[Contribution from the Department of Chemistry, University of Rochester, Rochester 20, New York]

Proton Magnetic Resonance Studies. I. Cyclophanes

By David J. Wilson, V. Boekelheide and Rodger W. Griffin, Jr.[1]

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The n.m.r. spectra of [2.2]paracyclophane and four [2.2]metacyclophanes in dilute carbon tetrachloride solutions are reported. The theory of ring currents partially explains the observed chemical shifts. The methylene proton resonances in [2.2]metacyclophane, 7,15-dimethyl[2.2]metacyclophane and 7,15-dimethoxy[2.2]metacyclophane are strikingly different from the corresponding resonances in 4,12-dimethyl[2.2]metacyclophane and [2.2]paracyclophane.

The availability of various cyclophanes from another investigation on the synthesis and properties of metacyclophane derivatives prompted us to study the proton magnetic resonance spectra of certain typical members of this group.[2] As shown in Fig. 3, the geometry of the [2.2]metacyclophane ring system is such that it requires the substituents at the 4- and the 12-positions to be in unusually close proximity to the π-electron system of the aromatic ring to which they are not directly attached. For this reason the (2.2) metacyclophanes appeared to be exceptionally well suited for testing the ring current theory proposed by Pople and others for explaining chemical shifts in aromatic molecules.[3]

The molecules selected for study were [2.2]-metacyclophane, 4,12-dimethyl[2.2]metacyclophane, 7,15-dimethyl[2.2]metacyclophane, 7,15-dimethoxy[2.2]metacyclophane and, for purposes of comparison, [2.2]paracyclophane. Their proton magnetic resonance spectra were determined using 5% solutions in carbon tetrachloride at 60 Mc. with a Varian Associates Model V4300 B spectrometer. All spectra were taken at 26° and the spectra were independent of concentration in the range 1–5% (weight-volume) in carbon tetrachloride. Audio side-band superposition was used; tetramethylsilane was the internal reference.[4a] The n.m.r. spectrum of metacyclophane is shown in Fig. 1, from which it is apparent that an AB_2 system is present at low fields (with the "B" lines weakly split by the protons in the 4- and 12- positions), a lone proton M weakly coupled to the B protons occurs at intermediate fields, and an X_2Y_2 system is present at high fields. Chemical shifts and spin–spin coupling constants which satisfactorily reproduce the spectrum are listed in Table I. (See ref. 3a, chapter 6, for the computational details and notation.)

The spatial relationships of [2.2]metacyclophane suggest that the lone protons M on the rings should be shifted to quite high fields relative to the AB_2 group and that there should be an appreciable chemical shift between the X and Y (methylene) protons if the ring current theory is applicable. The geometry of the model used was determined by the following bond distances and angles: C–H, 1.085 Å.; C–C (aromatic), 1.39 Å.; C–C, 1.54 Å.; C–C–C angle (aromatic), 120°; C–C–C angle (alkyl), 109°28′; H–C–H angle, 109° 28′; H-C-C angle (aromatic), 120°. A horizontal projection of the geometry is shown in Fig. 2, and the coördinates of the numbered points are listed in Table II. The methylene groups are twisted about the C–C bond about 18° from the symmetrically staggered configuration.

Table I

N.m.r. Spectral Parameters of [2.2]Metacyclophane

Chemical shifts are measured in τ units, spin-coupling parameters in c.p.s. The quantities K, L, M and N are defined on p. 139 of reference 3a. K and N may be interchanged without affecting the spectrum.

AB_2		M		X_2Y_2	
δ_A	2.75	δ_M	5.75	$\lvert K\rvert$	11.4
$\delta_B - \delta_A$	0.215	J_{BM}	1.2	$\lvert L\rvert$	14.7
J_{AB}	7.8			$\lvert M\rvert$	8.3
				$\lvert N\rvert$	7.8
				$\lvert\delta_Y - \delta_X\rvert$	0.96
				δ_X	7.01

Table II

Coördinates of Protons and Centers of Rings of [2.2]

The unit of distance is 1.39 Å.; point 7 lies in the center of one benzene ring and point 6 in the center of the other.

Metacyclophane point	X	Y	Z
1	0	−1.781	0
2	1.542	−0.890	0
3	0	1.781	0
4	2.416	0.552	−0.099
5	1.912	1.425	0.681
6	0	2.847	−0.826
7	0	0	0

These data allow us to compute from Johnson and Bovey's tables[4a] the difference in chemical shift between protons A and B, A and M and X and

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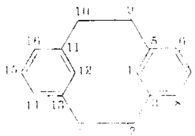
[1] National Science Foundation Predoctoral Fellow.

[2] The details of the synthesis and properties of these compounds will be reported elsewhere. The system of nomenclature follows that introduced by D. J. Cram and J. Abell (This Journal, **77**, 1179 (1955)) for the paracyclophanes. Thus, [2.2]metacyclophane and its numbering are



[3] (a) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw–Hill Book Company, Inc., New York, N. Y., 1959, p. 180. (b) E. D. Becker and R. B. Bradley, *J. Chem. Phys.*, **31**, 1413 (1959), and earlier references on ring-current theory listed here.

[4] (a) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958) (b) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958). The Tables are available on request from these authors.

Y, if we assume that the only contribution to these differences are those due to ring currents. The observed and calculated values are given in Table III. It is evident that the theory's prediction of the M proton shift is in good qualitative agreement with experiment but that the large difference found experimentally between protons X and Y cannot be accounted for by this means, nor can the difference in chemical shift between the A and B protons. (The very tentative assignment of the X protons as identified in Fig. 2 to the lower resonances of the X_2Y_2 system is made on the basis of ring current theory.)

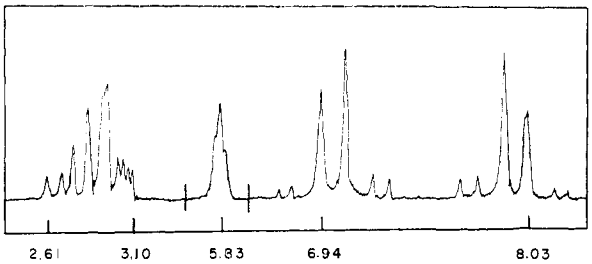


Fig. 1.—60 Mc. n.m.r. spectrum of [2.2]metacyclophane, horizontal scale is in τ-units; the two vertical bars in the spectrum indicate sections which have been omitted.

One reason for the discrepancy between theory and experiment as regards the difference in chemical shift between protons X and Y (and A and B) is the somewhat naive assumption that the only factor contributing to the shift between these chemically non-equivalent protons is the ring current effect. That these protons might have appreciably different chemical shifts in the absence of ring currents is suggested, for example, by the fact that there is a difference of 0.35 τ units between the proton *cis* and the proton *trans* to the alkyl group in heptene-1.[5] It seems unlikely that this shift is explicable in terms of the diamagnetic anisotropy of the methylenemethylene bonds, which should lead to a quite small effect.[6] Another possible reason for the discrepancy between theory and experiment is overlap of the π-orbitals in the two rings, with associated strains and distortions of the bonds. Such effects would, however, produce a reduction in the magnitude of the ring current, which would decrease the chemical shift. The diamagnetic anisotropy of the ring-methylene bonds would result in an additional shift of about 0.2 τ units (see reference 6, p. 117), which is in the right direction (*i.e.*, increasing the chemical shift between X and Y protons), However, the results obtained for [2.2]paracyclophane and 4,12-dimethyl[2.2]metacyclophane (mentioned below) confound all of the above explanations and leave the situation in chaos. Nonetheless, despite the limitations of ring current theory (previously noted by several authors), the theory here qualitatively accounts for a fact which would otherwise be most perplexing to interpret the position of the M proton resonance.

TABLE III

COMPARISON OF OBSERVED AND CALCULATED SHIFTS

	Obsd.	Calcd.
$(\delta_A - \delta_B)$	−0.215	+0.04
$(\delta_M - \delta_A)$	+3.00	+2.82
$(\delta_Y - \delta_X)$	+0.96	+0.28

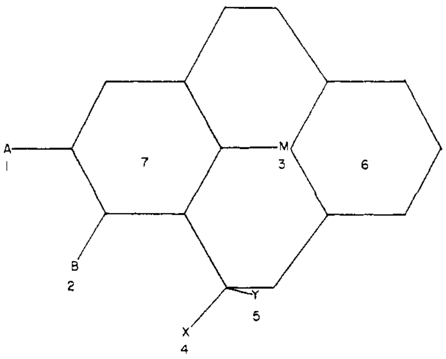


Fig. 2.—Horizontal projection of [2.2]metacyclophane, showing the locations of the protons.

4,12-Dimethyl[2.2]metacyclophane gives a spectrum which also qualitatively confirms the ring current theory. Of particular interest is the position of the methyl resonance, which at room temperature is a single peak occurring at 9.44 τ. (The methyl resonances in toluene and the xylenes occur at about 7.6–7.8 τ.) The influence of ring currents is again apparent. The methyl resonance shows no sign of being split into an AB_2 group at room temperature, indicating that internal rotation makes the methyl protons equivalent even though the methyl groups are crowded tightly against the benzene rings. The methyl line remains sharp down to minus 20 degrees. This is consistent with the suggestion of one of our referees that, due to tunneling, the barrier to the methyl group rotation would need to be of the order of 20 kcal. to affect the n.m.r. spectrum.

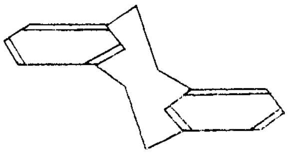


Fig. 3.—[2.2]Metacyclophane carbon skeleton.

The bridging methylene protons in this compound give rise to a poorly-resolved multiplet centered at 7.14 τ; the difference in chemical shift between the two types of methylene protons is less than 0.2 τ units. This would indicate that strain and C–C single bond diamagnetic anisotropies cannot account for the 0.96 τ unit split between the corresponding protons in the unsubstituted [2.2]-metacyclophane. The aromatic ring protons produce an AB_2 spectrum (the largest peak of which is

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[5] See reference 3a, p. 244.

[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 117.

at 3.06 τ) quite similar to that for [2.2]metacyclophane itself, except that in the methyl-substituted compound the chemical shift of the B protons is approximately 0.2 τ *less* than that of the A proton. The spectrum of [2.2]paracyclophane (described previously by Waugh and Fessenden[7]) was also taken. It consists of two relatively sharp peaks (of equal area) at 6.96 and 3.70 τ; the line at lower field is presumably due to the aromatic protons.

Two other [2.2]metacyclophanes were also studied; 7,15-dimethyl- and 7,15-dimethoxy[2.2]-metacyclophane. The spectrum of the former consists of five sets of peaks assigned as follows: a singlet at 3.21 τ (6, 8, 14, 16 protons); a singlet at 5.94 τ (4, 12 protons); two sextets, the main peaks of which occurred at 6.96, 7.09, 7.89 and 8.02 τ, which are very similar in structure to the dimethylene peaks in [2.2]metacyclophane (1, 1, 2, 2, 9, 9, 10, 10 protons); and a singlet at 7.64 τ (7, 15 methyl groups). The spectrum of the dimethoxy derivative was quite similar. The aromatic peak (3.45 τ) is unsplit, as is the peak (5.99 τ) of the central aromatic protons. Each of the two sets of dimethylene peaks is a large doublet (6.98, 7.11, 7.88 and 8.01 τ) flanked on each side by a smaller doublet. The methoxy peak (6.25 τ) is a sharp singlet.

The results of this work indicate that neither strain nor ring currents can readily account for the chemical shifts of the protons in the bridging dimethylene groups in cyclophanes. The drastic difference between the dimethylene lines in [2.2]-metacyclophane and 4,12-dimethyl[2.2]metacyclophane shows that considerable caution should be used in making spectral assignments on the basis of spectra of model compounds. The utility of ring current theory in the qualitative interpretation of spectra is again confirmed.

Acknowledgments.—We are indebted to Dr. Carl G. Krespan, of E. I. du Pont de Nemours & Company, for a sample of paracyclophane. This work was supported in part by a grant from the National Science Foundation.

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[7] J. S. Waugh and R. W. Fessenden, THIS JOURNAL, **79**, 846 (1957).