Deuterium Isotope Effect on the E.S.R. Spectrum of Annulene Radicals: a Reappraisal

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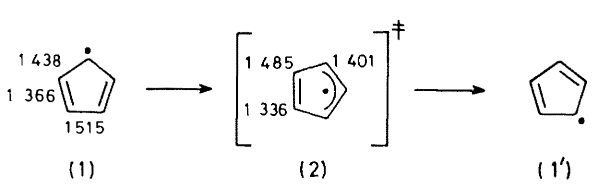
Summary. The deuterium isotope effect on the e.s.r. spectrum of the cyclopentadienyl radical is suggested to be the result of deuterium perturbation of the equilibrium between the positional isomers of the Jahn–Teller distorted radical and not of vibrational perturbation of the Hückel resonance integral, β.

The deuterium isotope effect on the e.s.r. spectrum of the cyclopentadienyl radical has recently been observed.[1,2] This effect has been attributed to vibrational perturbation of the Hückel resonance integral, β.[3] We prefer to revive an alternative explanation[4] and make it more quantitative. The cyclopentadienyl radical is a Jahn–Teller species[5] and cannot have D_{5h} symmetry. The fact that only one hyperfine coupling is found for $C_5H_5\cdot$ above 70 K[6,7] indicates that all five hydrogen atoms are equivalent on the e.s.r. time scale, *i.e.* that there is a fast pseudorotational process. The activation energy for this process is *ca.* 0.59 kJ mol^{-1} in a cyclopentadiene matrix[7] and is much lower in neon.[8] The observed spectral changes on deuterium substitution are then the result of a non-statistical distribution of deuterium over the three non-equivalent positions of the C_{2v} Jahn–Teller distorted $C_5H_4D\cdot$ radical.

We have used UHF/MINDO-3[9] semi-empirical molecular orbital theory to investigate Jahn–Teller annulene radical potential surfaces and to calculate the effect of deuterium on the positional equilibrium in their monodeuteriated counterparts. Bischof[10] has shown that UHF/MINDO-3 performs well for this type of radical.

Although the Born–Oppenheimer approximation[11] may not be valid for Jahn–Teller species[12] we have limited our calculations to the static Jahn–Teller effect, as have previous workers for the benzene radical anion.[13] This approximation should not affect our general conclusions, but may be important for quantitative calculations of the deuterium isotope effect.

Jahn–Teller distortion of an annulene radical can, in principle, lead to two structures, of which one is an energy minimum and the other is the pseudorotation transition state.[12,14] We can illustrate this process using the cyclopentadienyl radical, for which the 'dienylic' form (1) is a minimum and the 'en-allylic' form, (2) a transition state[10] (Scheme 1).† UHF/MINDO-3 gives a barrier of 0.429 kJ mol^{-1} for the process (1)→(2)→(1′), which is consistent with the observed low temperature e.s.r. spectrum of $C_5H_5\cdot$.[7,8] Recent *ab initio* calculations including vibronic coupling, but without configuration interaction (CI)[15] predict this barrier to be 14.63 kJ mol^{-1} and minimal basis set *ab initio* calculations with limited CI[16] find the two structures to be of prac-



Scheme 1. Pseudorotation of the cyclopentadienyl radical. The bond lengths (pm) are UHF/3—21G optimum values.

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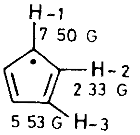
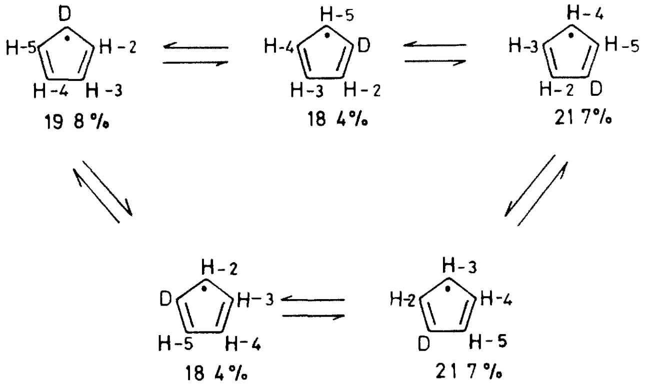
† Structure (2) was shown to be a transition state at UHF/MINDO-3 by diagonalising the force constant matrix; there was one negative eigenvalue.

tically identical energy. We have fully optimized (**1**) and (**2**) at the UHF/3–21G[17] split valence level and find the energy difference to be 4.41 kJ mol^{-1}. This barrier is likely to be decreased by CI. We emphasize that this pseudorotational behaviour of annulene radicals is a general phenomenon which has been noted by many authors.[10,12–15] The MINDO-3 calculated hydrogen hyperfine coupling constants[9] for (**1**) are as shown. The calculated average hyperfine coupling constant is 4.64 G, compared with the experimental value of 5·97 G.[4]



MINDO-3 calculated hydrogen hyperfine coupling constants for $C_5H_5\cdot$, (**1**)



SCHEME 2. MINDO-3 calculated equilibrium concentrations for $C_5H_4D\cdot$ at 198 K (see ref. 1). The equilibrium concentrations were calculated from the MINDO-3 calculated normal vibrational frequencies of (**1**) using a method similar to that of Kohler (see H.-J. Kohler, *Z. Chem.*, 1979, **19**, 235, and M. J. S. Dewar and G. P. Ford, *J. Amer. Chem. Soc.*, 1977, **99**, 1685). The calculations considered only zero point energy differences as Kohler has shown these to be the major contribution to the equilibrium perturbation.

If one of the hydrogen atoms in (**1**) is replaced by deuterium the equilibrium is no longer degenerate, but rather involves three distinguishable positional isomers within the five possible forms of $C_5H_4D\cdot$ (Scheme 2). This equilibrium is perturbed from a statistical distribution as the three positional isomers do not have the same zero point energies. The time averaged hydrogen coupling constants for H-2-(H-5) and H-3(H-4) in Scheme 2 are 4·56 and 4·67 G, respectively. The two sets of protons therefore have different time-averaged hyperfine coupling constants, as observed[1,2] (in an unperturbed statistical equilibrium no splitting would be observed). This process is exactly analogous to that used successfully to distinguish between fast-equilibrating and non-classical carbonium ions using ^{13}C n.m.r. spectroscopy.[18]

Similar calculations for other annulene radicals support our interpretation. The deuterium isotope effect for the benzene radical anion is calculated to be twice as large as for the benzene radical cation, in agreement with the observed isotope effect in the former[19] and with the fact that no effect was seen in a poorly resolved spectrum of the latter.[20] In general our calculated differences in the non-equivalent proton hyperfine splittings [for example, $\bar{a}$(H-2) $-$ $\bar{a}$(H-3) in $C_5H_4D\cdot$] are *ca.* 50% of the observed, probably a consequence of the dynamic Jahn–Teller effect. The agreement with experiment is greatly improved if experimental[7] hyperfine coupling constants are used in conjunction with the calculated equilibrium concentrations. As we consider the deuterium isotope effect to be an equilibrium phenomenon the difference between the two non-equivalent proton coupling constants should be larger at lower temperatures. This temperature dependence is, however, too small to observe by present techniques.[21]

This work was supported by the Fonds der Chemischen Industrie and by a von Humboldt Fellowship (to M. S.). We thank Prof. R. Sustmann for helpful discussions, Dr. P. Bischof for providing us with his UHF/MINDO-3 program, Prof. A. G. Davies for constructive suggestions, and the staff of the Regionales Rechenzentrum Erlangen for their co-operation.

(*Received, 15th November* 1979; *Com.* 1200.)

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