

Nonempirical Evaluation of π -Electron Charge-Density Dependence of Proton Isotropic Hyperfine Coupling Constants. An Application of the Valence-State Model*

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THE formula of McConnell,¹⁻³ $a = Q\rho$, relating the isotropic hyperfine coupling constant of a proton attached to an aromatic carbon to the π spin density ρ , has been extremely useful in elucidating electron paramagnetic resonance spectra. Apparent nonlinear deviations from McConnell's relation have been attributed to spin density in adjacent C-C bonds,⁴ $a = Q\rho + Q'\rho^{adj}$, and to excess π -electron charge density ϵ^{5-7} :

$$a = Q\rho + K\epsilon\rho. \quad (1)$$

It is the purpose of this Note to obtain a completely nonempirical estimate of the excess charge effect.

The "mechanism" behind Eq. (1) is the expansion and contraction of atomic orbitals (AO) accompanying the changes of π -electron charge.⁹ In calculating the ratio Q/K , Bolton⁶ estimated the AO changes from NMR data. We use the completely theoretical estimates based on the valence-state model.¹⁰⁻¹² Our results indicate the usefulness of this model for calculations of molecular properties.

Theoretical treatments of the proton coupling constant in a hypothetical "CH fragment" lead to^{1,3}

$$a/\rho \propto M(K_{\pi\sigma} - K_{\pi s})/\Delta E,$$

where K_{ij} is an exchange integral between Orbitals

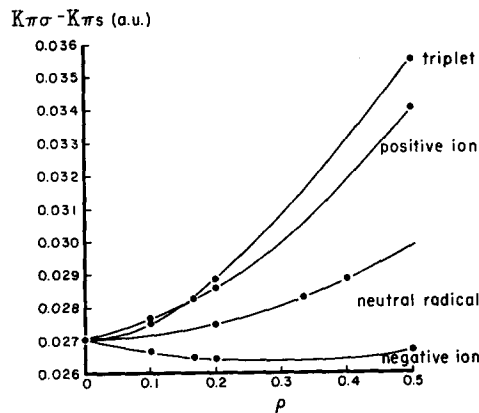


FIG. 1. $K_{\pi\sigma} - K_{\pi s}$ as a function of ρ for positive and negative ions, neutral radicals, and triplet states.

i and j , π is a $2p\pi$ carbon AO, s is a $1s$ hydrogen AO, σ is a carbon sp^2 σ hybrid pointing towards the hydrogen, ΔE is the $\sigma\sigma^*$ excitation energy of the CH bond, and M is either $(1 - \langle \sigma | s \rangle^2)^{-1}$ [molecular-orbital (MO) theory] or $(1 - \langle \sigma | s \rangle^4)^{-1}$ [valence-bond (VB) theory]. M is relatively insensitive to the AO changes involved here; we have taken M as a constant.

Calculation of $K_{\pi\sigma}$ and $K_{\pi s}$ is straightforward but calculation of ΔE is not. Indeed, simple VB theory predicts¹³ a ΔE with the wrong sign. We assume that ΔE changes are relatively small and consequently write

$$a/\rho \propto K_{\pi\sigma} - K_{\pi s}. \quad (2)$$

The AO's used in evaluating (2) are characterized in Table I. Certain assumptions (appropriate for alternant hydrocarbons in the single-configuration π -electron approximation) were made in obtaining

TABLE I. Slater-type atomic orbitals for carbon in alternant hydrocarbons.^a

Species	ρ π -electron spin density	ζ , Orbital exponent for basis functions ^b				Coefficients for orthogonalized $2s$ atomic orbital ^c	
		$1s$	$2s$	$2p\sigma$	$2p\pi$	c_{1s}	c_{2s}
Singlet ground state	0	5.6787	1.6649	1.6136	1.2929	-0.24872	1.02763
	0.1	5.6784	1.6724	1.6266	1.3080	-0.25051	1.02805
Positive ions	0.1667	5.6782	1.6772	1.6348	1.3217	-0.25171	1.02832
	0.2	5.6782	1.6795	1.6388	1.3300	-0.25234	1.02845
	0.5	5.6772	1.7001	1.6720	1.4670	-0.25740	1.02964
Negative ions	0.1	5.6790	1.6571	1.5996	1.2833	-0.24678	1.02719
	0.1667	5.6792	1.6517	1.5896	1.2796	-0.24543	1.02690
	0.2	5.6793	1.6489	1.5843	1.2786	-0.24479	1.02674
	0.5	5.6801	1.6214	1.5288	1.2878	-0.23814	1.02527
Triplet states (Neutral radicals)	0.1(0.2)	5.6787	1.6640	1.6114	1.3042	-0.24849	1.02758
	0.1667 (0.3333)	5.6786	1.6624	1.6077	1.3238	-0.24813	1.02749
	0.2(0.4)	5.6786	1.6614	1.6551	1.3371	-0.24791	1.02744
	0.5(1)	5.6779	1.6462	1.5666	1.5387	-0.24450	1.02662

^a Compiled from Refs. 11 and 12.

^b $\zeta=1$ was used for the hydrogen $1s$ orbital.

^c The orthogonalized $1s$ orbitals, which do not enter the present calculations, are also linear combinations of the $1s$ and $2s$ basis functions. See Refs. 11 and 12.

TABLE II. Values of Q/K .

		Q/K
Theoretical ^a	Positive ions	3.55
	Negative ions	8.92
	All ions	5.20
Experimental	Colpa and Bolton ^b	1.83
	Snyder and Amos ^c	2.11
	Bolton ^d	2.4

^a Theoretical Q/K 's are determined by the best fit of straight lines (in the least-squares sense) to $K_{\pi\sigma} - K_{\pi s}$ for appropriate subsets of the following values of ϵ : 0, ± 0.1 , ± 0.1667 , ± 0.2 .

^b Reference 5.

^c Reference 17.

^d Reference 8.

these AO's. The relevant assumptions are equivalent to: $\epsilon=0$ for neutral radicals and triplets; $\epsilon=\rho$ for positive ions; $\epsilon=-\rho$ for negative ions.

In Fig. 1, $K_{\pi\sigma} - K_{\pi s}$ is plotted¹⁴ versus ρ for positive and negative ions, neutral radicals, and triplet states.¹⁵ It is apparent that: (1) the dependence of $a(\rho, \epsilon)$ on ρ and ϵ is not as simple as in Eq. (1); (2) $a(\rho, \epsilon)$ has different functional dependences for differently charged radicals; (3) although $\epsilon=0$ for triplets (in the single-configuration MO theory of alternant hydrocarbons), the dependence of a on ρ is quite similar to the dependence for positive ions. Nevertheless, experimental values of ρ usually lie below 0.2, and for small ρ one may fit a/ρ by a straight line. The best fits in the least-squares sense of a/ρ for $\rho \leq 0.2$ yield the values of Q/K given in Table II.

On the basis of data given in Ref. 5 we have accounted for half the improvement possible¹⁶ by using a relation of Form (1), without calibrating Q/K to experimental data.

Considering the approximations in the valence-state and CH fragment models, the theoretical Q/K is reasonably close to the recent experimental values of Snyder and Amos¹⁷ and of Bolton.⁸ By a simple application of the valence-state model, the excess charge effect has been shown nonempirically to account for the order of magnitude of the deviations from McConnell's relation.

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¹ H. M. McConnell, *J. Chem. Phys.* **24**, 764 (1956).

² H. M. McConnell, *Proc. Natl. Acad. Sci. U.S.A.* **43**, 721 (1957).

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

⁴ G. Giacometti, P. L. Nordio, and M. V. Pavan, *Theoret. Chim. Acta* **1**, 404 (1963).

⁵ J. P. Colpa and J. R. Bolton, *Mol. Phys.* **6**, 273 (1963).

⁶ J. R. Bolton, *J. Chem. Phys.* **43**, 309 (1965).

⁷ The relative importance of the excess charge and the adjacent bond order effects is difficult to determine (see Ref. 8). Probably both effects should be taken into account simultaneously.

⁸ J. R. Bolton (private communication); $Q/K=2.4$, based on the ESR spectra of the positive and negative ions of nine alternant hydrocarbons.

⁹ J. Higuchi, *J. Chem. Phys.* **39**, 3455 (1963), derived a charge dependence for a based on a mechanism other than orbital changes. His calculations yield an ϵ dependence opposite to the experimental one.

¹⁰ H. J. Silverstone, H. W. Joy, and M. K. Orloff, *J. Am. Chem. Soc.* **88**, 1325 (1966).

¹¹ H. J. Silverstone and H. W. Joy (to be published).

¹² H. W. Joy and H. W. Silverstone (to be published).

¹³ H. S. Jarrett, *J. Chem. Phys.* **25**, 1289 (1956).

¹⁴ Calculations are carried out for a CH distance of 1.084 energy units are 1 a.u. = 27.21 eV.

¹⁵ Equation (2) can also be shown to hold for triplet states by a trivial generalization of the CH fragment model.

¹⁶ The best fit of a relation of the form $Q\rho + K\epsilon\rho$ to the experimental hyperfine splittings tabulated by Colpa and Bolton (Ref. 5) yielded $Q/K=31.2/17=1.83$. Calculation of the root-mean-square deviations $s(Q/K)$ of the experimental points from $31.2[\rho + \epsilon\rho(K/Q)]$ G for $Q/K = \infty, 5.20$, and 1.83 leads to $[s(\infty) - s(5.20)]/[s(\infty) - s(1.83)] = 0.49$.

¹⁷ L. C. Snyder and A. T. Amos, *J. Chem. Phys.* **42**, 3670 (1965); $Q/K=2.11$.

Upper Limit to the Electric-Field Effect on the NMR Spectrum of Nitromethane*

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RECENTLY, Sears and Hahn¹ reopened the question of the expected size of quadratic electric-field effects on the NMR of polar liquids by reporting some surprisingly negative results, including one which contradicts an earlier positive finding.² In view of the uncertainty of the experimental situation we wish to report another negative result alluded to rather unspecifically elsewhere.³

The unsaturated slow-passage proton spectrum of CH_3NO_2 was examined at 56.4 MHz using a parallel-plate cell consisting of two strips of aluminum separated by 0.244 cm of epoxy resin, which formed the edges and ends of the cell. The CH_3NO_2 was Eastman spectrograde, used as received. With no electric field applied the spectrum was a single line of irregular shape. Splitting it into a 1:2:1 triplet by modulation of the magnetic field gave resolved structure for modulation frequencies ≥ 4 Hz.

A potential difference of 5.0 kV applied across the cell with $\mathbf{E} \parallel \mathbf{H}_0$ produced no observable change in the spectrum. Using $r_{\text{HH}}=1.79 \text{ \AA}$, $\mu=3.46 \text{ D}$, $\epsilon=37$, an independent-particle model with Lorentz cavity boundary conditions^{4,1} predicts a splitting into a 1:2:1 triplet with spacings of 11.3 Hz. The experimental upper limit of the effect is thus about one-third of the Lorentz cavity prediction. In view of the inadequacies of the latter model³ this negative result is not surprising.

The effects of the static-field inhomogeneities in our cell, which give the observed ~ 4 -Hz linewidth, should be removable in a Carr-Purcell spin-echo experiment,⁵ leaving an echo-envelope beat from any induced spin-spin coupling. We attempted such an experiment and found the decay to be artificially shortened with the electric field on by effects arising from conduction in the sample. Similar effects were reported by Sears