and the demonstration that fluorine displacement from silicon occurs with either retention or inversion depending on the steric and polar requirements of the nucleophile.[11] Displacement of fluorine from silicon by bulky nucleopiles has been shown to be synthetically superior to displacement of chlorine: (a) R. West and G. A. Gornowicz, *J. Organomet. Chem.*, **28**, 25 (1971); (b) J. F. Hyde and J. W. Curry, *J. Am. Chem. Soc.*, **77**, 3140 (1955).
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Macro Rings. XLVII. Syntheses and Spectral Properties of Heteroannularly Disubstituted [2.2]Paracyclophanes[1]

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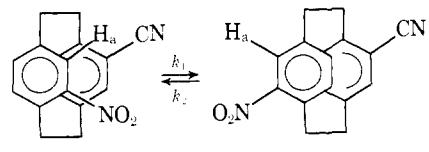
Abstract: The syntheses and structure determinations of 39 new, disubstituted [2.2]paracyclophanes are reported in which each benzene ring contains one substituent. No transannular directive effects were observed in the nitration of either 4-cyano- or 4-acetyl[2.2]paracyclophane. At 200°, pseudo-*o*- and pseudo-*p*-cyanonitro[2.2]paracyclophanes equilibrated to give an equilmolar mixture. The transannular effects of the positions of the substituents on the ^{1}H NMR and uv spectra of these compounds are described. Unlike their monosubstituted counterparts, the [2.2]paracyclophanes with a nitro group in one ring and an amino in the other are colored orange to red. The end absorption of the longest wavelength band of the isomers decreases in intensity in the order pseudo-gem > pseudo-meta > pseudo-para > pseudo-ortho. Transannular canonical charge transfer resonance structures can be drawn for the two most colored isomers, but not for the other two.

Former papers in this series reported the syntheses,[3a,b,c,d] substituent directive effects,[3b,d] and spectral properties[3a,3e] of a number of disubstituted [2.2]paracyclophanes. In bromination of monobromo-, mononitro-, monoacetyl-, and monocarbomethoxy[2.2]paracyclophanes, transannular substituent directive influences were found to be associated with inter-ring proton transfer as the rate-determining step.[3b] In bromination of 4-cyano[2.2]paracyclophane, or nitration of 4-nitro[2.2]paracyclophane, these directive effects were absent.[3b,d] The structures of the disubstituted [2.2]paracyclophane derivatives were determined by thermal interconversion through benzyl-benzyl diradical intermediates[3c] or from the patterns of ^{1}H NMR chemical shifts.[3e] Particularly useful were the downfield chemical shifts of the protons pseudo-gem to the halogen and cyano groups, and the unusually large ortho and small para chemical shifts compared to open-chain model compounds. Transannular substituent effects on the ultraviolet spectra and pK_a's of monosubstituted [*m.n*]paracyclophanes were found to be small.[3a]

The present paper reports the synthesis and spectral properties of 39 new disubstituted [2.2]paracyclophanes with one substituent in each ring. These compounds were prepared for the following reasons: (1) to examine the possibility of observing intramolecular charge-transfer effects on the uv spectra of appropriately substituted compounds; (2) to extend the knowledge of pseudo-gem ^{1}H NMR chemical shifts to substituents not yet examined; (3) to test further the generalizations about transannular, substituent-directing effects on electrophilic substitution; (4) to prepare compounds for a study of transannular substituent effects on the pK_a's of [2.2]paracyclophanecarboxylic acids and [2.2]paracyclophanylammonium ions. The results of this study are reported elsewhere.[4]

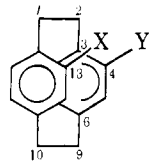
Results and Discussion

Syntheses. The new compounds reported here, and those disubstituted [2.2]paracyclophanes that served as starting materials, are formulated in a way (Chart I) that emphasizes the positions of the substituents relative to one another, and that names those relationships. Reduction with hydrogen and platinum of bromonitro isomers **1–4**,[3b] gave bromoamines **5–8**, respectively. With 2 mol of cuprous cyanide in *N*-methylpyrrolidone[5] at 205° for 24 hr, pseudo-gem-bromonitro compound **1** gave 14% of starting material, 24% of rearranged pseudo-meta-bromonitro compound **2**, 3% of pseudo-gem-cyanonitro compound **9**, and 27% pseudo-meta-cyanonitro isomer **10**. Under the reaction conditions, isomerizations **1** $\rightleftarrows$ **2** and **9** $\rightleftarrows$ **10** appear to occur. At equilibrium, [**2**]/[**1**] > 4.6 at 200°,[3c] but in the reaction mixture, [**2**]/[**1**] ~ 2. The total yield of cyanated product (~30%) exceeded that of isomerized starting material (24%). Thus the cyanation appears to occur slightly faster than the isomerization of starting material. Nitration of 4-cyano[2.2]paracyclophane[3e] gave a mixture of products from which pseudo-para- and pseudo-ortho-cyanonitro compounds **12** and **11** were isolated (8 and 4%, respectively). When heated at 200° in *N*-methylpyrrolidone for 30 hr, **11** equilibrated with **12**, and $K = k_1/k_2 \sim 1$. The reaction was followed by ^{1}H NMR integration of the doublets of H_a in **11** and **12**, and $k_1 \sim k_2 \sim 3 \times 10^{-5}$ sec^{-1}. Both the rate and equilibrium constants resemble those obtained for the

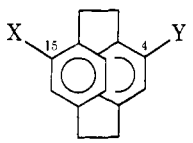


11 **12**

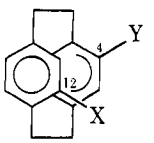
Chart I



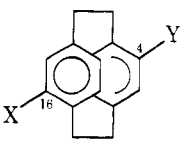
pseudo-gem



pseudo-meta

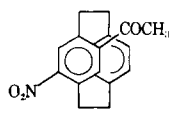


pseudo-ortho



pseudo-para

Compd no.	X	Y
1	NO_2	Br
5	NH_2	Br
9	NO_2	CN
13	NO_2	CO_2H
17	NO_2	NH_2



24

Compd no.	X	Y
2	NO_2	Br
6	NH_2	Br
10	NO_2	CN
14	NO_2	CO_2H
18	NO_2	NH_2
21	NO_2	$COCH_3$
25	NH_2	$COCH_3$
28	CN	CN
31	CN	CO_2H
34	CO_2H	CO_2H
37	NO_2	$NHCOCH_3$
39	NH_2	$NHCOCH_3$
41	NH_2	NH_2
43	CO_2CH_3	Br
45	CO_2H	Br
47	NO_2	CO_2CH_3
48	NH_2	CO_2CH_3

Compd no.	X	Y
3	NO_2	Br
7	NH_2	Br
11	NO_2	CN
15	NO_2	CO_2H
19	NO_2	NH_2
22	NO_2	$COCH_3$
26	NH_2	$COCH_3$
29	CN	CN
32	CN	CO_2H
35	CO_2H	CO_2H
44	CO_2CH_3	Br
46	CO_2H	Br

Compd no.	X	Y
4	NO_2	Br
8	NH_2	Br
12	NO_2	CN
16	NO_2	CO_2H
20	NO_2	NH_2
23	NO_2	$COCH_3$
27	NH_2	$COCH_3$
30	CN	CN
33	CN	CO_2H
36	CO_2H	CO_2H
38	NO_2	$NHCOCH_3$
40	NH_2	$NHCOCH_3$
42	NH_2	NH_2

equilibration of the pseudo-*o*- and pseudo-*p*-dibromo[2.2]paracyclophanes.[3c] These isomerization reactions undoubtedly occur through the benzyl diradical as a freely rotating intermediate.[3c]

Acid hydrolysis of nitrocyano isomers **9–12** gave the corresponding nitrocarboxylic acids, **13–16,** without any isomerization. When subjected to the Curtius rearrangement, the nitrocarboxylic acids **13–16** gave the corresponding nitroamines, **17–20.** Significantly, these nitroamines vary in color from orange to red. The color intensity increases in the order, pseudo-ortho, pseudo-para, pseudo-meta, and pseudo-gem (see future section for discussion). Catalytic reduction of nitroamines **18** and **20** gave the corresponding diamines, **41** and **42.**

Nitration of 4-acetyl[2.2]paracyclophane gave four nitroacetyl derivatives, the pseudo-meta compound **21** (4%), the pseudo-ortho isomer **22** (5%), the pseudo-para compound **23** (3%), and the homoannularly substituted para compound, **24** (0.7%). Most of the starting material and products were oxidized to ring-opened compounds in the reaction mixture, and therefore no conclusions can be drawn about directive effects in these reactions. The three transannularly substituted products, **21–23,** were catalytically reduced to the corresponding amino ketones, **25–27.**

Cyanation of pseudo-*m*-dibromo[2.2]paracyclophane[3b] gave (29%) the previously unprepared pseudo-meta-dicyano derivative, **28.** The pseudo-ortho- and pseudo-para-dicyano isomers (**29** and **30**) had been prepared previously.[3d] Partial acid hydrolysis of three dicyano compounds **28–30** gave the corresponding cyanocarboxylic acids, **31–33.** Full hydrolysis gave the corresponding diacids, **34–36.** Acetylation of pseudo-*m*- and pseudo-*p*-nitroamines **18** and **20** gave the corresponding nitroamides, **37** and **38,** catalytic reduction of which gave the corresponding aminoamides, **39** and **40.** Catalytic reduction of the pseudo-*m*- and pseudo-*p*-nitroamines **18** and **20** gave the corresponding diamines, **41** and **42.** Hydrolysis of the known[3b] pseudo-*m*- and pseudo-*o*-carbomethoxybromides, **43** and **44,** gave the corresponding bromocarboxylic acids, **45** and **46.** Treatment of pseudo-*m*-nitrocarboxylic acid (**14**) with diazomethane gave the nitro ester, **47,** reduction of which with hydrogen and platinum gave the amino ester, **48.**

Table I. Substituent Chemical Shift (SCS) Values for the Amino Group in 4-Amino[2.2]paracyclophane[a,b] and Aniline[c]

H orientation relative to NH_2	4-Amino[2.2]-paracyclophane	Aniline
Ortho	+0.98	+0.77
Meta	+0.10	+0.13
Para	+0.29	+0.40
Pseudo-gem	−0.77	
Pseudo-ortho	~+0.02	
Pseudo-para	−0.21	
Pseudo-meta	~+0.02	

[a] D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, 77, 6289 (1955), reported its synthesis, and B. E. Norcross, D. Becker, R. J. Cukier, and R. M. Schultz, *J. Org. Chem.*, 32, 220 (1967), reported part of its ^{1}H NMR spectrum. [b] δ for aromatic protons of [2.2]-paracyclophane (6.37 ppm) minus δ of protons of substituted [2.2]paracyclophanes. [c] Upfield chemical shifts from the aromatic protons of benzene (δ 7.27 ppm; see N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, Calif., 1966, pp 96–97).

Chemical Shifts in the ^{1}H NMR Spectra of the Disubstituted [2.2]Paracyclophanes.[6] The ^{1}H NMR spectra of the disubstituted [2.2]paracyclophanes proved to be a powerful tool in establishing the positions of the substituents relative to one another.[3e] Besides the usual chemical shift observed for protons ortho to substituents, the following substituents moved their pseudo-gem protons downfield: bromo, chloro, iodo, cyano, methyl, ethyl, hydroxy, acetoxy, and methoxy. The absorption appears as a doublet (J = 8 Hz) due to ortho, meta, and para proton splittings. If either X or Y of X,Y-[2.2]paracyclophane (X in one and Y in the other aromatic ring) is one of the above groups, the four possible isomers each exhibit a unique NMR aromatic proton pattern. The present study demonstrates the amino to be the most useful substituent for such structural assignments because it exerts a strong upfield shift on the ortho proton, and a strong downfield shift on the pseudo-gem proton (see Table I). The downfield shift (0.77 ppm) is between that of chlorine and bromine,[3e] and this pseudo-gem deshielding effect is qualitatively similar to the 1,3-diaxial deshielding effect of the amino group on the 18-CH_3 and 19-CH_3 protons in

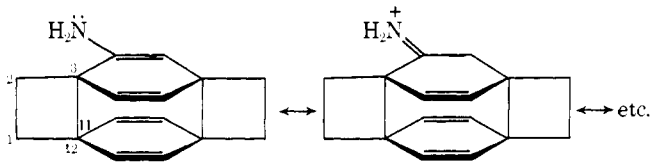
Table II. The ^{1}H NMR Chemical Shifts[a] (δ) of [2.2]Paracyclophanes Substituted with Groups X and Y

X	Y	Orientation of X and Y	Proton orientation relative to group X: Ortho	Meta	Para	Pseudo-gem	Pseudo-ortho	Pseudo-meta	Pseudo-para	CH_3	NH_2
NO_2	H[b]		7.20	6.59	6.76						
NO_2	CN	Pseudo-gem	7.41				6.88				
NO_2	CN	Pseudo-ortho	7.53								
NO_2	CN	Pseudo-para	7.20		7.20						
NO_2	CN	Pseudo-meta	7.19	7.02							
NO_2	$COCH_3$	Para	7.22	6.97						2.47	
NO_2	$COCH_3$	Pseudo-ortho	7.16			7.06				2.43	
NO_2	$COCH_3$	Pseudo-para	7.20					6.88		2.43	
NO_2	$COCH_3$	Pseudo-meta	7.23						6.95	2.44	
NO_2	CO_2H[c]	Pseudo-meta	7.34						7.24		
NO_2	CO_2Me	Pseudo-meta	7.22						7.15	3.92	
NH_2	H[b,d]		5.39	6.27	6.08	7.14	~6.35	~6.35	6.58		3.55
NH_2	Br	Pseudo-gem	5.65	6.37	6.06		6.80	6.42	6.42		~3.51
NH_2	Br[d]	Pseudo-ortho	~6.06	6.29	~6.06	7.19		6.32	6.52		3.36
NH_2	Br	Pseudo-para	5.36	6.20	6.63	7.10	6.31	6.44			3.36
NH_2	Br[d]	Pseudo-meta	5.43	6.94	6.05	7.18	6.35		6.56		3.30
NH_2	$COCH_3$	Pseudo-ortho	5.38	~6.18	~6.18	7.57		~6.54	~6.54	2.45	3.30
NH_2	$COCH_3$	Pseudo-para	5.38	6.20	6.01	7.33	6.39	6.83		2.46	~3.24
NH_2	$COCH_3$	Pseudo-meta	5.41	6.22	5.95	7.22	6.49		7.03	2.44	3.42
NH_2	CO_2Me[d]	Pseudo-meta	5.36	6.22	5.99	7.18	6.46		7.23	3.85	
NH_2	NO_2	Pseudo-gem	5.59	6.39	6.17		7.48	6.44	6.74		
NH_2	NO_2	Pseudo-ortho	5.54	6.35	6.15	7.92		6.67	6.67		3.41
NH_2	NO_2	Pseudo-para	5.38	6.29	6.11	7.46	6.45	7.14			
NH_2	NO_2	Pseudo-meta	5.41	6.35	6.03	7.32	6.59		7.31		
NH_2	NH_2	Pseudo-meta	5.47	6.95	6.01	6.95	6.01		5.47		3.38

[a] Taken on a Varian A-60-D spectrometer on dilute solutions (~2–20%) in deuteriochloroform with tetramethylsilane as internal standard. [b] D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, 77, 6289 (1955). [c] Carboxyl proton came at 11.00. Signal disappeared after addition of deuterium oxide. [d] Also measured on a Varian HA-100 spectrometer and assignment established by double resonance experiments.

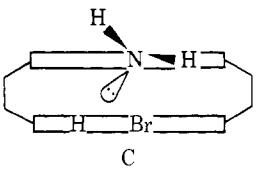
the 11β-amino steroids.[7] The ^{1}H NMR spectra of substituted amino[2.2]paracyclophanes often show all aromatic protons shifted from one another (Table II).

The ortho and para proton shifts of the amino and other electron withdrawing or releasing groups arises at least partially from changes in π-electron density associated with electron delocalization involving the substituent. The relatively small para and large ortho upfield shifts in the [2.2]paracyclophane derivatives (particularly the amino) possibly reflect damping due to the bent benzene rings of electron delocalization involving positions para to the conjugating substituents. The chemical shifts of the hydrogen cis to the substituent in vinyl derivatives are much larger than the corresponding ortho shifts in benzene derivatives.[8] The X-ray structure of [2.2]paracyclophane indicates the C-3 to C-12 distance to be 2.78 Å, and the C-4 to C-11 distance to be 3.09 Å.[9] Resonance structures A and B for 4-amino-[2.2]paracyclophane symbolize this suggestion.



A B

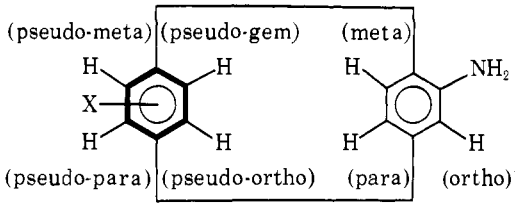
The proton ortho to an amino group is shifted downfield by introducing a substituent into the position pseudo-gem to the amino group (e.g., 0.20 ppm for a nitro and 0.26 ppm for a bromo substituent, see Table II). This result might reflect repulsion between the electron pairs of the amino and bromine groups, which sterically inhibits delocalization of the amino group's electron pair into its attached benzene. Repulsion between the amino group's electron pair and the π system of the nitro group would provide a similar effect. This conformational change also accounts for the fact that the proton pseudo-ortho to the amino group in pseudo-*gem*-aminobromo[2.2]paracyclophane is shifted more downfield by 0.45 ppm than in 4-amino[2.2]paracyclophane, although bromine does not have an ortho shift.[3e] Thus the electron cloud of the amino group may turn toward and deshield the pseudo-ortho proton (see structure C). A somewhat similar deshielding effect has been observed in crowded half-cage molecules.[10]



C

Introduction of a pseudo-*gem*-bromine atom into 4-nitro-[2.2]paracyclophane deshielded the proton ortho to the nitro group by 0.35 ppm. The explanation offered was that the bromine atom enforced copolanarity of the nitro group and its attached benzene ring, and thus increased electron delocalization in the two π systems.[3e] Compounds **1, 17,** and **9** provide a series of pseudo-gem-substituted 4-nitro-[2.2]paracyclophanes whose added substituents decrease in volume in the order, bromo, amino, and cyano. These substituents deshield the proton ortho to the nitro group by values of 0.35,[3e] 0.28, and 0.21 ppm, respectively (see Table II). The data therefore support the enforced copolanarity hypothesis. The cyano group which also deshields its ortho proton is axially symmetric. Thus the chemical shift of its ortho proton should not be subject to the same kind of conformational effects. However, a pseudo-gem nitro group induces an additional downfield shift of 0.13 ppm of the proton ortho to the cyano group (Table II). Although this effect is smaller than the effect of the cyano on the nitro

Table III. Substituent Chemical Shift[a] (SCS) Values for Substituents (X) in X-Substituted-4-amino[2.2]paracyclophanes[b]



Substituent (X)		Proton orientation relative to amino group						
Nature	Orientation	Ortho	Meta	Para	Pseudo-gem	Pseudo-ortho	Pseudo-para	Pseudo-meta
Br	Pseudo-gem	−0.26	−0.10	+0.02		~−0.45	+0.16	~−0.07
Br	Pseudo-ortho	~−0.67	−0.02	~+0.02	−0.05		+0.06	~+0.03
Br	Pseudo-para	+0.03	+0.07	−0.55	+0.04	~+0.04		~−0.09
Br	Pseudo-meta	−0.04	−0.67	+0.03	−0.04	0.00	+0.02	
NO_2	Pseudo-gem	−0.20	−0.12	−0.09		~−1.13	−0.16	~−0.09
NO_2	Pseudo-ortho	−0.15	−0.08	−0.07	−0.78		−0.09	~−0.32
NO_2	Pseudo-para	+0.01	−0.02	−0.03	−0.32	~−0.10		~−0.79
NO_2	Pseudo-meta	−0.02	−0.08	+0.05	−0.18	~−0.24	−0.73	~−0.24
$COCH_3$	Pseudo-ortho	+0.01	~+0.09	~−0.10	−0.43		~+0.04	−0.19
$COCH_3$	Pseudo-para	+0.01	+0.07	+0.07	−0.19	−0.04		~−0.48
$COCH_3$	Pseudo-meta	−0.02	+0.05	+0.13	−0.08	~−0.14	−0.45	
CO_2CH_3	Pseudo-meta	+0.03	+0.05	+0.09	−0.04	−0.11	−0.65	

[a] δ for aromatic protons of 4-amino[2.2]paracyclophane minus δ for corresponding protons of X-substituted-4-amino[2.2]paracyclophanes. [b] Calculated from the values of δ of Table II.

group's ortho proton shift, the effect is large enough to demonstrate that the enforced coplanarity hypothesis is not the sole reason for the enhanced downfield shift of the proton ortho to the nitro group in the presence of a pseudo-gem substituent.

An interesting remote deshielding effect is found in the movement downfield of protons pseudo-para to the amino groups of the cycles. In 4-amino[2.2]paracyclophane, the shift is 0.21 ppm. In pseudo-*m*-substituted-4-amino[2.2]paracyclophanes, this proton is ortho to the additional substituent, but is moved downfield relative to the monosubstituted cycle's ortho proton (by the remote amino group) by the following values (ppm): for nitro as the additional substituent, 0.11; for acetyl, 0.17; for carbomethoxy, 0.09; for bromo, 0.19; for amino as the additional substituent, −0.08 (see Tables I, II, and Table I of ref 3e). Although small, the effect is real and is difficult to rationalize. It is not observed with any substituents examined other than the amino.[3e]

The data in Table III demonstrate that the substituent chemical shift (SCS) values are almost additive for the pseudo-ortho, pseudo-meta, and pseudo-para isomers. The largest observed deviation from the reported CSC values[3e] is 0.25 ppm (in pseudo-*p*-aminobromo[2.2]paracyclophane). Thus the aromatic ^1H NMR spectrum of a pseudo-ortho, pseudo-meta, or pseudo-para disubstituted [2.2]paracyclophane can be predicted from the SCS values of each substituent and the aromatic proton signals of [2.2]paracyclophane itself (δ 6.37 ppm). This correlation simplifies the elucidation of the structure of the disubstituted [2.2]paracyclophanes. In the pseudo-gem series, the SCS values are not additive due to the proximity of the substituents. The same complication was found in steroid ^1H NMR spectra whose 18-CH_3 and 19-CH_3 proton chemical shifts could be calculated provided that substituents introduced did not interfere with one another sterically.[11]

Transannular Effects in the Ultraviolet Spectra of the Disubstituted [2.2]Paracyclophanes. The ultraviolet absorption spectra of the more interesting interannularly disubstituted [2.2]paracyclophanes are recorded in Figures 1–4. These spectra were taken to see if the absorption of one aromatic ring and its substituent was coupled with that of the other aromatic ring and its substituent. Figure 1 involves the four isomers with the electron-providing amino substituent in one ring, and the electron-withdrawing nitro substituent in the other. The three absorption bands at the shorter wavelengths of the four isomers range only from 210 to 216 nm (log ε ~4.5), 263 to 272 (~3.8), and 308 to 320 (~3.5). The curve shapes, wavelengths, and intensities of the pseudo-meta and pseudo-ortho compounds resemble one another, as do those of the pseudo-gem and pseudo-para isomers. The absorption bands at these shorter wavelengths do not differ greatly from those observed for 4-amino- and 4-nitro-[2.2]paracyclophane,[3a] respectively: ~222 (4.2) and 217 (4.3); 272 (3.4) and ≈260 (3.4); 323 (2.8) and 307 (3.5).[3a]

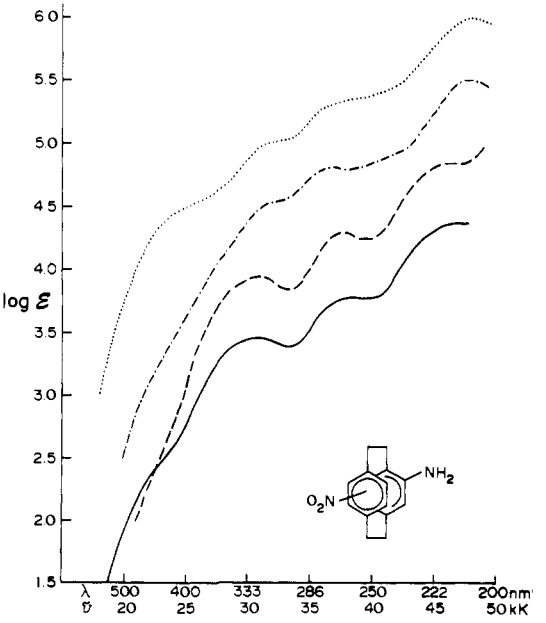


Figure 1. Ultraviolet absorption spectra of (···) pseudo-geminal, (-·-·-) pseudo-para, (- - -) pseudo-ortho, and (—) pseudo-meta isomer in ethanol. The upper three spectra are displaced upward on the ordinate by successive increments of 0.5 log unit.

The mono- and disubstituted [2.2]paracyclophanes differ strikingly in the longer wavelength region. Although the absorption bands of the disubstituted cycles overlap badly in

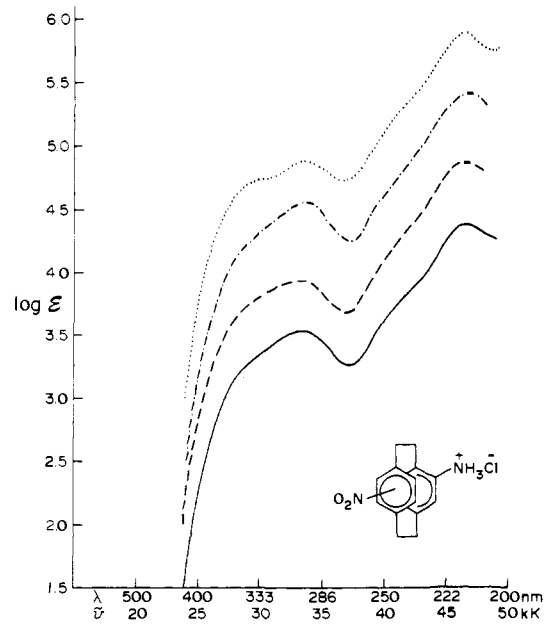


Figure 2. Ultraviolet absorption spectra of (•••) pseudo-geminal, (-•-•-) pseudo-para, (- - -) pseudo-ortho, and (—) pseudo-meta isomer in 1 *N* hydrogen chloride in ethanol. The upper three spectra are displaced upward on the ordinate by successive increments of 0.5 log unit.

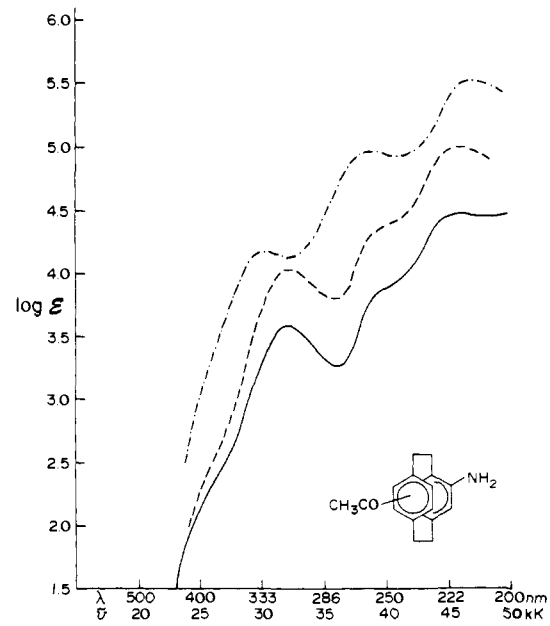


Figure 3. Ultraviolet absorption spectra of (-•-•-) pseudo-para, (- - -) pseudo-ortho, and (—) pseudo-meta isomer in ethanol. The upper two spectra are displaced upward on the ordinate by successive increments of 0.5 log unit.

this region, the curve shapes indicate points of inflection in the spectra of all four isomers. These occur at ~388 nm (log ϵ ~3.1) for the pseudo-gem, and at ~435 (~2.5) for the pseudo-meta isomers, and in between these values for the other two. The differences between the isomers in "end absorption" are the greatest. The wavelengths at which absorption reaches log ϵ 1.5 are as follows: pseudo-gem, 555 nm; pseudo-meta, 532; pseudo-para, 508; pseudo-ortho, 476. These differences are reflected in the red color of the pseudo-gem and meta crystalline isomers, and the orange color of the pseudo-para and meta crystalline isomers. In contrast, 4-amino[2.2]paracyclophane and 4-nitro[2.2]paracyclophane gave only enough "end absorption" to make them faintly yellow and no longer wavelength maxima or points of inflection were visible in their curves.[3a]

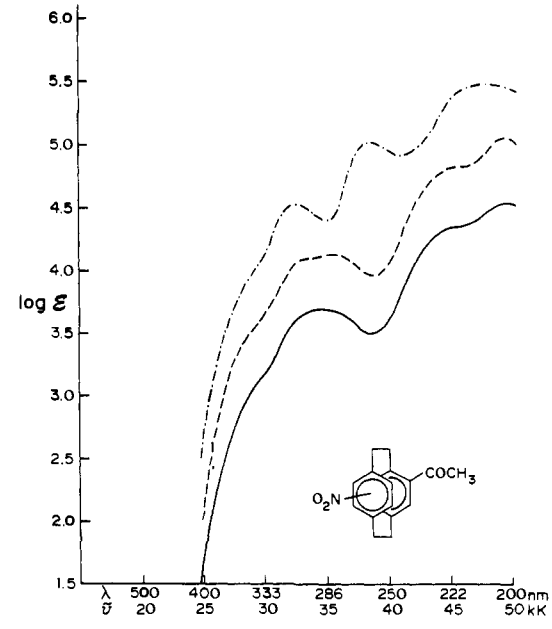


Figure 4. Ultraviolet absorption spectra of (-•-•-) pseudo-para, (- - -) pseudo-ortho, and (—) pseudo-meta isomer in *n*-hexane. The upper two spectra are displaced upward on the ordinate by successive increments of 0.5 log unit.

Figure 2 indicates that when the amino groups of the four nitroamines are protonated, the four isomers have almost identical spectra and the "end absorption" is cut off at a much shorter wavelength (λ ~420 nm at log ϵ 1.5). The curves are close to those expected from adding the spectra of 4-nitro[2.2]paracyclophane and protonated 4-amino-[2.2]paracyclophane. Thus when the electron pair of the amino group is localized by σ-bond formation, the coupling of the two absorbing units becomes much less prominent.

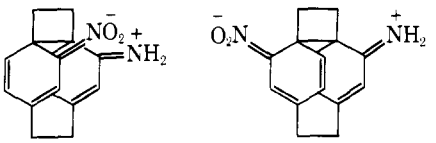
The curves of Figure 3 indicate a transannular electronic coupling of the amino and acetyl groups that resembles that of the amino and nitro groups of Figure 1. Although the same trends are visible in the differences in the curve shapes, the differences are not as great as with the nitroamines, and the "end absorption" does not extend to as long wavelengths (λ ranges from 416 to 435 nm at log ϵ 1.5).

When the two electron-withdrawing groups, nitro and acetyl, are substituted each in one ring, different spectral correlations emerge (Figure 4). The curves of the pseudo-meta and pseudo-ortho isomers are very similar to one another, and to that of the pseudo-para isomer at wavelengths longer than 300 nm. For example, the curves of all three isomers at λ 410 nm give log ϵ 1.5, each exhibits a point of inflection at λ ~333, and a band close to 300 nm. However, the curve of the pseudo-para isomer differs from the other two at shorter wavelengths.

Should transannular electronic effects be absent in these compounds, the spectra of the isomers should be the same, which they are not. The overlapping of bands and the complexity of the spectra limit the interpretation to the following.

The presence of long wavelength bands of enhanced "end absorption" and of color in the nitroamine derivatives suggests that intramolecular charge-transfer complexation between the benzene rings occurs to some extent. The transitions in question are of lower energy for the pseudo-gem and pseudo-meta than for the other two isomers. Interestingly, for only these two isomers, transannular dipolar

resonance structures can be drawn (D and E) which distrib-



D E

ute charge only on the functional groups. In these structures, the transannular σ bond is drawn where the benzene rings are closest. A structure similar to E can be drawn for pseudo-*m*-aminoacetyl[2.2]paracyclophane, which shows greater "end absorption" than the other two isomers of Figure 3.

Although the acetylnitro isomers of Figure 4 should exhibit much less charge transfer absorption, it is clear from the differences in spectra of the structural isomers that the charge distributions of the two absorbing units are different in the pseudo-para isomer on the one hand, and the pseudo-meta and pseudo-ortho isomers on the other.

Correlations between Structure and Other Physical Properties. As observed for other disubstituted [2.2]paracyclophane derivatives, the pseudo-para and gem derivatives usually have the higher melting points and are the less soluble of the isomers.[3e] The pseudo-meta isomers are always the lowest melting and most soluble. The pseudo-ortho derivatives vary widely in their melting behavior. With two exceptions, the polarity of the isomers in thin layer chromatography increases in the order pseudo-para, pseudo-meta, pseudo-ortho, and pseudo-gem. The pseudo-*o*-acetylnitro- and acetylbromo[2.2]paracyclophanes are less polar than their isomers probably for steric reasons. In models, the acetyl group is wedged between the methylene bridges and the pseudo-ortho substituent, with the oxygen oriented toward the transannular benzene ring. As a result, the polar carbonyl group is less available to polar surfaces. The same effect is visible with the pseudo-*o*-aminoacetyl which, although more polar than the pseudo-meta isomer, is equally polar to the pseudo-para isomer. Evidently the amino group is not large enough to inhibit binding as effectively as the bromo or nitro groups.

The mass spectra (at 70 and 12 eV) of all the disubstituted [2.2]paracyclophanes gave strong molecular ion peaks, as well as peaks for the substituted *p*-xylylene (or methylenetropylium) ion radicals. These spectra allowed the number of substituents in each ring to be determined. The intensity of the two xylyene fragments varied widely. The nitro-containing fragment was observed in spectra of only cyanonitro isomers. The other mixed nitro derivatives gave only peaks for the non-nitro-containing xylylene fragment.

The positions of the infrared spectral bands associated with the functional groups of the compounds reported here are not particularly dependent on the presence or position of a second substituent attached to the other benzene ring.

Experimental Section

General Procedure. Melting points are uncorrected. All solvents were reagent grade. The ^{1}H NMR measurements were made with a Varian A-60D and Varian HA-100 spectrometer on dilute solutions (ca. 2–20%) in deuteriochloroform with tetramethylsilane as internal standard. Infrared spectra were run in dichloromethane solutions on a Beckman IR-5 spectrophotometer. The mass spectra were obtained with an AEI Model MS9. Thin layer chromatograms were run using Baker and Merck silica gel G coated on glass plates with appropriate pentane–ethyl acetate mixtures as eluants. Iodine vapor was used to spot the plates. Silica gel for column chromatography was Baker chromatographic grade.

Aminobromo[2.2]paracyclophanes (5–8). The bromonitro compounds (**1–4**) of established structure[3e] were catalytically reduced by the following illustrative procedure. A mixture of 0.50 g of the pseudo-gem isomer (**1**), 30 ml of ethyl acetate, 10 ml of methanol, and 0.10 g of platinum oxide was stirred in an atmosphere of hydrogen until 3 mol of hydrogen was absorbed (5.5 hr). The mixture was filtered through a pad of Celite, the filtrate was evaporated, and the residue sublimed at 100–120° (0.01 Torr). The sublimate was recrystallized twice from dichloromethane–ether–pentane to give 0.26 g (57%) of **5**, mp 201–202.5°. Anal. Calcd for $C_{16}H_{16}BrN$: C, 63.59; H, 5.34. Found: C, 63.72; H, 5.37.

The preparation of the other three isomers, pseudo-meta, pseudo-ortho, and pseudo-para, gave respectively: mp 177–178.5°, 37% yield of **6** (C, 63.67; H, 5.50); mp 203–204.5°, 68% of **7** (C, 63.65; H, 5.29); mp 200–206°, 62% of **8** (C, 63.45; H, 5.48).

When 0.75 g of pseudo-*gem*-bromonitro[2.2]paracyclophane (**1**) was heated at 153° for 39 hr in a degassed solution of 11.5 ml of 0.8 *M* potassium methoxide in methanol in a sealed tube, a 19% yield of **5** and a 5% yield of **6** was obtained (products were separated chromatographically and compared with authentic samples).

Cyanonitro[2.2]paracyclophanes (9–12). The pseudo-gem (**9**) and pseudo-meta (**10**) isomers were obtained from pseudo-*gem*-bromonitro[2.2]paracyclophane (**1**) as follows. A mixture of 4.0 g of **1**, 30 ml of freshly distilled *N*-methylpyrrolidone and 2.22 g of cuprous cyanide was heated at 205° for 24 hr. Then 20 ml of a solution of 20 g of ferric chloride, 5 ml of concentrated hydrochloric acid, and 20 ml of water were added, and the mixture was kept at 60° for 30 min. The mixture was shaken with 150 ml of ether, the layers were separated, and the aqueous layer was washed six times with 100-ml portions of ether. The combined ether extracts were washed successively with 50% hydrochloric acid, water, 20% sodium hydroxide solution, and water. The solution was dried and evaporated to give 3.364 g of residue that was chromatographed on 300 g of silica gel. Ether–pentane, 3–10%, eluted isomerized starting material, pseudo-meta-bromonitro compound **2**, wt 0.944 g (24%), mp 115–116°. Ether–pentane, 10–15%, eluted 0.549 g (14%) starting material (**1**), mp 233–234°. Ether–pentane, 15–35%, eluted pseudo-meta-cyanonitro product, which after two recrystallizations from dichloromethane–ether gave 0.930 g (27%) of **10**, mp 162–163°. Anal. Calcd for $C_{17}H_{14}N_2O_2$: C, 73.36; H, 5.07. Found: C, 73.40; H, 5.12.

In a similar run with 25 g of **1**, after isolation of **1**, **2**, and **10**, the column was washed with 5–10% methanol–ether to give 2.03 g of material that was chromatographed again on 370 g of silica gel. Elution of this column with 25–40% ethyl acetate–pentane gave the pseudo-gem-cyanonitro product, which after three recrystallizations from dichloromethane–ether gave 0.592 g (3%) of **9**, mp 234–235° (C, 73.15; H, 5.19).

Nitration of 4-cyano[2.2]paracyclophane[12] gave **11** and **12.** To a solution of 17.7 g of the nitrile in 500 ml of glacial acetic acid at 100° was added with rapid stirring all at once 150 ml of 90% nitric acid. After 4 min, the solution was poured over 500 g of crushed ice. The resulting mixture was extracted six times with chloroform, and the combined extracts were washed with 20% sodium hydroxide solution and then water and were dried and evaporated. The residue was chromatographed on 1800 g of silica gel (500 ml fractions were cut). Product from fractions 27–28 (20% ethyl acetate–pentane) were recrystallized twice from dichloromethane–ether to give 1.325 g (7%) of pseudo-*p*-cyanonitro[2.2]paracyclophane (**12**), mp 236–237° (C, 73.17; H, 5.01). Fractions 29–36 contained mainly isomer **10** (^{1}H NMR spectrum). Fractions 37–38 (40% ethyl acetate–pentane) yielded after three recrystallizations from dichloromethane–ether 0.813 g (4%) of pseudo-*o*-cyanonitro-[2.2]paracyclophane (**11**), mp 209–211° (C, 73.50; H, 4.91).

Thermal Isomerization of Pseudo-*o*-cyanonitro[2.2]paracyclophane (11) to the Pseudo-Para Isomer (12). A degassed solution of 80 mg of **11** in 0.3 ml of pure *N*-methylpyrrolidone was heated in a sealed ^{1}H NMR tube at 200° for 44 hr. From time to time the tube was cooled, the ^{1}H NMR spectrum, and the isomerization was followed by integration of the two doublets at low field (proton ortho to the nitro group in **11** and **12**). Equilibrium was reached after ca. 30 hr, and the one-to-one mixture did not change with an additional 14 hr of heating.

Carboxynitro[2.2]paracyclophanes (13–16). Hydrolysis of pseudo-*m*-cyanonitro[2.2]paracyclophane (**10**) illustrates the procedure. A mixture of 0.400 g of **10**, 15 ml of glacial acetic acid, and 10 ml of concentrated hydrochloric acid was refluxed for 9 days. The mixture was cooled, shaken with water and ether, and

the ether layer was washed with water. The ether layer was extracted with 5% sodium hydroxide solution, and the extract was washed with ether. The basic solution was acidified with concentrated hydrochloric acid, and the acid that separated was filtered, dried, and recrystallized from ether–pentane and dichloromethane–pentane to give 0.266 g (63%) of **14**, mp 218.5–219.5°. Anal. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08. Found: C, 68.57; H, 5.20.

Similarly, pseudo-*gem*-carboxynitro[2.2]paracyclophane (**13**) was prepared in 45% yield, mp 287–289° (found: C, 68.39; H, 5.31). Although this reaction was carried out for 14 days, 45% of the starting material was recovered.

Similarly, pseudo-*o*-carboxynitro[2.2]paracyclophane (**15**) was prepared, 89% yield, mp 251–254° (found: C, 68.60; H, 5.17).

Similarly, pseudo-*p*-carboxynitro[2.2]paracyclophane (**16**) was prepared, 85%, mp 284–286° (found: C, 68.89; H, 5.36).

Aminonitro[2.2]paracyclophanes (17–20). The procedure is illustrated by the conversion of pseudo-*m*-carboxynitro[2.2]paracyclophane (**14**) to pseudo-*m*-aminonitro[2.2]paracyclophane (**18**). Acid **14**, 2.0 g was refluxed for 15 min with 2.90 ml of thionyl chloride in 60 ml of benzene, and the volatile components were evaporated under vacuum. The acid chloride produced was dissolved in 50 ml of acetone; the solution was cooled to 0° and was added in one portion to a stirred solution of sodium azide (1.7 g) in a mixture of 20 ml of water and 15 ml of acetone held at 0°. The mixture was allowed to stand at 25° for 30 min, and then 120 ml of water was added, the mixture was cooled, and the azide was collected and dried at 25° for 10 hr at 1 Torr over potassium hydroxide to give 1.69 g of material. The azide was dissolved in 35 ml of toluene, and the solution was heated to reflux for 20 min. Concentrated hydrochloric acid (40 ml) was added, and the mixture was heated under reflux for 30 hr. The solution was cooled, and the amine salt that separated was filtered. The salt was heated to reflux for 5 min with a mixture of 50 ml of chloroform and 10% potassium hydroxide solution. The chloroform phase was separated, washed with water, dried, and evaporated. The residual amine was sublimed at 135° (0.01 Torr) to give an orange-red sublimate which was recrystallized from dichloromethane–ether to give 1.128 g (68%) of orange-red crystals of **18**, mp 195.5–196°. Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01. Found: C, 71.75; H, 5.97.

Similarly from pseudo-*gem*-carboxynitro[2.2]paracyclophane (**13**) was obtained (63%) pseudo-*gem*-amino[2.2]paracyclophane (**17**) as deep orange crystals, mp 241–243° (C, 71.53; H, 6.07). From pseudo-*p*-carboxynitro[2.2]paracyclophane (**16**) was obtained (74%) pseudo-*p*-aminonitro[2.2]paracyclophane (**20**) as orange crystals, mp 226–229° (C, 71.60; H, 6.01). From pseudo-*o*-carboxynitro[2.2]paracyclophane (**15**) was obtained (63%) pseudo-*o*-aminonitro[2.2]paracyclophane (**19**) as orange crystals, mp 219–221° (C, 71.62; H, 6.14).

Acetylnitro[2.2]paracyclophanes (21–24). To a vigorously stirred solution of 10 g of acetyl[2.2]paracyclophane[12] in 500 ml of glacial acetic acid at 50° was added in one portion 100 ml of 90% nitric acid. During 4 min, the temperature rose to 62°, and the solution was poured onto 500 g of crushed ice. The reaction mixture was extracted with ether; the ether layers were washed with 20% sodium hydroxide and water, dried, and evaporated. The residue (6.45 g) was combined with similar material from another run (5.13 g), and chromatographed on 1300 g of silica gel with 125-ml fractions being cut. Fractions 53–61 (5% ethyl acetate–pentane) contained 0.29 g of starting material (TLC and ^{1}H NMR). Fractions 85–105 (5% ethyl acetate–pentane) contained 0.965 g (5%) of pseudo-*o*-acetylnitro[2.2]paracyclophane (**22**), mp 144.5–145.5° after two crystallizations from dichloromethane–ether–pentane. Anal. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80. Found: C, 73.30; 5.89.

Material from fractions 123–140 (5% ethyl acetate–pentane) was crystallized twice from dichloromethane–pentane to give 0.137 g (0.7%) of *p*-acetylnitro[2.2]paracyclophane (**24**), mp 142.5–143.5° (C, 73.28; H, 5.88). Fractions 147–180 (7% ethyl acetate–pentane) yielded after three crystallizations of the product from dichloromethane–ether–pentane, 0.547 g (3%) of pseudo-*p*-acetylnitro[2.2]paracyclophane (**23**), mp 149.5–150.5° (C, 73.06; H, 6.02). Fractions 181–186 (7–10% ethyl acetate–pentane) contained a mixture of **22** and **23** (0.068 g). Fractions 187–210 (7–10% ethyl acetate–pentane) gave material that was crystallized from dichloromethane–ether–pentane to give 0.788 g (4%) of pseudo-*m*-acetylnitro[2.2]paracyclophane (**21**), mp 117.5–118.5° (C, 73.25; H, 5.81).

Acetylamino[2.2]paracyclophanes (25–27). The procedure is illustrated with the reduction of pseudo-*o*-acetylnitro[2.2]paracyclophane (**22**) to pseudo-*o*-acetylamino[2.2]paracyclophane (**26**). A mixture of 0.080 g of **22**, 10 ml of ethyl acetate, and 50 mg of platinum oxide was shaken for 13 min during which time the theoretical amount of hydrogen was absorbed. The catalyst was filtered through a pad of Celite, and the filtrate was evaporated. The residue was sublimed at 130° (0.02 Torr), and the sublimate was recrystallized twice from dichloromethane–pentane to give 0.049 g (68%) of **26**, mp 146–148°. Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22. Found: C, 81.64; H, 7.22.

Similarly, 80 mg of pseudo-*p*-acetylnitro[2.2]paracyclophane (**23**) gave mg (60%) of pseudo-*p*-acetylamino[2.2]paracyclophane (**27**), mp 210–212° (C, 81.61; H, 7.04). Similarly, 90 mg of pseudo-*m*-acetylnitro[2.2]paracyclophane (**21**) gave 58 mg (72%) of pseudo-*m*-acetylamino[2.2]paracyclophane (**25**), mp 209–211° (C, 81.56; H, 7.37).

Pseudo-*m*-dicyano[2.2]paracyclophane (28). A mixture of 1.00 g of pseudo-*m*-dibromo[2.2]paracyclophane,[3d] 2.70 g of cuprous cyanide, and 20 ml of purified quinoline was heated at 215° for 24 hr under nitrogen. The black solution was poured into 80 ml of 15% ammonium hydroxide, and the mixture was extracted with 200 ml of ether. The ether extract was washed successively with 15% ammonium hydroxide, water, and 5 *N* hydrochloric acid. The ether solution was dried and evaporated, and the residue was chromatographed on 140 g of silica gel with 100 ml of elutate fractions cut of the following compositions: 1–5, pentane; 6–25, 95% pentane–ether; 26–35, 90% pentane–ether; 36–50, 85% pentane–ether; 50–56, 80% pentane–ether; 57–60, 75% pentane–ether; 61–75, 100% ether. Fractions 14–20 contained 76 mg of a mixture of pseudo-*gem*- and pseudo-*m*-bromocyano[2.2]paracyclophanes. Fractions 21–24 contained 36 mg of pseudo-*m*-bromocyano[2.2]paracyclophane. Fractions 36–47 contained a mixture of 363 mg of pseudo-*gem*- and pseudo-*m*-dicyano[2.2]paracyclophanes. Fractions 62–73 contained unknown material. Fractions 48–59 were recrystallized from ethyl acetate to give 204 mg (29%) of pseudo-*m*-dicyano[2.2]paracyclophane (**28**), mp 170–171°. Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46. Found: C, 83.46; H, 5.24. The other compounds, although identified by their ^{1}H NMR and mass spectra, were not obtained in a pure state.

Pseudo-*m*-cyanocarboxy[2.2]paracyclophanes (31–33) and Pseudo-*m*-dicarboxy[2.2]paracyclophanes (34–36). A mixture of 291 mg of pseudo-*m*-dicyano[2.2]paracyclophane (**28**), 15 ml of glacial acetic acid, and 10 ml of concentrated hydrochloric acid was refluxed for 89 hr. The reaction mixture was then shaken with 200 ml of water and 200 ml of ethyl acetate (200 ml). The ethyl acetate layer was dried, the solvent evaporated, and the 272 mg of residue was chromatographed on 140 g of silica gel with the following 100-ml fractions cut: 1–5, pentane; 6–10, 80% pentane–ether; 11–20, 60% pentane–ether; 21–30, 40% pentane–ether; 31–40, ether. Fractions 14–16 gave 50 mg of recovered **28.** Fractions 20–26 gave pseudo-*m*-cyanocarboxy[2.2]paracyclophane (**31**), which after recrystallization from ether–pentane gave 26 mg (8%) of material, mp 222.5–223.5°. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45. Found: C, 78.03; H, 5.31.

Fractions 29–37 gave pseudo-*m*-dicarboxy[2.2]paracyclophane (**34**), recrystallization of which from ethyl acetate gave 30 mg of material (9%), mp 283–283.5°. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.84; H, 5.47.

Similarly, pseudo-*o*-dicyano[2.2]paracyclophane (**29**)[3d] gave a mixture of pseudo-*o*-cyanocarboxy[2.2]paracyclophane (**32**) and pseudo-*o*-dicarboxy[2.2]paracyclophane (**35**). Compound **32** was obtained in 20% yield, mp 250–251°. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45. Found: C, 78.14; H, 5.47. Compound **35** was obtained in 7% yield, mp 320°. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.96; H, 5.44. Found: C, 72.83; H, 5.36.

Similarly, pseudo-*p*-dicyano[2.2]paracyclophane (**30**)[3d] was converted in 10% yield into pseudo-*p*-cyanocarboxy[2.2]paracyclophane (**33**), mp 264–264.5°. Anal. Calcd for $C_{18}H_{15}NO_2$: C, 77.96; H, 5.45. Found: C, 78.12; H, 5.44. Also obtained was pseudo-*p*-dicarboxy[2.2]paracyclophane (**36**) in 11% yield, mp 340°. Anal. Calcd for $C_{18}H_{15}O_4$: C, 72.96; H, 5.44. Found: C, 73.12; H, 5.42.

Acetamidonitro[2.2]paracyclophanes (37, 38). The cycle, pseudo-*p*-acetamidonitro[2.2]paracyclophane (**38**), was prepared from

pseudo-*p*-aminonitro[2.2]paracyclophane (**20**). A mixture of 70 mg of **20**, 4 ml of pyridine, and 4 ml of acetic anhydride was heated to 100° for 30 min, cooled, and mixed with 40 ml of water. The precipitate that formed was collected and recrystallized from ether to give 54 mg (77%) of needles of **38**, mp 227–228°. Anal. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85. Found: C, 69.82; H, 5.94.

Similarly, pseudo-*m*-aminonitro[2.2]paracyclophane (**18**) was converted (88%) to pseudo-*m*-acetamidonitro[2.2]paracyclophane (**37**), mp 184–185° (C, 69.58; H, 5.85).

Acetamidoamino[2.2]paracyclophanes (39, 40). The pseudo-*p*-acetamidoamino[2.2]paracyclophane (**40**) was prepared from pseudo-*p*-acetamidonitro[2.2]paracyclophane (**38**). A mixture of 40 mg of **38**, 30 ml of ethyl acetate, and 50 mg of platinum oxide was stirred under an atmosphere of hydrogen until the hydrogen uptake stopped. The solution was filtered through Celite, the filtrate evaporated, and the remaining white solid was recrystallized from dichloromethane–pentane to give 29 mg (80%) of yellow needles of **40**, mp 245–247° dec. Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.11; H, 7.19. Found: C, 76.77; H, 7.26.

Similarly pseudo-*m*-acetamidonitro[2.2]paracyclophane (**37**) was converted (55%) to pseudo-*m*-acetamidoamino[2.2]paracyclophane (**39**), mp 223–224° dec (C, 77.05; H, 7.33).

Diamino[2.2]paracyclophanes (41, 42). Catalytic reduction in ethyl acetate with a platinum oxide catalyst of pseudo-*m*-aminonitro[2.2]paracyclophane (**18**) gave after sublimation and recrystallization from ethyl acetane–pentane–ether a 55% yield of pseudo-*m*-diamino[2.2]paracyclophane (**41**), mp 222–226° (sealed tube mp 239–244°). Anal. Calcd for $C_{16}H_{18}N_2$: C, 80.63; H, 7.61. Found: C, 80.39; H, 7.36.

Similarly, pseudo-*p*-aminonitro[2.2]paracyclopane (**20**) gave (80%) pseudo-*p*-diamino[2.2]paracyclophane (**42**), mp 267–268° (sealed tube) (C, 80.67; H, 7.59).

Bromocarboxy[2.2]paracyclophanes (45, 46). A mixture of 317 mg of pseudo-*o*-bromocarbomethoxy[2.2]paracyclophane (**44**),[3b] 25 ml of 2 *N* sodium hydroxide, and 15 ml of absolute ethanol was refluxed for 5 days. The ethanol was evaporated and the basic aqueous solution was washed with chloroform and was acidified with hydrochloric acid. The precipitate that separated was collected and recrystallized from methanol to give 224 mg (68%) of pseudo-*o*-bromocarboxy[2.2]paracyclophane (**46**), mp 232–236°. Anal. Calcd for $C_{17}H_{15}BrO_2$: C, 61.65; H, 4.56. Found: C, 61.70; H, 4.62.

Similarly, pseudo-*m*-bromocarbomethoxy[2.2]paracyclophane (**43**)[3b] gave (82%), pseudo-*m*-bromocarboxy[2.2]paracyclophane (**45**), mp 218–219° (C, 61.88; H, 4.73).

Pseudo-*m*-carbomethoxynitro[2.2]paracyclophane (47). A solution of 88 mg of pseudo-*m*-carboxynitro[2.2]paracyclophane (**14**) in 20 ml of ether was treated with an excess of diazomethane in ether. The resulting solution was evaporated, and the residue was twice recrystallized from ether–pentane to give 60 mg (65%) of **47**, mp 130.5–132°. Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50. Found: C, 69.32; H, 5.50.

Pseudo-*m*-aminocarbomethoxy[2.2]paracyclophane (48). A mixture of 700 mg of pseudo-*m*-carbomethoxynitro[2.2]paracyclophane (**47**) was catalytically reduced with hydrogen and platinum oxide to give after recrystallization from ether 470 mg (74%) of **48**, mp 159–161°. Anal. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81. Found: C, 77.09; H, 6.83.

References and Notes

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Meta Bridging Reactions of Electron-Deficient Aromatics. I. Studies Directed toward a One-Step Synthesis of the 6,7-Benzomorphan Ring System. Facile Preparation of Potential Narcotic Antagonists

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Abstract: Reactions of a series of amidines with electron-deficient benzenes and naphthalenes have been shown to yield addition products. In certain cases, cyclization of the initial adducts occurs to yield the 6,7-benzomorphan ring system. The reaction is a new and useful preparation of such structures which, when appropriately functionalized, may have useful narcotic analgesic and antagonist activity. The reactivity of the amidine σ complex precursors to the bridged products is of considerable interest, and new facets of the chemistry of nitrogen base σ complexes are discussed.

In a previous series of papers, we have extensively studied the reactions of potential biscarbanions with electron-deficient aromatics to yield carbobicyclic [3.3.1] ring systems.[1-8] The reactions are base catalyzed and occur in two distinct steps. The first intermediate to rapidly form is an addition adduct (σ complex) **1** which slowly cyclizes to the final product **2**.[7] Our attempts to employ such a sequence with types of potential biscarbanion precursors in which the two potential nucleophilic sites were not flanking a single carbonyl carbon always failed,[8] and a general consideration of the requirements of the cyclization process led us to conclude that an sp^2 center adjacent to the nucleophilic site in