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Abstract

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Hyperfine Structure of the E.P.R. Spectra of α,α-Diphenyl-β-triphenylmethylhydrazyl and Its Derivatives

(Presented by Academician B. A. Arbuzov, 29 VI 1962)

The study of the isotropic hyperfine structure of solutions of the organic free radical α,α-diphenyl-β-picrylhydrazyl (DPPH) (^{1}) showed that the unpaired electron is localized mainly on the nitrogen atoms of the hydrazyl. It was found (^{2,3}) that the ratio of the hyperfine-structure constants A_1/A_2, characterizing the coupling of the unpaired electron with the α- and β-nitrogen atoms, respectively, is $\sim$ 0.84 (A_1 = 7.85 oersted; A_2 = 9.35 oersted). In a special investigation of deoxygenated solvents it was discovered that there is a probability, different from zero, of finding the unpaired electron also on the peripheral groups of the molecule, leading to a complex additional structure of the e.p.r. spectrum (^{4}). In (^{5}) the influence of various substituents in the para position of the phenyl groups on the distribution of electron density on the nitrogen atoms was studied. By replacing one of the hydrazyl atoms with the isotope N^{15}, which has nuclear spin $I = 1/2$, it was shown that the larger hyperfine-interaction constant (A_2) must be assigned to the nitrogen atom bound to the picryl group.

We have carried out an e.p.r. investigation of a free radical of the hydrazyl series in which the picryl group was replaced by triphenylmethyl; derivatives of this radical were also studied, obtained by introducing an NO_2 group into the para positions of the phenyl groups of triphenylmethyl and an OCH_3 group into the para position of one of the α-phenyls (see a, b, c, d in the caption to Fig. 1).

The indicated free radicals proved to be unstable in air. Therefore the oxidation of the corresponding hydrazines (as well as the subsequent e.p.r. measurements) was carried out in special instruments under vacuum. Pumping was performed after freezing the reaction mixture at a temperature of 77° K. We note that this procedure leads to partial degassing of the solvent and to better resolution of the e.p.r. spectrum. Benzene and chloroform were used as solvents. The e.p.r. spectra were recorded at a frequency $\nu = 9330$ Mc/s on an RE-1301 spectrometer at room temperature from solutions of sufficiently low concentration (< 0.001 mole/liter).

Photographs of the e.p.r. spectra of all the free radicals studied are shown in Fig. 1. It can be seen that the e.p.r. spectrum of each radical consists of seven principal, almost completely resolved components of the hyperfine structure, each of which in turn is structured. It is natural to assume that the principal hyperfine structure arises from the interaction of the unpaired electron with two N^{14} nitrogen atoms, which have nuclear spin $I = 1$, whereas the additional splittings are due to the influence of peripheral protons. Since, however, the available data are insufficient for identifying these protons, in the present article we shall not discuss the additional structure.

The presence of additional structure was not taken into account in the analysis of the experimental EPR spectra. The constants of the isotropic hyperfine interactions of the unpaired electron with the nitrogen atoms A_1 and A_2 were determined by constructing a theoretical nine-component spectrum with such A_1, A_2, and ΔH (the width of an individual peak between the points of maximum slope) that the position and shape of the lines coincided with the experimental spectra.

Fig. 1. EPR spectra of solutions of free radicals:

a) [chemical structure] $N - \dot{N} - C - (C_6H_5)_3$;

b) H_3CO–[chemical structure] $N - \dot{N} - C - (C_6H_5)_3$;

c) [chemical structure] $N - \dot{N} - C - (C_6H_4NO_2)_3$;

d) H_3CO–[chemical structure] $N - \dot{N} - C - (C_6H_4NO_2)_3$.

with the EPR spectra. It was assumed that each individual absorption line has a Gaussian shape and that the magnitude of the hyperfine splittings does not depend on the constant magnetic field. The calculations were carried out with the aid of the M-3-M electronic computer. The EPR curves to be analyzed were recorded under conditions of "overmodulation" of the additional structure. It turned out that comparable results are obtained only in the case when ΔH under the conditions of "overmodulation" is ~ 2 Oe. The obtained values of the constants A_1 and A_2, their sums, and ratios are given in Table 1.

The compounds are arranged in Table 1 in order of increasing ratio A_1/A_2, with $|A_1| < |A_2|$. From the data presented alone it is impossible to establish to which nitrogen atom the constant A_1 corresponds and to which A_2. We shall therefore use the data of work (^{5}), which are given in Table 2.

From the data of Table 2 it is seen that replacement of the hydrogen atoms in the para positions of the α, α-phenyl nuclei by methoxy groups leads to an increase in the electron density on the nearest α-nitrogen atom and, correspondingly, to a decrease in the electron density on the β-nitrogen atom. Since we have carried out an analogous substitution in

[chemical structure] $N - \dot{N} - C - (C_6H_5)_3$

and

[chemical structure] $N - \dot{N} - C - (C_6H_4NO_2)_3$, we believe that the influence of the $-OCH_3$ group on the distribution of the unpaired-electron density in the free radicals studied ···

Table 1

Parameters of the EPR spectrum of α, α-diphenyl-β-triphenylmethyl hydrazyl and its derivatives

Radicals	A_1/A_2	$A_1 + A_2$, Oe	A_1 (±0.20 Oe)	A_2 (±0.20 Oe)
[structural formula]	0.472	17.70	5.68	12.02
[structural formula]	0.502	17.80	5.95	11.85
[structural formula]	0.582	18.20	6.70	11.50
[structural formula]	0.604	18.33	6.91	11.42

Table 2

Parameters of the EPR spectrum of substituted hydrazyls dissolved in benzene (partially degassed) (^{5})

Radicals	A_α/A_β	$A_\alpha + A_\beta$, Oe	A_α (±0.20 Oe)	A_β (±0.20 Oe)
[structural formula]	0.836	16.96	7.72	9.25
DPPH	0.771	17.52	7.63	9.90
[structural formula]	0.618	17.43	6.66	10.78

in the radicals

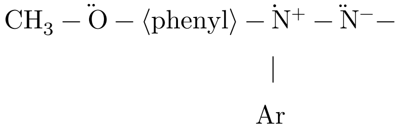
[structural formula] and [structural formula]

should have the same character. From the data in Table 1 it is seen that this substitution leads to an increase in the constant A_1 and a decrease in the constant A_2. This fact makes it possible to consider that the unpaired electron is more strongly associated with the β-nitrogen atom and more weakly with the α-nitrogen atom. This conclusion is also confirmed by the character of the influence of the NO_2 group on the delocalization of the unpaired electron. The data show that, both in DPPH and in the radicals we studied, introduction of this group leads to a decrease in the electron density on the nitrogen atom nearest to it.

Comparison of the data obtained by us with the results of work (^{5}) shows that replacement of the picryl group by triphenylmethyl leads to a marked increase in the density of the unpaired electron on the N_β atom and, accordingly, to a decrease in the density on N_α. In DPPH, owing to the presence of conjugation between the electrons of the nitrogen atoms and the peripheral groups of the molecule, the unpaired electron may be located both on the phenyl nuclei and on the picryl group. In α, α-diphenyl-β-triphenylmethylhydrazyl, delocalization of the unpaired electron is limited mainly to the two nitrogen atoms and the α-phenyls. At the same time, the presence of three electron-acceptor phenyl groups of triphenylmethyl results in a thickening of the electron density of the unpaired electron on the nitrogen atom N_β nearest to them. Decreas-

···by a narrowing of the delocalization region of the unpaired electron in diphenyltriphenylmethylhydrazyl, it is apparently possible also to explain the lower stability of this radical in comparison with DPPH.

Let us briefly consider the influence of substituents on the distribution of the electron density of the unpaired electron. Replacement of a hydrogen atom in the para position in one of the α-phenyls by a methoxy group leads, as a result of the conjugation effect, to a displacement of the electron cloud from the oxygen atom and makes the state



$$\begin{array}{c} \mathrm{CH_3} - \ddot{\mathrm{O}} - \langle\text{phenyl}\rangle - \underset{\displaystyle \begin{array}{c} | \\ \mathrm{Ar} \end{array}}{\dot{\mathrm{N}}^{+}} - \ddot{\mathrm{N}}^{-} - \end{array}$$

more probable than in the unsubstituted radical. When the para hydrogen atoms of the phenyls of triphenylmethyl are replaced by nitro groups, the electron density in the ortho and para positions with respect to these groups decreases. Owing to the appearance of a positive charge on the para-carbon atoms of the phenyl nuclei, the electron clouds of the bonds $-\mathrm{C} - \mathrm{C}\langle$, $-\dot{\mathrm{N}} - \mathrm{C}-$ and $-\dot{\mathrm{N}} ---\dot{\mathrm{N}} -$ are polarized, the degree of polarization decreasing along this series of bonds:

$$-\dot{\mathrm{N}} \rightarrow \dot{\mathrm{N}} \rightarrow -\mathrm{C} \rightarrow \left(-\langle \overset{+}{\text{phenyl}} \rangle - \mathrm{N} \begin{matrix} = \mathrm{O} \\ \backslash \mathrm{O} \end{matrix} \right)_3 . \tag{3}$$

As a result, the atom N_α proves to be charged more negatively than N_β. This, apparently, can qualitatively explain the greater density of the unpaired electron on the atom N_α as compared with the unsubstituted radicals, manifested in both cases in an increase of the ratio A_1/A_2.

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