Extended Hückel Theory Calculation of Electron Paramagnetic Resonance Hyperfine Coupling Constants

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Abstract: In this article we have analyzed various procedures for evaluating epr hyperfine coupling constants from the output of an extended Hückel calculation. Differences in the wave function for the lowest empty orbital of a neutral molecule and the orbital containing the unpaired electron in the radical anion derived from the molecule are discussed. The effect of using net atomic populations *vs.* gross atomic populations is evaluated. It is shown that in order to treat σ systems one must evaluate the total value of the wave function at the proton for the orbital containing the unpaired electron. It is not appropriate to use the net atomic poupulation, *i.e.*, the square of the hydrogen s-orbital coefficient, c_i^2, in the appropriate molecular orbital, as has been done for carbon in ring π systems. An evaluation of the total value of the wave function at various carbons in the ring π system is reported to illustrate why c_i^2 can be employed in these systems.

In order to relate observed proton coupling constants with unpaired electron densities in the adjacent π (carbon) system, McConnell[2-4] has proposed the relationship

$$A_i = Q\rho_i \tag{1}$$

where A_i is the nuclear hyperfine coupling constant, ρ_i is the unpaired electron density in the carbon $p_z(\pi)$ orbital, and Q is a proportionality constant. For several systems, the value of the proportionality constant Q has been found to be -22.5 gauss.[5,6] The electron densities calculated from simple Hückel theory have, in general, been found to give excellent agreement with experimental coupling constants for π systems. The unpaired electron density on an atom is usually evaluated from the coefficient of the atomic orbital in the molecular orbital containing the unpaired spin. This reflects the relative contribution of that atomic orbital to the molecular orbital, and the square of that atomic orbital coefficient is therefore proportional to the electron density contribution that the atomic orbital makes to the total molecular orbital. Hence one finds the substitution of squares of the atomic orbital coefficients from molecular orbitals containing an unpaired electron as an approximation of ρ_i in McConnell's equation (eq 1). This relationship has found widespread use in the analysis of π system electron spin resonance spectra.

The mechanism of odd-electron density transfer to the proton from a carbon π orbital is one of excited-state mixing. Such π-type contact interactions are referred to as indirect contact interactions in this discussion.

The foregoing situation is, of course, different from one in which the odd electron is formally in a σ orbital. In such a case, the contact interaction term can be used to relate the observed nuclear hyperfine splitting with unpaired electron density at a given site without recourse to excited-state mixing.

In contrast to the success of this approach when applied to π systems, the squares of the orbital coefficients resulting from extended Hückel calculations on σ systems usually do not correlate with A_i. This has caused some[7] authors to incorrectly conclude that the extended Hückel calculations are inadequate for σ systems. There are many theoretical reasons why closed-shell calculations should not work on open-shell systems, but most of these reasons also apply to π systems where many successful correlations are reported.

In this article we wish to report that one of the difficulties in the previous work on σ systems is associated with the incorrect approximation of using the square of the atomic orbital coefficient to evaluate ρ_i in eq 1. Rationalization of why this procedure is adequate for π systems is presented. In the course of this study we have also examined the effect of charge on the electron density calculation in benzonitrile.

Calculations

The extended Hückel theory (EHT) calculations were carried out essentially by the method previously described.[8] Coulomb integrals, H_{ii}, are approximated by charge-adjusted valence-state ionization potentials.[9] The valence-state ionization potentials were corrected using the equation

$$H_{ii} = H_{ii}^0 - Kq_i \tag{2}$$

where H_{ii} is the adjusted Coulomb integral, q_i the charge, and K a constant particular to each type orbital of each element.[10] The Wolfsberg–Helmholz arithmetic mean[11] with $K = 1.75$ was used to estimate H_{ij}.

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[1] Abstracted in part from the Ph.D. Thesis of H. Petersen, Jr., University of Illinois, 1966.

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[3] H. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 28, 107 (1958).

[4] H. McConnell, *ibid.*, 28, 1188 (1958).

[5] S. I. Weissman, R. Tuttle, and E. de Boer, *J. Phys. Chem.*, 61, 28 (1957).

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[7] R. H. Holm, G. W. Everett, Jr., and W. D. Horrocks, Jr., *J. Am. Chem. Soc.*, 88, 1071 (1966).

[8] P. C. Van der Voorn and R. S. Drago, *ibid.*, 88, 3255 (1966).

[9] J. Hinze and H. H. Jaffé, *ibid.*, 84, 540 (1962).

[10] L. C. Cusachs and J. W. Reynolds, *J. Chem. Phys.*, 43, 5160 (1965).

[11] M. Wolfsberg and L. Helmholz, *ibid.*, 20, 837 (1952).

Orbital exponents calculated according to Slater's rules[12] have also been corrected for charge in this investigation. An exponent of 1.2 was used for hydrogen.

The geometries of the radicals are illustrated in Figures 1–3. The cyclohexadienyl radical geometry has not been experimentally determined. The assumed geometry is shown in Figure 1. As the methylene carbon is four-coordinate, an essential sp^3 hybridization is assumed, with all C–H bond distances 1.09 A, a $H_7C_1H_8$ angle of 110°, a C_1C_2 (C_1C_6) bond distance of 1.54 A, a $C_1C_2C_3$ ($C_1C_6C_5$) bond angle of 123°, a C_2C_3 (C_5C_6) bond distance of 1.39 A, a $C_3C_4C_5$ bond angle of 120°, and a C_3C_4 (C_4C_5) bond distance of 1.40 A. The ring is assumed planar, with a plane containing $C_1H_7H_8$ at a right angle to the ring. The geometry of benzonitrile negative ion radical was assumed to be the same as that of the parent molecule[13] and is given in Figure 2. The geometry of the cyclopropyl radical has not been experimentally determined. Hydrogen atoms of the methylene groups are assumed to lie in planes perpendicular to and bisecting the CCC angles of the carbon ring, as indicated in Figure 3. The C_1 or apical carbon C–H bond is at an angle θ above and in a plane perpendicular to the ring. The C–C and C–H bond lengths and HCH bond angles are assumed to be the same as those of cyclopropane.[13]

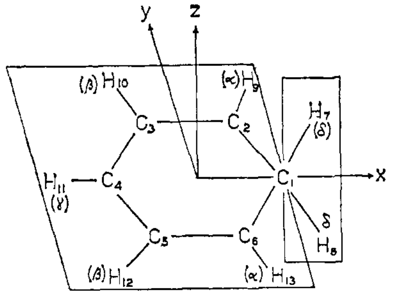

Figure 1. The cyclohexadienyl radical (assumed geometry).

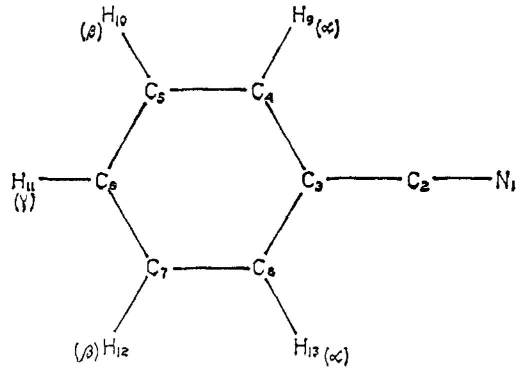

Figure 2. The benzonitrile negative ion radical (assumed geometry).

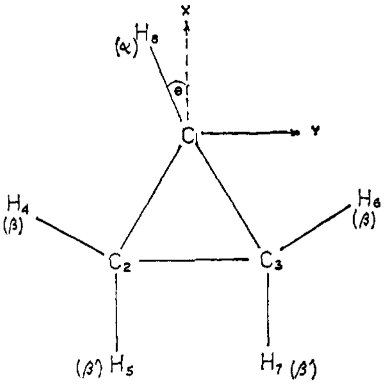

Figure 3. The cyclopropyl radical (assumed geometry).

Instead of using the atomic orbital coefficient in the MO containing the unpaired electron to relate electron density to coupling constants, we were interested in evaluating the total unpaired electron density at the nucleus of the atom (in the σ system examples covered here, the proton causing the splitting). Since unpaired electron density on other atoms in the molecule has a finite probability of being at the nucleus of the proton causing splitting, the total value of the wave function at the proton should be evaluated.

The output of this EHT calculation consists in part of adjusted orbital exponents for each orbital utilized in the basis set (except for 1s orbitals, for which no adjustment is carried out), Cartesian coordinates of the atoms in the molecule, and a tabulation of molecular orbitals in terms of basis set orbital coefficients. To evaluate the magnitude of a given *molecular* orbital at any point in space, the product of an *atomic* orbital of the basis set evaluated at the point and its corresponding coefficient in the molecular orbital is summed over the atomic orbitals in the basis set. Thus

$$\psi_{\mathrm{MO}j}(p) = \sum_i c_{ij}\phi_i(p) \qquad (3)$$

where $\psi_{\mathrm{MO}j}(p)$ is the value of the jth molecular orbital evaluated at point p, $\phi_i(p)$ is the value of the ith atomic orbital evaluated at point p, and c_{ij} is the coefficient of the ith atomic orbital in the jth molecular orbital. The square of the value of a molecular orbital at a point in space represents the electron density at that point due to the electron in that particular molecular orbital. Hence, the square of the sum in eq 3 represents the electron density at that point in space. A computer program was written that carries out this operation.

For σ systems, total unpaired electron density at the proton must be multiplied by a scaling factor to convert it to the coupling constant. The scaling factor for accomplishing this can be calculated from the constants in the equation

$$A\,(\text{gauss}) = \left[\frac{8\pi}{3(2.8025)}g\beta g_{\mathrm{N}}\beta_{\mathrm{N}}\left(\frac{1}{a_0^3}\right)\right]|\psi_{(p)}|^2$$

where $\psi_{(p)}$ is the value of the wave function for a Slater orbital at the point p, a_0 is the Bohr radius, and the other

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(12) C. A. Coulson, "Valence," Oxford University Press, London, 1961, p 40.

(13) "Tables of Interatomic Distances and Configurations in Molecules and Ions," Special Publications No. 11 and 18, The Chemical, Society, London, 1958.

symbols have their usual significance. The value 1596 is obtained and compares favorably with the value 1878 which we have arrived at empirically to scale the results of our calculation to the experimental A. The empirical scaling factor was arrived at before the theoretical one was calculated, and in view of the approximate level of our MO calculations, it was not considered meaningful to vary parameters to improve the fit. For π systems, ψ_{MO}^2 is evaluated at the carbon to which the hydrogen causing the splitting is attached because the hydrogens are orthogonal to the π system. A position 1 A up the z axis was selected, and the electron density at that point was multiplied by a π scaling factor. Although the magnitude of the scaling factor changed when positions other than 1 A were selected, good agreement with experimental coupling constants was always obtained from the ψ_{MO}^2 values. For example, good agreement was obtained with the value of the electron density calculated at the point of maximum probability in the p_z orbital, *i.e.*, at $2/(z - s)$, and also at $3/(z - s)$.

Results

The systems reported in this study are benzonitrile, benzonitrile negative ion radical, cyclohexadienyl radical, and cyclopropyl radical. The pertinent parts of the output are contained in Tables I–VI.

Table I. Matrix for the Benzonitrile Negative Ion Radical ψ^2 Evaluation of Proton Hyperfine Coupling Constants[a]

Coefficient[b]	Atom[c]	ψ at position[a] C_4	C_5	C_6
−0.5632	N_1	+0.0000	+0.0000	+0.0000
+0.3100	C_2	+0.0004	+0.0000	+0.0000
+0.4937	C_3	+0.0092	+0.0006	+0.0002
−0.3575	C_4	−0.0598	−0.0066	−0.0004
−0.1987	C_5	−0.0037	−0.0332	−0.0037
+0.5434	C_6	+0.0007	+0.0102	+0.0911
−0.1987	C_7	−0.0001	−0.0002	−0.0037
−0.3575	C_8	−0.0004	−0.0001	−0.0004
	ψ_{total}	−0.0537	−0.0293	+0.0831
	$\psi^2 \times 10^4$	28.84	8.59	69.06
	Scaling factor[d]	1066	1066	1066
	a_{H} (calcd), gauss	3.07	0.92	7.36

[a] A matrix for the contribution to ψ, for the MO containing the unpaired electron, at positions C_4, C_5, and C_6 from atoms in the basis set listed under the heading Atom. The carbon positions refer to a distance 1.0 A up the z axis from the carbon nucleus (in the p_z orbital). [b] These are p_z orbital coefficients; all in-plane orbital coefficients are zero. [c] See Figure 2 for numbering system. [d] The number required to scale ψ^2 to the values found for the hyperfine coupling constants from the epr spectrum. This value has been found to be constant in a large number of π systems that we have studied.

Table II. Benzonitrile Negative Ion Radical Proton Hyperfine Coupling Constants

	Calculated coupling constants, gauss				Exptl coupling constant,
	Direct scaling		Gross atomic population		
Atom	c_i^2	a_{H} (calcd)[a]	A	a_{H} (calcd)[b]	gauss[c]
C_4	0.1278	3.64	0.0968	3.51	3.63
C_5	0.0395	1.13	0.0293	1.06	0.30
C_6	0.2953	8.42	0.2321	8.42	8.42

[a] Scaling factor = 28.5. This scaling factor differs from that in Table I because ψ^2 was scaled there and c_i^2 is being scaled here. [b] Scaling factor = 36.3. [c] P. H. Rieger, I. Bernat, W. H. Reinmuth, and G. K. Fraenkel, *J. Am. Chem. Soc.*, **85**, 683 (1963).

Table III. Matrix for the Cyclohexadienyl Radical Total Unpaired Electron Density Calculation[a]

Coefficient	Atom[c]	ψ at position[a] C_2	C_3	C_4	δ
+0.1160[b]	C_1	+0.0015	+0.0001	+0.0000	+0.0131
−0.5700[b]	C_2	−0.0950	−0.0107	−0.0006	−0.0024
−0.0290[b]	C_3	−0.0005	−0.0048	−0.0005	+0.0000
+0.6045[b]	C_4	+0.0007	+0.0111	+0.1008	+0.0000
−0.0290[b]	C_5	+0.0000	+0.0000	−0.0005	+0.0000
−0.5700[b]	C_6	−0.0005	−0.0002	−0.0006	−0.0024
+0.1964	H_7	+0.0017	+0.0001	+0.0000	+0.1457
−0.1964	H_8	−0.0003	+0.0000	+0.0000	−0.0025
	ψ_{total}	−0.0925	−0.0045	−0.0985	+0.1514
	$\psi^2 \times 10^4$	85.59	0.20	97.04	229.1

[a] A matrix for the contribution to ψ, for the MO containing the unpaired electron, at positions C_2, C_3, C_4, and δ from atoms in the basis set listed under the heading Atom. Carbon positions refer to a distance 1.0 A up the z axis from the carbon (in the p_z orbitals) and δ to the hydrogen nucleus. [b] These are p_z orbital coefficients; all in-plane orbital coefficients are zero. [c] Atoms lettered as in Figure 1 where H_7 and H_8 are in a plane perpendicular to the ring.

Table IV. Cyclohexadienyl Radical ψ^2 Evaluation of Proton Hyperfine Coupling Constants

Position[a]	$\psi^2 \times 10^4$ [b]	SF[c]	a_{H} (calcd)	a_{H} (exptl)[d]	
$C_2(C_6)$	85.59	1066	9.12	8.99	10.2
$C_3(C_5)$	0.20	1066	0.02	2.65	0
C_4	97.04	1066	10.34	13.04	10.2
δ	229.1	1887	43.23	47.41	45.0

[a] The positions C_2 (C_6), C_3 (C_5), and C_4 refer to carbon p_z orbitals, and δ refers to the H_7 (H_8) nucleus (see Figure 1). [b] From Table III. [c] Scaling factors. The numbers required to scale ψ^2 to the values found for the proton hyperfine coupling constant from the epr spectrum. The proton is that attached to the carbon indicated under the position column. We have found these values to be constant for a large number of σ (1887) and π (1066) systems that we have studied. [d] The values in the first column were reported by R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963), and those in the second column are those by I. Chkheidze, *et al.*, *Proc. Acad. Sci. USSR, Chem. Sect.*, **130**, 201 (1960). Other values between these limits have also been reported.

Discussion

ψ^2 Evaluation. The results of the ψ^2 evaluation on benzonitrile negative ion radical are listed in Table I. By comparing the number in column C_4 (*i.e.*, position C_1), row C_4 (this quantity will be referred to as the local contribution to ψ and is proportional to c_i^2) with ψ total, it is seen that the two agree and the net of all other contributions to the MO at that point from other atoms (column C_4, rows C_2, C_3, etc.) largely cancel. This is also the case at positions C_5 and C_6. In view of this cancellation, it is possible to use c_i^2 to correlate with the coupling constants in this and related π systems. The a_{H} (calcd) values obtained from c_i^2 are listed in Table

Table V. Matrix for the Cyclopropyl Radical Total Unpaired Electron Density Calculation[a] ($\theta = 20°$)

Coefficient	Atom[a]	ψ at positions[a] α	β	β'
−0.1032	C_1	−0.0086	−0.0005	−0.0005
+0.9687		+0.0478	+0.0037	−0.0037
−0.1928		−0.0095	−0.0007	+0.0007
−0.0000		−0.0000	−0.0000	−0.0000
+0.0080	C_2	+0.0000	+0.0007	+0.0007
−0.0611		−0.0000	−0.0076	+0.0076
+0.0629		+0.0003	−0.0023	−0.0023
+0.0345		−0.0000	+0.0021	+0.0021
+0.0080	C_3	+0.0000	+0.0000	+0.0000
−0.0611		−0.0000	−0.0002	+0.0002
+0.0629		+0.0003	−0.0001	−0.0001
+0.0345		+0.0000	+0.0003	+0.0003
−0.1410	H_4	−0.0001	−0.1046	−0.0016
+0.1300	H_5	+0.0001	+0.0014	+0.0964
−0.1410	H_6	−0.0001	−0.0004	−0.0001
+0.1300	H_7	+0.0001	+0.0001	−0.0004
+0.0448	H_8	+0.0332	+0.0000	+0.0000
	ψ_{total}	+0.0633	−0.1080	+0.1003
	$\psi^2_{\text{total}} \times 10^3$	4.004	11.66	10.05
	a_H (calcd)[b]	7.56	22.00	18.96

[a] Values indicate contribution to ψ for MO containing the unpaired electron at positions α, β, and β' for atomic orbitals on atoms listed under the heading Atom. The carbon orbital coefficients are listed in the order 2s, $2p_z$, $2p_x$, and $2p_y$. Hydrogen coefficients are for 1s orbitals. See Figure 3 for the numbering system. The positions α, β, and β' refer to the H_3, H_4 (H_6), and H_5 (H_7) nuclei, respectively. [b] a_H is calculated using the scaling factor 1887.

Table VI. Benzonitrile Lowest Lying Unfilled Orbital. Comparison of Molecule and Negative Ion Basis Set Coefficients

	Basis set π-orbital coefficients			
	Molecule		Ion	
Atom[a]	c_i	c_i^2	c_i	c_i^2
N_1	−0.5701	0.3250	−0.5632	0.3172
C_2	+0.3820	0.1459	+0.3100	0.0961
C_3	+0.4410	0.1945	+0.4937	0.2437
C_4	−0.3772	0.1423	−0.3575	0.1278
C_5	−0.1783	0.0318	−0.1987	0.0395
C_6	+0.5132	0.2634	+0.5434	0.2953

[a] See Figure 2 for numbering system.

II. The scaling factor of 28.5 employed here to scale the c_i^2 values is close to the observed value of $|22.5|$, calculated from benzene negative ion studies.[14] We have tried several calculations involving different sets of orbital exponents and have found that the scaling factor for c_i^2 values for π systems is essentially insensitive to the choice of exponents.

The square of the p_z orbital coefficient in the π system containing the unpaired electron has been taken as proportional to the electron density at that position (and hence to the proton coupling constant). Cognizance should also be taken of the fact that some of the electron density in the MO is shared in bonds and that the *gross atomic population*, as defined by Mulliken and indicated below, would perhaps be a better measure of the electron density assignable to a particular atomic orbital. For purposes of illustration, consider a MO comprised of atomic orbitals ϕ_1 and ϕ_2.

$$\psi = c_1\phi_1 + c_2\phi_2$$

If N is the occupation number of the MO (1 in this case), the square of the wave function, integrated over all space, yields

$$1 = c_1^2 + c_2^2 + 2c_1c_2S_{12}$$

where S_{12} is the overlap of the two atomic orbitals, and N has been taken as 1. The squared terms represent *net atomic populations* and $2c_1c_2S_{12}$ the overlap population for the 1,2 orbital overlap. The *gross atomic population* (A) is defined as the net atomic population and one-half the overlap population. When this term, A, is summed in the case of benzonitrile negative ion radical (the overlap population now consists of seven terms, as there are eight nonzero coefficients in the MO) the results are found as listed in Table II. There is only a slight change in the predicted coupling constants, compared with the values calculated from c_i^2 terms. A slightly larger scaling factor, 36.3, is also required in this latter calculation. This results because the value of the overlap population summation is small compared with the c_i^2 terms and is composed of partially cancelling terms, the resulting sum being negative. Since the values calculated by both methods are so similar and the former are easier to calculate, the c_i^2 values can be generally employed for calculations on π systems.

It should be pointed out that a negative coupling constant is expected at the *meta* position.[7] In general, whenever the electron density on an atom is low, a negative coupling constant is possible because of the predominance of exchange-type interactions. Since the concept of negative electron density is foreign to the EHT treatment, we cannot hope to calculate the coupling constant if it is negative but will have to be satisfied with a low calculated electron density at that position.

It is of interest at this point to compare the magnitude of the ψ terms making up the total value of ψ at each π-orbital site for the cyclohexadienyl radical. These are listed in Table III. Note that at the C_3 position, contributions from p_z orbitals on atoms C_2 and C_4 essentially cancel. At other π positions, the total value of ψ is also very nearly that of the respective p_z orbital, other contributions being negligible. Hence, for the π system in this radical, the ratios of squares of p_z-orbital coefficients can also be reliably used as a measure of coupling constant ratios.[16] This result coupled

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(14) In the case of the cyclohexadienyl radical, Fessenden and Schuler[15] found that a Q of $|25.7|$ was required to account for features of that radical. In other[13] radicals these authors report Q varies from the benzene negative ion value. This can be interpreted as being caused by slight differences in the formal hybridization of the carbon atom in these several systems. A further discussion of this point will follow. It should also be pointed out that part of the difference in this scaling factor and $|22.5|$ arises from the fact that the EHT wave functions are normalized according to $\sum c_i^2 + \sum_{i \neq j} c_ic_jS_{ij} = 1$.

(15) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(16) Using the scaling factor of 28.5 for scaling the squares of p_z orbital coefficients as in the benzonitrile case, calculated values for the C_2, C_3, and C_4 positions in cyclohexadienyl radical are 9.26, 0.02, and 10.6 gauss, respectively.

with those on the benzonitrile negative ion radical illustrate why squares of p_z-orbital coefficients generally suffice for coupling constant correlations on π systems.

Conversion of the electron density at positions H_7 and H_8 in the cyclohexadienyl radical requires a different scaling factor because these hydrogens are not orthogonal to the π system; hence they contribute directly to the molecular orbital containing the unpaired electron. By examining a large number of systems[17] we have found the scaling factor of 1887 to be transferrable for cases where unpaired electron density is placed directly on the proton (as opposed to exchange interactions). The local contribution to the ψ term from H_7 is $+0.1457$, but the total value of ψ is $+0.1514$. If the local value for ψ is employed, the resulting value of a_H (scaling factor = 1887) is 40.06 gauss compared to the value of 43.23 gauss obtained using the total ψ. Although the use of total ψ produces a closer fit, the difference is hardly significant in this case.

A pronounced difference, however, illustrating the importance of the ψ^2 calculation, is seen in the results for the cyclopropyl radical, Table V. At the H_8 proton, the local contribution to ψ is $+0.0332$, but the total value of ψ at this point is almost twice that, $+0.0633$. Using the total ψ and the scaling factor of 1887 as before, excellent agreement is observed between calculated and experimental results. Experimentally, the α- and β-hydrogen coupling constants are found to be[15] 6.51 and 23.42 gauss, respectively. Since only a single β-hydrogen coupling constant is found and in view of the small value for the α coupling constant, the authors[15] conclude that H_8 is displaced from the plane of the carbon skeleton and is oscillating between positions above and below the ring. The experimental value is seen to be approximately the average of our calculated β and β' values.

Comparison of the Molecule and Ion c_i^2 Evaluation. Using the experimentally determined geometry of the molecule, EHT calculations were carried out on both benzonitrile and its negative ion radical. The lowest lying unfilled orbital in the molecule is of π symmetry and includes carbon p_z orbital coefficients from all atoms of the ring and the CN group. A comparison of this orbital in the molecule and in the ion is given in Table VI (refer to Figure 2 for molecular topology). The coefficients for C_7 and C_8 are identical with those for C_5 and C_4, respectively, as the molecule has a twofold rotation axis along the N_1–C_2 bond axis. All other coefficients are zero. A significant difference exists between c_i for corresponding orbitals in the ion and in the molecule. In particular, it is observed that the ratio of the squares of p_z orbital coefficients for atoms C_6 and C_4, c_6^2/c_4^2, in the ion (2.311) is in much closer agreement with the observed ratio of the coupling constants for these positions (2.320) than is that calculated from the molecule (1.851). Within the deviations generally observed in these calculations, however, the coupling constant correlations could be made with the coefficients from either the lowest lying empty molecular orbital in the molecule or the orbital containing the unpaired electron in the ion, in this instance. This does not imply, however, that only insignificant or relatively small changes are observed *in general* when an electron is added to a molecule. As an example, the effects on the ordering of orbitals immediately below the previously empty π orbital are very marked. The highest filled orbital is of π symmetry and is numbered 19 (where no. 1 is the highest empty orbital in the molecule). This orbital is lowered to no. 21 in the ion while orbitals 20 (π) and 21 (σ) in the molecule move up to 19 and 20, respectively, in the ion. Similar changes occur in other orbital orderings. It is not inconceivable that with the addition of an electron to a molecule, an orbital of different symmetry from the previously lowest lying empty orbital could contain the unpaired electron. This emphasizes the importance of using wave functions for the radical rather than those of the molecule from which the radical was derived when calculating epr coupling constants. When charge corrections are not made in the EHT calculations, these results suffer from the same disadvantage as using the wave function for the molecule since the molecule and ion become equivalent at this level of approximation.

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(17) R. S. Drago and H. Petersen, to be published.