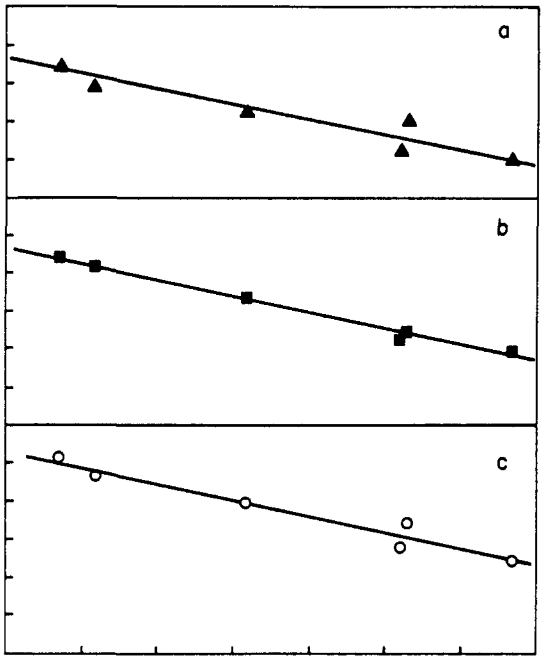
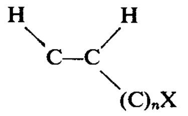


Figure 4. (a) Plot of calculated $J_{\mathrm{H^*D}}$ for type **4** compounds *vs.* calculated $J_{\mathrm{H^*A}}$ for the corresponding compounds. (b) Plot of $J_{\mathrm{H^*HC}}$ for type **3** compounds *vs.* corresponding $J_{\mathrm{H^*HA}}$ values. (c) Plot of $J_{\mathrm{H^*HB}}$ for type **2** compounds *vs.* corresponding $J_{\mathrm{H^*HA}}$ values. (See Table VII for structures **1–4**.)

the calculated values in the tables. A need for additional work in this area is indicated.

Most of the difficulties encountered with calculated substituent effects can be summarized as follows. The calculations generally yield a consistent pattern of results, in terms of the sign of substituent effects, for *cis* hydrogens, in systems which can be symbolized by structure I. In this generalized formula the symbol



I

$(C)_n$ represents a carbon chain of any type containing *n* carbons and connecting a *cis* HCCH moiety to an electronegative atom X (N, O, or F). For all the cases encountered in this study, and in a related study of substituted benzenes,[58] the signs of substituent effects computed for groups which contain these atoms fall into the pattern $n = 0(-)$, $n = 1(+)$, $n = 2(-)$, and $n = 3(+)$. This generalization holds for any of the carbon frameworks tested and is independent of the orientation of the $(C)_nX$ moiety. This suggests that an alternating, σ-inductive effect may be dominating the computed substitutent effects. The fact that the experimental results frequently disagree with the above patterns for $n > 0$ may imply that some important conjugation effects are not being treated adequately in the present calculations.

Summary and Conclusions

The theoretical method applied here is capable of reproducing several important experimental trends. These include the well-studied dependence upon the HCCH dihedral angle and the relationship to hybridization of the connecting carbons, as well as certain correlations between substituent effects in related types of molecules. However, difficulties have been encountered in reproducing experimental substituent effects in certain cases. Uncertainties associated with the molecular geometries employed in the calculations may account for some discrepancies.

Approximate Self-Consistent Molecular Orbital Theory of Nuclear Spin Coupling. V. Proton–Proton Coupling Constants in Substituted Benzenes[1a,b]

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Received December 1, 1969

Abstract: The SCF finite perturbation method is applied to the calculation of proton–proton coupling constants in 13 monosubstituted benzenes and 4 disubstituted benzenes. The Fermi contact mechanism is assumed and the INDO molecular orbital approximation is employed. Good agreement with experimental patterns is obtained for benzene and for some correlations of substituent effects in substituted benzenes. Additivity effects and the relationship to vicinal couplings in substituted ethylenes are discussed.

Experimental data on proton–proton constants (J_{HH}) in substituted benzenes abound in the chemical literature.[2,3] Because of the complex spin–spin splitting patterns in the proton spectra of monosubstituted benzenes, most of the earlier results were re-

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[1] (a) Research supported in part by a grant from the National Science Foundation; (b) papers I–IV in this series are given as ref 22–25; (c) Special NIH Fellow, on leave from the University of California, Davis; (d) Postgraduate Scholar of the National Research Council of Canada.

[2] (a) J. A. Pople, W. G. Schneider, and H. J. Berstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 258–265; (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1967, pp 770–774.

[3] A. A. Bothner-By, *Advan. Magn. Resonance*, 1, 195 (1965).

ported on di-, tri-, or tetrasubstituted compounds. This situation tended to obscure the potentially interesting roles of individual substituents in influencing the values of the coupling constants. More recently, the availability of instruments of higher resolution and computer techniques for the analysis of complex high-resolution nmr spectra[4] have made possible the complete analysis of the proton spectra of monosubstituted benzenes. Castellano and coworkers[5-9] and others[10-14] have published extensive sets of reliable J_{HH} values for these systems, and have described interesting correlations with the electronegativity of the substituent atoms.

Some recent attempts at calculating J_{HH} values in benzene[15,16] have been based on the Pople–Santry[17] treatment of Ramsey's second-order perturbation formula for the Fermi contact coupling.[18,19] There have apparently been no successful attempts to account theoretically for substituent effects on J_{HH} in substituted benzenes.

The present paper, devoted to J_{HH} in substituted benzenes, is the fifth in a series exploring a new theory of spin–spin coupling reported recently from this laboratory.[19-25] This theory employs a finite-perturbation approach which avoids the explicit consideration of excited states characteristic of the Ramsey formulation and the associated cancellation problems, without involving the average ΔE approximation.[17,18]

In its present form it pivots on the calculation of an unrestricted MO wave function in the INDO approximation,[26] under the influence of a Fermi contact perturbation h_B of the form given in eq 1. Within this

$$h_B = (8\pi/3)\beta\mu_B s_B^2(0) \qquad (1)$$

framework, a proton–proton spin–spin coupling constant is then given by

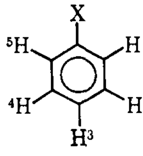
$$J_{H_AH_B} = h(4\beta/3)^2\gamma_H^2 s_A^2(0) s_B^2(0)\left[\frac{\partial}{\partial h_B}\rho_{s_As_A}(h_B)\right]_{h_B=0} \qquad (2)$$

where γ_H is the magnetogyric ratio of a proton, β is the Bohr magneton, $s_A^2(0)$ is the density of the hydrogen 1s orbital of atom A at its nucleus, and $\rho_{s_As_A}$ is the diagonal spin density matrix element corresponding to that orbital.

Results

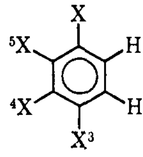
All calculations were based on eq 2 and used the standard geometrical model employed in earlier investigations.[21-27] Details of the computational methods have been described previously.[20,21]

Table I presents results on the calculation of the various J_{HH} values between ring protons for a variety of monosubstituted benzenes (**1**), with the corresponding experimental data. Except where specifically noted, planar conformations (excepting hydrogens in OCH_3) were chosen for compounds with potentially conjugating groups. In cases without a symmetry plane perpendicular to the plane of the benzene ring, computed values of J_{12} and J_{45} were not equal. In such cases, the values reported in Table I are the appropriate averages. For the calculation on phenyllithium, a monomeric structure with a C–Li bond length of 2.1 Å was arbitrarily chosen. As the actual structure of the solution species studied experimentally may be substantially different from this, the calculated results may not correspond closely with the experimental case and can only be interpreted as qualitatively representing the influence of an effectively electropositive substituent.



1

Table II presents calculated and experimental J_{HH} values for a few disubstituted benzenes (**2**). Again, planar geometries were used.



2

Table III summarizes calculated J_{HH} values for structurally related substituted benzenes and ethylenes.

Discussion

The results given in Table I show some patterns of general agreement between the computed and experimental J_{HH} values, as well as some conspicuous discrepancies. Considering the couplings within individual molecules, it is seen that the correct experimental order $J_{ortho} > J_{meta} > J_{para}$ is preserved in the calculations, as had been reported earlier for benzene,[19,21] for all but one of such pairs of protons. Phenyllithium gives the only exception to this order, *i.e.*, $J_{14} > J_{24}$; it also gives the only case of a negative computed J_{HH} value,

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(4) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(5) S. Castellano and C. Sun, *J. Amer. Chem. Soc.*, **88**, 4741 (1966).

(6) S. Castellano, R. Kostelnik, and C. Sun, *Tetrahedron Lett.*, **46**, 4635 (1967).

(7) S. Castellano, C. Sun, and R. Kostelnik, *ibid.*, **51**, 5205 (1967).

(8) S. Castellano and J. Lorenc, *J. Phys. Chem.*, **69**, 3552 (1965).

(9) H. Gunther and S. Castellano, *Ber. Bunsenges. Phys. Chem.*, **70**, 913 (1966).

(10) M. P. Williamson, R. J. Kostelnik, and S. M. Castellano, *J. Chem. Phys.*, **49**, 2218 (1968).

(11) K. Hayamizu and O. Yamamoto, *J. Mol. Spectrosc.*, **25**, 422 (1968).

(12) R. E. Mayo and J. H. Goldstein, *Mol. Phys.*, **10**, 301 (1966).

(13) J. M. Read, Jr., and J. H. Goldstein, *J. Mol. Spectrosc.*, **23**, 179 (1967).

(14) J. M. Read, Jr., R. E. Mayo, and J. H. Goldstein, *ibid.*, **21**, 235 (1966).

(15) J. N. Murrell and V. M. S. Gil, *Theor. Chim. Acta*, **4**, 114 (1966).

(16) S. Polezzo, P. Cremaschi, and M. Simonetta, *Chem. Phys. Lett.*, **1**, 357 (1967).

(17) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1963).

(18) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

(19) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *Chem. Phys. Lett.*, **1**, 465 (1967).

(20) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960 (1968).

(21) J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *ibid.*, **49**, 2965 (1968).

(22) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 1 (1970).

(23) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 11 (1970).

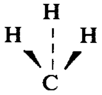
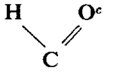
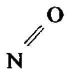
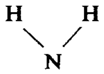
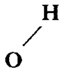
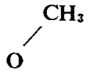
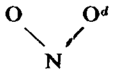
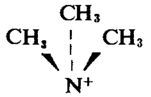
(24) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 4151 (1970).

(25) G. E. Maciel, J. W. McIver, Jr., N. S. Ostlund, and J. A. Pople, *ibid.*, **92**, 4497 (1970).

(26) J. A. Pople, D. D. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, **47**, 2026 (1967).

(27) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

Table I. J_{HH} Values for Monosubstituted Benzenes (1)

Substituent	Calculated[a,b]						Experimental						
X	J_{12}	J_{13}	J_{14}	J_{15}	J_{23}	J_{24}	J_{12}	J_{13}	J_{14}	J_{15}	J_{25}	J_{24}	Ref
Li	6.29 (−1.86)	3.49 (1.36)	2.56 (1.41)	−1.73 (−3.86)	8.94 (0.79)	1.36 (−0.77)	6.73 (−0.81)	1.54 (0.17)	0.77 (0.08)	0.74 (−0.63)	7.42 (−0.12)	1.29 (−0.08)	*e*
H	8.15 (0.0)	2.13 (0.0)	1.15 (0.0)	2.13 (0.0)	8.15 (0.0)	2.13 (0.0)	7.56 (0.0)	1.38 (0.0)	0.68 (0.0)	1.38 (0.0)	7.56 (0.0)	1.38 (0.0)	
	7.78 (−0.37)	2.27 (0.14)	1.27 (0.12)	1.89 (−0.24)	8.30 (0.15)	2.02 (−0.11)	7.64 (0.10)	1.25 (−0.12)	0.60 (−0.09)	1.87 (0.50)	7.53 (−0.01)	1.51 (0.14)	*g*
	7.68 (−0.47)	2.13 (0.00)	1.37 (0.22)	1.70 (−0.43)	8.27 (0.12)	1.91 (−0.22)	7.71 (0.17)	1.35 (−0.02)	0.62 (−0.07)	1.75 (0.38)	7.48 (−0.06)	1.25 (−0.12)	*e*
	7.78 (−0.37)	2.26 (0.13)	1.29 (0.14)	1.87 (−0.26)	8.27 (0.12)	1.97 (−0.16)	7.72 (0.16)	1.32 (−0.06)	0.64 (−0.04)	1.77 (0.39)	7.61 (0.05)	1.37 (−0.01)	*h*
	7.73 (−0.42)	2.21 (0.08)	1.29 (0.14)	1.84 (−0.29)	8.21 (0.06)	1.91 (−0.22)	7.79 (0.25)	1.28 (−0.09)	0.63 (−0.06)	1.76 (0.39)	7.68 (0.14)	1.30 (−0.07)	*i*
	7.95 (−0.19)	2.36 (0.23)	0.90 (−0.25)	2.78 (0.65)	7.86 (−0.29)	2.32 (0.19)	7.91 (0.35)	1.28 (−0.10)	0.56 (−0.12)	1.97 (0.59)	7.41 (−0.15)	1.36 (−0.02)	*j*
	8.37 (0.22)	2.04 (−0.09)	1.03 (−0.12)	2.64 (0.51)	8.15 (0.00)	2.25 (0.12)	8.02 (0.48)	1.11 (−0.26)	0.47 (−0.22)	2.53 (1.16)	7.39 (−0.15)	1.60 (0.23)	*j*
	8.69 (0.54)	1.87 (−0.26)	0.92 (−0.23)	2.92 (0.79)	7.97 (−0.18)	2.44 (0.31)	8.17 (0.63)	1.09 (−0.28)	0.49 (−0.20)	2.71 (1.34)	7.40 (−0.14)	1.74 (0.37)	*j*
	8.83 (0.68)	1.96 (−0.17)	0.94 (−0.21)	2.96 (0.83)	7.96 (−0.19)	2.49 (0.36)	8.30 (0.76)	1.03 (−0.34)	0.44 (−0.25)	2.74 (1.37)	7.36 (−0.18)	1.76 (0.39)	*j*
	8.02 (−0.13)	1.81 (−0.32)	1.01 (−0.14)	2.53 (0.40)	7.79 (−0.36)	2.20 (0.07)	8.36 (0.82)	1.18 (−0.19)	0.55 (−0.14)	2.40 (1.03)	7.47 (−0.07)	1.48 (0.11)	*j*
F	9.04 (0.89)	1.69 (−0.44)	0.82 (−0.33)	3.26 (1.13)	7.75 (−0.40)	2.62 (0.49)	8.36 (0.82)	1.07 (−0.30)	0.43 (−0.26)	2.74 (1.37)	7.47 (−0.07)	1.82 (0.45)	*k*
	8.45 (0.30)	1.66 (−0.47)	0.82 (−0.33)	3.22 (1.09)	7.18 (−0.97)	2.20 (0.07)	8.55 (1.01)	0.92 (−0.45)	0.48 (−0.21)	3.05 (1.68)	7.46 (−0.08)	1.70 (0.33)	*j*

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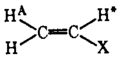
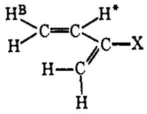
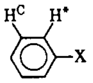
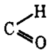
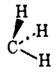
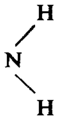
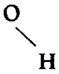
[a] Values in Hz. [b] Values in parentheses are the differences between particular J_{HH} values and the corresponding couplings in benzene. Calculated J_{HH} values are referenced to calculated benzene results; experimental J_{HH} values are referenced to experimental J_{HH} data. [c] For a molecular geometry with the HCO plane perpendicular to the benzene ring, the values 7.56, 2.28, 1.32, 1.73, 8.25, and 1.79 were obtained for J_{12}, J_{13}, J_{14}, J_{15}, J_{23}, and J_{24}, respectively. [d] For a molecular geometry with the NO_2 plane perpendicular to the benzene ring, the values 7.92, 1.89, 0.99, and 2.44 were obtained for J_{12}, J_{13}, J_{14}, and J_{15}, respectively. [e] S. Castellano, private communication. [f] Reference 14. [g] Reference 10. [h] Reference 8. [i] Reference 11. [j] Reference 7. [k] Reference 6.

Table II. Additivity Relationship in J_{HH} Values for Some Disubstituted Benzenes (2)

Substituents				Deviations from additivity in calculated values[a]							Deviations from additivity in experimental values[b]							
X	X^6	X^4	X^3	ΔJ_{12}	ΔJ_{13}	ΔJ_{14}	ΔJ_{15}	ΔJ_{23}	ΔJ_{24}	ΔJ_{25}	ΔJ_{12}	ΔJ_{13}	ΔJ_{14}	ΔJ_{15}	ΔJ_{23}	ΔJ_{24}	ΔJ_{25}	Ref
F	F	H	H	0.01 (8.64)[c]	−0.01 (2.17)	0.03 (0.52)		0.08 (7.43)	−0.01 (2.17)		0.04	0.12	0.06		0.24	0.12		f
F	H	F	H	0.01 (8.64)	0.10 (1.35)		−0.01 (2.81)	0.01 (8.64)		0.0 (0.49)	0.13	0.10		0.02	0.13		0.15	g
F	H	H	F	−0.01 (9.91)		0.08 (0.57)	−0.02 (3.73)		−0.02 (3.73)	0.08 (0.57)								
NO_2	H	H	NH_2	−0.02 (8.22)[d]		−0.04 (0.85)	0.04 (2.69)		0.03 (2.74)	−0.04 (0.85)	0.2		0.0	−0.3[c] or 0		0.0[e] or −0.3	0.0	h

[a] Computed from eq 3 using calculated J_{HH} values from Table I. [b] Computed from eq 3 using experimental J_{HH} values from Table I. [c] Values in parentheses are the J_{HH} values calculated for the disubstituted benzenes directly from eq 2. [d] Planar geometry employed in the calculation. [e] Experimental results do not distinguish between J_{15} and J_{24}. [f] R. Abraham, private communication. [g] D. B. MacDonald, *Chem. Commun.*, 686 (1967). [h] Reference 3.

Table III. Calculated J_{HH} Values in Three Systems[a]

			
X	$J_{H^*H^A}$[b]	$J_{H^*H^B}$[b]	$J_{H^*H^C}$
Li	23.03	8.24	6.29
	10.68	9.21	7.68
	9.21	9.39	7.78
H	9.31	9.69	8.15
	7.19	9.97	8.37
	5.20	10.32	8.69
F	4.74	10.56	9.04

[a] Values in Hz. [b] Taken from ref 25.

namely J_{15}. All other computed J_{HH} values are positive for all the compounds, in agreement with the experimental results.

The general trends for a given type of computed coupling constant, J_{ij}, for compounds with different substituents reflect some of the known experimental features. Castellano and coworkers[5] have noted tendencies toward larger values of J_{12} and J_{15} and toward smaller values of J_{13} and J_{14} with increasing electronegativity of the substituent atom attached to the ring. These trends were discussed as possible evidence for primarily σ-type spin coupling mechanisms. The computed values of Table I are suggestive of similar patterns, although there are some serious deviations from the experimental ordering.

Among the *meta* coupling constants (J_{13}, J_{15}, and J_{24}), the experimental results for all the substituted benzenes except benzaldehyde place J_{24} intermediate in value between J_{13} and J_{15}. This is true of the computed values as well, except for nitrosobenzene where the differences are small; however, for compounds in the upper portion of the table, the order of J_{13} and J_{15} is in some cases reversed from the experimental one.

If the *experimental* values of J_{12}, J_{13}, J_{14}, and J_{15} for C_6H_5X are arranged in order of decreasing or increasing algebraic value it is found that with each series the value for X = Li lies at one extreme and the one for X = F or $N(CH_3)_3^+$ lies at the other. In the ordering of each series, a closely grouped set of J_{HH} values corresponding to X = CH_3, C≡CH, CN, and CHO is separated from the Li position only by the entry for X = H. The same description applies to the computed J_{HH} values except that the CH_3, C≡CH, CN, CHO set (carbon substituent set) is not separated from Li in the ordering. Thus, aside from the reversed positions of values for X = H and X = a carbon substituent, this represents a pattern of overall agreement between experimental trends in substituent effects and the influence on computed J_{HH} values of substituent perturbations. Among the experimental results, only for J_{13} is this stated pattern violated at all; in this case the value for X = NO occurs

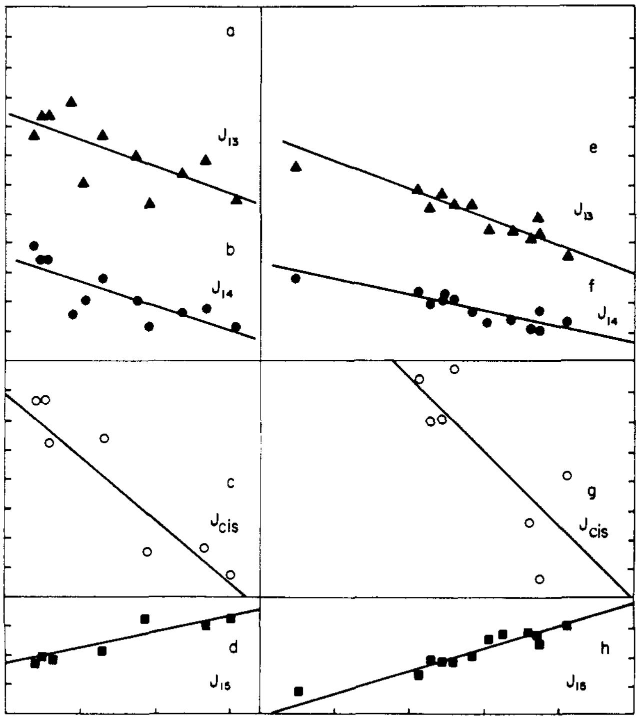


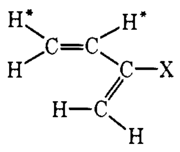
Figure 1. (a) Plot of calculated J_{13} *vs.* calculated J_{12} for monosubstituted benzenes. (b) Plot of calculated J_{14} *vs.* calculated J_{12} for monosubstituted benzenes. (c) Plot of calculated $^3J_{cis}$ for $CH_2{=}CHX$ compounds[25] *vs.* calculated J_{12} for the corresponding monosubstituted benzenes. (d) Plot of calculated J_{15} *vs.* calculated J_{12} for monosubstituted benzenes. (e) Plot of experimental J_{13} *vs.* experimental J_{12} for monosubstituted benzenes. (f) Plot of experimental J_{14} *vs.* experimental J_{12} for monosubstituted benzenes. (g) Plot of experimental $^3J_{cis}$ for $CH_2{=}CHX$ compounds[25] *vs.* experimental J_{12} for the corresponding monosubstituted benzenes. (h) Plot of experimental J_{15} *vs.* experimental J_{12} for monosubstituted benzenes. Points corresponding to lithium as the substituent are not included in (a), (b), (c), or (d); such points are included in (e), (f), (g), and (h), but were not employed in the least-squares analyses.

within the carbon substituent set. This exception also occurs in the computed results. Within experimental data for the carbon-substituent set, the internal ordering varies among the different J_{1j} values and is not reproduced by the calculations; however, the differences for a given J_{1j} type are small for both the computed and measured values. In the ordering of either the experimental *or* computed J_{1j} values for a given j, the entries at the opposite end from the Li extreme are those with N, O, or F atoms attached directly to the ring. The only breaks in this pattern are the computed values for X = H, which as noted above are out of order with the set CH_3, $C{\equiv}CH$, CN, CHO, and the J_{13} case noted above for both calculated and experimental values corresponding to X = NO.

Another area of qualitative agreement is found in the relationships among the computed values of the various J_{HH} values in substituted benzenes and in the analogous substituted ethylenes. The plots in Figures 1a, 1b, 1c, and 1d summarize some of these relationships, and bear substantial similarity to the plots relating the corresponding experimental data, given in Figures 1e, 1f, 1g, and 1h. Even in the presence of some serious reversals with respect to the experimental orders *within a given J_{1j} type*, the computed benzene J_{HH} values of different types relate satisfactorily *to each other* and to the *cis* vicinal couplings in the corresponding substituted ethylenes. The latter have previously been shown to be related properly to the corresponding *trans*-vicinal and geminal spin-spin couplings and to the average vicinal couplings in substituted ethanes.[25] Thus, the present method appears to present a rather consistent pattern of *related* substituent effects which is analogous with the experimental pattern, even though the method is less successful in accounting for strict experimental orders.

The plots of Figures 1a, 1b, and 1d are in general agreement with the qualitative conclusions obtained by Gil[28] from a simple application of Pople–Santry theory.[17] Gil concluded that J_{12} and J_{15} should vary in a similar manner with substituents, and that J_{13} and J_{14} should experience similar substituent effects.

In spite of the promising patterns described above, Table I provides many examples in which *individual* substituent effects (rather than general correlations) are not accounted for by the calculations. These limitations are particularly evident in the relationship between X = H and X = a carbon substituent, *e.g.*, X = CH_3, and with substituents with nitrogen attached directly to the ring. In seeking the source of these failures it is relevant to note that the order of the calculated substituent effects is apparently not due primarily to the presence of the benzene ring. Thus, the ordering of the calculated J_{12} values is exactly the same as that obtained for the structurally related vicinal ($^3J_{H^*H^*}$) values in the three series of compounds I, II, and III.[25] This is exactly opposite to the order that is obtained for the calculated *cis* vicinal coupling constants in vinyl compounds, IV.[25] Some of the relevant results are summarized in Table III. The associated alternation of sign of substituent effects has been discussed previously for systems of the type CH^3-CH^2-CH^1-X,[25,29,30] where experimental evidence shows that the dependence of $^3J_{23}$ upon the electronegativity of X is opposite in sign from that of $^3J_{12}$. Furthermore, the relative sensitivities of computed values of $^3J_{12}$ for *cis* vinyl hydrogens and J_{12} for substituted benzenes to the electronegativity of X are in qualitative agreement with the value $-{}^1/_{16}$ estimated from experimental data by Castellano and Kostelnik for the ratio $(\partial^3J_{23}/\partial\chi_x)(\partial^3J_{12}/\partial\chi_x)$ in CH^3-CH^2-CH^1-X systems. This is concluded from the least-squares slope in Figure 1c. Thus, the calculations roughly reproduce not only the correlations between the substituent effect trends of the various couplings within substituted benzenes, but also the correlations of substituent effects in the structurally related ethylene systems.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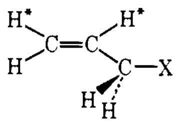
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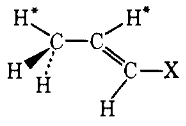
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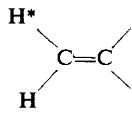
IV

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(28) V. M. S. Gil, *Mol. Phys.*, 15, 645 (1968).
(29) T. Schaefer, *Can. J. Chem.*, 40, 1 (1962).
(30) S. Castellano and R. Kostelnik, *J. Amer. Chem. Soc.*, 90, 141 (1968).

In searching for an explanation to the disagreements which are apparent in Table I, it is reasonable to consider geometrical or conformational influences. The calculated values were obtained on the basis of conformations shown in the table (regular type indicates a bond in the plane of the ring). However, some of the worst cases of disagreement occur with compounds for which either questions of substituent conformation do not arise (*e.g.*, benzene, phenylacetylene, benzonitrile) or conformational effects on the computed coupling constants are found to be relatively small, *e.g.*, toluene, benzaldehyde, and nitrobenzene. The small dependence of computed J_{HH} values on substituent orientation for the last two compounds implies a minor role of the π-electron system in determining these *calculated* substituent effects. This implication is consistent with the alternation pattern noted above and in a related study of substituted ethanes and ethylenes,[25] in that they both suggest the dominance of an alternating σ-inductive mechanism in the *computed* substituent effects. Barfield and Chakrabarti have indicated from examining the results of qualitative MO and previous theoretical results that J_{15} experiences substituent effects that are manifested in the σ framework.[31] In the present work the most serious cases of disagreement between the signs of calculated and experimental substituent effects may correspond to situations in which conjugation effects that are important in determining experimental couplings are overshadowed by the inductive effect in the calculations.

Other possible sources of error lie in the theoretical method itself at the level of approximation embodied in eq 2. One could question the reliability in general of theories at this level, or the reliabilities of the factors $s_{\mathrm{A}}^2(0)s_{\mathrm{B}}^2(0)$ and

$$\left[\frac{\partial}{\partial h_{\mathrm{B}}}\rho_{s_{\mathrm{A}}s_{\mathrm{A}}}(h_{\mathrm{B}})\right]_{h_{\mathrm{B}}=0}$$

used in this particular application. The latter factor is obtained from the unrestricted INDO wave functions. The former factor is taken as a constant which was obtained earlier on the basis of a least-squares fit with experimental results.[21]

Grant and Litchman[32] considered this same factor in an expression based on a simple valence-bond treatment of J_{CH} for substituted methanes. They suggested that variations in this factor may play a dominant role in the dependence of J_{CH} on the type of substitution. This was investigated for the $s^2(0)$ of carbon *via* the concepts of screening of the nuclear charge (effective nuclear charge) on the assumption that Slater's screening rules[33] could be applied to fractional electron densities.[34] In the first two papers in this series, we explored the same general approach for the $s^2(0)$ values of both nuclei in calculations of J_{CH} and J_{CC}.[22,23] The results given in those papers demonstrate that variation of these coupling constants with structural changes are dominated by changes in the factor

$$\left[\frac{\partial}{\partial h_{\mathrm{B}}}\rho_{s_{\mathrm{A}}s_{\mathrm{A}}}(h_{\mathrm{B}})\right]_{h_{\mathrm{B}}=0}$$

However, qualitative arguments using the above approach for guidelines suggested that variations of the $s^2(0)$ values might warrant significant corrections in the calculation of J_{CH}. We have attempted an adjustment of this type in calculations of geminal J_{HH}, where it was found not to give substantial improvement.[24] Similarly, the application of this adjustment here gave no general improvement, although certain conspicuous discrepancies were removed; *e.g.*, the incorrect sign of the $\mathrm{NO_2}$ substituent effect on J_{12} was corrected.

Additivity relationships among J_{HH} values in substituted benzenes have received some experimental attention.[11,35] On the assumption that substituent effects on J_{HH} values, with respect to benzene values, are additive, the expression given by Hayamizu and Yamamoto[11] can be used to predict the J_{HH} values in a disubstituted benzene from data on the corresponding monosubstituted benzenes. This expression is given by

$$J_{ij}^{n-x,m-y} = J_{ij}^{n-x} + J_{ij}^{m-y} - J_{ij}^{\mathrm{benzene}} \qquad (3)$$

where $J_{ij}^{n-x,m-y}$ is the value of the coupling constant for protons at positions i and j in a disubstituted benzene in which substituent x occupies position n and substituent y occupies position m, J_{ij}^{n-x} is the coupling between the protons at positions i and j in a monosubstituted benzene with substituent x occupying position n, and $J_{ij}^{\mathrm{benzene}}$ is the J_{ij} coupling in benzene itself. Equation 3 was applied here to the prediction of J_{HH} values of *p*-nitroaniline and *o*-, *m*-, and *p*-difluorobenzene from the J_{HH} values for fluorobenzene, aniline, and nitrobenzene given in Table I. The differences (ΔJ_{ij}) between the values computed directly from eq 2 and those predicted by eq 3 are given in Table II. It is seen that these deviations from the additivity relationship embodied in eq 3 are all small ($\Delta J_{ij} \leq 0.10$). This is in general agreement with the experimental results reported for a wide variety of disubstituted benzenes[14] (which did not include *p*-difluorobenzene). Hayamizu and Yamamoto considered the generally additive nature of the coupling constants, together with the correlations with electronegativity, as evidence for the predominant importance of the σ-electron framework in the coupling mechanism, as the π-electron structure was not expected to display a response suggesting a simple superposition of two substituent effects.[11] Table II includes cases where the deviations from additivity in experimental values are many times larger than the corresponding deviations from additivity in calculated values. This may also reflect a failure of the calculated results to give proper weight to conjugative effects which are experimentally important in certain cases. Thus, the smaller calculated deviations from additivity may reflect a dominant inductive effect in the calculations.

Summary

The computational method in its present form is capable of accounting for many of the dominant patterns of hydrogen–hydrogen coupling constants in benzene and substituted benzenes. Substituent effects are accounted for to the extent of reproducing empirical correlations among the couplings between individual proton pairs within the substituted benzenes or related

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(31) M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

(32) D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965).

(33) J. C. Slater, *Phys. Rev.*, **36**, 57 (1930).

(34) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).

(35) P. F. Cox, *J. Amer. Chem. Soc.*, **85**, 380 (1963).

compounds. Uncertainties in substituent conformations connot account for the discrepancies noted in comparing calculated with experimental couplings directly. A simple adjustment of the $s^2(0)$ values based upon Slater's rules does not give substantial improvement. The present method predicts a rather precise additivity relationship for substituent effects on the couplings, in general agreement with relevant experimental results

Oxygen-17 and Carbon-13 σ–π Parameters of the Carbonyl Group Calculated Using Localized σ Bonds

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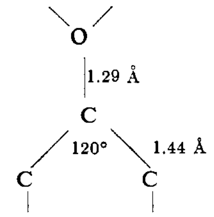
Abstract: σ–π polarization parameters for ^{17}O and ^{13}C were calculated semiempirically for the carbonyl group in the π fragment $(>C)_2C{=}O$. Three models were treated: model I with sp hybridization on oxygen, model II with sp^2 hybridization on oxygen, and model III with sp^2 hybridization on oxygen and a polarity parameter for the C–O bond. The method used was that of Melchior, in which localized σ bonds are constructed between each pair of atoms, each such bond being orthogonal to all others in the set. The excitation energies needed to evaluate the elements of the Q matrix were treated as parameters. However, the values of the intrabond excitation energies giving the best fit of calculated and "experimental" Q values were close to energies calculated for the corresponding bonds in small molecules. Experimental Q values were derived from the observed proton, ^{17}O, and ^{13}C hyperfine splittings in the *p*-benzosemiquinone radical. The following ranges of values were found for the elements of the $Q(^{17}O)$ and $Q(^{13}C)$ matrices: $Q_{OO}{}^{O} = 59 \pm 5$, $Q_{cross}{}^{O} = -7 \pm 1.9$, $Q_{CC}{}^{O} = -21 \pm 3.4$, $Q_{CC}{}^{C} = 44 \pm 5$, $Q_{cross}{}^{C} = 6.2 \pm 0.5$, and $Q_{OO}{}^{C} = -17.8 \pm 2$ G. It was found that, as Melchior predicts in general, the above values are relatively insensitive to the details of the σ-bonding scheme. The σ–π polarization parameters obtained for ^{17}O and ^{13}C compare well with those derived by other methods.

In π radicals the interaction between σ and π electrons is the physical basis for the interpretation of experimental hyperfine splitting constants in terms of the distribution of the unpaired electron in the π system. σ–π interaction constants for organic radicals have been estimated theoretically by a number of methods of varying sophistication and with varying success. A general theory for any atom in a π system has been presented by McLachlan, Dearman, and Lefevre,[2a] and rederived in a simpler fashion by Henning.[2b] The application of the theory to a particular molecular fragment requires some choice to be made for the molecular orbitals involved. In a few cases it has been possible to use the results of theoretical calculations on small molecules related to the fragment under consideration. More often a reasonable model system is used consisting of the usual LCAO π system and some choice of interatomic hybrids for the σ system. Recently in an important paper, Melchior[3] has shown that the neglect of overlap between the localized molecular orbitals of the basic σ set "leads to an artificial sensitivity of $Q_{AA}{}^{A}$ to σ-bonding details." This significant finding has encouraged us to reexamine the σ–π parameters for the carbonyl group, for which ^{13}C and ^{17}O hyperfine splittings have recently been observed in a large number of radicals.[4,5] In the present paper we derive values for the σ–π parameters of ^{13}C and ^{17}O in the fragment



which occurs in quinones. We use Melchior's method to construct the σ bonding and antibonding orbitals. All overlap integrals are included and all one-, two-, three-, and four-center exchange integrals are taken into account. Calculations were carried out for sp and sp^2 hybridization on oxygen, and also with a polarity parameter for the C–O bond.

The results compare favorably with those obtained by other methods,[5,6] and have the advantage that the various contributions to each σ–π parameter can be related to localized bonds, which are chemically easier to visualize than the molecular orbitals derived from SCF or CI calculations. Perhaps the most significant result is that, as Melchior predicts, the values found for the parameters are relatively insensitive to the details

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(1) (a) Technion—Israel Institute of Technology; (b) Weizmann Institute of Science.

(2) (a) A. D. McLachlan, H. H. Dearman, and R. Lefevre, *J. Chem. Phys.*, **33**, 65 (1960); (b) J. C. M. Henning, *ibid.*, **44**, 2139 (1966).

(3) M. T. Melchior, *ibid.*, **50**, 511 (1969).

(4) K. D. Sales, *Advan. Free Radical Chem.*, **3**, 139 (1969).

(5) (a) M. Broze and Z. Luz, *J. Chem. Phys.*, **51**, 738 (1969); (b) M. Broze, Z. Luz, and B. L. Silver, *ibid.*, **46**, 4891 (1967).

(6) M. R. Das and G. K. Fraenkel, *ibid.*, **42**, 1350 (1965).