

ESR SPECTRA OF CATION AND ANION OF AROMATIC HYDROCARBONS

Proton Hyperfine Splitting and Electron Density Relationship*

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Some features of the McConnell, Colpa-Bolton and Giacometti-Nordio-Pavan equations for A^H , the proton hyperfine splitting in the ESR spectra of cation and anion radicals of aromatic (alternant) hydrocarbons are explored. An extended Huckel molecular orbital type calculation is carried out on benzene (cation and anion) and A^H is correlated to the charge density on proton. Such correlation seems to explain the larger splitting constant (A^H) in cation, generally observed.

ESR Spectra of the neutral radicals and radical ions have been of considerable interest to a quantum chemist, because this technique helps in mapping the electron densities of the molecular species.¹ ESR spectra of anion and cation radicals of aromatic hydrocarbons, particularly the even alternants, have been of special interest. In these hydrocarbon ions the pi-electron densities occur in pair, i.e., the unpaired pi-electron density of cation and anions are the same.¹ Hence, the molecular properties depending upon the unpaired pi-electron density should be the same in anions. Since McConnell proposed² his equation for the hyperfine splitting constant due to proton, attempts were made to interpret the ESR spectra of the radicals and cation and anion radicals of aromatic hydrocarbon. When it was found that the A^H , the hyperfine splitting constant, of cation radicals is greater than those of anion radicals, attempts were made to explain this phenomenon by proposing more elaborate equations.^{3,4} All these equations correlated A^H to the pi-electron densities. In the present study the electron and charge densities on protons are calculated and correlated to A^H . An extended Huckel-type molecular orbital calculations on benzene cation and anion, taking into account all the sigma and pi-electrons, was performed to illustrate this point.

Results and Discussion

In aromatic hydrocarbons the 'active' electrons move in pi-orbitals which have node in the molecular plane containing protons. Thus an odd electron supposedly cannot interact with protons except through 'polarizing' sigma electrons. McConnell derived² equation 1, taking sigma-pi interaction,

$$A^H = Q_{\text{CH}}^H P_c \quad (1)$$

Q_{CH}^H being 'polarizing' parameter of sigma

core and P_c is the unpaired pi-electron density on the carbon atom to which hydrogen is attached. This equation has been widely used to interpret the ESR spectra of radicals and radical ions including aromatic hydrocarbon radical ions.

The alternant hydrocarbon anions and cations follow pairing theorem¹ and the unpaired electron (spin) density should be the same in these two ions. This means the cations and anions should have the same A^H . This is contradictory to the observation.⁵ The anions and cations of naphthalene, for example, have different A^H (see ref 5 and 7 for other examples), cation having larger A^H . Since the pairing theorem is much deep rooted and the McConnell equation was inadequate to explain A^H in these ion radicals alternative equation were proposed. Colpa and Bolton³ proposed,

$$A^H = A p_c + K E_p \quad (2)$$

where, $E = (q_c - 1)$ is the excess charge, A and K are constants. Giacometti, Nordio and Pavan proposed,⁴

$$A^H = B P_c + D P_{cr} \quad (3)$$

where p_{cr} is the bond order of the bond between the carbon atom, to which proton is attached and the contiguous carbon atoms (summation), B and D are constants. While Fraenkel *et al.* showed Copla-Bolton equation to be superior, Higuchi¹⁰ have proved this equation to be theoretically incorrect. Huckel-molecular orbital and more sophisticated molecular orbital method for pi-electrons have been used in conjunction with these equations.^{3,4,5} Full discussion are given by Amos and Snyder,⁵ and Fraenkel *et al.*⁷

These more-than-one-term equations (2 and 3) suffer from several other defects. The values of K and D are quite sensitive to the excess charge and bond orders and depends upon the type of molecular orbital methods employed. Besides, in some alternant hydrocarbons the second term in the above equations becomes zero and one gets back the McConnell equation. Other drawbacks

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of the above-mentioned equations are the use of pi-electron spin densities. A more direct approach would be to correlate A^H with the electron or charge densities on protons.

If one carries out all valence electron molecular orbital calculation, as is done in the present study on benzene (including sigma- and pi-orbitals) by constructing the symmetry orbital from D_{6h} symmetry and making the Huckel type assumptions (see appendix), it is found that, assuming a linear relationship between A^H and excess charge ($1-q_H$) on proton, the A^H in cation should be greater than in anion, as it should be^{5,7,8}, since the excess charge on proton in the case of benzene is greater in cation (Table 1). From Table 1 it is also evident that a simple McConnell equation correlating A^H to electron density on proton is inadequate. However, equation involving excess charge, on proton could explain the phenomenon. The equation relating the experimental A^H and the charge density of the radical on a particular proton could thus be:

$$\begin{aligned} A^H &= K(1-q_H) \quad \text{or} \\ A^H &= C + K(1-q_H) \end{aligned} \quad (4)$$

where K and C are constants, q is the charge density (on proton) as defined in the appendix.

We thus propose that an extended Huckel type molecular orbital, involving all the valence electrons, should be performed and the excess charge on the protons should be calculated and correlated with A^H if the hyperfine splittings of the cation and anion radicals are to be explained.

There is one aspect to be pointed out. In benzene cation and anion, the protons are equivalent, thus equation 4 is applicable. It will be interesting to find out if such simple relationship exists in the case when there are sets of non-equivalent protons (e.g. naphthalene cation and anion).

TABLE I

Species	P_H	$1-q_H$	P_C	A^H (expt)
Neutral	—	—	—	—
Cation	0	0.1230	0.166	4.44 ^a
Anion	0.0052	0.1176	0.16 ^c	3.75 ^a

(a) E.T. Kaiser and L. Kevan, *Radical Ions* (Interscience, New York, 1968).

(b) See ref. 5 and 9.

(c) Present calculations; Huckel calculation gives 0.166.

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Appendix

The n electron Hamiltonian for a molecule is given as:

$$H(1,2, \dots, n) = H^{\text{core}} + \sum_{i < j} \sum_{r, ij} \frac{1}{r_{ij}} \quad (\text{A-1})$$

In the Huckel method this Hamiltonian is simplified to

$$H(1,2, \dots, n) = \sum_m H_{\text{eff}}(m) \quad (\text{A-2})$$

thus

$$H_{\text{eff}}(m) v_i(m) = E_i v_i(m) \quad (\text{A-3})$$

A second assumption in the HMO method is the LCAO approximation, it is supposed that

$$v_i = \sum_p C_{ip} X_p \quad (i=1,2, \dots, n) \quad (\text{A-4})$$

where X_p 's are atomic orbitals. On applying the variation principle, the secular equation

$$\sum_p C_{ip} (H_{pq}^{\text{eff}} - S_{pq} E) = 0 \quad (i=1,2, \dots, n) \quad (\text{A-5})$$

which had the determinant

$$H_{pq}^{\text{eff}} - S_{pq} E = 0 \quad (p, q=1,2, \dots, n) \quad (\text{A-6})$$

are obtained and are to be solved. In HMO, we also define H_{pq} and S_{pq} ,

$$\begin{aligned} S_{pq} &= 0 \quad (p \neq q) \\ &= 1 \quad (p = q) \end{aligned}$$

for noncontiguous atoms: $H_{pq} = 0$

Instead of taking (A-4) as the solution of Schrodinger equation, one can use symmetry orbitals which are, in turn, the linear combination of atomic orbitals. These symmetry orbitals give rise to a simplified secular determinant which is solved for E . Various roots are used in (A-5) and the coefficient are determined.

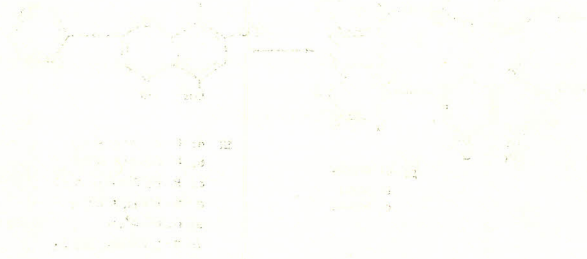
The charge density, q , on any atom i in the molecule is defined as:

$$q = \sum_j g_j C_{ij}^2 \quad (\text{A-7})$$

where j 's are filled m.o.'s and g_j is the population of the occupied molecular orbital.

In the benzene cation the highest occupied molecular orbital is the degenerated pi-orbital. In the anion the following degenerate orbitals are occupied by the unpaired electron.

$$\begin{aligned} &0.1765 H_4 - 0.4237 \Phi_4 + 0.888 \Psi_4 \\ \text{and } &0.1765 H_5 - 0.4237 \Phi_5 + 0.8887 \Psi_5 \end{aligned}$$



The charge densities on the atoms of the benzene cation and anion are given in Table 1. The charge densities on the atoms of the benzene cation are given in Table 1. The charge densities on the atoms of the benzene anion are given in Table 1.

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where H , Φ and ψ are semidelocalized symmetry orbitals and can be constructed from D_{6h} symmetry of benzene and the sp^2 hybridization of carbon atoms. H arises from considering hydrogens as six-membered ring, Φ and ψ come from sp^2 carbon orbitals.

TABLE 2.—BASIC INTEGRALS USED IN MO CALCULATION.

$I(s_H)$	13.6 eV	$I(sp^2)$	14.72 eV
$\beta_{s_H s_C}$	-5.00 eV	$\beta_{s_H s_C}$	-3.00 eV
$\beta_{\phi-H}$	-5.30 eV	$\beta_{\Psi-H}$	-1.667 eV
		$\chi-H$	
$\beta_{\Psi_j \chi_k} (j \neq k, \text{ adjacent})$			-5.50 eV.

Note: The subscripts H and C indicate hydrogen and carbon respectively.

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