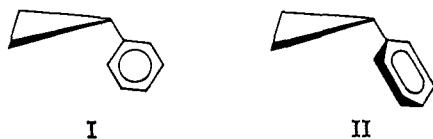


Determination of Conformational Preference in Arylcyclopropanes by Nuclear Magnetic Resonance¹

Sir:

The possibility of electronic interaction of a cyclopropane ring with unsaturated groups has been of interest to many workers.² Following Walsh's predictions of special geometric requirements for such interactions,³ Goodman and Eastman² examined the ultraviolet spectra of several rigid arylcyclopropane derivatives but were unable to obtain unambiguous results confirming a variation in conjugation consistent with the geometric variations employed. Continuing our n.m.r. studies on arylcyclopropanes,⁴ we believe we have uncovered evidence supporting Walsh's original hypothesis.

Two limiting conformations of phenylcyclopropane (I and II) can be envisioned. Conformation I, with the phenyl plane bisecting the three-membered ring, should have the largest electronic interaction between the π -electrons of the phenyl ring and the highly p-weighted σ -bonds of the cyclopropane. On the basis



of Walsh's hypothesis, and neglecting steric effects, I should correspond to the low-energy conformation of phenylcyclopropane.

The n.m.r. spectrum of *p*-deuteriophenylcyclopropane-III (1 mole %) in carbon disulfide shows an A_2B_2 multiplet for the aryl proton resonance.⁵ Analysis for chemical shifts and spin-coupling constants by conventional methods⁶ reveals unusually high shielding for the protons *ortho* to the cyclopropane ring. Figure 1 shows the difference of chemical shifts between the *ortho* and *meta* protons, $\nu_0(\delta_o - \delta_m)$,⁷ as a function of $1/T$ and measured at 60 Mc. On lowering the temperature the *ortho* protons experience a significant increase in shielding, while the total upfield shift of the *meta* protons is approximately 1 c.p.s. over the temperature range studied. In contrast, $\nu_0(\delta_o - \delta_m)$ of toluene is independent of temperature within the experimental error.

These observations are explained consistently by considering the magnetic susceptibility of the cyclopropane ring. It is well established that protons located near the threefold axis of the ring experience additional shielding, while deshielding is observed for protons in or near the ring plane.⁸ In conformation I one of the *ortho* protons lies directly over the center of the three-membered ring. The observed chemical shifts are the averages for both *ortho* and both *meta* protons, because even at low temperatures ($< -100^\circ$)

(1) Supported by Grant No. GP-1076 from the National Science Foundation.

(2) For a summary of leading references see A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

(3) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

(4) G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(5) Proton-deuterium coupling did not interfere seriously with the analysis.

(6) R. E. Richards and T. P. Schaefer, *Trans. Faraday Soc.*, **54**, 1280 (1958); B. Dischler and W. Maier, *Z. Naturforsch.*, **16a**, 318 (1961).

(7) The chemical shift, δ , is defined as negative for protons less shielded than tetramethylsilane.

(8) Cf. D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963), and references cited therein.

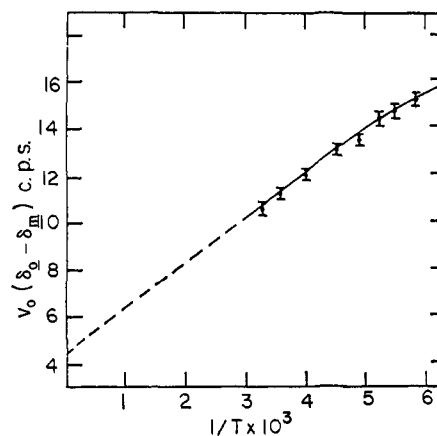


Figure 1. Difference in chemical shifts, $\nu_0(\delta_o - \delta_m)$ between *ortho* and *meta* protons of *p*-deuteriophenylcyclopropane (1 mole %) in carbon disulfide as a function of $1/T$.

the A_2B_2 spectral type is preserved. The ring current model^{8,9} and the point dipole approximation for localized, highly anisotropic single bonds¹⁰ predict a significant upfield shift for the averaged signal arising from the *ortho* protons in conformation I compared to the shift computed for the same protons in II. Using the ring current model and assuming structural parameters derived from related compounds, the calculated chemical shift difference, $\nu_0(\delta_o - \delta_m)$, can be expressed as a function of the torsional angle α ($\alpha_I = 0^\circ$, $\alpha_{II} = 90^\circ$) in terms of the Fourier series: $\nu_0(\delta_o - \delta_m) = 4.8 + 11.4 \cos 2\alpha + 0.7 \cos 4\alpha$. Although the calculated shifts must be regarded as extremely crude approximations, there can be little doubt that, qualitatively, the increasing shielding of the *ortho* protons indicates a decreasing average angle or a higher population of conformation I with decreasing temperature.

Similar results were obtained for *p*-chlorophenylcyclopropane, *p*-bromophenylcyclopropane, and *p*-methoxyphenylcyclopropane. Complications arise in the latter molecules, presumably because of the larger dipole moments which induce solvent-solute and solute-solute interactions. In the corresponding toluenes $\nu_0(\delta_o - \delta_m)$ is temperature dependent even in very dilute solutions. However, if one corrects the temperature dependence of $\nu_0(\delta_o - \delta_m)$ obtained for the cyclopropanes by the temperature dependence observed for the corresponding toluenes, the resulting slopes of the $\nu_0(\delta_o - \delta_m)$ vs. $1/T$ plots are very nearly the same as that obtained for III.

The order of magnitude of the energy difference between I and II can be estimated by using a method similar to one which was applied to biphenyl with moderate success.¹¹ Assuming a classical rotor and a simple potential curve of the form $E_\alpha = E_0 + V/2(1 - \cos 2\alpha)$, the average $\cos \alpha$ as a function of temperature is given by the expressions

$$\langle \cos 2n\alpha \rangle = I_n(x)/I_0(x), \quad x = V/2RT$$

where $I_n(x)$ are modified Bessel functions of order n with argument x . Selecting the value of V to obtain

(9) The method employed is equivalent to the one described by C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958), with a ring radius of 0.88 Å and 4.5 circulating electrons. Good results were obtained with these empirical values on a large number of polycyclic compounds (S. Winstein and J. I. Brauman, private communication).

(10) K. Tori and K. Kitahonoki, *J. Am. Chem. Soc.*, **87**, 386 (1965).

(11) R. J. Kurland and W. B. Wise, *ibid.*, **86**, 1877 (1964).

the best agreement with experiment one finds 1.4 kcal./mole as the energy difference between I and II.¹²

The conformational preference for I cannot be attributed to steric effects because on the basis of internuclear distances nonbonded interactions should be more severe in I than in II. Furthermore, it has been shown that the structural equivalent of II becomes the more stable conformation when steric effects are amplified by introducing methyl groups at the cyclopropane ring *cis* to the phenyl ring.⁴ We therefore believe that electronic effects similar to those proposed by Walsh must be responsible for lowering the potential energy in conformation I.

(12) Because of the many assumptions inherent in this treatment there is little justification for attaching limits of uncertainties to this value.

(13) A. P. Sloan Foundation Research Fellow.

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Carbon-13 Nuclear Magnetic Resonance Spectra of Transition Metal Cyclopentadienyl and Carbonyl Derivatives

Sir:

C¹³ n.m.r. spectra of transition metal cyclopentadienyl and carbonyl derivatives have been relatively little investigated. Previous reports include measurements of the carbon magnetic shieldings in ferrocene,¹

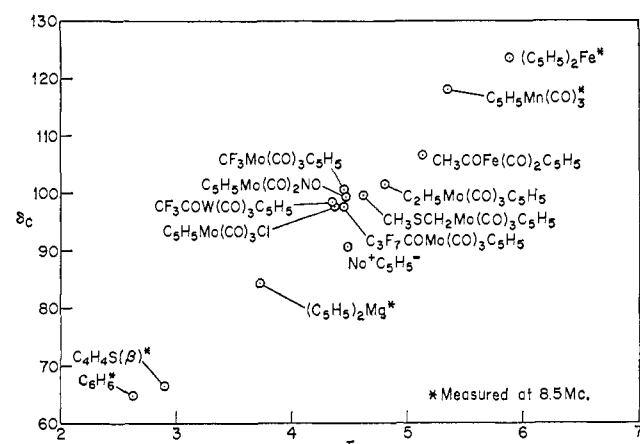


Figure 1. H^1 vs. C^{13} chemical shift in aromatic metal complexes.

iron pentacarbonyl,²⁻⁴ iron dicarbonyl nitrosyl,³ and nickel tetracarbonyl.^{3,4} We have undertaken an investigation of the C¹³ spectra of a more extensive and varied series of compounds and wish now to report our initial results.

Some of the cyclopentadienyl derivatives which we studied are listed in Table I. All of the cyclopentadienyl carbon resonances were doublets, with a carbon-hydrogen spin-spin coupling of approximately 175 c.p.s. Of particular interest is the fact that the plot in Figure 1 of the carbon shieldings against the shieldings of the corresponding protons is almost a straight line, collinear with the similar line for aromatic rings.⁵

(1) P. C. Lauterbur, *J. Am. Chem. Soc.*, **83**, 1838 (1961).

(2) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958).

(3) R. Bramly, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(4) J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964).

Table I. Cyclopentadienyl Resonances^a

Compound	C ¹³ shielding, p.p.m. ^b	H ¹ shielding, p.p.m. ^c
(C ₅ H ₅) ₂ Mg	84.2 ^d (C ₆ H ₆)	3.72 (Et ₂ O)
C ₅ H ₅ Na	90.7 ^e (THF ^f)	4.48 (THF)
C ₅ H ₅ Mo(CO) ₃ Cl	97.9 (C ₆ H ₆)	4.37 (CHCl ₃)
C ₃ F ₇ COMo(CO) ₃ C ₅ H ₅	97.9 (C ₆ H ₆)	4.45 (CHCl ₃)
CF ₃ COW(CO) ₃ C ₅ H ₅	98.7 (C ₆ H ₆)	4.35 (CHCl ₃)
C ₅ H ₅ Mo(CO) ₂ NO	99.2 (CH ₂ Cl ₂)	4.47 (CS ₂)
CH ₃ SCH ₂ Mo(CO) ₃ C ₅ H ₅	99.6 (CH ₂ Cl ₂)	4.62 (CS ₂)
CF ₃ Mo(CO) ₃ C ₅ H ₅	100.9 (C ₆ H ₆)	4.45 (CHCl ₃)
C ₂ H ₅ Mo(CO) ₃ C ₅ H ₅	101.1 (C ₆ H ₆)	4.80 (CS ₂)
CH ₃ COFe(CO) ₂ C ₅ H ₅	106.3 (C ₆ H ₆)	5.13 (CS ₂)
C ₅ H ₅ Mn(CO) ₃	118 ^d (C ₆ H ₆ , CH ₃)	5.35 (CS ₂)
(C ₅ H ₅) ₂ Fe	123.6 ^d (CS ₂)	5.89 (CS ₂)

^a Solvent given in parentheses. ^b To high field from CS₂. ^c τ -scale: G. V. D. Tiers, *J. Phys. Chem.*, **68**, 1151 (1958). Spectra measured at 60 Mc. ^d Spectrum measured at 8.5 Mc.; other carbon spectra measured at 25.143 Mc. ^e H. Spiesecke and W. G. Schneider, *Tetrahedron Letters*, 468 (1961). ^f Tetrahydrofuran.

Table II. Carbonyl Resonances^a

Compound	C ¹³ shielding, p.p.m. ^b
CO	11.5 ^{c,d} (gas)
Ni(CO) ₄	1.2 ^{d,e} (neat liquid)
C ₃ F ₇ Fe(CO) ₄ I	-6 ^d (CHCl ₃)
Fe(CO) ₂ (NO) ₂	-14 ^f (neat liquid)
[Fe(CO) ₃ SCH ₃] ₂	-16.6 ^d (CHCl ₃)
Fe(CO) ₅	-16.8 ^d (neat liquid)
C ₅ H ₅ Fe(CO) ₂ I	-20.9 ^d (CHCl ₃)
C ₇ H ₈ Mo(CO) ₄ ^g	-22.4, -26.0 ^d (CHCl ₃)
C ₇ H ₈ Mo(CO) ₄ ^g	-22.0, -25.4 (CH ₂ Cl ₂)
C ₅ H ₅ Mo(CO) ₃ Cl	-32.6 (CH ₂ Cl ₂)
C ₅ H ₅ Mo(CO) ₂ NO	-34.5 (CH ₂ Cl ₂)

^a Solvent given in parentheses. ^b To high field from CS₂. ^c R. Ettinger, P. Blume, A. Patterson, Jr., and P. C. Lauterbur, *J. Chem. Phys.*, **33**, 1547 (1960). ^d Spectrum measured at 8.5 Mc.; other spectra measured at 25.143 Mc. ^e J. B. Stothers and P. C. Lauterbur, *Can. J. Chem.*, **42**, 1563 (1964). ^f R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962); measured at 12.069 Mc. ^g C₇H₈ is bicyclo[2.2.1]heptadiene (norbornadiene).

The variations in carbon and hydrogen shieldings in aromatic rings seem to be dominated by the local π -charges, and a similar interpretation of the shieldings in cyclopentadienyl rings might be attempted. It appears to be very unlikely, however, that the charge separations implied by such a simple theory can be reconciled with other considerations.⁶ No convincing explanation of these results within the framework of the current approximate shielding theory has been found. It may be suggested tentatively that molecular currents similar to those responsible for high-field carbon and hydrogen shifts in acetylenes and three-membered rings may be responsible for the anomalies.⁷

(5) P. C. Lauterbur, *Tetrahedron Letters*, No. 8, 274 (1961); H. Spiesecke and W. G. Schneider, *ibid.*, No. 8, 468 (1961).

(6) For example, ferrocene would be expected to be several orders of magnitude more reactive to electrophilic substitution than benzene or even cyclopentadienide ion, in disagreement with experimental results. [For suitable reviews of the chemistry of cyclopentadienyl derivatives see P. L. Pauson, *Quart. Rev.* (London), **9**, 391 (1955); E. O. Fischer and H. P. Fritz, *Advan. Inorg. Chem. Radiochem.*, **1**, 55 (1959); G. Wilkinson and F. A. Cotton, *Progr. Inorg. Chem.*, **1**, 1 (1959).]

(7) A fairly close analogy between the carbon-carbon triple bond and the metal-cyclopentadienyl bond may be drawn. The latter may be regarded as being made up of a σ -bond between the ring A orbitals and a metal hybrid orbital and two perpendicular π -bonds formed between