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Abstract

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Hyperfine Structure in the E.P.R. of Certain Derivatives of Benzoylhydrazyl Free Radicals

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In the present communication we give the results of an investigation, by the E.P.R. method, of a series of derivatives of benzoylhydrazyl free radicals (see Table 1).

Some free radicals of the hydrazyl series with various groups at the β-nitrogen atom have been studied in works (1-7). Information was obtained on the influence of the nature and position of various substituents on the distribution of spin density over the molecule; the constants of the isotropic h.f.s. and the contribution to the h.f.s. from peripheral protons, etc., were determined.

In particular, in (5) radicals derived from diphenylbenzoylhydrazyl were investigated.

The E.P.R. spectra were explained by an equiprobable distribution of spin density over the two nitrogen atoms N^{14} of the hydrazyl. For derivatives with mono-ortho- and di-ortho-para-nitro groups in benzene, additional splittings were found, which the authors of (5) ascribe to the nitrogen of the ortho-nitro group. However, in the E.P.R. spectra of the free radicals

$$\mathrm{Ph_2{-}N{-}\dot{N}{-}}\begin{matrix}\text{benzene ring}\\ \text{with } \mathrm{NO_2} \text{ substituent}\end{matrix}$$

and

$$\mathrm{Ph_2{-}N{-}\dot{N}{-}}\text{benzene ring bearing } \mathrm{NO_2} \text{ groups} \qquad (4)$$

such additional splittings are absent. Therefore, one aspect of our work was to clarify the role of the ortho-nitro group of the benzoyl residue and the possibility that the group C=O participates in conjugation.

The study of dioxane solutions with free-radical concentrations of 10^{-3} mole/l was carried out at room temperature on an RE-1301 spectrometer (ν = 9320 MHz). The choice of solvent was due to the good solubility in it of the starting hydrazines.* The solution of hydrazine and lead dioxide in a special apparatus was partially degassed (at liquid-nitrogen temperature). Then, on warming to room temperature, oxidation was carried out, after which

the apparatus was transferred into the resonator cavity. E.P.R. signals could be recorded for periods from several minutes to 1 hour, depending on the type of radical. Evacuation of the samples increased the lifetime of the radicals in solution and also led to a noticeable narrowing of the E.P.R. lines.

In all the free radicals studied, h.f.s. was observed which can be explained by the predominant interaction of the unpaired electron with the nuclei of the N^{14} nitrogen atoms of the hydrazyl and by a weaker interaction with the nuclei of peripheral atoms. Free radicals with α-naphthyl in position G_1 gave a characteristic h.f.s. (Fig. 1), which made it possible to combine them into one group (I), distinct from radicals with $G_1 = C_6H_5$ (group II,

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* In CCl_4, contrary to the data of (5), it is not possible to create a concentration of the starting hydrazines of 10^{-3} mole/l either for radicals of group II or for radicals of group I.

Fig. 2). The additional splittings of the "nitrogen" EPR lines in group I radicals are quadruplets (see the outer components of the EPR spectra in Fig. 1), which should naturally be assigned to two ortho and one para protons of the α-phenyl ring. Consequently, the EPR spectra of I are described by the spin Hamiltonian

$$\hat{\mathcal{H}} = g\beta HS + A_1 I_{N_1} S + A_2 I_{N_2} S + A_3 \sum_{i=1}^{3} I_i S. \qquad (1)$$

Here $S = 1/2$ is the electron spin, $I_{N_1} = I_{N_2} = 1$ are the nuclear spins of nitrogen N^{14}, A_1 and A_2 are the corresponding constants of the isotropic hyperfine coupling of the unpaired electron with the nuclei of the nitrogen atoms, and A_3 is the constant of coupling of the unpaired electron with protons, where $I_i = 1/2$ is the spin of the hydrogen nucleus.

Analysis of the experimental EPR spectra was carried out by comparing them with theoretically calculated spectra until optimal agreement was obtained by selecting the ratio of the constants A_1/A_2, their sum $A_1 + A_2$, the value A_3, and the width of an individual EPR line, δH. Calculations of the theoretical spectra were performed on an electronic computer using a special program (7). It was assumed that each line of the nine-component EPR spectrum from two nonequivalent nitrogen atoms is split into a quartet with an intensity ratio $1 : 3 : 3 : 1$ by 3 equivalent protons. The theoretical curves obtained (Fig. 3) testify to the correctness of the choice made.

(Figure: Fig. 1. EPR spectra of benzoylhydrazyl radicals 1-5 (group I))

Fig. 1. EPR spectra of benzoylhydrazyl radicals **1-5** (group I)

For the spectra of radicals II it is characteristic that each of the main h.f.s. components, due to the hydrazyl nitrogens, is split into more than 10 additional lines.

(Figure: Fig. 2. EPR spectra of benzoylhydrazyl radicals 6–10 (group II))

Fig. 2. EPR spectra of benzoylhydrazyl radicals **6–10** (group II)

Since the β-parts of the molecules of radicals of groups I and II are identical, these additional splittings may be assigned to the protons of nonequivalent α-phenyls. A detailed analysis of the EPR spectra of II could not be carried out because of insufficient line resolution. The values of A_1 and A_2

in this case were estimated from spectra recorded under "overmodulation" conditions. All obtained parameter values are collected in Table 1.

Table 1

Parameters of EPR spectra of benzoylhydrazyl radicals with the general formula

$$\mathrm{Ph-N-\dot{N}-C(=O)-}G_2 \quad (G_1 \text{ on } \dot{N})$$

No.	G_2	G_1 = naphthyl group as shown		G_1 = phenyl group as shown						
		A_1/A_2	$A_1+A_2\pm$ 0.2 oersted	$A_1\pm$ 0.2 oersted	$A_2\pm$ 0.2 oersted	$\delta H\pm$ 0.3 oersted	$A_3\pm$ 0.3 oersted		A_1/A_2	$A_1+A_2\pm$ 0.5 oersted
1	phenyl	0.91	18.2	8.67	9.53	1.98	1.65	6	0.94	17.5
2	*o*-nitrophenyl	0.75	17.80	7.65	10.15	2.35	2.49	7	0.84	17.0
3	*m*-nitrophenyl	0.80	18.0	8.01	9.99	1.98	1.98	8	0.86	17.4
4	*p*-nitrophenyl	0.75	17.28	7.43	9.85	2.63	2.42	9	0.84	17.3
5	dinitrophenyl, as shown	0.70	17.72	7.55	10.17	3.28	3.01	10	0.76	16.0

It is known that the constants A_1 and A_2 of the isotropic h.f.s. rather reliably characterize the magnitudes of the spin density on the corresponding atoms ([4]). The dependence between A_1 and A_2 and the nature of the substituents

introduced both into the α- and into the β-parts of hydrazyl radicals has been described in detail in ([2,4,7]).

(Figure: Theoretical spectra selected for radicals of group I)

Fig. 3. Theoretical spectra selected for radicals of group I

It was shown that substituents with donor or acceptor properties lead, respectively, to an increase or decrease in the spin density on the neighboring nitrogen atom of the hydrazyl. This effect is associated with the presence of conjugation of the lone pair of electrons of the α-nitrogen with the orbital of the unpa-

of the unpaired electron of the β-nitrogen and is common to all free radicals of the hydrazyl series.

From the data in Table 1 it is seen that introduction of an NO_2 group in the ortho or para position of the benzoyl residue decreases the ratio A_1/A_2 from 0.91 to 0.75 for radicals of group I and from 0.94 to 0.84 for radicals of group II, while leaving the sum $A_1 + A_2$ practically unchanged. Taking into account what was set forth above and the magnitude of the change in spin density under the influence of the NO_2 group ([4,7]), these facts can be understood by assuming that in benzoylhydrazyl radicals, in contrast to DPPH and its numerous derivatives, the spin density on the α-nitrogen atom is greater than on the β-nitrogen atom. Further, it follows from the data in Table 1 that replacement of one phenyl in the α-position by α-naphthyl decreases the ratio A_1/A_2 from 0.94 to 0.91 (for DPPH such replacement leads to an increase of A_1/A_2 from 0.83 to 0.88 ([4])). This also confirms the assumption made that the spin density on N_α is greater than on N_β.

The increase of spin density on N_α in benzoylhydrazyl radicals in comparison with substituted DPPH, for which $A_\beta > A_\alpha$ ([7]), is probably due to the carbonyl group. If the distribution of spin density in benzoylhydrazyl radicals is represented by the structures

$$\begin{array}{l} G_1 \ \dot{N} - N - C - G_2 \\ \qquad\quad \| \\ \quad \text{Ph} \quad O \\ \qquad\quad | \\ \quad \text{Ph} \quad O^- \end{array} \qquad\qquad G_1 \ \overset{+}{N} - \dot{N} = C - G_2$$

(a) (b)

then it is seen that the assumption of the greater probability of structure (b) reflects the property of the double $C = O$ bond–its polarity ([8]). The results obtained by us could be naturally explained by the predominant interaction of the unpaired electron with the nitrogen atoms of the hydrazyl and by a weaker interaction with the protons of the α-part of the molecule. Hyperfine interactions with the remaining magnetic nuclei contribute only to the width of the individual components of the h.f.s. It is noteworthy that δH in the

benzoylhydrazyl radicals studied (see Table 1) is considerably smaller than in DPPH and its derivatives ($\delta H \sim 5$ oersted) ([4]), and is comparable with δH for hydrazyl radicals in which triphenylmethyl or pentaphenylcyclopentadienyl residues stood in the β-position ($\delta H \sim 2$ oersted) ([2,1]). The presence of two single bonds $-\dot{N}-C-C$ in these radicals considerably hinders the interaction of the unpaired electron with the β-residue. The experiments described in the present work show that the carbonyl group $C=O$ also impedes delocalization of the unpaired electron. As a result, the spin density on the phenyl of the benzoyl group has a small value. However, bearing in mind the conclusions made in work ([5]), we repeated the experiment with samples 7 and 9 under the conditions described in ([5]). The results of the measurements are identical with those set forth above (see Table 1).

Finally, we carried out treatment of the oxidized products with hydroquinone, followed by isolation of the initial hydrazines. This unambiguously indicates that the radicals investigated by us by the e.p.r. method have the structure given in Table 1.

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