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Theory of Deuterium Effect on the ESR Spectra of Cyclic Polyene Radicals
A Semiempirical Approach

M. Rossi, P. L. Nordio, and G. Giacometti
Institute of Physical Chemistry, University of Padova, Padova, Italy

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The effect of substituting one hydrogen atom with a deuterium atom on the spin density distribution of cyclic aromatic mononegative ions is theoretically investigated. Vibronic interaction with CH modes is considered and evaluated on the basis of a semiempirical approach which makes use of experimental I.R. results. The predictions are consistent with the available experimental data.

Die Auswirkung einer einfachen Deuteriumsubstitution auf die Verteilung der Spindichte bei einfach-negativen aromatischen Ionen wird theoretisch untersucht. Die Vibrationswechselwirkung mit CH-Schwingungen wird mit Hilfe einer semiempirischen Näherung untersucht. Die Voraussagen stimmen mit den experimentellen Daten überein.

L'effet de la substitution d'un atome d'hydrogène par un atome de deutérium sur la distribution de densité de spin dans les ions aromatiques négatifs est étudiée théoriquement. L'interaction vibronique avec les modes C–H est considérée et évaluée sur une base semi-empirique utilisant des résultats expérimentaux de spectroscopie infra-rouge. Les prédictions ne contredisent pas les données expérimentales existantes.

Introduction

A recent ESR investigation [1] has shown that the twofold degeneracy of the ground electronic state of the benzene negative ion is lifted on deuterium substitution. On the contrary deuteration does not alter the proton hyperfine splitting in the cyclooctatetraene radical anion [2].

Two simple models have been proposed to provide a qualitative explanation of the deuterium effect. A. Carrington *et al.* [2] suggest that the answer is to be found in the dependence of the CH stretching vibrational frequencies on the electronic charge of the C-atom. The effect would be absent in cyclooctatetraene since, from a static Jahn-Teller point of view, the H nuclei are still equivalent in the favoured b_{2g} distorsion.

On the other hand, Karplus *et al.* [3] believe that the effect is produced by the out of plane C–H vibrational modes which perturb the Hückel resonance integral β. By using a simple orbital following approximation, a reasonable value of β (40 Kcal/mole) reproduces the experimental result.

In the present work we do not assume any *a priori* theoretical model but we evaluate semiempirically the parameters, which describe the coupling between electronic and CH vibrational motions. To this aim we make use of the results of an experimental work [4] on the lowering of vibrational frequencies of aromatic hydrocarbon radical anions compared with that of the corresponding neutral molecules. The knowledge of these vibronic coupling parameters allows us to calculate a detailed vibronic wave function of the degenerate ground state and, therefore, the splitting produced by deuterium perturbation.

The resulting spin densities are in good agreement with experiment and it turns out that the most active vibration in producing the effect is the out of plane CH bending in agreement with Karplus views.

Theoretical Treatment

It is well known that in the case of two or more states separated by small energy differences a correct wave function for a polyatomic molecule cannot be written simply as a product of an electronic and a vibrational part. Following the method proposed by McConnell and McLachlan [5] we approximate the two complex conjugate wave functions Φ_a and Φ_b corresponding to the ground state degenerate levels of a cyclic polyene radical anion with the expression:

$$\Phi_a = (\Phi_b)^* = S \cdot \left[\omega_\lambda \chi_v^0 + \omega_{-\lambda} \sum_m c_m \chi_v(K_m^1, K_m^2, \ldots)\right] \tag{1}$$

where $S = \left[1 + \sum_m c_m^2\right]^{-1/2}$ is the normalization factor, χ_v^0 is the vibrational ground state w.f. of the neutral molecule and $\chi_v(K_m^1, K_m^2, \ldots)$ is the w.f. for the vibrational state having the 1st normal mode excited at the $(K_m^1)^{\text{th}}$ level the second mode at the $(K_m^2)^{\text{th}}$ level *etc.*, and

$$\omega_\lambda = \omega_{-\lambda}^* = \frac{1}{\sqrt{N}} \sum_{n=0}^{N-1} \gamma^{\lambda n} p_n ; \; \gamma = \exp\left(\frac{2\pi i}{N}\right) \tag{2}$$

N is the number of carbon atoms of the cyclic polyene, p_n is the $2p_z$ atomic orbital centered on the n^{th} carbon nucleus. First order perturbation theory gives:

$$c_m = \frac{\langle \omega_{+\lambda} \chi_v^0 | H | \omega_{-\lambda} \chi_v(K_m^1, K_m^2, \ldots)\rangle}{E_v(K_m^1, K_m^2, \ldots)} \tag{3}$$

where E_v is the energy of the vibrational state defined by the wave function χ_v.

The perturbation Hamiltonian representing deuterium substitution at position r will have the form (using massweighted coordinates)

$$H'_r = \sum_{i=1}^{3} \frac{\hbar^2}{4} \frac{\partial^2}{\partial q_{ri}^2} \tag{4}$$

which is the kinetic energy difference between deuterium and hydrogen nuclei. The suffix i distinguishes the three vibrational coordinates of the r^{th} nucleus: stretching, in-plane bending and out-of-plane bending motions.

If we approximate, to simplify the algebraic treatment, the CH normal vibrational modes with the expression (see Ref. [6]):

$$Q_{vi} = \frac{1}{\sqrt{N}} \sum_{n=1}^{N-1} \gamma^{nv} q_{ni} \tag{5}$$

and take $r = 0$, we have:

$$H'_0 = \frac{\hbar^2}{4N} \sum_{i=1}^{3} \sum_{v,v'=0}^{N-1} \frac{\partial^2}{\partial Q_{v,i} \partial Q_{v',i}} . \tag{6}$$

This perturbation mixes the term $\omega_\lambda \chi_v^0$ which appears in Φ_a with those terms $\omega_\lambda \chi_v(K_m^1, K_m^2, \ldots)$ in Φ_b which have two excited quanta belonging to one of the three possible sets of CH modes.

To evaluate the splitting caused by deuteration we need to calculate the coefficients c_m corresponding to these excited states. The integral which appears in Eq. (3) may be performed by first integrating on electronic coordinates. By using Eq. (2) and the usual approximations of π-electron theory we obtain

$$\langle \omega_\lambda | H | \omega_{-\lambda} \rangle = \frac{1}{N} \sum_{n=0}^{N-1} \gamma^{2\lambda n} \{ 2\gamma^\lambda \beta_{n,n+1} + \alpha_n \} \,. \tag{7}$$

The dependence of the electronic integrals α's and β's upon the vibrational coordinates is obtained by series expansion of the right hand side of Eq. (7). It is evident that the terms by which H' mixes Φ_a and Φ_b come from the second order coefficients

$$D^{(2)} = \frac{1}{2Nm} \sum_{n=0}^{N-1} \sum_{i=1}^{3} \gamma^{2\lambda n} \sum_{jj'} \frac{\partial^2}{\partial q_{ji} \partial q_{j'i}} \cdot (2\gamma^\lambda \beta_{n,n+1} + \alpha_n) q_{ji} q_{j'i} \tag{8}$$

where q_{ji} are CH mass weighted vibrational coordinates.

Of course, many other terms appear in the complete vibronic function, but they are omitted here since they are not affected by the perturbing Hamiltonian.

It is a reasonable approximation to assume that $\beta_{n,n+1}$ depends essentially on coordinates of the n^{th} and $(n+1)^{\text{th}}$ hydrogen nuclei and α_n essentially on those of the n^{th} nucleus, therefore:

$$\sum_{jj'} \frac{\partial^2}{\partial q_j \partial q_{j'}} \alpha_n q_j q_{j'} \simeq q_n^2 \frac{\partial^2 \alpha_n}{\partial q_n^2} \equiv \alpha'' q_n^2 \tag{9}$$

$$\begin{aligned} \sum_{jj'} \frac{\partial^2}{\partial q_j \partial q_{j'}} \beta_{n,n+1} q_j q_{j'} &\simeq \frac{\partial^2 \beta_{n,n+1}}{\partial q_n^2} q_n^2 + \frac{\partial^2 \beta_{n,n+1}}{\partial q_{n+1}^2} q_{n+1}^2 + \frac{2\partial^2 \beta_{n,n+1}}{\partial q_n \partial q_{n+1}} q_n q_{n+1} \\ &\equiv \beta''(q_n^2 + q_{n+1}^2) + 2\beta^* q_n q_{n+1} \,. \end{aligned} \tag{10}$$

By using the inverse transformation:

$$q_n = \frac{1}{\sqrt{N}} \sum_{\nu=0}^{N-1} \gamma^{-\nu n} Q_\nu \tag{11}$$

we have, after some algebra:

$$D^{(2)} = \frac{1}{mN} \sum_{\nu=1}^{N-1} \sum_{i=1}^{3} \left[\frac{\alpha_i''}{2} + 2\beta_i'' \cos\left(\frac{2\pi\lambda}{N}\right) + 2\gamma^\lambda \gamma^\nu \beta_i^* \right] Q_\nu Q_{\nu-2\lambda} \,. \tag{12}$$

The result of the integration on nuclear coordinates in Eq. (3) is different from zero only if $\chi_v(K_m^1, K_m^2, \ldots)$ has one excited quantum in the two modes Q_ν and $Q_{\nu-2\lambda}$. Then Eq. (1) will assume the form:

$$\begin{aligned} \Phi_a = \Phi_b^* = S \cdot \Bigg\{ & \omega_\lambda \chi_v^0 - \omega_{-\lambda} N^{-1} \sum_{i,\nu} \left[\frac{\alpha_i''}{2} + 2\beta_i'' \cos\left(\frac{2\pi\lambda}{N}\right) + 2\gamma^\lambda \gamma^\nu \beta^* \right] \\ & \cdot \frac{\langle 0 | Q_{\nu i} | 1 \rangle \langle 0 | Q_{-\nu-2\lambda} | 1 \rangle}{\varepsilon_{\nu,i} + \varepsilon_{\nu-2\lambda,i}} \chi_v(\ldots, 1^\nu, \ldots, 1^{-\nu-2\lambda}, \ldots) + \cdots \Bigg\} \end{aligned} \tag{13}$$

where $\varepsilon_{\nu,i}$ is the excitation energy of the $Q_{\nu,i}$ normal mode. We shall have therefore:

$$\begin{aligned} H'_{ab} = \langle \Phi_a | H' | \Phi_b \rangle \simeq & -\frac{\hbar^2 S^2}{mN^2} \sum_{i,\nu} \left[\frac{\alpha_i''}{2} + 2\beta_i'' \cos\left(\frac{2\pi\lambda}{N}\right) + 2\gamma^\lambda \gamma^\nu \beta^* \right] \\ & \cdot \frac{\langle 0 | Q_{\nu i} | 1 \rangle \langle 0 | Q_{\nu-2\lambda,i} | 1 \rangle \left\langle 0 \left| \frac{\partial}{\partial Q_{\nu,i}} \right| 1 \right\rangle \left\langle 0 \left| \frac{\partial}{\partial Q_{-\nu-2\lambda,i}} \right| 1 \right\rangle}{\varepsilon_{\nu,i} + \varepsilon_{-\nu-2\lambda,i}} \,. \end{aligned} \tag{14}$$

Since the frequencies of CH normal modes in each of the three types of vibration are within a narrow band we shall approximate the energies $\varepsilon_{v,i}$ with their average value $\bar{\varepsilon}_i$ and since:

$$\langle 0|Q_{v,i}|1\rangle \left\langle 0\left|\frac{\partial}{\partial Q_{vi}}\right|1\right\rangle = \frac{1}{2}$$

we obtain:

$$H'_{ab} = -\frac{\hbar^2 S^2}{8N m_{\mathrm{H}}} \sum_{i=1}^{3} \left[\frac{\alpha''_i}{2} + 2\beta''_i \cos\left(\frac{2\pi\lambda}{N}\right)\varepsilon_i^{-1}\right] \tag{15}$$

where the term in β^* has disappeared, because $\sum \gamma^n = 0$. According to the sign of H'_{ab} the symmetric function $\frac{1}{\sqrt{2}}(\Phi_a + \Phi_b)$ or the antisymmetric one $\frac{1}{\sqrt{2}}(\Phi_a - \Phi_b)$ will be stabilized.

Semiempirical Evaluation of the Vibronic Coupling Parameters

We can make use, now, of the measurements [4] of the shifts in the CH frequencies of some aromatic hydrocarbons after reduction to mononegative ions.

The energy of the negative ion is, in the Hartree-Fock approximation:

$$E = E_0 + \varepsilon \tag{16}$$

where E_0 is the energy of the neutral molecule and ε is the energy of the first antibonding π orbital.

If we write $\pi = \sum_i c_i p_i$ we have:

$$E = \sum_i [P_{ii}\alpha_i + 2(P_{i,i+1} \cdot \beta_{i,i+1} + P_{i,i-1}\beta_{i,i-1})] \tag{17}$$

where $P_{ij} = c_i c_j$.

The force constant k_n of the n^{th} vibration will be:

$$k_n = \frac{\partial^2 E_0}{\partial q_n^2} + \frac{\partial^2 \varepsilon}{\partial q_n^2} = k_0 + \Delta k = k_0 + P_{nn}\alpha'' + 2[P_{n,n+1} + P_{n,n-1}]\beta'' \,. \tag{18}$$

There are two hydrocarbon molecules whose frequency shifts are tabulated in reference [4]: naphthalene and anthracene. If we choose for instance naphthalene negative ion (similar conclusions could be drawn by considering the other molecule) we have, in the Hückel framework, the average values:

$$P_{n,n} = 0.12\,;\; 2(P_{n,n-1} + P_{n,n+1}) = -0.15$$

hencefore

$$0.12\alpha'' - 0.15\beta'' = 2\frac{\Delta\nu}{\nu}k\,. \tag{19}$$

a) Out of Plane Vibrational Modes

For this vibrational coordinate [7] $k \simeq 3 \cdot 10^4$ dynes/cm, and from the tables in Ref. [4] we can extract an average frequency shift of the order of a ten per cent of the unshifted frequency.

It follows:

$$0.12\alpha'' - 0.15\beta'' = -6.10^4 \text{ dynes/cm}\,. \tag{20}$$

If we express, assuming with Karplus [3] the simple orbital following model, the β integral in the form:

$$\beta = \beta_0 \cos\theta$$

we have:

$$\beta'' = -\beta_0 r_{\mathrm{CH}}^{-2} .$$

If now we use the value $\beta_0 = 54$ Kcal/mole fitted on the electronic spectra of naphthalene [8] and of a series of similar molecules and $r_{\mathrm{CH}} \simeq 1$ Å, we see that we can satisfy rather well Eq. (20) by neglecting the α'' term[1, 2].

b) In Plane Stretching Vibrational Modes

In this case $k \simeq 5 \cdot 10^5$ dynes/cm [9] and the frequency shift is of the order of one per cent. Since β is negligible with respect to α and there is no reason to believe that the stretching motion affects more strongly β than α, we can reasonably guess that α'' strongly predominates β'', therefore $\alpha'' \simeq -0.8 \cdot 10^5$ dynes/cm and $\beta'' \simeq 0$.

c) In Plane Bending Vibrational Modes

Here $\frac{\Delta\nu}{\nu} \simeq 0.015$ and $k \simeq 3 \cdot 10^4$ dynes/cm [8]. Since in this case also, α'' would predominate β'', we have $\alpha'' < 10^4$ dynes/cm and the effect of these vibrations can be neglected in comparison with that of the preceding ones.

Results and Conclusions

On evaluating H_{ab} by considering only the most important contributions, we obtain:

$$\begin{aligned} H_{ab} &= -\frac{\hbar^2 S^2}{8 N m_{\mathrm{H}}} \left[\frac{\alpha''_S}{2\bar{\varepsilon}_S} + \frac{2\beta''_b}{\bar{\varepsilon}_b} \cos\left(\frac{2\pi\lambda}{N}\right) \right] \\ &= \frac{S^2}{N} \frac{3}{4} \cdot 10^{-13} \left[0.8 - 5.8 \cos\left(\frac{2\pi\lambda}{N}\right) \right] \mathrm{erg} \end{aligned} \tag{21}$$

where the suffixes s and b label stretching and bending constants respectively.

Now we have to evaluate the factor $S^2 = \left(\sum_m c_m^2\right)^{-1}$. The greatest c_m value corresponds to the coupling with carbon skeleton vibrations that we have not yet considered, since they do not contribute directly to the matrix element H_{ab}. These contributions have been calculated very accurately by McConnell and McLachlan [5] for benzene. From their work we can extract the value $S^2 \simeq 0.7$. A similar value for S^2 can be assumed for C_8H_8.

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[1] The fact that $\Delta\nu$ in reference (4) is found to be proportional to the spin density ϱ_i is not in contrast with our conclusion, although the factor $P_{ii} \equiv \varrho_i$ is associated with α'' in Eq. (18) and not with β''. In fact the quantity $(P_{i,i+1} + P_{i,i-1})$ is also proportional to P_{ii} in these systems, as can be easily verified.

[2] We have also performed a more rigorous evaluation of α'' and β'', by solving the two separate equations:

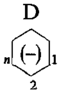
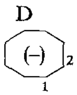
$$\Delta K_\nu = \frac{\partial^2 \varepsilon}{\partial Q_\nu^2} = \sum_i P_{ii} \frac{\partial^2 \alpha_i}{\partial Q_\nu^2} + 2\left(P_{i,i+1} \frac{\partial^2 \beta_{i,i+1}}{\partial Q_\nu^2} + P_{i,i-1} \frac{\partial^2 \beta_{i,i-1}}{\partial Q_\nu^2} \right) \quad (\nu = 1, 2)$$

where Q_ν stands for the two B_{1u} bending out of plane modes. If we write Q_ν as a linear combination of the q_i and develop the second order derivatives on the right hand side we get α'' and β'' times constants which can be evaluated by means of the value $S' = \partial S / \partial Q_\nu$ (kindly fournished to us by Dr. B. Schully). The results are practically identical to the preceeding ones; this fact confirms the validity of the orbital following model.

Before calculating the resulting spin density on the basis of thermal mixing we must consider that vibronic coupling (essentially the one involving skeleton vibrations) smoothes out the difference in spin density between the two states. Whereas in benzene we use once again the McConnell and McLachlan results [5], in C_8H_8 we use the treatment proposed by Nordio *et al.* [6] which is much less refined, but sufficient for our need.

In the Table the numerical results of the calculation are presented.

Table. *Calculated deuterium effect on spin densities of C_6H_6 and C_8H_8*

	$\Delta E = 2 \cdot H_{ab}$ (cm^{-1})	$e^{-\frac{\Delta E}{kT}}$	$\frac{a_{H_1}}{a_{H_2}}$
	25	1.25	0.9
	6	1.05	0.97

The calculated ratio among the two different spin densities for $C_6H_5D^-$ is in good agreement with the experimental one which is 0.87 [10]. For $C_8H_7D^-$ the calculated ratio produces a difference between the two spin densities which is less than the ESR linewidth for this case, hence not in contrast with the experimental result (no deuterium effect).

Finally our results seem to confirm Karplus' opinion that coupling through out of plane vibrations is the most important one and that inside this coordinate the contribution of the resonance integral predominates on that of the coulomb integral (see Eq. [21]). However, it is less true that we can neglect the effect of the stretching modes especially in C_8H_8, where the contribution of β'' vanishes, because of the factor $\cos\left(\frac{2\pi\lambda}{N}\right)$ in Eq. (15).

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Dr. M. Rossi
Institute of Physical Chemistry
University of Padova
Padova, Italy