The Nuclear Magnetic Resonance Spectra of Five Cyclopentadienides

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Abstract: The nmr parameters for sodium indenyl, triphenylphosphonium cyclopentadienide, pyridinium cyclopentadienide, trimethylammonium cyclopentadienide, and diazocyclopentadiene have been determined. The bond orders for several of these molecules and some related structures were calculated by the ω' technique. It has been found that the bond orders and vicinal proton coupling constants for five-membered ring compounds follow a linear relationship which allows one to draw inferences regarding the aromaticity of these substances.

The requirements of the modern electronic definition of aromaticity can be met by five-membered ring compounds in which all ring atoms are conjugated and six π electrons are available in the ring.[1] The cyclopentadienide ion is often cited as being aromatic in this sense.

Six π electrons can also be made available to the five-membered ring by attachment of appropriate exocyclic groups. Among such structures one might list the fulvenes and the various ylides which have been synthesized from cyclopentadiene. While dimethylfulvene and diphenylfulvene have been shown to have substantial thermochemical resonance energies (*ca.* 12 kcal/mole), the nmr parameters[2] and chemical properties[3] characterize these compounds as dienelike rather than aromatic.

The chemistry of the ylides derived from cyclopentadiene has been little explored. A review of what is known is given later. In view of the theoretical significance of these compounds, it seemed of interest and importance that their nmr parameters be determined.

Since Jonathan, Gordon, and Dailey[4] have shown that there is a correlation between bond order and vicinal proton coupling constants in a series of six-membered aromatic compounds, we have also explored this relation in the five-membered series.

Experimental Section

The ylides used in this study were prepared by methods in the literature: triphenylphosphonium cyclopentadienide as by Ramirez and Levy;[5] pyridinium cyclopentadienide as by Lloyd and Sneezum;[6] trimethylammonium cyclopentadienide as by Spooncer;[7] and diazocyclopentadiene as reported by DePuy and Doering.[8] Solids were recrystallized immediately before use and gave melting points agreeing with the literature. Diazocyclopentadiene was distilled. In one case, a mild explosion was experienced. All compounds, other than the first, were unstable, and determinations were carried out on sealed, degassed samples immediately after preparation.

All nmr spectra were determined with a Varian A-60 at ambient temperature. The spectrum of trimethylammonium cyclopentadienide was also run on a Varian HA-100. Six or more sweeps were recorded, and the line positions averaged. Tetramethylsilane was added as an internal standard in each case.

The spectrum of the triphenylphosphonium cyclopentadienide in deuteriochloroform was a perturbed AA'BB' spectrum owing to coupling with the phosphorus. Spectrum simplification was carried out by spin decoupling the phosphorus.[9] The parameters for the five-membered ring are given in Table I.

Table I. Nmr Parameters

Cyclopentadienides	τ^a	Δ_{AB}, cps	J_{12}	J_{23}	J_{13}	J_{14}
Triphenylphosphonium	3.64	10.20	3.84	2.80	1.89	2.16
Pyridinium	4.12	23.13	4.19	2.34	1.50	2.18
Trimethylammonium	5.44	10.69	3.84	2.96	2.26	1.74
Diazo	3.67	47.06	4.93	2.70	1.87	2.20
Dimethylfulvene[d]	3.70[b]	7.30[c]	5.45	2.40	1.50	2.40
Diphenylfulvene[d]	3.70[b]	24.54[c]	5.17	2.21	1.38	1.94
Indenylsodium			J_{45}	J_{56}	J_{46}	J_{47}
Six ring	. . .	53.53	7.97	6.17	1.13	0.80
Five ring	. . .	39.50	$J_{12} = 3.23$			

[a] Center of ring proton spectrum. [b] Chemical shifts (cps) in carbon tetrachloride. [c] Determined in dimethyl sulfoxide. [d] Reference 2.

The spectra of pyridinium cyclopentadienide, trimethylammonium cyclopentadienide, and diazocyclopentadiene were run on *ca.* 10% solutions in dimethyl sulfoxide, acetonitrile, and carbon tetrachloride, respectively. This choice of solvents was dictated by solubility considerations. Unfortunately, no one solvent was sufficiently good for the whole series. The spectra of the cyclopentadiene ring in each case was that of an AA'BB' system. In the first two, the upfield half of the spectrum was broadened owing to coupling with the nitrogen. The spectrum of the diazocyclopentadiene was completely symmetrical with no broadening. It closely approximated an AA'XX' case.

The analyses of these spectra followed considerations presented elsewhere.[2] Since the spectra resembled those of the previously studied fulvenes, none are presented here. The calculated parameters are given in Table I. The assignments of the various coupling constants also follow from previous considerations.[2]

Solutions of indenylsodium in tetrahydrofuran were prepared from freshly distilled indene and tetrahydrofuran sealed in the nmr tube with metallic sodium. The unreacted sodium was centrifuged to the top of the tube and remained stuck there when the tube was inverted and placed in the instrument. The spectrum was identical with that previously reported by Schaefer and Schneider[10]

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(1) See (a) P. L. Pauson, "Non-Benzenoid Aromatic Compounds," D. Ginsberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, p 108; (b) W. von E. Doering, "Theoretical Organic Chemistry," Butterworth and Co., Ltd., London, 1959, p 36.

(2) W. B. Smith and B. A. Shoulders, *J. Am. Chem. Soc.*, **86**, 3118 (1964).

(3) J. H. Day, *Chem. Rev.*, **53**, 167 (1953).

(4) N. Jonathan, S. Gordon, and B. P. Dailey, *J. Chem. Phys.*, **36**, 2443 (1962).

(5) F. Ramirez and L. Levy, *J. Org. Chem.*, **21**, 488 (1956).

(6) D. Lloyd and J. S. Sneezum, *Chem. Ind.* (London), 1221 (1955); *Tetrahedron*, **3**, 334 (1958).

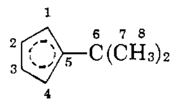
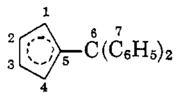
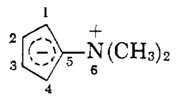
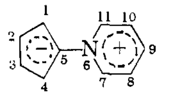
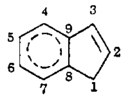
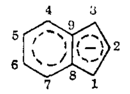
(7) W. Spooncer, Ph.D. Thesis, University of Washington, 1955.

(8) W. von E. Doering and C. H. DePuy, *J. Am. Chem. Soc.*, **75**, 5955 (1953).

(9) The normal and phosphorus-decoupled spectra were determined for us by Dr. C. A. Reilly, Shell Development Corp., Emeryville, Calif. Dr. Reilly also carried out the spectral analyses with the aid of his MARIP program. In addition to the values given in Table I, Dr. Reilly also reported J_{HP}'s of ±3.6 cps to proton 2 and ±5.6 cps to proton 1. The phosphorus appeared at −9.8 ppm from trimethyl phosphate. We wish to express our great appreciation to Dr. Reilly for his efforts on this problem.

(10) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963).

Table II. MO Parameters and Results

 $h_7 = -0.1$ $h_8 = -0.5$ $k_{15} = 0.93$ $k_{12} = 1.08$ $k_{23} = 0.93$ $k_{56} = 1.08$ $k_{67} = 0.90$ $k_{79} = 2.5$ $p^{12} = 0.828, p^{23} = 0.444$ $\Delta E = 0.894, 1.237;\ \mu = 3.5$ D.	 $k_{15} = 0.93$ $k_{12} = 1.08$ $k_{23} = 0.93$ $k_{56} = 1.08$ $k_{67} = 0.90$ $p^{12} = 0.814, p^{23} = 0.460$ $\Delta E = 0.980$	 *a* $h_5 = 1.0$ $h_6 = 2.0$ $k_{15} = 0.93$ $k_{13} = 1.08$ $k_{23} = 0.93$ $k_{56} = 0.70$ $p^{12} = 0.705, p^{23} = 0.564$ $\Delta E = 1.428, \mu = 9.4$	*b* $h_5 = 1.0$ $k_{15} = 0.93$ $k_{13} = 1.08$ $k_{23} = 0.93$ +1 *exo* charge $p^{12} = 0.762, p^{23} = 0.516$ $\Delta E = 2.062$
 $h_6 = 1.50$ $h_5 = 0.40$ $h_7 = 0.40$ $k_{15} = 0.93$ $k_{12} = 1.08$ $k_{23} = 0.75$ $k_{56} = 0.75$ $p^{12} = 0.752, p^{23} = 0.540$ $\Delta E = 0.405, 0.833;\ \mu = 13.2$	 $k_{12} = 0.10$ $k_{49} = 0.94$ $k_{18} = 0.10$ $k_{45} = 1.04$ $k_{23} = 0.99$ $k_{56} = 1.04$ $k_{39} = 0.86$ $p^{23} = 0.928$ $\Delta E = 0.693, 0.994;\ \mu = 0.2$	 $k_{12} = 0.99$ $k_{18} = 0.90$ $k_{49} = 0.94$ $k_{45} = 1.04$ $k_{56} = 1.04$ $p^{12} = 0.668, p^{45} = 0.723, p^{56} = 0.589$ $\Delta E = 1.026, \mu = 1.2$	

and consisted of an AB_2 system partially superimposed on the spectrum of an AA′BB′ system. The lines were readily assigned and analyzed by conventional procedures. These results are also given in Table I.

Molecular Orbital Calculations

The π bond orders for the molecules of interest in this study were calculated using a modified ω' technique.[11] The bond resonance integrals could be modified during iteration or an initial fixed set could be used. The variations of the bond resonance integrals with each successive iteration results in a rapid convergence for anion radicals while the normal ω or ω' technique, in general, does not. An atom *exo* to the π electron system can be included to allow for the modification of a particular coulomb integral or to perturb a particular region of the π electron system.

The calculations of the π-bond orders in this article are for fixed values of the bond resonance integrals. The π-bond orders for nonradical systems were found not to change significantly from those obtained when the variation of bond resonance integral portion of the program was included provided the initial set of bond resonance integrals were based on bond alternations.[12]

The initial values of the bond resonance integrals were estimated by assuming a reasonable set of bond lengths and bond angles for each molecule referring, where possible, to structures of known geometry. Hyperconjugation was included for dimethylfulvene, and the three hydrogen atoms were treated as a composite atom. Hyperconjugation of the methylene group was also provided in the indene calculation. Trimethylammonium cyclopentadienide was calculated in two ways. In the first case, the nitrogen atom was included in the π electron system with a small value of the C–N bond resonance integral. In the second, the system was treated as a five-atom problem with an external perturbation from a unit positive charge in the appropriate geometric location. Diphenylfulvene was calculated for one cycle only because of the time required for iteration on the IBM 1620.

The parameters used in these calculations are given in Table II. The initial form of bond resonance integrals and coulomb integrals were taken as $\alpha = \alpha_0 + h_r\beta_0$ and $\beta_{rs} = k_{rs}\beta_0$, respectively. If no value is listed for a given integral in Table II then $h_r = 0$ for the coulomb integrals and $k_{rs} = 1.0$ for the bond resonance integrals between adjacent atoms. Bonds symmetrical to those listed are not relisted. Bond orders (p), excitation energies (ΔE in units of β), and the π-electron dipole moments (μ in Debyes) are also listed in Table II.

Results and Discussion

The nmr parameters for triphenylphosphonium cyclopentadienide, pyridinium cyclopentadienide, trimethylammonium cyclopentadienide, diazocyclopentadiene, and sodium indenyl in a variety of solvents are given in Table I. The previously determined values for dimethylfulvene and diphenylfulvene are included for comparison.[2]

The wide range of solvents employed here was necessitated by solubility and stability considerations. While there is no doubt that such solvent changes will alter the chemical shifts of the protons in the various molecules in this study, there is reason to assume that no major alterations in coupling constants occur. It is known that geminal coupling constants vary widely with solvent polarity.[13] However, vicinal coupling constants in both vinyl and aromatic systems

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(11) (a) A. Streitwieser, A. Heller, and M. Feldman, *J. Phys. Chem.*, **68**, 1224 (1964); (b) W. Kuhn, *Tetrahedron Suppl.*, **2**, 88, 389, 437 (1963).

(12) W. H. Watson, unpublished results. A discussion of the two approaches and a comparison of the results will be published later.

(13) V. S. Watts and J. H. Goldstein, *J. Chem. Phys.*, **42**, 228 (1965).

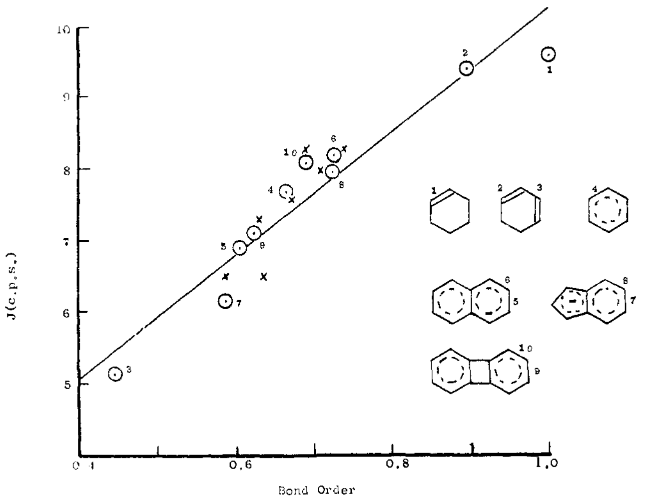

Figure 1. Plot of proton coupling constants for six-membered rings *vs.* bond orders. Points marked x are from ref 4.

vary only 2–3% over wide ranges of solvent polarity.[13,14] The change of vicinal coupling constants in diphenylfulvene was 0.1 cps or less in passing from carbon tetrachloride to dimethyl sulfoxide.[2]

In attempting to assess the aromaticity of the systems in this study one might presumably utilize either the chemical shift or spin coupling parameters. The affect of the magnetic anisotropy of aromatic rings on proton chemical shifts has been discussed at great length, and Jackman and Elvidge[15] have proposed the downfield shift of such protons as a quantitative measure of aromatic character. It has not always been certain, however, how this criterion may be applied,[16,17] and recently a theoretical objection to their proposal has been raised.[18] Certainly, there are often a number of objections which can be raised against most models chosen for comparison with the proposed aromatic system, and practical matters, such as the influence of solvents of widely different polarity, the change in charge densities on the ring carbons introduced by the exocyclic group, and the magnetic anisotropy of the exocyclic group, all rule against the applicability of chemical shifts in any attempt to determine the aromaticity of the compounds reported here.

As mentioned previously, Jonathan, Gordon, and Dailey[4] have found a linear relationship between bond order and the vicinal proton coupling constants for a limited number of six-membered aromatic compounds. The original relation has now been extended (Figure 1) by use of more recent data including values at both the high and low ends of the bond-order scale.[19] The least-squares fit for these data gave J (cps) $= 8.65p + 1.66$ where p is the bond order. The probable error in J for a given value of p was ± 0.27 cps.

Two points may be made regarding the data in Figure 1. First, the literature value of 6.0 cps for J_{ortho} in benzene coupled with $p = 0.667$ gives a point far off the least-squares line.[20] This value of J was determined by the liquid crystal technique. Recently, Reavill and Bernstein have analyzed the spectrum of a deuterated benzene and arrived at $J_{ortho} = 7.7$ cps.[21] This value is in excellent agreement with the other data in Figure 1 and was consequently included in our calculations.

The second point is that the modified ω′ treatment of the charged nonalternant anion, sodium indenyl, provides p values consistent with the other data in Figure 1 and suggests that this adjustment of the simple HMO technique is satisfactory for systems of this type. It is well known that simple HMO calculations often do not give satisfactory results in nonalternant systems.

The J–p relation of Jonathan, Gordon, and Dailey[4] does have a basis of justification in current theory. Karplus,[22] in his valence-bond treatment of the spin-coupling phenomenon, has shown that vicinal coupling constants decrease linearly with increasing length of the intervening carbon–carbon bond. This statement is subject to the condition that the internal bond angles and hybridization remain constant, a condition which is met presumably by the compounds in Figure 1. Since the relation of bond order to bond length is essentially linear over the range of bond orders encompassed by the plot, the observed linear behavior is not surprising. Moreover, the Karplus equation predicts a decrease in J of about 60% in going from a true double bond to a single bond, a value in keeping with the results of Figure 1. While the variation of J with bond length may be considered the more fundamental relation, the bond length–bond order correlation and the ability to calculate bond orders for many compounds where no bond length measurements have been carried out support the use of the J–p plot.

The data for a number of five-membered carbocyclic compounds is plotted in Figure 2 using data from the literature[19] and the results of this study. The least-squares line was determined as J (cps) $= 7.12p - 1.18$ and the probable error in J for a given value of p was found to be ± 0.22 cps. The need to plot the five-membered series on a separate graph is occasioned by the change of internal bond angles in passing to the five-membered rings.[22] Again, it is noted that the difference between the J values at the extremes of the plot change by about the 60% required by the Karplus equation.

The results for the trimethylammonium and pyridinium cyclopentadienide as well as sodium indenyl are incorporated in Figure 2. The fact that these charged nonalterant systems fit the curve as well as the neutral

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(14) H. M. Sutton and T. Schaefer, *Can. J. Chem.*, 43, 3116 (1965).

(15) L. M. Jackman and J. A. Elvidge, *J. Chem. Soc.*, 859 (1961).

(16) R. J. Abraham, R. C. Sheppard, W. A. Thomas, and S. Turner, *Chem. Commun.*, 3, 43 (1965). See, however, J. A. Elvidge, *ibid.*, 8, 160 (1965).

(17) E. M. Elveth, J. A. Berson, and S. L. Manatt, *J. Am. Chem. Soc.*, **87**, 2901 (1965).

(18) J. Musher, *J. Chem. Phys.*, **43** 4081 (1965).

(19) The bond orders and J values of Jonathan, Gordon, and Dailey[4] are plotted in Figure 1. Other J values used in Figures 1 and 2 were taken from (a) indene, D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, 36, 2346 (1962); (b) cyclopentadiene and cyclohexadiene, S. L. Manatt and D. D. Elleman as quoted by J. B. Lambert, L. J. Durham, P. Lepoutre, and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3896 (1965); (c) cyclopentene and cyclohexene, P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963); (d) azulene, W. G. Schneider, H. J. Bernstein, and J. A. Pople, *ibid.*, **80**, 3497 (1958); (e) pentalenyl dianion, T. J. Katz and M. Rosenberger, *ibid.*, **84**, 865 (1962); (f) biphenylene, A. R. Katritzky and R. E. Reavill, *Rec. Trav. Chim.*, **83**, 1230 (1964). Bond orders were taken from (g) azulene, R. Pariser, *J. Chem. Phys.*, **25**, 1112 (1957); (h) biphenylene, J. D. Roberts, A. Streitwieser, and M. Regan, *J. Am. Chem. Soc.*, 74, 4579 (1952); (i) pentalenyl dianion, A. J. Silvestri, L. Goodman, and A. J. Dixon, *Tetrahedron*, **18**, 1329 (1962).

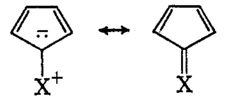
(20) L. C. Snyder and E. W. Anderson, *J. Am. Chem. Soc.*, **86**, 5023 (1964).

(21) R. Reavill and H. J. Bernstein, private communication.

(22) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

systems again supports the contention that the MO technique employed produced reliable results.

The cyclopentadiene ylides have been cited as examples of nonbenzenoid aromatic compounds which may be represented by resonance contributing forms such as



I II

Only forms of type I, however, can contribute to trimethylammonium cyclopentadienide.

The small amount of available data on the chemistry of these compounds may be briefly summarized as follows. The triphenylphosphonium ylide is stable indefinitely in air, couples with benzenediazonium chloride, and has a dipole moment suggesting about equal contributions from I and II;[5,23] the pyridinium ylide is unstable in air and is readily hydrogenated;[6] and the diazo compound is thermally unstable, decomposes on standing, and is also readily hydrogenated.[8] Little is known about the trimethylammonium ylide though we observed it to decompose less rapidly in the nmr tube than the pyridinium compound.

Based on chemical reactivity, only the triphenylphosphonium ylide can be construed as aromatic in the sense of benzene and its derivatives. The degree to which the members meet the electronic criteria of aromatic compounds can be inferred from the bond orders. Streitwieser[24] has suggested that in π systems single bonds will have $p < \sim 0.4$, aromatic bonds have $p = 0.5\text{--}0.7$, and that double bonds are characterized by $p > 0.8$. From the MO calculations of p for the trimethylammonium ylide and the pyridinium ylide (Table II), one finds both sets, p^{12} and p^{23}, to be more in the aromatic region than the values for the fulvenes. Furthermore, the trimethylammonium compound has more aromatic-type bonding than the pyridinium ylide, in keeping with our observations on their relative stabilities and the nmr coupling constants.

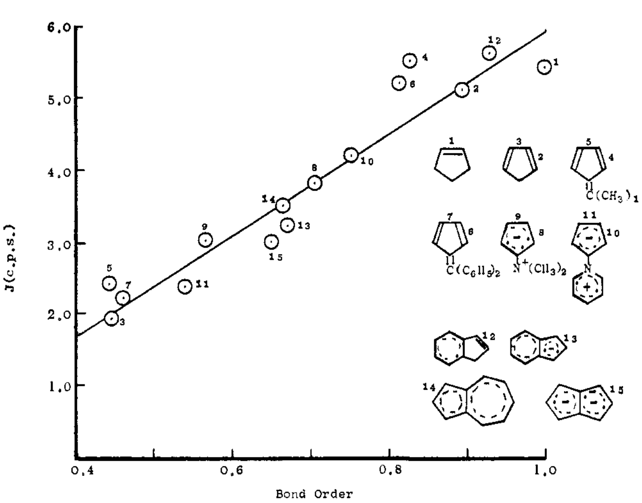


Figure 2. Plot of proton coupling constants for the five-membered rings *vs.* the bond orders.

No MO calculations for the triphenylphosphonium ylide or diazocyclopentadiene were carried out owing to the lack of suitable parameters for the exocyclic group. However, the bond orders calculated from the *J–p* relation were p^{12}, p^{23} = 0.705, 0.559 and 0.858, 0.545, respectively, indicating substantial aromatic behavior for the former and dienoid character for the latter.

In conclusion, it is evident that practical considerations, theoretical criticisms aside, preclude the use of chemical shift data to rule on the aromaticity of the cyclopentadienides of this study. The *J–p* relation may be applied to either five- or six-membered carbocyclic compounds and is of utility in reaching qualitative conclusions on aromaticity in these systems. As more bond length data become available one may hope the quantitative nature of this relation will improve.

Acknowledgment. We wish to express our gratitude to the Robert A. Welch Foundation for their generous support of this work.

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(23) F. Ramirez and S. Levy, *J. Am. Chem. Soc.*, **79**, 67 (1957).

(24) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 172.