Macro Rings. XXXVIII. Determination of Positions of Substituents in the [2.2]Paracyclophane Nucleus through Nuclear Magnetic Resonance Spectra[1]

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Abstract: The use of nuclear magnetic resonance (nmr), infrared (ir), and mass spectra to determine the structures of disubstituted (aromatic) [2.2]paracyclophanes is described. Besides the usual chemical shift in the nmr observed for protons *ortho* to substituents, the following 4-substituted [2.2]paracyclophanes exhibit downfield shifts for their pseudo-*gem* protons:[2] bromo, chloro, iodo, cyano, methyl, ethyl, hydroxy, acetoxy, and methoxy. The absorption appears as a doublet ($J = 8$ Hz) with further small splittings (1 to 2 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, then the four possible isomers (not counting enantiomers) each exhibits a unique nmr aromatic proton resonance pattern. When X and Y are pseudo-*gem*, no signal for a proton pseudo-*gem* to the down-shifting group is observed. When X and Y are pseudo-*meta*, the proton pseudo-*gem* to the down-shifting group is split by its *ortho* and *para* protons, and appears as a doublet ($J = 8$ Hz). When X and Y are pseudo-*ortho*, the proton pseudo-*gem* to the down-shifting group is split only by its *meta* and *para* protons, and appears as a broad singlet or close doublet. When X and Y are pseudo-*para*, the proton pseudo-*gem* to the down-shifting group is split by its *meta* and *ortho* protons, and appears as a doublet of doublets ($J_1 = 8$ Hz, $J_2 = 2$ Hz). The structures of 40 disubstituted [2.2]paracyclophanes have been assigned on this basis. A unique halogen–aromatic ring absorption has been observed in the infrared spectra of all [2.2]paracyclophanes substituted with halogen, and occurs from 1029 to 1099, depending on the nature of the halogen and other substituents. This band was useful for analysis of mixtures. The carbonyl stretching frequency of pseudo-*gem*-bromoacetyl[2.2]paracyclophane was found to be moved to 1663 cm^{-1} from 1666–1668 cm^{-1} for the other isomers. This frequency decrease may be due to transannular $Br\cdots C{=}O$ interactions. The mass spectra of the substituted [2.2]paracyclophanes at low ionizing voltages (12 eV) show predominant fragmentation to the substituted *p*-xylylene (or elements thereof) ion radicals. Thus, the mass spectrum provides a convenient analytical tool for the determination of the number of substituents on each aromatic ring of a polysubstituted [2.2]paracyclophane. Correlations between structures and other physical properties of disubstituted [2.2]paracyclophanes have been summarized. For example, pseudo-*gem* isomers tend to melt higher, to move slower on tlc, and to be more insoluble than the other isomers.

Central to the problem of directive effects during electrophilic substitution of [2.2]paracyclophane derivatives is the task of structure determinations. Initially, this problem appeared formidable since there are eight substitutable aromatic protons and seven isomers (not counting optical) when two of these positions are substituted. Thus, the discovery that nmr spectra could provide unambiguous structure identification for most such isomers was key to the present work. Many products of disubstitution of [2.2]paracyclophane were described in papers XXXV[3a] and XXXVII[3c] of this series, and both thermal isomerizations (paper XXXVI)[3b] and functional group interconversions[3a,c] related them structurally. Although many structural *relationships* were established, few complete structures were determined. This paper elucidates the constitutions of these compounds in an unambiguous way largely by use of nmr spectra aided by mass spectra, infrared spectra, and correlations of physical properties. The results represent a striking testimonial to the power of the spectral tool for making subtle structural distinctions.

Structure Elucidation by Use of Nmr Spectra of Substituted Paracyclophanes

The nmr spectra of the [1.*n*]-,[4a] the [*m*]-,[4b–d] and [*m.n*]paracyclophanes[5a] have been reported previously. All of the aromatic resonances of the [*m.n*]paracyclophanes with $4 \geqslant m$ or $n \geqslant 2$ are between τ 3.34 and 3.63 (deuteriochloroform with tetramethylsilane as standard). The smaller the values of *m* and *n*, the higher the upfield shift. These upfield shifts have been assigned to anisotropy effects of one ring on the protons of the other, and to rehybridization of the benzene carbons as a result of ring deformation.[5] Effects of the former type have been observed in 1,8-diphenylnaphthalene[6a] and janusene.[6b] Only small shifts of the aromatic proton resonances can be attributed to rehybridization since the resonance of [8]paracyclophane aromatic protons at τ 2.95 is similar to that

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[2] The colloquial nomenclature is self-evident: pseudo-*gem* denotes two transannularly adjacent positions on the benzene rings; pseudo-*ortho*, pseudo-*meta*, and pseudo-*paras* pecify *ortho*, *meta*, and *para* relationships displaced from the usual homoannular into a transannular context.

[3] (a) H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3505 (1969); (b) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3517 (1969); (c) H. J. Reich and D. J. Cram, *ibid.*, **91**, 3527 (1969).

[4] (a) D. J. Cram and L. A. Singer, *ibid.*, **85**, 1084 (1963); (b) J. S. Waugh and R. W. Fessenden, *ibid.*, **79**, 846 (1957); (c) D. J. Cram and M. Goldstein, *ibid.*, **85**, 1063 (1963); (d) D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).

[5] (a) D. J. Cram and R. C. Helgeson, *ibid*, **88**, 3515 (1966); (b) R. C. Helgeson and D. J. Cram, *ibid.*, **88**, 509 (1966).

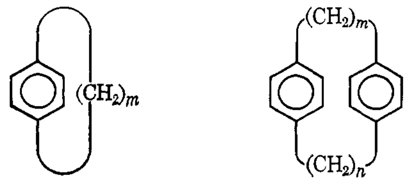
[6] (a) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963); (b) S. J. Cristol and D. C. Lewis, *J. Am. Chem. Soc.*, **89**, 1476 (1967).

Table I. The Nmr Chemical Shifts[a] (τ) of [2.2]Paracyclophanes Substituted with Groups X and Y

			Proton (orientation relative to group X)								
X	Y	Orientation of X and Y	*ortho*	*meta*	*para*	pseudo-*gem*	pseudo-*ortho*	pseudo-*meta*	pseudo-*para*	CH_3	Ref[c]
Cl	H					2.88					*b*
Cl	Cl	Pseudo-*para*	3.72	3.57	2.98	2.98	3.57	3.72	Y		3c
Br	H					2.84					*b,d,e*
Br	Br	Pseudo-*ortho*	2.78			2.78	Y				3c
Br	Br	Pseudo-*meta*	3.45	2.86	3.57	2.86	3.57	Y	3.45		3c
Br	Br	Pseudo-*para*	3.47	3.54	2.83	2.83	3.54	3.47	Y		3c
Br	Br	*para*	3.51	3.51	Y	2.84	3.55	3.55	2.84		3c
I	H		3.19			2.77					*d*
$COCH_3$	H		3.14							7.60	*b*
$COCH_3$	Br	Pseudo-*ortho*	2.39				Y			7.48	3a
$COCH_3$	Br	Pseudo-*meta*	3.02	2.79	3.42			Y		7.57	3a
$COCH_3$	Br	Pseudo-*para*	3.13		2.69		3.67		Y	7.56	3a
$COCH_3$	Br	Pseudo-*gem*	2.85			Y				7.37	3a
$COCH_3$	Br	*para*	3.14	3.44	Y				2.87	7.57	3a
CO_2Me	H		2.86							6.12	3a
CO_2Me	Br	Pseudo-*ortho*	2.31							6.14	3a
CO_2Me	Br	Pseudo-*meta*	2.80	2.79	3.42			Y		6.12	3a
CO_2Me	Br	Pseudo-*para*	2.91		2.69				Y	6.12	3a
CO_2Me	Br	Pseudo-*gem*	2.66	3.47	3.33	Y				6.14	3a
CO_2Me	Br	*para*	2.91		Y				2.85	6.10	3a
CO_2Me	CO_2Me	Pseudo-*para*	2.70	3.53	3.33	3.33	3.53	2.70	Y	6.12	3c
CH_3	H		3.98			3.28				7.98	3a
CH_3	CH_3	Pseudo-*para*	3.92	3.73	3.33	3.33	3.73	3.92	Y	7.89	3c
CH_3	Br	*para*	3.90	3.57	Y	3.18			2.79	7.97	3a
CH_3	Br	*ortho*	Y			3.33	3.02			7.93	3a
NO_2	H		2.80	3.41	3.24						*b*
NO_2	Br	Pseudo-*ortho*	2.16				Y				3a
NO_2	Br	Pseudo-*meta*	2.70	2.70	3.28			Y			3a,3b
NO_2	Br	Pseudo-*para*	2.81		2.56				Y		3a
NO_2	Br	Pseudo-*gem*	2.45			Y					3a
NO_2	Br	*para*	2.82	3.34	Y				2.88		3a
NO_2	NO_2	Pseudo-*gem*	2.68	3.17	3.17	Y	2.68	3.17	3.17		3c
NO_2	NO_2	Pseudo-*ortho*	2.47	3.06	2.88	2.47	Y	2.88	3.06		3c
NO_2	NO_2	Pseudo-*meta*	2.63	3.16	3.16	3.16	3.16	Y	2.63		3c
NO_2	NO_2	Pseudo-*para*	2.80	3.40	3.10	3.10	3.40	2.80	Y		3c
CN	H		3.25			3.09					8
CN	Br	Pseudo-*ortho*	2.56			3.08	Y				3a,3c
CN	Br	Pseudo-*meta*	3.15	2.68	3.30	3.06	3.44	Y			3a
CN	Br	Pseudo-*para*	3.27	3.45	2.63	3.07	3.52		Y		3a,3c
CN	CN	Pseudo-*ortho*	2.87	3.33	3.22	2.87	Y	3.22	3.33		3c
CN	CN	Pseudo-*para*	3.21	3.37	2.88	2.86	3.37	3.21	Y		3c
OH	H		4.52			3.03					*b*
OH	Br	Pseudo-*meta*	4.44	2.88		3.02		Y			*e*
OH	Br	Pseudo-*para*	4.45	3.59	3.02	3.18	3.64	3.52	Y		*e*
OH	OH	Pseudo-*ortho*	3.72	3.62	3.92	3.72	Y	3.92	3.62		3c,[f]
OH	OH	Pseudo-*para*	4.31	3.74	3.48	3.48	3.74	4.31	Y		3c,[f]
OCH_3	H		4.40	3.62	3.76	3.27				6.38	*b,e*
OCH_3	OCH_3	Pseudo-*ortho*	3.89	3.61	3.83	3.89	Y	3.83	3.61	6.33	3c
OCH_3	OCH_3	Pseudo-*para*	4.40	3.65	3.61	3.61	3.65	4.40	Y	6.35	3c
OAc	Br	Pseudo-*para*	3.96	3.53	2.92	3.12	3.56		Y	7.70	3a
OAc	OAc	Pseudo-*para*	4.01	3.54	3.19	3.19	3.54	4.01	Y	7.72	3c

[a] Taken on a Varian A-60 spectrometer on dilute solutions (5–20%) in deuteriochloroform with tetramethylsilane as internal standard. [b] D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.*, **77**, 6289 (1955). [c] Either prepared or referred to in this reference. [d] See Experimental Section. [e] D. J. Cram and A. C. Day, *J. Org. Chem.*, **31**, 1227 (1966). [f] Taken in hexadeuterioacetone solution with tetramethylsilane as internal standard.

of open-chain model compounds such as 1,4-di(p-tolyl)-butane at τ 2.95[5a] or 1,2-di(p-tolyl)ethane[5b] at τ 3.05 (latter in carbon tetrachloride). The aromatic ring of [8]paracyclophane is distorted as much as those in [2.2]paracyclophane.[7]



I($m = n = 2$)

An nmr study of 4-substituted [2.2]paracyclophanes[8] showed that one of the aromatic protons was shifted upfield for electron-donating substituents (ethyl and methoxy) and downfield for electron-withdrawing substituents (nitro, acetyl, and bromo). This resonance was assigned to the *ortho* proton. The center of gravity of the remainder of the aromatic protons similarly exhibited upfield or downfield shifts depending on the nature of the substituent. Since the majority of these protons were on the unsubstituted ring, a transannular shift was involved.

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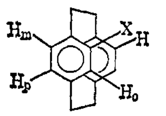
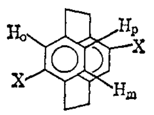
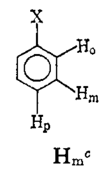
(7) N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Amer. Chem. Soc.*, **85**, 1171 (1963).

(8) L. A. Singer and D. J. Cram, *ibid.*, **85**, 1080 (1963).

Table II. The Substituent Chemical Shift (SCS) Values[a] for *ortho*, *meta*, and *para* Protons in [2.2]Paracyclophanes and Substituted Benzenes







X	H_o[b]	H_m[b]	H_p[b]	H_o[b]	H_m[b]	H_o[c]	H_m[c]	H_p[c]
Cl				0.09	−0.06	−0.02	0.08	0.13[d,e]
Br				−0.16	−0.09	−0.22	−0.09	0.03[e]
I	−0.44					−0.40	−0.25	0.03[e]
OH	0.89					0.54	0.17	0.46[d,f,g]
OCH_3	0.77	−0.01	0.13	0.77	0.02	0.45	0.08	0.42[d,e]
OAc				0.38	−0.09			
CH_3	0.35			0.29	0.10	0.17	0.09	0.19[h]
CN	−0.38			−0.42	−0.26	−0.27	−0.10	−0.22[d]
$COCH_3$	−0.49					−0.64[i]		
CO_2CH_3	−0.77			−0.93	−0.10	−0.72	−0.10	−0.20[d,f]
NO_2	−0.83	−0.22	−0.39	−0.83	−0.23	−0.95	−0.20	−0.33[e]

[a] In parts per million. [b] Chemical shift from the aromatic resonance of [2.2]paracyclophane (τ 3.63). [c] Chemical shift from benzene (τ 2.73). [d] R. R. Fraser and R. N. Renaud, *J. Am. Chem. Soc.*, **88**, 4365 (1966). [e] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, **35**, 731 (1961). [f] J. L. Garnett, L. J. Henderson, W. A. Sollich, and G. V. D. Tiers, *Tetrahedron Letters*, 516 (1961). [g] J. C. Schug and J. C. Deck, *J. Chem. Phys.*, **37**, 2618 (1962). [h] F. A. Bovey, F. P. Hood, III, E. Pier, and H. E. Weaver, *J. Am. Chem. Soc.*, **87**, 2060 (1965). [i] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "Nmr Spectra Catalog," Varian Associates, Palo Alto, Calif., 1962, p 192.

In the present work the spectra of a number of 4-substituted [2.2]paracyclophanes were examined in more detail along with those of the large number of disubstituted [2.2]paracyclophanes.[3] Table I records the chemical shifts of the aromatic protons of these substances. As noted previously,[3] electron-donating substituents (ethyl, methyl, hydroxy, methoxy, and acetoxy) cause their *ortho* protons to be shifted upfield, and electron-withdrawing substitutents (nitro, carbomethoxy, acetyl, and iodo) downfield. However, the spectra of many of the 4-substituted [2.2]paracyclophanes including the bromo, chloro, iodo, cyano, methyl, ethyl, hydroxy, acetoxy, and methoxy derivatives give a resonance for one proton downfield from the remainder of the aromatics, appearing as a doublet (J = 8 Hz) with further small splittings (1 to 2 Hz). This pattern is characteristic of a proton split by *ortho*, *meta*, and *para* protons, and therefore has been assigned to the proton directly transannular (pseudo-*gem*)[2] to the functional group. Figure 1 records the nmr spectra of 4-nitro- and 4-bromo[2.2]paracyclophane which illustrate these generalizations.

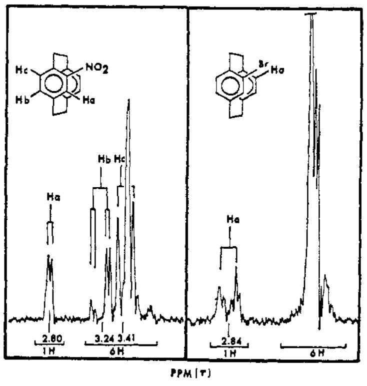
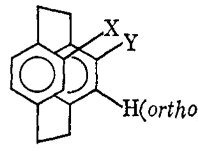
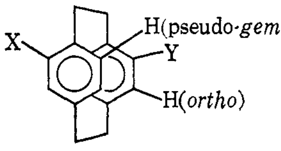


Figure 1. The aromatic region of the nmr spectra of 4-nitro[2.2]paracyclophane and 4-bromo[2.2]paracyclophane.

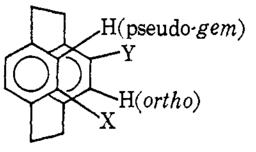
These observations serve as the basis for structura assignments to the disubstituted [2.2]paracyclophanes. Consider a disubstituted [2.2]paracyclophane containing one group Y that has a substantial pseudo-*gem* downfield shift. Chemical degradation[3c] or mass spectral (see future section) evidence indicates whether both functions are on the same or on different benzene rings. If the groups are on different rings, four isomers are possible, pseudo-*gem*, pseudo-*ortho*, pseudo-*meta*, and pseudo-*para*.[2] The spectrum of each isomer is unique. For the pseudo-*gem* isomer, no signal for a proton pseudo-*gem* to Y is observed. For the pseudo-*meta* isomer, the proton pseudo-*gem* to Y is split by its *ortho* and *para* protons, and appears as a doublet (J = 8 Hz). For the pseudo-*ortho* isomer, the proton pseudo-*gem* to Y is split only by its *meta* and *para* protons, and so appears as a broad singlet or close doublet. For the pseudo-*para* isomer, the pseudo-*gem* proton is split by its *meta* and *ortho* protons, and appears as a doublet of doublets (J_1 = 8 Hz, J_2 = 2 Hz). Figures 2 and 3 provide illustrations of assignments of structures based on nmr spectra.



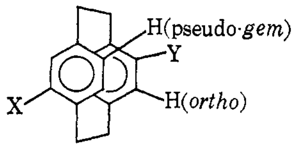
pseudo-*gem*



pseudo-*meta*



pseudo-*ortho*



pseudo-*para*

The assignment of the downfield doublet of doublets or broad doublet in a number of monosubstituted [2.2]paracyclophanes to the proton pseudo-*gem* to the substituent has been abundantly confirmed by the internal consistency of structural assignments made on

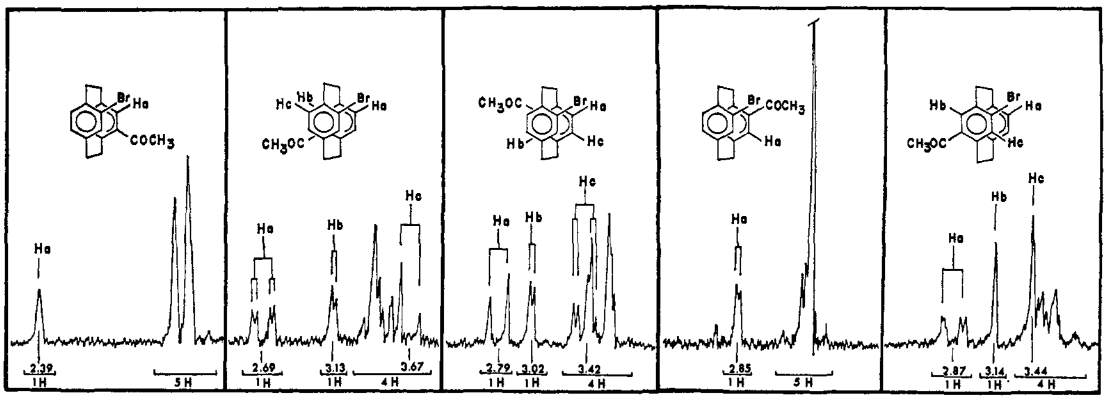


Figure 2. The aromatic regions of the nmr spectra of pseudo-*o*-, pseudo-*p*-, pseudo-*m*-, pseudo-*gem*-, and *p*-bromoacetyl[2.2]paracyclophanes.

this basis of a large number of disubstituted compounds. The validity of the method is established by the many thermal equilibrations of isomer pairs[3b] (pseudo-*gem* ⇄ pseudo-*meta* and pseudo-*ortho* ⇄ pseudo-*para*), the values of the equilibrium constants,[3b] the many functional group interconversions,[3a,c] and the correlations of structure with other physical properties (see future sections).

ortho **Chemical Shifts in [2.2]Paracyclophane (I) Derivatives.** The *ortho* shifts observed in [2.2]paracyclophane derivatives are qualitatively similar to those in benzene derivatives (Table II). The greatest difference is the considerably larger *ortho* shift and smaller *para* shift observed for electron-donating groups in the cyclic system compared to open-chain compounds. The difference between *ortho* and *para* protons in 4-methoxy[2.2]paracyclophane is 0.64 ppm, for the hydroxy derivative, approximately 0.7 ppm, and for the methyl derivative, approximately 0.2 ppm. The corresponding values for anisole, phenol, and toluene are 0.03, 0.09, and −0.01 ppm, respectively (Table II). The similar large *para* shifts in hindered phenols such as 2,6-dimethylphenol,[9] which has a *para* SCS (substituent chemical shift)[10] value of 0.41 ppm, and 2,4-dimethylphenol, which has a 0.1-ppm difference between *ortho* and *para* protons,[11] show that steric inhibition of resonance or insulation from "through space"[12] effects by the alkyl bridges in the [2.2]paracyclophanes is not responsible for the small *para* shifts.

The *ortho* and *para* shifts for benzenes substituted with electron-donating groups such as these follow the Hammett σp relation and are generally considered to arise from changes in the π-electron density of the ring positions due to resonance interactions with the substituent.[12-15] Likely, the small *para* shifts in the [2.2]paracyclophanes are a result of the distortion of the benzene rings[16] which would be expected to reduce resonance interaction with the *para* position. The chemical shifts of the *cis* hydrogen in vinyl derivatives are much larger than the corresponding *ortho* shifts in benzenes.[12] The larger *ortho* shifts in the paracyclophanes could then be a result of increased double bond character in the bent rings, possibly through contributions from resonance structures such as A. Such contributors to the hybrid of compound II appear favored because of the proximity of the bridgehead carbon atoms (2.78 Å),[16] although the X-ray crystal structure has not been refined to a point of revealing bond-length differences in the benzene rings.[16] Structure A also correlates some unusual infrared frequencies observed in [2.2]paracyclophanes (see below).

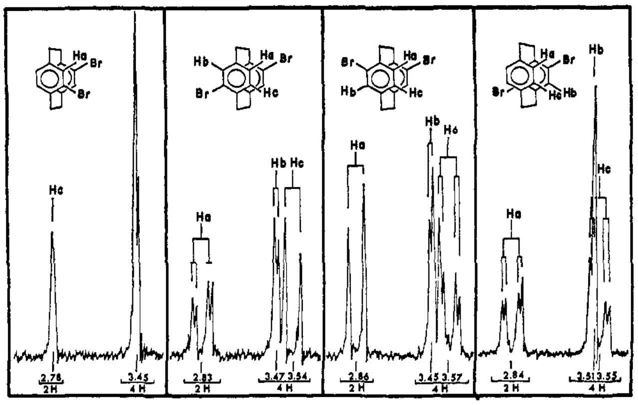
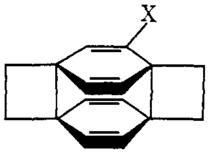


Figure 3. The aromatic region of the nmr spectra of the pseudo-*o*-, pseudo-*p*-, pseudo-*m*-, and *p*-dibromo[2.2]paracyclophanes.



A

The downfield *ortho* shifts for functional groups such as acetyl, carbomethoxy, and nitro have been suggested as arising from resonance interactions,[13,14] from field effects,[17] from the anisotropy of the magnetic susceptibility of the functional group,[18-20] and from

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[9] R. R. Fraser, *Can. J. Chem.*, **38**, 2226 (1960).

[10] M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.*, **88**, 3318 (1966).

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[12] W. B. Smith and J. L. Roark, *J. Am. Chem. Soc.*, **89**, 5618 (1967).

[13] Footnote *d* in Table II.

[14] J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, **39**, 1722 (1963).

[15] P. Diehl, *Helv. Chim. Acta*, **44**, 829 (1961).

[16] P. K. Gantzel and K. N. Trueblood, *Acta Cryst.*, **18**, 958 (1965); K. N. Trueblood, private communication.

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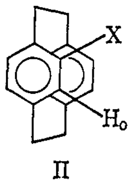
[19] P. R. Wells, *Australian J. Chem.*, **17**, 967 (1964).

[20] H. Conroy, *Advan. Org. Chem.*, **2**, 320 (1960).

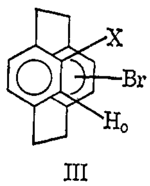
incipient hydrogen bonding between oxygen and the proton involved (Van der Waal's dispersion effect).[18,20,21] Support for the latter two is obtained from the considerably smaller *ortho* shifts observed in benzonitrile than in acetophenone, methyl benzoate, or nitrobenzene (Table II). The cyano group has resonance and inductive capabilities comparable to these groups. Diehl[15] has assigned the lower *ortho* shift of cyano to a shielding magnetic anisotropy effect.

Table III lists the SCS values of the *ortho* protons in nitro-, carbomethoxy-, acetyl-, and hydroxy-substituted [2.2]paracyclophanes resulting from introduction of bromine into various positions on the ring. The *ortho* SCS values in the pseudo-*meta* isomers are consistently more negative than in the pseudo-*para* isomers. It is of interest to note that transannular conjugative interactions such as are represented by canonical structure B for pseudo-*p*-bromoacetyl[2.2]paracyclophane predict a chemical-shift difference in this direction. The effect is small, however, and conformational or long-range magnetic interactions may be involved.

Table III. The Substituent Chemical Shift[a] (SCS) Values for *ortho* Protons in Bromo-X-[2.2]paracyclophanes (III)



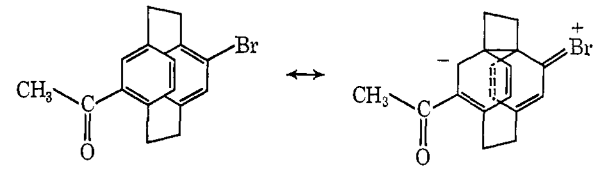
II



III

X	Structure Pseudo-*para*	 Pseudo-*meta*	 Pseudo-*ortho*	 Pseudo-*gem*	H_o in II (τ)
$COCH_3$	−0.01	−0.12	−0.75	−0.27	3.14
CO_2CH_3	+0.05	−0.06	−0.55	−0.20	2.86
NO_2	+0.01	−0.10	−0.64	−0.35	2.80
CN	+0.02	−0.10	−0.69		3.25
OH	−0.07	−0.08			4.52

[a] Defined as the substituent chemical-shift difference between H_o in II and III.



pseudo-*para* B

The chemical shift of the *ortho* proton in the pseudo-*ortho* isomers represents the sum of the pseudo-*gem* shift by bromo and the *ortho* shift by the X group. The SCS values in Table III for the pseudo-*ortho* isomers should then amount to the usual pseudo-*gem* shift of bromo (−0.8 ppm), since the *ortho*-X shift has been subtracted, assuming that the two interactions are additive.[14,15]

The introduction of two substituents on one side of the paracyclophane system as in the pseudo-*ortho* or pseudo-*gem* isomers would be expected to tilt the benzene rings apart on the substituted side. This would increase the bromo to pseudo-*gem* hydrogen distance in the pseudo-*ortho* isomer, and result in a smaller shift. A change in the ring current effect of one ring on the other would also be expected. The fact that in the pseudo-*ortho* isomer the *ortho* SCS values are smaller than expected, while in the pseudo-*gem* isomer the *ortho* shift is larger by 0.2 to 0.4 ppm than in the monosubstituted paracyclophanes, shows that this is not the predominant effect.

Conformational changes in the X group are not likely to be responsible for the smaller SCS value in the pseudo-*ortho* isomer, because the axially symmetric cyano compound also shows this effect. In the pseudo-*gem* isomer, however, the probable explanation involves an enforced coplanarity of X with the benzene ring due to the presence of the bromine. This results in closer proximity of the oxygen to the *ortho* hydrogen and greater resonance interaction with the ring, hence a larger *ortho* shift. In this connection the nmr spectrum of the presently unavailable pseudo-*gem*-bromocyano-[2.2]paracyclophane would be informative, since on the conformational argument this compound should show a normal *ortho* shift. The dependence of shifts of this type on the angle between the plane of the functional group and the plane of the aromatic system has been observed in other cases[19,22,23] (see also a different point of view[12]).

The Pseudo-*gem* Shift in Substituted [2.2]Paracyclophanes. The pseudo-*gem* shifts observed are summarized in Table IV. Groups such as nitro, carbomethoxy, and acetyl show no detectable pseudo-*gem* shift. For example, the protons pseudo-*gem* to the ester groups in pseudo-*p*-dicarbomethoxy[2.2]paracyclophane come at τ 3.33, 0.20 ppm downfield from the aromatic protons in [2.2]paracyclophane. This displacement is that expected for a *para* shift, and no influence of the pseudo-*gem*-carbomethoxy group is evident. The study on the magnetic anisotropy of the nitro group by Yamaguchi[22] would have indicated a small upfield pseudo-*gem* shift for the nitro group.

The shifts show no correlation with either resonance or inductive parameters of the groups and must therefore be the result of a through-space interaction which uniformly leads to downfield shifts.

In a study of methyl chemical shifts in keto-hydroxy-, chloro-, and cyanosteroids by Zürcher,[24] dispersion effects were considered insignificant at distances greater than 2.2 Å on the basis of rapid fall-off with distance and some chemical-shift considerations. Magnetic anisotropy effects needed to be considered only in correlation of shifts involving the keto group. The shifts observed for chloro-, hydroxy-, and cyano-substituted compounds could be adequately correlated using only dipole interactions. Inclusion of magnetic effects did not improve the calculated shifts. In aromatic systems, however, field effects are generally inadequate to account for the observed chemical shifts.[12,14] The largest shifts observed by Zürcher[24] were for 1,3-diaxial interactions, geometrically similar to the paracyclophane pseudo-*gem* interactions, suggesting that similar effects may be involved.

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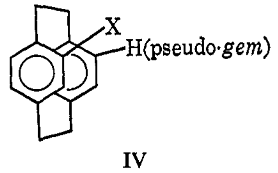
(21) G. O. Dudek, *Spectrochim. Acta*, **19**, 691 (1963).

(22) I. Yamaguchi, *Mol. Phys.*, **6**, 103 (1963).

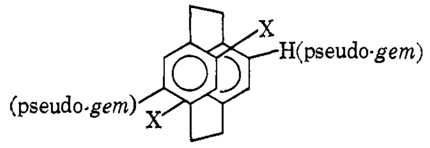
(23) R. W. Frank and M. A. Williamson, *J. Org. Chem.*, **31**, 2420 (1966).

(24) R. F. Zürcher, *Progr. Nucl. Magnetic Resonance Spectry.*, **2**, 205 (1967).

Table IV. The Substituent Chemical Shift (SCS) Values[a] for Pseudo-*gem* Protons in 4-Substituted [2.2]Paracyclophanes (IV) and Pseudo-*para*-disubstituted [2.2]Paracyclophanes (V)



IV

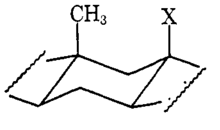


V

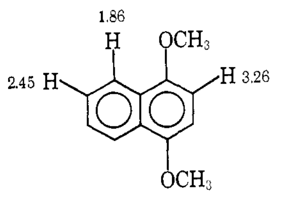
Compd	Cl	Br	I	OH	OCH_3	OAc	CH_3	CN	NO_2
IV[b]	−0.75	−0.80	−0.86	−0.60	−0.37		−0.35	−0.54	
V[b,c]	−0.65	−0.80			−0.02	−0.44	−0.29	−0.77	−0.53

[a] In parts per million. [b] Defined as the difference between the chemical shift of the pseudo-*gem* proton in IV or V and the aromatic resonance of [2.2]paracyclophane (τ 3.63). [c] Sum of *para* SCS and pseudo-*gem* SCS values.

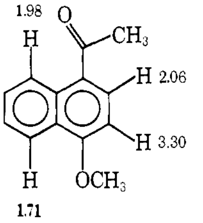
Comparison of the *peri* proton chemical shifts in VI, VII, and other compounds[21] with the chemical shifts in naphthalene itself ($H_1 = \tau$ 2.34, $H_2 = \tau$ 2.69)[25] reveals the presence of a substantial downfield *peri* shift, amounting to 0.5 ppm for methoxy, 0.4 ppm for hydroxy, and as high as 1.0 ppm for acetyl. Dudek[21] suggested that these shifts arise from hydrogen bonding (which is known to cause downfield shifts[26]) between the oxygen and the *peri* proton. The oxygen to hydrogen distance in VI is estimated at 2.4 Å, less than the distance in some hydrogen bonds. In the paracyclophane the pseudo-*gem* shift for methoxy (−0.36 ppm) is considerably smaller than for the hydroxy (−0.60 ppm), but steric requirements for particular conformations are drastically different for the two functions. The pseudo-*gem* and *peri* shifts in the two systems undoubtedly have a common origin.



X	SCS
Cl	−0.317
OH	−0.240
CN	−0.283



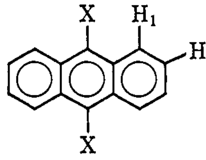
VI



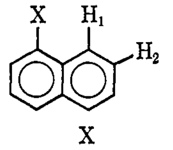
VII

The oxygen to pseudo-*gem*-hydrogen distance in 4-hydroxy[2.2]paracyclophane can be estimated at 2.9–3.0 Å if one assumes the same geometry as in [2.2]-paracyclophane,[16] and normal aromatic C–O (1.46 Å) and C–H (1.08 Å) bond lengths. The similarity in magnitude of the hydroxy *peri* and pseudo-*gem* shifts in spite of the greater distance in the paracyclophane would seem to argue against dispersion interactions being responsible for the effect, since these have a large dependence on distance.

Table V. The Substituent Chemical Shift (SCS) Values[a] for Protons *peri* to 9-Halogen-Substituted Anthracene (IX) and 1-Substituted Naphthalene (X)



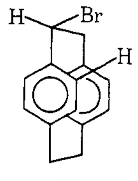
IX



	IX			X	
X	H_1	H_2	H_1-SCS	H_1	SCS
H	2.09	2.61[b]	0	2.34[b]	0
Cl	1.48	2.40[c]	−0.61		
Br	1.43	2.40[d]	−0.66	1.83[b]	−0.51

[a] In parts per million. [b] Reference 25. [c] Footnote *h* in Table II, p 618. [d] Footnote *h* in Table II, p 619.

Substantial *peri* shifts occur in 1-halonaphthalenes and 9-haloanthracenes as well. The data in Table V show that introduction of chlorine or bromine at the 9 and 10 positions in VIII results in a downfield shift of 0.6 ppm at the 1 position, but only 0.2 ppm at the 2 position. In the extensive study of bromonaphthalenes by Paviot and Hoarau[25] the marked *peri* shift of −0.5 ppm in 1-bromonaphthalene was assigned primarily to magnetic anisotropy effects, with a substantial contribution from the electric field effect. One of the aromatic protons in 1-bromo[2.2]paracyclophane (VIII) is shifted downfield from the remainder.[27] A similar interaction appears to be involved.



VIII

The pseudo-*gem* shifts for the halogens increase from chloro to iodo, as expected for a magnetic anisotropy or dispersion interaction. The differences are small considering the change in size and atomic number and probably reflect a blend of opposing effects.

The absence of lone pair or π electrons and substantial resonance or inductive capabilities in the methyl group renders the pseudo-*gem* shift observed in 4-methyl[2.2]paracyclophane (−0.35 ppm) and other alkyl derivatives somewhat more surprising than the observation of such shifts in the other functional groups of Table IV. This shift is much larger than the methyl *peri* shift in naphthalene (−0.05 to −0.10

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(25) J. Paviot and J. Hoarau, *J. Chim. Phys.*, 64, 1415 (1967).

(26) T. Schaefer, W. F. Reynolds, and T. Yonemoto, *Can. J. Chem.*, **41**, 2969 (1963).

(27) R. E. Singler and D. J. Cram, unpublished results.

Table VI. Useful Infrared Bands of Aromatic Ring-Substituted (X and Y) [2.2]Paracyclophanes[a]

Substituents X	Substituents Y	Band assign.	Band positions (cm^{-1}) for various isomers: Pseudo-*gem*	Pseudo-*ortho*	Pseudo-*para*	Pseudo-*meta*	*para*
Br	CH_3CO	C=O	1663	1666	1668	1666	1666
Br	CH_3CO	Br—Ar	1034	1036	1036	1035	1073
Br	CO_2CH_3	C=O	1705	1707	1707	1707	1707
Br	CO_2CH_3	C—O	1078	1079	1078	1079	1087
Br	CO_2CH_3	C—O	1271	1269	1269	1271	1267
Br	CO_2CH_3	Br—Ar	1036	1036	1035	1036	1099 (sh)
Br	NO_2	NO_2	1520	1517	1517	1515	1511
Br	NO_2	NO_2	1323	1342	1342	1342	1339
Br	NO_2	Br—Ar	1036	1037	1035	1036	1088

[a] Taken in chloroform solutions on a Beckman IR-5 spectrophotometer, except for the carbonyl frequencies of the acetyl and carbomethoxy derivatives, which were taken on a Perkin-Elmer 421 ir spectrophotometer.

ppm[28]) and the 1,3-diaxial methyl shifts[29] which have been observed in certain cyclohexane derivatives.

Groups such as CH_2Cl, CH_2Br, CH_2I, CH_2OH, and CH_2OCH_3 substituted in the 4 position of [2.2]paracyclophane cause only small pseudo-*gem* shifts (~ -0.2 ppm). Evidently the substituent of the methyl group has a pronounced effect on the pseudo-*gem* shift. Similarly, methoxy has a much smaller pseudo-*gem* shift than hydroxy.

In summary, many analogies to the [2.2]paracyclophane pseudo-*gem* shifts are known, but the origin of these shifts is not understood, and they do not seem to have been considered as a group in previous studies of chemical shifts in crowded molecules. Evidently, the *peri*, 1,3-diaxial, pseudo-*gem*, and related types of steric interactions result in downfield shifts for many groups, and their origin probably lies in a combination of effects.

Coupling Constants of Aromatic Protons in Substituted [2.2]Paracyclophanes. The *ortho* coupling in substituted [2.2]paracyclophanes generally amounts to 7.7 to 7.9 Hz, essentially identical with the coupling in *p*-xylene (8.0 Hz)[30] or benzene (7.7 Hz).[31] Couplings of 1.8 to 1.9 Hz with *meta* protons are observed. The peak width of proton resonances coupled only to *para* protons (and, possibly, to the bridge protons) is 1.3 to 1.5 Hz, indicating the presence of small additional splitting.

The Bridge Protons in the [2.2]Paracyclophanes. The side chain protons of [2.2]paracyclophane appear at τ 6.95,[5a] and substituted [2.2]paracyclophanes generally give a complex multiplet from τ 6.3 to 7.5. Carbomethoxy-, acetyl-, or nitro-substituted [2.2]paracyclophanes generally appear to have the signal for one proton in the bridge shifted downfield to τ 6 and as low as τ 5.6 for the pseudo-*gem* isomers. This shift is another example of the influence of a nearby carbonyl group on the shielding of protons, as in the *ortho* and *peri* shifts discussed previously.

The pattern of the side chain protons can give structural information in certain cases. For example, in pseudo-*m*-dibromo[2.2]paracyclophane, each of the bridges should form a symmetric A_2B_2 pattern. The spectrum clearly shows two superimposed symmetric multiplets centered at τ 6.83 and 7.06, confirming the structural assignment made on the basis of the aromatic absorption pattern. The pseudo-*gem*- and *meta*-disubstituted [2.2]paracyclophanes should also give a pattern such as this for the bridge protons. The structures of the four heteroannular dinitro[2.2]paracyclophanes were assigned using the symmetry properties of the bridge proton resonances.[3c] The complete analysis of the coupling constants and chemical shifts of the side-chain protons in 1-bromo[2.2]paracyclophane (VIII) has been reported.[32]

The Infrared Spectra of Substituted [2.2]Paracyclophanes

The potentiality of infrared spectroscopy for structure determination of aromatic systems has been widely exploited. Because of the extreme utility of the nmr spectra for structure determination in the [2.2]paracyclophane system, infrared spectroscopy was not explored to the fullest extent possible.

Acetyl[2.2]paracyclophanes. The carbonyl frequency in 4-acetyl[2.2]paracyclophane appears at 1666 cm^{-1}. The frequencies for the bromoacetyl compounds (see Table VI) fall in the region 1666–1668 cm^{-1}, except for the pseudo-*gem* isomer, which appears at 1663 cm^{-1}. This slight lowering may be due to direct interaction between the bromine and carbonyl groups. Carbonyl frequency decreases have been observed for interaction of nitrogen and carbonyl groups across intramolecular space in steroids and eight- and nine-membered rings.[33a] The effect could also result from increased conjugation with the benzene ring because of the greater coplanarity due to the presence of the pseudo-*gem* substituent (acetomesitylene absorbs at 1701 cm^{-1}, acetophenone at 1692 cm^{-1}[33b]).

The carbonyl frequency for the acetyl derivatives falls below the range for normal aryl ketones (1680 to 1700 cm^{-1}[33b]). This result is again an indication of the semiaromatic character of the [2.2]paracyclophane system (α,β-unsaturated ketones absorb at 1665 to 1685 cm^{-1}[33b]), and suggests that structures such as A contribute to the resonance hybrid.

Carbomethoxy[2.2]paracyclophanes. The infrared spectra of the esters exhibit the same lowering of the carbonyl frequency as do the ketones. The absorption for 4-carbomethoxy[2.2]paracyclophane and the bromo-substituted esters is at 1707 cm^{-1}, whereas ordinary

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(28) (a) P. R. Wells and P. G. E. Alcorn, *Australian J. Chem.*, 16, 1108 (1963); (b) C. MacLean and E. L. Mackor, *Mol. Phys.*, 3, 223 (1960).

(29) E. L. Eliel, M. H. Gianni, T. H. Williams, and J. B. Stothers, *Tetrahedron Letters*, 741 (1962).

(30) A. D. Cohen, N. Sheppard, and J. J. Turner, *Proc. Chem. Soc.*, 118 (1958).

(31) W. B. Smith, W. H. Watson, and S. Chiranjeevi, *J. Am. Chem. Soc.*, **89**, 1438 (1967).

(32) E. B. Whipple and Y. Chiang, *J. Chem. Phys.*, **40**, 713 (1964).

(33) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1958: (a) p 149; (b) p 132; (c) p 178; (d) p 297; (e) p 264; (f) p 328; (g) p 81.

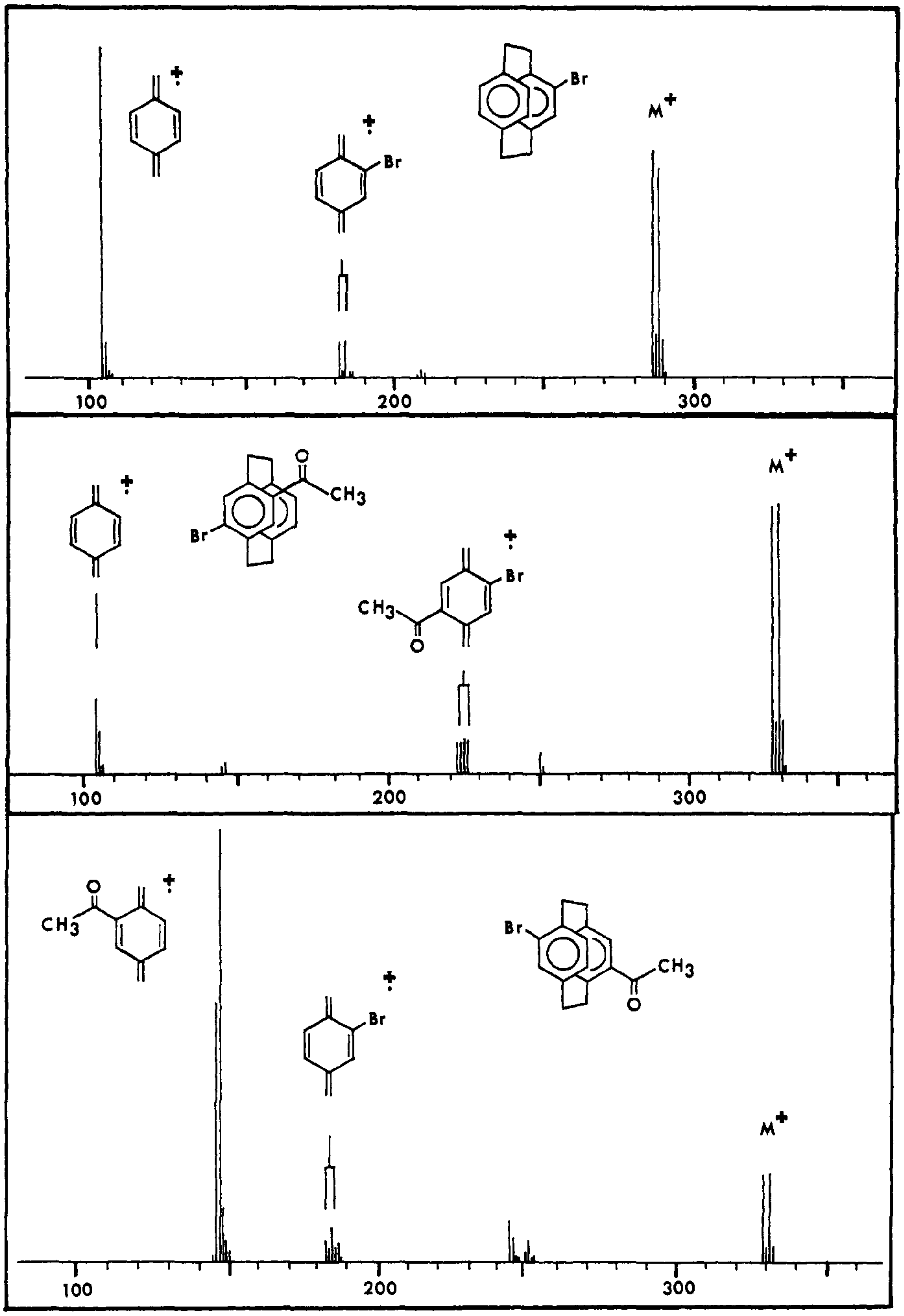


Figure 4. Mass spectra at 12 eV of 4-bromo[2.2]paracyclophane (top), *p*-bromoacetyl[2.2]paracyclophane (middle), and pseudo-*p*-bromoacetyl[2.2]paracyclophane (bottom) taken on an AEI Model MS-9 instrument.

aryl esters absorb at 1717–1730 cm^{-1}.[33c] No significant lowering of the carbonyl frequency of pseudo-*gem*-bromocarbomethoxy[2.2]paracyclophane could be detected.

The single bond C–O stretch absorptions come in a region where there are many other bands, but the strongest bands from 1000 to 1400 cm^{-1} can usually be assigned to this vibration.[33c] On this basis the two C–O frequencies come at approximately 1080 and 1270 cm^{-1} (see Table VI) in the paracyclophane esters. Bellamy quotes the ranges 1250–1300 cm^{-1} and 1100–1150 cm^{-1} for benzoates.[33c]

Nitro[2.2]paracyclophanes. The nitro valence vibrations in the nitro[2.2]paracyclophanes (see Table VI) are again somewhat lower than is usual for aromatic compounds. Thus, the frequencies for these cycles (1340 and 1515 cm^{-1}) are closer to the values for dialkylnitroethylenes (1346 and 1515 cm^{-1} [33d]) than to the aromatic nitro absorptions (1360 and 1530 cm^{-1} [33d]).

Cyano[2.2]paracyclophanes. The nitriles which have been obtained during the present study all have C≡N absorption at 2225 cm^{-1}, as expected for conjugated nitriles (2221 to 2240 cm^{-1} [33e]).

Halogenated[2.2]paracyclophanes. The strongest absorption in the infrared spectrum of 4-bromo[2.2]paracyclophane (other than possibly the C–Br stretch at 500 to 600 cm^{-1} [33f] which was not examined) and of the pseudo-*p*-, pseudo-*m*-, and pseudo-*o*-dibromides

Table VII. Melting Points[a] and Polarities (R_f Values on Thin Layer Chromatography) of Aromatic Ring Disubstituted (X and Y) [2.2]Paracyclophanes

	Substituents		Isomer				
Physical property	X	Y	Pseudo-*gem*	Pseudo-*ortho*	Pseudo-*para*	Pseudo-*meta*	*para*
Mp (°C)	Br	CH_3CO	182	144	170	86	123
R_f (tlc)[b]	Br	CH_3CO	0.30	0.46	0.34	0.35	0.36
Mp (°C)	Br	CO_2CH_3	160	74	160	93	157
Mp (°C)	Br	NO_2	236	224	216	119	172
R_f (tlc)[b]	Br	NO_2	0.29	0.34	0.55	0.53	0.56
Mp (°C)	NO_2	NO_2	268	246	250	200	
R_f (tlc)[c]	NO_2	NO_2	0.33	0.39	0.64	0.60	
R_f (tlc)[d]	NO_2	NO_2	0.17	0.23	0.69	0.57	
Mp (°C)	Br	Br		207	251	123	197
Mp (°C)	Br	CN		182	221	126	
R_f (tlc)[b]	Br	CN		0.35	0.48	0.49	

[a] Uncorrected. [b] Thin layer chromatography on silica gel G with 15% ethyl acetate–cyclohexane as developer. [c] Thin layer chromatography on silica gel G using 50% ethyl acetate–cyclohexane as developer. [d] Thin layer chromatography on alumina G using 15% ethyl acetate–cyclohexane.

appears at 1036 cm^{-1}. In the *p*-dibromide this absorption is shifted to 1049 cm^{-1}, and was used for detection and crude estimation of this isomer in mixtures.[3c]

Examination of a series of brominated [2.2]paracyclophanes revealed that the absorption at 1036 ± 2 cm^{-1} was characteristic of compounds having one ring substituted with one bromine. No exception to this generalization has been observed. In the monosubstituted [2.2]paracyclophanes other than chloro, bromo- and iodo, the absorption was absent, and in the *p*-bromoacetyl and bromonitro[2.2]paracyclophanes it was shifted to 1073 and 1088 cm^{-1}, respectively. The *p*-bromocarbomethoxy[2.2]paracyclophane had strong C–O absorption at 1087 cm^{-1}, and this absorption appeared to overlap with the Br–Ar absorption (shoulder at 1099 cm^{-1}). The pseudo-*o*- and pseudo-*p*-dicyano[2.2]paracyclophanes had no strong absorptions from 1000 to 1100 cm^{-1}. In 4-chloro[2.2]paracyclophane and pseudo-*p*-dichloro[2.2]paracyclophane the corresponding vibration appeared at 1046 cm^{-1}, whereas in 4-iodo[2.2]paracyclophane strong absorption at 1029 cm^{-1} was evident.

The origin of this halogen–ring vibration is not known. It appears in 2,5-dimethylbromobenzene (1042 cm^{-1}). The aromatic C–H in-plane deformation modes appearing in this region are usually weak, and a number of bands are present.[33g] In the halogenated [2.2]-paracyclophanes only one medium or strong band is observed. This characteristic frequency (termed "Br–Ar" in Table VI) proved extremely useful in the present work,[3a,c] especially during the dibromination study,[3c] since it provided a convenient method of analysis for compounds not differing appreciably in polarity, nmr spectrum, or solubility.

The Mass Spectra of Substituted [2.2]Paracyclophanes

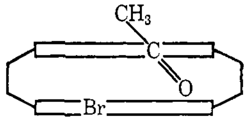
The mass spectra of [2.2]paracyclophanes at low ionizing voltages (12 eV) show predominant fragmentation to substituted *p*-xylylene (or methylenetropylium) ion radicals. The mass spectrum thus provides a convenient analytical tool for the determination of the number of substituents (including deuterium[3a]) on each ring. Figure 4 gives three examples of the fragmentation patterns of substituted [2.2]paracyclophanes.

Correlation between Structure and Other Physical Properties of the [2.2]Paracyclophanes

The normal correspondence between high symmetry and stable crystal structure is clearly evident in the substituted [2.2]paracyclophanes. The parent hydrocarbon is highly symmetric, and is extremely insoluble (mp 286°), whereas the monosubstituted compounds are generally lower melting and quite soluble, since all elements of symmetry have been destroyed. The introduction of two identical substituents can give seven isomeric compounds, four of which are *meso* (*ortho*, *meta*, pseudo-*gem*, and pseudo-*para*) and three are racemates (*para*, pseudo-*ortho*, and pseudo-*meta*). Only a limited number of such disubstituted compounds are known, but the pseudo-*para* isomer is always extremely insoluble and high melting.

When the two substituents are different, all elements of symmetry are lost, but the physical properties still correlate somewhat with the "quasi-symmetry" present by considering the two groups to be the same. Thus, the compounds which are quasi-*meso* (pseudo-*para* and pseudo-*gem*) are invariably the least soluble and usually the highest melting of the isomers. The pseudo-*meta* isomers are always low melting and soluble but are usually highly crystalline, whereas the pseudo-*ortho* isomers provide poorly defined crystals, and vary widely in their melting point behavior (see Table VII).

During column or thin layer chromatography (tlc) the pseudo-*gem* isomer is consistently more polar than the other known isomers (see Table VII). The pseudo-*para* and pseudo-*meta* isomers are always inseparable by chromatography but usually have a sufficient solubility difference to allow reasonably complete separation on this basis. The pseudo-*ortho* isomers are generally more polar than the pseudo-*para* isomers, as expected, since they should have a higher dipole moment. The only exception encountered was pseudo-*o*-bromoacetyl-[2.2]paracyclophane, which proved considerably less polar than the other isomers. It is believed that this arises from a specific conformational effect where the smaller carbonyl group, which is forced below the plane of the ring by repulsion between the methyl group and the nearby *ortho* and bridge hydrogens, is protected from polar sites on the chromatographic support by the large bromine atom (conformation C).



C

The pseudo-*gem*-bromoacetyl- and -bromocarbomethoxy[2.2]paracyclophanes have longer retention times on vapor phase chromatography (vpc) as well. The separation is sufficient to allow reasonably accurate analysis of mixtures of these with other isomers.[3a] Thermal isomerization occurs during vpc analysis of paracyclophanes even at the lowest temperatures and retention times accessible, resulting in some loss of accuracy. Under the minimum conditions where the pseudo - *gem* - bromocarbomethoxy[2.2]paracyclophane could be separated from the other isomers, approximately 1.5% isomerization occurred.

Experimental Section

General. All of the compounds employed in this investigation have been previously prepared except 4-iodo[2.2]paracyclophane, and were brought to analytical purity for the physical measurements (see Table I for references to their preparation). The instruments employed are referred to in the footnotes of the appropriate tables or in the legends of the figures. Thin-layer chromatograms were run on Brinkmann silica gel G or alumina G coated on glass or Pyrex plates with ethyl acetate–cyclohexane as developer. Iodine vapor was used to spot the plates.

4-Iodo[2.2]paracyclophane. A modified procedure[34] (recorded here) was used for preparation of 4-bromo[2.2]paracyclophane which served as starting material for the iodo derivative. A mixture of 53.3 g (0.256 mol) of [2.2]paracyclophane, 42.3 g (0.264 mol) of bromine, 0.3 g of iron filings, 400 ml of carbon tetrachloride, and 1200 ml of dichloromethane was stirred at 25° for 2 hr. The crude product isolated by the usual procedure was chromatographed on 600 g of alumina with 10% ether–pentane as eluent. Crystallization of the product from ether gave 55 g of 4-bromo[2.2]paracyclophane, mp 136–138° (lit.[35] 132–134°). Sublimation of the residues provided an additional 5.5 g of material, total yield 82%. This material contained trace amounts of dibrominated material (vpc analysis) which could be removed by recrystallization from dichloromethane.

This bromo derivative was converted to 4-iodo[2.2]paracyclophane as follows. A solution of 0.5 g of bromo compound (1.74 mmol) and 3.2 mmol of *n*-butyllithium (2.0 ml of 1.6 *M* hexane solution) in 10 ml of ether was stirred under nitrogen for 1.5 hr. To this mixture was added a solution of 0.81 g of iodine (3.3 mmol) in 10 ml of ether. Only about half of this solution was used before the reaction mixture became clear and the brown iodine color persisted. The reaction mixture was worked up by adding water, and washing with 10% sodium bisulfite solution and saturated sodium chloride solution. The vpc of the crude product showed the presence of only [2.2]paracyclophane and the iodo compound. Chromatography of this material on 60 g of alumina with pentane as eluent gave a small amount of hydrocarbon material (possibly 4-butyl[2.2]paracyclophane) followed by 4-iodo[2.2]paracyclophane. The crude material was difficult to purify; crystallization from dichloromethane gave 90 mg of 4-iodo[2.2]paracyclophane, mp 144–146°, further recrystallization of which gave 146.5–148.5°. *Anal.* Calcd for $C_{16}H_{15}I$: C, 57.50; H, 4.52. Found: C, 57.65; H, 4.45.

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(34) Footnote *e* of Table I.

(35) Y. L. Yeh, U. S. Patent 3,155,172 (1962).