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Abstract

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Electron Paramagnetic Resonance of meta-Substituted α,α-Diphenyl-β-picrylhydrazyls

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Derivatives of the stable organic free radical α,α-diphenyl-β-picrylhydrazyl (DPPH) have repeatedly been studied by the method of electron paramagnetic resonance (EPR) ($^{1-6}$). Various substituents have been introduced into the DPPH molecule in the para position of the α-phenyls ($^{2-4,6}$) and into the para and ortho positions of the picryl residue (^{1,5,6}). The present communication gives the results of an EPR study of new stable free radicals—derivatives of the hydrazyl series with substituents in the meta position of the picryl group of the molecule. The general formula of the free radicals studied is

$$\text{[[structural formula: hydrazyl radical with } G \text{ group, picryl ring bearing } NO_2 \text{ groups and substituent } R\text{]]},$$
$$\text{where } G = \text{[[phenyl group]]},\ \text{[[naphthyl-like fused-ring group]]},$$
$$R = -OCH_3,\ -Cl,\ -CH_3,\ -H,\ -N\text{[[piperidyl ring with } H\text{]]},\ -N\text{[[morpholine ring with } H \text{ and } O\text{]]}.$$

Measurements were carried out on polycrystalline samples and in solutions.

The EPR spectra of solutions of the radicals were recorded at room temperature on an RE-1301 spectrometer ($\nu_1 = 9290$ MHz). The concentration of radicals in the measured samples did not exceed 0.001 mol/l. Benzene was used as the solvent. To eliminate the effect of oxygen on the resolution of the EPR spectra, the solutions were partially degassed (^{4,6}). A solution of the radical in an evacuated ampoule remains stable for several days. Characteristic EPR spectra of the radicals studied are shown in Fig. 1.

In all cases, five lines of hyperfine structure are observed, caused by the isotropic interaction of the unpaired electron with two nitrogen atoms N^{14} (nuclear spin $I_N = 1$) of the hydrazyl. The constants of this interaction $|A_1|$ and $|A_2|$ were determined with the aid of the M-3M electronic computer by constructing nine-component spectra and automatically fitting the theoretical spectrum to the experimental one. This procedure is described in detail in (^{6}). The values found for the hyperfine-structure constants, their sum and ratio, and also the width of an individual hyperfine component between the points of maximum slope δH are given in Table 1.

Data from previous studies ($^{4-6}$) show that introduction of substituents into the para position of the α-phenyls and into the para or ortho positions of β-picryl regularly changes the distribution of spin density on the atoms

Table 1

Parameters of the EPR spectra of hydrazyl radicals with the general formula

(Figure: structural formula)

No.	G	R	$\nu_1 =$ 9290 MHz, $T =$ 293°K	$\nu_1 =$ 32000 MHz, $T =$ 293°K									
			A_1/A_2	$A_1 + A_2 \pm$ 0.2 Oe	$A_1 \pm$ 0.2 Oe	$A_2 \pm$ 0.2 Oe	$\delta H \pm$ 0.1 Oe	g_1	g_2	g_3	$g_\perp^{\text{eff.}}$	$g_\parallel^{\text{eff.}}$	$\langle g \rangle$
I	phenyl	$-OCH_3$	0.98	17.39	8.61	8.78	5.48	2.0041	2.0039	2.0030	2.0040	2.0030	2.0037
II	phenyl	$-CH_3$	0.98	17.39	8.61	8.78	5.48	2.0044	2.0039	2.0032	–	–	2.0038
III	phenyl	$-Cl$	0.98	17.39	8.61	8.78	5.48	2.0041	2.0036	2.0026	–	–	2.0034
IV	phenyl	$N\langle H \rangle$	0.98	17.39	8.61	8.78	5.48	2.0041	2.0034	2.0032	2.0033	2.0041	2.0036
V	phenyl	$N\langle H \rangle O$	0.98	17.39	8.61	8.78	5.48	2.0041	2.0034	2.0032	2.0033	2.0041	2.0036
VI	phenyl	$-H$	0.83	17.68	8.03	9.65	5.25	2.0040	2.0038	2.0031	2.0039	2.0031	2.0036
VII	naphthyl	$-H$	0.88	16.79	7.86	8.93	5.16	2.0042	2.0035	2.0032	2.0034	2.0042	2.0036
VIII	naphthyl	$-CH_3$	0.98	17.39	8.61	8.78	5.48	2.0047	2.0042	2.0033	–	–	2.0041

Note. The relative error of measurement of g_i $(i = 1, 2, 3)$ is $\Delta g_{\text{rel}} = 0.0001$; the absolute error of measurement of g_i $(i = 1, 2, 3)$ is $\Delta g_{\text{abs}} = 0.0002$.

of the hydrazyl nitrogen in accordance with the nature of the substituent. At the same time (see Table 1), the nature of the substituent in the meta position is not manifested at all in the hyperfine structure of the EPR spectra (Fig. 1). This is not surprising, if one bears in mind that groups located meta to one another in the benzene ring are not in the same system of conjugated bonds (^{7}). However, the obtained values of the isotropic HFS constants $|A_1|$ and $|A_2|$ show that the introduced substituents significantly changed the ratio of the constants A_1/A_2, from 0.83 for DPPH (VI) and from 0.88 for the α-naphthyl radical (VII) to 0.98 for all meta-substituted radicals (I–V). In (^{4}) it was shown that the spin density in unsubstituted DPPH is greater on the β-nitrogen. The values of 0.98 that have been found indicate an equalization of the spin density on the hydrazyl nitrogen atoms in radicals with substituents in the meta position.

In ($^{4-6}$) it was established that the most probable cause of the increase in spin density on the α-nitrogen atom is an enhancement of the acceptor properties of the β-part of the molecule. Since in the free radicals studied only the NO_2

groups, which were present even before substituents were introduced into the meta position, can be responsible for such an increase, we come to the conclusion that the observed manifestation of the influence of substituents in the meta position indicates an increase in the conjugation of the p-orbitals of the hydrazyl nitrogen atoms, on which the unpaired electron may be located, with the π-system of the β-residue. When considering the bonds of the hydrazyl nitrogen atoms in the approximation of a planar structure of the radical molecule, it is natural to assume ([8]) that the three bonding orbitals of the α-nitrogen are sp-hybrids, and the lone pair of electrons occupies the remaining p-orbital. The bonding orbitals of the β-nitrogen are either sp- or sp^2-hybrids. In both cases the unpaired electron is located in a p-orbital, while the lone pair of electrons is in a p-orbital or in an sp^2-hybrid orbital. Delocalization of the unpaired electron over

in the radical molecule occurs as a result of the formation of a common molecular orbital containing the π-electron orbitals of the phenyl rings and the p-orbitals of the nitrogen atoms in the hydrazyl. The introduction of substituents in the meta position of the picryl group apparently changes its orientation relative to the plane of the conjugated system. This, in turn, changes the degree of overlap of the orbital of the atom N_β, on which the unpaired electron is located,* with the p-orbital of the ring carbon. The observed increase in spin density on N_α probably indicates an increase in such overlap.

(Figure: Fig. 1)

Fig. 1. Hyperfine structure of the EPR spectra at $\nu_1 = 9290$ MHz of:
a –I–V, *b* –VII, *v* –VI

This explanation presupposes a dependence of the spin density on N_α on the structure of the meta substituents, leading to various deviations from the original structure of the molecule. However, the accuracy of estimating the ratio A_1/A_2 when $A_1/A_2 \sim 1$ becomes low. A considerably more sensitive parameter of the molecular shape is the g-factor and its anisotropy. Therefore, to confirm the assumptions put forward about certain physical properties, we measured the anisotropy of the $\vec{g}$-tensor in these substances. The measurements were carried out on evacuated microcrystalline samples on a spectrometer with frequency $\nu_2 = 36000$ MHz at room temperature. Calibration of the constant magnetic field was performed by means of proton NMR ([9]). The values of the components of the $\vec{g}$-tensor were determined from analysis of the EPR line shapes ([10,11]) (see Fig. 2). The obtained values are given in Table 1. It is evident from it that, although the average values of the $\vec{g}$-tensor $\langle g \rangle$ in free radicals with substituents in the meta position differ very little from one another and from $\langle g \rangle$ for DPPH, the character of the anisotropy of $\vec{g}$ in them changes considerably.

(Figure: Fig. 2)

Fig. 2. EPR spectra in polycrystalline samples at $\nu_2 = 32000$ MHz of:
1 –II, 2 –VIII, 3 –III, 4 –I, 5 –IV, 6 –V, 7 –VII, 8 –VI

* It is possible that, in the nonplanar structure of the radical molecule, the probability increases of finding the unpaired electron on the second orbital of the nitrogen atom, which does not participate in the formation of the chemical bond.

It may be assumed that in a planar aromatic free radical the unpaired electron is located in a nonbonding π-orbital and that the deviation of the g-factor from the value for a free electron, g_{free}, is due to admixture into this π-state of σ-bonding and σ^*-antibonding states. Then, from qualitative theoretical considerations it follows (12) that in this case the $\vec{g}$-tensor must have axial symmetry, with $g_\perp > g_{\text{free}}$, and $g_\parallel \sim g_{\text{free}}$ ($g_{\text{free}} = 2.0023$). For a nonplanar free radical the symmetry of the g-tensor is lowered. Therefore the low symmetry of the $\vec{g}$-tensor found experimentally is a consequence of the low symmetry of the free-radical molecule.

From the data in Table 1 it follows that all the free radicals studied have three different values of the components of the $\vec{g}$-tensor. At the same time, in some of these radicals two components of $\vec{g}$ differ little from one another. This indicates that the symmetry of $\vec{g}$ in these cases is close to axial. For convenience, these radicals may be characterized by only two values of $\vec{g}$: $g_{\perp\text{eff}}$ and $g_{\parallel\text{eff}}$. These values are given in Table 1. Thus, axial symmetry is observed to a good approximation for DPPH (VI) (10,14), whose molecule apparently has a structure close to planar.

Replacement of phenyl in the α-position by α-naphthyl leads to the reverse order of the values of the components of $\vec{g}$: $g_\parallel = 2.0042$; $g_\perp = 2.0034$. Accordingly, there is every reason to expect significant deviations from a planar arrangement of various groups in the molecule of the α-naphthyl radical (6). The measured values of $\vec{g}$ in the hydrazyl radicals with substituents in the meta position of picryl also indicate the absence of coplanarity in these compounds. It is noteworthy that radicals IV and V, with substituents having different properties but analogous geometry, are characterized by completely identical values of the $\vec{g}$-tensor (again $g_\parallel > g_\perp$), whereas radical III, with a bulky substituent—the chlorine atom—exhibits strong anisotropy of the $\vec{g}$-tensor.

As a result, we arrive at the conclusion that the deviations observed in hydrazyl free radicals with substituents in the meta position in the distribution of spin density and in the values of the components of the $\vec{g}$-tensor from the analogous characteristics in DPPH have a common cause—the change in the shape of their molecules.

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