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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. II. Spin Densities in Paramagnetic Species[1a]

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Abstract: A recent version of approximate self-consistent molecular orbital theory (intermediate neglect of differential overlap or INDO) is used to calculate electron spin density distributions and nuclear hyperfine constants in a number of paramagnetic organic radicals and ions. It is found that calculated hyperfine constants are in reasonable agreement with experimental values in most cases. Since all valence electrons are handled explicitly, the method is not restricted to π-electron systems.

This series of papers[2] is concerned with the application of approximate self-consistent-field (SCF) molecular orbital (MO) theory to the electronic structure of organic molecules. Approximate schemes under consideration are based on the Hartree–Fock–Roothaan equations for molecular orbitals taken as linear combinations of atomic orbitals (LCAO),[3] with approximations introduced in the calculation of atomic and molecular integrals entering the matrix elements of the Hartree–Fock Hamiltonian operator. The various acceptable levels of approximation have been introduced and discussed in related series of papers[4,5] (for a review see ref 6). Calculations have been reported with complete neglect of differential overlap[4] (CNDO) and intermediate neglect of differential overlap[5] (INDO), and these methods have been tested extensively by calculating geometries and the electric dipole moments of a variety of polyatomic molecules.[2,4,5]

The preceding paper in this series[2] focused on the electronic charge distribution of selected organic molecules, and calculations on the CNDO level were found to give a satisfactory account of trends in electric dipole moments of diamagnetic organic molecules. The study reported herein is concerned with paramagnetic organic molecules, *e.g.*, free radicals, radical cations, and radical anions. Here in addition to the *total* electronic charge distribution, which is the *sum* of the density of α and β electrons at any point in the system, it is possible to study the *unpaired* electron distribution, known as the spin density, which is essentially the *difference* in α-electron density and β-electron density at any point in the system.

The spin density at or near any magnetic nuclei in a paramagnetic molecule is related to the hyperfine interaction between electron and nuclear magnetic moments and is measured experimentally by the hyperfine coupling constants obtained from the electron spin resonance (esr) spectrum. In an LCAO theory, the isotropic (orientationally averaged) part of the hyperfine coupling constants of a given magnetic nucleus reflects the unpaired electron population of s atomic orbitals centered on the nucleus, and the anisotropic part of the hyperfine constants reflects the unpaired electron

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[2] J. A. Pople and M. Gordon, *J. Am. Chem. Soc.*, 89, 4253 (1967).

[3] C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

[4] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, 43, 3129 (1965); J. A. Pople and G. A. Segal, *ibid.*, 43, S136 (1965); 44, 3289 (1966); D. P. Santry and G. A. Segal, *ibid.*, 47, 158 (1967).

[5] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, 47, 2026 (1967).

[6] J. A. Pople, D. L. Beveridge, and N. S. Ostlund, *Intern. J. Quant. Chem.*, in press.

population of p or d orbitals of the atom. Since there are generally several magnetic nuclei in a paramagnetic organic molecule, it is possible to determine experimentally the spin density at several points in the system.

The aim of this paper is to examine whether the INDO approximate SCF–MO theory is capable of calculating the spin density distribution of an organic molecule in a satisfactory manner. Most previous work in this area has been concerned with π-electron radicals and radical ions where the σ electrons are not all handled explicitly. The INDO method, on the other hand, deals with all valence electrons on the same basis and can handle all types of radicals within the same framework. Satisfactory results in a study of this sort would indicate that approximate SCF–MO calculations will be useful in predicting magnitudes *and signs* of hyperfine coupling constants, and in interpreting known hyperfine coupling constants in terms of electronic structure by molecular orbital theory.

Method

The pertinent details of the methods employed in the approximate SCF–MO calculation of isotropic hyperfine coupling constants are most conveniently considered in two categories: (a) the calculation of the molecular electronic wave function and (b) the calculation of isotropic hyperfine coupling constants from this wave function.

The special considerations involved in calculating single determinant MO electronic wave functions for paramagnetic (and thus open shell) systems are enumerated in detail in ref 5. To accommodate negative as well as positive spin densities, one must use a spin-unrestricted orbital wave function with different orbitals for different spins. The general form of the unrestricted wave function for a system with p α electrons and q β electrons ($p \geq q$) is

$$\Psi = |\psi_1^\alpha(1)\alpha(1)\psi_2^\alpha(2)\alpha(2)\cdots \psi_p^\alpha(p)\alpha(p)\psi_1^\beta(p+1)\beta(p+1)\cdots \psi_q^\beta(p+q)\beta(p+q)| \quad (1)$$

where the ψ_i^α and ψ_i^β are taken as linear combinations of valence-shell atomic orbitals ϕ_μ

$$\begin{aligned} \psi_i^\alpha &= \sum_\mu c_{\mu i}^\alpha \phi_\mu \\ \psi_i^\beta &= \sum_\mu c_{\mu i}^\beta \phi_\mu \end{aligned} \quad (2)$$

The linear expansion coefficients $c_{\mu i}^\alpha$ and $c_{\mu i}^\beta$ are determined by solving a set of coupled algebraic equations in the standard self-consistent field manner, with approximations introduced in the evaluation of the atomic and molecular integrals involved. Density matrices P^α and P^β for α and β electrons, respectively, are defined as

$$\begin{aligned} P_{\mu\nu}^\alpha &= \sum_i^p c_{\mu i}^\alpha c_{\nu i}^\alpha \\ P_{\mu\nu}^\beta &= \sum_i^q c_{\mu i}^\beta c_{\nu i}^\beta \end{aligned} \quad (3)$$

Electronic wave functions based on spin-unrestricted determinants of molecular orbitals are not in general eigenfunctions of the $\mathbf{S}^2$ operator and contain contaminating contributions from states of higher multiplicity. An extensive study of the effect of the contaminating spin components on calculated isotropic hyperfine coupling constants has been carried out for calculations on the level of approximation considered herein.[7] It was concluded that no serious errors were introduced in hyperfine coupling constants by assuming that the effect of the contaminating spin components is negligible.

In the previous paper in this series,[2] calculations on the CNDO level of approximation were shown to be capable of accommodating electronic charge distribution in a satisfactory and generally useful manner. In the calculation of unpaired electron densities, the CNDO approximations are too extreme to give a proper account of the spin polarization contribution to the unpaired electron density.

It is important to retain the one-center atomic exchange integrals (neglected in CNDO theory) as they introduce quantitatively the effect of Hund's rule, according to which electrons in different atomic orbitals on the same atom will have a lower repulsion energy if their spins are parallel. This type of interaction has important consequences on the unpaired electron distribution in the system for it means that the attracting power of a particular atomic orbital for electrons of a particular spin will depend on the unpaired electron population of other orbitals on the same atom. In fact, for π-electron radicals (planar molecules with the odd electron occupying a molecular orbital of π symmetry), retention of one-center exchange integrals is necessary to introduce any spin density at all into the σ system, as required for a nonzero isotropic hyperfine coupling constant. The INDO method[5] is an extension of the CNDO method in which differential overlap is neglected in all *polycenter* interelectron repulsion integrals and one-center atomic exchange integrals are retained. This is the lowest level of approximation that one may hope to accommodate hyperfine coupling phenomena *generally*, and thus calculations considered in the present study are of the INDO type. Complete specification of the INDO calculations is presented in ref 5, in which preliminary results on the methyl and ethyl radicals are reported. It is important to note that *none* of the disposable parameters involved in the determination of the molecular orbitals are chosen on the basis of experimentally observed hyperfine coupling constants.

The isotropic hyperfine coupling constant a_N of magnetic nucleus N is related to the electronic wave function of the system Ψ by

$$a_\text{N} = (4\pi/3)g\beta\gamma_\text{N}\hbar\langle \mathbf{S}_z\rangle^{-1}\langle\Psi|\rho(\mathbf{r}_\text{N})|\Psi\rangle \quad (4)$$

where g is the electronic g factor, β is the Bohr magneton, γ_N is the gyromagnetic ratio of nucleus N, and $\mathbf{r}_\text{N}$ is the position vector of nucleus N. The quantity $\rho(\mathbf{r}_\text{N})$ is the spin density operator evaluated at the nuclear position of atom N, defined as

$$\rho(\mathbf{r}_\text{N}) = \sum_k 2\mathrm{s}_{zk}\delta(\mathbf{r}_k - \mathbf{r}_\text{N}) \quad (5)$$

where $\mathbf{r}_k$ is the position vector of the kth electron, s_{zk} is the component of the electron spin angular momentum operator, and $\delta(\mathbf{r})$ is the Dirac δ function. With Ψ defined as in eq 1, the expectation value of the spin

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(7) D. L. Beveridge and P. A. Dobosh, *J. Chem. Phys.*, in press.

Table I. Analysis of Linear Relation[a] between Observed a_N and Calculated $\rho_{s_N s_N}$ (Eq 9)

Nucleus	No. of data points	$(4\pi/3)g\beta\gamma h\langle S_z\rangle^{-1}$ $\lvert\phi_{s_N}(\mathbf{r}_N)\rvert^2$, G	Std dev,[b] G	Correlation coeff[c]	$\lvert\phi_{s_N}(\mathbf{r}_N)\rvert^2$, au^{-3}
^{1}H	141	539.86	7.29	0.8797	0.338
^{13}C	26	820.10	23.78	0.9253	2.042
^{14}N	29	379.34	2.34	0.7561	3.292
^{17}O	5	888.68	2.67	0.5188	41.082
^{19}F	9	44829.20	22.22	0.9224	29.840

[a] Constrained to origin. [b] Calculated as $\sqrt{\Sigma(a - a_{\text{calcd}})^2/(n - 1)}$. [c] Calculated as $(n\Sigma\rho a - \Sigma\rho\Sigma a)/\sqrt{[n\Sigma\rho^2 - (\Sigma\rho)^2][n\Sigma a^2 - (\Sigma a)^2]}$.

density operator becomes

$$\langle\Psi|\rho(\mathbf{r}_N)|\Psi\rangle = \sum_{\mu\nu}\rho_{\mu\nu}\phi_\mu(\mathbf{r}_N)\phi_\nu(\mathbf{r}_N) \qquad (6)$$

where $\rho_{\mu\nu}$ is the unpaired electronic population

$$\rho_{\mu\nu} = P_{\mu\nu}{}^{\alpha} - P_{\mu\nu}{}^{\beta} \qquad (7)$$

Up to this point, the theoretical considerations of isotropic hyperfine coupling constant apply generally to a spin-unrestricted molecular orbital wave function. In order to evaluate eq 6 at a level of approximation commensurate with the approximations involved in integral evaluation in the wave-function determination, we assume that all contributions to the summation are negligible unless both ϕ_μ and ϕ_ν are centered on atom N. Of the atomic functions centered on atom N, only s functions have nonvanishing densities at the nucleus and contribute to the isotropic hyperfine coupling constant. With these approximations, the expectation value of the spin density operator at the nucleus of atom N reduces to the single term

$$\langle\Psi|\rho(\mathbf{r}_N)|\Psi\rangle = \rho_{s_N s_N}|\phi_{s_N}(\mathbf{r}_N)|^2 \qquad (8)$$

where $\rho_{s_N s_N}$ is the unpaired electronic population of the valence s orbital of atom N and $|\phi_{s_N}(\mathbf{r}_N)|^2$ is the density of the valence s orbital of atom N evaluated at the nucleus. Substituting eq 8 into eq 4, the final expression for the isotropic hyperfine coupling constant is

$$a_N = \{(4\pi/3)g\beta\gamma_N\hbar\langle s_z\rangle^{-1}|\phi_{s_N}(\mathbf{r}_N)|^2\}\rho_{s_N s_N} \qquad (9)$$

The quantity in brackets on the right-hand side of eq 9 is a constant for each type of magnetic nucleus to be considered. The quantities involved in this term are all fundamental constants with the exception of $|\phi_{s_N}(\mathbf{r}_N)|^2$, which involves some special consideration. The integrals calculated in the wave-function determination were evaluated over Slater orbitals. In this analytical form for atomic functions, all radial nodes are collapsed to a point node at the nucleus, and thus spurious values for $|\phi_{s_N}(\mathbf{r}_N)|^2$ are obtained. Alternatively, one may evaluate this quantity using SCF atomic orbitals, but, since the calculations were not carried out in this basis, these are not strictly appropriate. The procedure adopted for determining $|\phi_{s_N}(\mathbf{r}_N)|^2$ involves recognizing the linear relation implied by eq 9 and selecting this quantity to give the best linear relation between the observed a_N and calculated $\rho_{s_N s_N}$ in a least-squares sense. This is the only disposable parameter involved which was selected on the basis of experimentally observed hyperfine coupling constants. The values adopted for $|\phi_{s_N}(\mathbf{r}_N)|^2$ for each magnetic nucleus considered are listed in Table I along with the statistics of the least-squares calculations involved.

The values for ^{1}H, ^{13}C, and ^{14}N compare reasonably well with the corresponding values calculated from atomic Hartree–Fock wave functions,[7] and, of course, only qualitative agreement can be expected. For ^{17}O and ^{19}F the values obtained in this work are somewhat higher than the corresponding Hartree–Fock atomic values, and the oxygen value is anomalously higher than the fluorine value. Consideration of more extensive and representative data, especially for oxygen, is necessary before making further comment on this point.

Calculations

Molecular orbital calculations were carried out on a variety of molecules composed of first-row atoms, and ^{1}H, ^{13}C, ^{14}N, ^{17}O, and ^{19}F isotropic hyperfine coupling constants were considered. As with the study of charge distributions and dipole moments in the preceding paper, standard bond lengths and angles were used for the molecular geometries. The detailed model proposed previously is, however, not really suitable for radicals and radical ions, where it is frequently difficult to classify bonds by type (single, double, etc.). We shall, therefore, adopt for the present study a rather cruder scheme in which the internuclear distances chosen depend entirely on the nature of the two atoms involved. We shall henceforth refer to these geometries as model B, with those of the previous paper being model A. The bond lengths for model B are listed in Table II, with the rules for bond angles being the same as in paper I.

Table II. Standard Bond Lengths (Model B) in Ångstroms

	H	C	N	O	F
H	0.74	1.08	1.00	0.96	0.92
C		1.40	1.37	1.36	1.35
N			1.35	1.30	1.36
O				1.48	1.42
F					1.42

Molecules chosen were generally those for which a reasonable knowledge of the molecular geometry could be inferred from chemical intuition, and molecules which required explicit consideration of several interconverting conformations were not included, with the exception of ethyl radical. Even with these limitations a number of exceptions to the standard model were necessary, and these are noted in Table IV.

Table III. Observed and Calculated Isotropic Hyperfine Coupling Constants for C^{13}

Radical	Atom or group	a_N, G	
		Calcd	Exptl
Methyl		45.0	(+)38.34[a]
Fluoromethyl		92.7	(+)54.80[b]
Difluoromethyl		145.1	(+)148.80[b]
Trifluoromethyl		184.6	(+)271.60[b]
Ethyl	CH_3	−12.4	(−)13.57[b]
	CH_2	39.9	(+)39.07[a]
Vinyl	α	178.0	(+)107.57[a]
	β	−14.5	(−)8.55[a]
Ethynyl	1	−2.5	
	2	342.8	
Allyl	1	28.0	
	2	−16.6	
Phenyl	1	151.3	
	2	−4.8	
	3	10.7	
	4	−2.6	
Cyclopentadienyl		4.1	
Tropyl		3.5	
Benzyl	1	−12.3	
	2	11.7	
	3	−8.5	
	4	10.5	
	CH_2	32.6	
Phenoxy	1	−10.7	
	2	7.0	
	3	−5.5	
	4	6.3	
Cyclohexadienyl	2	17.9	
	3	−13.7	
	4	17.8	
	CH_2	−17.6	
Perinaphthenyl	1	13.9	
	2	−10.3	
	4	−9.3	
	13	6.7	
Benzene$^-$		4.0	(+)2.80[c]
Cyclooctatetraene$^-$		3.0	(+)1.28[d]
trans-Butadiene$^-$	1	18.6	
	2	−1.2	
Naphthalene$^-$	α	9.3	(+)7.10[e]
	β	−0.3	(−)1.20[f]
	9	−4.3	
Anthracene$^-$	1	4.6	3.57[g]
	2	0	−0.25[g]
	9	12.4	8.76[g]
	11	−3.4	−4.59[g]
Anthracene$^+$	2	0.2	(+)0.37[g]
	9	11.8	8.48[g]
	11	−3.3	(−)4.50[g]
Phenanthrene$^-$	1	8.2	
	2	−5.7	
	3	6.9	
	4	−2.2	
	9	7.5	
	11	−3.8	
	12	2.1	
Pyrene$^-$	1	9.9	
	2	−7.1	
	4	2.9	
Stilbene$^-$	1	6.2	
	2	−5.2	
	3	7.4	
	4	−4.9	
	5	5.8	
	6	−3.2	
	7	7.4	
Biphenylene$^-$	1	−3.0	
	2	3.0	
	10	5.2	
Azulene$^-$	1	−1.8	
	2	4.9	
	9	1.3	
	4	11.7	
	5	−10.2	
	6	16.9	
Fluoranthene$^-$	1	7.5	
	2	−6.4	
	3	12.0	
	7	−1.2	
	8	1.3	
	11	−7.0	
	12	1.6	
	13	−0.4	
	14	2.4	
Benzonitrile$^-$	1	8.4	
	2	3.6	
	3	−5.2	
	4	14.0	
	CN	−6.6	(−)6.12[h]
Phthalonitrile$^-$	1	8.5	
	3	−6.1	
	4	6.0	
	CN	−6.4	
Isophthalonitrile$^-$	1	4.9	
	2	−5.8	
	4	12.3	
	5	−9.1	
	CN	−4.3	
Terephthalonitrile$^-$	CN	−6.7	(−)7.83[h]
	1	9.7	8.81[h]
	2	−0.7	(−)1.98[h]
1,2,4,5-Tetracyanobenzene$^-$	1	7.2	
	3	−7.3	
	CN	−5.3	
p-Nitrobenzonitrile$^-$	1	7.5	
	2	−5.2	
	3	5.5	
	4	−2.3	
	CN	−4.5	
Nitrobenzene$^-$	1	−5.2	
	2	6.1	
	3	−5.2	
	4	7.1	
m-Dinitrobenzene$^-$	1	0.3	
	2	−2.4	
	4	13.2	
	5	−9.4	
p-Dinitrobenzene$^-$	1	6.1	
	2	0.1	
o-Benzosemiquinone$^-$	1	−6.6	
	3	3.2	
	4	−1.1	
p-Benzosemiquinone$^-$	1	−6.9	(−)0.59[i]
	2	1.0	(+)0.40[i]
2,5-Dioxo-1,4-benzosemiquinone^{3-}	1	3.1	
	3	−7.9	
1,4-Naphthosemiquinone$^-$	1	−8.3	
	2	1.3	
	5	−1.5	
	6	0.2	
	9	1.4	
9,10-Anthrasemiquinone$^-$	1	−1.7	
	2	0.4	
	9	−9.6	
	11	1.8	
Pyrazine$^-$		−1.8	(−)2.88[j]
N,N-Dihydropyrazine$^+$		0.1	
Pyridazine$^-$	3	−7.6	
	4	5.1	
s-Tetrazine$^-$		−12.2	
1,5-Diazanaphthalene$^-$	2	−2.5	
	3	0.9	
	4	6.5	
	9	−4.8	
Phthalazine$^-$	1	11.9	
	5	9.1	
	6	−0.2	
	9	−4.5	

Table III (*Continued*)

Radical	Atom or group	a_N, G		Radical	Atom or group	a_N, G	
		Calcd	Exptl			Calcd	Exptl
Quinoxaline$^-$	2	−1.2		1,4,5,8-Tetraazaanthracene$^-$	2	−0.2	
	5	3.3			9	8.4	
	6	−0.2			11	−4.3	
	9	−4.1		*p*-Dicyanotetrazine$^-$	Ring	−10.6	
Dihydroquinoxaline$^+$	2	0.2			CN	3.5	
	5	−0.1		*p*-Nitrobenzaldehyde$^-$	CHO	−9.5	
	6	0.2		*p*-Cyanobenzaldehyde$^-$	CHO	−2.7	
	9	−0.2			CN	−4.1	
Phenazine$^-$	1	2.6		4-Cyanopyridine$^-$	CN	−10.1	
	2	−0.2					
	11	−3.8					

[a] R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967). [b] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965). [c] J. R. Bolton, *Mol. Phys.*, 6, 219 (1963). [d] H. L. Strauss and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1738 (1963). [e] T, R. Tuttle, Jr., and S. I. Weissman, *ibid.*, **25**, 189 (1956). [f] T. R. Tuttle, Jr., *ibid.*, **32**, 1579 (1960). [g] See ref 18. [h] P. H, Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963). [i] See ref 23. [j] E. W. Stone and A. H. Maki, *J. Chem. Phys.*, **39**, 1635 (1963).

Table IV, Observed and Calculated Isotropic Hyperfine Coupling Constants for ^1H

Radical	Atom or group	a_N, G		Radical	Atom or group	a_N, G	
		Calcd	Exptl			Calcd	Exptl
Methyl		−22.4	(−)23.04[a]	Stilbene$^-$	1	−3.7	(−)1.90[s]
Fluoromethyl[mm]		−7.8	(−)21.10[b]		2	2.0	(+)0.86[s]
Difluoromethyl[mm]		21.9	(+)22.20[b]		3	−3.9	(−)3.80[s]
Ethyl[nn]	CH$_2$	−20.4	(−)22.38[a]		4	1.9	(+)0.32[r]
	CH$_3$	27.6	(+)26.87[a]		5	−3.4	(−)2.96[s]
Vinyl	α	17.1	(+)13.40[a]		7	−5.2	(−)4.36[s]
	β_1	55.1	(+)65.00[a]	Biphenylene$^-$	1	0.2	(+)0.21[t]
	β_2	21.2	(+)37.00[a]		2	−2.1	(−)2.86[t]
Formyl		74.9	(+)137.00[c]	Azulene$^-$ [oo]	1	0	(+)0.27[u]
Ethynyl		32.7	(+)16.10[d]		2	−3.0	(−)3.95[u]
Allyl	1	−14.6	(−)13.93[a]		4	−7.0	(−)6.22[u]
	1′	−14.9	(−)14.83[a]		5	3.9	(+)1.34[u]
	2	6.9	(+)4.06[a]		6	−9.4	(−)8.82[u]
Phenyl	2	18.7	(+)19.50[e]	Fluoranthene$^-$ [oo]	1	−4.4	(−)3.90[v]
	3	6.1	(+)6.50[e]		2	2.2	(+)1.30[v]
	4	3.9			3	−6.4	(−)5.20[v]
Cyclopentadienyl[oo]		−4.8	(−)5.60[f]		7	0.2	
Tropyl[oo]		−3.2	(−)3.95[g]		8	−0.9	
Benzyl	−CH$_2$	−17.0	(−)16.35[h]	Benzonitrile$^-$ [qq]	2	−3.3	(−)3.63[w]
	2	−6.4	(−)5.14[h]		3	1.1	(+)0.30[w]
	3	3.6	(+)1.75[h]		4	−8.0	(−)8.42[w]
	4	−5.6	(−)6.14[h]	Phthalonitrile$^-$ [qq]	3	1.5	(+)0.33[x]
Phenoxy	2	−4.1	(+)6.60[i]		4	−4.0	(−)4.24[x]
	3	2.2	(+)1.96[i]	Isophthalonitrile$^-$ [qq]	2	1.5	(+)0.08[w]
	4	−3.4	(−)10.40[i]		4	−7.6	(−)8.29[w]
Cyclohexadienyl[oo]	CH$_2$[pp]	97.6	(+)47.71[a]		5	2.6	(+)1.44[w]
	2	−11.1	(+)8.99[a]	Terephthalonitrile$^-$ [qq]		−1.0	(−)1.59[w]
	3	5.1	(+)2.65[a]	1,2,4,5-Tetracyanobenzene$^-$ [qq]		2.2	(+)1.11[w]
	4	−9.8	(−)13.04[a]	*p*-Nitrobenzonitrile$^-$ [qq,rr]	2	1.8	(+)0.76[y]
Perinaphthenyl	1	−7.5	(−)7.30[j]		3	−3.5	(−)3.12[y]
	2	4.3	(+)2.80[j]	Nitrobenzene$^-$ [rr]	2	−3.6	(−)3.39[z]
Benzene$^-$		−3.6	(−)3.75[k]		3	1.9	(+)1.09[z]
Cyclooctatetraene$^-$ [oo]		−2.6	(−)3.21[l]		4	−3.8	(−)3.97[z]
trans-Butadiene$^-$	1	−9.8	(−)7.62[m]	*m*-Dinitrobenzene$^-$ [rr]	2	0.4	(+)3.11[aa]
	1′	−10.3	(−)7.62[m]		4	−7.8	(−)4.19[aa]
	2	−0.8	(−)2.79[m]		5	3.2	(+)1.08[aa]
Naphthalene$^-$	1	−5.3	(−)4.90[n]	*p*-Dinitrobenzene$^-$ [rr]		−1.0	(−)1.12[aa]
	2	−0.9	(−)1.83[n]	*m*-Fluoronitrobenzene$^-$ [rr]	2	−3.7	(−)3.30[bb]
Anthracene$^-$	1	−2.7	(−)2.74[o]		4	−3.7	(−)3.30[bb]
	2	−0.6	(−)1.51[o]		5	1.8	(+)1.10[bb]
	9	−6.8	(−)5.34[o]		6	−3.4	(−)3.00[bb]
Anthracene$^+$	1	−2.9	(−)3.08[p]	*p*-Fluoronitrobenzene$^-$ [rr]	2	−3.8	(−)3.56[y]
	2	−0.6	(−)1.38[p]		3	2.2	(+)1.16[y]
	9	−6.6	(−)6.49[p]	3,5-Difluoronitrobenzene$^-$ [rr]	2	−3.5	(−)3.26[cc]
Phenanthrene$^-$	1	−4.6	(−)3.60[q]		4	−3.6	(−)3.98[cc]
	2	1.2	(+)0.72[q]	*o*-Benzosemiquinone$^-$	3	−1.9	(−)3.65[dd]
	3	−3.8	(−)2.88[q]		4	0.2	(+)0.95[dd]
	4	0.6	(+)0.32[q]	*p*-Benzosemiquinone$^-$		−0.9	(−)2.37[ee]
	9	−5.0	(−)4.32[q]	2,5-Dioxo-1,4-semiquinone^{3-}		2.4	(+)0.79[ff]
Pyrene$^-$	1	−5.5	(−)4.75[r]	1,4-Naphthosemiquinone$^-$	2	−1.0	(−)3.23[ee]
	2	2.5	(+)1.09[r]		5	0.6	(+)0.65[ee]
	4	−1.9	(−)2.08[r]		6	−0.1	(−)0.51[ee]

Table IV (*Continued*)

Radical	Atom or group	a_N, G Calcd	a_N, G Exptl
9,10-Anthrasemiquinone⁻	1	0.8	(+)0.96[ee]
	2	−0.2	(−)0.55[ee]
Pyrazine⁻		−2.0	(−)2.64[gg]
N,N-Dihydropyrazine⁺	NH	−10.1	(−)8.30[hh]
	CH	−2.1	(−)3.26[hh]
Pyridazine⁻	3	1.1	(+)0.16[gg]
	4	−3.6	(−)6.47[gg]
s-Tetrazine⁻		2.5	(+)0.21[gg]
1,5-Diazanaphthalene⁻	2	−0.6	(−)1.69[ii]
	3	−1.5	(−)2.95[ii]
	4	−3.8	(−)5.77[ii]
Phthalazine⁻	1	−6.4	(−)5.91[gg]
	5	−5.2	(−)4.64[gg]
	6	−0.9	(−)2.14[gg]
Quinoxaline⁻	2	−1.8	(−)2.32[jj]
	5	−2.0	(−)3.32[jj]
	6	0.4	(−)1.00[jj]
Dihydroquinoxaline⁺	1	−9.8	(−)7.17[kk]
	2	−2.3	(−)3.99[kk]
	5	−0.5	(−)0.78[kk]
	6	−0.7	(−)1.38[kk]
Phenazine⁻	1	−1.7	(−)1.93[jj]
	2	−0.4	(−)1.61[jj]
1,4,5,8-Tetraazaanthracene⁻	2	−1.0	(−)2.73[jj]
	9	−4.4	(−)3.96[jj]
p-Nitrobenzaldehyde⁻ [ss]	2	−0.6	(−)1.23[y]
	3	−0.4	(−)0.44[y]
	5	−0.4	(−)0.44[y]
	6	−0.6	(−)2.37[y]
	CHO	1.4	(−)3.10[y]
p-Cyanobenzaldehyde⁻ [qq,ss]	3	1.2	(+)0.19[ll]
	2	−2.5	(−)2.73[ll]
	6	−2.5	(−)3.14[ll]
	5	1.3	(+)0.71[ll]
	CHO	−1.8	(−)5.56[ll]
4-Cyanopyridine⁻ [qq]	2	−1.3	(−)1.40[w]
	3	−1.5	(−)2.62[w]

[a] See ref 13. [b] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965). [c] F. J. Adrian, E. L. Cochran, and V. A. Bowers, *ibid.*, **36**, 1661 (1962). [d] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **40**, 213 (1964). [e] J. E. Bennett, B. Mile, and A. Thomas, *Proc. Roy. Soc.* (London), A**293**, 246 (1966). [f] See ref 15. [g] See ref 15b. [h] See ref 14. [i] T. J. Stone and W. A. Waters, *Proc. Chem. Soc.*, 253 (1962). [j] P. B. Sogo, M. Nakazaki, and M. Calvin, *J. Chem. Phys.*, **26**, 1343 (1957). [k] T. R. Tuttle, Jr., and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 5342 (1958). [l] T. J. Katz and H. L. Stevens, *J. Chem. Phys.*, **32**, 1873 (1960). [m] See ref 17. [n] A. Carrington, F. Dravnieks, and M. C. R. Symons, *J. Chem. Soc.*, 947 (1959). [o] See ref 18. [p] I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, **43**, 2712 (1965). [q] S. H. Glarum and L. C. Snyder, *ibid.*, **36**, 2989 (1962). [r] G. J. Hoijtink, J. Townsend, and S. I. Weissmann, *ibid.*, **34**, 507 (1961). [s] R. Chang and C. S. Johnson, Jr., *ibid.*, **41**, 3273 (1964). [t] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 285 (1962). [u] I. Bernal, P. H. Rieger, and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 1489 (1962). [v] E. DeBoer and S. I. Weissman, *J. Am. Chem. Soc.*, **80**, 4549 (1958). [w] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *ibid.*, **85**, 683 (1963). [x] A. Carrington and P. F. Todd, *Mol. Phys.*, 6, 161 (1963). [y] A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852, 3532 (1961). [z] D. H. Geske and A. H. Maki, *ibid.*, **82**, 2671 (1960). [aa] See ref 21. [bb] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963). [cc] M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 955 (1965). [dd] B. Venkataremen, B. G. Segal, and G. K. Fraenkel, *ibid.*, **30**, 1006 (1959). [ee] See ref 22. [ff] D. C., Reitz, F. Dravniecks, and J. E. Wertz, *ibid.*, **33**, 1880 (1960). [gg] E. W. Stone and A. H. Maki, *ibid.*, **39**, 1635 (1963). [hh] J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 465 (1962). [ii] J. C. M. Henning, *J. Chem. Phys.*, **44**, 2139 (1966). [jj] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962). [kk] B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 1455 (1964). [ll] P. H. Rieger and G. K. Fraenkel, *ibid.*, **37**, 2813 (1962). [mm] Calculated equilibrium bond angles (ref 11). [nn] Free rotation of methyl group simulated (ref 5). [oo] Ring(s) assumed to be regular polygon. [pp] HCH angle, 109.5°. [qq] C–N bond length, 1.16 Å. [rr] N–O bond length, 1.24 Å. [ss] C–O bond length, 1.36 Å, and O *cis* to H_2.

Results and Discussion

Using the values for $|\phi_{s_N}(\mathbf{r}_N)|^2$ listed in Table I and the $\rho_{s_N s_N}$ computed from the INDO molecular orbitals for each molecule, isotropic hyperfine coupling constants a_N were calculated for each atomic nucleus in each compound. A comparison of the calculated a_N with observed values is presented for ^1H, ^{13}C, ^{14}N, ^{17}O, and ^{19}F in Tables III–VII. In preparing these tables, assignments were made on the basis of the calculated spin densities for cases where the assignment of experimentally observed hyperfine coupling constants was not unequivocally established. In addition, the signs of most of the hyperfine coupling constants listed in Tables III–VII are not known experimentally, and here again assignments were made entirely on the basis of the calculations.

Considering the level of approximation involved, the over-all results are seen to be quite satisfactory. An indication of the quality of the results follows from the linear relationship between the observed a_N and calculated $\rho_{s_N s_N}$, as reflected in the standard deviations and correlation coefficients listed in Table II. From Table IV, we observe that 92% of the proton hyperfine coupling constants are calculated within 3 G, evidence that calculations of this type will be predictive in a semiquantitative sense. For ^{13}C, ^{14}N, and ^{19}F, the number of data points is not as large as for protons, but the over-all results are satisfactory, especially in light of the fact that contributions from inner shells and vibronic effects are neglected. The correlation is not as good for ^{17}O, where there is an insufficient number of data points for a critical test. Also included in Tables III–VII are a number of calculated hyperfine coupling constants for which no experimental data have been reported.

Radicals and radical ions considered may be broadly divided into two classes. The first includes those in which the odd electron is primarily associated with a molecular orbital with nonvanishing amplitude at the nuclear positions (σ-type radicals such as vinyl, formyl, phenyl). The other, more numerous, class consists of planar systems in which the singly occupied molecular orbital is of π type and hyperfine interaction only occurs by means of indirect effects (α and β electrons in the σ system experiencing different environments because of the different local α and β π-electron densities). Most previous theoretical calculations have treated these two types separately. Independent electron calculations of the extended Hückel type[8] have given a partially satisfactory account of some of the σ systems, but these methods are inherently incapable of giving true values for π systems. Similar con-

(8) (a) G. A. Petersson and A. D. McLachlan, *J. Chem. Phys.*, **45**, 628 (1966); (b) W. T. Dixon, *Mol. Phys.*, **6**, 201 (1965).

Table V, Observed and Calculated Isotropic Hyperfine Coupling Constants for ^{14}N

		a_N, G	
Radical	Group	Calcd	Exptl
Benzonitrile$^-$		2.4	(+)2.15^a
Phthalonitrile$^-$		1.9	(+)1.80^b
Isophthalonitrile$^-$		1.3	(+)1.02^a
Terephthalonitrile$^-$		2.0	(+)1.81^a
1,2,4,5-Tetracyanobenzene$^-$		1.4	(+)1.15^a
p-Nitrobenzonitrile$^-$	CN	1.1	(+)0.76^c
	NO_2	4.7	(+)7.15^c
Nitrobenzene$^-$		7.1	(+)10.32^c
m-Dinitrobenzene$^-$		0.5	(+)4.68^d
p-Dinitrobenzene$^-$		−0.0	(−)1.74^d
m-Fluoronitrobenzene$^-$		6.6	(+)12.60^e
p-Fluoronitrobenzene$^-$		7.1	(+)9.95^f
3,5-Difluoronitrobenzene$^-$		6.1	(+)8.09^f
Pyrazine$^-$		8.3	(+)7.21^g
N,N-Dihydropyrazine$^+$		7.8	(+)7.60^h
Pyridazine$^-$		7.7	(+)5.90^g
s-Tetrazine$^-$		5.8	(+)5.28^g
1,5-Diazanaphthalene$^-$		5.9	(+)3.37^i
Phthalazine$^-$		0.3	(+)0.88^g
Quinoxaline$^-$		7.3	(+)5.64^j
Dihydroquinoxaline$^+$		7.7	(+)6.65^k
Phenazine$^-$		7.2	(+)5.14^j
1,4,5,8-Tetraazaanthracene$^-$		3.3	(+)2.41^j
p-Dicyanotetrazine$^-$	Ring	5.9	(+)5.88^l
	CN	−0.9	(−)0.16^l
p-Nitrobenzaldehyde$^-$		−0.5	(+)5.83^c
p-Cyanobenzaldehyde$^-$		1.0	(+)1.40^m
4-Cyanopyridine$^-$	Ring	8.3	(+)5.67^a
	CN	2.7	(+)2.33^a

[a] P. H. Rieger, I. Bernal, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963). [b] A. Carrington and P. F. Todd, *Mol. Phys.*, 6, 161 (1963). [c] A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852, 3532 (1961). [d] See ref 21. [e] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963). [f] M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 955 (1965). [g] E. W. Stone and A. H. Maki, *ibid.*, 39, 1635 (1963). [h] J. R. Bolton, A. Carrington, and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 465 (1962). [i] J. C. M. Henning, *J. Chem. Phys.*, **44**, 2139 (1966). [j] A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962). [k] B. L. Barton and G. K. Fraenkel, *J. Chem. Phys.*, **41**, 1455 (1964). [l] A. Carrington, P. Todd, and J. dos Santos-Veiga, *Mol. Phys.*, 6, 101 (1963). [m] P. H. Rieger and G. K. Fraenkel, *J. Chem. Phys.*, **37**, 2813 (1962).

Table VI, Observed and Calculated Isotropic Hyperfine Coupling Constants for ^{17}O[a]

	a_N, G	
Radical	Calcd	Exptl
p-Benzosemiquinone$^-$	−8.7	(−)9.53^b
1,4-Naphthosemiquinone$^-$	−9.3	(−)8.58^b
9,10-Anthrasemiquinone$^-$	−9.9	(−)7.53^b
2,5-Dioxo-1,4-semiquinone^{3-}	−3.6	(−)4.57^b
Nitrobenzene$^-$	−4.3	(−)8.84^c

[a] The signs of the ^{17}O isotropic hyperfine coupling constants take account of the fact that the magnetic moment of the ^{17}O nucleus is negative. [b] M. Broze, Z. Luz, and B. L. Silver, *J. Chem. Phys.*, **46**, 4891 (1967). [c] W. M. Garlick and D. H. Geske, *J. Am. Chem. Soc.*, **87**, 4049 (1965).

Table VII, Observed and Calculated Isotropic Hyperfine Coupling Constants for ^{19}F

		a_N, G	
Radical	Atom	Calcd	Exptl
Fluoromethyl		71.3	(+)64.30^a
Difluoromethyl		87.1	(+)84.20^a
Trifluoromethyl		159.5	(+)142.40^a
Monofluoroacetamide		34.4	54.60^b
Difluoroacetamide	1′	31.5	75.00^c
	1	39.0	75.00^c
m-Fluoronitrobenzene$^-$		−4.0	(−)3.70^d
p-Fluoronitrobenzene$^-$		6.3	(+)8.41^e
3,5-Difluoronitrobenzene$^-$		−3.8	(−)2.73^f

[a] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965). [b] See ref 24. [c] See ref 25. [d] P. B. Ayscough, F. P. Sargent, and R. Wilson, *J. Chem. Soc.*, 5418 (1963). [e] A. H. Maki and D. H. Geske, *J. Am. Chem. Soc.*, **83**, 1852, 3532 (1961). [f] M. Kaplan, J. R. Bolton, and G. K. Fraenkel, *J. Chem. Phys.*, **42**, 955 (1965).

siderations apply to the calculations of Atherton and Hinchliffe,[9] carried out on the CNDO level of approximation, The second class of radicals is usually handled by considering the π electrons in detail and then using the McConnell relation[10] connecting the unpaired electron population of a carbon π orbital with hyperfine interactions with carbon and hydrogen nuclei in the immediate vicinity, The method presented here, on the other hand, since it treats all valence electrons on an equal footing, is able to give a comprehensive account of both types of radicals within a single theoretical framework. The fact that moderately good agreement is achieved for both classes without additional parameterization is one of the most encouraging features.

Among the simple radicals, the results for methyl, fluorinated methyls, and ethyl have been discussed elsewhere,[5,11] (It should be noted that for fluorinated methyls the results quoted are for calculated equilibrium bond angles leading to significant nonplanarity at the carbon atom.[10]) For the remaining σ-type radicals, the theory reproduces a number of experimental features satisfactorily. The calculations on vinyl and formyl (using model B with all angles 120°) show the observed major difference between the hydrogen constants at the α position. The theory also distinguishes between the two β hydrogen positions, predicting that the interaction is greatest *trans* to the site of the unpaired electron, These results parallel those obtained by extended Hückel[8] and CNDO[9] methods, The carbon calculations predict that the C_β constant in vinyl is negative, as it probably is in ethyl. The theoretical results for ethynyl show similar features. The C_β constant is predicted to be small and negative, but this is sensitive to bond lengths. A more realistic choice of 1.2 Å for the carbon–carbon triple bond gives positive constants for both C_α and C_β,

Application of the theory to phenyl gives results in better agreement with experiment than previous calculations. The hydrogen spin densities are predicted to be all positive with magnitudes in the order *ortho* > *meta* > *para*, This is an improvement over the Hückel-type calculations of Petersson and McLachlan[8a] and Dixon[8b] who obtained a rather large value for the *para* position. The carbon predictions are interesting, as they indicate sign alternation around the ring (a result which cannot be obtained by any independent-electron calculations of the Hückel type), No experimental data on the carbon hyperfine constants for phenyl appear to be available,

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(9) N. M. Atherton and A. Hinchliffe, *Mol. Phys.*, **12**, 349 (1967).

(10) H. M. McConnell, *J. Chem. Phys.*, 24, 764 (1956); S. I. Weissman, *ibid.*, **25**, 190 (1956); R. Bersohn, *ibid.*, **24**, 1066 (1956); H. M. McConnell and D. B. Chestnut, *ibid.*, 28, 107 (1958).

(11) D. L. Beveridge, P. A. Dobosh, and J. A. Pople, *ibid.*, in press.

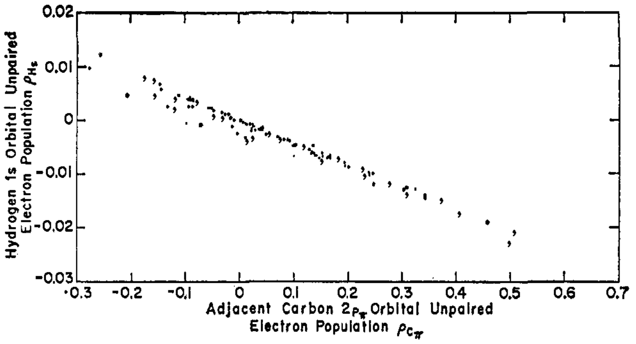

Figure 1.

For the π-type hydrocarbon radicals, the results of this theory mostly parallel previous calculations which treat π electrons separately and handle σ–π interactions on a local basis.[12] As previously mentioned, the McConnell relation in its simplest form[10]

$$a_H = Q\rho_{C_\pi} \qquad (10)$$

implies a direct proportionality between the unpaired electron population of the carbon $2p\pi$ orbital of a conjugated carbon atom, ρ_C, and the 1s orbital unpaired electron population, ρ_{H_s}, of hydrogen atoms bonded to the carbon atom in the principal valence structure, with Q being the constant of proportionality and usually taken to be about -23 G. Since both ρ_{C_π} and ρ_{H_s} are calculated explicitly in the course of an INDO molecular orbital calculation, the extent to which the McConnell relation holds up on this level of approximation may be directly examined. The quality of the linear relation obtained in plotting ρ_{C_π} *vs.* the corresponding ρ_{H_s} for a number of positions in a variety of molecules reflects the extent to which the McConnell relation holds. A plot of this type, including all appropriate cases taken from the molecules listed in Table IV, is given in Figure 1. The McConnell relation is observed to hold remarkably well, and the slope of the line leads to a theoretical value for Q of -22 G.

Another notable feature of the calculations on π radicals is that the two hydrogens in the 1 position of allyl are separated in this theory, the prediction being that 1′ (*cis* to the third carbon atom C_3) has the hyperfine constant of larger magnitude. However, the calculated separation between the two positions is considerably smaller than that observed experimentally.[13] The results for benzyl predict that the magnitude of the proton hyperfine interaction at the *para* position is smaller than the corresponding magnitude at the *ortho* position, The experimental results show the opposite ordering.[14] This failure of self-consistent field theories has also been noted in π-electron treatments,[14] and its origin is not yet understood. The theoretical results for the phenoxy radical show up the same difficulty,

The radicals cyclopentadienyl (C_5H_5) and tropyl (C_7H_7) were treated as having carbon structure as regular polygons, Both these systems are predicted to be in degenerate electronic states and are therefore distorted according to the Jahn–Teller theorem. This distortion is neglected and the theoretical values quoted are averages over the two components of the Jahn–Teller state. The calculated proton hyperfine constants are approximately in the ratio 5:7 as observed experimentally.[15]

Cyclohexadienyl shows a large hyperfine constant for the methylene protons,[13] It was pointed out by Whiffen[16] that this was best interpreted in terms of a delocalized π-type molecular orbital in the pentadienyl fragment which interacted strongly with the CH_2 group. The results of the INDO calculations (using a regular hexagon for the carbon atoms and a tetrahedral H–C–H angle) overemphasize this effect and give too large a proton hyperfine constant. This is probably due to the unsatisfactory nature of the geometrical model which assumes a C–C bond length of 1.40 Å for all C–C bonds. If the calculations are repeated with the same geometry for the pentadienyl C_5 fragment but with a length of 1.48 Å for the C–C bond to the CH_2 group, the predicted value of a_H (methylene) falls to 71.5.

The next section of the table deals with hydrocarbon anions and cations, for which there is an extensive body of experimental data. The calculations on butadiene anion give a rather smaller value for the proton constant at the 2 position than that observed by Levy and Myers.[17] This may again be partly due to the unsatisfactory geometrical model which assumes three equal C–C bond lengths. Using model A geometry (a C–C single-bond length of 1,46 Å and a double-bond length of 1,34 Å), the calculated two-proton constant changes to -1.24 G. The carbon hyperfine constant in position 2 is predicted to be slightly negative, but this is also sensitive to bond length and becomes positive if model A is used. The INDO calculations again differentiate between the two hydrogens in the 1 position, the 1′ (*cis* to C_3) having the hyperfine constant of largest magnitude,

For polycyclic anions and cations, the results of the present theory agree for the most part with previous π-electron treatments. For naphthalene and anthracene, the general agreement is good for both carbon and hydrogen, the negative carbon constants observed in anthracene[18] being correctly reproduced. However, calculated values at the 2 position are rather too small, For some of the higher polycyclic ions, assignments are still somewhat uncertain. Those given in the tables are made to give best fit between the experimental data and the calculations of this paper. It may be noted that the assignment for phenanthrene anion differs from that proposed by Colpa and Bolton,[19] The results for the cations parallel those of the corresponding anions fairly closely, indicating that the pairing results discussed by Bolton and Fraenkel[18] hold well at this level of approximation.

The good results for the azine and cyanobenzene ions in the tables are very encouraging, particularly since the calculations involve no additional parameterization to fit the data, The agreement covers hydrogen,

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(12) A. T. Amos and L. C. Snyder, *J. Chem. Phys.*, **42**, 3670 (1965).

(13) R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963).

(14) A. Carrington and I. C. P. Smith, *Mol. Phys.*, **9**, 137 (1965).

(15) (a) S. Ohnishi and I. Nitta, *J. Chem. Phys.*, **39**, 2848 (1963); (b) D. E. Wood and H. M. McConnell, *ibid.*, **37**, 1150 (1962).

(16) D. H. Whiffen, *Mol. Phys.*, **6**, 223 (1963).

(17) D. H. Levy and R. J. Myers, *J. Chem. Phys.*, **41**, 1062 (1964).

(18) J. R. Bolton and G. K. Fraenkel, *ibid.*, **40**, 3307 (1964).

(19) J. P. Colpa and J. R. Bolton, *Mol. Phys.*, **6**, 273 (1963).

carbon, and nitrogen constants in all the compounds considered. We are not able to report the results for some other nitrile anions studied experimentally (such as tetracyanoethylene) because of convergence difficulties with the calculations. The experimental data on nitrobenzene and dinitrobenzene anions are also fairly well reproduced. It is particularly interesting that the sharp drop in the nitrogen hyperfine constant from nitrobenzene to *p*-dinitrobenzene is accounted for. The standard model for all these compounds is planar, so this effect can be interpreted without appealing to nonplanarity at the nitrogen atoms as proposed by Symons.[20] The calculations on *m*-dinitrobenzene suggest that the assignment of the two- and five-proton hyperfine constants by Maki and Geske[21] may be incorrect.

The results for quinones are less satisfactory. Calculated proton hyperfine constants for hydrogens in *p*-benzosemiquinone ion are less than experimental values as are those of the corresponding protons (2, 3) in 1,4-naphthosemiquinone.[22] Fairly large negative carbon constants are predicted for the carbon atoms in the carbonyl groups, but only a small value is found experimentally in *p*-benzosemiquinone.[23]

The fluorine isotropic hyperfine coupling constants are generally well reproduced with the notable exception of the two fluoroacetamide radicals, which are calculated to be much lower than the observed values.[24,25] Although these radicals are thought to be planar in the crystal, the fluorine coupling constants observed for the monofluoro and difluoro species are quite comparable to those observed for fluoromethyl and difluoromethyl radicals, respectively, and the latter are almost certainly nonplanar.[11] Thus the planar model B geometry may be an inappropriate choice for these molecules. Further study of these molecules is being undertaken and the results will be reported in a subsequent publication.

Conclusions

On the basis of the agreement between calculated and observed hyperfine coupling constants listed in Tables III-VI, we conclude that spin-unrestricted molecular orbital calculations carried out with the INDO approximations for atomic and molecular integrals are quite capable of accommodating isotropic hyperfine coupling phenomena in polyatomic molecules. Calculations on this level of approximation should be useful in providing a basis for the assignment of positions and signs of hyperfine coupling constants when used in close conjunction with the available experimental data. To facilitate applications of this sort, the authors are making copies of the FORTRAN-63 computer program used in these calculations available through the Quantum Chemistry Program Exchange.[26] It also seems likely that wave functions of this type could be used to calculate and interpret anisotropic hyperfine coupling constants, *g* tensors, and other features of the electronic structure of free radicals.

(20) M. C. R. Symons, *Advan. Phys. Org. Chem.*, **1**, 283 (1963).

(21) A. H. Maki and D. Geske, *J. Chem. Phys.*, 33, 825 (1960).

(22) G. Vincow and G. K. Fraenkel, *ibid.*, 34, 1333 (1961).

(23) M. R. Das and B. Venkataraman, *Bull. Coll. Amp. Eindhoven*, 21 (1962).

(24) R. J. Cook, J. R. Rowlands, and C. H. Whiffen, *Mol. Phys.*, 7, 31 (1963).

(25) R. J. Lontz and W. Gordy, *J. Chem. Phys.*, 37, 1357 (1962).

(26) Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind.

Calculation of the Chemical Shift of a Series of Polyenylic Ions by the "Free-Electron Model"

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Abstract: The correlation of the chemical shift with the "free-electron model" is demonstrated for a series of polyenylic ions.

The applicability of the free-electron, or particle in a box, model to the discussion of the electronic spectra of a series of polyene ions has been amply demonstrated in the literature.[1] Recently Sorensen[2] reported both the electronic and the nmr spectra of a series of polyenylic ions and discussed the results in terms of phenomenological equations. The linear relation given by Sorensen for the electronic spectra can be readily obtained using free-electron theory and a single empirical parameter. The results of the calculations for the electronic spectra can then be used to predict the chemical shift of the nmr spectra. Although the correlation of electronic spectra is not surprising, the correlation of the chemical shift by free-electron theory has not been reported.

The Electronic Spectra

The polyenylic-ion series discussed may be represented by

$$[(CH_3)_2C{=}CH(CH{=}CH)_{n-2}{=}C(CH_3)_2]^+$$

The energy levels are given by the particle in a box treatment as $E_m = m^2h^2/8m_ea^2$, where a, the length of the box, depends on n_c, the number of carbons in the π-electron system, and on the semiempirical pa-

(1) For a review see R. Platt, *et al.*, "Free Electron Theory of Conjugated Molecules," John Wiley and Sons, Inc., New York, N. Y., 1964.

(2) T. S. Sorenson, *J. Am. Chem. Soc.*, 87, 5080 (1965).