[2.2](2,6)Pyridinoparacyclophane-1,9-diene. A Perpendicular Orientation of Two Aromatic Rings[1a]

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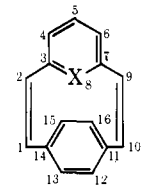
Abstract: Subjection of 2,11-dithia[3.3](2,6)pyridinoparacyclophane (**8**) to the two-step reaction sequence of a Stevens rearrangement followed by a Hofmann elimination has provided [2.2](2,6)pyridinoparacyclophane-1,9-diene (**4**). Alternatively, oxidation of **8** to the corresponding bissulfone **10** followed by pyrolysis gave [2.2](2,6)pyridinoparacyclophane (**5**). Although [2.2](2,6)pyridinoparacyclophane (**5**) shows a temperature-dependent nmr spectrum and is clearly undergoing conformational flipping, no such temperature dependence is observed for the nmr spectrum of [2.2](2,6)pyridinoparacyclophane-1,9-diene (**4**) and it would appear that the ground state of the molecule corresponds to a perpendicular orientation of the two aromatic rings. This orientation in the solid state has been confirmed by a single crystal X-ray analysis of **4**.

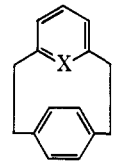
In accompanying papers,[2,3] we have presented studies on the rates of conformational flipping for [2.2]metaparacyclophane (**1**), [2.2]metaparacyclophane-1,9-diene (**2**), and their derivatives. The sensitivity of the rate of conformational flipping to such effects as nonbonded interactions and changes in bond angle is demonstrated by the much higher rate of flipping for **1** ($\Delta G^{\ddagger}_{-96}$ = 8.3 kcal/mol) than **2** ($\Delta G^{\ddagger}_{157}$ = 20.6 kcal/mol). Furthermore, the rate of conformational flipping is very sensitive to the nature of the substituent at the 8 position, as well as to the effect that remote polar groups have on that substituent.[3] For example, substitution of deuterium for hydrogen, as in **3**, leads to a rate increase of about 20%.

In view of the extensive studies on piperidine derivatives, it is clear that in the "conformational rivalry between the nonbonding electron pair on nitrogen and the proton on nitrogen" that the nonbonding electron pair has the smaller steric bulk.[4] Similarly, in the conformational flipping of derivatives of [2.2]metacyclophane, where the critical steric interaction is that at the 8 and 16 positions, the ordering of steric size is the interaction of =N– and =N– is smaller than =N– and =CH–, which is smaller than =CH– and =CH–.[5,6] The present study was undertaken to compare the steric size, as measured by rates of conformational flipping, of nitrogen and its nonbonded electron pair with carbon bonded to hydrogen in the [2.2]metaparacyclophane series, where presumably the critical interaction is that between the substituent at the 8 position and the π-electron cloud of the para-bridged ring.

The syntheses of the [2.2](2,6)pyridinoparacyclophane derivatives were accomplished following the general procedures employed in our related studies.[2,3,7] The

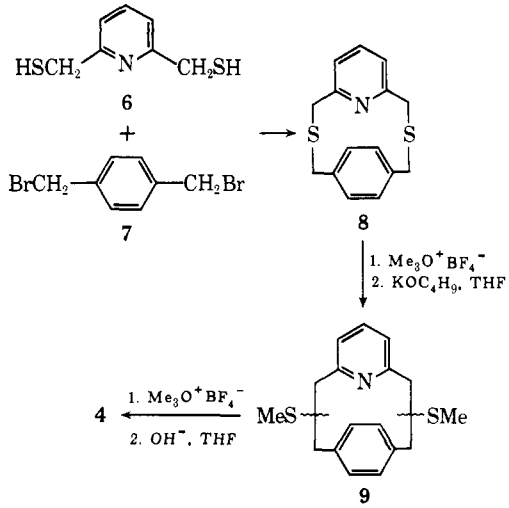


1, X = -CH-
4, X = -N-
11, X = -N$^+$H-



2, X = -CH-
3, X = -CD-
5, X = -N-
12, X = -N$^+$H-

condensation of 2,6-bis(mercaptomethyl)pyridine (**6**) with *p*-xylylene dibromide (**7**) occurred smoothly to give 2,11-dithia[2.2](2,6)pyridinoparacyclophane (**8**) in 48% yield. The formation of **8** could also be accomplished by the reaction of 2,6-bis(bromomethyl)pyridine and *p*-xylylene dibromide with sodium sulfide, but the yield *via* this procedure was only 36%. A Stevens rearrangement of **8** readily effected ring contraction giving **9**, as a mixture of isomers in 33% yield. Subjection of **9** to a Hofmann elimination then gave the desired [2.2]-(2,6)pyridinoparacyclophane (**4**) in 42% yield.



In terms of the general application of these procedures, it is worth noting that they proceed effectively even in the presence of a basic moiety such as the pyridine ring. The sulfide linkages are sufficiently more nucleophilic than the pyridine nitrogen that, by employing exactly 2 equiv of methylating agent (Meerwein's

(1) (a) We thank the National Science Foundation for their support of this investigation. (b) Fulbright-Hayes Scholar from the University of Warsaw, Warsaw, Poland, 1972–1973.

(2) V. Boekelheide, P. H. Anderson, and T. A. Hylton, *J. Amer. Chem. Soc.*, **96**, 1558 (1974).

(3) S. Sherrod, R. daCosta, R. A. Barnes, and V. Boekelheide, *J. Amer. Chem. Soc.*, **96**, 1565 (1974).

(4) R. A. Y. Jones, A. R. Katritzky, A. C. Richards, R. J. Wyatt, R. J. Bishop, and L. E. Sutton, *J. Chem. Soc. B*, 127 (1970); *cf.* M. J. Cook, R. A. Y. Jones, A. R. Katritzky, M. M. Manas, A. C. Richards, A. J. Sparrow, and D. L. Trepanier, *J. Chem. Soc., Perkin Trans 2*, 325 (1973).

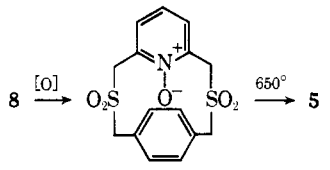
(5) I. Gault, B. J. Price, and I. O. Sutherland, *Chem. Commun.*, 540 (1967); J. R. Fletcher and I. O. Sutherland, *ibid.*, 1504 (1969).

(6) F. Vögtle, *Tetrahedron Lett.*, 3623 (1968).

(7) R. H. Mitchell and V. Boekelheide, *J. Amer. Chem. Soc.*, **96**, 1547 (1974).

reagent), methylation occurs exclusively on sulfur. This preference of a sulfide linkage over a pyridine nitrogen during methylation has been noted previously.[8]

Although the conversion of **4** to give **5** could be accomplished directly by hydrogenation over a palladium–charcoal catalyst, it was more convenient for obtaining larger quantities to prepare **5** by an alternate procedure. Oxidation of **8** with an excess of *m*-chloroperbenzoic acid in chloroform gave the corresponding bissulfone *N*-oxide **10**. Attempts to avoid *N*-oxide formation by using lesser amounts of *m*-chloroperbenzoic acid led to mixtures of *N*-oxides containing sulfoxides and monosulfones. However, pyrolysis of **10** at 650–680° gave [2.2](2,6)pyridinoparacyclophane (**5**) in 66% yield. It was unexpected, but gratifying, that under the conditions of the pyrolysis the *N*-oxide function was lost as well as the sulfone moieties. Also, if the conventional formulation of sulfone pyrolyses as involving an intermediate diradical is correct, it is surprising that such highly strained molecules as the [2.2](2,6)pyridinoparacyclophanes should be formed in such good yield.



10

From a comparison of the temperature dependence of the nmr spectra of [2.2]metaparacyclophane (**2**) and [2.2]metaparacyclophane-1,9-diene (**1**),[2] the temperatures for coalescence of signals for **2** and **1** were found to be +157 and −96°, respectively, at 100 MHz. This corresponds to $\Delta G^{\ddagger}$ values of 20.6 and 8.3 kcal/mol for their rates of conformational flipping. The lower barrier for conformational flipping for **1** as compared to **2** is attributed to various factors including (1) the differing bond angles which do not require as deep an intrusion of the C–H bond on the 8 position into the para-bridged aromatic π-electron cloud for **1** as for **2**, (2) the conjugative stabilization between the meta-bridged aromatic ring and the olefinic linkages which occur at the transition state of **1** but not for **2**, and (3) the repulsive nonbonded interactions of the methylene hydrogens at the transition state for **2** but not for **1**. Thus, by analogy, it was expected that the energy barrier for conformational flipping should be smaller for **4** than for **5**. This was found to be the case. The nmr spectrum of [2.2](2,6)pyridinoparacyclophane-1,9-diene (**4**) shows the four protons of the para-bridged ring as a singlet at τ 3.16, and this spectrum is unaltered by cooling the solution to the lowest temperatures (−110°) experimentally feasible for measurement. On the other hand, the nmr spectrum of [2.2](2,6)pyridinoparacyclophane (**5**) at room temperature shows the para-bridged ring protons as a singlet at τ 3.36, but when a solution in carbon disulfide is cooled this splits into two signals at τ 2.87 and 4.32. The coalescence temperature is −43.5°, so that, applying the method of Calder and Garratt,[9] the $\Delta G^{\ddagger}_{-43.5}$ for the conformational flipping of **5** is calculated to be 10.7 kcal/mol. The much smaller energy barrier for conformational flipping in the case of **5** as compared to **2** provides clear evidence that nitrogen with its lone pair engenders much less steric interaction than an aromatic carbon–hydrogen bond on intrusion into an aromatic π-electron cloud.

The fact that the nmr spectrum of **4** is unchanged even at the lowest temperatures experimentally feasible could be attributed to a very low energy barrier to conformational flipping or it could indicate that the two aromatic rings in **4** are perpendicular to each other. In the case of **1**, a single crystal X-ray analysis showed the meta-bridged aromatic ring to be inclined 41° from perpendicular to the para-bridged ring.[10] A single crystal X-ray analysis of [2.2](2,6)pyridinoparacyclophane-1,9-diene (**4**) has now shown that the two aromatic rings are in fact perpendicular.[11] Whether this perpendicularity is true for solutions of **4** as well as for its crystalline state is not, of course, certain. However, the lack of temperature dependence of the nmr spectrum of **4** is suggestive that it may be so.

Both **4** and **5** behave as typical pyridine bases, readily forming salts and complexes. In the hope of studying the steric interactions of the protonated ammonium ion in this series, we prepared the fluoroborate salts, **11** and **12**. The nmr spectrum of **12** was clearly temperature dependent and coalescence of the signals for the two types of para-bridged ring protons occurred at −5.6° in perdeuterioacetone, an appreciably higher temperature than for the free base **5**. This would, of course, be expected in view of the work of Katritzky and others suggesting a smaller steric size for the nonbonded electron pair on nitrogen as compared to the proton on nitrogen. However, when the experiment was repeated using perdeuteriomethanol as solvent rather than perdeuterioacetone, coalescence of the two signals for the para-bridged ring protons occurred at 21.0°. This is strong evidence that, in the case of the fluoroborate salt **12**, the temperature of coalescence is not a true measure of the rate of conformational flipping of the pyridinium ion. Rather, it suggests that there is a facile equilibrium between the salt **12** and the corresponding free base **5**. Since conformational flipping would be expected to be much more rapid for the free base **5** than its salt **12**, the coalescence temperature becomes dependent on the rate of equilibration between the salt **12** and the free base **5**. This rate, in turn, will depend heavily on the basicity of the solvent. Since it has been shown that acetone is appreciably more basic than methanol,[12] the fact that the coalescence temperature for **12** is appreciably lower in acetone than in methanol is in accord with this interpretation.

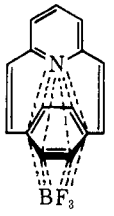
$$\mathbf{12} + \text{solvent} \rightleftharpoons \mathbf{5} + \text{solvent}\cdot\text{H}^{+}$$

In contrast, the nmr spectrum of solutions of the fluoroborate salt **11**, derived from [2.2](2,6)pyridinoparacyclophane-1,9-diene, in perdeuterioacetone did not show any temperature dependence even at the lowest temperatures (−100°) feasible. Either equilibration between the salt **11** and the corresponding free base **4** is extremely rapid leading to an appreciable concentration of **4**, or the protonated species **11** is symmetrical, presumably with the two aromatic rings being perpendicular. For comparison the boron trifluoride complex of

(8) V. Boekelheide and J. A. Lawson, *Chem. Commun.*, 1558 (1970).
(9) I. C. Calder and P. J. Garratt, *J. Chem. Soc. B*, 660 (1967).
(10) A. W. Hanson, *Acta Crystallogr., Sect. B*, 27, 197 (1971).
(11) L. H. Weaver and B. W. Matthews, *J. Amer. Chem. Soc.*, 96, 1581 (1974).
(12) E. A. Guggenheim, J. E. Mayer, and F. C. Tompkins, "International Encyclopedia of Physical Chemistry, Topic 15, Vol. 4, Macmillan, New York, N. Y., 1965, p 294.

4 was prepared. In this case the BF_3 group, if directly attached to nitrogen, is too bulky to allow conformational flipping. However, the nmr spectrum of a perdeuterioacetone solution of the boron trifluoride complex of **4** was symmetrical, showing the four protons of the para-bridged ring as a singlet at τ 2.62. Again the spectrum was not temperature dependent within the experimentally accessible range.

Although the fluoroborate salt **12** is white (uv (CH_3CN) 257 nm (ϵ 4340)), both the fluoroborate salt **11** and the boron trifluoride complex of **4** are yellow. Their spectra are quite similar with an absorption band at 243 nm (ϵ *ca.* 15,000) with a strong shoulder at 343 nm (ϵ *ca.* 2000) and tailing out into the visible. At present it is not clear what exact assignment of structure should be made for **11** and for the boron trifluoride complex. A speculative structure for the boron trifluoride complex of **4** which would account for its ultraviolet and visible spectrum as well as the lack of temperature dependence of its nmr spectrum is shown by **13**. Regardless of whether this is the correct structure for the boron trifluoride complex of **4** or not, this speculation raises the intriguing question of whether molecules can be suitably devised such that electrostatic interaction (bond formation?) between functional groups can occur directly through an aromatic ring.



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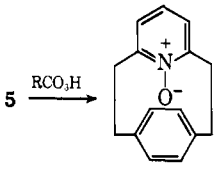
Treatment of [2.2](2,6)pyridinoparacyclophane (**5**) with *m*-chloroperbenzoic acid readily converted it to the corresponding *N*-oxide, **14**. As would be expected, a group as bulky as the *N*-oxide prevents conformational flipping and the nmr spectrum of **14** showed the para-bridged protons as two signals at τ 2.64 and 3.86.



14

Experimental Section[13]

2,11-Dithia[3.3](2,6)pyridinoparacyclophane (8). To a stirred solution of 2.20 g of sodium hydroxide in 2 l. of ethanol there was added dropwise a solution of 4.43 g of 2,6-bis(mercaptomethyl)-pyridine (**6**)[14] and 6.84 g of *p*-xylylene dibromide in 500 ml of benzene over a period of 12 hr. After the mixture had been stirred an additional 10 hr at room temperature, it was filtered and the filtrate concentrated under reduced pressure. The residue was taken up in dichloromethane, washed with cold brine solution, and dried, and the solution was concentrated. Sublimation of the residue gave 3.35 g (48%) of a white crystalline powder. A sample, recrystallized from methanol, yielded white crystals: mp 177–178°; uv (cyclohexane) 232 nm (ϵ 7880) and 274 (2600); nmr ($CDCl_3$) an AB_2 multiplet at τ 2.45–2.96 (3 H, pyridine-*H*), a singlet at 3.11 (4 H, benzene-*H*), a singlet at 6.12 (4 H, $ArCH_2$), and a singlet at 6.46 (4 H, $ArCH_2$); mass spectrum (70 eV) *m/e* (rel intensity) 273 (100), 139 (62), 134 (81), and 104 (33).[15]

Alternatively, the formation of **8** could be accomplished by the simultaneous addition from two Hershberg funnels of a solution of 27.0 g of 2,6-bis(bromomethyl)pyridine and 8.5 g of *p*-xylylene dibromide in 900 ml of benzene and a solution of 48.0 g of sodium sulfide nonahydrate in 900 ml of ethanol dropwise with rapid stirring to a mixture of 1.5 l. of ethanol and 500 ml of benzene. When the reaction mixture was worked up as before, there was isolated 9.8 g (36%) of white crystals, identical in all respects with those described above.

Stevens Rearrangement of 8 to Give 9. To a solution of 756 mg of **8** in 50 ml of dichloromethane there was added with stirring 1.26 g of trimethyloxonium fluoroborate.[16] The resulting precipitate was collected by filtration, washed with ethyl acetate, and dried to give 1.33 g (100%) of the bis(methylsulfonium) fluoroborate of **8**. This was dissolved in 100 ml of tetrahydrofuran containing 750 mg of potassium *tert*-butoxide. After the mixture had been stirred for 25 min at room temperature, it was concentrated and the residue was taken up in dichloromethane. The organic layer was washed with water, dried, and concentrated. Chromatography of the residue over silica gel using a 1:19 mixture of ethyl acetate and dichloromethane for elution gave 220 mg (26%) of white crystals: mp 152–153°; nmr ($CDCl_3$) a broad multiplet at τ 2.0–3.0 (5 H, ArH), a singlet at 3.11 (2 H, ArH), and a singlet at 8.05 (6 H, SCH_3); mass spectrum (70 eV) *m/e* (rel intensity) 301 (100), 254 (86), 239 (30), 181 (27), and 103 (17).

Hofmann Elimination of 9 to Give 4. To a solution of 220 mg of **9** in 50 ml of dichloromethane there was added with stirring 65 mg of trimethyloxonium fluoroborate.[16] The resulting precipitate was collected by filtration, washed with ethyl acetate, and dried to give 370 mg (100%) of a white solid. This was dissolved in 100 ml of tetrahydrofuran and stirred at room temperature for 15 hr with an excess of ion exchange resin (Amberlite IRA-400, OH^-). After decantation from the ion exchange resin, the solution was concentrated. Chromatography of the residue over silica gel using benzene for elution gave 147 mg (42%) of white crystals: mp 157–158°; uv (cyclohexane) 232 nm (ϵ 32,000), 242 (30,800), and 292 (1760); nmr ($CDCl_3$) an AB pattern at τ 2.61 and 3.67 (4 H, J = 10 Hz, –CH=CH–), an AB_2 pattern at 2.76 and 3.27 (3 H, J = 8 Hz, pyridine-*H*), and a singlet at 3.16 (4 H, para-bridged benzene-*H*); mass spectrum (70 eV) *m/e* (rel intensity) 205 (69), 204 (100), 150 (38), and 102 (19).

The fluoroborate salt 11 was prepared by mixing a solution of ordinary commercial boron trifluoride etherate in ether with an ethereal solution of [2.2](2,6)pyridinoparacyclophane-1,9-diene (**4**). The resulting yellow precipitate was collected, washed with ether, and dried. Recrystallization from methanol containing a few drops of ether gave bright yellow crystals: mp 207–210°; uv (CH_3CN) 218 nm (ϵ 22,000), 243 (15,350), and 343 (sh, 2032); nmr (CD_3COCD_3) an AB_2 pattern at τ 1.50 and 2.08 (3 H, J = 10 Hz, pyridine-*H*), an AB at 1.75 and 2.95 (4 H, J = 13 Hz, –CH=CH–), and a singlet at 2.50 (4 H, para-bridged benzene-*H*).

The boron trifluoride complex of 4 was prepared by dissolving 16 mg of **4** in carefully dried ether and adding excess boron trifluoride etherate which had been freshly distilled from calcium hydride. The yellow precipitate was collected, washed with dry ether, and sublimed at 10^{-3} mm to give 15 mg of yellow crystals: mp 204–206°; uv (CH_3CN) 218 nm (ϵ 21,820), 243 (14,980), and 343 (sh, 1920); nmr (CD_3COCD_3) an AB_2 pattern at τ 1.70 and 2.25 (3 H, J = 10 Hz, pyridine-*H*), an AB at 1.92 and 3.06 (4 H, J = 13 Hz, –CH=CH–), and a singlet at 2.62 (4 H, para-bridged benzene-*H*).

2,2,11,11-Tetraoxo-2,11-dithia[3.3](2,6)pyridinoparacyclophane *N*-Oxide (10). To a solution of 340 mg of **8** in 40 ml of chloroform cooled in a Dry Ice bath there was added dropwise a solution of 1.26 g of *m*-chloroperbenzoic acid (85% pure) in 35 ml of chloroform over a period of 1.5 hr. The mixture was stirred an addi-

(13) Elemental and mass spectral analyses were determined by Dr. S. Rottschaefer, University of Oregon Microanalytical Laboratories. Infrared spectra were measured with a Beckman IR-5a; ultraviolet and visible spectra with a Cary 15; nmr spectra with a Varian XL-100 spectrometer; and mass spectra with a Consolidated Model 21-110 instrument. We thank the National Science Foundation for funds supporting the purchase of the Varian XL-100. All elemental analyses of new compounds gave experimental values within 0.4% of the calculated values.

(14) R. A. Partyka, U. S. Patent 3,290,319, (1966); *Chem. Abstr.*, **66**, 115,609k (1967).

(15) We thank I. D. Reingold for the details of this particular experiment.

(16) H. Meerwein, *Org. Syn.*, **46**, 120 (1966).

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°; 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° 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 resublimation this yielded white crystals: mp 80.5–81.5°; 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°; ir (KBr) 3450–2500 (N^+–H) and 1580 and 1560 cm^{-1} (–C=C–); uv (CH_3CN) 257 nm (ϵ 4340); nmr (CD_3COCD_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, $ArCH_2$). This nmr spectrum was temperature dependent (T_c −5.6°) 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°; 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 Ar*H*), an AB_2 multiplet at 3.17 (3 H, pyridine-*H*), a narrow multiplet at 3.86 (2 H, para-bridged benzene Ar*H*), 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 *Fdd*2, 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 reports[1] 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]metaparacyclophane-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 2*mm* 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).