

Deuterium Isotope Effect on the Electron Spin Resonance Spectrum of the Cyclopentadienyl Radical

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Summary The e.s.r. spectrum shows that, in the radical $C_5H_4D\cdot$, the unpaired electron occupies the ψ_A and ψ_S molecular orbitals with the probability 0.515:0.485, which is consistent with a model which assumes a vibrational perturbation of the Hückel resonance integral β .

THE e.s.r. spectra of substituted annulene radicals provide a sensitive probe of the interaction of the substituents with the π -electron system. In this way, deuterium has been shown to break the orbital degeneracy of the benzene^{1,2} and naphthalene³ radical anions, but no effect could be

detected in the benzene radical cation,⁴ cycloheptatrienyl radical,⁵ or cyclo-octatetraene radical anion.⁶ We describe here the breaking of the orbital degeneracy of the cyclopentadienyl radical by deuteration, which enables an unambiguous choice to be made between the two alternative theories which have been proposed to account for the isotope effect.

The $C_5H_4D\cdot$ radical was prepared by the photolysis of $Bu_3SnC_5H_4D$ as described previously.⁷

In π -radicals, $a(H)/a(D)$ is usually less than the value of 6.514 which is calculated from the nuclear magnetogyric ratios,[†] whereas for the cyclopentadienyl radical,

[†] The only exceptions we are aware of are the [1-²H]phenalenyl radical [$a(H)/a(D) = 6.54 \pm 0.01$] (ref. 8) and the [1,4-²H₂]-2,3,5,6-tetramethoxybenzene radical cation [$a(H)/a(D) = 6.61 \pm 0.05$] (ref. 9). In both of these, the effect arises because hyperfine coupling to the hydrogen or deuterium atom by spin polarisation from the proximate carbon, and by hyperconjugation from the adjacent carbons due to the out-of-plane vibration, has the same sign.

TABLE. Observed e.s.r. hyperfine coupling constants for the $C_5H_4D\cdot$ radical, and values calculated for different occupancies by the unpaired electron of the ψ_A and ψ_S orbitals.

	Hyperfine coupling constants/G		
	$a(H_{2,5})$	$a(H_{3,4})$	$a(D)$
Observed ^{a,b}	6.14	5.92	0.89
Calc. for 1.000 ψ_A	10.86	4.15	0.00
Calc. for 1.000 ψ_S	1.14	7.86	1.84 ^c
Calc. for 0.500 ψ_A + 0.500 ψ_S	6.00	6.00	0.92 ^c
Calc. for 0.515 ψ_A + 0.485 ψ_S	6.15	5.95	0.89 ^c

^a At $-75^\circ C$ in cyclopropane. ^b Line width $\Delta H_{pp} = 0.22 G$.
^c Calculated from $(Q - \sum_{i=2-5} a_i)/6.514$.

$a(H)(C_5H_5\cdot)/a(D)(C_5H_4D\cdot) = 6.74$ (see Table). This implies that the deuterium is attached to a site of low spin density so that $a(D)$ by spin polarisation is small, that is that the deuterium breaks the degeneracy of the ψ_A and ψ_S orbitals so that the unpaired electron occupies predominantly the ψ_A orbital of higher energy in which c_1 is zero (see Figure). This was confirmed by computer simulation of the triplets $M_1^H = -1, 0, +1$, $M_1^D = -1, 0, +1$, which showed further partial resolution, to give the hyperfine coupling constants shown in the Table.

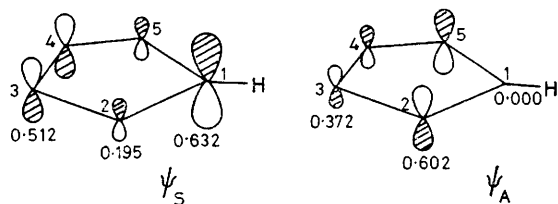


FIGURE. Hückel coefficients for the ψ_S and ψ_A M.O.s of the cyclopentadienyl radical.

The calculated coupling constants for the radical in the $\psi_S^2 \psi_A^1$ and $\psi_A^2 \psi_S^1$ configurations are derived from equation (1), where c_i is the appropriate Hückel coefficient

$$a_1 = c_i^2 Q \quad (1)$$

as shown in the Figure,^{7,10} and the McConnell Q is taken to be $29.98 G$.⁷ The unpaired electron is seen to occupy principally the ψ_A M.O. with the probabilities $\psi_A : \psi_S =$

$0.515 : 0.485$, whence ΔE , the separation between the two energy levels, is $100 J mol^{-1}$.

The effect of the deuterium in breaking the degeneracy of the ψ_S and ψ_A M.O. has been considered in terms of its electronegativity effect on the coulomb integral, α , or its vibrational effect on the resonance integral β .^{2,8,†}

Deuterium releases electrons more powerfully than hydrogen,¹¹ and its introduction should destabilise ψ_S , which has a high coefficient at C(1), but not affect ψ_A in which c_1 is zero. On this argument, the $C_5H_4D\cdot$ radical should have predominantly the configuration $\psi_A^2 \psi_S^1$.

Out-of-plane vibration of hydrogen at C(1) will reduce any overlap of the $p\pi$ orbitals between C(1) and its neighbours C(2) and C(5), destabilising ψ_S which is bonding in this region, but leaving ψ_A unaffected as $c_1 = 0$. The amplitude of vibration of deuterium will be less than that of hydrogen, with a smaller destabilising effect on ψ_S . On this argument, ψ_S in $C_5H_4D\cdot$ should lie below ψ_A , and the radical would have predominantly the configuration $\psi_S^2 \psi_A^1$.

Our results, therefore, unequivocally favour the model in which the deuterium exerts its effect predominantly through a vibrational perturbation of the resonance integral β .[‡]

On this model, the energy shift of an orbital when deuterium is introduced is given by equation (2), where δ is the change in β when hydrogen is replaced by

$$\Delta E = 2c_i(\delta_{i,i+1}c_{i+1} + \delta_{i,i-1}c_{i-1}) \quad (2)$$

deuterium.^{2,12} A rough estimate for $C_6H_5D\cdot$ gives $\delta = ca. 0.0025 \beta$, and the experimental best fit for a series of deuteriobenzenes gives $\delta 0.002 \beta^2$. If we accept $\delta = ca. 0.002 \beta$ for both $C_6H_5D\cdot$ and $C_5H_4D\cdot$, and $\beta = ca. 167 kJ mol^{-1}$, equation (2) gives $\Delta E(C_6H_5D\cdot) = ca. 225 J mol^{-1}$, and $\Delta E(C_5H_4D\cdot) = ca. 165 J mol^{-1}$, in qualitative agreement with the values of $235 J mol^{-1}$ and $100 J mol^{-1}$ which are observed.

The cyclopentadienyl radical provides the first example in the series of annulene radicals of a detectable deuterium isotope effect in compounds other than the [6]-annulene radical anions,[¶] and establishes that the model assuming perturbation of the resonance integral remains satisfactory when the radical is electrically neutral.

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† An alternative model has also been considered which is based on the fact that the various hydrogen nuclei in an annulene radical may be rendered inequivalent by Jahn-Teller distortion (ref. 6).

‡ In the $C_6H_5D\cdot$ radical anions, the coulombic and vibrational effect both operate to raise the energy of ψ_S (ref. 2), but in the [1,4,5,8-²H₄]- and [2,3,6,7-²H₄]-naphthalene radical anions, the two types of perturbation act in opposite directions, and the spectra are consistent only with the model of a dominant perturbation of the resonance integral (ref. 3).

¶ Professor H. Sakurai has informed us that he too has been able to observe the deuterium isotope effect in the $C_5H_4D\cdot$ radical.

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