BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 2263—2264 (1971)

Dipolar Interaction in TEMPAD Biradical

Jun Yamauchi, Teruaki Fujito,* Akira Nakajima,* Hiroaki O. Nishiguchi*, and Yasuo Deguchi*
The Institute for Chemical Research, Kyoto University, Uji
* *Department of Chemistry, Faculty of Science, Kyoto University, Kyoto*

(Received February 6, 1971)

There have been a number of investigations regarding the magnetic properties of organic solids, especially those of stable free radicals. In addition to the measurement of the paramagnetic susceptibility, the electron spin resonance (ESR) has been used in the study of triplet states of aromatic molecules after the first successful experiments by Hutchison and Mangum[1] and by van der Waals and de Groot.[2] A molecule in a triplet state has degenerate Zeeman levels which are lifted even in the absence of an external magnetic field as a result of dipolar interaction between the unpaired electrons. This dipolar splitting can be obtained in rigid glassy solvents or in diamagnetic host crystals.

When one molecule with a single unpaired electron interacts with another, the problem can be reduced to a question of linear antiferromagnets. Soos adopted the pseudospin method to deal with a linear array of tightly bound electrons which are coupled to their neighbors.[3] In this case, the Hamiltonian can be described as follows:

$$H = \sum \{J(1+d)\boldsymbol{S}_{2i-1}\boldsymbol{S}_{2i} + J(1-d)\boldsymbol{S}_{2i}\boldsymbol{S}_{2i+1}\}, \qquad (1)$$

Where d is an alternation parameter, and J, an exchange integral. Because of the interpair exchange interaction, $J(1-d)$, the triplet states may propagate along the linear chains. These mobile triplet states are called "triplet excitons". The magnetic susceptibilities of $(\phi_3AsCH_3)^+(TCNQ)^-_2$ and $(\phi_3PCH_3)^+(TCNQ)^-_2$ can be well explained if one assumes $d \sim 1$ in Eq. (1).[4] Chesnut and Phillips first observed the ESR spectra of these molecules characterized by fine structure splittings.[5] The dipolar interaction was found by reducing the exchange interaction between triplet excitons at lower temperatures.

The TEMPAD biradical, shown in Fig. 1, has two unpaired electrons in a molecule and may be considered to have a dominant intramolecular spin interaction which forms the triplet state. The weak exchange interaction between the triplet entities may cause the triplet excitons to propagate in the crystal. These facts are confirmed, to some extent, by the magnetic susceptibility measurements.[6] The susceptibility of the TEMPAD biradical is not completely explained by the singlet-triplet model; a slight deviation from the model was observed. It was found that the triplet states in the radical are not actually localized in lattice sites, but are a little mobile because of the weak intertriplet interaction, which presumes the existence of the $J(1-d)$ interaction. However, it has not yet been clarified whether the exchange interaction which causes triplet states is the intra- or inter-molecular interaction. On the other hand, the fine structure arising from the dipole-dipole interraction between electron spins may be observed when the triplet entities are reduced by lowering the temperature. Therefore, we observed the ESR spectra of the TEMPAD biradical at a very low temperature in order to confirm the existence of triplet states and find a zero-field splitting.

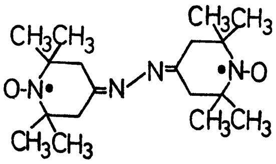

Fig. 1. Structural formula of TEMPAD biradical, bis-(2,2,6,6-tetramethylpiperidine-4-azine)-1,1′-dioxyl.

The sample was prepared from 2,2,6,6-tetramethyl-4-piperidone, following the same process as that of Rassat *et al.*[7] After recrystallization from ether, a pure sample, mp 182°C, was obtained.

The ESR absorption spectra were observed by the use of a JES-S10E type X-band spectrometer with an 80-Hz field modulation. The details of the experiments at very low temperatures will be described

---

[1] C. A. Hutchison and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958).

[2] J. H. van der Waals and M. S. de Groot, *Mol. Phys.*, **2**, 333 (1959).

[3] Z. G. Soos, *J. Chem. Phys.*, **43**, 1121 (1965); W. Duffy, Jr. and K. P. Barr, *Phys. Rev.*, **165**, 647 (1968).

[4] Z. G. Soos and R. C. Hughes, *J. Chem. Phys.*, **46**, 253 (1967).

[5] D. B. Chesnut and W. D. Phillips, *ibid.*, **35**, 1002 (1961).

[6] A. Nakajima, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc. Jap.*, **24**, 1175 (1968).

[7] R. Briere, R. M. Dupeyre, H. Lemaire, C. Morat, A. Rassat, and P. Rey, *Bull. Soc. Chim. Fr.*, **1965**, 3290.

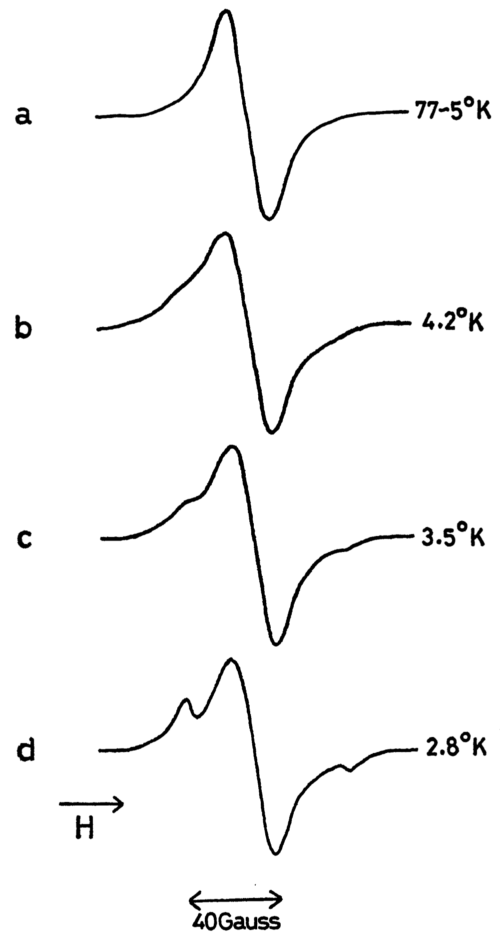

Fig. 2. Temperature dependence of the ESR absorption of a powder of TEMPAD biradical.

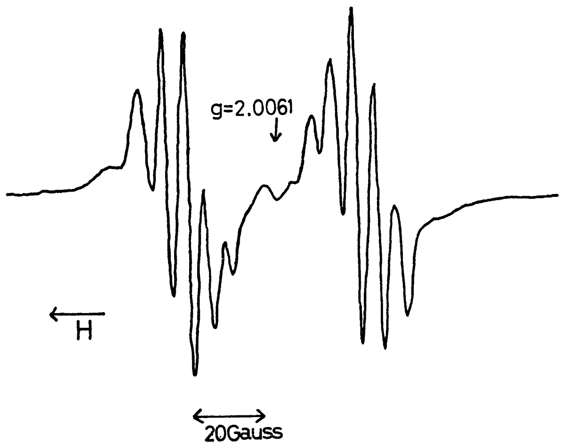

Fig. 3. ESR spectrum of a crystal of TEMPAD biradical diluted in the corresponding diamine for an arbitrary orientation.

elsewhere.[8] The ESR measurements were carried out in powder samples. Fig. 2-a shows an exchange-narrowed Lorentz-type absorption in the higher-temperature region. When the temperature is lowered, the side peaks (Figs. 2-b, c, and d) appear. The newly-appeared doublet can be ascribed to the dipole-dipole interaction between the unpaired electrons. The spacing of the doublet resonances is evaluated as 76.6 gauss. If one assumes a localized spin density, the distance between the unpaired electrons can be calculated from the relation:

$$g\beta\langle 1/r^3\rangle = 38.3,$$

where g is a g-factor, β, a Bohr's magneton, and $<1/r^3>$, an average distance between the unpaired electrons. $r\sim 8$ Å is quite well in accord with the distance between the unpaired electrons in a molecule, that is, $r\sim 9$ Å. On the other hand, the doublet splitting is also found at room temperature in the TEMPAD biradical diluted in the corresponding diamine. Although the spectrum, shown in Fig. 3, has not yet been completely analyzed, the dipole-dipole interaction is 40 gauss in order of magnitude; this corresponds to the intramolecular dipole-dipole interaction between the unpaired electrons. Hence, the doublet in Fig. 2 may be ascribed to the intramolecular dipole-dipole interaction.

The triplet-state population at the temperature where the doublet resonance starts to appear can be calculated to be 5% from this relation:

$$\rho = 1/[1+(1/3)\exp(\Delta/kT)],$$

where ρ is the density of the triplets, and $\Delta(\Delta/k = 26.4°\mathrm{K}^{6)})$, the separation between lower singlet and upper triplet states. This phenomenon is similar to the cases of $(\phi_3\mathrm{AsCH_3})^+(\mathrm{TCNQ})_2^-$ and $(\phi_3\mathrm{PCH_3})^+(\mathrm{TCNQ})_2^-$, which also exhibit dipole-dipole interaction at a triplet density of $\rho\sim 0.04$. Therefore, we may conclude that the dipole-dipole interaction can be observed by decreasing the exchange interactions between triplet entities in the solid state and that it can be ascribed to the intramolecular interaction between the unpaired electrons in a molecule.

---

[8] J. Yamauchi, This Bulletin, to be published.