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The Proof of a Triplet Ground State in the *N*,*N*′-Di-*t*-butyl-*m*-phenylenebinitroxide Biradical

Kazuo Mukai, Hiroshi Nagai, and Kazuhiko Ishizu*
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790

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Synopsis. The magnetic susceptibility of the *N*,*N*′-di-*t*-butyl-*m*-phenylenebinitroxide biradical has been measured in the temperature range from 60 to 300 K. The susceptibility follows the Curie-Weiss law, with a paramagnetic Curie constant of 0.90±0.04 K·emu/mol and a Weiss constant of −19±2 K. This susceptibility suggests that the ground state of the biradical is a triplet and that an intramolecular pure triplet approximation, $2J \gg kT$, is reliable in the temperature region below 300 K. The negative Weiss constant is due to the negative exchange interaction, $J' < 0$, between the triplets.

Recently, Calder *et al.*[1] have succeeded in the synthesis of *N*,*N*′-di-*t*-butyl-*m*-phenylenebinitroxide, which is a fairly stable nitroxide biradical, as is shown in Fig. 1. The biradical has π-conjugated monoradical halves linked by a central phenylene π bridge, so the magnitude of the intramolecular spin-spin interaction in the biradical can be expected to be greater than those in σ-bridged nitroxide biradicals.[2,3] Actually, they observed a large ESR zero-field splitting in rigid media, indicating the existence of the triplet state in the biradical. They also proposed that the triplet is the ground state, from a study of the temperature dependence of the ESR signal intensity measured in the solid-state matrix. It is not very clear, however, from the above-mentioned results whether or not the observed triplet state is the ground state; there remains the possibility that they observed an excited triplet state which is thermally populated at that temperature; this would be true if the exchange interaction with a negative value, J, were smaller than the thermal excitation.

In order to clarify the level scheme of the spin system of the biradical, the magnetic susceptibility of the solid nitroxide biradial has been measured in the temperature range between 60 and 300 K.

In recent years, several stable π-conjugated bi- or tri-radicals, in which monoradical parts are linked with each other at the *meta*-position of a central phenyl group, have been prepared.[4–9] The existence of a triplet or quartet state in these radicals is also confirmed by ESR measurements in rigid media at 77 K.[6–11] However, the properties of the ground state in these radicals have not been fully established, except in the cases of a few radicals.[4,12] Studies of the temperature dependence of the static magnetic susceptibility are essential if we are to investigate the level scheme of the spin systems of these polyradicals.

Experimental

The biradical was prepared by the method of Calder *et al.*[1] An orange crystalline compound (mp 67—69 °C) (lit, 68—70 °C) was obtained by the oxidation with silver oxide of the corresponding dihydroxylamine in purified chloroform and by subsequent rapid recrystallization from *n*-hexane in a dry-ice–acetone bath.

The susceptibility measurements were carried out with a Shimadzu-type MB-2 magnetic torsion balance, equipped with a low-temperature cryostat. The temperatures were measured using an AuCo-Cu thermocouple. Manganese Tutton salt was used for the calibration of the thermometers and the field gradient.

Results and Discussion

The inverse molar susceptibilities obtained for the nitroxide biradical are shown in Fig. 1 as a function of the temperature. The data have been corrected for the diamagnetic contribution of $\chi_{\rm dia} = -0.17\times10^{-3}$ emu/mol calculated by Pascal's method. The susceptibility follows the Curie-Weiss law, with a Curie constant of 0.90±0.04 K·emu/mol and a Weiss constant of −19±2 K.

Calder *et al.*[1] have observed ESR spectra due to

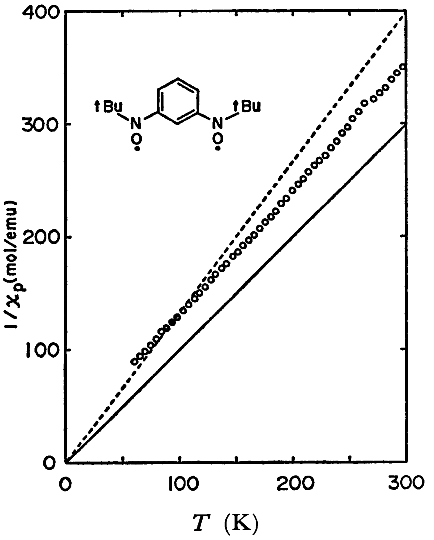

Fig. 1. Inverse molar susceptibility of *N*,*N*′-di-*t*-butyl-*m*-phenylenebinitroxide biradical *vs.* temperature. Solid and broken lines represent the Curie laws with Curie constants of 1.00 and 0.75 K·emu/mol, respectively.

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* To whom correspondence should be addressed.

transitions between the triplet states of the biradical in glassy media, as has been mentioned above. Therefore, the present susceptibility should be interpreted, in a first approach, by the singlet-triplet equilibrium (ST) model, in which the molar susceptibility is given by the following expression:

$$\chi_m = 2N_0g^2\beta^2/\{kT[3+\exp(-2J/kT)]\},$$

where the symbols have their usual meanings. At the high temperature limit, $|2J| \ll kT$, the susceptibility follows the Curie law and the Curie constant is 0.75 K·emu/mol from the above equation, regardless of the sign of the J parameter. This susceptibility corresponds to that of the noninteracting spin 1/2 particles. On the other hand, at the low-temperature limit, $|2J| \gg kT$, the Curie constant is 1.00 K·emu/mol for the positive J parameter. The positive exchange interaction requires the presence of the triplet ground state. This intramolecular triplet can behave as a pure triplet at low temperatures, because the exchange-interaction energy is much greater than the thermal excitation energy. If the J parameter is negative, the susceptibility falls off rapidly to zero after passing through its maximum at $T_{max} = -1.25\ J/k$. Accordingly, the Curie law does not hold in this temperature region.

Our experimental results show that the susceptibility of the biradical follows the Curie-Weiss law, with a Curie constant of 0.90 K·emu/mol in the temperature region below 300 K. This value is larger than the Curie constant of 0.75 K·emu/mol for noninteracting spin 1/2 particles, and is rather close to that of 1.0 K·emu/mol for pure triplet ($S=1$) ones. The discrepancy between the observed and calculated Curie constants for the pure triplet is probably due to the following two reasons: (i) the nitroxide biradical is not very stable and gradually changes to its diamagnetic aminoquinone imine *N*-oxide form by means of spontaneous topochemical change,[1] and (ii) the existence of a small amount of a monoradical impurity has been observed at the ESR spectra in a rigid solution at 77 K as a central singlet between the absorptions due to zero-field splitting.[1] These facts may explain the decrease in the Curie constant. The observed negative Weiss constant ($\theta = -19$ K) is due to the negative exchange interaction, $J' < 0$, between the triplets. All these results are very similar to those for *m*-phenylene-bis-verdazyl, whose magnetic susceptibility has also been explained as a contribution from its pure triplet ground state.[12]

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