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Abstract

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DISTRIBUTION OF SPIN DENSITY IN AROMATIC METAL KETYLS

(Presented by Academician B. A. Arbuzov, January 23, 1963)

The application of the simple molecular-orbital method (MO LCAO) for calculating spin densities in free radicals with heteroatoms agrees well with experimental data (1–4), provided the parameters δ and γ, which are introduced into the calculation to account for heteroatoms, are chosen properly. The Coulomb integral of the heteroatom is chosen in the form $\alpha + \delta\beta$, and the resonance integral for the carbon–heteroatom bond is assumed equal to $\gamma\beta$, where α is the Coulomb integral of the carbon atom and β is the resonance integral of the C–C bond.

The present work is a continuation of calculations for determining the spin density in metal ketyls (4)—free radicals containing oxygen as the heteroatom. The distribution of spin density was calculated by the MO LCAO method in diphenyl-K-ketyl, di-α-naphthyl-K-ketyl, di-β-naphthyl-K-ketyl, and phenyclone-K-ketyl:

[chemical structural formulas: diphenyl-K-ketyl; di-α-naphthyl-K-ketyl; di-β-naphthyl-K-ketyl; phenyclone-K-ketyl]

As before, it was assumed that ketyl formation occurs through transfer of an electron from the metal atom to the lowest vacant level of the corresponding ketone. In the calculation, in each case about 45 values of the parameters δ and γ were used; the values of δ were chosen from 0 to 2, and γ from 1 to 2 (1,5).

Table 1 contains the values of the spin density in diphenyl-K-ketyl for one pair of values of δ and γ. The spin density in the ortho positions in the first ring is usually 3–4 times greater than the density in the ortho positions in the second ring. The density in the meta positions of the second ring is always less than the spin density in the meta positions of the first

Table 1

$$\delta = 2, \quad \gamma = 1$$

Atom position	Spin density	Atom position	Spin density
1	0.0649	8	0.0214
2	0.3022	9	0.0001
3	0.0070	10	0.0218
4	0.0792	11	0.0001
5	0.0015	12	0.0214
6	0.0827	13	0.0015
7	0.0011	14	0.0792

rings approximately 10-fold. Changes in δ have a very slight effect on the spin-density distribution at constant γ. Variations of γ from 1 to 2 lead to a change in the spin density on the carbon atom of the carbonyl group and on oxygen, and also on the atoms of the first ring. The spin density in the second ring remains almost constant.

Experimental values of the spin densities could be found from the hyperfine structure of the e.p.r. spectra of this ketyl. However, dibiphenyl-K-ketyl is not soluble in ordinary solvents and gives a narrow singlet line (6). Nevertheless, one may suppose that the total width of the spectrum should be of the order of 11 G, since the calculation shows that 50% of the total spin density is located on atoms not bonded to protons. The largest splittings will be due to the ortho and para protons; moreover, as in the ketyls studied earlier (6–8), the ortho and para positions in each ring are equivalent.

Table 2

$$\delta = 2, \quad \gamma = 1$$

Atom position	Di-α-naphthyl ketyl	Di-β-naphthyl ketyl
1	0.045	0.0674
2	0.203	0.3156
3	0.006	0.0070
4	0.120	0.0331
5	0.001	0.0029
6	0.123	0.0364
7	0.000	0.0018
8	0.055	0.0391
9	0.001	0.0001
10	0.053	0.0397
11	0.004	0.0004
12	0.013	0.1490

Table 2 gives data on the spin densities in di-α-naphthyl-K-ketyl and di-β-naphthyl-K-ketyl.

In di-α-naphthylketyl, about 30% of the total spin density is concentrated on atoms not bonded to protons, while in di-β-naphthylketyl, for some values of δ and γ, this part of the spin density amounts to about 50%.

In di-α-naphthylketyl, four pairs of atoms have spin densities close in magnitude (positions 4 and 6; $4'$ and $6'$; 8 and 10; $8'$ and $10'$). In studying this radical by the e.p.r. method, a hyperfine structure consisting of five quintets should be obtained. In di-β-naphthylketyl the positions 8 and 10; $8'$ and $10'$ are equivalent. A considerable density is concentrated in positions 12 and $12'$. For some values of δ and γ, splittings from protons in positions 4 and $4'$ may occur.

Table 3

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

Atom position	Spin density	Atom position	Spin density
1	0.1608	9	0.0396
2	0.0179	10	0.0615
3	0.1521	11	0.0102
4	0.0025	12	0.0146
5	0.0396	13	0.0065
6	0.0003	14	0.0179
7	0.0408	15	0.0034
8	0.0003	16	0.0207

Changes in δ in both cases have little effect on the spin-density distribution. For di-β-naphthylketyl, changes in γ at constant δ have little effect on the spin densities at atoms that can give splittings, with the exception of atom $4(4')$ (with increasing γ, the spin density at this atom decreases sharply). For di-α-naphthylketyl, an increase in γ leads to a small decrease in the spin density on atoms 4 and 6 ($4'$ and $6'$) and to an increase in the spin density on atoms 8 and 10 ($8'$ and $10'$).

Calculation of the spin density in phenylcyclone-K-ketyl shows that the greatest density on the carbon atoms bonded to protons is concentrated in the ortho and para positions of the phenyl groups (Table 3). The hyperfine structure of the e.p.r. spectrum of this ketyl should consist of 7 lines, which, at sufficient resolution, may split further as a result of the interaction of the unpaired electron with protons in positions 12 and 14 ($12'$ and $14'$). Almost 70% of the total spin density falls on atoms not

associated with protons, and therefore the total width of the spectrum should be small.

A preliminary investigation of this radical by the EPR method, carried out by V. M. Kazakova in Ya. K. Syrkin' s laboratory, showed that seven components of the hyperfine structure are indeed observed; these are not completely split by additional interaction with other protons (^{9}). The experimentally estimated equivalence of the ortho and para positions in the phenyl groups (seven lines arose through interaction with 6 equivalent protons) is in complete agreement with the theoretical calculation not only qualitatively, but also quantitatively. The experimental spin densities at positions 5, 7, 9, ($5', 7', 9'$) are equal to 0.040.

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