Layered Compounds. XVI.[1] NMR Spectra of Multilayered [2.2]Paracyclophanes

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The NMR spectra of multilayered [2.2]paracyclophanes (I—XVI), in which benzene rings are closely stacked, have been examined. The assignment of the signals was made not only by integral strength, but also by solvent effect and the Nuclear Overhauser effect. The steric compression effect of transannular methyl groups on aromatic protons was observed in methylated cyclophanes. Enhanced ortho substitution shift was also observed. All the aromatic protons shift to remarkably higher field due to the anisotropy of stacked benzene rings as the number of layers increases. The shielding effect caused by these rings was empirically estimated.

In the NMR spectra of a series of [*m.n*]paracyclophanes, the aromatic protons appear at higher field beyond the usually accepted range of alkylbenzenes with decreasing number of methylenes in the bridges, *m* and *n*.[2] The upfield shift was considered to be ascribed to the anisotropy effect of one benzene ring on the aromatic protons of the other ring, and to the rehybridization effect of benzene carbon atoms due to ring deformation. By comparing the aromatic protons of [*m*]paracyclophanes ($m=7$—10)[3—5] with those of their open chain model compounds, the former effect is considered to be mainly responsible for the upfield shift, the latter effect being regarded as minor. Janusene,[6] [2.2]metacyclophane,[7] and [13]helicene,[8] in which aromatic rings are constructed parallel to overlap each other, also exhibit such an upfield shift of aromatic protons due to anisotropy of other aromatic rings.

According to X-ray crystallographic analyses,[9,10] both [2.2]paracyclophane and quadruple-layered [2.2]paracyclophane are of rigidly fixed structures with benzene rings fully superposed. We thus anticipated that the aromatic protons of multilayered [2.2]-paracyclophanes, consisting of two or more of [2.2]-paracyclophane system, would be affected by the anisotropy of more remote benzene rings besides the neighboring rings and that these cyclophanes would be appropriate model compounds for the study of magnetic anisotropy. The present paper reports a study on chemical shifts of aromatic protons in a series of multilayered [2.2]paracyclophanes (I—XVI), synthesis of which was described in the preceding paper.[1]

Results and Discussion

Assignment of Aromatic Protons. The NMR spectra of layered cyclophanes (I—XVI) are summarized in Table 1. Except for I, III, and IV, most of them show a few signals of aromatic protons depending upon magnetic environment. The signals are mostly assigned to the corresponding protons with the aid of integral strengths. However, there are some compounds with more than two layers, whose aromatic protons are difficult to assign by their integral strengths alone, *e.g.*, VI (Hb and Hc), XI, and XIV (Hb—He). In these cases, the solvent effect was found to be fairly

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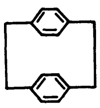

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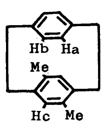

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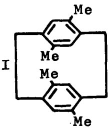

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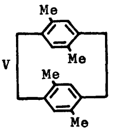

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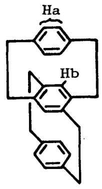

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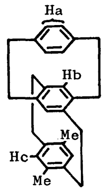

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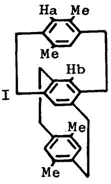

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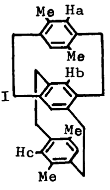

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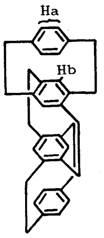

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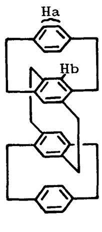

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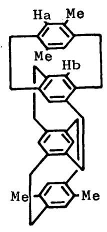

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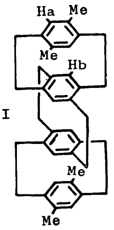

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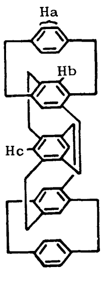

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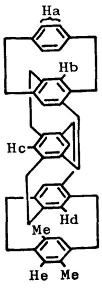

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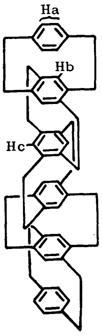

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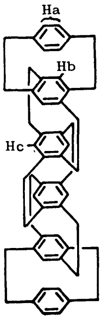

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Table 1. NMR spectra of layered compounds (τ value)

Compound		Aromatic proton		$\Delta\tau$[a]	Benzylic proton		Methyl proton	
		$\mathrm{CCl_4}$	$\mathrm{CDCl_3}$		$\mathrm{CCl_4}$	$\mathrm{CDCl_3}$	$\mathrm{CCl_4}$	$\mathrm{CDCl_3}$
p-Xylene		3.05(s)	2.94(s)	0.11			7.72(s)	7.69(s)
Durene		3.26(s)	3.10(s)	0.16			7.88(s)	7.85(s)
I		3.65(s)	3.53(s)	0.12	6.99(s)	6.94(s)		
II	Ha (2H)	3.32(A_2B_2)	3.22(A_2B_2)	0.10	6.5—7.7(m)		7.95(s)	7.90(s)
	Hb (2H)	3.74(A_2B_2)	3.64(A_2B_2)	0.10				
	Hc (2H)	4.12(s)	4.00(s)	0.12				
III		3.75(s)	3.64(s)	0.11	6.8—7.6(A_2B_2)		8.04(s)	7.98(s)
IV		3.93(s)	3.81(s)	0.12	6.5—7.4(A_2B_2)		7.85(s)	7.78(s)
V	out. Ha (8H)	3.92(s)	3.81(s)	0.11	6.8—7.7(m)			
	inn. Hb (2H)	4.65(s)	4.60(s)	0.05				
VI	out. Ha (4H)	3.88(s)	3.77(s)	0.11	6.8—7.8(m)		8.17(s)	8.11(s)
	inn. Hb (2H)	4.30(s)	4.25(s)	0.05				
	out. Hc (2H)	4.36(s)		0.11				
VII	out. Ha (4H)	4.33(s)	4.21(s)	0.12	6.7—7.7(m)		8.11(s)	8.07(s)
	inn. Hb (2H)	3.94(s)	3.88(s)	0.06				
VIII	out. (2H)	4.33(bs)	4.17(s)	0.16	6.7—7.8(m)		8.13(s)	8.10(s)
	Ha or Hc (2H)		4.21(s)	0.12				
	inn. Hb (2H)		4.28(s)	0.05				
IX	out. Ha (8H)	4.02(s)	3.91(s)	0.11	6.7—7.9(m)			
	inn. Hb (4H)	4.88(s)	4.85(s)	0.03				
X	out. Ha (8H)	4.02(s)	3.88(s)	0.14	6.9—7.9(m)			
	inn. Hb (4H)	4.90(s)	4.87(s)	0.03				
XI	out. Ha (4H)	4.43(s)	4.31(s)	0.12	6.8—8.1(m)		8.19(s)	8.16(s)
	inn. Hb (4H)	4.53(s)	4.48(s)	0.05				
XII	out. Ha (4H)	4.45(s)	4.32(s)	0.13	6.8—8.1(m)		8.20(s)	8.16(s)
	inn. Hb (4H)	4.52(s)	4.48(s)	0.04				
XIII	out. Ha (8H)	4.04(s)	3.93(s)	0.11	6.8—8.0(m)			
	inn. Hb (4H)	4.97(s)	4.93(s)	0.04				
	inn. Hc (2H)	5.12(bs)	5.08(bs)	0.04				
XIV	out. Ha (4H)	4.04(s)	3.91(s)	0.13	6.9—8.1(m)		8.24(s)	8.19(s)
	inn. Hb (2H)	4.96(s)	4.91(s)	0.05				
	inn. Hc (2H)	5.08(s)	5.05(s)	0.03				
	inn. Hd (2H)	4.64(s)	4.60(s)	0.04				
	out. He (2H)	4.47(s)	4.35(s)	0.12				
XV	out. Ha (8H)	4.06(s)	3.95(s)	0.11	7.1—8.3(m)			
	inn. Hb (4H)	5.00(s)	4.96(s)	0.04				
	inn. Hc (4H)	5.20(s)	5.17(s)	0.03				
XVI	out. Ha (8H)		3.95(s)		6.9—8.2(m)			
	inn. Hb (4H)		4.95(s)					
	inn. Hc (4H)		5.19(s)					

a) $\Delta\tau=\tau(\mathrm{CCl_4})-\tau(\mathrm{CDCl_3})$

effective for assignment of the protons. Thus, it was anticipated that the aromatic protons of outer benzene rings (outer ArH) would be strongly affected by solvent, while those of inner benzene rings (inner ArH) would not be influenced so much since they are closely sandwiched between the upper and lower benzene rings. The signals for aromatic protons of single- and double-layered compounds and for outer ArH of more than two layered ones (Table 1) display somewhat larger differences (0.10—0.16 ppm) between chemical shifts in carbon tetrachloride and in deuteriochloroform, while those for inner ArH give smaller differences (0.03—0.06 ppm). On the basis of such a solvent effect, assignments can be made for Hb (inner ArH) and Hc (outer ArH) of VI, and Ha (outer ArH) and Hb (inner ArH) of XI and XII. Dimethyl fivelayered compound XIV shows an integral ratio 2 : 1 : 1 : 1 : 1 of five aromatic proton signals at τ 4.04 (Ha), 4.47 (He), 4.64 (Hd), 4.96 (Hb), 5.08 (Hc) in carbon tetrachloride, and the assignment of those protons seems to be difficult at first. However, Ha, Hb, and Hc can be determined by comparison with the corresponding ones of non-substituted compound XIII, which are easily assigned by the integral strengths. The remaining protons, Hd and He, are distinguished as inner ArH and outer ArH, respectively, on the ground of the solvent effect.

Nuclear Overhauser Effect (NOE). In the spectrum of compound II, the aromatic protons of non-methylated benzene ring appear nonequivalently as

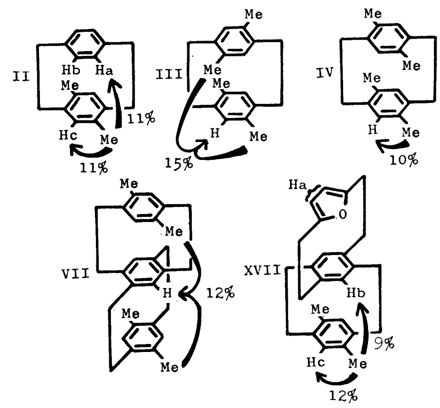
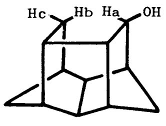


Fig. 1. Nuclear Overhauser effects of some layered cyclophanes in deuteriochloroform.

A_2B_2 pattern, possibly due to transannular proximity effect of methyl groups of the opposed benzene ring. Since NOE has successfully been used to assign such protons, we have attempted it on some layered compounds, whose aromatic protons could not be assigned by either the integral strength or the solvent effect. NOE was observed on the peaks at τ 3.22 and 4.00 and not for τ 3.64 peak of the compound II when methyl protons were irradiated in deuteriochloroform (Fig. 1). Since the peak at τ 4.00 is assigned to Hc proton from signal pattern, the peak at τ 3.22 is of the proton Ha at pseudo-gem position to methyl group and the remaining one at τ 3.64 of Hb at pseudo-ortho position.[11] The difference in the extent of NOE on aromatic protons of III and IV is related to the relative positions of the protons to methyl groups of opposed ring, that is, a larger value of the effect for compound III is attributable to both effects of pseudo-gem and ortho methyl groups.

The NOE caused by pseudo-gem methyl group was also observed on aromatic protons of triple-layered cyclophane VII and furanophane XVII. A value for the inner ArH of VII indicates an NOE depending upon efficient relaxation by the two methyl groups closely sandwiching the proton. On the other hand, the inner ArH of XVII exhibits a 9% area increase by irradiating the methyl group, and the protons which are unaffected by the saturation of methyl protons can easily be assigned to furan protons. In contrast to NOE on aromatic protons by saturation of methyl protons, the effect between aromatic protons was not detected on this series of compounds, *e.g.*, no change was observed in the areas of Ha and Hb when Hc of II was saturated. This seems to be well explained in terms of smaller interaction (dipole-dipole relaxation)[12] and longer transannular distances of H–H than those of CH_3–H.

Steric Compression Effect (CE). Hydrogen atoms which are significantly compressed with each other exhibit generally downfield shifts in NMR spectra.[13] This steric deshielding effect was found to be larger in more rigid compounds. Winstein reported unusually large deshielding effects (1—4 ppm) for the compounds with a half-cage structure related to the bird-cage hydrocarbons.[14] For example, the steric compression effect on Ha due to proximity of Hb in compound XVIII was seen to be in excess of 1 ppm. The effect has been observed also in layered cyclophanes containing proximate aromatic rings. Reich and Cram have described in NMR spectra of 4-substituted [2.2]-paracyclophanes that the protons pseudo-gem to the substituent displayed downfield shifts.[15] Similar steric compression effects of transannular methyl groups have been observed in the present multilayered [2.2]paracyclophanes. For example, obvious downfield shifts recognized by comparing the chemical shifts of Ha in dimethyl[2.2]paracyclophane (II) and of the aromatic protons in tetramethyl[2.2]paracyclophane (III) with those of the corresponding protons, to which pseudo-gem position is not substituted with methyl group. A similar deshielding of compressed protons is also observed for Hb of VI, VIII, XI, and XII and Hd of XIV (Table 1). An average value of these compression effects, σ_{CE} (pseudo-gem shift), of methyl groups, -0.36 ppm, is nearly equal to the value for 4-methyl-[2.2]paracyclophane given by Reich and Cram.[15] Of greater interest is a downfield shift of Hb in triplelayered compound VII, for the proton is a unique one sandwiched in between two methyl groups, that is, compressed from both upper and lower sides. They appear at lower field by twice (0.71 ppm) the above mean value for one methyl group. It is noteworthy that VII presents a novel example of steric compression on both sides and there is an additivity among steric compression shifts.



XVIII

Whether bridged methylene groups of multilayered [2.2]paracyclophanes exert a similar effect can be solved with non-methylated multilayered cyclophanes such as the tripled one V. Thus, two types of outer aromatic protons in V, namely pseudo-gem and pseudo-ortho to methylene group, should exhibit different chemical shifts, provided that the methylene group can exert steric compression effect on the protons in question. However, this is not the case actually. They appear as a singlet pattern to demonstrate equal magnetic environment. This result may be interpreted in terms of out-of-plane bending of the methylene groups toward the opposite side to the proton in question.

A steric compression effect between two methyl groups themselves was also found in tetramethyl[2.2]-paracyclophane (IV). All methyl groups are eclipsed with each other, and their pseudo-gem distances

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[11] Nomenclature of pseudo-gem and pseudo-ortho was taken according to D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 3505 (1969).

[12] R. A. Bell and J. K. Saunders, *Can. J. Chem.*, **48**, 1114 (1970).

[13] B. V. Cheney, *J. Amer. Chem. Soc.*, **90**, 5386 (1968), and literatures cited therein.

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[15] H. J. Reich and D. J. Cram, *ibid.*, **91**, 3534 (1969).

are expected to be maintained within van der Waals distance (4.0 Å) on the basis of X-ray crystallography of [2.2]paracyclophane.[9] Thus, a difference in the chemical shifts of methyl protons of III and IV, 0.19 ppm, is related to the mutual compression effect between two methyl groups.

Enhanced Ortho Substitution Shifts. Reich and Cram reported that introduction of a substituent into the benzene ring of [2.2]paracyclophane caused a considerably large ortho shift compared to the corresponding open chain compounds, and that the enhancement of ortho shift might be due to the increased double bond character at C_4–C_5 bond in the bent ring.[15] On the other hand, the ortho substitution shifts in [3.3]paracyclophane are close to the normal, since the benzene rings are distorted from their planar configuration only by 6.4° in contrast to 15° for [2.2]-paracyclophane.[16]

The enhanced ortho shift σ_{OE} is observed also in methylated layered cyclophanes (Table 1). Thus, ortho protons to methyl groups appear at higher field by an average 0.42 ppm than the corresponding protons of non-substituted cyclophanes, *e.g.*, outer protons n each pair of VII *vs.* V, XI *vs.* IX, and XIV *vs.* XIII. The value 0.21 ppm, obtained by substracting the difference between durene and *p*-xylene (0.21 ppm) from the above average value, is the enhanced ortho substituent effect of methyl group in the layered [2.2]-paracyclophane system. Only one exception is the ortho shift in IV, 0.28 ppm. It is probable that strong mutual repulsion between the methyl groups may hinder electron delocalization of the moiety containing the methyl and its ortho proton.

Magnetic Anisotropy. Table 1 also shows that all the aromatic and methylene protons are shifted to a remarkably higher field as the number of layers increases. The more prominent of these is the upfield shift of inner aromatic protons caused by magnetic anisotropy of both upper and lower benzene rings. It is anticipated that there may exist a certain regularity among the chemical shifts of the aromatic protons, since each benzene ring is stacked at regular intervals in this series of multilayered cyclophanes.[10] From a number of examinations of the spectral data, the shielding effects due to additionally stacked benzene rings were estimated empirically (Table 2). It can be seen that the additional effect becomes less effective as the additional benzene ring lies further away from the proton in question.

Table 2. Shielding effect of additional benzene ring (ppm)

	Empirical	Calculated[a]
σ_1 (neighboring ring)	0.69	0.417
σ_2 (next ring but one)	0.22	0.157
σ_3 (next ring but two)	0.10	0.057
σ_4 (next ring but three)	0.03	0.028
σ_5 (next ring but four)	0.02	0.014

a) Values were calculated according to Johnson-Bovey's method.

It is known that the aromatic protons of [7]- and [8]-paracyclophanes[3,4] and [8][8]paracyclophane[17] appear within conventional range for alkyl benzenes, though they are in different steric environments due to individual ring deformation. Thus, their ring deformations hardly affect the chemical shifts of their own aromatic protons. It is known from X-ray crystallography of quadruple-layered cyclophane XII that the outside ring is distorted in a boat shape, and the inside ring in a twist shape,[10] and the ring deformations are considered not to differ so much in magnitude from those in [*m*]- and [8][8]-paracyclophanes. We assumed that the magnetic anisotropies of outside and inside benzene rings in multilayered cyclophanes were equal in magnitude in spite of different ring distortion.

From Table 2, the chemical shift of a given aromatic proton can be calculated by adding shielding effects of additional benzene rings to the chemical shift of the aromatic proton in standard alkylbenzene, *p*-xylene (τ 3.05) or durene (τ 3.26). For example, a calculated value of Ha in XIII is τ 4.09 ($3.05+\sigma_1+\sigma_2+\sigma_3+\sigma_4$), for Hb τ 4.96 ($3.26+2\sigma_1+\sigma_2+\sigma_3$), and for Hc τ 5.08 ($3.26+2\sigma_1+2\sigma_2$). Such a treatment

Table 3. Additivity of chemical shifts for aromatic protons of layered cyclophanes (τ value)

Compound		Obsd	Calcd	Deviation
I		3.65	3.74	+0.09
II	Ha	3.32	3.38	+0.06
	Hb	3.74	3.74	0
	Hc	4.12	4.16	+0.04
III		3.75	3.80	+0.05
IV		3.93	3.95[a]	+0.02
V	out. Ha	3.92	3.96	+0.04
	inn. Hb	4.65	4.64	−0.01
VI	out. Ha	3.88	3.96	+0.08
	inn. Hb	4.30	4.28	−0.02
	out. Hc	4.36	4.38	+0.02
VII	out. Ha	4.33	4.38	+0.05
	inn. Hb	3.94	3.92	−0.02
IX	out. Ha	4.02	4.06	+0.04
	inn. Hb	4.88	4.86	−0.02
XI	out. Ha	4.43	4.48	+0.05
	inn. Hb	4.53	4.50	−0.03
XIII	out. Ha	4.04	4.09	+0.05
	inn. Hb	4.97	4.96	−0.01
	inn. Hc	5.12	5.08	−0.04
XIV	out. Ha	4.04	4.09	+0.05
	inn. Hb	4.96	4.96	0
	inn. Hc	5.08	5.08	0
	inn. Hd	4.64	4.60	−0.04
	out. He	4.47	4.51	+0.04
XV	out. Ha	4.06	4.11	+0.05
	inn. Hb	5.00	4.99	−0.01
	inn. Hc	5.20	5.18	−0.02

a) Not consider σ_{OE}

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[16] M. Sheehan and D. J. Cram, *J. Amer. Chem. Soc.*, **91**, 3544 (1969).

[17] M. Nakazaki, K. Yamamoto, and S. Tanaka, *Tetrahedron Lett.*, **1971**, 341.

is also applicable to the cases of methyl derivatives by considering the secondary effects of methyl group such as σ_{CE} and σ_{OE}. In the case of XIV, the calculated value for Ha, Hb, and Hc are the same as those of XIII, but for Hd τ 4.60 ($3.26+2\sigma_1+\sigma_2+\sigma_3+\sigma_{CE}$) and for He τ 4.51 ($3.26+\sigma_1+\sigma_2+\sigma_3+\sigma_4+\sigma_{OE}$). These calculated values are in excellent agreement with the observed ones (Table 3), supporting the view that the evaluation of each shielding magnitude is reasonable. However, we see a tendency of slightly positive deviation for outer protons and negative for inner protons. This may reflect the fact that in multilayered compounds, π-electron density is richer on the inner benzene ring than on the outer ring as a result of the transannular electronic interaction.

On the other hand, magnetic anisotropy of benzene ring was calculated by means of the ring current equation of Johnson and Bovey,[18] where 3.03 Å was used for the average distance between two adjacent benzene rings and 2.40 Å for the distance from the center of the benzene ring to its own ring proton. The calculated values thus obtained are not quite equal to the empirically evaluated ones, the former values being less by a factor of about 0.6, but both are in good correlation (Table 2). The results show that our data for shielding effect can be used satisfactorily to anticipate chemical shifts of similarly constructed compounds, and that for more exact evaluation of magnetic anisotropy of benzene ring, one must take into account not only ring current but also the secondary effects such as anisotropies of carbon-carbon and carbon-hydrogen σ-bonds.

Experimental

NMR spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer on dilute solutions (~10%) in carbon tetrachloride and/or deuteriochloroform using tetramethylsilane as an internal standard. The signals were measured by frequency counter with a precision of about ±1 cps. For NOE measurements a Varian HA-100 spectrometer was used. The effects were measured in degassed deuteriochloroform solution as area increase using the electronic integrator of the instrument. The errors are within ±5%.

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[18] C. E. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).