond angles in the two molecules are remarkably similar, differing at most by 2.6°. On the other hand, in [2.2]paracyclophane-1,9-diene, in which the linkages are both para, and the two aromatic rings are parallel, the molecule is less strained and the bonds corresponding to those at C(3) and C(4) are both close to 120°.⁷

(7) C. L. Coulter and K. N. Trueblood, *Acta Crystallogr.*, **16**, 667 (1963).

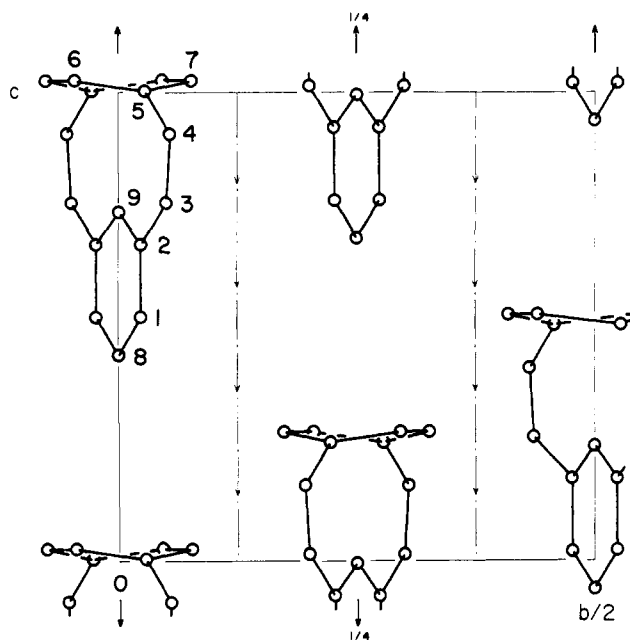


Figure 4. The molecular packing seen parallel to *a*.

The distortion of the highly strained para-bridged ring is illustrated in Figure 3, and may be characterized by the angles α and β , which are compared, in Table V, with values observed for related compounds. The nitrogen of the pyridine ring lies only 2.51 Å from the plane of the unsubstituted atoms of the para-bridged ring, substantially closer than the approach of 2.71 Å observed for the corresponding carbon of [2.2]meta-paracyclophane-1,9-diene (Table V). Some other

short intramolecular distances are also illustrated in Figure 3, and summarized in Table V.

The crystal packing is illustrated in Figure 4 and the closest intermolecular distances are listed in Table VI.

Table VI. Closest Intermolecular Distances (Å)

C(1)–C(3)	3.802 (10)	C(6)–H(8)	2.94 (38)
C(8)–C(6)	3.847 (11)	C(7)–H(8)	2.94 (38)
C(8)–C(7)	3.842 (11)	H(6)–H(7)	2.66 (07)
C(2)–H(3)	2.97 (28)	H(1)–H(6)	2.94 (16)
C(1)–H(3)	2.84 (28)	H(1)–H(7)	2.88 (17)

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Supplementary Material Available. A listing of structure factor amplitudes (Table II) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-1581.