The Ground Spin States of Tris[p-(N-oxyl-N-tert-butylamino)phenyl] amine, -Methyl, and -Borane. Prospects of Further Studies

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IN DEDICATION TO THE LATE PROFESSOR OLIVIER KAHN FOR HIS PIONEERING CONTRIBUTIONS TO THE FIELD OF MOLECULAR MAGNETISM

An exploratory study has been carried out on new poly(aminoxyl) radicals as potential bridging ligands for $2p/3d$-hybrid-spin metal complexes having network structures. Temperature dependence of the magnetic susceptibility data on the title amine **N** in the range 2–300 K was analyzed to show that its ground state was a doublet with a quartet state lying 559 K (= 1.11 kcal mol^{-1}) above the doublet. B3LYP/6-31G*//B3LYP/6-31G computations on a simplified model molecule (**N′**) confirmed the doublet ground state by 0.84 kcal mol^{-1}. The methyl compound (**C**) is a triplet diradical with a singlet state lying 410 K above the triplet. The hexamethyl derivative (**B′**) of the title borane **B** has a doublet ground state with an energy gap to a quartet state by 9.9 K. The electronic structures are described qualitatively by p-(N-oxyl-tert-butylamino)phenyl homologues of $(\cdot H_2C)_3X$ in which $X = N$, $C\cdot$, and B atoms, and carries two, one, and no π-electrons, respectively. **N** and **B′** showed two reversible redox waves. Mn^{II}(hfac)$_2$ and **C** gave a black–violet crystalline complex in which the $3d$ and $2p$ spins ordered at 60 K. © 2001 Academic Press

INTRODUCTION

Cross-conjugated bis- and tris(aminoxyl) radicals have not only the aligned spins of their own merit but also basic oxygen atoms for forming conjugate bonds with magnetic metals ions, thus providing ample opportunities for building block approaches to network-structured magnetic materials (1–3). Bis(hexafluoroacetylacetonato)manganese(II), Mn(hfac)$_2$, and tris(aminoxyl) radicals **1** and **2** (see Scheme 1) having quartet ground states, for example, form by self-assembly of two- and three-dimensional network structures in which spins order at 3.4 and 46 K, respectively (3). As a part of our continued efforts to explore new oligoradicals as building blocks, we report in this paper on a series of three stable radicals that carry three *tert*-butylaminoxyl radicals attached to the *p*-positions of triphenylamine, triphenylmethyl, and triphenylborane (**N**, **C**, and **B**, respectively). When **C** is viewed as a *p*-penyleneaminoxyl analogue of trimethylenemethane $(\cdot H_2C)_2C{=}CH_2$ (TMM) (4), **N** and **B** have one more and one less, respectively, π-electron at the central atom than **C** (Chart 1). It is of great interest to see whether such a simple picture is applicable to the understanding of ground spin states of **N**, **C**, and **B** that will be best manifested by temperature dependence of their paramagnetic susceptibility data.

RESULTS, ANALYSIS AND DISCUSSION

1. Synthesis

N, **C**, and **B′** were prepared as described previously (5). Since the reactions of the organolithium compound obtained by lithiation of *N*-(p-bromophenyl)-*N-tert*-butyl-*O-tert*-butyldimethyl-silylhydroxyamine with boron trifluoride etherate gave complex mixtures in which the expected triarylborane derivative was not found, a recourse was had to prepare its 2,2′,2″,6,6′,6″-hexamethyl derivative **B′**.

2. Crystal and Molecular Structures

X-ray crystallographic data and experimental parameters for radicals **N**, **C**, and **B′** have been reported previously (5).[2] The essence of the crystal and molecular structures is as follows.

[2] The crystallographic data (excluding structure factors) for the structure of **N** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC-101263. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + (44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk). X-ray crystal structural data on **C** and **B′** are available free of charge via the Internet at http://pubs.acs.org.

[1] To whom correspondence should be addressed: University of the Air, 2-11 Wakaba, Mihama-ku, Chiba 261-8586, Japan. Fax: 81-43-298-4379.

SCHEME 1.

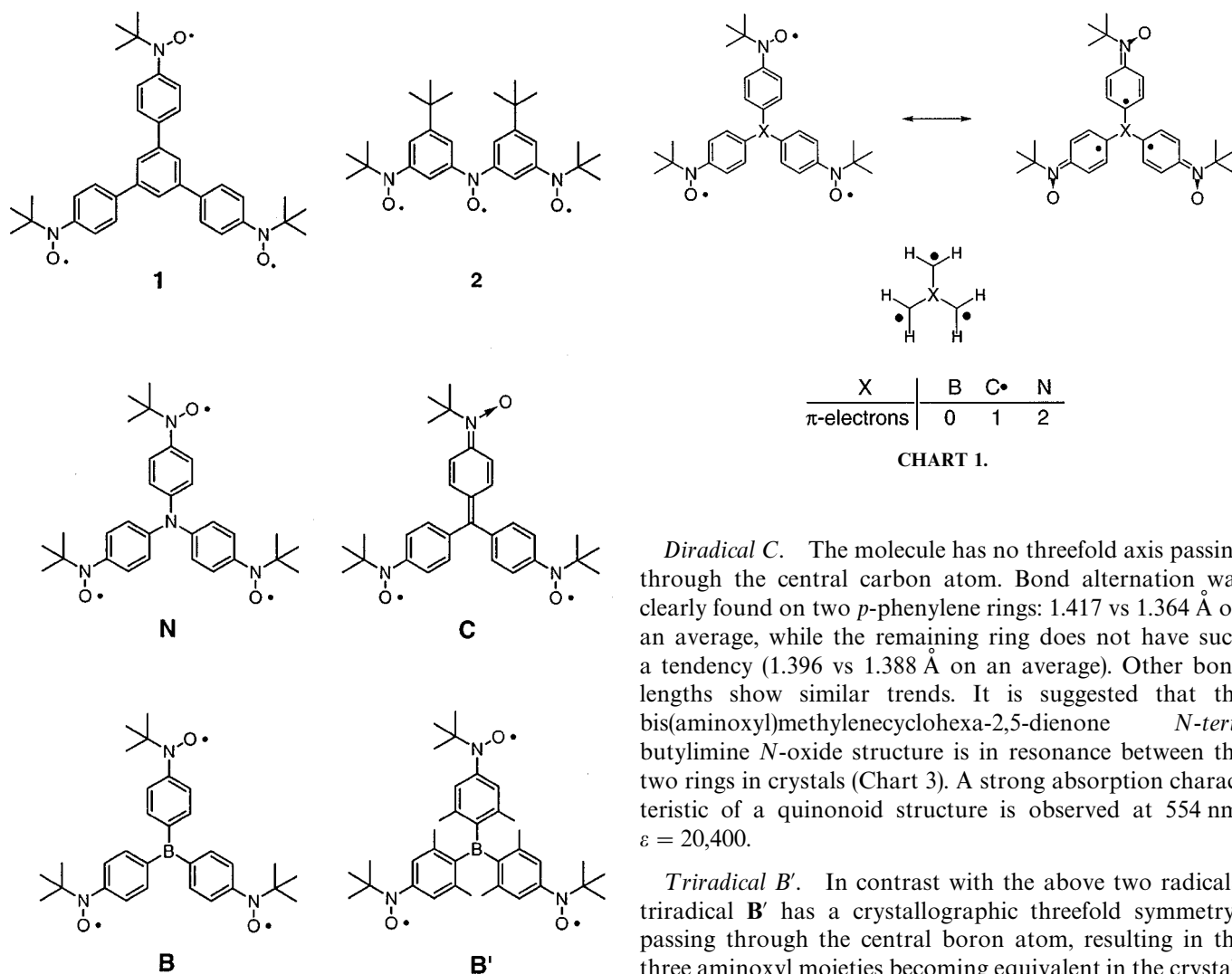| X	B	C•	N
π-electrons	0	1	2

CHART 1.

Triradical N. The molecule has no threefold axis passing through the central nitrogen atom, which is located only 0.04 Å out of the plane defined by the three carbon atoms attached to the nitrogen. One *p*-phenylene rings is tilted more (57.3°) than the other two. Any bond alternation is less than 0.02 Å in the *p*-phenylene rings of **N**. The bonds connecting the aminoxyl nitrogen atom with the ring are in the range 1.41–1.42 Å, values only slightly shorter than 1.43–1.45 Å in typical phenylaminoxyls (6). Therefore, the contribution of a quinonoid structure is judged to be insignificant (Chart 2). Triradical **N** exhibits a broad absorption band at 450–800 nm (λ_{max} 534 nm, $\varepsilon = 5500$). Although its absorption coefficient is not very strong compared with that of quinonoid system **C**, the long-wavelength absorptions may be due to weak CT transitions from the amine nitrogen to the aminoxyl groups.

Diradical C. The molecule has no threefold axis passing through the central carbon atom. Bond alternation was clearly found on two *p*-phenylene rings: 1.417 vs 1.364 Å on an average, while the remaining ring does not have such a tendency (1.396 vs 1.388 Å on an average). Other bond lengths show similar trends. It is suggested that the bis(aminoxyl)methylenecyclohexa-2,5-dienone *N-tert*-butylimine *N*-oxide structure is in resonance between the two rings in crystals (Chart 3). A strong absorption characteristic of a quinonoid structure is observed at 554 nm, $\varepsilon = 20,400$.

Triradical B′. In contrast with the above two radicals, triradical **B′** has a crystallographic threefold symmetry[3] passing through the central boron atom, resulting in the three aminoxyl moieties becoming equivalent in the crystalline state. The aryl groups are tilted by 49.2° with respect to the borane valence plane. The shortest intermolecular distance between the aminoxyl oxygen atoms of the neighboring molecules is 3.99 Å.

3. EPR Spectra in Fluid and Solid Solutions

Triradical N. X-band EPR spectra of **N** in degassed 2-methyltetrahydrofuran (MTHF) solution were obtained in the temperature range 8.5–300 K. At 300 K the EPR spectrum centering at $g = 2.006$ consisted of a septet in a ratio of 1:3:6:7:6:3:1 due to hyperfine coupling with the three equivalent nitrogen nuclei, suggesting that the exchange interaction is much larger than the hyperfine interaction ($|J| \gg |a_N|$). The spectrum was simulated by an isotropic hyperfine couplings with three equivalent nitrogen atoms ($a_N = 4.06\,\text{G}$), six equivalent *meta*-hydrogens

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[3] Symmetry operation: $x, -y, \frac{1}{2} + z$.

CHART 2.

FIG. 1. Temperature dependence of $\chi_{mol}T$ of triradical **N** at a constant field of 5000 Oe. The solid curve is the theoretical one described in text.
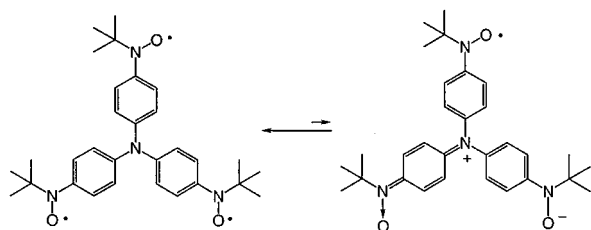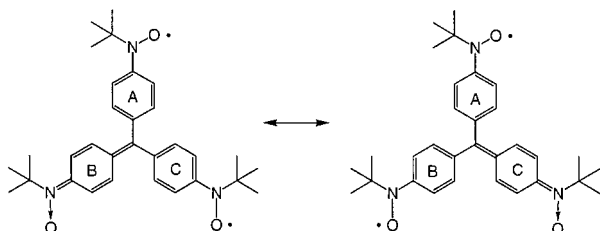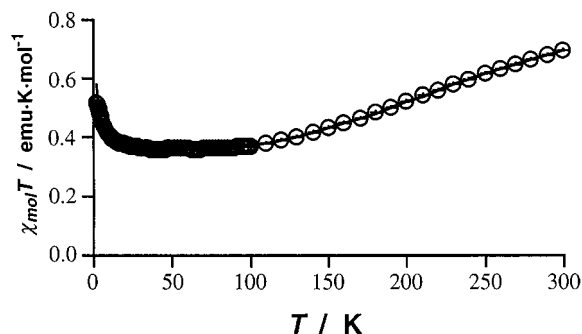
($a_H = 0.8$ G), six equivalent *ortho*-hydrogens ($a_H = 0.4$ G), and a nitrogen atom ($a_N = 0.5$ G).

In frozen solution, **N** showed a strong main peak with a pair of weak outer shoulders separated by 20.3 G in the $\Delta m_s = 1$ region. Most of the former is due to a doublet species. The latter was simulated by assuming a dipole–dipole interaction with $|D/hc| = 0.0019$ cm^{-1} and $|E/hc| = 0$ cm^{-1}. The D value corresponds to a mean distance of 11.2 Å for the unpaired electrons (7). No signal arising from the $\Delta m_S = 2$ or 3 transitions was detected. The intensity of the main peak decreased as the temperature was increased in the range 8.5–100 K in good agreement with a Curie law. This result is not decisive as to determine rigorously whether the ground state is a quartet, doublet, or degenerate quartet/doublet state.

Diradical C. The EPR spectrum of biradical **C** in degassed MTHF solution at room temperature exhibits a well-resolved complex pattern, dominated by the presence of different conformers and their hyperfine splitting (8).

Triradical B′. The EPR spectra of triradical **B′** centering at $g = 2.0058$ consisted of a septet ($|a_N| = 4.11$ G) due to hyperfine coupling with the three equivalent nitrogen nuclei. In a frozen solution, **B′** showed a large main peak with a very weak outer shoulder and no signal arising from the $\Delta m_s = 2$ or 3 transitions was observed.

4. Molar Paramagnetic Susceptibility

Triradical N. The temperature dependence of the molar paramagnetic susceptibility χ_{mol} at 5000 G is presented as

CHART 3.

a $\chi_{mol}T$ vs T plot in Fig. 1. At 300 K, the observed $\chi_{mol}T$ value amounts to 0.695 emu K mol^{-1}. This value is considerably smaller than the theoretical 1.125 emu K mol^{-1} for a triradical having three independent spins, implying that the coupling favoring the antiparallel alignment of the spins is operative even at 300 K. The $\chi_{mol}T$ value decreased linearly (theoretically speaking it should be a part of a sigmoidal curve) as the temperature was lowered until it remained almost constant at approx. 0.375 emu K mol^{-1} from 100 down to 20 K. This constant value is typical of a paramagnetic species having a single isolated spin; **N** behaves as if it had only one spin per molecule under these conditions. As the temperature was decreased below 20 K, the $\chi_{mol}T$ values increased to reach a value of 0.58 emu K mol^{-1} at 2 K.

A further proof of the ground doublet state in **N** was furnished by similar magnetic susceptibility measurements on a dilute sample (5%) of **N** in poly(vinyl chloride) in which a possible intermolecular coupling would be considerably diminished. Under these conditions, the $\chi_{mol}T$ values were flat below 20 K and the continuous increase observed for the crystalline sample was not detected. It was confirmed that the increase is due to the interaction between the adjacent molecules, that there is no intramolecular magnetic interaction populating the quartet state at the cryogenic temperature, and that the ground state must be a doublet state. The doublet–quartet energy gap is estimated to be greater than 300 K (> 0.6 kcal mol^{-1}). The origin of the ferromagnetic interaction between the neighboring molecules in crystals may be located at contacts O1–C12′ (3.272(4) Å) and O3–C25′ (3.131(3) Å) along the chain made by the molecules aligned in the direction of the c axis (Fig. 2).

The magnetic interaction in a nonsymmetric triangular triradical system can be written by the spin Hamiltonian

$$H = -2(J_{12}S_1S_2 + J_{23}S_2S_3 + J_{31}S_3S_1), \qquad [1]$$

where J_{ij} is the exchange coupling parameter between S_i and S_j. The molar susceptibility is given by
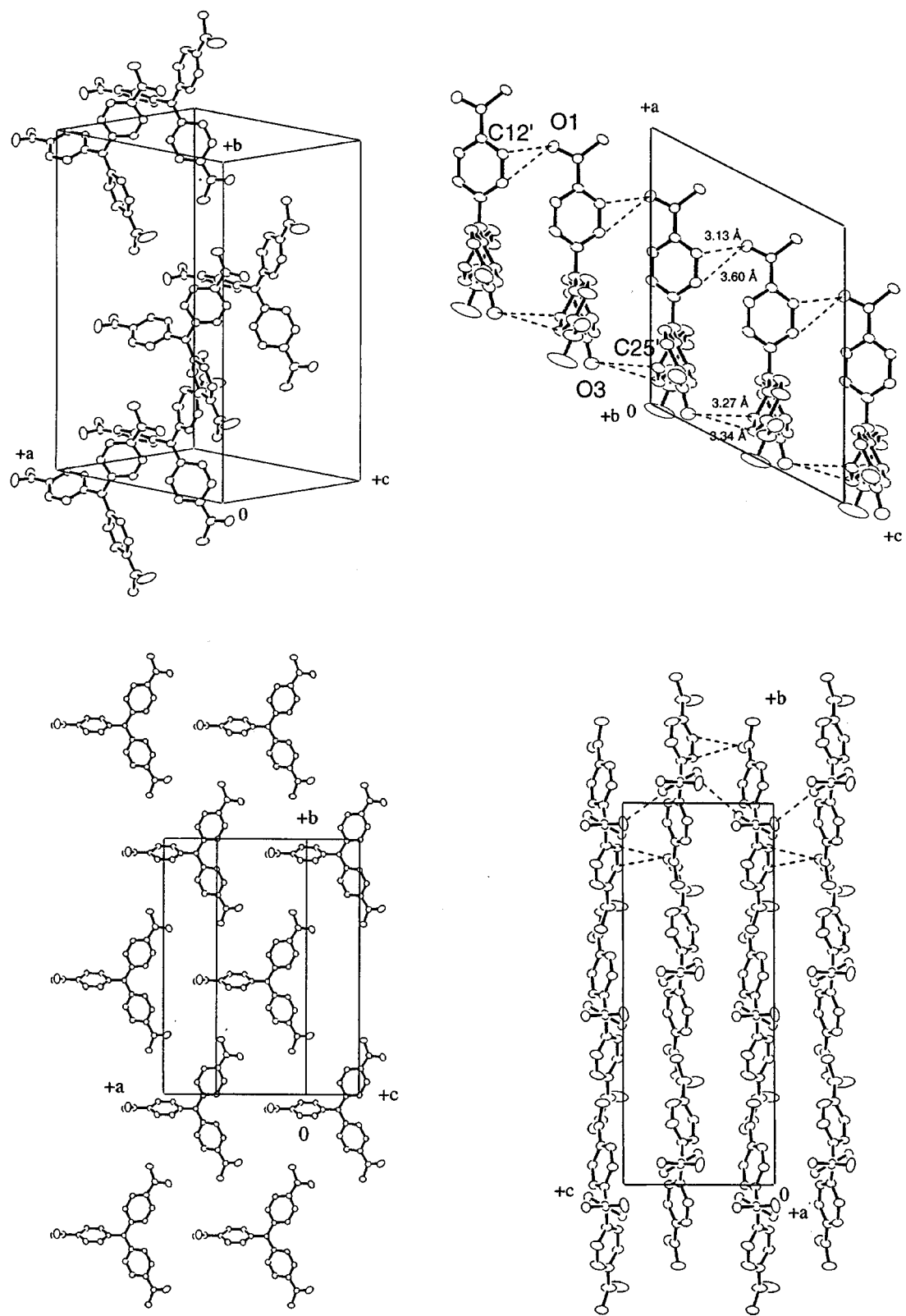
FIG. 2. Ball-and-stick presentation of the crystal structure of **N**. The methyl groups are omitted for clarity. Broken lines indicate the short contacts between the neighboring molecules (see text).

$$\chi_{\mathrm{mol}}T = f \frac{Ng^2\mu_B^2}{4k_B} \cdot \frac{1 + \exp(-\Delta_1/k_B T) + 10\exp(-\Delta_2/k_B T)}{1 + \exp(-\Delta_1/k_B T) + 2\exp(-\Delta_2/k_B T)}$$

$$\cdot \frac{T}{(T-\theta)}, \qquad [2]$$

where Δ_1 and Δ_2 are given by

$$\Delta_1 = 2(J_{12}^2 + J_{23}^2 + J_{31}^2 - J_{12}J_{23} - J_{23}J_{31} - J_{31}J_{12})^{1/2}$$
$$[3]$$

$$\Delta_2 = \Delta_1/2 - (J_{12} + J_{23} + J_{31}), \qquad [4]$$

which are energy differences defined as in Fig. 3 (9). In principle the spin Hamiltonian should contain terms due to the Zeeman, dipole–dipole, and hyperine interactions in addition to the exchange term. They are estimated to be 0.7 K (1 K = 0.695 cm^{-1}) at a field of 5000 G, 1.0×10^{-2} K for two spins at a distance of 5 Å, and 1.3×10^{-3} K for $a = 100$ G, respectively. Therefore these terms may be neglected in the present discussion of the exchange interaction as strong as 10–500 K ($|J| \gg |a_N|$).

A purity factor f was introduced to account for all the experimental errors of weighing a sample, calibrating a SQUID susceptometer, etc., in addition to the paramagnetic purity of a radical sample. Any interradical interaction is taken into account by a mean-field theory.

When Eq. [2] is used for the fitting of the temperature dependence of the magnetic susceptibility on **N** in the range 2–300 K, three J_{ij} parameters are required. It is apparent that the three J_{ij} parameters must be highly correlated, and there are too many parameters to determine three kinds of J values uniquely from the fitting of Eq. [2] to the experimental temperature dependence of $\chi_{\mathrm{mol}}T$ data by a least-squares fitting procedure. Therefore, we decided to fit the expression of the magnetic susceptibility as a function of Δ_1 and Δ_2 to the experimental data. The best-fit parameters by means of a least-squares method were $\Delta_1 = 1015 \pm 444$ K, $\Delta_2 = 559 \pm 9$ K, $\theta = 0.75 \pm 0.02$ K, and $f = 0.958 \pm 0.004$.

Since the eigenvalues for Eq. [1] are given by

$$E(\tfrac{3}{2}) = -\tfrac{1}{2}\cdot(J_{12} + J_{23} + J_{31}) \qquad [5]$$

$$E(\tfrac{1}{2}) = \tfrac{1}{2}\cdot(J_{12} + J_{23} + J_{31}) \pm (J_{12}^2 + J_{23}^2 + J_{31}^2$$
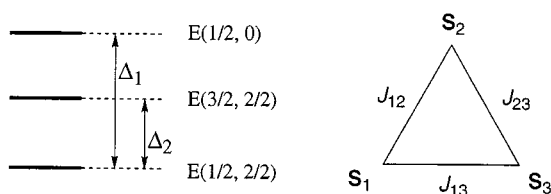$$- J_{12}J_{23} - J_{23}J_{31} - J_{31}J_{12}), \qquad [6]$$

FIG. 3. The energy level diagram for two doublets and one quartet states originating from the triangular interaction of three spin $\frac{1}{2}$.
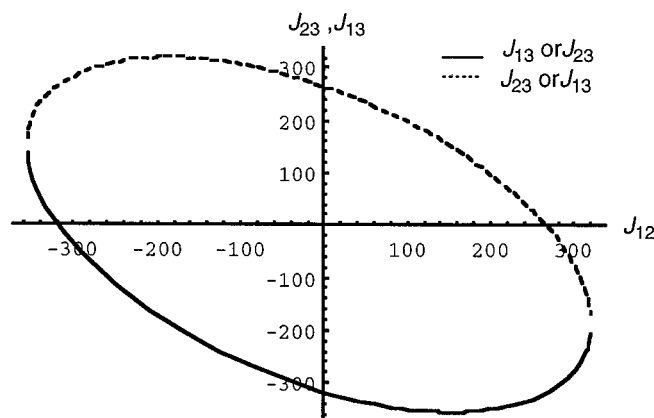

FIG. 4. A general relation among the exchange coupling parameters $J_{12} + J_{23} + J_{31}$.

the ground doublet state is concluded to lie below an excited quartet state by $\Delta_2 = 559 \pm 9$ K (= 1.11 kcal mol^{-1}) (see Fig. 3).

In principle, J_{23} and J_{31} are given as functions of J_{12}. This is shown in Fig. 4. A large standard deviation in Δ_1 makes it unrealistic to determine the exchange coupling parameter J values separately. It was only by making the following assumptions were numerical values for J obtained.

(1) For a regular triangle that is applicable to a triradical having a threefold symmetry axis (6b), $J = J_{12} = J_{23} = J_{31}$ in Eqs. [3] and [4], and $J/k_B = -135 \pm 3$ K. Since $\Delta_1 = 0$, the ground doublet state is doubly degenerate. Note that this antiferromagnetic coupling is almost comparable in magnitude to the ferromagnetic coupling of $J/k_B = 205$ K in **C**, although in opposite sign (*vide infra*). A superexchange mechanism has been evoked in organic di- and tricarbenes (10) but there is no example of organic free radicals in which such strong interaction as in **N** has been determined quantitatively. The superexchange interaction is a concept introduced in coordination chemistry to explain the interaction between two magnetic metal ions through a bridging diamagnetic atom, e.g., in M–O–M. One of the most important factors contributing to the interaction is a charge transfer from the diamagnetic bridging atom to the metal ions. Depending on the symmetry of the magnetic orbitals at the metal ions, the interaction becomes antiferro- or ferromagnetic. It is very often the case indeed to detect the LMCT band for such systems. Spin polarization does not accompany a charge transfer as the difference in energy of the electron repulsion between α vs α and α vs β is concerned.

(2) For isosceles triangles, $J_{12} = J_{31} \neq J_{23}$ in Eqs. [3] and [4], there are several possibilities and no unique set of J parameters was obtained (6b). Since the torsion angle of ring C with respect to the central nitrogen–aromatic carbon bond is almost twice as large as those of rings A and B, the
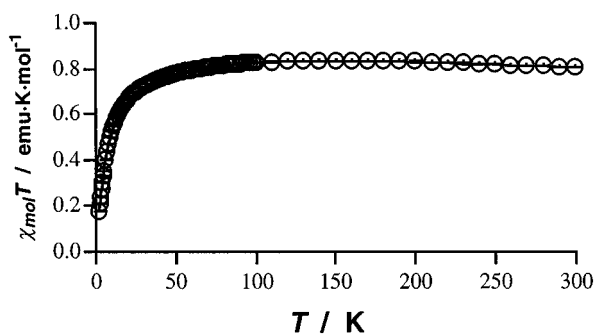
FIG. 5. Temperature dependence of $\chi_{mol}T$ of biradical **C** at a constant field of 5000 Oe. The solid curve is the theoretical one described in the text.

aminoxyl radical on ring C may be regarded as isolated from the rest: $J_{23} = J_{31} = 0$. Then $J = J_{12} = -270 \pm 3$ K from Eqn. [3] and [4]. If $J_2 = 0$ for some reasons, then $J_{23} = J_{31} = -171 \pm 2$ K.

Triradical **N** may be regarded as an organic counterpart of bridged trinuclear metal complexes exhibiting the superexchange interaction (11), e.g., [Cu$_3$(pao)$_3$OH] (11a) and μ^3-oxo-bridged trinuclear Fe(III) acetate complexes (11c). The interaction between any two radical centers through the nitrogen atom carrying a lone pair of electrons is antiferromagnetic, leaving the remaining one electron spin intact. The spin states are typically frustrated in that the ground state is degenerate. In crystals, however, the molecular structure is frozen to one of the tautomeric structures due probably to the crystal field.

Diradical C. Crystalline samples of **C** gave $\chi_{mol}T$ vs T plots as shown in Fig. 5. The $\chi_{mol}T$ value is as high as 0.80 emu K mol^{-1} at 300 K, suggesting that the ferromagnetic coupling for aligning the two spins in parallel is on the order of ~ 300 K. As the temperature is lowered, the $\chi_{mol}T$ value increases steadily, aiming at 1.0 emu K mol^{-1}, but reaches a maximum of 0.83 emu K mol^{-1} at around 150 K, and then decreases continuously. Application of the Bleaney–Bowers–type equation (12)

$$\chi_{mol}T = f \frac{21Ng^2\mu_B^2}{k} \cdot \frac{1}{3 + \exp(-2J/k_BT)} \cdot \frac{T}{(T - \theta)} \quad [7]$$

for an equilibrated singlet–triplet model, with Weiss constant θ for an antiferromagnetic mean molecular field, gave the best fit parameters $2J/k_B = 410 \pm 10$ K, $f = 0.893 \pm 0.002$, $\theta = 7.375 \pm 0.06$ K.

Matsumoto *et al.* synthesized 1,1-bis[p-(N-*tert*-butyl-N-hydroxyamino)phenyl]-2-methylpropene **3** similar to **C**, and showed that **3** had a small exchange coupling of $2J/k_B = 15.3$ K (13). Hosokoshi and coworkers determined a much larger exchange coupling of 319 K between nitronyl nitroxide and *tert*-butylaminoxyl radicals in **4**, whereas the

exchange coupling between imino nitroxide and *tert*-butylaminoxyl radical in **5** is less than 200 K (14). A contribution of the quinonoidal resonance forms seems to be important in strengthening the magnitude of the exchange coupling in **C** and **4**. **C** may also be regarded as the aminoxyl counterpart of Yang's diradical in which the molecule has approximate D_3 symmetry with propeller blades of quinonoidally distorted six-membered rings in the same direction (15).

Triradical B′. The $\chi_{mol}T$ value of a microcrystalline sample of **B′** was 1.07 emu K mol^{-1} at 300 K, a value close to a theoretical 1.125 emu K mol^{-1} for three isolated spins. As the temperature is lowered, the $\chi_{mol}T$ value started to decrease steadily at approx. 200 K; the magnetic susceptibility is dominated by antiferromagnetic interactions. Since it is not clear whether the antiferromagnetic interaction is intra- or interradical molecules, another measurement was carried out for a film sample made by casting a 6% solution of **B′** in poly(vinyl chloride). Under these conditions, the continuous decrease in $\chi_{mol}T$ in the range 300–50 K was absent (Fig. 6). In order to understand the magnetic interactions more quantitatively, a regular triangle three-spin model suggested by X-ray crystal structure analysis of **B′** was applied to the $\chi_{mol}T$ vs T plot. By assuming that the remaining decrease in $\chi_{mol}T$ values at temperatures below approx. 50 K is due to intraradical coupling, the $\chi_{mol}T$ vs
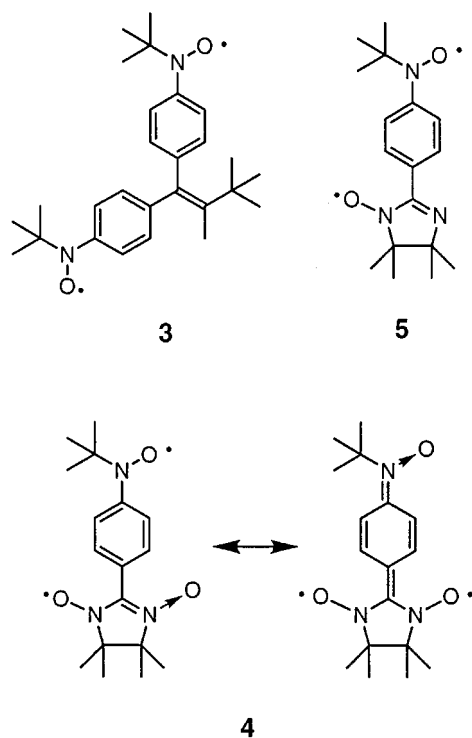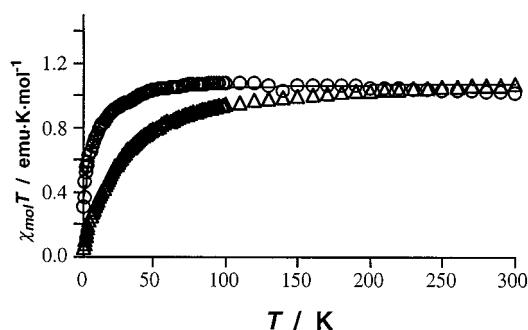

SCHEME 2.

FIG. 6. Temperature dependence of $\chi_{mol}T$ of triradical **B′** in neat crystals (△) and 6% PVC film (O) at a constant field of 5000 Oe. The solid curve is the theoretical one described in text.

T plots were analyzed on the basis of a regular triangle coupling: the spin Hamiltonian given by Eq. [1] where $J = J_{12} = J_{23} = J_{31}$. The temperature dependence of the molar susceptibility is given by Eq. [8], where all symbols have their usual meaning. The best fit to the observed points was reached by $3J/k_B = -9.9\ \mathrm{K} \pm 0.3$ and $f = 0.956 \pm 0.004$ and $\theta = 0$:

$$\chi_{mol}T = f\frac{Ng^2\mu_B^2}{4k_B}\cdot\frac{1 + 5\exp(-3J/k_BT)}{1 + \exp(-3J/k_BT)}\cdot\frac{T}{(T-\theta)}. \quad [8]$$

Ground doublet states are doubly degenerate and concluded to be more stable than a quartet state by $3J/k_B = 9.9\ \mathrm{K}$. This result is in accord with the expectation from MO theory. The weakened absolute J value between *tert*-butylaminoxyl radicals in **B′** is considered to be caused by the large torsion angles of the benzene rings (49.2°) comparable to those of trimesitylborane (16) and/or the lack of π-electrons on the boron atom. Even though perturbed by six *ortho* methyl groups, the interaction is intramolecular and it is likely that the antiferromagnetic interaction would be much stronger in the sterically less-biased **B** for which the torsion angle is expected to be approx. 30° (17).

5. Ab Initio Molecular Orbital Studies on N

In order to delineate the electronic structures and obtain an estimate on the energy gap between doublet and quartet states of **N**, ab initio MO studies based on the density functional theory (DFT) were carried out. First, the molecule of **N** was simplified to **N′** by replacing all the N-*tert*-butyl with N-methyl groups. All the geometric parameters were optimized for **N′** by taking electron correlation into account in the framework at the B3LYP/6-31G level of theory on a Gaussian94 program (19). None of the optimized structures have any threefold axis. The torsion angles of the three rings with respect to the plane defined by the three

quaternary ring carbons attached to the central nitrogen atom are 23.9°, 26.8°, and 46.7° for the doublet and 33.6°, 36.6°, and 45.7° for the quartet. The latter is much closer to a C_3 structure. The computed bond lengths and angler[4] agree with those observed by X-ray crystallography for the doublet state of **N**. For these optimized structures, B3LYP/6-31G* computations were performed to obtain the DFT energy values of -1257.34292593 and -1257.34162401 Hartree for the doublet and quartet states of **N′**, respectively. The former is more stable than the latter by 0.84 kcal mol^{-1} ($= 423\ \mathrm{K}$).

Whereas the central amine nitrogen atom does not carry high net spin density in both states (the Mulliken spin density of 0.0093 and 0.0314 for the doublet and quartet states, respectively), it has high α and β spin densities in the 100th magnetic orbital and the 99th doubly occupied MO, respectively, in the ground doublet state. The operation of a superexchange mechanism through the lone pair of electrons on the central nitrogen atom is suggested with two spins on the aminoxyl radical centers coupled antiferromagnetically, with one spin remaining intact.

It is well established that the positive spin density (α spin) is polarized at the para carbon atom of the phenyl ring in N-*tert*-butyl-N-phenylaminoxyls. The three α spins thus polarized are to interact through the central nitrogen, carbon, and boron atoms as in $(\cdot\mathrm{H_2C})_3X$ where $X = \mathrm{N}$, C·, and B, respectively. In other words, the results obtained in this work should also be interpreted in terms of a series of three-time phenylogs of trimethylenemethane TMM. The numbers of the π-electrons in the simplified $\mathrm{CH_2} = X(\mathrm{CH_2}\cdot)_2$ are four for $X = \mathrm{C}$ in the carbon analog, leaving two electrons for two degenerate orbitals, making the triplet electronic configuration most stable (see Fig. 7). In the amino analog, the number of π-electrons is five, making the two orbitals doubly occupied and leaving only one SOMO. Similarly, in the borane analogue, the central atom does not supply any π-electron, making the total number of the relevant π-electrons three. Here again only one SOMO is generated. Taking the effects of dynamic electron correlation into account by CASPT2 single-point calculations at the geometries optimized via the CASSCF methodology, Borden and Brown showed that $^2A_2$ and $^2B_1$ states are nearly degenerate ground states and excited $^4A_2''$ states are 38.0 and 23.4 kcal mol^{-1} above the ground states for trimethyleneamine and trimethyleneborane, respectively.[5] The ground spin states of **N** and **B′** observed in this study are justified by this theoretical study. The much smaller magnitude of the observed gaps are due to the partial
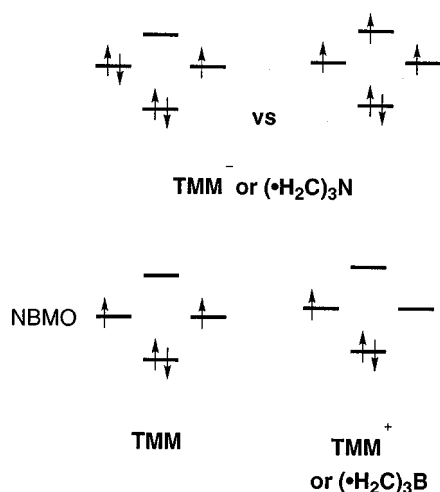
FIG. 7. Ground state electron configuration in the basic structural units of **N**, **C**, and **B**.

Potential / **V** (vs SCE)

FIG. 8. Cyclic voltammograms for **N** and **B′**.

α spins polarized at the ring carbon atoms attached to the central nitrogen and boron atoms (see Chart 1).

The antiferromagnetic coupling in molecular systems is nothing but a partial bonding. The triangular antiferromagnetic coupling among three $\frac{1}{2}$ spins leading to a doublet ground state in **N** corresponds therefore to the π-bonding in cyclopropane-1,2,3-triradical in which any two spins interact antiferromagnetically owing to the strong overlap of the spin-containing orbitals and a π-bond is formed to give a cyclopropenyl radical. The π-bond energy of $J \approx -60 \ kcal \ mol^{-1}$ may be regarded as a measure of the antiferromagnetic interaction in this case.

6. Cyclic Voltammetry

The electrochemical oxidation of aminoxyl radicals was studied by cyclic voltammetry. The results are summarized in Fig. 8 and Table 1. When the three triarylamines **N**, **6**, and **8** are compared, we note that the first and the second waves are at 0.3 and 1.0 V, respectively. The relative heights are 1:2, 1:1, and 1:0. It is clear from these observations that the first and second oxidation waves of **N** are due to the amino nitrogen and the aminoxyl group, respectively. The product obtained reversibly by one-electron oxidation is considered to have a resonance structure given by Chart 4. In this sense, the first wave should be described as due to the *p*-aminophenylaminoxyl chromophore. A similar spin-pairing interaction is suggested in the electrochemistry of 4,4′,4″-tris(tricyanovinyl)triphenylamine (19). If the first wave were not coupled with one of the aminoxyl groups and the second wave were due to the oxidation of the isolated aminoxyls, the relative intensities should have been 1:3 and 1:2 for **N** and diradical **6**, respectively. The potential of the second wave is similar to that of diradical **7**, a typical
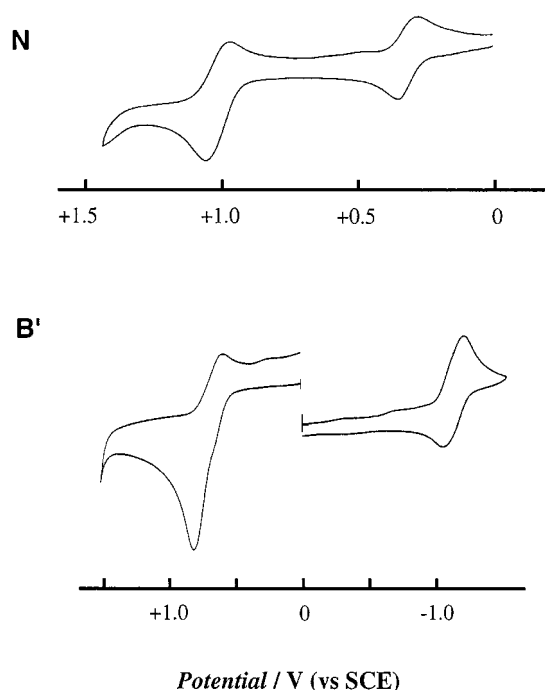
arylaminoxyl. Since the oxidation potential of TEMPO is 0.4 V (20), only slightly more positive than 0.3 V, the first wave of **N** may also be viewed as the oxidation of the aminoxyl substituted with a moderately electron-donating diarylamino group.
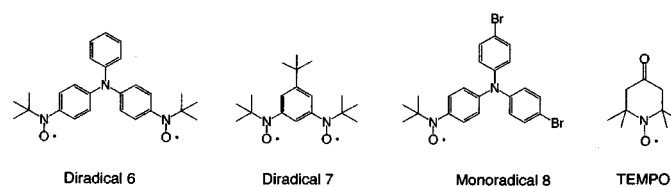
TABLE 1

| Aminoxyl radical | Oxidation potentials | | Conditions |
	Eox1/V	Eox2/V	
N	0.31	0.99	1
Diradical **6**	0.31	0.96	
Diradical **7**		1.01[a]	
Monoradical **8**	0.28		
TEMPO		0.4	
B[b]		0.69	2

Note. Condition (1): Reference electrode, SCE; working and counter electrodes, Pt; solvent, CH_2Cl_2; supporting electrolyte, TBAClO$_4$ (0.1 M); sweep rate, 100 mV/s.
Condition (2): Reference electrode, Ag/AgNO$_3$; others are equal.
[a] Irreversible.
[b] Reduction wave at −1.13 V.

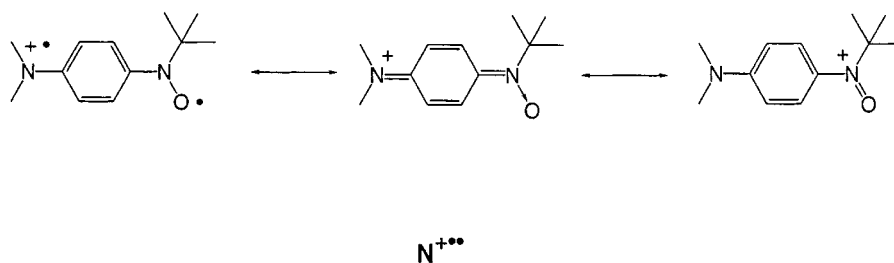Diradical 6   Diradical 7   Monoradical 8   TEMPO

CHART 4.

Whereas **B′** is reduced to the stable borate, it seems to undergo three-electron oxidation to give a trication at 0.69 V. In this sense, the second wave of the triarylamines should be regarded as aminoxyls substituted with electron withdrawing group(s).

The product obtained reversibly by one-electron oxidation of **N** is considered to have a resonance structure given by Chart 4 and isoelectronic with **C**. Therefore this cation diradical should be a triplet with a reasonably large gap with the exited singlet. The redox activity of **N** thus promises an interesting entry into magnetic materials controlled by electrochemistry. Efforts are in progress to isolate the cation diradical salt **N$^{+\cdot\cdot}$X$^-$** or to find this species on the surface of the electrode.

7. The Manganese(II) Complex with C

One of the objectives of this work was to explore new aminoxyl radicals as bridging ligands for magnetic metal ions. The oxygen atoms of aminoxyl radicals have enough Lewis basicity and are coordinated to magnetic metal ions to build tailored extended magnetic structures (2, 3). Two most typical examples are ferri/ferromagnets made of bis(hexafluoroacetylacetonato)manganese(II) Mn(hfac)$_2$ with tris(aminoxyl) radicals **1** and **2** and having ordering temperatures (T_C) of 3.4 and 46 K, respectively. They have a graphite-like honeycomb network structure (3a) and a crossed parallel structure (3e, h) analogous to the silicon sublattice of ThSi$_2$, respectively. Thus, polyradicals having aminoxyl radicals arranged trigonally in cross conjugation are of importance in constructing high T_C 2p–3d hybrid spin magnets.

When Mn(hfas)$_2$ and diradical **C** were mixed in a 3:2 molar ratio in n-heptane-dichloromethane-diethyl ether, fine black–violet needles were obtained. Elemental analysis revealed that its composition was not consistent with a 2:3 complex, but agreed better with a 2:2.8 complex or a 2:3 complex containing 0.5 molecule of n-heptane per formula unit. We have not succeeded in obtaining single crystals of this complex amenable for X-ray crystal structure analysis. By analogy with the network structures of Mn(hfac)$_2$ with **1** and **2**, we assumed that the complex has also an extended network structure.

Temperature dependence of its paramagnetic susceptibility revealed a strong ferromagnetic interaction as revealed by its Weiss constant θ of 87 K (Fig. 9a). Temperature dependence of its magnetization was measured at low field of 5 Oe. The field-cooled magnetization (FCM) revealed the typical features of a ferromagnetic transition at T_C of 60 K. If the field was switched off below T_C, a remnant magnetization was observed. The zero-field-cooled magnetization (ZFCM) was obtained by cooling the sample below 60 K in
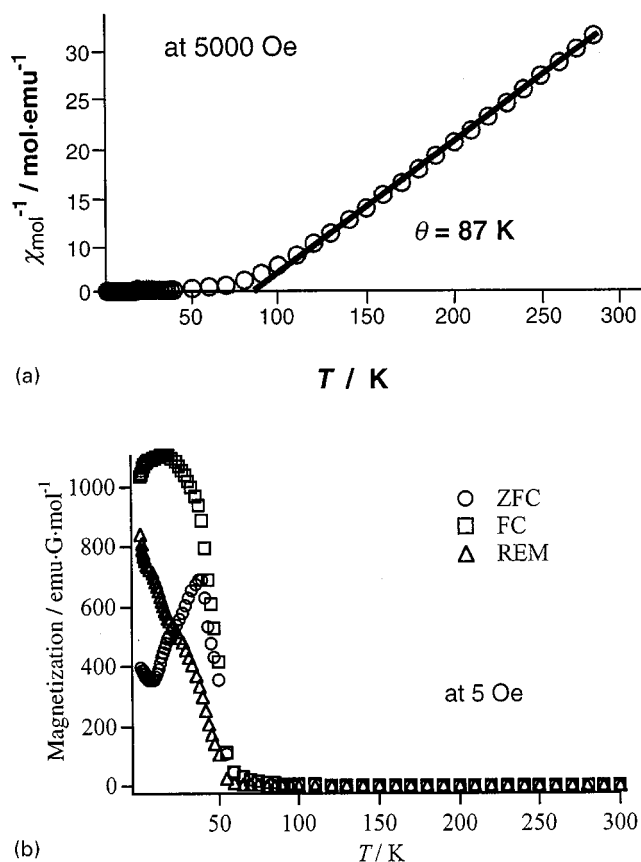

FIG. 9. (a) Plots of reciprocals of χ_{mol} vs temperature. (b) Temperature dependence of various magnetization data of the crystalline complex of Mn(II)(hfac)$_2$ with **C** (see text and Experimental section).

zero field and then applying the field and heating. The ZFCM was lower than the FCM at any temperature range below T_C probably due to the difficulty in moving the domain walls by the weak applied field. ZFCM showed a maximum at the temperature just below T_C. Some anomaly was found at 15–20 K (Fig. 9b). A hysteresis loop with the coercive field of 18 Oe was obtained when the field was swept at 5 K.

CONCLUSIONS

We have shown that tris[p-(N-oxyl-N-$tert$-butyl-amino)phenyl] amine, -methyl, and -borane have doublet, triplet and doublet ground states, respectively. Ferro- and antiferromagnetic coupling units are dictated by the topology of the π-orbitals (1, 4a, 21). Thus one of the most important messages pertinent to the design of new molecule-based magnets is the unequivocal demonstration that the number of the π-electrons is also important in determining the positive and negative coupling of the spin centers connected by the same topology.

Further studies are in progress to monitor electrochemical interconversion of doublet N and triplet cation diradical salt $N^{+\cdot\cdot}X^-$. Structural elucidation of the complex of Mn(hfac)$_2$ with diradical C is indispensable to disclose the origin of its T_C as high as 60 K.

EXPERIMENTAL SECTION

1. Materials

^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-270 instrument. IR spectra were obtained on a Hitachi I-5040 spectrometer. Mass spectra were obtained on a JEOL JMS-HX110A instrument. All solvents used in the reactions were purified by the reported methods. THF was purified by distillation from sodium-benzophenone ketyl under a dry nitrogen atmosphere, just before use. All reactions were performed under an atmosphere of dry nitrogen unless otherwise specified. All reactions were monitored by thin-layer chromatography carried out on 0.2-mm E. Merck silica gel plates (60F-254) using UV light as a detector. Column chromatography was performed using silica gel (Wakogel C-200, 200 mesh) or neutral alumina (ICN, activity grade IV or Nacalai, alumina-activated 200 mesh, inactivated with 6% H$_2$O). Powder poly(vinyl chloride) ($n \approx 1100$) used for the preparation of polymer film samples was purchased from Wako Pure Chemical Industries Ltd.

The radical samples N, C, and B' were prepared as described previously (5).

The manganese (II) Complex with C. A solution of 60 mg (0.127 mmol) of Mn(hfac)$_2$ in 80 ml of n-heptane was obtained by zeotropic distillation of water from a suspension

of Mn(hfac)$_2 \cdot 2$H$_2$O in this solvent. The 50-ml cooled solution was diluted with 20 ml of anhydrous diethyl ether. To this solution was added 43 mg (0.085 mmol) of diradical C in 40 ml of dichloromethane. The mixed solution was kept at room temperature under a stream of dry nitrogen to deposit fine black–violet needles. Anal. Found: C, 46.86; H, 3.87; N, 3.41%, Calcd for (1) a 2:3 complex (C$_{92}$H$_{84}$F$_{36}$Mn$_3$N$_6$O$_{18}$): C, 45.84; H, 3.51; N, 3.45%; (2) a 2:2.8 complex: C, 46.66; H, 3.64; N, 3.63%; and (3) a 2:3 complex containing 0.5 molecule of n-heptane per formula unit: C, 46.62; H, 3.77; N, 3.42%.

Samples of N, C, and B' diluted in polymer films. PCV powder (50 mg) and a polycrystalline sample of radical N, C, or B' (5–6 wt%) were dissolved in CH$_2$Cl$_2$ (ca. 5 ml) on a watch glass and the solvent was slowly evaporated. The obtained PVC films were dried under reduced pressure overnight at room temperature.

2. Crystallography

The intensity data for N and C were collected on a Rigaku RAXIS-IV imaging plate area detector with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71070$ Å). Indexing was performed form three oscillations that were exposed for 4.0 min. The crystal-to-detector distance was 110.00 mm with the detector at a zero swing position. Readout was performed in the 0.100-mm pixel mode. The data were collected at a temperature of $-100°$C to a maximum 2θ value of 55°. A total of 205.0° (for N) and 185.0° (for C) oscillation images were collected, each being exposed for 60 min. (for N) and 100 min. (for C). The intensity data for B' were collected on a Rigaku AFC7R diffractometer with graphite-monochromated MoK$_\alpha$ radiation ($\lambda = 0.71070$ Å). The data were collected at a temperature of 23°C using the ω–2θ scan technique to a maximum 2θ value of 55°. The structures of N and C were solved by a direct method with MULTAN 88 and refined by the full-matrix least-squares method. The structure of B' was solved by a direct method with SHELXS-86 and refined by the full-matrix least-squares method. All of the nonhydrogen atoms were refined anisotropically. The final cycle of the least-squares refinement was based on 2461 (for N), 1597 (for C), and 1519 (for B') observed reflections ($I > 3.0\sigma(I)$ for N and B', $I > 1.5\sigma(I)$ for C) and 335 (for N and C) and 199 (for B') variable parameters with R ($R_w = 0.039$ (0.054) (for N), 0.058 (0.055) (for C), and 0.050 (0.072) (for B'). All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corp.

3. Magnetic Measurement

Fine crystalline samples or polymer film samples were mounted in a capsule (Japan Pharmacopoeia NO. 5, 4.5

o.d. × 11 mm) and measured on a Quantum Design MPMS-5S SQUID susceptometer at 5000 G. The data were corrected for the diamagnetic contribution in the range $-3.7 - -6.7 \times 10^{-5}$ emu G of sample capsules and holding straws used. Contribution of the diamagnetic susceptibility ($-1.7 - -2.2 \times 10^{-4}$ emu_G) of the polymer matrix was determined by measuring the susceptibility of the same amount of similar PVC films made in the absence of dissolved free radicals. Corrections for the diamagnetic contribution from the free radical molecules were made by using Pascal's constants.

The ZFCM was obtained by cooling the sample below a T_C of 60 K in zero field and applying the field and heating. The FCM was obtained by cooling within the field of 5 Oe.

4. Computational Studies

The computational work was performed on a NEC HSP computer and the library program GAUSSIAN94 at the Computer Center, Institute for Molecular Science in Okazaki.

5. Cyclic Voltammetry

The voltammogram was obtained on a BAS CV-50W Voltammetric Analyzer with a sweep rate of 100 mV/s. SCE and Ag/AgNO$_3$ reference electrodes and Pt working and Pt counter electrodes were used for the measurements. Dichloromethane was used as a solvent to which tetra-*n*-butylammonium perchlorate (0.1 M) was added as a supporting electrolyte.

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