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ENDOR Studies of 1,3,5-Triphenylverdazyl Radical and Its Methyl Derivatives. V.

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Synopsis. The ENDOR spectra of 1,3,5-triphenylverdazyl radical and its methyl derivatives were observed in toluene, and the effects of methyl substitution on the proton hyperfine coupling constants were investigated.

Verdazyls, a series of very stable neutral radicals containing four nitrogen nuclei, were previously studied by Kuhn, Neugebauer, and Trischmann.[1,2] Recent studies of the magnetic susceptibility of 1,3,5-triphenylverdazyl and its methoxy or methyl derivatives have clarified some interesting magnetic properties in these radicals,[3-5] as is explained by the one-dimensional Heisenberg model or the linear Ising model. The X-ray diffraction analyses[6,7] of the above verdazyls revealed the variety of molecular packing. The magnetic property is very sensitive to both the packing of the radical molecules in the crystal and the distribution of the unpaired electron on the radical. ESR is a frequently used method for determining the distribution of the unpaired electron on radical molecules. However, the ESR spectra of verdazyl radicals usually show only nine line splittings ($a^N=6G$[1]) due to the four nitrogen atoms in verdazyls.

Electron nuclear double resonance (ENDOR) spectroscopy is a valuable method for the determination of proton isotropic hyperfine couplings of organic radicals in solution, since the effective resolution is much higher than for ESR.[8] However, due to the quadrupole moment of the nitrogen atom, the observation of ENDOR spectra of the radicals which include nitrogen atoms is generally difficult compared to those of other radicals. Particularly, in the case of verdazyl radicals, four nitrogens are contained in the heterocyclic ring. Thus, we carefully selected adequate temperature, solvent, radical concentration, ESR and NMR powers, and ESR and NMR modulations.[9]

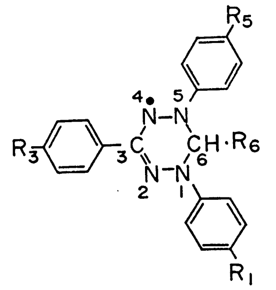

Fig. 1. The verdazyl radicals (I—V).

Radical	R_1,R_5	R_3	R_6
I	H	H	H
II	H	CH_3	H
III	CH_3	H	H
IV	CH_3	CH_3	H
V	H	H	CH_3

In the present paper, proton hyperfine splitting constants measured from the solution ENDOR spectra of the 1,3,5-triphenylverdazyl radical and its methyl derivatives in toluene are reported, in order to present fundamental data which are essential for a more detailed understanding of the magnetic properties of these radicals.

Experimental

Verdazyls (I—V) (see Fig. 1) were prepared by the method of Kuhn and Trischmann,[1] followed by recrystallization from an acetone–ethanol mixture. They were identified by their elementary analyses and melting points, and the values obtained were in good agreement with those presented in the literature.[1] The radical concentrations were determined by their magnetic susceptibilities in the temperature range from 77 to 300 K. The respective spin concentrations were 100% as $S=1/2$, within the limit of the experimental error. The paramagnetic susceptibility measurements were carried out with a Shimadzu type MB-2 magnetic torsion balance, equipped with a low temperature cryostat. The ENDOR spectra were recorded by a JEOL type ES-EDX-1 spectrometer, operated with 80 Hz magnetic field modulation. About 150 watts of the continuous radio wave frequency modulated at 6.5 kHz were running inside of the cavity for NMR excitation.[10]

Results and Discussion

The ESR spectra of 1,3,5-triphenylverdazyl (I) and its methyl derivatives (II), (III), (IV), and (V) show only nine line splittings due to four nitrogens in the heterocyclic ring. We were unable to resolve splittings from the protons. The nitrogen hyperfine splittings, a^N, observed in 2-methyltetrahydrofuran (2-MeTHF)

Table 1. Hyperfine splitting constants of verdazyl radicals (in Gauss)

Radical	a^{N} a)	a^{H}_{p}	a^{H}_{o}	a^{H}_{m}, $a^{H}_{3\text{-}o}$	$a^{CH_3}_{3\text{-}p}$	$a^{CH_3}_{6}$
I	5.79	1.22_2	1.11_2	0.42_5	—	—
II	5.67	1.21_8	1.11_3	0.42_4	0.30_0	—
III	5.75	1.29_3	1.12_4	0.41_9	—	—
IV	5.62	1.29_0	1.12_4	0.41_3	0.30_2	—
V	5.60	1.26_5	1.15_4	0.42_2	—	0.97_6

a) The values in 2-MeTHF observed by ESR.

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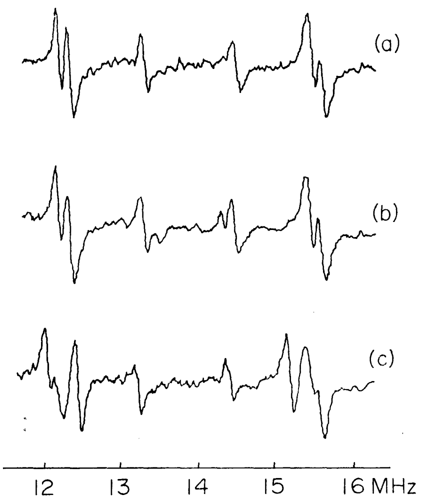

Fig. 2. ENDOR spectra of (a) verdazyl (I) at −78 °C, (b) verdazyl (II) at −74 °C, and (c) verdazyl (V) at −70 °C in toluene.

at room temperature are listed in the first column of Table 1.

Figure 2 shows three typical ENDOR spectra of the verdazyls in toluene at temperature $-70\sim-80$ °C. Toluene, chloroform, 2-MeTHF and *n*-heptane were used as solvents, and it was found that toluene is the most suitable solvent for the verdazyls.

The ENDOR spectrum of 1,3,5-triphenylverdazyl radical (I) (see Fig. 2(a)) clearly exhibits three different proton hyperfine splittings (1.22_2, 1.11_2, and 0.42_5 G). The orbitals containing the unpaired electron of the 1,3,5-triphenylverdazyl have, at least in the Hückel approximation, a node in 3-phenyl ring, giving a zero spin density on the phenyl ring. In the McLachlan approximation, the orbitals are spin polarized so as to yield nonvanishing spin densities in the 3-phenyl ring of the radical.[11] However, these spin densities are not large enough to account for the above proton hyperfine splittings. In fact, aryl-substituted verdazyls with selectively introduced D-, Cl-, Br-, F- and ethoxycarbonyl groups give well resolved ESR spectra[12] at room temperature, and the observed proton hyperfine splittings are explained as splittings ($a_o^H=a_p^H=1.06$—1.09 G, $a_m^H=0.41$—0.49 G) in equivalent 1,5-phenyl rings. On the other hand, recent NMR study[13] of 1,3,5-triphenylverdazyl in $CDCl_3$ shows paramagnetic shift lines due to all protons contained in the verdazyl radical. The hyperfine splittings are assigned for 1,5-phenyl ring protons ($a_6^H=1.195$, $a_o^H=1.12$ and $a_m^H=0.425$ G), for 3-phenyl ring protons ($a_p^H=0.31$, $a_o^H=0.425$, and $a_m^H=0.16$ G), and for C-6-methylene protons in the verdazyl ring ($a_6^H=0.027$ G[14]). A comparison of the hyperfine splittings obtained in the present ENDOR study with those of ESR and NMR studies indicates that the hyperfine splittings (1.22_2 and 1.11_2 G) arise from the *para* and *ortho* protons respectively in the 1,5-phenyl rings, and 0.42_5 G from both *meta* protons in the 1,5-phenyl rings and *ortho* protons in the 3-phenyl ring. The verdazyl (III) also shows three pairs of similar hyperfine splittings.

As shown in Fig. 2(b), in addition to the above three splittings of verdazyl (I), a pair of signals with weak intensity and smaller splitting (0.30_0 G) is clearly observed for verdazyl (II), in which the *para* proton in the 3-phenyl ring is substituted by methyl group. This signal is attributed to the methyl protons. Verdazyl (IV) also shows four pairs of similar hyperfine splittings. These values are listed in Table 1. Hyperfine splittings of *ortho* and *para* ring protons remain constant within experimental error, indicating that methyl substitution does not affect the distribution of the unpaired electron. The small increase in hyperfine splitting of the *para* proton observed for verdazyls (III) and (IV) is explained as a larger Q-value for the methyl proton than for the ring α-proton.

In addition to the hyperfine splittings of 1.26_5, 1.15_4, and 0.42_2 G due to 1,3,5-phenyl ring protons, an abnormally large hyperfine splitting (0.97_6 G) was observed for verdazyl (V), in which one of C-6-methylene protons is substituted by a methyl group. C-6-Methylene protons have small hyperfine splittings of about 0.03 G,[13,14] and thus this large hyperfine splitting should be attributed to the substituted methyl γ-protons. We usually cannot expect such a large splitting for a γ-proton. However, the Stuart model shows that the methyl protons locate just above the 1- and 5-nitrogen atoms having large spin densities and should couple more strongly, because of hindered rotation of C-6-methylene group. In fact, X-ray studies have revealed such a configuration, with the shortest distance of 2.72 Å between the 1-nitrogen and the methyl protons.[15] A small change in hyperfine splittings of *ortho* and *para* proton was also observed for verdazyl (V). This arises from the variation of the distortion angle of the 1,5-phenyl rings connected to the centeral verdazyl ring by substituted methyl group.

In conclusion, as was expected, the effect of the methyl substitution on the spin distribution is fairly small. Therefore, these radicals are useful for the study of how molecular packing affects the magnetic properties of the organic radical crystalline.

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