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Abstract

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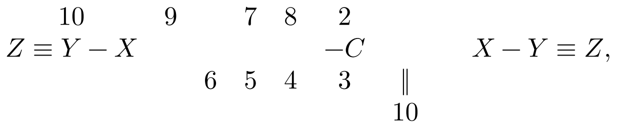
DISTRIBUTION OF SPIN DENSITY IN METAL KETYLS CONTAINING METHYL GROUPS

(Presented by Academician B. A. Arbuzov on 23 VIII 1963)

The spectra of electron paramagnetic resonance (e.p.r.) of certain aromatic and aliphatic radicals containing methyl groups reveal a distinct hyperfine structure caused by the interaction of the unpaired electron with the protons of the methyl groups. The transfer of the density of the unpaired electron to the methyl groups can be explained, in a quantum-chemical treatment, by hyperconjugation of the methyl groups with the rest of the system of conjugated bonds of the radical over which the unpaired electron is delocalized. For aromatic radicals, similar calculations by the LCAO MO method were carried out by Bersohn (^1) (methyl-substituted ions of benzosemiquinone) and by Bolton and co-workers (^2) (ions of 9- and 9,10-methylanthracene).

In the present work the molecular-orbital method was applied to the study of the distribution of spin density in di-*p*-tolyl-K-ketyl. The formation of the ketyl is assumed to occur by transfer of an electron from the metal atom to the lowest vacant level of ditolyl ketone. According to the presently accepted scheme of hyperconjugation (^3), it was assumed that the three eigenfunctions of the hydrogen atoms of the methyl groups combine with one another, giving three so-called "group eigenfunctions." The distribution of the electron clouds for two such group functions has a form analogous to the orbitals of π-electrons, the nodal planes of the two functions being perpendicular to one another. The third group function has the symmetry of a σ-bond. Thus, the three hydrogen atoms of a methyl group are combined into one "pseudo-H_3 atom," and all three simple C—H bonds are represented in the form of a "quasi-triple bond" H_3 C— . The carbon atom of the methyl group now has *sp* hybridization, and through the *p*-orbital of this atom one of the group π-orbits of the pseudoatom will take part in conjugation with the π-orbitals of the benzene rings and the carbonyl group.

The hyperconjugation scheme in ditolyl ketone may be written conventionally in the form:



$$\begin{array}{cccccccc} 10 & 9 & & 7 & 8 & 2 & & \\ Z \equiv Y - X & & & & & -C & & X - Y \equiv Z, \\ & & 6 & 5 & 4 & 3 & \| & \\ & & & & & & 10 & \end{array}$$

where X is the carbon atom of the ring bonded to the methyl group, Y is the carbon atom of the methyl group, and Z is the pseudoatom H_3.

The parameters for the Coulomb integrals of atoms X, Y, Z and for the resonance integrals of the bonds Z—Y, Y—X were chosen, in agreement with the available literature data (⁀1, ⁀4), as follows:

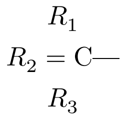
$$\begin{aligned} &\alpha_Z = \alpha_C - 0.3, \quad \beta_{ZY} = 2\beta_{CC}, \\ &\alpha_Y = \alpha_C - 0.1, \quad \beta_{YX} = 0.9\beta_{CC}. \\ &\alpha_X = \alpha_C, \end{aligned}$$

Here α_C and β_{CC} are, respectively, the Coulomb integral of a carbon atom and the resonance integral of a CC bond. For the oxygen atom the Coulomb integral was chosen in the form $\alpha_O = \alpha_C + \delta\beta_{CC}$, and the resonance integral of the C=O bond as $\beta_{CO} = \gamma\beta_{CC}$.

The spin-density distribution was found for 50 values of γ and δ, with γ varying from 1 to $\sqrt{5}$, and δ from 0 to 2.

Table 1 gives the spin-density values in ditolyl-K-ketyl at $\delta = 0.5$ and $\gamma = 2$. The experimental spin-density values, found from the hyperfine-splitting constants of the EPR spectrum of di-*p*-tolyl-K-ketyl, are taken from the work of V. M. Kazakova and Ya. K. Syrkin (^{5}).

The case considered above refers to the so-called C—H hyperconjugation, i.e., hyperconjugation of three simple C—H bonds. However, there also exists another type of conjugation—C—C hyperconjugation. As Mulliken (^{6}) indicates, the three simple bonds in the system



$$\begin{array}{c} R_1 \\ R_2 = \text{C}— \\ R_3 \end{array}$$

must analogously take part in hyperconjugation, regardless of whether R_1, R_2, R_3 are hydrogen atoms or methyl groups, although quantitatively some difference in the strength of the hyperconjugation should be expected.

Table 1

$$\delta = 0.5, \ \gamma = 2$$

Atom position	Spin densities	Spin densities
	experimental	theoretical
1	–	0.166
2	–	0.063
3	–	0.099
4, 8	0.043	0.058
5, 7	0.009 ± 0.001	0.019
6	0.125	0.117
9	–	0.001
10	–	0.015

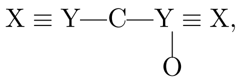
The EPR method gives quite evident proof of the existence of C–C hyperconjugation. In the spectra of certain radicals containing tert-butyl groups, hyperfine structure is observed, caused by interaction of the unpaired electron either with a C^{13} atom located in the β-position to the conjugated system containing the unpaired electron (2-tert-butyl-benzosemiquinone (^{7}), hexamethylacetone ketyl (^{8})), or with γ-protons (2,5-di-tert-butyl-benzosemiquinone (^{9}), hexamethylacetone ketyl (^{8})).

For the K-ketyl of hexamethylacetone, V. M. Kazakova and Ya. K. Syrkin (^{10}) first found a narrow singlet line, indicating considerable localization of the unpaired electron at the carbonyl carbon. Later, Hirota and Weissman (^{8}), using an instrument of higher resolution, found hyperfine structure of the spectrum, whose line intensities corresponded to interaction with 18 equivalent protons. In addition, an additional splitting arose owing to the presence of the isotope C^{13} in the methyl position and in the central position of the carbon atom. Splitting by C^{13} from the quaternary carbon atom was not found.

We have attempted to calculate the spin density in the ketyl of hexamethylacetone by the LCAO MO method. In doing so, we assumed that the hyperconjugation scheme in this case is the same as that considered above, but the role of H is now played by the $\mathrm{CH_3}$ groups, and the pseudoatom is

$$\left(> \mathrm{C} \right)_3 \equiv .$$

The hyperconjugation scheme in the ketone may be represented conventionally as:



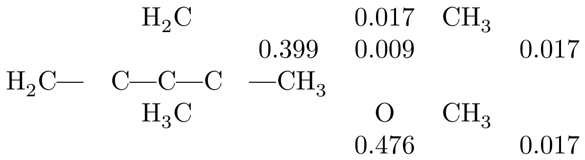
$$\mathrm{X} \equiv \mathrm{Y}—\mathrm{C}—\underset{\displaystyle \overset{|}{\mathrm{O}}}{\mathrm{Y}} \equiv \mathrm{X},$$

where X is the pseudoatom $\left(> \mathrm{C} \right)_3$, and Y is the quaternary carbon atom of the butyl group.

The Coulomb integral of the pseudoatom was assumed to be equal to $\alpha_X = \alpha_C - 0.6\beta_{CC}$, proceeding from the considerations that the electronegativity of the butyl group is less than the electronegativity of the CH_3 group, for which the Coulomb-integral parameter is usually chosen from 0 to -0.3. The resonance integral of the X—Y bond was taken equal to $\beta_{XY} = 3\beta_{CC}$, and the resonance integral

bond Y—C—$\beta_{YC} = 1.2\,\beta_{CC}$. The spin density was found for several values of the parameters δ and γ for the Coulomb integral of the oxygen atom $\alpha_O = \alpha_C + \delta\beta_{CC}$ and for the resonance integral of the $C = O$ bond $\beta_{CO} = \gamma\beta_{CC}$.

Below are the data for the spin density at $\delta = 0$ and $\gamma = 2.1$:



When δ is increased from 0 to 1, there is a slight decrease in the spin density on the methyl groups and on the quaternary carbon atom, and an increase in the spin density on the central carbon atom.

The results obtained can be compared with the available experimental data, and the semiquantitative agreement between theory and experiment is as follows:

1. The spin density on the quaternary carbon atom is always small, which is consistent with the absence of splitting from C^{13} in this position.
2. If the splitting is caused by an unpaired electron located on the $2s$-atomic orbital of carbon, then it is equal to 1200 oersteds. ([11]). In the present case the splitting from C^{13} of the central carbon atom is equal to 49.6 oersteds. Hence the "*s*-character" of the unpaired-electron orbital is represented by the value $49.6/1200 = 0.041$. If the $2p$-density calculated by us is taken as 100%, then this spin "*s*-density" accounts for 7-10%. This agrees with the calculation of the spin density in the $C^{13}H_3$ radical, where the "*s*-density" accounts for 3% ([12]).
3. If the orbital of the unpaired electron has sp^3 hybridization, then the splitting is equal to 1/4 of 1200 oersteds. Taking into account the fact that the splitting from C^{13} at the methyl carbon atoms is equal to 7.6 oersteds, we find the fraction of the "*s*-density" of the unpaired electron at the methyl groups. It is not difficult to see that it is equal to 0.025, i.e., the spin density calculated by us (0.017) is in fact an "*s*-density." This is natural, since the carbon atoms of the methyl groups in fact contain no π-electrons.

The hyperconjugation scheme used in the present calculations is very crude and approximate, but nevertheless, even in a simple approximation of the molecular-orbital method it makes it possible to obtain reasonable estimates for the spin density both in aromatic and in aliphatic radicals.

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Note: Figure translations are in progress. See original paper for figures.