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(20) All irradiations were carried out on nitrogen-purged solutions through a Pyrex filter by a 450-W high-pressure mercury vapor lamp at room temperature for 6 h. The product mixture was extracted into methylene chloride.
(21) 1,4-Dicyanobenzene is consumed by a base-catalyzed reaction to form the methyl imidate.[22] During the reduction of alkyl halides upon treatment with alkali naphthalenes, a major competing reaction is coupling of the radical with the anion radical to give ultimately dihydroalkylnaphthalenes.[23] This type of reaction may account for the consumption of the sensitizer during reaction.
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Syntheses, Properties, and Photoelectron Spectra of Substituted and Layered [2.2](2,6)Pyridinoparacyclophanes

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Abstract: Syntheses of methyl-substituted [2.2](2,6)pyridinoparacyclophanes **15, 16,** and **17,** as well as their corresponding 1,9-dienes, **19, 20,** and **21,** are reported. The triple-layered [2.2](2,6)pyridinoparacyclophanes **23, 24,** and **30** have also been prepared. The temperature-dependent NMR behavior of the simple [2.2](2,6)pyridinoparacyclophanes is in accord with a geometry where the pyridine ring is more or less parallel to the benzene ring, but undergoing rapid conformational flipping with an energy barrier of about 12 kcal/mol. The triple-layered cyclophane **30** shows a similar behavior, but with a slightly smaller energy barrier (11 kcal/mol). However, the apparent geometry of the corresponding 1,9-dienes has the pyridine ring essentially perpendicular to the benzene ring. This is true also of the triple-layered cyclophane **23,** where both pyridine rings are almost perpendicular to the central benzene ring. The [2.2](2,6)pyridinoparacyclophanes show enhanced basicity compared to simple model pyridine derivatives, whereas their 1,9-diene analogues show greatly reduced basicity. Photoelectron spectra have been measured for a number of the [2.2](2,6)pyridinoparacyclophanes and their corresponding 1,9-dienes and orbital assignments have been proposed for their lower energy ionization potentials.

In a previous study,[2] syntheses of [2.2](2,6)pyridinoparacyclophane (**14**) and its corresponding 1,9-diene **18** were reported together with the interesting observation that the NMR spectrum of **14** is temperature dependent, indicating conformational mobility, whereas the NMR spectrum of **18** is temperature independent. Furthermore, an X-ray crystallographic analysis of [2.2](2,6)pyridinoparacyclophane-1,9-diene (**18**) showed the two aromatic rings in this molecule to be essentially perpendicular to each other.[3] To gain a better understanding of the physical and chemical properties of this type of structure, we have now prepared a series of methyl-substituted derivatives and three triple-layered analogues.

The syntheses of the methyl-substituted derivatives are summarized in Scheme I. In each case, the intermediate dithiacyclophane (**6–9**) was converted to the corresponding ring-contracted compound (**10–13**) by the benzyne–Stevens rearrangement procedure.[4] Benzyne was generated thermally from 1-(2′-carboxyphenyl)-3,3-dimethyltriazene,[5] and overall this proved to be a much more efficient and convenient procedure than the simple Stevens rearrangement reported earlier for the parent case (**6**).[2] Treatment of the phenylthiacyclophanes (**10–13**) with Raney nickel catalyst gave the [2.2](2,6)pyridinoparacyclophanes (**14–17**) in good yield, whereas oxidation of the phenylthiacyclophanes (**10–13**) to the corresponding bissulfoxides, followed by thermal elimination, gave the [2.2](2,6)pyridinoparacyclophane-1,9-dienes (**18–21**) in fair to good yields.

The first property examined for these methyl-substituted [2.2](2,6)pyridinoparacyclophanes was their nuclear magnetic resonance behavior. Each of the [2.2](2,6)pyridinoparacyclophane-1,9-dienes (**18–21**) showed a symmetrical pattern in its ^{1}H NMR spectrum, which was temperature independent. Thus, either the barrier to conformational flipping in these compounds is quite low or, as is more likely, these compounds

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Scheme I

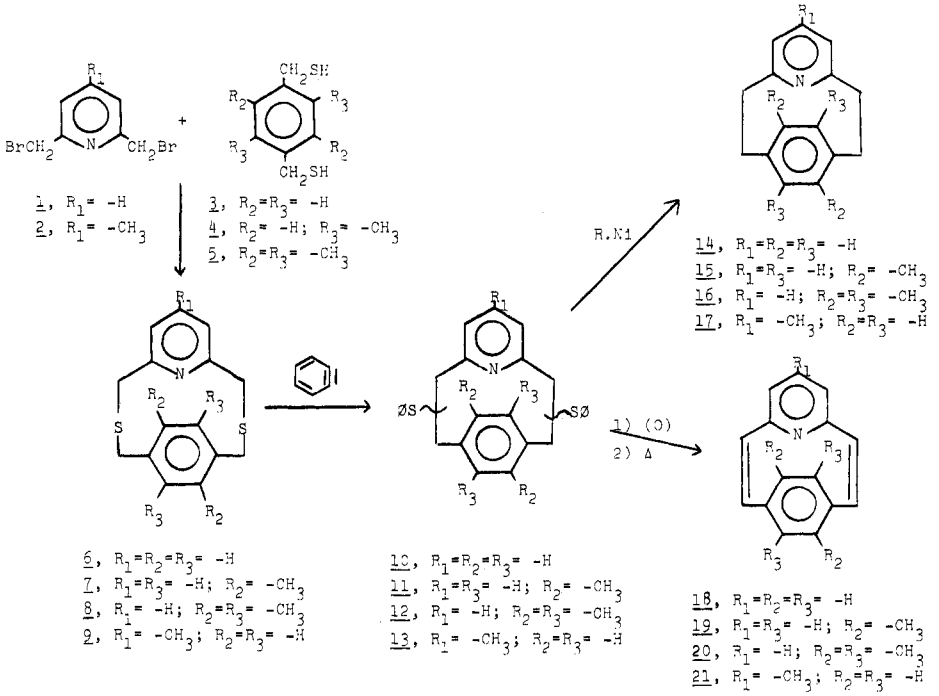


Table I. Relationship of the C-D Infrared Stretching Frequency Shifts for Various Pyridines and the pK_a Values for the Corresponding Protonated Amines

	compounds	pK_a	$\Delta\nu$, cm^{-1}
1.	pyridine	5.23[a]	28
2.	2-methylpyridine	5.97[a]	39
3.	3-methylpyridine	5.68[a]	32
4.	2,6-dimethylpyridine	6.75[a]	47
5.	2,4,6-trimethylpyridine	7.43[a]	53
6.	**14**	7.95[b]	58
7.	**15**	7.48[b]	53
8.	**16**	7.38[b]	52
9.	**6**	7.10[b]	49
10.	**7**	6.64[b]	45
11.	**8**	6.46[b]	42

[a] Literature values.[9] [b] Measured values.

have a perpendicular orientation of the aromatic rings in solution, as well as in the crystalline state.[3]

The ^{1}H NMR spectra of the [2.2](2,6)pyridinoparacyclophanes **15** and **16** measured in perdeuterioacetone were temperature dependent, showing a coalescence temperature at −25 °C, which, by the method of Calder and Garratt,[6] corresponds to $\Delta G^{\ddagger}_{25\,°C}$ = 12 kcal/mol for the conformational flipping process. Because the values observed for these compounds were somewhat at variance with that found earlier for **14**,[2] the coalescence temperature for **14** was remeasured in deuterioacetone and found to be −29 °C, essentially the same as for **15** and **16**. Furthermore, the coalescence temperature for **15** was unchanged when measured in carbon disulfide, indicating very little, if any, solvent dependence for the conformational flipping process. Since coalescence temperatures are not a very accurate measure of kinetic parameters, a solution of **15** in perdeuterioacetone was carefully examined at −61, −68, and −74 °C by the selective pulse NMR technique of Dahlquist, Longmuir, and DuVernet.[7] The value of $\Delta G^{\ddagger}_{61\,°C}$ by this method was found to be 12.51 kcal/mol. Clearly, the presence of methyl groups on the para-bridged benzene ring has very little effect on the conformational flipping process of these pyridinoparacyclophanes.

It was expected that the differences in geometry between the [2.2](2,6)pyridinoparacyclophanes (**14–16**) and their corresponding dienes (**18–20**) would be reflected by differences in their relative basicities. For this measurement, we elected the convenient and accurate infrared method first suggested by Lord, Nolin, and Stidham[7] and later used by Richman and Simmons.[8] The infrared stretching frequency for the carbon–deuterium bond in deuteriochloroform is shifted to lower frequencies by the presence of solutes that undergo hydrogen bonding. In an ideal situation, the magnitude of the frequency shift can be directly related to the pK_a of a protonated amine in aqueous solution. Since the generality of this method had not been demonstrated previously, we measured the C-D frequency shift for a broad range of amines whose pK_a values in aqueous solution were available from the literature (see Table I). Within a series, such as that of tertiary amines, and especially if the series were limited to pyridine derivatives, the correlation is very good and gives a straight-line plot of pK_a against deuteriochloroform C-D infrared frequency shifts.

A comparison of amines from different series, for example, comparing primary and tertiary amines, is not so satisfactory. Presumably this is due to the fact that solvation plays an important role in pK_a values in aqueous solution, but not in deuteriochloroform, and this effect varies markedly depending upon the type of amine under consideration.

Using this C-D infrared frequency shift method, we found [2.2](2,6)pyridinoparacyclophane (**14**) to have a pK_a of 7.95, a value of 1.20 pK_a units more basic than 2,6-dimethylpyridine, a model reference compound. Apparently the increased basicity of **14** is the result of internal electron donation from the benzene ring to the pyridine ring within the cyclophane framework. Compound **15**, with a pK_a of 7.48, is less basic than **14**, and presumably this decrease in basicity is the result of steric hindrance by the methyl groups on the para-bridged benzene ring. Compound **16**, with four substituent methyl groups, has a pK_a of 7.38, showing a continuation of the trend of decreased basicity with increased steric hindrance.

If the increased basicity of the [2.2]pyridinoparacyclophanes is due to electron donation from the benzene ring, an increase in distance between the pyridine and benzene rings should lessen this effect. This is found to be true. The dithiapyridinophanes **6**, **7**, and **8**, where the rings are separated by three atom bridges rather than two, are appreciably less basic than

14, 15, and **16,** and, in fact, are in the same range of basicity as the model pyridine derivatives.

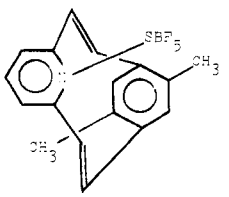
In contrast to the strong basicity of the [2.2](2,6)pyridinoparacyclophanes, the corresponding [2.2](2,6)pyridinoparacyclophane-1,9-dienes (**18, 19,** and **20**) showed no measurable effect on the infrared stretching frequency of the C–D bond of deuteriochloroform. Thus, by this technique they are off the scale and so are much weaker bases than their saturated counterparts (**14, 15,** and **16**) and also much weaker bases than reference models such as 2-vinylpyridine (pK_a = 4.92).[9] The striking difference in basicity between the two series is, in our opinion, due to the difference in geometry of the molecules. Electron donation from the benzene ring to the pyridine should still be possible, and to about the same extent, for the pyridinophane-1,9-dienes. However, if the two rings are perpendicular to each other in the pyridinophane-1,9-diene series, as is known to be true in the crystalline state,[3] the nitrogen lone pair is buried in the cavity of the electron π cloud of the benzene ring, and so is not easily approached by a Lewis acid.

As had been reported earlier,[2] treatment of **14** with moist boron trifluoride etherate gives the corresponding fluoroborate salt as white crystals, whereas **18** reacts with moist boron trifluoride etherate to give a yellow crystalline fluoroborate. Similarly, **15** and **16** formed white crystalline fluoroborate salts, but **19** and **20** gave yellow salts. The NMR spectra of the fluoroborate salts of **14, 15,** and **16** are temperature dependent, with a coalescence temperature of about 15 °C for solutions in deuteriomethanol. As expected, protonation of the pyridine nitrogen raises the energy barrier for conformational flipping.

On the other hand, the NMR spectra of the yellow fluoroborate salts of the 1,9-dienes (**18, 19,** and **20**) were symmetrical and independent of temperature, at least to the lowest temperatures (−100 °C) experimentally feasible. This raised the question of whether these molecules were undergoing very easy and rapid conformational flipping, or whether protonation was occurring to give a symmetrical ion.

Since the pyridinophane-1,9-dienes (**18, 19,** and **20**) showed no interaction with europium shift reagent, it was not possible to employ this simple NMR technique for ascertaining the site of complexation. In an alternate approach, a ^{13}C NMR study was made to see the effect of protonation on ^{13}C chemical-shift values for various positions in the skeletal framework. Both **15** and **19,** as well as their protonation species, were examined, and the results are summarized in Table II in the Experimental Section. The pattern of ^{13}C chemical-shift changes on protonation is very similar in both series. Although not conclusive, these results certainly suggest that **19** is protonated on nitrogen and that the pyridinium ring is undergoing extremely rapid conformational flipping.

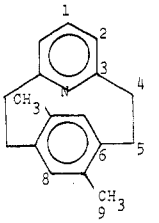
Finally, it was found that **19** undergoes complex formation with antimony pentafluoride in deuteriochloroform. That bonding of the antimony pentafluoride moiety occurs directly to the pyridine nitrogen is evident from its NMR spectrum. The bulky antimony pentafluoride group prevents conformational flipping, and so the two methyl groups and two aromatic protons attached to the benzene ring show different signals, as is required for structure **22.** In view of these results, the



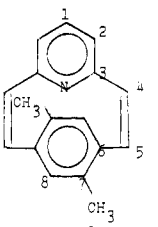
22

possibility raised earlier that [2.2](2,6)pyridinoparacyclophane-1,9-diene (**18**) might be undergoing complex formation on the open face of the para-bridged benzene ring[2] can now be dismissed.

Table II. ^{13}C NMR Chemical Shifts of Compounds **15** and **19** on Conversion to Their Protonated Fluoroborate Salts



15



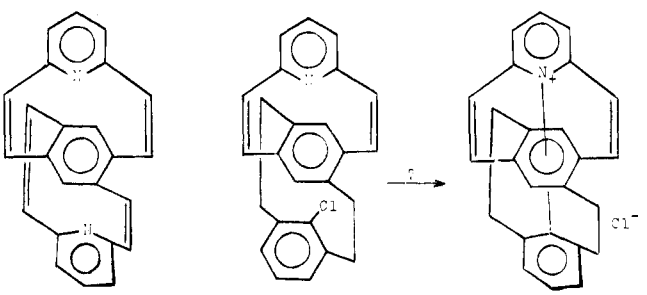
19

carbon	free base	fluoroborate salt[a]	free base	fluoroborate salt[a]
1	137.6[b]	145	136.7[b]	146.6
2	120.8	125.4	122.1	127.0
3	160.5	156.7	153.8	147.4
4	37.2	32.7 or 33.3	129.9 or 142.1	127.1 or 143.1
5	32.9			
6	134.2 or 135.3	135.8 or 136.6	135.3 or 135.5	136.7 or 138.6
7				
8	132.9	132.5	132.8	130.7
9	17.8	17.4	18.1	17.8

[a] The fluoroborate salts were prepared by treating **15** and **19,** respectively, in ether with moist boron trifluoride etherate. [b] The signals listed are in parts per million downfield from tetramethylsilane.

Triple-Layered Cyclophanes

The probability that the benzene and pyridine rings in the [2.2](2,6)pyridinoparacyclophane-1,9-dienes are perpendicular to each other still left the possibility, though, that in a properly designed molecule one might observe interactions occurring directly through the π-electron cavity of a benzene ring. For this purpose we considered the two types of triple-layered cyclophanes shown by structures **23** and **24.** For the case of **23,** it seemed that, if each pyridine ring were essentially perpendicular to the central benzene ring, direct interaction between the two pyridine nitrogens might be possible. For the case of **24,** interaction might occur to expel a chloride ion and give the ion **25.**

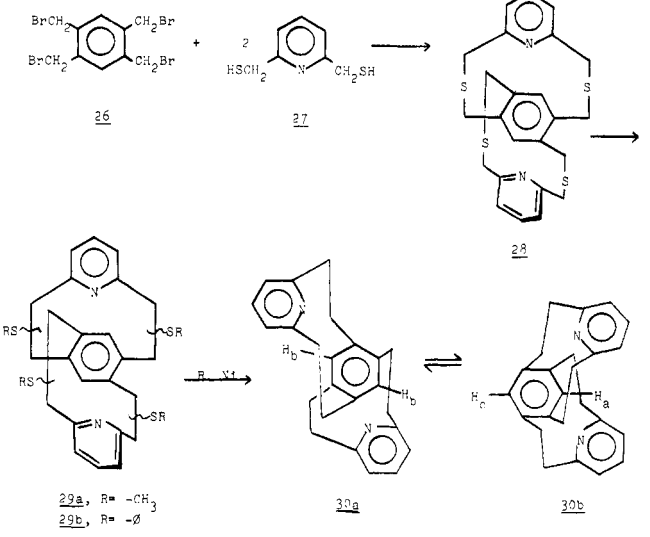


23 24 25

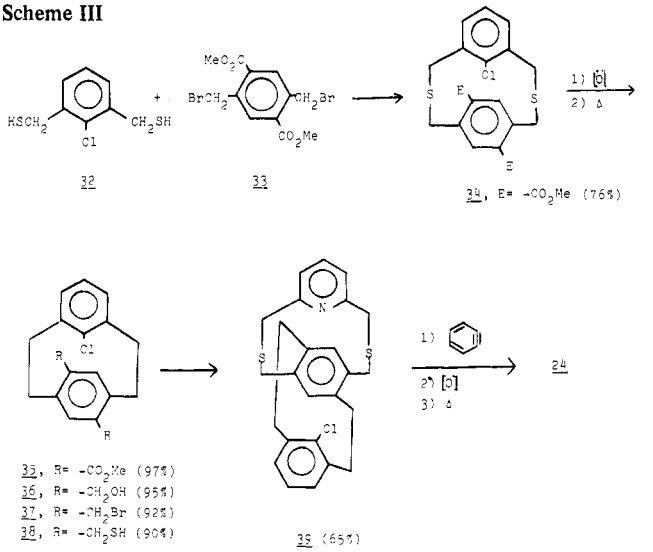
The key to the synthesis of **23,** as summarized in Scheme II, was the observation that 1,2,4,5-tetrakis(bromomethyl)benzene (**26**) underwent coupling with 2 equiv of 2,6-bis(mercaptomethyl)pyridine (**27**) to give thiacyclophane **28** in 34% yield. Ring contraction of **28** using the Wittig rearrangement[10] led to **29a** as a mixture of isomers. All attempts to convert **29a** to **23** by a Hofmann elimination reaction were unsuccessful. However, treatment of **29a** with Raney nickel catalyst gave **30,** the corresponding triple-layered cyclophane with saturated bridges.

Although the NMR spectrum of **30** at room temperature shows the benzene protons as a singlet at τ 4.10, this is a

Scheme II

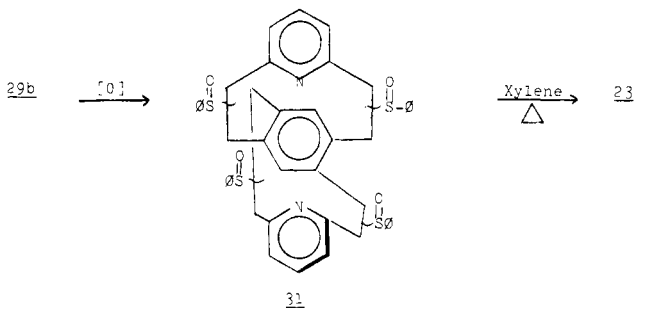


Scheme III



time-averaged spectrum. At low temperature (−70 °C), this signal is resolved into three separate ones at τ 2.5 (H_c), 4.18 (H_b), and 5.59 (H_a) in an approximate ratio of integrated areas of 1:2:1. This is what would be expected for **30** if it exists as a mixture of interchanging conformers **30a** and **30b**, where the resolved signals correspond to H_a, H_b, and H_c. The coalescence temperature was found to be −39 °C, corresponding to a value of $\Delta G^{\ddagger} = 11$ kcal/mol for the conformational flipping process. Thus, the behavior of the triple-layered pyridinophane **30** is remarkably similar to that of the simple [2.2](2,6)pyridinoparacyclophanes (**14, 15,** and **16**).

Eventually, it was found that heating **28** with 1-(2′-carboxyphenyl)-3,3-dimethyltriazene in chlorobenzene proceeded to give the phenylthio derivative **29b** as a mixture of isomers in 55% yield. Oxidation of **29b** to the corresponding tetrasulf-



oxide **31** followed by pyrolysis then yielded the desired tetraene **23** in 23% yield.

An X-ray crystallographic examination of **23** has been made by Hanson, and the molecule has twofold rotation symmetry about an axis through the nonsubstituted carbon atoms of the benzene ring.[11] The central benzene ring has a twist-boat conformation with the pyridine rings bent away from true perpendicularity to the benzene ring by about 15°. Each pyridine nitrogen lies 2.52 Å from the mean plane of the benzene ring, and so the nitrogen to nitrogen distance is 5.04 Å. It had been hoped that it would be possible to examine the monoprotonated derivative of **23** to see whether or not the ion had a symmetrical structure. However, **23** showed very little basicity and it was not possible to prepare such a species. The ultraviolet spectrum of **23** is very similar to that of the simple [2.2](2,6)pyridinoparacyclophane-1,9-dienes (**18, 19,** and **20**), having absorption bands at 247 (ϵ 21 430), 253 (22 140), 260 (18 630), and 294 nm (7380), but with a strong absorption tail well out into the visible (ϵ 477 at 420 nm and 239 at 470 nm), giving the compound its yellow color.

The synthesis of **24** was accomplished in a stepwise fashion following the usual procedures for making cyclophanes via dithiacyclophane intermediates and is summarized in Scheme III.

The ^{1}H NMR spectrum of **24** is in accord with the pyridine ring being perpendicular to the central benzene ring, whereas the chlorobenzene ring is roughly parallel and does not undergo conformational flipping. Thus, the two protons of the central benzene ring appear as separate singlets. The most interesting property of **24** is its mass spectrum, which shows *m/e* signals at 369 and 334 with very little fragmentation below this. The signal at 369 corresponds to the parent molecular ion of **24,** whereas the signal at 334, which shows seven times the intensity of the parent molecular ion, fits that of the positive ion depicted in structure **25**. A high-resolution mass spectrum confirmed that the molecular composition of the two ions agrees with these assignments. In the case of the mass spectra of the precursor compounds, **34–39,** the parent molecular ion is always the most intense signal and a significant amount of fragmentation does occur. Thus, the possibility exists that **24,** on electron bombardment in the gas phase, undergoes chloride ion displacement to give the novel positive ion shown by **25.** Obviously, it would be highly desirable to obtain **25** in sufficient quantity to examine its properties. Unfortunately, numerous experiments attempting to convert **24** to **25** by thermal, photochemical, or metal-catalyzed reactions have been completely without success.

Photoelectron Spectra

Of particular interest to our studies was the extent of interaction of the π-electron cloud of the benzene ring with the π-electron cloud of the pyridine ring and the lone pair on pyridine, and for this purpose we measured the photoelectron spectra of these compounds. The first five vertical ionization potentials of the [2.2](2,6)pyridinoparacyclophanes (**14, 15,** and **16**) and their probable correlation and orbital assignments are summarized in Figure 1. The assignments are based on analogy to appropriate model compounds and, although not completely certain, seem very reasonable. Thus, the first two ionization potentials in each case are assigned to the π_3 and π_2 benzene ring orbitals. On this basis, the first two ionization potentials appearing at 7.57 eV for **16,** a hexa-substituted benzene derivative, compare well with the observed value of 7.90 eV for the first two ionization potentials of hexamethylbenzene.[12]

The third and fourth ionization potentials appear to relate to the n orbital of the pyridine nitrogen and the π_3 orbital of

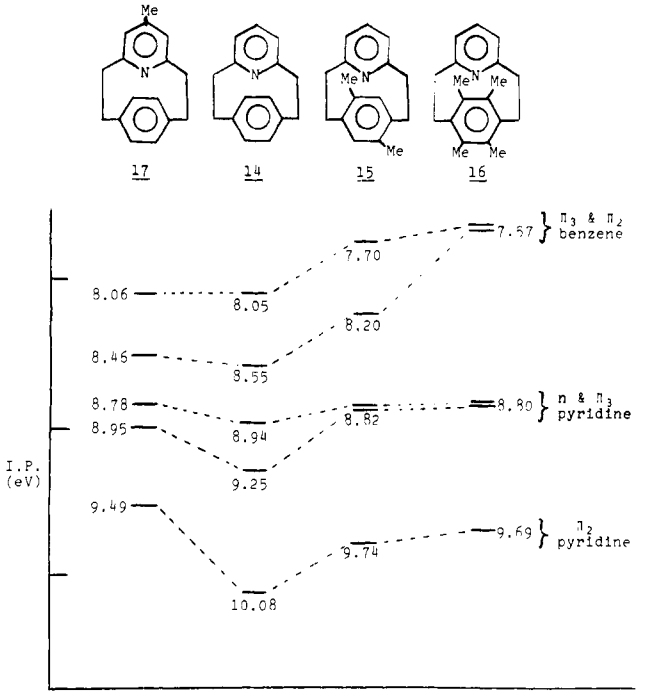


Figure 1. Photoelectron spectra of compounds **14, 15, 16,** and **17.** A plot of their first five vertical ionization potentials, their correlation, and orbital assignments.

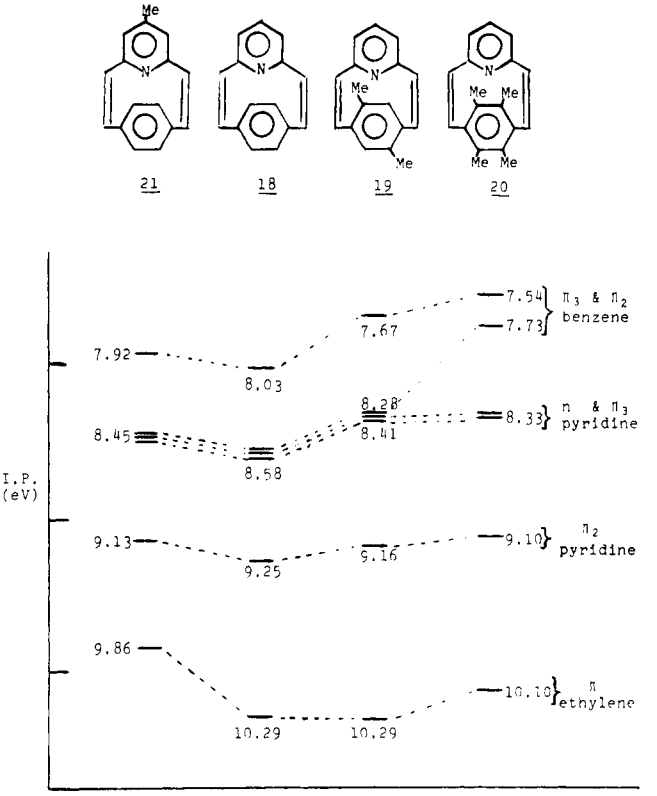


Figure 2. Photoelectron spectra of compounds **18, 19, 20,** and **21.** A plot of their first six vertical ionization potentials, their correlation, and orbital assignments.

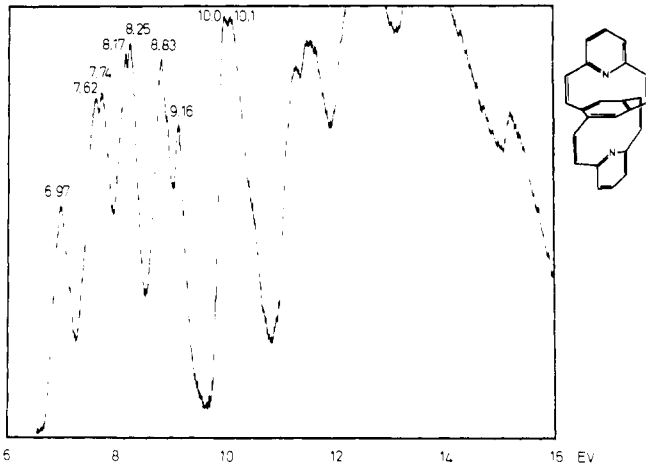


Figure 3. Photoelectron spectrum of **23.** Vertical ionization potentials are given in electron volts.

the pyridine ring, but it was not obvious which was which. To settle this question, it seemed easiest to look at a substituent effect that would distinguish between the two choices, and so we prepared **17** (see Scheme I), the analogue of **14** having a methyl group in the γ position. It is known from the work of Heilbronner et al. that γ-methyl substitution on pyridine lowers the ionization potential for the n band by almost 0.1 eV, whereas the π_3 band of pyridine is lowered somewhat more.[13] Similarly, Ramsey has observed that on going from 2,6-lutidine to 2,4,6-collidine, the ionization potential for the n band shifts from 9.30 to 9.20 eV.[14] As can be seen in comparing **17** to **14** in Figure 1, the ionization potential for the third band shifts to a lower value by 0.16 eV, whereas that of the fourth band shifts by 0.30 eV. Thus, the assignment of the third ionization potential to n and the fourth to the π_3 orbital of pyridine seems a better fit for the effect of methyl substitution. This leaves the assignment of the fifth ionization potential to the π_2 orbital of pyridine.

The first six vertical ionization potentials of the [2.2]-(2,6)pyridinoparacyclophane-1,9-dienes (**18, 19, 20,** and **21**) are given in Figure 2. Their assignment to the various molecular orbitals follows in a straightforward fashion from the previous discussion.

Thus, the photoelectron spectra of the [2.2]pyridinoparacyclophanes (**14–17**) and the [2.2]pyridinoparacyclophane-1,9-dienes (**18–21**) show nothing exceptional to reflect their unusual geometry. Also, the two series show a surprisingly good correspondence with each other. However, the photoelectron spectrum of the triple-layered pyridinophane **23** (Figure 3) does show an exceptionally low first ionization potential. The remaining ionization potentials through the 10.1-eV band bear, at least superficially, a rough correspondence to the simple [2.2](2,6)pyridinoparacyclophane-1,9-dienes. The data on hand are inadequate to make any detailed interpretation of the spectrum of **23** or to suggest an explanation for the origin of the surprisingly low first ionization potential.

Experimental Section[15]

4-Methyl-2,6-bis(bromomethyl)pyridine (2). The synthesis of 4-methyl-2,6-bis(bromomethyl)pyridine was accomplished by a convenient, but poor yielding, route starting with 2,4,6-collidine.[16] To 63.8 g of collidine there was added dropwise with stirring at room temperature 90 g of an aqueous 30% hydrogen peroxide solution over a period of 1 h. The mixture was then boiled under reflux for 22 h and concentrated. After careful addition of 175 mL of acetic anhydride to the residual oil, the solution was boiled under reflux for 1 h and again concentrated. To the dark brown oil was added another 92 g of an aqueous 30% hydrogen peroxide solution, and the mixture was boiled under reflux until it showed a negative test with starch–iodine paper (38 h). It was again concentrated, 125 mL of acetic anhydride was added, and the mixture was boiled under reflux for 1 h. After concentration, the residual oil was vacuum distilled and a fraction was collected at about 100 °C at 0.05 mm. This was taken up in 5% aqueous hydrochloric acid solution, washed with ether, made basic, and extracted with ether. The ether extract was washed with water, dried, and concentrated. This gave 3.64 g of an orange oil whose properties (NMR, singlets at τ 2.90, 4.82, and 7.62; mass spectrum,

m/e 237) are in accord with its identification as 4-methyl-2,6-bis(acetoxymethyl)pyridine. Without further purification, this crude product was dissolved in 35 mL of aqueous 48% hydrobromic acid solution and boiled under reflux for 5 h. The solution was then concentrated, an additional 35 mL of aqueous 48% hydrobromic acid was added, and the solution was boiled under reflux an additional 12 h. After the solution had been neutralized with base, it was extracted with chloroform. The chloroform extract was washed with water, dried, and concentrated. Chromatography of the residual solid over silica gel using benzene as eluent led to the isolation of 596 mg of white crystals: mp 85.0–85.5 °C; NMR singlets at τ 2.80 (2 H, Ar*H*), 5.50 (4 H, ArC*H*$_2$Br), and 7.63 (3 H, C*H*$_3$); mass spectrum *m/e* 277, 279, and 281. Anal. ($C_8H_9NBr_2$) C, H, N.

7-Methyl-2,11-dithia[3.3](2,6)pyridinoparacyclophane (9). To a stirred solution of 200 mg of sodium hydroxide in 500 mL of 95% ethanol there was added dropwise with stirring under a nitrogen atmosphere a solution contining 365 mg of 1,4-bis(mercaptomethyl)benzene and 596 mg of 4-methyl-2,6-bis(bromomethyl)pyridine in 100 mL of benzene over an 8-h period. After the mixture had been allowed to stir for another 18 h at room temperature, it was partitioned between water and chloroform. The organic layer was washed with water, dried, and concentrated. Crystallization of the residue from methanol gave 500 mg (85%) of white crystals: mp 173–175 °C; NMR singlets at τ 3.12 (6 H, Ar*H*), 6.14 (4 H, ArC*H*$_2$), 6.52 (4 H, ArC*H*$_2$), and 7.76 (3 H, C*H*$_3$); mass spectrum *m/e* 287. Anal. ($C_{16}H_{17}NS_2$) C, H, N.

Benzyne–Stevens Rearrangement of 6 to Give 10. The preparation of **6** needed for this experiment was carried out by coupling **1** and **3** following the procedure described above for the preparation of **9**. The product **6**, isolated in 92% yield, corresponded in all respects to the sample of **6** described previously.[2] To a solution of 280 mg of **6** in 250 mL of chlorobenzene boiling under reflux there was added dropwise a solution of 1.16 g of 1-(2′-carboxyphenyl)-3,3-dimethyltriazene[17] in 100 mL of chlorobenzene. When half the solution had been added, addition was interrupted to allow the mixture to boil under reflux for 4 h. Then, another quarter of the solution was added, boiling was allowed for another 4 h, addition was continued, and at the end the mixture was boiled under reflux for an additional 12 h. After concentration under reduced pressure, the residue was chromatographed over silica gel using ethyl acetate for elution. The main fraction of eluate gave 399 mg (90%) of **10** as a mixture of isomers. For the further conversion of **10** to **14** or **18**, there was no need to separate these isomers and the mixture was used directly.[18] Anal. ($C_{27}H_{23}NS_2$) C, H, N.

Conversion of 10 to 18. To a solution of 314 mg of the mixture of isomers corresponding to **10** in 100 mL of chloroform at 0 °C there was added 309 mg of *m*-chloroperbenzoic acid (85%), and the mixture was stirred for 16 h. After the solution had been extracted with 5% aqueous sodium hydroxide solution, it was washed with water, dried, and concentrated to give 355 mg of the bissulfoxide derived from **10**. Without further purification, this was dissolved in 100 mL of xylene and boiled under reflux for 23 h. After concentration, the residual solid was purified by chromatography over silica gel using benzene for elution to give 45 mg of white crystals: mp 157–158 °C; identical in all respects with an authentic sample of **18**.[2]

Benzyne–Stevens Rearrangement of 9 to Give 13. This was carried out as described above for the preparation of **10**. From 299 mg of **9** there was obtained 315 mg (69%) of a mixture of isomers corresponding to **13**.[18] Anal. ($C_{28}H_{25}NS_2$) C, H, N.

5,8-Dimethyl-2,11-dithia[3.3](2,6)pyridinoparacyclophane (7). The coupling of 1,4-dimethyl-2,5-bis(mercaptomethyl)benzene (**4**) with 2,6-bis(bromomethyl)pyridine (**1**) to give **7** was carried out following the general procedure described for the preparation of **9**. The product **7** was isolated in 35% yield after recrystallization from methanol as white crystals: mp 160–161 °C; NMR τ 2.56 and 2.91 (3 H, AB_2 m, Py*H*), 3.31 (2 H, s, Ar*H*), 6.14 (4 H, AB q, J = 13 Hz, ArC*H*$_2$), 6.47 (4 H, s, PyC*H*$_2$), and 7.85 (6 H, s, C*H*$_3$); mass spectrum *m/e* 301; UV (CH_3CN) 270 nm (ϵ 4600) and 235 (12 240). Anal. ($C_{17}H_{19}NS_2$) C, H, N.

Benzyne–Stevens Rearrangement of 7 to Give 11. This was carried out following the general procedure given previously for the preparation of **10**. From 1.01 g of **7** there was isolated 1.05 g (69%) of **11** as a mixture of isomers that was used directly for the preparation of **15** and **19**.[18] Anal. ($C_{29}H_{27}NS_2$) C, H, N.

4,7-Dimethyl[2.2](2,6)pyridinoparacyclophane (15). To a solution of 185 mg of the mixture of isomers corresponding to **11** in 50 mL of benzene was added a spatula of Raney nickel catalyst, and the resulting mixture was boiled under reflux for 1 h. After removal of the catalyst and solvent, the residual solid was purified by thin-layer chromatography over silica gel using a 4:1 mixture of benzene–ethyl acetate for elution. The solid from the main fraction of eluate was sublimed at 45 °C and 0.005 mm pressure to give 70 mg (72%) of white crystals: mp 64–66 °C; NMR τ 2.74 and 3.24 (3 H, AB_2 m, Py*H*), 3.60 (2 H, m, Ar*H*), 6.60–7.60 (8 H, m, ArC*H*$_2$), and 7.90 (6 H, s, C*H*$_3$); mass spectrum *m/e* 237; UV (CH_3CN) 300 nm (ϵ 530), 265 (2700). Anal. ($C_{17}H_{19}N$) C, H, N.

4,7-Dimethyl[2.2](2,6)pyridinoparacyclophane-1,9-diene (19). The preparation of **19** was carried out following the general procedure described earlier for the preparation of **18**. Oxidation of 621 mg of **11** with *m*-chloroperbenzoic acid in chloroform gave 721 mg of the corresponding bissulfoxide (mass spectrum, *m/e* 485). This on pyrolysis in xylene solution gave as product, after recrystallization from 2-propanol, 169 mg (53%) of white crystals: mp 143–144 °C; NMR τ 2.67 and 3.16 (3 H, AB_2 m, Py*H*), 3.10 (4 H, AB q, J = 11 Hz, C*H*=C*H*), 3.43 (2 H, s, Ar*H*), and 7.98 (6 H, s, C*H*$_3$); mass spectrum *m/e* 233; UV (CH_3CN) 294 nm (ϵ 3521), 242 (23 090), and 228 (24 410). Anal. ($C_{17}H_{15}N$) C, H, N.

5,6,8,9-Tetramethyl-2,11-dithia[3.3](2,6)pyridinoparacyclophane (8). The coupling of 2,3,5,6-tetramethyl-1,4-bis(mercaptomethyl)benzene (**5**) with 2,6-bis(bromomethyl)pyridine (**1**) was carried out following the general procedure described for the preparation of **9**. The product **8** was isolated in 63% yield after crystallization from 2-propanol as white crystals: mp 136–138 °C; NMR τ 2.68 and 3.00 (3 H, AB_2 m, Py*H*), 6.06 (4 H, s, ArC*H*$_2$), 6.62 (4 H, s, ArC*H*$_2$), and 7.92 (12 H, s, C*H*$_3$); mass spectrum *m/e* 329; UV (CH_3CN) 270 nm (ϵ 2120) and 243 (7823). Anal. ($C_{19}H_{23}NS_2$) C, H, N.

Benzyne–Stevens Rearrangement of 8 to Give 12. This was carried out following the general procedure described previously for the preparation of **10**. From 1.12 g of **8** there was obtained 880 mg (54%) of **12** as a mixture of isomers that was used directly for the preparation of **16** and **20**.[18] Anal. ($C_{31}H_{31}NS_2$) C, H, N.

4,5,7,8-Tetramethyl[2.2](2,6)pyridinoparacyclophane (16). This was prepared following the general procedure given for the preparation of **15**. From 125 mg of **12** there was obtained, after recrystallization from 2-propanol, 52 mg (76%) of white plates: mp 153–154 °C; NMR τ 2.80 and 3.34 (3 H, AB_2 m, Py*H*), 6.89 and 7.38 (8 H, A_2B_2 m, ArC*H*$_2$), and 7.98 (12 H, s, C*H*$_3$); mass spectrum *m/e* 265; UV (CH_3CN) 305 nm (ϵ 320), 270 (1560), and 235 (5570). High-resolution mass spectrum 265.184 (calcd mol wt 265.183).

4,5,7,8-Tetramethyl[2.2](2,6)pyridinoparacyclophane-1,9-diene (20). This was prepared following the general procedure described earlier for the preparation of **18**. Oxidation of 551 mg of **12** with *m*-chloroperbenzoic acid gave 600 mg of the bissulfoxide. Pyrolysis of this in xylene, followed by recrystallization of the product from 2-propanol, gave 149 mg (50%) of white crystals: mp 156–158 °C; NMR τ 3.16 (4 H, AB q, J = 10.5 Hz, C*H*=CH), 2.70 and 3.22 (3 H, AB_2 m, Py*H*), 8.10 (12 H, s, C*H*$_3$); mass spectrum *m/e* 261; UV (CH_3CN) 285 nm (ϵ 4420), 260 (16 670), 252 (22 990), 243 (24 300), and 228 (29 820). Anal. ($C_{19}H_{19}N$) C, H, N.

15-Methyl[2.2](2,6)pyridinoparacyclophane (17). This was prepared following the general procedure given for the preparation of **15**. From 100 mg of **13** there was obtained, after preparative TLC using a 1:1 mixture of acetone–dichloromethane for elution, 15 mg (31%) of crystals: mp 78–80 °C; NMR τ 3.36 (2 H, s, Py*H*), 3.39 (4 H, s, Ar*H*), 6.96 and 7.46 (8 H, A_2B_2 m, ArC*H*$_2$), and 7.78 (3 H, s, C*H*$_3$); mass spectrum (high resolution) *m/e* 223.135 (calcd mol wt for $C_{16}H_{17}N$, 223.136).

15-Methyl[2.2](2,6)pyridinoparacyclophane-1,9-diene (21). This was prepared following the general procedure described earlier for the preparation of **18**. Oxidation of 103 mg of **13** with *m*-chloroperbenzoic acid gave 111 mg of the bissulfoxide. Pyrolysis of this in xylene, followed by preparative TLC using a 1:1 mixture of dichloromethane and petroleum ether (30–60 °C), gave 15 mg (30%) of white crystals: mp 120–121 °C; NMR τ 3.04 (4 H, AB q, C*H*=C*H*), 3.08 (4 H, s, Ar*H*), 3.28 (2 H, s, Py*H*), and 7.82 (3 H, s, C*H*$_3$); mass spectrum (high resolution) *m/e* 219.105 (calcd mol wt for $C_{16}H_{13}N$, 219.105).

Complex of 19 with Antimony Pentafluoride. The ^{1}H NMR spectrum of 1 mg of **19** in 5 mL of a solution of deuteriochloroform containing two drops of antimony pentafluoride showed signals at τ 1.54 (1 H, t, J = 8 Hz, Py*H*), 2.00 (1 H, d, J = 8 Hz, Py*H*), 2.11 (1 H, d, J = 8 Hz, Py*H*), 3.45 (4 H, q, J = 13 Hz, C*H*=C*H*), 3.18 (1 H, q,

J = 2 Hz, ArH), 4.50 (1 H, q, J = 2 Hz, ArH), 7.77 (3 H, d, J = 2 Hz, CH_3), and 8.35 (3 H, d, J = 2 Hz, CH_3).

2,6,10,14-Tetrathia-4-pyrida-4-[2,6],8-benza-8-[1,4;2,5],12-pyrida-12-[2,6]spiro[7.7]pentadecaphane (28).[19] To a solution of 3.0 g of sodium hydroxide in 2.5 L of 95% ethanol was added, dropwise with stirring under a nitrogen atmosphere at room temperature, a solution of 4.80 g of 2,6-bis(mercaptomethyl)pyridine (**27**) and 6.30 g of 1,2,4,5-tetrakis(bromomethyl)benzene (**26**) in 800 mL of benzene over a period of 48 h. After the mixture had been stirred an additional 9 h, it was concentrated, and the residual solid was partitioned between chloroform and water. The chloroform extract was washed successively with aqueous brine, dried, and concentrated. Chromatography of the residue over silica gel using a 1:1 mixture of benzene and ethyl acetate gave a main fraction (R_f ~0.5) of useful product. This was placed in a Soxhlet and extracted with benzene, which, on concentration and addition of hexane, gave 1.76 g (27%) of white crystals, mp 247–251 °C. The solid from the mother liquor was again chromatographed over silica gel and recrystallized from benzene–hexane to give an additional 460 mg (7%) of **28.** The combined products were recrystallized from benzene to give white crystals: mp 252–253 °C; NMR τ 2.60 and 2.96 (6 H, AB_2 m, PyH), 3.56 (2 H, s, ArH), 6.17 (8 H, AB q, J = 13 Hz, ArCH_2), and 5.58 (8 H, s, PyCH_2); mass spectrum m/e 468. Anal. ($C_{24}H_{24}N_2S_4$) C, H, N.

3-Pyrida-3-[2,6],6-benza-6-[1,4;2,5],9-pyrida-9-[2,6]spiro[5.5]-undecaphane (30). The Wittig rearrangement of **28** to give **29a** was carried out as follows. To a stirred solution of 93 mg of **28** and 0.24 mL of tetramethylethylenediamine in 15 mL of dry benzene under a nitrogen atmosphere there was added 1.05 mL of a 1.5 M solution of *n*-butyllithium in hexane. After the solution had been stirred at room temperature for 3.5 h, there was added 90 μL of methyl iodide, and the mixture was stirred an additional 17 h. It was then washed with water, dried, and concentrated. Preparative TLC over silica gel using a 4:1 mixture of benzene and ethyl acetate allowed the separation of 18 mg of product from the main fraction of eluate, which was a mixture of isomers but whose mass spectrum (m/e 524) indicated it to be the desired Wittig product **29a.** This was dissolved in 10 mL of absolute ethanol, Raney nickel catalyst was added, and the mixture was boiled under reflux for 24 h. After removal of the solvent and catalyst, the residual solid was purified by preparative TLC over silica gel using acetone for elution to give 6.1 mg of an amorphous solid: NMR τ 2.80 and 3.36 (6 H, AB_2 m, PyH), 4.10 (2 H, s, ArH), and 6.85–7.60 (16 H, m, ArCH_2); mass spectrum m/e 340; high-resolution mass spectrum, 340.193 (calcd mol wt for $C_{24}H_{24}N_2$, 340.194).

3-Pyrida-3-[2,6],6-benza-6-[1,4;2,5],9-pyrida-9-[2,6]spiro[5.5]-undecaphane-1,4,7,10-tetraene (23).[19] The benzyne–Stevens rearrangement of **28** to give **29b** was carried out as described for the preparation of **10.** From 293 mg of **28,** there was obtained after chromatography over silica gel using benzene for elution 265 mg (55%) of a solid whose NMR spectrum was in accord with its being a mixture of isomers corresponding to **29b.** This was also supported by its mass spectrum, m/e 772 (calcd mol wt for $C_{48}H_{40}N_2S_4$, 772). This was then converted to **23** following the general procedure used for the conversion of **10** to **18.** The product was purified by preparative TLC over silica gel using benzene for elution, followed by recrystallization of the product from a mixture of dichloromethane and 2-propanol to give 5.1 mg (23%) of yellow crystals: mp 203–204 °C; NMR τ 2.63 and 3.13 (6 H, AB_2 m, PyH), 4.04 (4 H, AB q, J = 11 Hz, CH=CH), and 4.52 (2 H, s, ArH); mass spectrum m/e 332; UV (EtOH) 294 nm (ϵ 7380), 260 (18 630), 253 (22 140), and 247 (21 430). Anal. $C_{24}H_{16}N_2$) C, H, N.

1,3-Bis(mercaptomethyl)-2-chlorobenzene (32). A mixture of 11.7 g of 1,3-bis(bromomethyl)-2-chlorobenzene and 7.1 g of thiourea in 300 mL of ethanol was boiled under reflux for 0.5 h and then cooled. The crystals, which separated, were collected and dried to give 17.8 g (100%) of white crystals (mp 253–254 °C) of the corresponding bis(thiouronium) bromide. A 2.0-g portion of these crystals was added to a solution of 11.5 g of sodium hydroxide in 100 mL of water and boiled under reflux for 17 h. After the solution had cooled, it was acidified and extracted with hexane. The hexane extract was washed with brine, dried, and concentrated. This gave 600 mg (66%) of a colorless oil: NMR τ 2.62–2.90 (3 H, m, ArH), 6.16 (4 H, d, J = 8 Hz, ArCH_2), and 8.06 (2 H, t, J = 8 Hz, SH). Anal. ($C_8H_9S_2Cl$) C, H.

14-Chloro-5,8-dicarbomethoxy-2,11-dithia[3.3]metaparacyclophane (34). The coupling of 260 mg of 1,3-bis(mercaptomethyl)-2-chlorobenzene (**32**) and 484 mg of dimethyl 2,5-bis(bromomethyl)-terephthalate (**33**)[20] was carried out following the general procedure described for the preparation of **9**, but substituting methanol for ethanol as solvent. The product, after recrystallization from benzene, gave 410 mg (76%) of white crystals: mp 158–160 °C; NMR τ 2.20 (1 H, s, ArH), 2.70–3.10 (4 H, m, ArH), 5.14–6.64 (8 H, m, ArCH_2), 6.03 (3 H, s, OCH_3), and 6.14 (3 H, s, OCH_3); mass spectrum m/e 422 and 424; IR ($CHCl_3$) 1720 cm^{-1} (C=O); UV (CH_3CN) 313 nm (ϵ 1890) and 260 (5820). Anal. ($C_{20}H_{19}ClO_4S_2$) C, H.

2,2,11,11-Tetraoxo-14-chloro-5,8-bis(carbomethoxy)-2,11-dithia-[3.3]metaparacyclophane. To a solution of 1.0 g of **34** in 250 mL of chloroform at 0 °C there was added 2.8 g of *m*-chloroperbenzoic acid (85%), and the solution was stirred for 15 h. The solution was washed successively with a 10% aqueous sodium hydroxide solution and water, dried, and concentrated. This gave 1.1 g (96%) of white crystals: mp 336–338 °C; NMR (CF_3CO_2D) τ 2.58 (1 H, s, ArH), 3.36 (1 H, s, ArH), 2.98–3.64 (3 H, m, ArH), 4.97–6.68 (8 H, m, ArCH_2), 6.74 (3 H, s, OCH_3), and 6.92 (3 H, s, OCH_3). Anal. ($C_{20}H_{19}ClO_8S_2$) C, H.

12-Chloro-4,7-bis(carbomethoxy)[2.2]metaparacyclophane (35). Pyrolysis of 2,2,11,11-tetraoxo-14-chloro-3,5-bis(carbomethoxy)-2,11-dithia[3.3]metaparacyclophane was carried out at 0.01 mm pressure with the preheater at 380 °C and the oven at 600 °C. From an 80-mg sample of the bissulfone, there was obtained 57 mg (97%) of **35.** The slightly yellow product was recrystallized from 2-propanol to give white crystals: mp 155–157 °C; NMR τ 2.06 (1 H, s, ArH), 3.05–3.35 (4 H, m, ArH), 5.58–7.48 (8 H, m, ArCH_2), 6.03 (3 H, s, OCH_3), and 6.22 (3 H, s, OCH_3); mass spectrum m/e 360, 358; IR ($CHCl_3$) 1720 cm^{-1} (C=O); UV (CH_3CN) 332 nm (ϵ 1475) and 263 (8605). Anal. ($C_{20}H_{10}ClO_4$) C, H.

12-Chloro-4,7-bis(hydroxymethyl)[2.2]metaparacyclophane (36). To a boiling mixture of 151 mg of lithium aluminum hydride in 75 mL of anhydrous ether there was added dropwise a solution of 370 mg of **35** in 75 mL of dry tetrahydrofuran. After the mixture had been boiled under reflux for an additional 0.75 h, it was cooled and acidified with aqueous hydrochloric acid. The organic layer was separated, washed with brine, dried, and concentrated. The residual solid was recrystallized from ethyl acetate to give 296 mg (95%) of white crystals: mp 175–200 °C; NMR τ 2.82 (1 H, s, ArH), 3.03–3.30 (3 H, m, ArH), 4.00 (1 H, s, ArH), 4.05 (2 H, AB q, J = 12 Hz, ArCH_2OH), 5.77 (2 H, AB q, J = 12 Hz, ArCH_2OH), 6.37–7.75 (8 H, m, ArCH_2), and 8.37 (2 H, br s, OH); mass spectrum m/e 304, 302; IR ($CHCl_3$) no carbonyl. Anal. ($C_{18}H_{19}ClO_2$) C, H.

12-Chloro-4,7-bis(bromomethyl)[2.2]metaparacyclophane (37). To a solution of 130 mg of **36** in 20 mL of benzene there was added 10 drops of phosphorus tribromide, and the mixture was heated on a steam bath for 20 min. After the solution had been washed successively with brine and water, it was dried and concentrated. The residual solid was chromatographed over silica gel using benzene for elution. The product from the main fraction of eluate was recrystallized from a benzene–cyclohexane mixture to give 169 mg (92%) of white crystals: mp 169–172 °C; NMR τ 2.90 (1 H, s, ArH), 3.00–3.30 (3 H, m, ArH), 4.08 (1 H, s, ArH), 5.33 (2 H, AB q, J = 10 Hz, CH_2Br), 5.96 (2 H, AB q, J = 10 Hz, CH_2Br), and 6.40–7.70 (8 H, m, ArCH_2); mass spectrum m/e 430, 428, 426. Anal. ($C_{18}H_{17}ClBr_2$) C, H.

12-Chloro-4,7-bis(mercaptomethyl)[2.2]metaparacyclophane (38). A mixture of 579 mg of **37** and 600 mg of sodium thiolacetate in 100 mL of dimethylformamide was heated at 112 °C for 3.5 h. It was then diluted with 200 mL of water and extracted well with ether. The ether extract was washed well with water, dried, and concentrated to give 530 mg (94%) of 12-chloro-4,7-bis(acetylthiomethyl)[2.2]metaparacyclophane as a pale yellow oil: NMR τ 2.95–3.25 (4 H, m, ArH), 4.17 (1 H, s, ArH), 5.62 (2 H, AB q, J = 13 Hz, CH_2S), 6.34 (2 H, AB q, J = 14 Hz, CH_2S), 6.5–8.0 (8 H, m, ArCH_2), 7.70 (3 H, s, CCH_3), and 7.78 (3 H, s, C(=O)CH_3); mass spectrum m/e 420, 418; IR ($CHCl_3$) 1685 cm^{-1} (C=O). This was dissolved in 100 mL of dry ether and added dropwise to a boiling solution of 340 mg of lithium aluminum hydride in 100 mL of dry ether. The reaction mixture was then decomposed by addition of water and aqueous acid. The ether layer was separated, washed with water, dried, and concentrated to give 404 mg (96%) of a pale yellow oil: NMR τ 3.04 (1 H, s, ArH), 3.08–3.30 (3 H, m, ArH), 4.15 (1 H, s, ArH), 6.01 (2 H, AB of d, J_{AB} = 14 Hz, J = 7 Hz, CH_2SH), 6.30–7.78 (10 H, m, ArCH_2 + CH_2SH), 8.31 (1 H, t, J = 7 Hz, CH_2SH), and 8.65 (1 H, t, J = 7 Hz, CH$_2$SH); mass spectrum m/e 334.

2,6-Dithia-11^2-chloro-4-pyrida-4-[2,6],8-benza-8-[1,4;2,5]-11-benza-11-[1,3]spiro[7.5]tridecaphane (39).[19] The coupling of 100 mg

of **38** with 84 mg of **1** was carried out following the general procedure described previously for the preparation of **9**. The product, after recrystallization from a benzene-ethyl acetate mixture, gave 85 mg (65%) of white crystals: mp 219–220 °C; NMR (τ 2.63 (1 H, t, J = 8 Hz, PyH), 2.94 (1 H, d, J = 8 Hz, PyH), 3.06 (1 H, d, J = 8 Hz, PyH), 3.10–3.40 (3 H, m, ArH), 3.42 (1 H, s, ArH), 4.48 (1 H, s, ArH), 5.88 (2 H, AB q, J = 13 Hz, ArCH_2S), and 6.18–7.92 (14 H, m, ArCH_2, ArCH_2S, and PyCH_2S); mass spectrum m/e 439, 437; UV (CH_3CN) 280 nm (ϵ 4370) and 268 (8112). Anal. ($C_{25}H_{24}NS_2Cl$) C, H, N.

9²-Chloro-3-pyrida-3-[2,6],6-benza-6-[1,4;2,5],9-benza-9-[1,3]-spiro[5.5]undecaphane-1,4-diene (24).[19] The benzyne-Stevens rearrangement of 148 mg of **39** was carried out following the general procedure described previously for the preparation of **10.** After the product had been purified by chromatography over silica gel, there was isolated 164 mg (81%) of a mixture of isomers having the expected NMR and mass spectral (m/e 515 and 513) properties for the benzyne-Stevens, ring-contracted product. This was directly oxidized with m-chloroperbenzoic acid (85%) in chloroform to give 188 mg of the corresponding bissulfoxide. A solution of this in 50 mL of toluene was boiled under reflux for 18 h. After concentration, the residual solid was chromatographed over silica gel using a 1:1 mixture of dichloromethane and petroleum ether (30–60 °C) for elution, to give 29 mg (39%) of yellow crystals: mp 226–228 °C; NMR τ 3.01 (2 H, AB q, J = 11 Hz, ArCH), 3.31 (2 H, AB q, J = 11 Hz, ArCH), 2.6–3.4 (7 H, m, ArH), 4.56 (1 H, s, ArH), 6.5–7.9 (8 H, m, ArCH_2); mass spectrum (high resolution) 369.127 (calcd mol wt for $C_{25}H_{20}NCl$, 369.128); UV (EtOH) 290 nm (ϵ 6550), 260 (18 480), 251 (24 860), and 246 (24 860). Anal. ($C_{25}H_{20}NCl$) C, H, N.

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A Study of the Synthesis and Properties of [2.2.2.2](1,2,4,5)Cyclophane[1]

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Abstract: The synthesis of [2.2.2.2](1,2,4,5)cyclophane (**9**), the first tetra- (two-atom bridged) cyclophane, is reported. The key to its successful synthesis (see Schemes I and II) lay in combining the traditional approach and formation of dithiacyclophane **3** followed by sulfur expulsion to give **4,** with the use of transannular reactions special to [2.2]paracyclophanes: (1) electrophilic substitution of **4** giving exclusively chloromethylation at positions pseudogem to the ester groups, and (2) transannular carbene insertion converting **13** to **9.** Alternatively, **11** was obtained in quantitative yield by a transannular pinacol rearrangement of tetraol **7.** An X-ray crystallographic analysis of **9** shows each of the benzene rings to be in a highly strained boat conformation. This is reflected in the ease with which the benzene rings react with dienophiles such as perfluoro-2-butyne and dicyanoacetylene to give the corresponding mono- and bis(barrelene) adducts, **17–19** and **22.** Addition of singlet oxygen to **9** likewise occurs readily to give the corresponding epidioxide **23** and from this a series of transformation products. The copper-catalyzed thermal addition of ethyl diazoacetate to **9** has been utilized to provide a synthesis of [2.2.2.2](1,2,4,5)-7′-methyltropylioparacyclophane (**37**). Birch reduction of **9** to give **14** followed by addition of dichlorocarbene led to **15.** Lithium metal reduction of **15** then gave the caged hydrocarbon **16.** However, all attempts to effect solvolytic ring opening of **15** to give a cyclophane with a cyclooctatetraene moiety in each deck were unsuccessful. Irradiation of **17,** though, does give a cyclophane containing a cyclooctatetraene moiety.

Since the first report on the synthesis and properties of [2.2]paracyclophane,[2] there has been a tremendous interest in the "bent and battered benzene rings of cyclophane chemistry."[3a] Of particular interest are the multibridged cyclophanes in which each of the bridges has two carbon links.[3b] Aside from the [2.2]paracyclophanes and the trivial case of [2.2]orthocyclophanes, the known examples of such multibridged cyclophanes include both syn and anti isomers of the [2.2]metacyclophanes,[4] [2.2]metaparacyclophanes,[5,6] [2.2.2](1,3,5)cyclophanes,[7] [2.2.2](1,2,4)cyclophanes,[8] [2.2.2](1,2,4)(1,3,5)cyclophanes,[9] and [2.2.2](1,2,5)cyclophanes.[9] We became interested in extending the series to examples of tetrabridged cyclophanes and, from an inspection of molecular models, it appeared that of the various possibilities

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