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The Proton Magnetic Resonance in the DPPH–Benzene Complex

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The proton magnetic resonance in single crystals of the DPPH-benzene complex has been measured around three Cartesian axes. All the spectra are highly complex, but some lines are clearly identified around all axes. The principal values of their anisotropic hyperfine tensors have been evaluated, in addition to the isotropic hyperfine coupling constants. In the crystalline state, the unpaired electron-spin distributions of one phenyl group is almost twice as large as that of the other phenyl group, as is to be expected from the crystal structure. Besides, the unpaired electron-spin delocalization is larger in the crystalline state than that in solution, particularly on the picryl group and on one phenyl group.

In the proton NMR spectra of some organic free radicals in polycrystalline states, some lines have been shifted from the free-proton position because of the exchange-narrowed hyperfine interaction.[1–5]

Anderson *et al.* have observed the proton resonance of a polycrystalline sample of the 1 : 1 DPPH–benzene complex at 4.2 K.[3] By deuterium substitution, the large central component and the largest downfield-shifted component were attributed to the benzene protons and to the picryl group protons respectively, but the other three components were not identified. Moreover, they reported that the single crystal spectrum is highly complex, containing as many as 15 resolvable peaks in certain orientations.

On the other hand, the ESR spectra of DPPH in mixed organic solvents have been measured, and the high resolution of the Electron-Nuclear Double Resonance (ENDOR) technique has been utilized to obtained precise values for the twelve proton hyperfine couplings of DPPH in a mineral oil solution.[6,7,8] Those results indicate that the unpaired electron-spin distributions of the two phenyl groups are equal in solution.

Recentyl the crystal structure of the 1 : 1 DPPH–benzene complex has been determined by Williams.[9] He reported that the molecular configuration around the α-nitrogen is approximately trigonal planar, with the phenyl groups twisted at angles of 49 and 22°. From his results, the unpaired electron-spin distribution of the two phenyl groups can be expected to be different in the crystalline state. In order to obtain more information about the unpaired electron-spin distribution in the crystalline state and the contribution of the anisotropic hyperfine interaction to the proton resonance shift, we have measured the NMR of protons in the DPPH–benzene complex single crystal around three Cartesian axes at 4.2 K, employing a higher frequency of 40.0 MHz. We have evaluated the principal values of the anisotropic hyperfine tensors for the identified lines. The single crystal and polycrystalline NMR data show that the unpaired electron-spin distribution of one phenyl group is almost twice as large as that of the other phenyl group.

Experimental

α,α-Diphenyl-β-picryl hydrazyl (DPPH) was prepared by the oxidation of commercially-obtained α,α-diphenyl-β-picryl hydrazine (DPPH$_2$) with PbO$_2$ and was recrystallized several times from a benzene solution. The single crystals of the DPPH-benzene complex used in the measurements was grown by the slow evaporation of the solvent from the benzene solution and had the dimensions of $10\times5\times4$ mm^3.

An x, y, z Cartesian axis system was defined for convenience from its shape. The x-axis was selected parallel to the long edge, and the z-axis, normal to the metallic lustrous face containing the long edge. All the NMR measurements were carried out using a Robinson-type spectrometer[10] at 40.0 MHz, with an 80-Hz field modulation and a field sweep. The angular dependence of the NMR spectra was obtained by rotating the magnet around the x, y, and z axes, with the magnet set perpendicular to the magnetic-field direction.

Results and Discussion

The 4.2 K proton resonance spectrum of a polycrystalline DPPH-benzene complex agrees well with the results reported by Anderson *et al.*,[3] as is shown in Fig. 1(a). Figs. 1(b) and (c) present relatively well-resolved spectra of the single crystal of the DPPH–benzene complex in a certain orientation, measured at 4.2 K and 1.5 K respectively. The angular dependences around the x, y, and z axes measured at 4.2 K are shown in Figs. 2(a), (b) and (c) respectively. The crystal structure obtained by Williams shows that

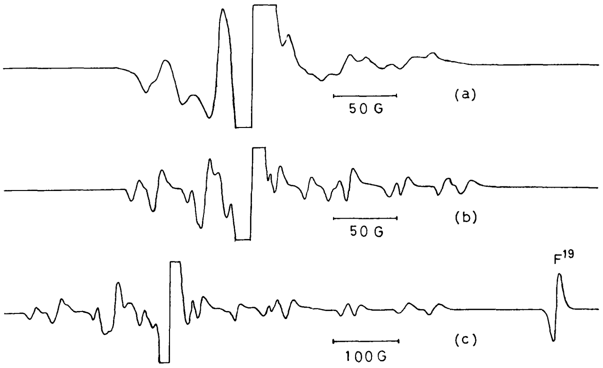

Fig. 1. Proton magnetic resonance absorption derivative curves (a) of the polycrystalline DPPH–benzene complex at 40.0 MHz, 4.2 K, (b), (c) of the single crystal of DPPH–benzene complex at 40.0 MHz, 4.2 K and 1.5 K. The static magnetic field is lying in the xy-plane and makes an angle 20° with the x-axis.

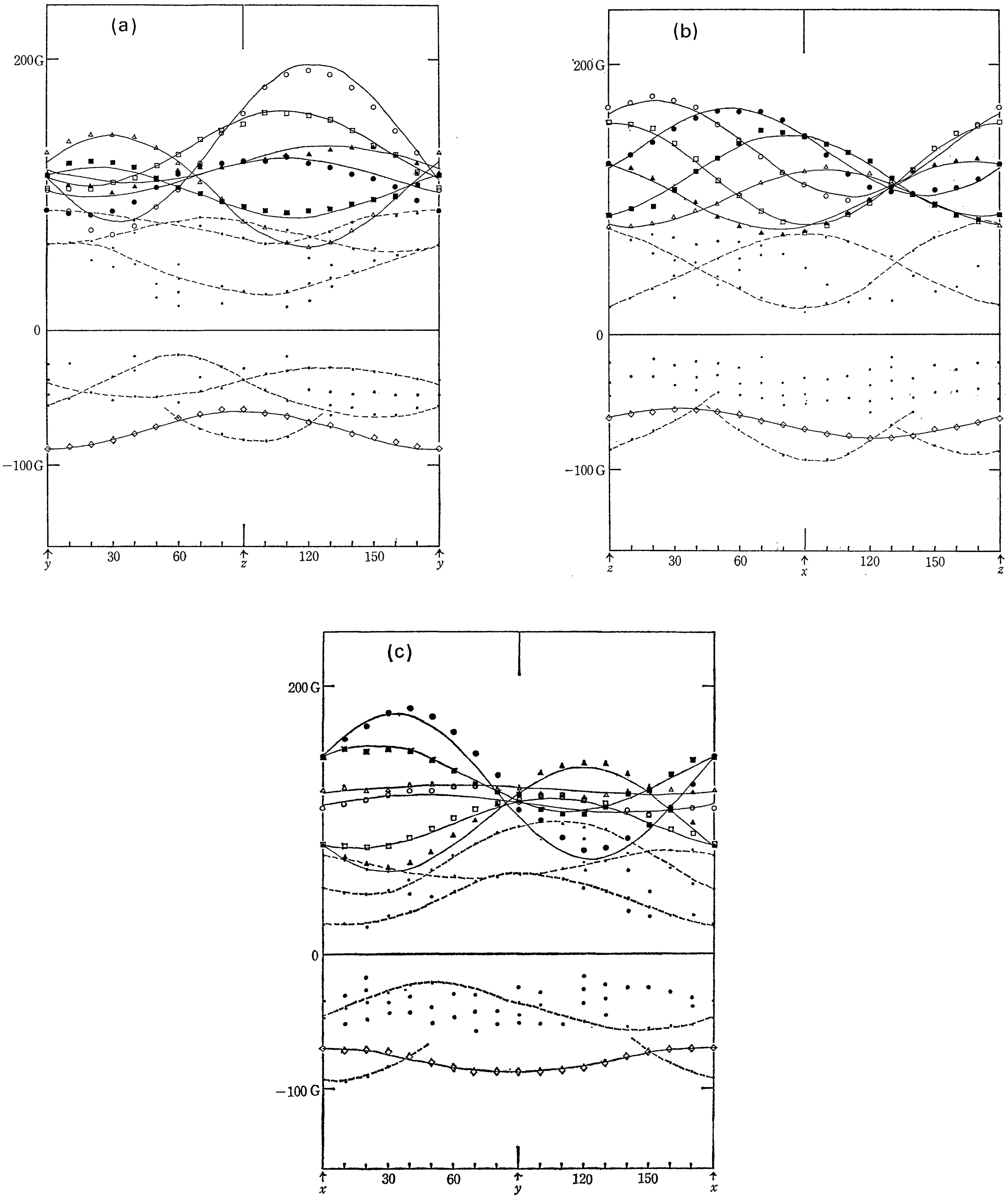

Fig. 2. Angular variation of NMR spectral line positions (a) around the x-axis, (b) around the y-axis, (c) around the z-axis.

The solid curve is the angular variation calculated by the least-square method.

—○— No. **1**, —●— No. **2**, —□— No. **3**, —■— No. **4**, —△— No. **5**, —▲— No. **6**, —◇— No. **7**

there are two DPPH molecules with unequivalent orientations in the crystal unit cell.[9] If the spectrum of the single crystal is completely resolved, 24 lines will be observed at most because of the anisotropic hyperfine interaction, except for the unshifted benzene proton lines. Around any axis we could identify six upfield-shifted lines and one downfield-shifted line, whose intensity is twice as strong as the others. In addition, two downfield-shifted lines can be partially identified around some axes.

The spin Hamiltonian for a free radical in which one proton interacts with one unpaired electron is:

$$\mathscr{H} = -g_N\beta_N\mathbf{H}\cdot\mathbf{I} + \mathbf{S}\cdot\mathbf{T}\cdot\mathbf{I}$$

in which the hyperfine term, $\mathbf{S}\cdot\mathbf{T}\cdot\mathbf{I}$, consists of an isotropic part, $a_H\mathbf{S}\cdot\mathbf{I}$, arising from the Fermi contact interaction and an anisotropic part, $\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{I}$, due to the electron-nuclear dipolar interaction. Here, $\mathbf{T}$, a_H, and $\mathbf{D}$ are the total coupling tensor, the isotropic hyperfine coupling constant, and the traceless dipolar coupling tensor respectively. The other symbols are used with their conventional significances. If the electron-spin relaxation, T_e, satisfies the condition of $|a_H T_e| \ll 1$, $\mathbf{S} = (\langle S_\alpha \rangle, 0, 0)$, which leads to the following equation: $\chi H = -g\beta\langle S_\alpha \rangle$. Here, $\langle S_\alpha \rangle$ is the α component of a vector **S** (parallel to the magnetic field, **H**) and χ is the static magnetic susceptibility per molecule, formulated by $\chi = g^2\beta^2 S(S+1)/3k(T-\theta)$, provided that it obeys the Curie-Weiss law. The other symbols have their usual significances. To first order, therefore, the nuclear resonance signal shifts from the free-proton position to the high field by this amount:

$$\Delta H = -(\chi H/g\beta g_N \beta_N)T_{\alpha\alpha}$$

where $T_{\alpha\alpha}$ is the $\alpha\alpha$ component of the total tensor, **T**.

We reported in the previous paper[11] that, at 4.2 K, the static magnetic susceptibility per molecule of the DPPH–benzene complex obeys the Curie-Weiss law, with the Weiss constant $\theta = -0.5$ K. Although the anisotropy of the ESR g-value becomes larger as the temperature is lowered, it can be neglected in comparison with the magnitude of the anisotropic hyperfine interaction.[12] Consequently, from the angular variation of $T_{\alpha\alpha}$ around three Cartesian axes, it is possible to determine **T**. The tensor components with respect to the xyz-system were determined by the least-square method. Then, the **T**-tensor was diagonalized to obtain the principal values. The isotropic hyperfine coupling constant and the principal values, A, B, and C, of the anisotropic tensor, **D**, for each identified lines are summarized in Table 1, together with the direction cosines of the tensor. The isotropic hyperfine coupling constants of the six lines resemble each other and agree approximately with those obtained from the polycrystalline NMR spectrum, as will be shown afterwards. Using the results for the α-proton tensor in $\dot{C}H(COOH)_2$,[13] we expect the anisotropic principal values to be $+1.35$, -0.03 and -1.32 for $a_H = -2.60$, and to be -0.84, $+0.02$ and $+0.82$ for $a_H = +1.62$. Those values do not agree well with the measured values listed in Table 1, especially in the case of the latter. Probably the anisotropic term does not depend only upon the spin density on the carbon atom adjacent to the proton, but also upon those on the second-nearest carbon atoms and the nitrogen atoms. Such an effect is serious in the case of the latter, for the positive spin densities on the second-nearest carbon atoms are larger than the negative ones on the carbon atom adjacent to the proton, as will be shown afterwards.[14] The direction of the principal hyperfine axes deviates considerably from that of the

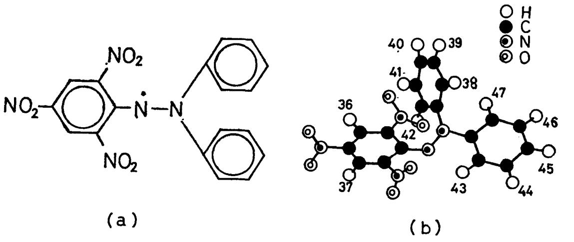

Fig. 3. (a) Molecular structure of DPPH (b) the shape of the DPPH molecule in the DPPH–benzene crystal. Williams' notation is used for the protons.

TABLE 1. ISOTROPIC HYPERFINE CONSTANTS, THE PRINCIPAL VALUES AND THE DIRECTION COSINES OF ANISOTROPIC HYPERFINE TENSORS

No.	a_H (Gauss)		Principal values (Gauss)	Direction cosines		
				x	y	z
1	-2.86 ± 0.11	A	$+1.28\pm0.11$	-0.427	0.735	0.527
		B	$+0.28\pm0.11$	0.884	0.461	0.074
		C	-1.56 ± 0.11	0.188	-0.497	0.847
2	-2.75 ± 0.14	A	$+1.40\pm0.14$	-0.554	0.743	0.375
		B	-0.04 ± 0.14	-0.073	-0.493	0.867
		C	-1.36 ± 0.14	0.829	0.453	0.327
3	-2.59 ± 0.06	A	$+0.84\pm0.06$	0.956	0.283	0.031
		B	$+0.17\pm0.06$	-0.276	0.898	0.343
		C	-1.01 ± 0.06	0.069	-0.338	0.939
4	-2.58 ± 0.06	A	$+0.74\pm0.06$	-0.005	-0.390	0.921
		B	$+0.15\pm0.06$	-0.463	0.817	0.344
		C	-0.89 ± 0.06	0.886	0.425	0.185
5	-2.42 ± 0.07	A	$+1.09\pm0.07$	0.116	-0.488	0.865
		B	-0.27 ± 0.07	0.992	0.094	-0.080
		C	-0.82 ± 0.07	-0.042	0.868	0.495
6	-2.41 ± 0.09	A	$+1.12\pm0.09$	0.838	0.495	0.230
		B	-0.39 ± 0.09	-0.401	0.272	0.876
		C	-0.73 ± 0.09	-0.370	0.825	-0.427
7	$+1.62\pm0.03$	A	-0.40 ± 0.03	0.520	0.000	0.854
		B	$+0.07\pm0.03$	0.854	-0.016	-0.520
		C	$+0.33\pm0.03$	0.014	1.000	-0.008

α-proton tensor. This cannot be explained by the experimental error. The relation between the directions of the principal hyperfine axes and the molecular structure was not discussed in this paper. Figs. 3(a) and (b) present the molecular structure of DPPH and the shape of the DPPH molecule in the DPPH–benzene crystal respectively. Williams' notation is used for the protons.

Now let us assign the proton resonance signals to the protons of the DPPH molecule. As there are two DPPH molecules with unequivalent orientations in the crystal unit cell, the six upfield-shifted lines are reduced to three for one molecule. In considering the theoretical results, we can expect the isotropic hyperfine coupling constants of two *ortho* protons to be approximately equal to that of one *para* proton.[2,15] Therefore, the three lines are attributable to two *ortho* protons and one *para* proton of the phenyl group twisted at an angle of 22°. These protons correspond to the largest upfield-shifted component in the polycrystalline spectrum. The downfield-shifted lines are assigned to *meta* protons of the picryl group, as has been determined by Anderson *et al.*[3] Another upfield-shifted component in the polycrystalline spectrum is probably due to two *ortho* protons and one *para* proton of the phenyl group twisted at an angle of 49°, and the other two downfield-shifted components (partially resolved), to the *meta* protons of two phenyl groups.

On the basis of the assignment of the polycrystalline NMR spectrum, the isotropic hyperfine coupling constants have been evaluated. The results are tabulated, together with the ESR[7] and ENDOR[8] results of DPPH in the solution state, in Table 2. The results in Table 2 indicate that the unpaired electron-spin distribution of one phenyl group is almost twice as large as that of the other phenyl group in the crystalline state. Further, in spite of the nonplanarity of the hydrazyl skeleton, the unpaired electron-spin delocalization is larger in the crystalline state than in solution, particularly on the picryl group and on one of the two phenyl groups. This fact may be related to the high stabilization of this radical in the crystalline state, in addition to the steric hindrance of the *o*-nitro groups reported by Williams.[9] In the case of a solution, a DPPH molecule may undergo dynamical changes in the hydrazyl skeleton and in the twist angle of the rings.

TABLE 2. ISOTROPIC HYPERFINE CONSTANTS OBTAINED BY THE NMR SPECTRA IN THE CRYSTALLINE STATE, THE ESR SPECTRA AND THE ENDOR SPECTRA IN SOLUTIONS

Notation of proton	a_H-NMR[a] (Gauss)	a_H-ESR[b] (Gauss)	a_H-ENDOR[c] (Gauss)
H 36, 37	+1.6	0.377	1.0
H 44, 46	+1.1	0.754	0.67, 0.75
H 39, 41	+0.6	0.754	0.67, 0.75
H 38, 40, 42	−1.5	1.885	2.0, 1.9
H 43, 45, 47	−2.6	1.885	2.0, 1.9

a) This work, b) Ref. 7, c) Ref. 8

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