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Abstract

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STUDY OF THE FREE RADICAL α, α-DIPHENYL-β-PENTAPHENYLCYCLOPENTADIENYLHYDRAZYL BY THE E.P.R. METHOD

In a number of works ([1]-[5]), the influence of various substituents in free radicals of the hydrazyl series on the characteristics of electron paramagnetic resonance (e.p.r.) spectra was studied. In this connection, primary attention was devoted to the influence of substituents on the e.p.r. line width of free radicals in the crystalline state and on the magnitude of the hyperfine-structure constants (h.f.s.), which characterize the coupling of the unpaired electron with the nitrogen atoms of the hydrazyl. In work ([4]) it was shown that the strongest change in the relative magnitude of the h.f.s. constants from the α- and β-nitrogen atoms is observed when the picryl group is replaced by a triphenylmethyl group. In this case the ratio of the h.f.s. constants proved to be 0.47, as compared with 0.79 for the classical α,α-diphenyl-β-picrylhydrazyl (DPPH). At the same time, in the e.p.r. spectrum of the radical studied, with a triphenylmethyl β-part, in addition to the principal h.f.s. components due to interaction of the unpaired electron with the nuclei of the nitrogen atoms, an additional structure was observed, attributed to the influence of peripheral protons. Because of insufficient experimental data, the proton structure was not discussed in work ([4]).

In the present work an e.p.r. study is described of yet another free radical: α, α-diphenyl-β-pentaphenylcyclopentadienylhydrazyl

[structural formula of α,α-diphenyl-β-pentaphenylcyclopentadienylhydrazyl] (I)

The synthesis of this radical was carried out according to the following scheme:

$$(C_6H_5)_2NH \xrightarrow{HONO} (C_6H_5)_2N{-}NO \xrightarrow[\text{acetic acid}]{\text{Zn dust}} (C_6H_5)_2N{-}NH_2 \xrightarrow[\text{in } CHCl_3]{\text{Br}{-}C(C_6H_5)\text{-pentaphenylcyclopentadienyl fragment}}$$
$$\rightarrow (C_6H_5)_2N{-}NH{-}C(C_6H_5)\text{-pentaphenylcyclopentadienyl fragment } (I_h)$$
$$\xrightarrow[\text{in } CHCl_3]{PbO_2} (C_6H_5)_2N{-}\dot{N}{-}C(C_6H_5)\text{-pentaphenylcyclopentadienyl fragment (I)}$$

The bromopentaphenylcyclopentadiene starting material required for the reaction was obtained by the method described by Ziegler ([6]).

Hydrazine (I_h) consists of shiny, faintly pale-green crystals, melting with decomposition at 188—190°. The compound obtained dissolves well in chloroform, benzene, and toluene, less readily in alcohol and dioxane, and is insoluble in ether and water. In glacial acetic acid the hydrazine dissolves with a violet coloration. Yield 85–87%.

Found, %:	C 89.13;	H 5.82;	N 4.65
$C_{47}H_{36}N_2$. Calculated, %:	C 89.80;	H 5.73;	N 4.45

The free radical—hydrazyl (I)—is obtained by oxidizing a solution of hydrazine (I_h) in chloroform with lead dioxide, followed by precipitation with dry ether ([7]). In contrast to the extremely unstable triphenylmethyl-substituted radicals, diphenylpentaphenylcyclopentadienylhydrazyl is stable, and it proved possible to isolate it in the crystalline state. The small bright-orange crystals of the radical melt with decomposition above 180°. Hydrazyl (I) dissolves well in benzene, chloroform, alcohol, and acetonitrile with an intense cherry-red coloration. In glacial acetic acid the radical dissolves with a green coloration, and in dioxane with a bright-red coloration. Yield of hydrazyl (I) 70–80%.

Found, %:	C 88.86;	H 6.09;	N 4.70
$C_{47}H_{35}N_2$. Calculated, %:	C 89.95;	H 5.58;	N 4.46

The EPR spectrum of the synthesized radical was studied in solutions and in the crystalline state. Benzene, chloroform, and acetonitrile were used as solvents. The paramagnetic absorption of the radical solutions was investigated at room temperature on a standard RE-1301 radiospectrometer with oscillating magnetic-field frequency

$$\nu_1 = 9330 \text{ MHz}.$$

In partially degassed solutions ([2]) of radical (I) of sufficiently low concentration (less than $1 \cdot 10^{-3}$ mol/l), an h.f.s. is observed consisting, as in the case of substitution of the picryl group in DPPH by triphenylmethyl, of seven principal almost completely resolved components. Each of these seven lines is in turn split into four more (Fig. 1). No dependence of the spectrum on the solvent is observed. The main components of the h.f.s. are due to the interaction of the unpaired electron with two nitrogen atoms N^{14}, having nuclear spin $I = 1$. Analysis of the spectrum makes it possible to determine that the constants of isotropic hyperfine interactions of the unpaired electron with these nitrogen atoms are

$$A_1 = 5.8 \pm 0.2 \text{ Oe}$$

Fig. 1. EPR spectrum of α,α-diphenyl-β-pentaphenylcyclopentadienylhydrazyl in chloroform ($1 \cdot 10^{-3}$ mol/l, $\nu_1 = 9330$ MHz)

Figure 1: Fig. 1. EPR spectrum of α,α-diphenyl-β-pentaphenylcyclopentadienylhydrazyl in chloroform ($1 \cdot 10^{-3}$ mol/l, $\nu_1 = 9330$ MHz)

and

$$A_2 = 11.6 \pm 0.2 \text{ Oe}$$

$$(A_1 + A_2 = 17.4 \text{ Oe}, \quad A_1/A_2 = 0.5).$$

In the case of DPPH,

$$A_1 + A_2 = 16.85 \pm 0.4 \text{ Oe}, \quad A_1/A_2 = 0.79 \ (^2).$$

This indicates that the unpaired electron in hydrazyl (I) is localized mainly on the nitrogen atoms.

Fig. 1. EPR spectrum of α, α-diphenyl-β-pentaphenylcyclopentadienylhydrazyl in chloroform ($1 \cdot 10^{-3}$ mol/l, $\nu_1 = 9330$ MHz).

The fact that the spectra of (I) and α, α-diphenyl-β-triphenylmethylhydrazyl differ hardly at all in the values of the constants A_1 and A_2, in their sum, and in their ratio, despite the very large difference in the structure of their β-parts, permits the conclusion that the additional structure is not connected with the protons of the β-group. It therefore remains to assume that the additional h.f.s. is due to the protons of the α-phenyls. The presence of four additional components indicates ···

preferential coupling of the unpaired electron with only three protons. If one takes into account that the 3,5- and 2,4,6-protons of phenyl are nonequivalent, the additional structure can be explained by coupling of the unpaired electron with the 2,4,6-protons of one of the α-phenyls, assuming that the plane of the other is not coplanar with the plane of the cloud of the p-electrons of the nitrogen atoms.

To determine the constant a of the hyperfine interactions of the unpaired electron with protons, we constructed a spectrum consisting of four lines of Gaussian form with an intensity ratio of $1 : 3 : 3 : 1$ and studied the shape of the spectrum as a function of the width of the components ΔH_n at half intensity. The calculations were performed on an M-3M electronic computer. It turned out that the theoretical spectrum agrees well with the experimental one at a ratio $\Delta H_n/a = 0.65$ (the comparison was made with the outer lines of the spectrum

Fig. 2. Theoretical curve for $\Delta H_n/a = 0.65$ (the first derivative is shown)

Figure 2: Fig. 2. Theoretical curve for $\Delta H_n/a = 0.65$ (the first derivative is shown)

Fig. 3. Absorption line at $\nu_3 = 36\,000$ MHz from a finely crystalline sample of radical (I)

Figure 3: Fig. 3. Absorption line at $\nu_3 = 36\,000$ MHz from a finely crystalline sample of radical (I)

shown in Fig. 1, which are distorted less than the others by the overlapping adjacent lines). This made it possible to determine the value $a = 1.7$ Oe and $\Delta H_n = 1.1$ Oe. The theoretical curve for $\Delta H/a = 0.65$ is shown in Fig. 2.

Fig. 2. Theoretical curve for $\Delta H_n/a = 0.65$ (the first derivative is shown)

In work (5), using DFPG derivatives as an example, it was noted that the EPR method can be used to estimate the relative stability of related free radicals by studying the HFS of solutions containing, along with molecules of free radicals of one substance, molecules of unoxidized hydrazines of another substance. The EPR spectrum of the synthesized radical (I) differs sharply from the spectrum of DFPG. Therefore, in our case it was easy to estimate the relative stability of these radicals. It turned out that, a short time after the addition to the DFPG solution of an equivalent amount of α,α-diphenyl-β-pentaphenylcyclopentadienylhydrazine, an EPR spectrum characteristic of radical (I) is observed. The addition of diphenylpicrylhydrazine to a solution of radical (I), even in an amount 1.5-2 times greater than the equivalent amount, does not lead to a change in the EPR spectrum. These facts show that hydrazyl (I) possesses greater chemical stability than DFPG. Knowing the extreme instability of the triphenylmethyl-substituted radical (4), this conclusion proves to be rather unexpected. Let us recall here that, according to EPR data, both in diphenylpentaphenylcyclopentadienylhydrazyl and in diphenyltriphenylmethylhydrazyl the region of delocalization of the unpaired electron is mainly limited to two nitrogen atoms and the α-phenyls. Apparently, the stability of hydrazyl (I) is determined by steric factors limiting the possibility of chemical interaction of (I) with molecules of other substances. On the other hand, it is possible that, as has already been noted more than once (2), it is not legitimate to compare the magnitudes of HFS constants and electron densities for substances with strong differences in the structure of any parts of their molecules.

Fig. 3. Absorption line at $\nu_3 = 36\,000$ MHz from a finely crystalline sample of radical (I)

The study of the electron paramagnetic absorption of free radical (I) in the crystalline state was carried out at frequencies $\nu_2 = 300$ MHz and $\nu_3 = 36\,000$ MHz. At the frequency ν_2, the line width ΔH at half intensity of the absorption curve was measured; at the frequency ν_3, the anisotropy of the g-factor was

measured. The measurement technique and apparatus are described in works (8, 9). The measurements were carried out on evacuated samples. The results obtained are given in Table 1.

The ratios of the fourth moment of the absorption line to the second, calculated from the data at ν_2,

$$r = \langle \Delta H^4 \rangle^{1/4} / \langle \Delta H^2 \rangle^{1/2},$$

show that, despite the comparatively large line width ΔH, the exchange interactions are strong. The data given in Table 1 refer to a microcrystalline sample into which, apparently, solvent molecules enter in addition to the radical molecules. In samples not containing solvent, the values of ΔH and r may prove to be somewhat different.

Table 1

	ΔH, Oe	ΔH, Oe	r	r	g-tensor
	295°K	77°K	295°K	77°K	295°K
$(C_6H_5)_2N-$ N − C(C_6H_5)-cyclopentadienyl fragment with five C_6H_5 groups	15.7 ± 0.3	10.5 ± 0.3	1.43	1.45	$g_1 = 2.0039 \pm 0.0001 g_2 = 2.0051 \pm 0.0001 g_3 < g_1$

Narrowing of the EPR line upon lowering the temperature from room temperature to 77°K was observed earlier [10] for DPPH containing crystallization-bound cyclic solvent molecules, and was attributed to the dependence of nonsecular broadening on the correlation time [11].

A theoretical analysis of the EPR line shape of microcrystalline substances with anisotropic parameters [12] makes it possible to find the g-tensor of free radicals from measurements at high frequencies. A photograph of the EPR line at frequency ν_3 from microcrystalline radical (I) is shown in Fig. 3. From the shape of this line only two values of the g-tensor can be determined. However, the gentle slope of the EPR curve on the side of strong magnetic fields permits one to assume that this part of the line is also structural.

The appreciable difference between the g-factor of the synthesized radical (I) and the value of the g-factor of the related DPPH shows that the structure of the molecule of the free radical substantially affects the residual spin-orbit coupling and the anisotropy of the g-factor.

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