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Antiferromagnetic Exchange Interaction among the Three Spins Placed in an Isosceles Triangular Configuration in 2,4-Dimethoxy-1,3,5-benzenetriyltris(*N-tert*-butyl nitroxide)

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Abstract: 2,4-Dimethoxy-1,3,5-benzenetriyltris(*N-tert*-butyl nitroxide) (**3**) was prepared by lithiation of 2,4-dimethoxy-1,3,5-tribromobenzene followed by the reaction with 2-methyl-2-nitrosopropane and subsequent oxidation with Ag_2O. The triradical crystallizes in the orthorhombic space group *Pnma* (no. 62) with four molecules in the unit cell of dimensions $a = 18.200(3)$ Å, $b = 19.018(3)$ Å, and $c = 6.659(5)$ Å. X-ray analysis for an orange plate single crystal of **3** revealed that the three nitroxide radicals in a molecule have large dihedral angles (90° and 79°) between N−O bonds and the benzene ring plane in the all-syn conformation and the distances between them are 5.44 and 5.28 Å. An EPR spectrum of triradical **3** in frozen toluene solution showed quartet signals ($g = 2.0062$, $|D/hc| = 0.010$, and $|E/hc| = 0.0004$ cm^{-1}) in addition to the signals at $g = 4.019$ and 6.035 due to $\Delta m_s = 2$ and 3 transitions, respectively. Temperature dependence of molar susceptibility for a microcrystalline sample obtained by SQUID measurements suggested that the antiferromagnetic interaction produces a doublet ground state in triradical **3**. Experimental data were fitted in terms of the equation derived from an isosceles triangular three spin system ($H = -2J(S_{A1}S_B + S_BS_{A2} + \alpha S_{A1}S_{A2})$) with negative J's to afford two sets of the best fitting parameters: $J/k_B = -41.5$ K, $\alpha = 0.31$ and $J/k_B = -22.3$ K, $\alpha = 2.29$. The former J/k_B value is more consistent with $J/k_B = -39.7$ K for the reference biradical, 1-bromo-2,4-dimethoxy-3,5-benzenediylbis(*N-tert*-butyl nitroxide) (**4**). In triradical **3**, therefore, the ground spin state would be a doublet with the stronger antiferromagnetic interaction between the spins at 1 and 3 positions and 3 and 5 positions polarizing the ferromagnetic alignment of the 1 and 5 spins, providing the first demonstration of an organic triradical showing competing interactions.

Introduction

In the design and construction of organic super-high-spin molecules, the *m*-phenylene framework has been extensively employed as a versatile coupling unit for connecting unpaired electrons ferromagnetically. Typical examples are super-high-spin polycarbenes[1] and poly(triphenylmethyl)s[2] and stable high-spin poly(*N-tert*-butyl nitroxide)s[3] containing *m*-phenylene units as backbones. In some *m*-phenylene and its substituted derivatives carrying two spin centers,[4−7] however, the ground states are found to become singlets ruling out the general rule that the *m*-phenylenes serve as robust ferromagnetic coupling units. By taking advantage of these observations, i.e., singlet ground states of **1**[4] and **2**,[8] we became interested in designing a three-spin system that would show competing interactions and/or spin frustration in the context of molecular magnetism.

When the local spins S_A, S_B, and S_C are placed at the corner of a triangle (Scheme 1) and the exchange coupling represented by J 's between any two of them are ferromagnetic (J_{AB}, J_{BC}, and J_{AC} are positive),[3b,9] nothing is special about the electronic structure of the system; the ground state should be a quartet. On the other hand, when they are antiferromagnetic, the spins would find it difficult to decide which way to align in the ground state.[10,11] For $|J_{AB}| = |J_{BC}| > |J_{AC}|$ or $|J_{AB}| = |J_{BC}| < |J_{AC}|$, the ground state spins will be illustrated as in Scheme 1b,c.

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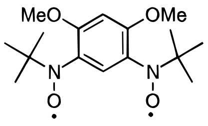

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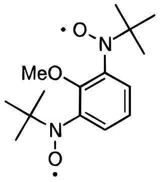

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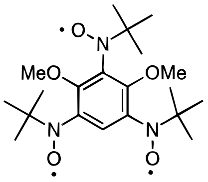

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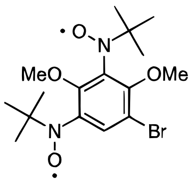

4

For $J_{AB} = J_{BC} = J_{AC} < 0$, by symmetry or accidental degeneracy, the spins will have two kinds of ground states.

A stable triradical, 2,4-dimethoxy-1,3,5-benzenetriyltris(*N*-*tert*-butyl nitroxide) (**3**) was designed by consolidating the chemical formulas of dinitroxide diradicals **1** and **2** into one. Preparation of **3** and analysis of its magnetic properties were performed in this study to understand competing through-bond interactions in an organic triangular spin system. A reference compound, 5-bromo-2,4-dimethoxy-1,3-phenylenebis(*N*-*tert*-butyl nitroxide) (**4**) having a partial structure of **3** was also prepared and its magnetic coupling was investigated.

Experimental Section

General Methods. UV−vis spectra were recorded on a JASCO UVDEC 610C spectrometer. ^{1}H NMR spectra were measured on a JEOL 270 Fourier transform spectrometer using $CDCl_3$ as the solvent and referenced to TMS. FAB mass spectra (FABMS) were recorded on a JEOL JMS-SX102 spectrometer. Melting points were obtained with a MEL-TEMP heating block and are uncorrected. Elemental analyses were performed in the Analytical Center of Faculty of Science in Kyushu University.

X-ray Crystal and Molecular Structure Analysis. All the X-ray data were collected using Cu Kα radiation on a Rigaku AFC5R four-circle diffractometer. Pertinent crystallographic parameters and refinement data are collected in Table 1. The structures of **3** and **4** were solved in *Pnma* (no. 62) and $P\bar{1}$ (no. 2), respectively, by direct methods and refinement converged using the full-matrix least squares of the TEXAN Ver. 1.6 program (Molecular Structure Corp.). All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at standard positions (C−H, 0.96 Å; C−C−H, 109.5°, 120 °, or 180°) and refined isotropically using a rigid model.

EPR Spectra and Magnetic Measurements. EPR spectra were recorded on a Bruker ESP 300 X-band (9.4 GHz) spectrometer equipped with a Hewlett-Packard 5350B microwave frequency counter. An Air Products LTD-3-110 liquid helium transfer system was attached for the low-temperature measurements. Sample solutions were placed in 5 mm o.d. quartz tubes, degassed by three freeze-and-thaw cycles, and sealed.

Magnetic susceptibilities were measured on a Quantum Design MPMS2 SQUID susceptometer. Data were corrected for the magnetization of a sample holder and capsule used and for diamagnetic contributions which were estimated from Pascal's constants.

Materials. Solvents (diethyl ether and toluene) used for the reactions and spectral measurements were all distilled under high-purity N_2 after drying with sodium/benzophenone ketyl. Dichloromethane was distilled under high-purity N_2 after drying with calcium hydride. All reactions were stirred under an atmosphere of N_2. Anhydrous magnesium sulfate was used as the drying agent. Solvents were removed on a rotary evaporator unless otherwise stated. 1,3,5-Tribromo-2,4-dimethoxybenzene was prepared by a procedure reported in the literature.[12]

Scheme 1

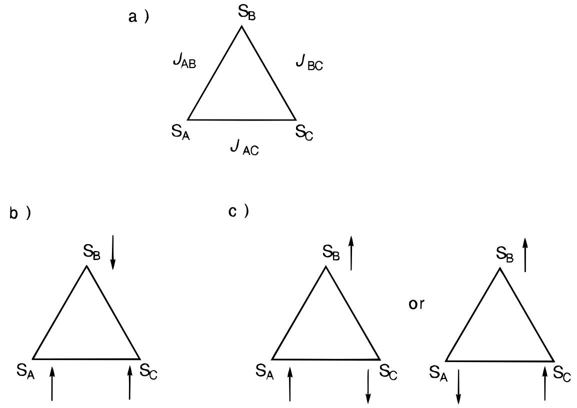

Table 1. Crystallographic Parameters and Refinement Data for Triradical **3** and Biradical **4**

	triradical **3**	biradical **4**
emp form	$C_{20}H_{34}N_3O_5$	$C_{18}H_{25}N_2O_4Br$
form wt	396.51	389.29
cryst color, habit	orange, plate	orange, block
cryst dimens (mm)	0.50 × 0.30 × 0.10	0.70 × 0.50 × 0.50
cryst system	orthorhombic	triclinic
lattice params		
a (Å)	18.200(3)	10.074(1)
b (Å)	19.018(3)	11.2037(8)
c (Å)	6.659(5)	9.3047(7)
α (deg)		96.570(3)
β (deg)		91.604(8)
γ (deg)		63.674(7)
V (Å$^{3)}$	2304(1)	934.7(1)
space group	*Pnma*	$P\bar{1}$
Z	4	2
D_{cald} (g/cm^3)	1.143	1.383
no. of obsns	551 ($I > 3.00\sigma(I)$)	2486 ($I > 3.00\sigma(I)$)
no. of variables	137	209
residuals: R; R_w	0.071; 0.055	0.049; 0.052

2,4-Dimethoxy-1,3,5-benzenetriyl(*N*-*tert*-butyl nitroxide) (3). To the solution of 4.13 g (11.0 mmol) of 1,3,5-tribromo-2,4-dimethoxybenzene in 120 mL of anhydrous ether was added 31 mL (66.0 mmol) of a 2.13 M solution of *tert*-butyllithium in *n*-pentane at −78 °C. After being stirred for 4 h, a solution of 3.1 g (35.6 mmol) of 2-methyl-2-nitrosopropane in 35 mL of anhydrous ether was added dropwise. The reaction mixture was stirred for 1 h at −78 °C and then left overnight at room temperature. After the usual workup, 0.50 g (ca. 11% yield) of crude hydroxylamine containing a small amount of the corresponding triradical was obtained as a brown solid. The obtained mixture was used for the oxidation without separation and purification of the hydroxylamine derivative.

To a solution of 0.10 g of this crude hydroxylamine in 30 mL of anhydrous ether was added 0.17 g of freshly prepared Ag_2O. The suspension was stirred for 2 h and filtered. A red solution was left in a refrigerator and 0.096 g (0.24 mmol, 96%) of red precipitate was collected by filtration. Recrystallization from MeOH−H_2O gave triradical **3** as orange plates. Mp (dec.): 166 −167 °C. UV−vis spectrum (in CH_2Cl_2): λ_{max} 481, 366 (sh), 294 nm. Mass spectrum (Fab, *m*-nitrobenzyl alcohol matrix): *m*/*z* 396 (M^+). Anal. Calcd for $C_{20}H_{34}N_3O_5$: C, 60.58; H, 8.64; N, 10.60. Found: C, 60.55; H, 8.60; N, 10.56.

5-Bromo-2,4-dimethoxy-1,3-phenylenebis(*N*-*tert*-butyl nitroxide) (4). This was prepared in a manner similar to that for triradical **3** using 4 mol equiv of *tert*-butyllithium. Orange bricklike crystals were obtained from *n*-hexane. Mp (dec.): 95−96 °C. UV−vis spectrum (in CH_2Cl_2): λ_{max} 481, 368 (sh), 294, 283 nm. Mass spectrum (Fab,

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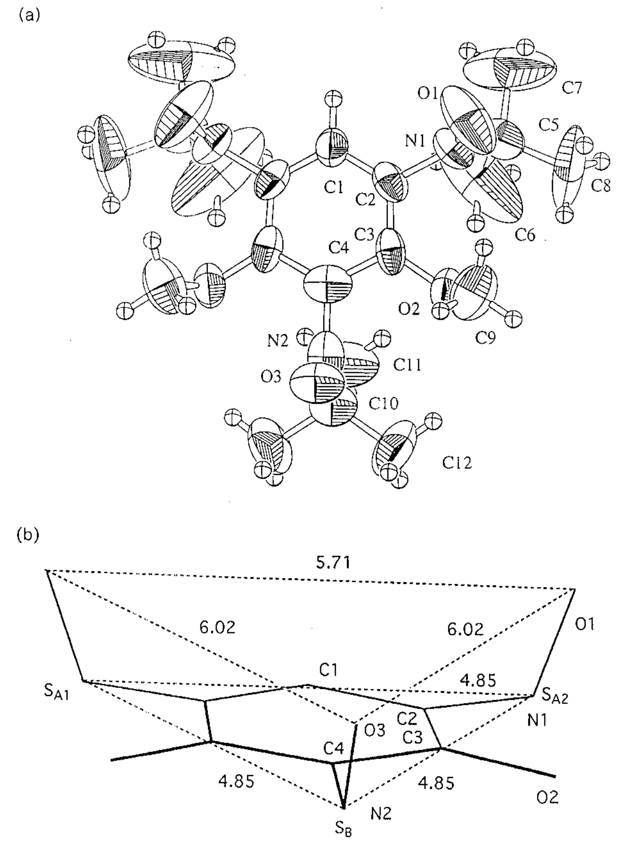
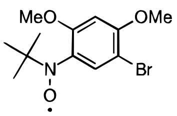


Figure 1. Molecular structure of triradical **3:** (a) ORTEP drawing with a thermal ellipsoid plot at the 30% probability level and (b) a stick model showing distances (Å) between the radical centers (*tert*-butyl and methyl groups are omitted for the sake of clarity).

m-nitrobenzyl alcohol matrix): m/z 392, 390 ($M^+ + H$), 391, 389 (M^+). Anal. Calcd for $C_{16}H_{25}N_2O_4Br$: C, 49.37; H, 6.47; N, 7.20. Found: C, 49.62; H, 6.52; N, 6.98.

Results and Discussions

Preparations of Triradical 3 and Biradical 4. Triradical 2,4-dimethoxy-1,3,5-benzenetriyltris(*N*-*tert*-butyl nitroxide) (**3**) was prepared by lithiation of the corresponding tribromo compound followed by the reaction with 2-methyl-2-nitrosopropane and subsequent oxidation with Ag_2O. The recrystallization from $MeOH-H_2O$ gave orange-brick single crystals of **3**. As a reference compound, diradical 5-bromo-2,4-dimethoxy-1,3-phenylenebis(*N*-*tert*-butyl nitroxide) (**4**) was prepared in a manner similar to the procedure for **3** by using 4 mol equiv of *tert*-butyllithium in place of 6 equiv. In preparation of **4**, the detection of 5-bromo-2,4-dimethoxy-1-(*N*-*tert*-butyl-*N*-oxyamino)benzene (**5**) suggested that the reaction at the 3-position of benzene was faster in the lithiation of bromide than others and nucleophilic reaction with 2-methyl-2-nitrosopropane was the slowest by steric effects of both sides of methoxy groups. Both radicals in solution were relatively persistent at the room temperature, and no change of signal intensity in EPR spectra was observed after 1 week.



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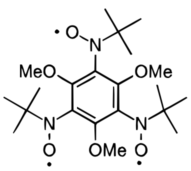

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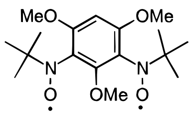

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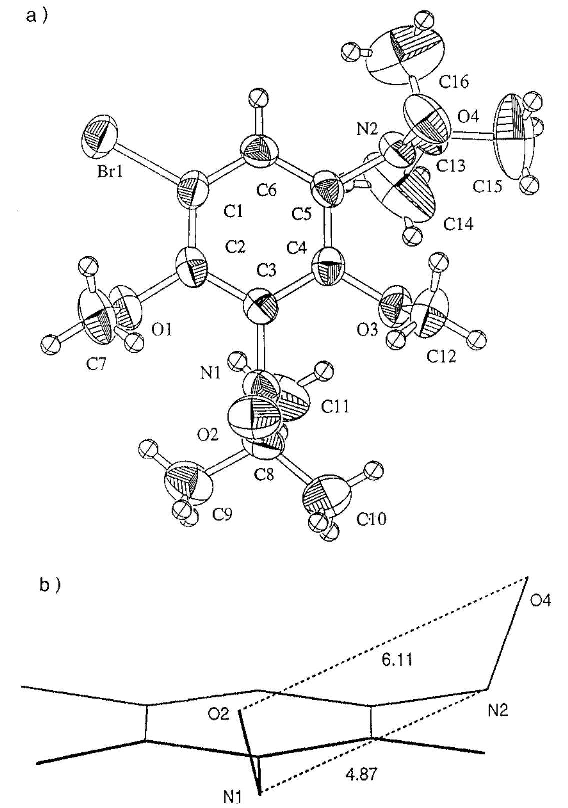

Figure 2. Molecular structure of triradical **4:** (a) ORTEP drawing with a thermal ellipsoid plot at the 30% probability level and (b) a stick model showing distances (Å) between the radical centers (*tert*-butyl and methyl groups are omitted for the sake of clarity).

Synthesis of analogous triradical 2,4,6-trimethoxy-1,3,5-benzenetriyltris(*N*-*tert*-butyl nitroxide) (**6**), which is expected to produce the three-hold symmetrical triangular spin system ($J_{AB} = J_{BC} = J_{AC}$ in Scheme 1a) and exhibit a spin-frustration behavior, was attempted by using 2,4,6-trimethoxy-1,3,5-tribromobenzene in a manner similar to the procedure for **3**. Unfortunately, only 2,4,6-trimethoxy-1,3-phenylenebis(*N*-*tert*-butyl nitroxide) (**7**) was obtained as a main product and **6** remained a target of our synthetic effort.

X-ray Molecular Structure of Triradical 3 and Biradical 4. Crystallographic data and experimental parameters for radicals **3** and **4** are summarized in Table 1. ORTEP drawings and their stick models containing representative bond lengths are given in Figures 1 and 2 for **3** and **4**, respectively. In the molecular structure of **3**, there is an approximate mirror plane passing through the middle nitroxide, S_B, and perpendicular to the benzene ring. The three nitroxide radicals, two S_A's and one S_B, have large dihedral angles of 90° and 79° for S_B and S_A, respectively, with respect to the benzene ring in all-syn conformation.[13] The average distances between two nitrogens and two oxygens are 5.44 and 5.28 Å for $r(S_AS_B)$ and $r(S_AS_A)$, respectively, to make an isosceles triangular three-spin system (Figure 1b) as expected.

As shown in Figure 2, the molecular structure of biradical **4** has a similar *syn* conformation; the corresponding dihedral angles are 79° and 83° for $S_{A'}$ and $S_{B'}$, respectively, and the corresponding average distance $r(S_{A'}S_{B'})$ between the nitroxide radicals is 5.49 Å.

Magnetic Properties of Triradical 3 and Biradical 4. A. In EPR Measurements. An X-band EPR spectrum of

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[13] In biradical **1**,[4] the two nitroxide groups are in the syn conformation and their dihedral angles with the benzene ring plane and distance, $r(S_AS_A)$, between them are 65.1, 75.3°, and 5.13 Å, respectively.

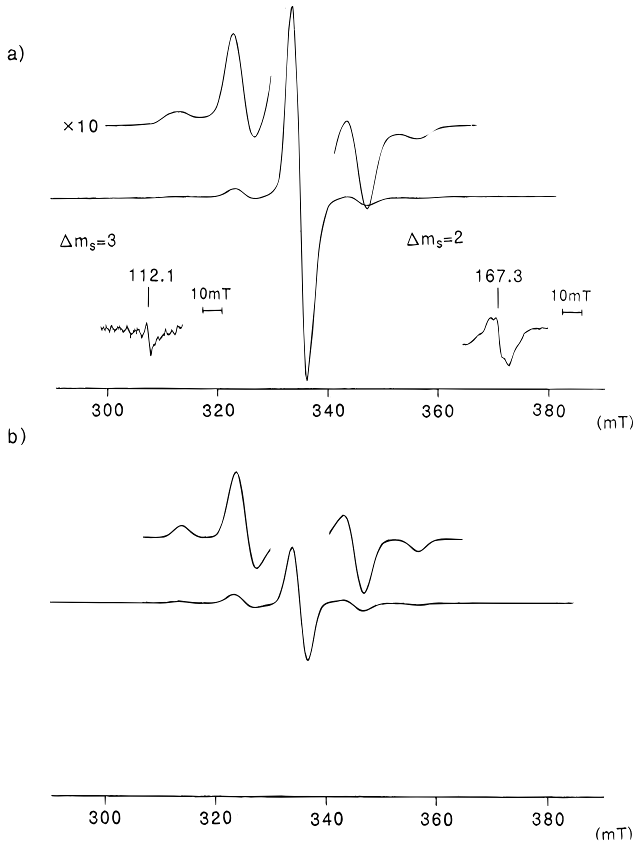

Figure 3. (a) X-band EPR (9.411 GHz) spectrum of triradical **3** in frozen toluene at 10 K. (b) Simulated spectrum for a randomly oriented quartet species.

triradical **3** in toluene solution at room temperature showed one broad signal with $\Delta H_{pp} = 25$ G at $g = 2.0064$. In the corresponding spectrum of **3** in frozen solution at 6.5 K (Figure 3a), a fine structure characteristic of a randomly oriented quartet species was observed at $g = 2.006$ in addition to signals ($g = 4.019$ and 6.035) due to $\Delta m_s = 2$ and 3 transitions, respectively.

The quartet spectrum was simulated (Figure 3b)[14] to afford $g = 2.0062$ and zero-field splitting parameters $|D/hc| = 0.010$ and $|E/hc| = 0.0004$ cm^{-1}. The simulation is, however, only partly satisfactory in that the central signal of the observed five-line fine structure is too strong. Overlap of a signal due to a doublet species is suggested.[15] A doublet state produced by the exchange interaction among the three radical centers in **3** is more reasonably postulated to be responsible for the signal rather than the contribution of a monoradical impurity. Temperature dependence of the intensity of the signal at $g = 4.019$ due to the $\Delta m_s = 2$ transition in the range 6.5−100 K revealed that the plot of signal intensity vs inverse temperature below 10 K deviated slightly downward from a linear relationship, suggesting that the quartet is thermally populated under these frozen solution conditions and the energy gap with the ground doublet state(s) may be small.[16]

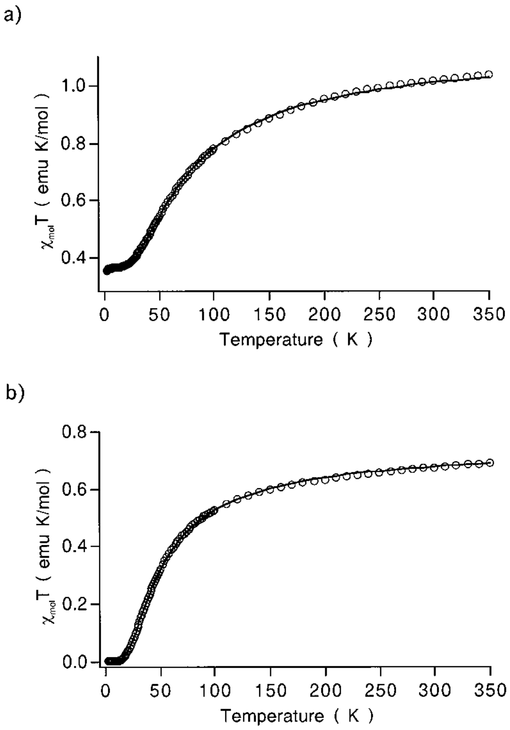

Figure 4. Temperature dependence of the molar magnetic susceptibility (χ_{mol}) as expressed by $\chi_{mol}T$ vs T plots for (a) triradical **3** and (b) biradical **4**. The solid curves are theoretical ones as described in text.

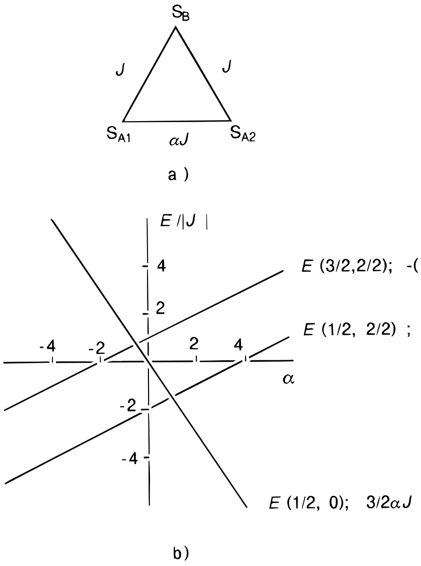

Figure 5. (a) Illustration of an isosceles triangular three-spin model for triradical **3** and (b) variation of the spin state energies with α.

The EPR spectrum for **4** in frozen toluene solution showed characteristic triplet signals with $|D/hc| = 0.016$, and $|E/hc| \cong 0.0$ cm^{-1} in addition to a signal ($g = 4.014$) due to the $\Delta m_s = 2$ transition.

B. In SQUID Measurements. Magnetic susceptibilities of crystalline samples of triradical **3** and biradical **4** were measured on a SQUID susceptometer/magnetometer in the temperature range 2−350 K at constant fields of 200 and 500 mT, respectively. Temperature dependence of the molar magnetic susceptibility (χ_{mol}) for both radicals are shown in Figure 4.

The $\chi_{mol}T$ value of **3** was 1.039 emu K mol^{-1} at 350 K. As the temperature was decreased, the values gradually decreased until 16 K, reached a constant value of $\chi_{mol}T = 0.365$ emu K mol^{-1} in the range 16−4 K, and started to decrease again below 4 K. The observed value of 0.365 emu K mol^{-1} at low

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[14] The simulation of the EPR fine structure was performed by using a program based on the second-order perturbation theory and provided by Professors K. Ito and K. Takui of Osaka City University.

[15] In an EPR spectrum of a sample of **3** doped in poly(vinyl chloride) (PVC) film (**3**:PVC = 1:200 w/w) prepared under conditions similar to those for the recrystallization, a shoulder was more clearly observed for the central signal and the signal intensity due to the quartet species vs 1/T plot did not obey Curie's law.

[16] The observed discrepancy of thermal behavior of **3** obtained from EPR spectrometry and SQUID susceptometry may be explained by the difference of conformation in the crystalline state and solid solutions; in the latter, the dihedral angle between the planes of nitroxide radicals and benzene ring might be smaller.

temperature is consistent with a theoretical value of 0.374 emu K mol^{-1} for a spin-only magnetic moment with $S = {}^{1}/_{2}$, suggesting that the ground state must be a doublet state.

In order to understand these magnetic interactions quantitatively, an isosceles triangular three-spin model (Figure 5a) suggested by the X-ray crystal structure analysis of **3** was applied to the $\chi_{\mathrm{mol}}-T$ plot. The Heisenberg spin Hamiltonian

$$H = -2J(S_{A1}S_B + S_BS_{A2} + \alpha S_{A1}S_{A2}) \qquad (1)$$

for such a system gives an energy diagram (Figure 5b) consisting of two doublet and one quartet states when J is negative. The nature of ground state spin in this system depends on the α value, $\alpha > 1$ or < 1, as illustrated in Scheme 1a,c ($S_A = S_{A1}$, $S_C = S_{A2}$), respectively. When $\alpha = 1$, this system becomes a symmetrical triangular one and two doublet states are degenerated. As expected from Figure 5b, however, eq 2[17] derived

$$\chi_{\mathrm{mol}}T = \frac{Ng^2\mu_B^{\,2}}{4k_B}\,\frac{1 + \exp(2(\alpha - 1)J/k_BT + 10\exp(1 + 2\alpha)J/k_BT}{1 + \exp(2(\alpha - 1)J/k_BT + 2\exp(1 + 2\alpha)J/k_BT}\,\frac{T}{T - \theta} \qquad (2)$$

from the model has two solutions: one for $0 < \alpha < 1$ and the other for $1 < \alpha < 4$.

Actually, eq 2 was fitted to the experimental data to give two sets of best-fit negative J's: $J/k_B = -22.31 \pm 0.53$ K, $\alpha = 2.29 \pm 0.08$, $\theta = -0.18 \pm 0.01$ and $J/k_B = -41.46 \pm 0.23$ K, $\alpha = 0.31 \pm 0.02$, $\theta = -0.18 \pm 0.01$. The theoretical curve is shown by a solid curve in Figure 4a. The $\chi_{\mathrm{mol}}T-T$ plot for biradical **4** is shown in Figure 4b and was simulated by a Bleaney−Bowers-type equation[17] to give the best-fit parameters: $g = 2.0058$, $J/k_B = -39.65 \pm 0.18$ K, $\theta = -9.66 \pm 0.24$ K, which is represented by a solid curve in Figure 3b.

While the ground-state spin in an isosceles triangular triradical **3** in the solid state could not be determined uniquely by fitting of eqs 1 and 2 to the experimental data, the J/k_B value of −41.5 K is closer to −39.7 K for the reference compound **4**, suggesting that the α value might be 0.31 (see Scheme 1b).[16] If this is the case, stronger $S_{A1}-S_B$ and $S_{A2}-S_B$ antiferromagnetic interactions are concluded to polarize $S_{A1}-S_{A2}$ ferromagnetically, providing the first demonstration of the organic triradical showing competing interactions.

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Supporting Information Available: X-ray crystallographic data for triradical **3** and biradical **4** including tables of atomic coordinates, bond angles, and bond lengths (32 pages). See any current masthead page for ordering and Internet access instructions.

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[17] In eq 2, all the symbols have their usual meanings and $g = 2.0066$ as determined by the EPR spectrum of a powder sample of **3**.

[18] Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451. For fitting to the experimental data, $g = 2.0058$ as obtained by the EPR spectrum of a powder sample of **4**.