Fig. 12.—The appearance of the OH band of dilute phenol in (a) perfluoroöctane + hexane (8:1 w./w.); (b) perfluoroöctane + CCl₄ (7:1 w./w.); concn. of phenol <0.02 molar; 1-mm. cells.

Solvent mixtures	ν_{OH} phenol, cm.⁻¹ (max.)
Cyclohexane + CCl₄ (20:17 v./v.)	3614 (symmetrical)
CCl₄ + CS₂ (3:2 v./v.)	3606 (slight asymmetry on low freq. side)
Cyclohexane + CS₂ (1:1 v./v.)	3608 (definite asymmetry on low freq. side)
Hexane + CS₂ (10:7 v./v.)	3614 (definite asymmetry on low freq. side)
Perfluoroöctane + hexane (8:1 w./w.)	3639, 3624 (see text and Fig. 12a)
Perfluoroöctane + CCl₄ (7:1 w./w.)	3642, 3623 (see Fig. 12b)
FC-75ᵃ satd. with CCl₄	3640, 3623 (similar to above)
FC-75ᵃ satd. with cyclohexane	3640 (slight asymmetry on low freq. side)

ᵃ FC-75 is a mixture of perfluorocyclic ethers (Minnesota Mining and Mfg. Co.). Its behavior is very much like that of perfluoroöctane, and it is much more readily available. The free band of phenol in FC-75 is at 3645 cm.⁻¹; there is no tendency to hydrogen bond to the oxygen atom in this solvent. Perfluorotributylamine (FC-47) behaves similarly in these respects, but solubilities are lower in this solvent.

solvents and the presence of more than one band or of an asymmetry in the observed band have been taken as evidence for specific interactions, e.g., hydrogen bonding, between one of the solvents in the mixture and the solute.[5] This type of evidence should be taken with caution, since it does not take into account the possible presence of non-equivalent sites in the solvent mixture. This is illustrated by the behavior of phenol in mixtures of hexane and perfluoroöctane. The OH stretching frequency of phenol is 3654 cm.⁻¹ in the vapor phase,[27] 3644 cm.⁻¹ in perfluoroöctane and 3621 cm.⁻¹ in hexane. The spectrum of phenol in a mixture of hexane and perfluoroöctane shows two partially overlapped but well defined bands with apparent

maxima at 3639 and 3624 cm.⁻¹ (Fig. 12a). It is hardly possible to attribute the lower frequency band to the presence of a hydrogen bonded complex, phenol.. hexane; the prevalence of this effect in mixtures of presumed "inert" solvents (Table XII) suggests that another cause may be responsible. The system perfluoroheptane–isoöctane has been studied by small angle X-ray measurements[59]; evidence of clusters up to 140 perfluoroheptane molecules has been found. It is possible that such clustering in solvent mixtures such as perfluoroöctane–hexane gives sites essentially similar to the pure solvents and this is responsible for the behavior reported in Table XII.

(59) G. W. Brady, J. Chem. Phys., 32, 45 (1960); G. W. Brady and J. I. Petz, ibid., 34, 332 (1961); G. W. Brady and H. L. Frisch, ibid., 35, 2234 (1961).

Proton Spin–Spin Coupling in Aromatic Molecules. p-Disubstituted Benzenes

BY P. F. COX

Nuclear magnetic resonance spectra of several p-disubstituted benzene derivatives have been obtained at 60 Mc./sec. The aromatic proton spectra were analyzed in terms of the relative chemical shift of the two aromatic proton types and the spin coupling constants between proton pairs. It was possible to obtain these solutions of the spin Hamiltonian without the use of numerical or iterative techniques. While the coupling constant did not vary greatly in the compounds studied, a definite relationship was found between the coupling constants and the electronegativity of the atoms attached to the aromatic ring.

The p-disubstituted benzene derivatives are a fruitful class of compounds to study by nuclear resonance. Because of symmetry of the spin coupling Hamiltonian, the spectra are relatively simple and may be easily analyzed in terms of chemical shift and spin coupling parameters. Richards and Schaefer[1] have examined the spectra of several p-disubstituted benzene derivatives and noted qualitative correlation between chemical shift and the substituent groups. Small differences

in spin coupling constants were reported, but no attempt was made to correlate their magnitude with the substituent group. Schaefer and Schneider[2] have reported the effect of solvent on the chemical shift of aromatic protons in p-substituted toluenes and fluorobenzenes.

McConnell has examined the mechanism for spin coupling of aromatic protons.[3] The observed coupling constant between proton N and N' is composed of con-

(1) R. E. Richards and T. P. Schaefer, Trans. Faraday Soc., 54, 1280 (1958).

(2) T. Schaefer and W. G. Schneider, J. Chem. Phys., 32, 1218 (1960).
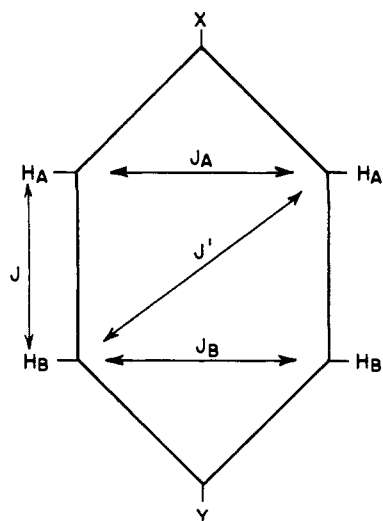
(3) H. M. McConnell, J. Mole. Spectry., 1, 11 (1957).

Figure 1.

Fig. 2.—Energy levels and observed transitions for an A_2B_2 proton group.

tributions from electrons in σ-bonding orbitals and electrons in π-bonding orbitals.

$$J_{N.N'} = J^{\sigma}_{N.N'} + J^{\pi}_{N.N'}$$

The contribution from π-electrons is given by[3]

$$J^{\pi}_{NN'} = \beta^2 Q^2 \eta^2_{NN'}/h\Delta E$$

in which β is the electronic Bohr magneton, Q is an effective hyperfine interaction constant, $\eta_{NN'}$ is the π bond-order between carbons N and N′, h is Planck's constant, and ΔE is an effective electronic excitation energy between the ground-state singlet molecular orbital and excited triplet states.

TABLE I

Compound	Position of peaks relative to center of spectrum					
p-Chloroiodo- benzene	9.85	12.34	14.46	18.92	20.96	23.61
p-Bromoiodo- benzene	4.22	6.41	8.59	12.99	15.08	17.38
p-Chlorophenol	6.05	9.03	11.36	15.63	17.95	21.04
p-Bromophenol	11.61	14.72	17.04	21.32	23.64	26.75
p-Chloroaniline	5.14	7.94	10.22	14.44	16.77	19.54
p-Chlorotoluene	2.25	4.18	6.50	10.51	12.85	14.77
p-Bromotoluene	5.25	7.19	9.40	13.73	15.58	17.83
p-Iodotoluene	14.66	16.70	18.53	23.05	24.92	27.14
p-Chloroaceto- phenone	7.75	9.93	11.93	16.57	18.56	20.77
p-Isopropyl- phenol	2.64	4.83	7.18	11.22	13.55	15.78
p-Nitroanisole	24.77	28.20	30.48	35.20	37.45	40.93
p-Hydroxy- benzoic acid	23.64	26.33	28.35	32.93	34.98	37.68
p-Chloronitro- benzene	14.00	16.76	18.86	23.56	25.70	28.50

Changes in the symmetry and energy of π-molecular orbitals with the addition of substituents is well known. These changes should be reflected in the observed proton coupling constants in substituted benzenes. The short range coupling constants are particularly sensitive to changes in the σ-bonding orbitals.[3] These changes in σ-orbitals may be either the result of inductive effects or the result of changes in bond order and electron density of the π-orbitals. A detailed study of proton coupling should provide additional insight into the nature of these changes.

Experimental

A Varian Associates DP-60 high resolution spectrometer was used in obtaining the n.m.r. spectra. Spectral line positions were measured by interpolation between 15.0 c.p.s. side bands from the principal peak of each group of lines. The audio
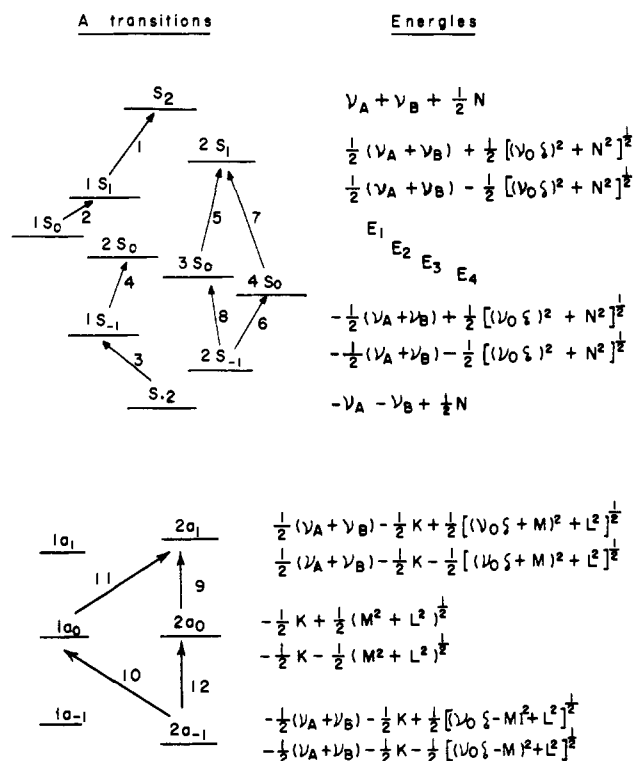
oscillator was set by observation of Lissajous patterns of the oscillator output $vs.$ 60 c.p.s. line current. At least six spectra were calibrated for each hydrocarbon investigated. The probable error in measurement of relative line positions was less than ± 0.05 c.p.s. The probable error in determination of spin coupling constants from the observed line positions was of the same order of magnitude.

In order to minimize solvent effects, the spectra were obtained from a 5 mole per cent solution of each of the substituted benzenes in cyclohexane. The solubility of the more polar molecules was limited in cyclohexane, and the spectra were obtained from saturated solutions.

The observed line positions in c.p.s. are given in Table I.

Analysis of Spectra.—An excellent analysis of the n.m.r. spectra of an A_2B_2 proton group has been given by Pople, Schneider, and Bernstein.[4] The essential features of this analysis were used in obtaining the coupling constants and relative chemical shifts from the observed spectra.

The relative chemical shift, $\nu_0\delta$, is defined as the difference in the chemical shift of the two proton groups.

$$\nu_0\delta = \nu_a - \nu_b$$

The coupling constants are defined in Fig. 1.

Pople, Schneider, and Bernstein have derived explicit expressions for the energy of each of the spin states except the S_0 states.[4] These energies are given in Fig. 2 with the observed A transitions. The spectra of p-bromoiodobenzene are given in Fig. 3 with assignment of the observed lines to the transitions.

From the frequency of transitions 1 and 3, the values of $\nu_0\delta$ and N may be obtained. The fourth order secular equation corresponding to the S_0 states may be expanded (1) as a function of K and L

$$(K + E_n)\{E_n^3 + NE_n^2 - [N^2/4 + (\nu_0\delta)^2]E_n - N^3/4\} -$$
$$L^2/4 [(\nu_0\delta)^2 + 3N^2/4 - 3E_n^2] = 0 \quad (1)$$

In which E_n are the energies of the S_0 spin states. Two of the energies of these states may be determined from the spectrum directly. Referring to the energy level diagram (Fig. 2), we note that

$$E_3 = {}^1/_2(\nu_3 - \nu_5)$$

and

$$E_4 = {}^1/_2(\nu_6 - \nu_7)$$

By substitution of the value of N and $\nu_0\delta$ previously obtained into (1) and successive substitution of E_3 and E_4, a pair of linear expressions are derived from which K and L may be obtained.

(4) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw–Hill Book Company, New York, N. Y., 1959, pp. 138–151.
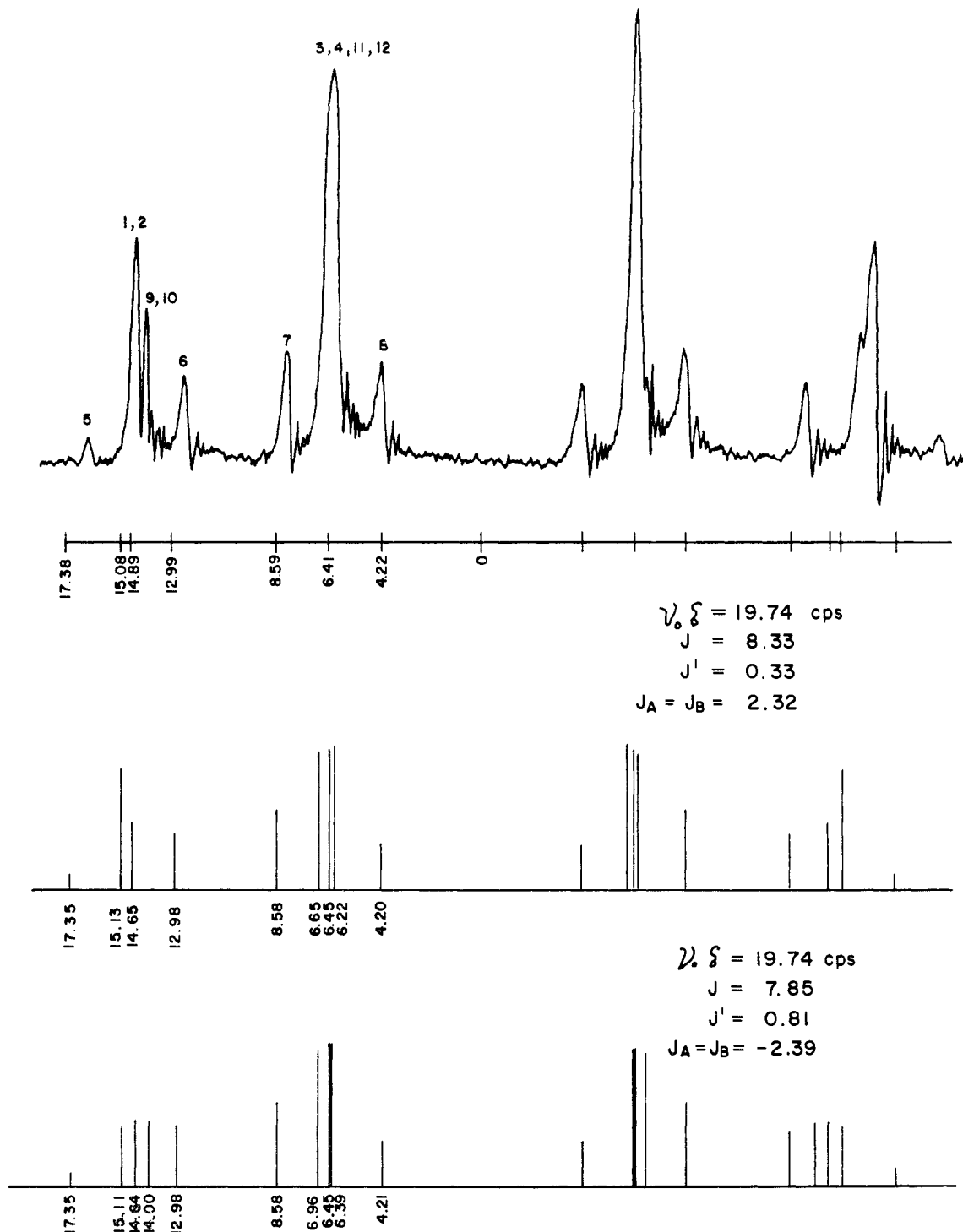
Fig. 3.—High resolution spectrum of p-bromoiodobenzene with assignment of A transitions. Frequency is in c.p.s. from the center of the spectrum. Two calculated spectra are given below the main spectrum.

Because of the uncertainty in the assignment of the observed transitions, the algebraic signs of E_3 and E_4 may not be determined. If both are assumed to have the same sign, no solution is obtained ($L^2 < 0$). Two values of K and L may be obtained, depending upon which energy is assumed negative. The calculated spectra[5] are given below the experimental spectrum in Fig. 3. Case I, in which K is positive, gives a better fit in this instance; however, in most of the observed spectra, lines (1, 9, 10, and 11) appeared as one broad peak. It was not possible to determine the value of M, since the transitions between asymmetric spin states could not be resolved.

(5) A program written at Mellon Institute and adapted by this Laboratory for use on an IBM 7090 computer was used for the calculation of these two spectra. See A. A. Bothner-By and C. Naar-Collin, *J. Am. Chem. Soc.*, **83**, 231 (1961).

The coupling constants for the p-disubstituted benzenes studied are given in Table II. In these calculations it was assumed that all coupling constants were of the same sign.

Discussions

In the interpretation of data on proton coupling constants in these substituted benzenes, two parameters appeared to be of significance—the type of π-molecular orbitals and the electronegativity of the atoms which are bonded to the aromatic ring. Each of these compounds has π-molecular orbitals which may be derived by a perturbation of one of the structures I–III.
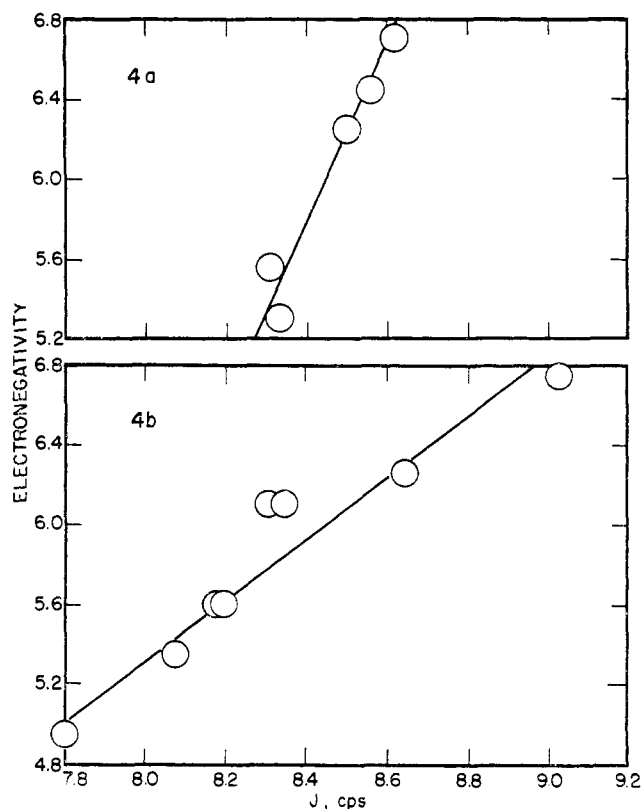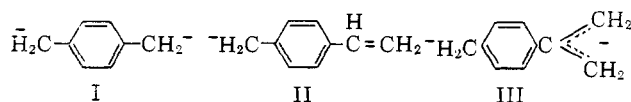
Fig. 4.—Relationship between *ortho* coupling constants and the sum of the electronegativity of atoms attached to the ring: (a) compounds of type I; (b) compounds of types II and III.

I   II   III

The classification of substituent groups is given in Table III.[6]

TABLE II

COUPLING CONSTANTS

Compound	J	J'	$\frac{1}{2}(J_A + J_B)$	$\nu_0\delta$
	Type I			
p-Chloroiodobenzene	8.31	0.31	2.38	32.24
p-Bromoiodobenzene	8.33	.33	2.32	19.74
p-Chlorophenol	8.62	.30	2.80	25.51
p-Bromophenol	8.56	.36	2.77	37.31
p-Chloroaniline	8.50	.34	2.67	23.05
	Type II			
p-Chlorotoluene	8.20	0.47	2.30	14.65
p-Bromotoluene	8.08	.40	2.15	21.37
p-Iodotoluene	7.80	.42	2.07	40.84
p-Chloroacetophenone	8.18	.43	2.23	27.15
p-Isopropylphenol	8.31	.41	2.45	16.20
	Type III			
p-Nitroanisole	9.03	0.23	2.88	65.02
p-Hydroxybenzoic acid	8.35	.29	2.38	60.68
p-Chloronitrobenzene	8.65	.29	2.49	41.51

The relationship between the observed coupling constants and the sum of the electronegativity[7] of the atoms attached to the carbons of the ring is shown in Fig. 4 and Fig. 5.

The range of values for the p-proton coupling constants was small, and no significant relationship was

(6) A similar classification of substituents has been given by H. H. Jaffé, *J. Am. Chem. Soc.*, **76**, 5843 (1954).

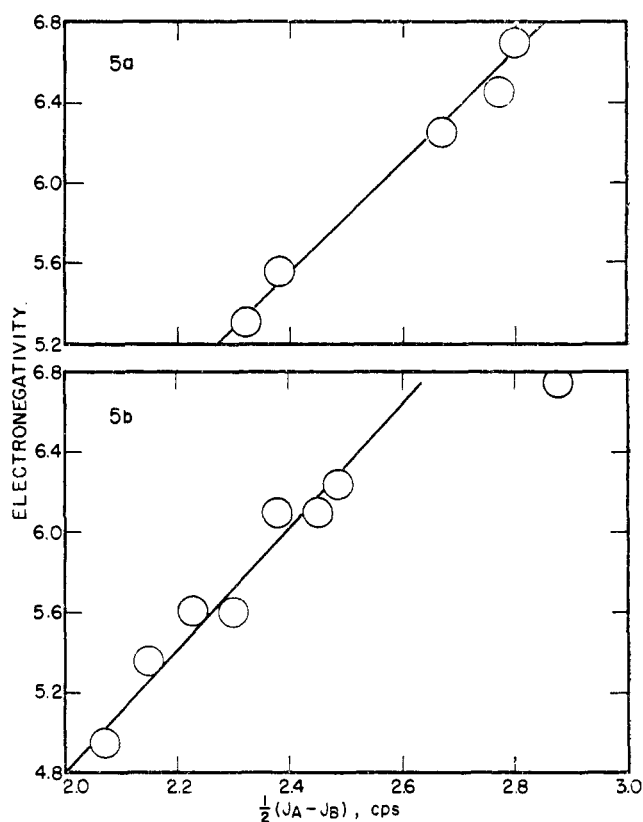(7) J. Bellugue and R. Daudel, *Rev. Sci.*, **84**, 541 (1946).

Fig. 5.—Relationship between the average *meta* coupling constants and the sum of the electronegativity of atoms attached to the ring: (a) compounds of type I; (b) compounds of types II and III.

noted between them and the electronegativities; however, it was found that within a given compound type the measured p-proton coupling constants were within the experimental error.

TABLE III

Group	—CH₃⁽⁻⁾	—CH=CH₂	$\overset{\textstyle CH_3}{\underset{\textstyle CH_3}{C}}$
	–Cl	–CH₃[a]	–NO₂
	–Br	–CH(CH₃)₂[a]	–COOH
	–I	–COCH₃	
	–OH		
	–OCH₃		

[a] Assuming hyperconjugation.

While a definite relationship appeared to exist between the proton–proton coupling constants and the electronegativities of the atoms adjacent to the ring, it is not clear whether the changes in proton coupling constants in these compounds are the result of changes in the σ-electronic system or changes in the π-orbitals. The range of the observed coupling constants is less than the total contribution of the π-electrons to the proton coupling constants estimated by McConnell.[3,8]

An attempt is now being made to correlate the observed data with a molecular orbital description of the π-electronic system.

(8) H. M. McConnell, *J. Chem. Phys.*, **30**, 126 (1959).