PARAMAGNETIC RESONANCE IN VARIOUS FORMS OF α,α-DIPHENYL-β-PICRYLHYDRAZYL

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PARAMAGNETIC RESONANCE IN VARIOUS FORMS OF α,α-DIPHENYL-β-PICRYLHYDRAZYL

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In studying paramagnetic resonance in finely crystalline samples of α,α-diphenyl-β-picrylhydrazyl (DPPH) at frequencies of 300 and 9400 MHz, A. E. Arbuzov et al. (^{1}) showed that the width of the absorption line depends substantially on the nature of the solvent used at the final stage of preparation of the radical (^{2}), on atmospheric oxygen, and on the frequency at which the experiment is carried out.

We have carried out measurements of paramagnetic resonance at a frequency of 36 000 MHz at room temperature in single crystals of DPPH obtained from chloroform, carbon disulfide, and benzene, as well as in polycrystalline samples prepared from several solvents. Single crystals of DPPH were grown by slow evaporation of the solvents. It was observed that, with this method of crystallization, favorable conditions are created for twinning. All the crystals selected for the work, grown from solutions in benzene and chloroform, proved to be twins. The chloroform crystals of DPPH had an elongated plate-like form. Therefore, on them it was possible easily to detect the plane of intergrowth of the twin and to separate one individual from the other. For the benzene samples this could not be done.

From the data available in the literature (^{3}) it is known that single crystals grown from a benzene solution of DPPH belong to the monoclinic system, whereas single crystals of DPPH obtained from chloroform (^{3}), carbon disulfide, or carbon tetrachloride (^{4}) belong to the triclinic system.

In the millimeter-wave range, the components depending on the magnitude of the constant magnetic field are resolved much better than at lower frequencies. Therefore, small differences in the g-factors can be measured with sufficiently high accuracy. Our measurements showed that in all the indicated single crystals —even triclinic ones—there is a direction such that, upon rotation about it, the value of the g-factor changes hardly at all.* This direction may be regarded, to an approximation corresponding to the accuracy of the measurements, as the axis of magnetic symmetry of the crystal, as was done by V. Gordy et al. (^{4}). It is reasonable to suppose that the axis of magnetic symmetry is directed along the —N—N— bond in DPPH. Bearing in mind the reservations made above, we used, to describe the paramagnetic resonance in all three types of DPPH single crystals, the spin Hamiltonian customary for the case of axial symmetry,

$$\hat{\mathscr{H}} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) \tag{1}$$

with spin 1/2.

* Upon rotation of a DPPH single crystal relative to the direction taken as the axis of magnetic symmetry, the values of the g-factor varied from 2.0041 to 2.0038.

The obtained values of the g-factors and the linewidths of the paramagnetic resonance in DPPH single crystals are given in Table 1. The linewidths ΔH were measured at half intensity. In the apparatus for observing paramagnetic resonance, an electromagnet of the SP-13B type was used, which made it possible to obtain sufficient homogeneity of the constant magnetic field at the location of the sample. The single crystals used for the measurements had dimensions of approximately 0.5 × 0.1 × 0.1 mm. Increasing the dimensions of finely crystalline samples to 0.5 × 0.5 × 0.5 did not lead to any noticeable broadening of the absorption line. Calibration of the constant magnetic field during the measurements was carried out from the proton nuclear magnetic resonance signal. The values of the DPPH g-factors were extrapolated to the g-factor of metallic lithium dispersed in rubber, for which the value 2.0023 is accepted (^{5}). We note that our principal attention was directed not so much to the absolute values of g, as to their change as a function of the nature of the solvent and of the orientation of the single crystals. The accuracy of the g-factor measurements was ±0.0002.

Table 1

g-factors and linewidths of the paramagnetic resonance (in oersteds) in DPPH single crystals

Solvent	$g_{\perp}$	$g_{\parallel}$	$\Delta H_{\perp}$	$\Delta H_{\parallel}$
Benzene	2.0039 ± 0.0003	2.0030 ± 0.0003	Not more than 5	Not more than 5
Chloroform	2.0040	2.0030	1.4 ± 0.1	2.0 ± 0.1
Carbon disulfide	2.0041	2.0031	1.9 ± 0.2	2.4 ± 0.2

It follows from Table 1 that the g-factors of all DPPH single crystals, within the accuracy of the measurements, have the same absolute magnitude. In all types of DPPH single crystals a small, but far beyond the experimental errors, anisotropy of the g-factor is observed. In single crystals obtained from chloroform and carbon disulfide, the anisotropy of the paramagnetic-resonance linewidth, first discovered by Livingston and Zeldes (^{6}), was also measured. There had been no clarity on this question, since in the report of Kikuchi and Singer (^{7}) it was indicated that the absorption-line width does not depend on the orientation of the DPPH single crystal within the experimental errors of ±20%. Our data confirm the reality of this anisotropy. Measurements of DPPH obtained from benzene did not give such unambiguous results.

The benzene samples had a larger number of faces. Examination of them under the microscope failed to reveal signs of twinning. However, both the resonance measurements and the X-ray structural investigation lead one to believe that in this case we were not dealing with individual crystals. Most probably, each resonance curve obtained from DPPH samples with benzene represented a superposition of two curves, very sensitive to orientation with respect to the constant magnetic field. This affected the distortion of the shape of the curve. At certain orientations two clearly resolved peaks were observed. All this led to a change in the width of the absorption curve from approximately 5 to 9 oersteds. Analysis of the results obtained made it possible to trace the anisotropy of the g-factor also for benzene DPPH single crystals. It may be considered that the width of the resonance curve corresponding to a single crystal does not exceed 5 oersteds in this case. We also carried out measurements of paramagnetic resonance in finely crystalline DPPH samples obtained from benzene, chloroform, carbon disulfide, and carbon tetrachloride. These measurements were made in order to determine whether the magnitude of the "isotropic" g-factor depends on the type of solvent and what the tendency is for the absorption-line widths to change with frequency. The results obtained are given in Table 2. The data refer to samples of approximately the same degree of dispersion, placed in Pyrex ampoules from which the air was pumped out to a high vacuum.

Thus, it may be considered that the magnitude of the g-factor and its anisotropy do not depend on the solvent from which the DPPH samples crystallized.

The width of the paramagnetic-resonance line in the benzene sample exceeds the absorption-line widths in DPPH samples obtained from solutions in chloroform, carbon disulfide, and carbon tetrachloride, which indicates stronger exchange interactions in the latter.

Table 2

g-factors and widths of paramagnetic-resonance lines (in oersteds) in various DPPH samples

Solvent	36000 MHz, polycryst. g	36000 MHz, polycryst. ΔH	36000 MHz, monocryst. ΔH	300 MHz, ΔH
Benzene	2.0038	7.2 ± 0.2	5	6.8
Chloroform	2.0038	5.4 ± 0.2	1.6	1.7
Carbon disulfide	2.0038	4.7 ± 0.2	2.1	1.3

Solvent	36000 MHz, polycryst. g	36000 MHz, polycryst. ΔH	36000 MHz, monocryst. ΔH	300 MHz, ΔH
Carbon tetrachloride	2.0038	5.6 ± 0.2	–	1.9

The results of our measurements can be compared with the data (1) obtained at a frequency of 300 MHz for finely crystalline DPPH samples. The weak anisotropy of the g-factor of DPPH has absolutely no effect on the shape of the absorption line at this frequency. Therefore, the values of the widths obtained at a frequency of 300 MHz for polycrystals should properly be compared with the values calculated by the formula $\Delta H_{\text{isotr}} = {}^1/_3(\Delta H_\parallel + 2\Delta H_\perp)$ for single crystals, where $\Delta H_\parallel$ and $\Delta H_\perp$ were measured in the range of 36000 MHz. It is evident from Table 2 that, with increasing frequency, the absorption line in a benzene single crystal of DPPH, i.e., in DPPH containing crystallization-bound cyclic solvent molecules, narrows appreciably, as was shown in (1). In single crystals containing noncyclic solvent molecules (chloroform, carbon disulfide, carbon tetrachloride), however, no change of ΔH with frequency occurs. Indeed, ΔH in the chloroform single crystal has practically the same value at frequencies of 300 and 36000 MHz. The slight difference in the widths of the paramagnetic-resonance lines in finely crystalline DPPH samples obtained from chloroform and carbon tetrachloride at a frequency of 300 MHz is retained at a frequency of 36000 MHz. A comparison of ΔH in DPPH samples crystallized from solvents with noncyclic molecules (see (1)) shows that the increase in the width at a frequency of 9400 MHz in comparison with 300 MHz corresponds precisely to the magnitude of the anisotropy of the g-factor, which is already manifested at this frequency. As for the DPPH single crystal grown from carbon disulfide, it should be borne in mind that DPPH prepared from this solvent is most strongly subject to the influence of atmospheric oxygen, and in the present work very small single crystals were used that had been stored in air for 2 months.

Finally, it should be noted that atmospheric oxygen, while causing considerable broadening of the absorption lines in DPPH obtained from solvents whose molecules contain no rings (1,8), does not influence the magnitude of the g-factor of this free radical.

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