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N. S. GARIFYANOV, A. V. ILYASOV, Yu. V. YABLOKOV

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Abstract

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N. S. GARIFYANOV, A. V. ILYASOV, Yu. V. YABLOKOV

ELECTRON PARAMAGNETIC RESONANCE IN LIQUID AND SUPERCOOLED SOLUTIONS OF CERTAIN FREE RADICALS

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In studying liquid solutions of the organic free radicals 2,2,6,6-tetramethylpentamethylene nitroxide (TMPMOA) and Banfield and Kenyon' s radical, one of the authors (^{1}) discovered the influence of the solvent on the electron paramagnetic resonance (EPR) spectrum. It turned out that in polar solvents the width δH of the components of the hyperfine structure (h.f.s.) is smaller, and the splitting constant A is larger, than the values observed in nonpolar solvents. A similar influence of the solvent on the EPR spectrum was also observed for phosphonyl radicals (^{2}). The change in the h.f.s. parameters of radicals in polar solvents, compared with the values in nonpolar media, was explained by the author (^{1}) as the formation around the radical molecule of a solvation shell that hinders broadening of the h.f.s. lines by the Heitler—Teller mechanism (^{3}). In addition, the solvation environment of the paramagnetic molecule affects the electric field in the region of localization of the unpaired electron, which is manifested in a change of the h.f.s. constants.

In works ($^{4-7}$), in studying the spectrum of α,α-diphenyl-β-picrylhydrazyl (DPPH), an h.f.s. practically independent of the solvent was found, consisting of five lines. This structure (^{4}) in DPPH is due to the interaction of the unpaired electron with two nitrogen nuclei N^{14}. It was also found that the constants A_1 and A_2, characterizing the coupling of the unpaired electron with the α- and β-nitrogen atoms, are not identical ($^{7-9}$). In degassed solutions of DPPH in benzene, the ratio $A_1/A_2 = 0.77^*$ (^{9}). Anisotropic hyperfine interactions in diluted single crystals of DPPH were studied in (^{10}). Lord and Blinder obtained parameters characterizing the anisotropic hyperfine coupling in DPPH and carbazyl by analyzing the EPR spectra of these radicals in hardened Duco cement and methyl methacrylate (^{7}).

In this article we present the results of a further study of the influence of the nearest environment of the paramagnetic molecule on the h.f.s. parameters of α,α-diphenyl-β-picrylhydrazyl and 2,2,6,6-tetramethylpentamethylene nitroxide. Measurements were made at a frequency $\nu = 9320$ MHz in the temperature interval 77—300° K on a standard RE-1301 radiospectrometer. Methanol,

ethanol, a glycerin-methanol mixture, benzene, toluene, chloroform, and also polystyrene diluted with benzene or chloroform were used as solvents. The study of these radicals in liquid and supercooled solutions made it possible to obtain information on both isotropic and anisotropic hyperfine interactions.

The supercooled glassy state is obtained by freezing alcoholic solutions. In nonpolar solutions, however, the supercooled state could be obtained only in a highly viscous polystyrene medium.

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* In our measurements for partially degassed solutions of DPPH in benzene, $A_1/A_2 = 0.83$.

It should be noted that upon freezing pure nonpolar solutions of DPPH, a single absorption line of the crystalline radical is observed. In (^{5}), the single line in a frozen benzene solution of DPPH is explained by the appearance of direct exchange interaction between radical molecules, or indirect interaction through benzene molecules. As shown below, in supercooled solutions of DPPH a well-resolved h.f.s. is observed. This indicates that in these solutions exchange interaction through solvent molecules does not arise.

The study of EPR spectra in liquid and supercooled (solid) solutions makes it possible to investigate the isotropic and anisotropic parts of the hyperfine structure in one and the same medium. At the same time, the use of different solvents that form a supercooled state permits information to be obtained on the influence of the solvent on the anisotropic h.f.s. In addition, rapid preparation of supercooled solutions becomes especially important in the study of unstable free radicals.

Fig. 1. EPR spectrum in liquid deoxygenated solutions of DPPH (0.001 mole/l): *a* —in benzene, *b* —in a methanol-glycerol mixture (60 : 40)

The observed EPR spectrum in liquid and supercooled solutions of radicals is described by a spin Hamiltonian consisting of a Zeeman term $\hat{\mathcal{H}}_z$ and the operator of hyperfine interactions $\hat{\mathcal{H}}_{\text{st}}$:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_z + \hat{\mathcal{H}}_{\text{st}}. \tag{1}$$

The latter term may be represented in the form

$$\hat{\mathcal{H}}_{\text{st}} = A\hat{\mathbf{S}}\hat{\mathbf{I}} + \hat{\mathbf{S}}B'\hat{\mathbf{I}}, \tag{2}$$

where the first term describes the isotropic, so-called contact, interaction, and the second the anisotropic (dipole-dipole) interaction. The tensor B' in the molecular coordinate system is represented by a diagonal matrix with zero trace (^{11}):

$$B_{xx} + B_{yy} + B_{zz} = 0. \tag{3}$$

For axial symmetry ($B_{xx} = B_{yy}$), Hamiltonian (2) can be rewritten in the form

$$\hat{\mathscr{H}}_{\mathrm{st}} = A^{*} \hat{I}_z \hat{S}_z + B^{*} (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y), \tag{4}$$

where

$$A^{*} = A + 2B, \qquad B^{*} = A - B, \qquad B = \tfrac{1}{2} B_{zz}.$$

Equations (5) relate the anisotropic constants A^{*} and B^{*} to the constant B, used by Lord and Blinder (^{7}) to characterize the anisotropic part of the h.f.s. In solid solutions, the values of the constants A and A^{*} are determined directly from the h.f.s. spectra of radicals in the liquid and supercooled states; then B can be calculated from equation (5).

In liquid solutions of DPPH, the observed h.f.s. is described by the isotropic part of spin Hamiltonian (2) with $A = A_1 + A_2$. It turned out that in degassed liquid solutions of diphenylpicrylhydrazyl the h.f.s. parameters

noticeably depend on the nature of the solvent (Fig. 1). The determination of the constants A_1 and A_2 from the spectra of liquid DFPG solutions, as well as of the width δH between the points of maximum and minimum of the first derivative of an individual line of the nine-component spectrum, was carried out on an M-3-M electronic computer. The obtained values of A_1, A_2, and δH are given in Table 1.

Table 1

Parameters of h.f.s. in degassed DFPG solutions ($C = 0.001$ mol/l)

Solvent	Isotropic structure ($T =$ 300° K): $A_1 + A_2$ ($\pm$0.2 e)	Isotropic structure ($T =$ 300° K): A_1/A_2	Isotropic structure ($T =$ 300° K): δH ($\pm$0.2 e)	Anisotropic structure ($T =$ 77° K): $B_1 + B_2$ ($\pm$0.2 e)	Anisotropic structure ($T =$ 77° K): B_1 ($\pm$0.7 e)	Anisotropic structure ($T =$ 77° K): B_2 ($\pm$0.7 e)
Benzene	17.6	0.83	5.24	–	–	–
Toluene	17.6	0.83	5.24	–	–	–
Chloroform	17.6	0.83	5.24	–	–	–
Polystyrene with benzene	17.6	0.83	5.24	11.6	5.36	6.24
Methanol	17.8	0.86	5.26	11.8	5.62	6.28

Fig. 2. EPR spectrum in supercooled methanol solutions: a –DFPG (10^{-3} mol/l), b –TMPMOA (10^{-4} mol/l)

Figure 1: Fig. 2. EPR spectrum in supercooled methanol solutions: a –DFPG (10^{-3} mol/l), b –TMPMOA (10^{-4} mol/l)

Solvent	Isotropic structure ($T =$ 300° K): $A_1 + A_2$ (±0.2 e)	Isotropic structure ($T =$ 300° K): A_1/A_2	Isotropic structure ($T =$ 300° K): δH (±0.2 e)	Anisotropic structure ($T =$ 77° K): $B_1 + B_2$ (±0.2 e)	Anisotropic structure ($T =$ 77° K): B_1 (±0.7 e)	Anisotropic structure ($T =$ 77° K): B_2 (±0.7 e)
Methanol-glycerol mixture (60 : 40%)	18	0.92	5.73	11.9	5.76	6.14

In alcoholic and polystyrene supercooled solutions of DFPG, practically the same anisotropic h.f.s. is observed, with the distance between components about 2 times greater than the distances in the isotropic h.f.s. (Fig. 2a). The increase in hyperfine splitting is caused by the appearance of an anisotropic term in the spin Hamiltonian (2). The constants $B = B_1 + B_2$ were determined from the spectrum of the anisotropic h.f.s.; approximate values of B_1 and B_2 were then calculated under the assumption that $A_1 - A_2 \sim 2(B_1 - B_2)$. Table 1 gives the values of the h.f.s. parameters for which the best agreement is obtained between the theoretically constructed curves and the experimental spectra.

Fig. 2. E.p.r. spectrum in supercooled methanol solutions: *a* –DFPG (10^{-3} mol/l), *b* –TMPMOA (10^{-4} mol/l).

As is seen from the data of Table 1, the ratio of the isotropic h.f.s. constants noticeably depends on the solvent. It is natural to suppose that, as in the case of TMPMOA (1), a solvation shell forms around the radical molecule in polar solutions. This leads to a change in the hyperfine coupling of the unpaired electron with the α- and β-nitrogen atoms. The constancy of the sum $A_1 + A_2$, within the limits of experimental error, indicates that the total coupling of the unpaired electron with both nitrogen atoms of the hydrazyl is preserved.

The constants of the anisotropic structure obtained by us (Table 1) differ from the values reported in work (7). This is possibly due to the fact that, when calculating B_1 and B_2 from the spectra in Duco cement (solvent–acetone), Lord and Blinder used isotropic parameters obtained in a non-deoxygenated benzene solution. From the data of Table 1 it is seen that the quantities B_1 and B_2 do not exhibit any appreciable

dependence on the solvent. This may be connected both with a different distortion of the solvate complex in frozen solutions and with insufficient accuracy in determining the parameters B_1 and B_2.

In supercooled solutions of tetramethylpentamethylene nitrogen oxide an anisotropic h.f.s. is observed, consisting of three lines of unequal intensity (Fig. 2b). Both in liquid and in supercooled solutions the spectrum of TMPMOA does not depend on atmospheric oxygen. The constant A^* was determined directly from the experimental spectrum as the distance between the components of the anisotropic h.f.s.; the value B was then calculated from relations (5). The values of B obtained are given in Table 2. It should be noted that, with the values of B given in Table 2, good agreement between theoretically constructed curves and experimental spectra is obtained only for $A, B > 0$ and $\Delta g < 0.001$. Measurement of the g-factor of TMPMOA at a frequency $\nu = 36000$ MHz showed that the anisotropy Δg is not more than 0.002.

Table 2

H.f.s. constants in solutions of TMPMOA
($C = 0.001$ mol/l)

Solvent	Isotropic structure ($T = 300^\circ$ K) $A \pm 0.2$ Oe	Anisotropic structure ($T = 77^\circ$ K) $B \pm 0.2$ Oe
Polystyrene with benzene	15.6	9.4
Methanol	16.3	10.2
Methanol-glycerol mixture (60 : 40%)	16.8	10.1
Ethanol-water mixture (40% water)	17.4	10.0

As can be seen from the data in Table 2, the constant B, which characterizes the anisotropic hyperfine coupling in alcoholic supercooled solutions of TMPMOA, is larger in comparison with the value in a nonpolar medium (polystyrene). Such an influence of the solvent can, as in the case of liquid solutions, be explained by the action of the nearest environment of the radical molecule in a polar medium. Thus, the nearest environment (solvate shell) of a paramagnetic molecule can affect the density of the unpaired electron at the nitrogen nucleus, which is manifested in the values of the constants of isotropic and anisotropic h.f.s.

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Physicotechnical Institute
of the Kazan Branch of the Academy of Sciences of the USSR

Institute of Organic Chemistry
of the Academy of Sciences of the USSR
Kazan

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