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## ESR Study of Spin-Spin Interactions in Verdazyl Biradicals. II

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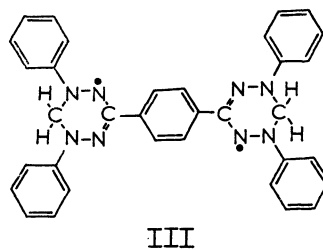
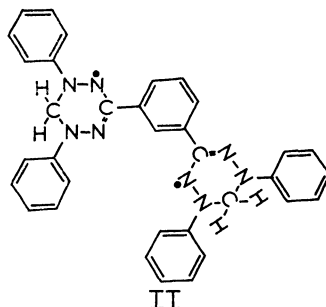
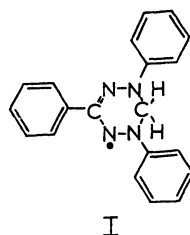
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The verdazyls, a series of very stable free radicals containing four nitrogen nuclei, were recently studied by Kuhn, Neugebauer and Trischmann<sup>1,2)</sup>. Preliminary susceptibility measurements showed the presence of one unpaired electron per molecule. The combination of two 3-verdazyl residues by a 1,3- or 1,4-phenylene bridge gives fully-conjugated, nearly planar, green biradicals with properties which correspond to those of the simple verdazyls. The results of the paramagnetic susceptibility measurements revealed that the two unpaired electrons in the  $\pi$ -electron system of each biradical are practically free from coupling down to 77°K, in contrast to the case with the other stable biradicals.<sup>3-5)</sup>

However, all of the bi- and tri-radicals of this series shows less well resolved ESR spectra than those of the monoradicals. Fischer<sup>6)</sup> proposed that, judging from the results of HMO theory, each biradical has a node in the odd electron orbitals at the aryl system connecting the radical parts and should, consequently, exhibit little intramolecular spin exchange, and that, further, through step-by-step polarographic oxidation, the broadening of lines in the ESR spectra can be attributed mainly to dipole-dipole interaction, and not to

electron exchange and or slow molecular tumbling motion as a consequence of the large molecular size.

The purpose of this note is to present new ESR spectra which not only yield the quantitative values of dipole-dipole interaction in these verdazyl biradicals, but also show existence of a triplet state in these radicals due to electron-exchange in-



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1) R. Kuhn and H. Trischmann, *Angew. Chem.*, **75**, 294 (1963); *Mh. Chem.*, **94**, 457 (1964).

2) R. Kuhn, F. A. Neugebauer and H. Trischmann, *Angew. Chem.*, **76**, 691 (1964); *Mh. Chem.*, **97**, 525 (1966).

3) R. Kuhn and H. Katz, *Angew. Chem.*, **46**, 478 (1933); E. Muller and I. Müller-Rodloff, *Ann.*, **521**, 81 (1936).

4) R. Kuhn and W. Blau, *Ann.*, **615**, 99 (1958).

5) K. Mukai, K. Ishizu and Y. Deguchi, *J. Phys. Soc. Jap.*, **27**, 783 (1969).

6) P. H. H. Fischer, *Tetrahedron*, **23**, 1939 (1967).

teraction. This has been accomplished through the observation of the dipolar splitting of two verdazyl biradicals in 2-MeTHF at 77°K.

### Experimental

1,3,5-triphenyl-verdazyl (I), mp 142.0—142.1°C (lit, 140—141°C), 1,3-bis-(1,5-diphenyl-verdazyl-3-yl) benzene (II), mp 182.2—183.3°C (lit, 184—185°C), and 1,4-bis-(1,5-diphenyl-verdazyl-3-yl) benzene (III), mp 197.5—198.0°C (lit, 195—196°C) were prepared from the corresponding formazans according to the method of Kuhn, Neugebauer and Trischmann.<sup>1,2)</sup> After the formation of the s-tetrazyl ring with formaldehyde for I and II and with paraformaldehyde for III, the reaction mixture was neutralized with sodium hydroxide. A dark green crystalline compound was isolated from the DMF-solution, it was recrystallized three times from acetone-methanol for the I radical and from dioxane-methanol for the II radical, but in the case of the III radical it was washed two times with hot acetone.

All the ESR measurements were carried out using a JES-3BX spectrometer equipped with 100 kc/sec field modulation.

### Results and Discussion

We followed the ESR spectrum of a 2-MeTHF solution of the verdazyl biradical (II) in a sealed, degassed system. A nine-line, considerably-overlapped ( $a_N=6.0$  gauss) spectrum, as noted by Kuhn *et al.*<sup>2)</sup> in a benzene solution, was observed. When this solution was frozen to a rigid glass at 77°K, the broad ESR spectrum clearly showed that it was a triplet species, as is shown in Fig. 1(a).

On the other hand, the spectrum of the verdazyl biradical III in 2-MeTHF at room temperature presents 17 overlapped lines ( $a_N=2.8$  gauss), unlike the one observed by Kuhn *et al.* Fig. 2 shows such a spectrum. The existence of the triplet state in the III biradical was also confirmed by ESR measurement in a rigid solution at 77°K, as is shown in Fig. 1(b).

These spectra at 77°K can be interpreted on the basis of a randomly-oriented set of triplets with axial symmetry<sup>\*2</sup>; thus the values of the dipolar splitting,  $D$ , are 52.7 gauss for the II biradical and 43.1 gauss for the III biradical, as one half of the outer two lines splitting. The observed increase in the splitting constants,  $D(\text{II}) > D(\text{III})$ , is consistent with the structure. Using a model of two-point dipoles, that is the relation  $D=(3/2)$

<sup>\*2</sup> We have tentatively calculated the zero-field splittings,  $D$  and  $E$ , for the biradical III, assuming the distribution of the 1/4 unpaired electron on each nitrogen atom, and, further, using a model of a one-point dipole.<sup>7)</sup> These values are  $D=47.1$  gauss and  $E=1.0$  gauss respectively. Therefore, in this note, we shall assume  $E=0$  in interpreting the spectra.

7) D. A. Wiersma and J. Kommandeur, *Mol. Phys.*, **13**, 241 (1967).

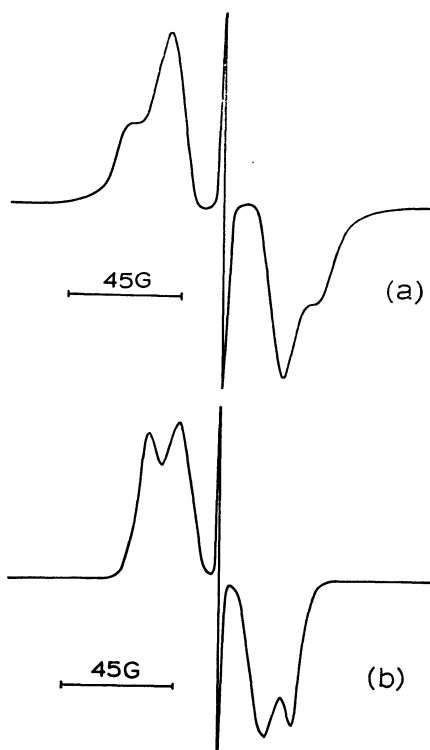


Fig. 1. ESR spectra of the two verdazyl biradicals in 2-MeTHF at 77°K.  
(a) Biradical(II) (b) Biradical(III)

$g\mu_B r^{-3}$ , the average interelectronic distances in the II and III biradicals are calculated as 8.1 Å and 8.7 Å respectively. The relative intensity of central singlet varied with the samples, that is, with the radical concentration of the samples. Since the monoradical I in 2-MeTHF solution at 77°K gives a singlet ESR spectrum of a line width of about 10 gauss, the central singlet spectra of the biradicals of  $\Delta H_{\text{msl}}=5-10$  gauss in Fig. 1(a) and (b) may be due to unknown species of monoradicals produced as by-products of the synthesis.

The ESR spectrum of a 2-MeTHF solution of the (I) monoradical at room temperature consists of a nine-line, well-resolved ( $a_N=5.8$  gauss) spec-

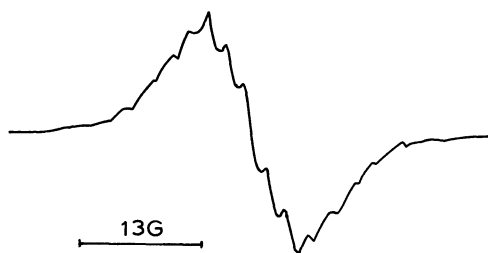


Fig. 2. ESR spectra of the verdazyl biradical (III) in 2-MeTHF at room temperature.

trum. On the other hand, the ESR measurements of two verdazyl biradicals in a rigid solution at 77°K indicate that a triplet state exists in these radicals. If there is strong scalar exchange interaction,  $J$ , between the two electrons such that  $J \gg a_N$ , the spectrum will consist of 17 lines separated by  $a_N/2$ , corresponding to an interaction with 8 nearly-equivalent nitrogen nuclei<sup>8)</sup>. In fact, the ESR spectrum of the III verdazyl biradical in 2-MeTHF shows 17 lines of  $a_N = 2.8$  gauss. However, in the ESR spectrum of the II biradical, a hyperfine interaction with only four nearly equivalent nitrogen nuclei seems indicated, although the distance between the two verdazyl rings is smaller in the II biradical than in the III biradical and thus a larger exchange interaction in the former may be expected. This is probably because of the poorer resolution due to a larger dipolar broadening in the II biradical than in the III biradical.

Spin concentrations for the three species of verdazyl radicals were obtained from the results of the paramagnetic susceptibility measurements<sup>9)</sup>

at room temperature, after correcting for the diamagnetic contribution calculated by the Pascal method. The values were 97% for the I radical, 110% for II, and 104% for III, assuming the Curie law. The magnetic susceptibilities of usual organic radical solids, including several verdazyl radicals,<sup>10)</sup> follow the Curie-Weiss law, and the values of the Curie-Weiss constant,  $\theta$ , are negative, showing a inter-molecular negative exchange interaction. These facts show the possibility of intra-molecular positive spin coupling for such molecules as the II and III biradicals which have no  $C_3$  or greater symmetry. We are now planning to measure the magnetic susceptibility over the temperature range of 1.8°K—300°K in order to clarify the above experimental results.

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8) C. P. Slichter, *Phys. Rev.*, **99**, 479 (1955).

9) M. Mekata, *J. Phys. Soc. Jap.*, **17**, 796 (1962).

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