A ^{13}C Nuclear Magnetic Resonance Study of [*n*]Paracyclophanols: Chemical Shifts and Spin–Lattice Relaxation

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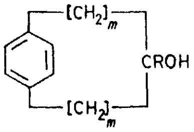
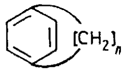
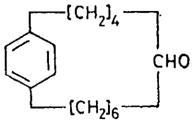
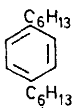
^{13}C Chemical shifts and ^{13}C spin–lattice relaxation times (T_1) of symmetric [9]—[15]paracyclophanols are observed in $CDCl_3$. Assignment of the aliphatic bridge carbons is performed by the use of $Eu(fod)_3$ and by assuming additivity of the usual substituent parameters. The aliphatic and aromatic carbon shifts are not sensitive to differences in the geometry of the carbon skeleton. The aromatic tertiary carbons are non-equivalent when internal rotation of the benzene ring is slow or inhibited. The T_1 data are explained in terms of conformational flexibility, intermolecular association, and internal rotation.

THE unusual geometry and the resulting strain in [*n*]paracyclophanes have been extensively investigated by means of u.v. spectroscopy,[1] *X*-ray diffraction,[2] and semiempirical calculations.[3] It is well known that ^{13}C chemical shifts sensitively reflect differences in geometry and conformation but reports of ^{13}C n.m.r. studies on cyclophanes are surprisingly few and are all concerned with elucidation of ring-current effects on ^{13}C chemical shifts.[4]









(1) *m* = 4, R = H
(2) *m* = 5, R = H
(3) *m* = 6, R = H
(4) *m* = 7, R = H
(7) *m* = 5, R = Me
(8) *m* = 7, R = Me

(5) *n* = 9
(6) *n* = 11

(9)

(10)

In the hope of elucidating geometrical and conformational effects on the ^{13}C chemical shifts in [*n*]paracyclophanes, we measured the ^{13}C n.m.r. spectra of the symmetrical [9]—[15]paracyclophanols (1)—(4) in $CDCl_3$. These compounds were selected because signals can be easily assigned with the help of a paramagnetic shift reagent and without needing to use deuteriated samples.[4d] Further, we have studied ^{13}C spin–lattice relaxation in compounds (1)—(4) to obtain information on internal rotation.

TABLE 1

^{13}C Chemical shifts (p.p.m. downfield from Me_4Si) of [*n*]paracyclophanols and related compounds in $CDCl_3$

	Aromatic carbon		Aliphatic carbon								
Compound	Quaternary	Tertiary	1	2	3	4	5	6	7	8	CH_2
(1)	140.0	129.8 129.4	35.4	29.7	21.3	36.5	71.6				
(2)	140.3	129.2 129.1	36.1	29.0	27.0	24.0	35.0	70.0			
(3)	139.6	128.6	35.1	29.6	26.1	27.4	23.6	35.9	69.4		
(4)	139.2	128.4	35.0	30.2	27.9	26.5	28.5	23.1	35.6	71.9	
(5)	139.4	128.9	35.3	29.3	23.3	28.0	26.1				
(6)	140.2	129.1	35.9	29.2	25.8	28.4	26.9	27.6			
(7)	140.0	129.1 129.0	36.7	29.0 [c]	28.6 [c]	25.0	40.5	72.6			29.0
(8)	139.4	128.6	35.4	30.3 [d]	28.2 [e]	27.0 [e]	29.3 [d]	22.6	40.5	72.9	28.7
(9) [a]	140.5 140.1	129.3 129.1 [b] 128.9									
(10)	139.8	128.1	35.6	31.6	29.1	31.8	22.6	14.0			

[a] Shows 11 signals with equal intensities in the aliphatic region. [b] Double-intensity signal. [c-e] Assignments may be reversed.

RESULTS AND DISCUSSION

Signal Assignments.—The ^{13}C chemical shifts of the compounds examined are presented in Table 1. The aromatic carbon signals were assigned by means of off-resonance partial decoupling and by taking account of the characteristic chemical shifts and spin–lattice relaxation times (T_1). Assignment of the aliphatic bridge carbons of compounds (1)—(4) was performed by the use of $Eu(fod)_3$. In this case, a pseudo-contact contribution to the induced shifts (L.I.S.) was assumed to be the dominant influence, as has been confirmed for several alkanols.[5] The observed L.I.S. values agreed with those calculated using the pseudo-contact term of

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[1] N. L. Allinger, L. A. Freiberg, R. B. Hermann, and M. A. Miller, *J. Amer. Chem. Soc.*, 1963, **85**, 1171.

[2] N. G. Newton, T. J. Walter, and N. L. Allinger, *J. Amer. Chem. Soc.*, 1973, **95**, 5652; N. L. Allinger, T. J. Walter, and N. G. Newton, *ibid.*, 1974, **96**, 4588.

[3] N. L. Allinger, J. T. Sprangue, and T. Liljefors, *J. Amer. Chem. Soc.*, 1974, **96**, 5100.

[4] (*a*) R. H. Levin and J. D. Roberts, *Tetrahedron Letters*, 1973, 135; (*b*) K. Sakamoto and M. Oki, *Chem. Letters*, 1976, 257; (*c*) T. Kaneda, T. Inoue, Y. Yasufuku, and S. Misumi, *Tetrahedron Letters*, 1975, 1543; (*d*) T. Kamata, T. Inoue, and S. Misumi, presented at the 8th Symposium on Structural Organic Chemistry, Kyoto, October 1975, No. 1A03.

[5] W. D. Horrocks and J. P. Sipe, *J. Amer. Chem. Soc.*, 1971, **93**, 6800; R. J. Cuchley, D. R. Anderson, and S. R. Lipsky, *J.C.S. Chem. Comm.*, 1972, 636.

McConnel and Robertson;[6] Table 2 summarizes the results for compound (1) as a typical example. The results thus obtained for compounds (1)—(4) were used to assign the bridge carbon signals of other cyclophanes by assuming additivity of the OH and CH_3 substituent parameters. The assignment obtained for [11]paracyclophane (5) was consistent with that based on selective decoupling of a deuteriated sample.[4d] As an additional aid for the assignment of the central bridge carbons the lower signal intensity was used. The methyl carbon assignment of compounds (7) and (8) was also confirmed from the off-resonance spectra. The hexyl carbon signals of the open-chain model (10) were assigned by taking account of the usual phenyl substituent effects and confirmed by the T_1 values which became larger on going towards the terminal methyl, a segmental motion,[7] as will be described later.

TABLE 2

Comparison between observed and predicted LIS values for compound (1)

Carbon		1	2	3	4	5	10,13	11,12 [c]	14,15
	δ	35.4	29.7	21.3	36.5	71.6	140.0	129.8	129.4
LIS	Obs.[a]	2.1	3.3	7.2	12.0	42.2	3.5	1.5	3.4
	Calc.[b]	0.2	1.3	7.2	13.8	41.1	3.4	1.7	3.9

[a] δ for a 1 : 1 mixture of compound (1) and $Eu(fod)_3$ minus δ for compound (1). [b] LIS = $K(3\cos^2\theta - 1)/r^3$, where θ and r for each carbon were obtained by direct measurement of Dreiding models for probable conformation previously described.[12] An O–Eu distance of 2 Å, a C–O–Eu angle of 142°, and an Eu–O–C–H dihedral angle of 125° were taken. [c] Carbons closer to the OH group in space (*e.g.* C_A in Scheme 1).

Aliphatic region. For all the paracyclophanols, carbons γ to the hydroxy group are most shielded (Table 1). In hydrocarbons (5) and (6), those γ to the benzene ring are most shielded, as previously pointed out for several [*n*]paracyclophanes and related compounds.[4d] These and the other carbon shifts may be explained mainly in terms of additivity of the usual substituent parameters.

TABLE 3

Substitutent effects on aliphatic carbon shieldings

Carbon	1	2	3	4	5	6
Substituent effects of the *p*-hexylphenyl group in compound (10)						
$\delta_{(10)} - \delta$ [a]	+21.7	+8.7	−2.9	−0.2	−0.3	+0.1
Substituent effects of the *p*-phenylene groups in hydrocarbons (5) and (6)						
$\delta_{(5)} - \delta_{CH_2}$ [b]	+8.3	+2.3	−3.7	+1.0	−0.9	
$\delta_{(6)} - \delta_{CH_2}$ [b]	+8.9	+2.2	−1.2	+1.4	−0.9	+0.6
Substituent effects of the hydroxy groups in cyclophanols (1) and (2)						
$\delta_{(1)} - \delta_{(5)}$	+0.1	+0.4	−2.0	+8.5	+45.5	
$\delta_{(2)} - \delta_{(6)}$	+0.3	−0.2	+1.2	−4.4	+8.1	+42.4

[a] δ for hexane taken from ref. 8, p. 56. [b] Average chemical shift, 27.0 (±1.0) p.p.m., for large cycloalkanes.[11]

Table 3 includes several comparisons between the observed chemical shifts. Evidently the *p*-hexylphenyl group in the open-chain model (10) has almost the same substituent parameters as those of the phenyl group itself.[8] The hydroxy substituent parameters in cyclophanols (1) and (2) are similar to those in the less strained cyclo-octanol [9] and cyclododecanol,[10,*] but the γ-effect in compound (1) is relatively small. It is also noticed that the γ-effect of the *p*-phenylene group in hydrocarbon (5) is −2.5 p.p.m. larger than in the larger hydrocarbon (6), suggesting a more eclipsed relationship between the benzene ring and the γ-carbons in compound (5).[3] In Table 1, all C(1) chemical shifts lie in the narrow range 35.0—36.1 p.p.m. with an intermediate value of 35.6 p.p.m. for the planar model (10) and do not reflect any deviation of the phenyl–C(1) bonds from planarity.[2,3] It thus appears that the bridge carbon chemical shifts are determined mainly by the usual substituent effects and are practically insensitive to the differences in geometries.

The lack of importance of ring-current effects in determining ^{13}C chemical shifts [4] is apparent from the fact that no linear correlation of chemical shift variation with ring size exists between the central bridge carbon, for which electronegativity and steric effects by the benzene ring are negligible, and the attached proton, as Table 4 shows. The carbon shift differences among compounds (1)—(4) are 2.5 p.p.m. or less, comparable with those in 13—17-membered cycloalkanes (2.0 p.p.m. or less),[11] and may thus be largely ascribed to differences in conformations.

TABLE 4

Chemical shifts for the central bridge carbons and attached protons

Compound	δ_C ($CDCl_3$) (p.p.m.)	δ_H (CCl_4)
(1)	71.6	2.70
(2)	70.0	2.80
(3)	69.4	3.00
(4)	71.9	3.40
(5)	26.1	0.33
(6)	27.6 [a]	0.68 [b]
(7)	72.6	
(8)	72.9	

[a] Lit.,[4d] 27.7 p.p.m. [b] Value in $CDCl_3$ taken from ref. 4*d*.

Aromatic region. Table 5 shows the differences in aromatic carbon shifts ($\Delta\delta$) between [*n*]paracyclophanes and the planar model (10) together with the angles of deformation of the benzene rings from planarity (θ). No apparent trend exists between $\Delta\delta$ and θ. The same is also true of cyclophanols (1)—(4). It thus appears that ring deformation is not an important factor in determining aromatic carbon shifts.

Cyclophanols (1), (2), and (7) show doublets with equal intensities due to the tertiary carbons, while the larger compounds (3), (4), and (8) show singlets (Table 1).

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[*] The α-, β-, and γ-carbon shifts of cyclododecanol are 44.3, 7.7, and −3.8 p.p.m. (in $CDCl_3$) from those of cyclododecane (24.9 p.p.m.).[11]

[6] H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, 1958, **29**, 1361.

[7] G. C. Levy, *Accounts Chem. Res.*, 1973, **6**, 161.

[8] J. B. Stothers, 'Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York, 1972, p. 97.

[9] J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *J. Amer. Chem. Soc.*, 1970, **92**, 1338.

[10] N. Mori and T. Takemura, unpublished data.

[11] J. J. Burke and P. C. Lauterbur, *J. Amer. Chem. Soc.*, 1964, **86**, 1870. Original data converted using δ_{CS_2} 192.8 p.p.m.

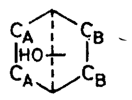
This phenomenon corresponds to the attached-proton case [12] and may be explained in terms of a through-space effect of the hydroxy group in connection with internal rotation of the benzene ring. In the smaller cyclophanols, the rotation of the benzene ring is slow on the n.m.r. time scale,[12] so the hydroxy group may stay, on a time average, above one side of the benzene ring to cause non-equivalence of the two carbon pairs, *e.g.* C_A and C_B in Scheme 1. In the larger cyclophanols, the environments of C_A and C_B are averaged by the fast rotation of the aryl ring,[12] so all the tertiary carbons experience equal magnitudes of the hydroxy effect and are thus equivalent.

TABLE 5

Ring deformation effects on aromatic carbon shifts in [*n*]paracyclophanes

n	Δδ (p.p.m.) [a] Quaternary carbon	Tertiary carbon	θ(°) [b]
9	−0.4	+0.8	15
10	(−0.5)	(+0.9)	5
11	+0.4 (+0.1)	+1.0 (+0.6)	5
12	(−0.2)	(+0.3)	5

[a] Δδ = δ of [*n*]paracyclophane minus δ of planar model (10), Values in parentheses were derived using data in ref. 4*d*. [b] Degree of ring bending from planarity.[1,12]



SCHEME 1

TABLE 6

Hydroxy effects on aromatic carbon shieldings

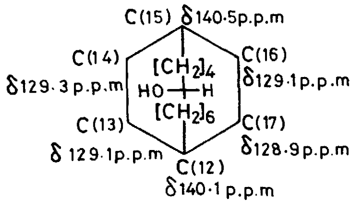
		Tertiary carbon	Quaternary carbon
$\Delta\delta_{A-B}$[a]	(1)	0.4 ± 0.0	0.0
	(2)	0.1 ± 0.0	0.0
	(7)	0.1 ± 0.0	0.0
$\Delta\delta_{(1)-(5)}$		0.9 ± 0.2(C_A) 0.5 ± 0.2(C_B)	0.6 ± 0.2
$\Delta\delta_{(2)-(6)}$		0.1 ± 0.2(C_A) 0.0 ± 0.2(C_B)	0.1 ± 0.2

[a] $\Delta\delta_{A-B}$ = δ_A for C_A minus δ_B for C_B.

In either case, the two quaternary carbons should be equivalent.

The hydroxy effect causes a downfield shift, because the aromatic carbons in cyclophanols (1) and (2) are deshielded compared with those in hydrocarbons (5) and (6) (Table 6). Further evidence is the result predicted from pseudo-contact considerations that C_A is deshielded compared with C_B (Table 2). This result is indicative of a spatial-distance dependence of the hydroxy effect, and this is also apparent from the fact that the shift differences between compounds (1) and (5) are larger than those between (2) and (6) (Table 6). The multiplet in the spectrum of the unsymmetrical cyclophanol (9) may be explained in terms of the distance dependence of the hydroxy effect. This compound shows two quaternary carbon and three tertiary carbon signals, the one at δ 129.1 p.p.m. having double intensity. Moreover, the aromatic protons give a multiplet suggesting slow rotation of the benzene ring.

An examination of models indicates that the hydroxy group is nearest to C(14) and furthest from C(17). Thus the assignments in Scheme 2 seem reasonable.



SCHEME 2

Judging from the number of C–C bonds intervening between the hydroxy group and the aromatic carbons, the hydroxy effect may be a through-space, but not a through-bond, effect. This should arise through intramolecular OH · · · π bonding,* magnetic anisotropy, steric proximity, or an electric field effect. The first factor is excluded because the OH · · · π bonding is present in compounds (1)—(3) but not in the others.[12] Moreover, the acetate of compound (1) in which the OH · · · π bonding is not expected shows ^{13}C and ^{1}H spectra [14] similar to those of compound (1). The electric

TABLE 7

^{13}C Spin–lattice relaxation values, T_1/s

Compound	Aromatic carbon Quaternary	Tertiary	Aliphatic carbon 1	2	3	4	5	6	7	8
(1)	9.0	2.6 [a] 2.1 [b]	1.1	1.3	1.3	1.5	1.4			
(2)	8.1	0.8 [c]	0.4	0.4	0.4	0.5	0.4	0.6		
(3)	6.0	0.7	0.3	0.3	0.5	0.5	0.3	0.4	0.6_5	
(4)	5.5	0.8	0.2_5	0.3	0.4	0.3	0.3	0.4	0.3	0.6_5
(5)	44.8	5.3	2.6	2.5	2.5	2.4	2.3			
(6)	12.6	1.6	0.9	1.0	1.0	1.1	1.2	1.6		
(10)	15.1	2.6	1.0	1.1	1.4	2.1	2.4	2.9		

[a] Value for carbon with shift 129.8 p.p.m. [b] Value for carbon with shift 129.4 p.p.m. [c] Average time for the carbons with shifts 129.1 and 129.2 p.p.m.

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* Cram *et al.* posited intramolecular OH · · · π bonding to explain the aromatic proton multiplet of [8]paracyclophan-4-ol.[13]

[12] N. Mori, T. Takemura, and T. Ohkuma, *Bull. Chem. Soc. Japan*, 1977, **50**, 179.

[13] D. J. Cram, C. S. Montgomery, and G. R. Knox, *J. Amer. Chem. Soc.*, 1966, **88**, 515.

[14] N. Mori and T. Takemur, unpublished data [δ($CDCl_3$) 139.9 (quaternary carbons), 130.0, and 129.4 p.p.m. (tertiary carbons)].

field effect seems most probable, but we shall reserve judgment until *decisive proof* is obtained. A further study is under way.

^{13}C *Spin–Lattice Relaxation*.—The following discussion assumes that the relaxation mechanism of the protonated carbons is dominated by ^{13}C–^{1}H dipolar interactions, as shown by similar aromatic compounds[15] and large cycloalkanes.[16]

Inspection of the results in Table 7 shows that for all compounds, except (5), T_1 for C(1) is short relative to the values for the other methylene carbons. This indicates that the internal motion of the 1-methylene group is most restricted. In open-chain compound (10), segmental motion of the side chains is shown by an increase in T_1 on going towards the terminal methyl group. In hydrocarbon (6) also, a similar but less pronounced motion of the bridge chain is apparent from the decrease in T_1 on going towards the central methylene group. However, such motion is not found in the smaller compound (5).

The effects of intermolecular association in cyclophanols (1) and (2) are evident from the much shorter T_1 values for all carbon atoms than for hydrocarbons (5) and (6), indicating more restricted overall reorientation in the former molecules. Interestingly, the ratio of $1/NT_1$ for the carbon atom adjacent to the central bridge carbon to $1/NT_1$ for this atom increases in the order 0.47, 0.75, 0.81, and 1.1, in going from compound (1) to (4). Here, N is the number of attached protons. If the ratio is a measure of the anchoring effect of the hydroxy group, this effect decreases with the increasing molecular weight or ring size. In the largest compound (4), anchoring seems not effective at the concentration examined, because the ratio is comparable with those in hydrocarbons (5) and (6) (0.96 and 1.3, respectively).

A comparison between the aromatic tertiary carbon atom and C(1) is also of interest. In each of compounds (1), (2), (5), and (6), both carbons show almost the same $1/NT_1$ values, suggesting that the internal rotations of the benzene ring and the 1-methylene group are restricted to similar degrees or so slow as to be negligible compared with the overall molecular reorientation. In the larger cyclophanols (3) and (4) and in the open-chain model (10), the value for the aromatic tertiary carbon is smaller than that for C(1), suggesting that the benzene ring is rotating more rapidly than the 1-methylene group.

EXPERIMENTAL

Materials.—All compounds, except for [11]paracyclophan-5-ol (9) and *p*-dihexylbenzene (10) are known.[12] [11]Paracyclophane (6) (previously prepared by catalytic hydrogenation of [11]paracyclophadiyne)[4d] was obtained by Clemensen reduction of [11]paracyclophan-5-one, liquid, b.p. 135—136 °C at 2 mmHg (Found: M^+, 230.202 0. Calc. for $C_{17}H_{26}$: M, 230.203 4); δ(CDCl$_3$): 7.03 (4 H, s), 2.58 (4 H, m), 1.56 (4 H, m), 1.18 (4 H, m), and 0.79 (10 H, m).

Compound (9) was obtained by the LiAlH$_4$ reduction of the above ketone, m.p. 65.5—66.0 °C (from hexane); δ(CCl$_4$): 7.03 (4 H, m), 2.83 (1 H, m, CH), 2.60 (4 H, m), 1.63 (4 H, m), 1.20 (4 H, m), 0.80 (8 H, m), and 0.54 (1 H, s, OH at infinite dilution) (Found: C, 82.65; H, 10.7. $C_{17}H_{26}O$ requires C, 82.85; H, 10.65%); $\nu_{max.}$ (dilute CCl$_4$) 3 608 (π-bonded OH) and 3 628 cm^{-1} (free OH).

Compound (10) was prepared by the Grignard reaction of *p*-bis-(6-bromohexyl)benzene followed by hydrolysis, b.p. 133 °C at 11.5 mmHg; δ(CDCl$_3$) 7.00 (4 H, s), 2.52 (4 H, t, J 7.5 Hz), 1.30 (16 H, m), and 0.88 (6 H, t, J 6 Hz); Found: C, 87.8; H, 12.05. $C_{18}H_{30}$ requires C, 87.75; H, 12.25%).

Measurements.—^{13}C Spectra were measured at natural abundance for 0.2—0.3M solutions in CDCl$_3$ at ambient temperature, using a JEOL PFT-100 spectrometer operating at 25.15 MHz in the Fourier transform mode. The deuterium resonance of the solvent served as an internal lock. Chemical shifts were determined from proton noise-decoupled spectra and are given in p.p.m. downfield from internal tetramethylsilane (accurate to ±0.1 p.p.m.). Measurement conditions were as follows: pulse width, 13 μs; repetition time, 3 s; spectral width, 4 kHz; data points, 819 2.

^{13}C Spin–lattice relaxation times (T_1) were determined using the partially relaxed Fourier transform method[17] on degassed sample solutions. A recycle time was set to be at least five times that of the longest T_1 to be measured. At least eight τ values in the (180°—τ—90°) pulse sequence were used in determining any T_1 value. The 90° pulse width was 25.5 μs. The T_1 values obtained are accurate to ±10%.

[8/133 *Received, 26th January, 1978*]

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[16] S. Berger, F. R. Kreissl, and D. J. Roberts, *J. Amer. Chem. Soc.*, 1974, **96**, 4348.

[17] A. Allerhand, D. Doddrell, V. Glushko, D. W. Cochran, E. Wenkert, D. J. Lawson, and F. R. N. Gurd, *J. Amer. Chem. Soc.*, 1971, **93**, 544.