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Cyclohexadienyl – a Homoaromatic Radical?

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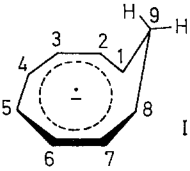
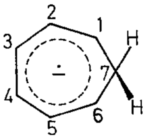
A reinterpretation of the hyperfine coupling constants of the ESR spectrum of cyclohexadienyl radical is given in terms of a homoaromatic model in agreement with the Woodward-Hoffmann symmetry rules.

The interest on homoaromatic species has recently touched the field of odd electron systems with the findings related to the monohomocyclooctatetraene anion radical (I) [1].



I

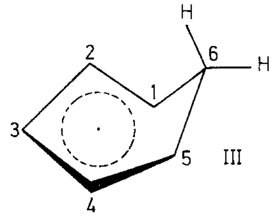
We now know that radicals of the type $(CH)_n\overset{*}{C}H_2$ $\left(* = \begin{matrix} \dot{-} \text{ for } n \text{ odd} \\ \cdot \text{ for } n \text{ even} \end{matrix}\right)$ may assume a configuration typical of the stable homoaromatic species with the methylene carbon atom not in the plane of the CH carbons. It has also been proposed that the important factor which determines the preference of the homoaromatic structure over the classical planar one [which is found in the case of $n = 6$, a classical cycloheptatrienyl radical anion (II)] is the symmetry of the singly occupied orbital [2].



II

In analogy with the Woodward-Hoffmann rule concerning the stereochemistry of cyclizations [3], one can say that to allow the formation of a homoaromatic species from a classical one, we need a rotation of the two C–CH_2 bonds in a 'disrotatory mode' and the consequence is a repulsive situation if the orbital is antisymmetric, while it is energetically favored if the orbital is symmetric.

In agreement with these predictions, we wish to submit that the species with $n = 5$, cyclohexadienyl radical, is in fact a monohomocyclopentadiene system (III). The evidence we use relies again on the interpretation of the electron proton coupling constants of this radical as determined by ESR spectroscopy.



III

In a recent paper [4] it has been shown that all experimental ESR data on alicyclic short-lived free radicals containing β-protons can be rationalized by assuming an angular dependence of the proton hyperfine coupling of the well established type [5]:

$$a_{\mathrm{H}}^{\beta} = B\varrho \cos^2 \vartheta \tag{1}$$

with $B = 58.6$ gauss, where ϱ is the spin density of the α-carbon atom and ϑ is the dihedral angle between p_z orbital and C–H bond.

This value of the constant B is also consistent [6] with the coupling constants of ethyl, propyl and *t*-butyl radicals and has been used by many authors [7] in order to investigate the conformation of aliphatic free radicals. The methylene protons hyperfine coupling constants of cyclohexadienyl radicals have been instead accounted for by taking $B = 47$ gauss [6, 8][1].

A very resolved ESR spectrum has been recorded by Fessenden and Schuler [6] and the measured splittings are reported in the Table together with the 'experimental' spin densities on the CH carbon atoms. The latter are obtained from

Table. *Coupling constants and spin densities for cyclohexadienyl*

Position	a_{H}(exp) Gauss	ϱ_{exp} [a]	ϱ_{theor} [b]	ϱ_{theor} [c]
1,5	8.99	0.349	0.322	0.360
2,4	2.65	−0.103	−0.058	−0.100
3	13.04	0.506	0.466	0.380

[a] See text ($Q_{\mathrm{exp}} = 25.7$).
[b] Homoconjugated model. McLachlan's calculation ($\lambda = 1.2$).
[c] Classical model (Ref. [10]).

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[1] A value of 47 gauss for B was used also for the saturated radical cyclopentyl. In this case, however, the erroneous assumption was made of a planar conformation suggested by the equivalence of the four β-protons ($\cos^2 \vartheta = \frac{3}{4}$, for all of them). If one assumes instead a more likely situation in which there is high frequency of interconversion between two symmetrical half char conformations [cfr. the case of cyclopentanone: Le Fevre, C. G., R. J. Le Fevre, S. J. Barr, and N. Pearson: J. Amer. chem. Soc. **81**, 4915 (1959)], the equivalence of four protons is maintained and the mean value of $\cos^2 \vartheta$ becomes $\frac{5}{8} = (\frac{1}{2}\cos^2 0° + \frac{1}{2}\cos^2 60°)$. Under this assumption a B value of 58 gauss fits the experimental data.

McConnell's equation [9] and a value of 26 gauss for Q obtained from the experimental total width of the spectrum by taking in proper account the methylene proton splittings (47.7 gauss) and the fact that spin densities at positions 2 and 4 are negative.

Using Eq. (1) from the experimental methylene proton coupling and from the 'experimental' spin densities on the ortho carbon atoms we can calculate $B\cos^2\vartheta$. It must be pointed out that the spin densities on the ortho carbon atoms must be taken into account according to Whiffen [8b)], so that the value of ϱ which appears in Eq. (1) has to be taken equal to $(|\varrho_1^{1/2}|+|\varrho_5^{1/2}|)^2$.

The value of $B\cos^2\vartheta = 35.5$ gauss is consistent with a B value of 58 if $\cos^2\vartheta$ is taken as $\frac{5}{8}$ which is the average value we would expect for a homoconjugated conformation in which there is rapid ring inversion.

Further evidence comes from the CH protons constants.

If one assumes a classical conformation, the ring system is treated as a slightly perturbed open chain and the ratio of a_3 to $a_{1,5}$ is predicted to be very close to one both on the basis of valence bond or of simple molecular orbital calculations [6] and also on the basis of more rigorous methods [10]. If, on the other hand, one assumes the homoconjugated conformation, the ring system is to be treated as a slightly perturbed pentatomic ring with a direct interaction between the p_z orbitals of carbon atoms 1 and 5 which is described in similar systems by a resonance integral of 0.7β [11]. The perturbation of releasing the bond between atoms 1 and 5 lifts the degeneracy of the first two degenerate orbitals of the C_5H_5 system by lowering the energy of the one which is antisymmetric with respect to the plane passing through carbon atom 3 so that the singly occupied orbital will be the symmetric one. Fig. 1 shows the Hückel spin densities of the pentadienyl and cyclopentadienyl singly occupied orbitals and it is already quite apparent at this level of approximation that the $a_3/a_{1,5}$ ratio for cyclopentadienyl is much closer to the experimental one.

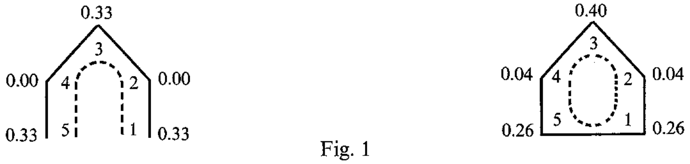

Fig. 1

A refinement in the calculation is however necessary because we assumed negative spin densities on atoms 2 and 4 contrary to the simple Hückel results. By using the very simple McLachlan's method [12] of calculating spin densities we obtain the results given in the Table and it is probable that a more refined calculation would still improve the agreement with experiment.

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