Tris[*p*-(*N*-oxyl-*N*-*tert*-butylamino)phenyl]amine, -methyl, and -borane Have Doublet, Triplet, and Doublet Ground States, Respectively

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Abstract: *N*,*N*,*N*-Tris[*p*-(*N*-oxyl-*tert*-butylamino)phenyl]amine (**N**) was obtained as dark violet plates by lithiation of tris(4-bromophenyl)amine, followed by reaction with 2-methyl-2-nitrosopropane and oxidation of the resulting tris(hydroxyamine) with Ag_2O. An X-ray crystal and molecular structure analysis of the monoclinic single crystal with space group *Cc* showed that it has neither C_3 symmetry nor zwitterionic quinonoid structure. An EPR spectrum in MTHF solution at room temperature consisted of seven lines ($a_N = 4.06$ G (3N) at $g = 2.0058$). The temperature dependence of the magnetic susceptibility data on **N** in the range 2−300 K was analyzed in terms of a triangular coupling model for three $S = 1/2$ spins to give a set of best-fit parameters which placed a doublet state as the ground state with a quartet state lying 559 K ($= 1.11$ kcal mol^{-1}) above it. B3LYP/6-31G*//B3LYP/6-31G computations were performed on both spin states of a model molecule (**N′**) in which all three *N*-*tert*-butyl groups in **N** were replaced with *N*-methyl groups. The doublet state was found to be more stable than the quartet state by 0.84 kcal mol^{-1}. Tris[*p*-(*N*-oxyl-*tert*-butylamino)phenyl]methyl (**C**) gave a monoclinic single crystal with space group *Cc* (no. 9) and has been shown to have a benzoquinoneimine *N*-oxide type diradical structure. Temperature dependence of its magnetic susceptibility showed that **C** has a triplet ground state with a singlet state lying 410 K above the triplet. Reactions of the corresponding organolithium compounds with $BF_3 \cdot OEt_2$ were not applicable to give tris[4-(*N*-oxyl-*tert*-butylamino)phenyl]borane (**B**) but its 2,2′,2′′,6,6′,6′′-hexamethyl derivative (**B′**). In the trigonal crystal with space group $R\bar{3}$ (no. 148), the three benzene rings are tilted by 49.2° with respect to the valence plane of the boron atom. The magnetic susceptibility data on **B′** were consistent with a doublet ground state with an energy gap to a quartet state by 9.9 K ($= 0.0197$ kcal mol^{-1}). All the results together with ab initio MO studies are consistent with a picture that the ground spin states of title compounds **N**, **C**, and **B** are doublet, triplet, and doublet, respectively. The electronic structures are explained qualitatively by *p*-(*N*-oxyl-*tert*-butylamino)phenyl homologues of $(\bullet H_2C)_3X$ in which X = N, C•, and B atoms, and two, one, and no π-electrons are contained, respectively.

Introduction

Studies of *N*,*N*,*N*-tris[*p*-(*N*-oxyl-*N*-*tert*-butylamino)phenyl]amine, -methyl, and -borane (**N**, **C**, and **B**, respectively) have 2-fold significance. First, organic free radicals having two or more basic coordinating centers serve as bridging ligands for magnetic metal ions to make hybrid-spin chains or networks consisting of organic 2p and metal 3d spins by self-assembly.[1−3] Thus bis(hexafluoroacetylacetonato)manganese(II) with triplet bis- and quartet tris-aminoxyl radicals formed complexes in which spins ordered in the range 3.4−46 K.[3] New polyradicals having aminoxyl radicals arranged trigonally in cross-conjugation are of importance in constructing high T_C 2p−3d hybrid spin magnets.[4] To increase basicity of the aminoxyl oxygen

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10.1021/ja9920819 CCC: $19.00

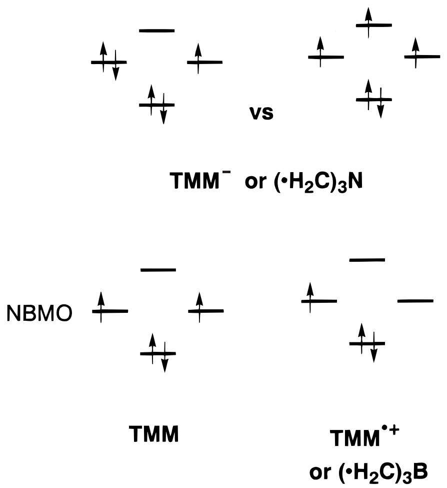
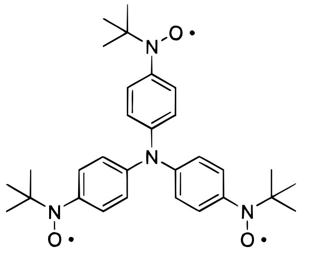


Figure 1. Ground-state electron configuration in the basic structural units of **N**, **C**, and **B**.

atoms serving as ligating sites, it was deemed worthwhile to synthesize tris[*p*-(*N*-oxyl-*tert*-butylamino)phenyl]amine (**N**).[5]



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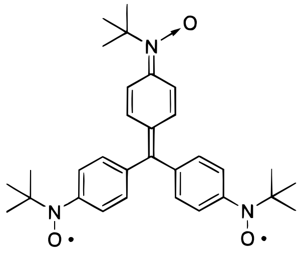

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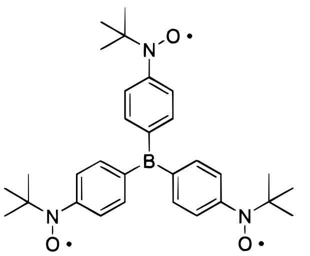

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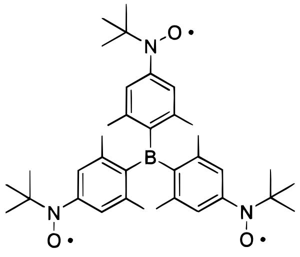
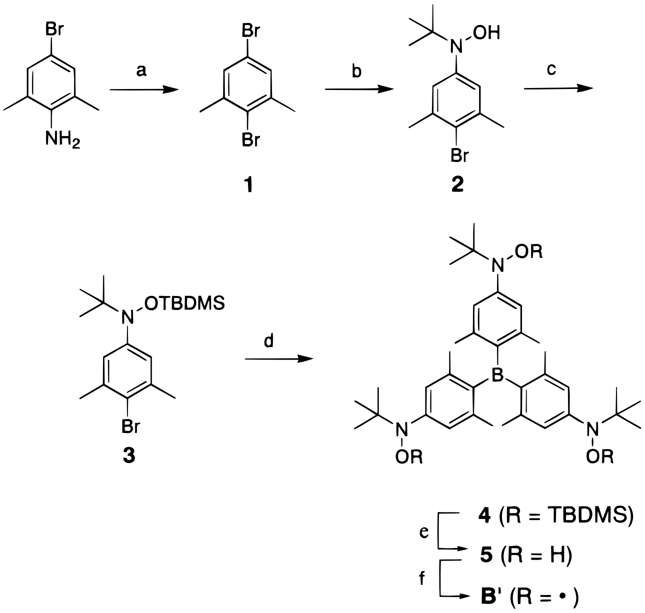


B'

Second, simplified models of **B**, **C**, and **N** by truncation of three phenylene units and replacement of the *N-tert*-butylaminoxyls with •H_2C radicals may be regarded as trimethylene derivatives $(\bullet H_2C)_3X$ (X = B, C•, and N) (Figure 1).[6] The carbon analogue is triplet trimethylenemethane (TMM). Since the corresponding amine has one more π-electron than the methane, the former is expected to become isoelectronic with the anion radical of the latter and therefore a doublet monoradical. The π-electron is one less in borane analogue **B** which corresponds to the cation radical of TMM. It is of great interest to see if such a simplified picture is applicable to the understanding of the ground-state electron configuration of **N**, **C**, and **B**.

Scheme 1[a]



[a] Reagents and conditions: (a) $NaNO_2$, concd H_2SO_4, CuBr, aq HBr, 53%; (b) Mg, 1,1-dimethylnitrosoethane, Et_2O, 31%; (c) *tert*-butyldimethylchlorosilane, imidazole, DMF, 97%; (d) *n*-BuLi, Et_2O, BF_3•Et_2O, 13%; (e) AcOH, THF, 54% (f) Ag_2O, CH_2Cl_2, 98%.

Results and Analyses

Synthesis. 1. Triradical N. Tris(4-bromophenyl)amine was lithiated with excess *tert*-butyllithium and treated with 2-methyl-2-nitrosopropane to give the corresponding tris(hydroxyamine). Triradical **N** was obtained by oxidation of this hydroxyamine derivative with Ag_2O in CH_2Cl_2.[5]

2. Diradical C. Diradical **C** was prepared as described previously.[4]

3. Tris[2,6-dimethyl-4-(*N*-oxyl-*tert*-butylamino)phenyl]borane B′. *O*-Silylation of *N*-(*p*-bromophenyl)-*N*-*tert*-butylhydroxyamine was followed by lithiation with *tert*-butyllithium. The organolithium compound thus obtained was allowed to react with boron trifluoride etherate to give a complex mixture in which the expected triarylborane derivative was not found. Therefore, our recourse was to prepare its 2,2′,2″,6,6′,6″-hexamethyl derivative **B′**. The synthesis outlined in Scheme 1 started from commercially available 4-bromo-2,6-dimethylaniline which was converted to **1**. The Grignard reagent prepared from **1** and 1.0 equiv of magnesium was coupled with 2-methyl-2-nitrosopropane to give **2**. After protection of the hydroxyamino group with a *tert*-butyldimethylsilyl group in quantitative yield, **3** was lithiated with *tert*-BuLi and coupled with 1/3 equiv of BF_3•Et_2O to give triarylborane **4**. **B′** was obtained by means of the desilylation of **4** with acetic acid in THF followed by the oxidation with Ag_2O in dichloromethane.

X-ray Crystal and Molecular Structure. Crystallographic data and experimental parameters for radicals **N**, **C**, and **B′** are summarized in Table 1.

1. Triradical N.[5,7] A single crystal of **N** for an X-ray diffraction measurement was obtained by slow evaporation of a *n*-heptane−dichloromethane solution of **N**. The molecular structure of **N** is reproduced in Figure 2. The molecule has no

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[5] A preliminary account of this paper appeared in Itoh, T.; Matsuda, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1791.

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[7] The crystallographic data (excluding structure factors) for the structure have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101263. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12, Union Rode, GB- Cambridge CB2 1EZ, UK (fax: int. code +(44)1233-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic Parameters for N, C, and B′

	N	**C**	**B′**
formula	$C_{30}H_{39}N_4O_3$	$C_{31}H_{39}N_3O_3$	$C_{36}H_{51}B_1N_3O_3$
fw	503.66	501.68	584.63
crystal color	dark violet	reddish purple	reddish brown
crystal description	plate	prismatic	prismatic
crystal system	monoclinic	monoclinic	trigonal
space group	*Cc* (no. 9)	*Cc* (no. 9)	$R\bar{3}$ (no. 148)
a/Å	13.11(1)	13.35(1)	19.777(2)
b/Å	23.081(5)	23.542(4)	
c/Å	10.410(2)	10.134(2)	16.393(3)
β/deg	116.80(5)	117.72(1)	
V/Å^3	2811(2)	2820(1)	5552.9(7)
Z	4	4	8
D_{calcd}/(g cm^{-3})	1.190	1.153	1.190
no. of reflections	2874	1923	2630
obsd data	2461	1597	1519
	($I > 3.00\sigma(I)$)	($I > 1.50\sigma(I)$)	($I > 3.00\sigma(I)$)
R	0.039	0.058	0.050
R_w	0.054	0.055	0.072

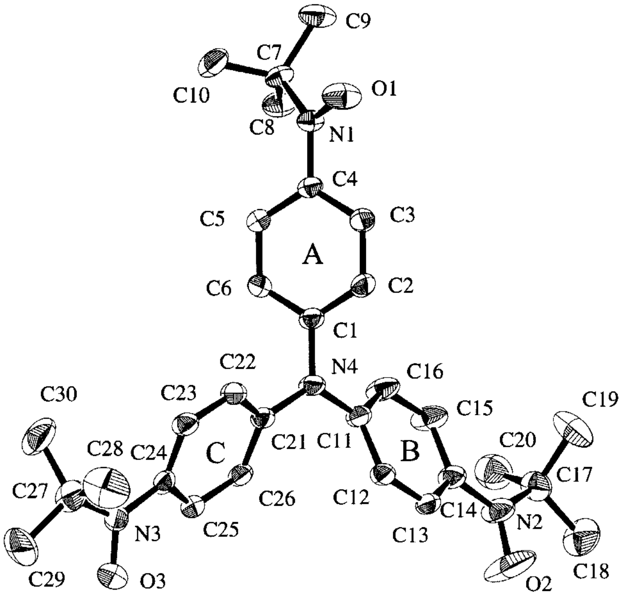


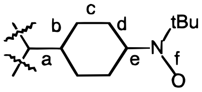
Figure 2. ORTEP drawing of **N** with thermal ellipsoid plot at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): N4−C1 1.412(4), N4−C11 1.421(4), N4−C21 1.428(4), N1−O1 1.291(3), N2−O2 1.285(4) N3−O3 1.294(3), N1−C4 1.417(4), N2−C14 1.414(4), N3−C24 1.413(4), C1−N4−C11 122.1(2), C1−N4−C21 118.9(2), C11−N4−C21 118.7(2), O1−N1−C4 116.9(2), O2−N2−C14 116.9(3), O3−N3−C24 116.6(2).

3-fold axis passing through the central nitrogen atom. Intramolecular distances between the oxygen atoms of the aminoxyl groups are 9.73 Å (O1−O2), 11.30 Å (O2−O3), and 11.41 Å (O3−O1), whereas the shortest intermolecular distance between O1 and O2′ of neighboring molecules is 4.84 Å.[8] N4 is located only 0.04 Å out of the C1C11C21 plane from which the three *p*-phenylene rings labeled A, B, and C are tilted by 29.9°, 34.3°, and 57.3°, respectively. The C−C bond lengths of the *p*-phenylene rings are not very much indicative of a potential contribution of quinonoid structures. The bonds connecting the aminoxyl nitrogen atom with the benzene ring are in the range 1.41−1.42 Å and only slightly shorter than 1.43−1.45 Å in typical phenylaminoxyls[9] (Table 2).

Table 2. Comparison of the Bond Lengths (Å) and Angles (deg) in **N**[a])

ring	A	B	C
a	1.412	1.421	1.428
	(1.425)	(1.426)	(1.427)
	[1.427]		
b[b]	1.400	1.393	1.400
	(1.410)	(1.409)	(1.409)
	[1.409]		
c[b]	1.380	1.383	1.388
	(1.391)	(1.391)	(1.391)
	[1.393]		
d[b]	1.405	1.403	1.400
	(1.411)	(1.410)	(1.410)
	[1.409]		
e	1.417	1.414	1.413
	(1.405)	(1.407)	(1.407)
	[1.409]		
f	1.291	1.285	1.294
	(1.323)	(1.322)	(1.322)
	[1.322]		
ϕ	29.9	34.3	57.3
	(23.9)	(26.8)	(46.7)
	[33.6]	[36.6]	[45.7]

[a] The bond lengths and angles for ab initio calculated doublet and quartet states are in () and [ ], respectively. In the last case near *C*3 symmetry does not reveal meaningful difference in bond lengths among the rings. [b] Average of two nearly equivalent bond lengths on the same ring.



2. Diradical C. A single crystal of **C** for an X-ray diffraction measurement was obtained by recrystallization from Et_2O at −30 °C. The crystal structure of **C** is reproduced in Figure 3. The molecule has no 3-fold axis passing through the central carbon atom. Bond alternation was clearly found on two *p*-phenylene rings B and C: 1.417 Å vs 1.364 Å on an average, while ring A does not have such a tendency (1.396 Å vs 1.388 Å on an average) (see Table 3). The bond connecting the aminoxyl nitrogen atom with the benzene ring is normal 1.429 Å for ring A, but shorter (1.415 and 1.382 Å) for rings B and C.[9] Rings B and C are more coplanar with the plane defined by the C2C12C22 plane (27° and 24°, respectively) and the dihedral angles of aminoxyl moieties with the phenylene rings to which

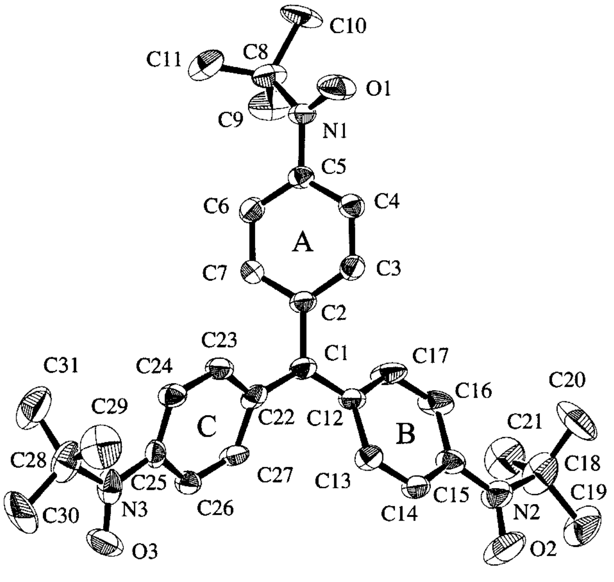


Figure 3. ORTEP drawing of **C** with a thermal ellipsoid plot at a 50% probability level. The hydrogen atoms are omitted for clarity.

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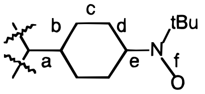
[8] Symmetry operation: *x*, -*y*, 1/2 + *z*.

[9] (a) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847. (b) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, *J. Phys. Chem.* **1993**, *97*, 13267. (c) Hanson, A. W. *Acta Crystallogr.* **1953**, *6*, 32.

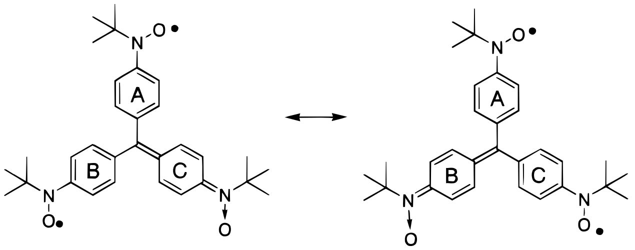
Table 3. Comparison of Bond Length (Å) in C

	ring		
	A	B	C
a	1.492	1.427	1.425
b[a]	1.402	1.427	1.419
c[a]	1.388	1.366	1.363
d[a]	1.392	1.418	1.406
f	1.283	1.296	1.293
e	1.429	1.415	1.382

[a] Bond lengths are averaged over assumed symmetry.



Scheme 2. Quinonoidal Resonance Structures Extending over Two Rings B and C in C at Least in the Solid State



they are attached are 26.9° (ring A), 2.8° (ring B) and 9.3° (ring C). It is suggested that, whereas ring A is tilted by 50° and there is no bond alternation detected on this ring, the bis(aminoxyl)methylenecyclohexa-2,5-dienone *N-tert*-butylimine *N*-oxide structure is in resonance between rings B and C in crystals (Scheme 2).

3. Triradical B′. A single crystal of **B′** for an X-ray diffraction measurement was obtained by recrystallization from *n*-hexane/CH_2Cl_2 (2:1) at −30 °C. The molecular structure of **B′** is reproduced in Figure 4. In contrast with the above two radicals, triradical **B′** has a crystallographic 3-fold symmetry 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 neighboring molecules is 3.99 Å (Figure 5).

EPR Spectra in Fluid and Solid Solutions. 1. 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 (Figure 6), 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 ($a_N = 4.06$ G), six equivalent *meta*-hydrogens ($a_H = 0.8$ G), six equivalent *ortho*-hydrogens ($a_H = 0.4$ G), and a nitrogen atom ($a_N = 0.5$ G).

In a 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 $|E/hc| = 0$. The *D* value corresponds to a mean distance of 11.2 Å for the unpaired electrons.[10] No signal arising from the $\Delta m_s = 2$ or 3 transitions were 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 to determine rigorously whether the ground state is quartet, doublet, or degenerate quartet/doublet states.

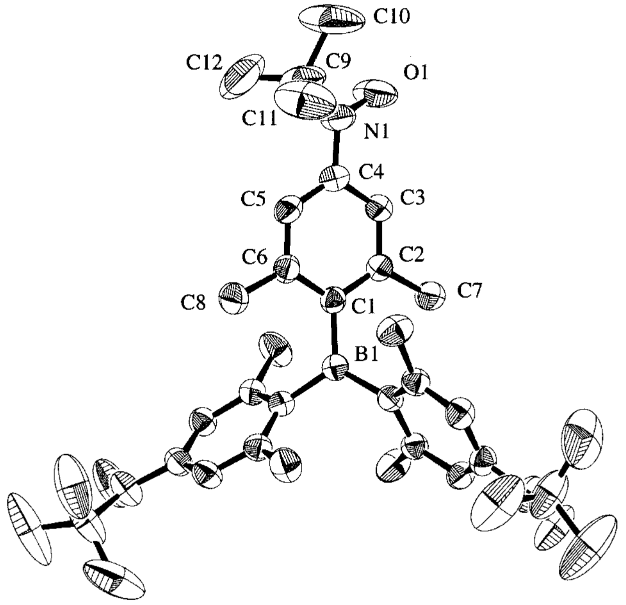


Figure 4. ORTEP drawing of **B′** with thermal ellipsoid plot at 50% probability level. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1−C1 1.573(2), C1−C2 1.417(3), C2−C3 1.383(3), C3−C4 1.387(3), C4−C5 1.388(3), C5−C6 1.377(3), C6−C1 1.417(3), C2−C7 1.508(3), C6−C8 1.516(3), C4−N1 1.416(3), N1−O1 1.266(2), B1−C1−C2 121.0(2), B1−C1−C6 121.9(2), C1−C2−C3 120.6(2), C2−C3−C4 121.5(2), C3−C4−C5 118.3(2), C4−C5−C6 121.5(2), C5−C6−C1 120.8(2), C6−C1−C2 117.1(2), O1−N1−C4 117.3(2), N1−C4−C3 118.0(2), N1−C4−C5 123.6(2).

2. 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.[4]

3. 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.

Molar Paramagnetic Susceptibility. 1. Triradical N. The magnetic susceptibility data of **N** were acquired on a SQUID susceptometer/magnetometer. The temperature dependence of the molar paramagnetic susceptibility (χ_{mol}) at 5000 G is given as a $\chi_{mol}T$ vs T plot in Figure 7. At 300 K, the observed $\chi_{mol}T$ value amounts to 0.695 emu K mol^{-1}, a value considerably smaller than the theoretical one of 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 ca. 0.375 emu K mol^{-1} from 100 down to 20 K. This constant value is typical of a paramagnetic species having 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.

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(10) (a) Lakcharst, G. R.; Rosantsev, E. G. *Izv. Akad. Nauk SSSR Ser. Khim.* **1968**, *8*, 1708. (b) Veciana, J.; Rovira, C.; Ventosa, N.; Crespo, M. I.; Palacio, F. *J. Am. Chem. Soc.* **1993**, *115*, 57. (c) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 2396.

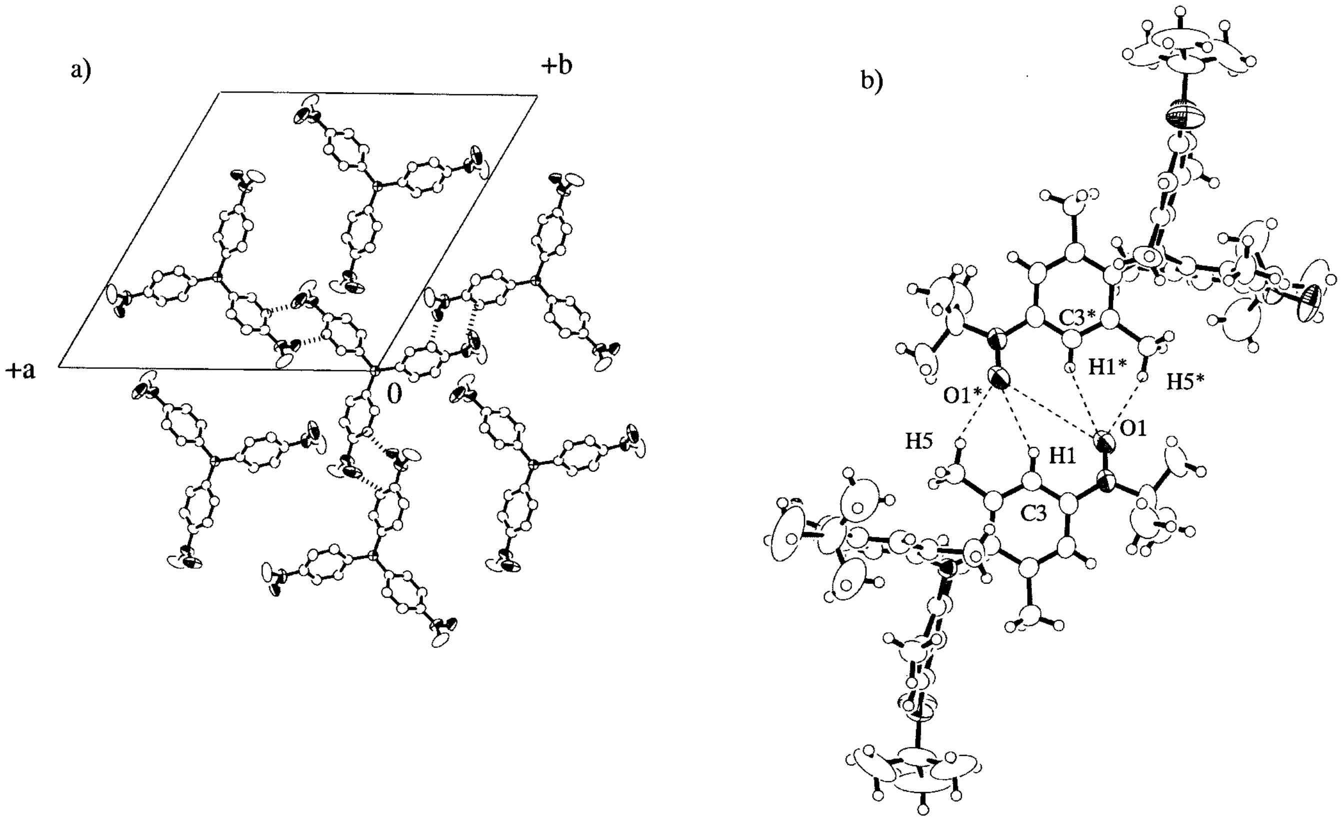

Figure 5. (a) Projection along the *c*-axis of **B′**. The methyl groups are omitted for clarity. (b) Crystal structures of **B′** in which the nearest molecules are shown. Broken lines indicate the short contacts between the neighboring molecules: O1−H1* 2.66 Å, O1−O1* 3.99 Å, O1−H5* 2.45 Å.

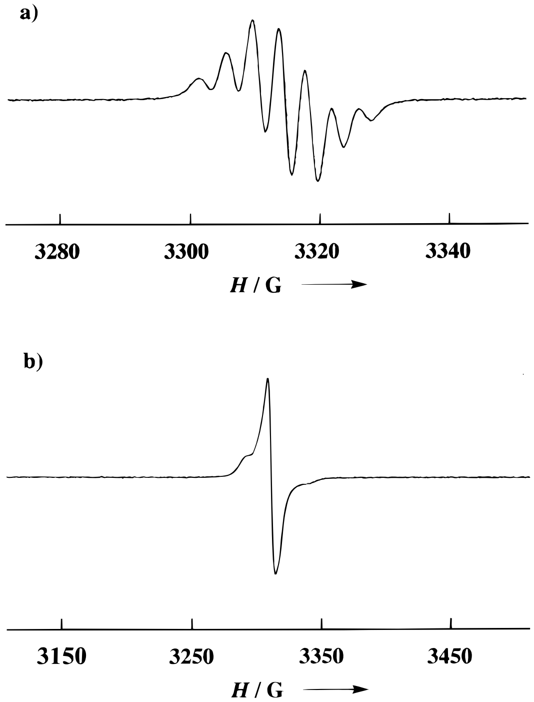

Figure 6. X-band EPR spectra of **N** in 10 mM MTHF solution (a) at room temperature (9.327 GHz) and (b) 8.5 K (9.330 GHz).

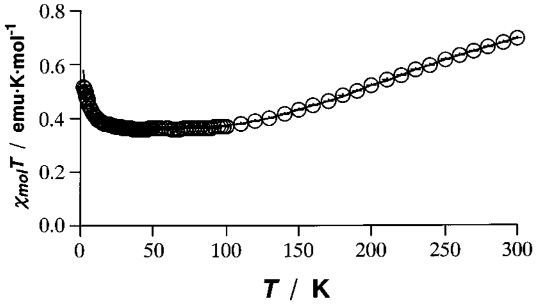

Figure 7. Temperature dependence of $\chi_{\mathrm{mol}}T$ of triradical **N** at a constant field of 5000 Oe. The solid curve is the theoretical one described in text.

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 possible intermolecular coupling would be considerably diminished. Under these conditions, the $\chi_{\mathrm{mol}}T$ 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.[6] 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.

The magnetic interaction in a nonsymmetric triangular triradical system can be written by spin Hamiltonian of eq 1, where J_{ij} is the exchange coupling parameter between $\mathbf{S_i}$ and $\mathbf{S_j}$.[11] The molar susceptibility is given by eq 2, where Δ_1 and

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[11] In principle the spin Hamiltonian should contain terms due to the Zeeman, dipole−dipole, and hyperfine 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 ($|J| \gg |a_{\mathrm{N}}|$).

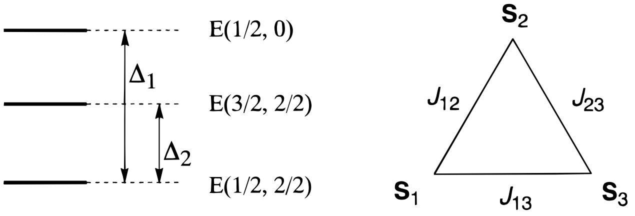

Figure 8. Energy level diagram for the two spin doublets and the spin quartet originating from the interaction of $S_1 = S_2 = S_3 = 1/2$.

Δ_2 are given by eqs 3 and 4 which are energy differences defined as in Figure 8.[12]

$$\mathrm{H} = -2(J_{12}\mathbf{S_1S_2} + J_{23}\mathbf{S_2S_3} + J_{31}\mathbf{S_3S_1}) \tag{1}$$

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

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

$$\Delta_2 = \Delta_1/2 - (J_{12} + J_{23} + J_{31}) \tag{4}$$

A purity factor f was introduced to account for all the experimental errors of weighing a sample, calibration of 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 Js 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 is given by:

$$E(3/2) = -1/2(J_{12} + J_{23} + J_{31}) \tag{5}$$

$$E(1/2) = 1/2(J_{12} + J_{23} + J_{31}) \pm (J_{12}{}^2 + J_{23}{}^2 + J_{31}{}^2 - J_{12}J_{23} - J_{23}J_{31} - J_{31}J_{12}) \tag{6}$$

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 Figure 8). A large standard deviation in Δ_1 makes it unrealistic to determine the exchange coupling parameters Js. It was only by making the following assumptions when numerical values for J were obtained. (1) For a regular triangle which is applicable to a triradical having a 3-fold symmetry axis,[9b] $J = J_{12} = J_{23} = J_{31}$ in eqs 3 and 4, and $J/k_{\mathrm{B}} = -135 \pm 3$ K. Since $\Delta_1 = 0$, the ground doublet state is doubly degenerate.

(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.[9b] 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 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 eqs 3 and 4. If $J_{12} = 0$ for some reasons, then $J_{23} = J_{31} = -171 \pm 2$ K.

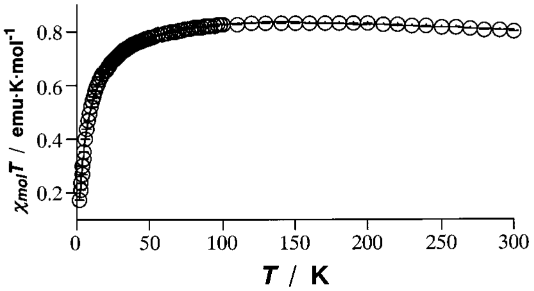

Figure 9. Temperature dependence of $\chi_{\mathrm{mol}}T$ of biradical **C** at a constant field of 5000 Oe. The solid curve is the theoretical one described in the text.

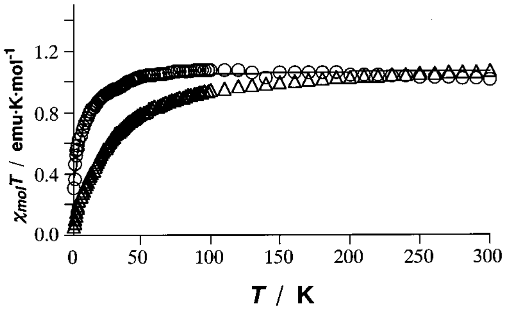

Figure 10. Temperature dependence of χmol$T$ of triradical **B′** in neat crystals (Δ) and 6% PVC film (O) at a constant field of 5000 Oe. The solid curve is the theoretical one described in text.

2. Diradical C. Our new measurements in the present study on crystalline samples of **C** gave $\chi_{\mathrm{mol}}T$ vs T plots as shown in Figure 9. The $\chi_{\mathrm{mol}}T$ value is already 0.80 emu K mol^{-1} at 300 K, suggesting that the ferromagnetic coupling making the two spins to align in parallel between the two unpaired electrons is in the order ~300 K. As the temperature is lowered, the $\chi_{\mathrm{mol}}T$ value increased steadily to reach a maximum of 0.83 emu K mol^{-1} at around 150 K and then decreased continuously. Previously, a limited quality of **C** restricted us from detecting the steady increase of $\chi_{\mathrm{mol}}T$ values with decreasing temperature.[4] Application of Bleaney−Bowers-type equation (eq 7)[13] for an equilibrated singlet−triplet model, with Weiss constant θ for an antiferromagnetic mean molecular field, gave the best fit parameters: $2J/k_{\mathrm{B}} = 410 \pm 10$ K, $f = 0.893 \pm 0.002$, $\theta = 7.375 \pm 0.06$ K.

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

3. Triradical B′. The $\chi_{\mathrm{mol}}T$ 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 $\chi_{\mathrm{mol}}T$ value started to decrease steadily at ca. 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 $\chi_{\mathrm{mol}}T$ in the range 300−50 K was absent (Figure 10). To understand the magnetic interactions more quantitatively, a regular triangle

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[12] (a) Bencini, A.; Benelli, C.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1985**, *24*, 695. (b) Reference 1a, pp 211−228.

[13] Bleany, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

three-spin model suggested by X-ray crystal structure analysis of **B′** was applied to $\chi_{\mathrm{mol}}T$ plot. By assuming that the remaining decrease in $\chi_{\mathrm{mol}}T$ values at temperatures below ca. 50 K is due to intraradical coupling, the $\chi_{\mathrm{mol}}T$ vs 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 6, where all symbols have their usual meaning. The best fit to the observed points was reached by $3J/k_B = -9.9$ K ± 0.3 and $f = 0.956 \pm 0.004$ and $\theta = 0$.

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

Ground doublet states which are doubly degenerate are thus concluded to be more stable than a quartet state by $3J/k_B = 9.9$ K.

Ab Initio Molecular Orbital Studies on N. 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 at the B3LYP/6-31G level of theory on a Gaussian94 program.[14] The optimized structures for which the pertinent bond lengths and angles are given in Table 2 and the Supporting Information have no 3-fold 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 more closer to a C_3 structure. The computed bond lengths and angles agree with those observed 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 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, 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, demonstrating the operation of a superexchange mechanism through the lone pair of electrons on the central nitrogen atom, with two spins on the aminoxyl radical centers coupled antiferromagnetically, with one spin remaining intact.

Discussion

Molecular Structures of N, C, and B′. 1. Triradical N. It was difficult to show from the X-ray crystal structure that the *p*-phenylene rings have a tendency to assume the quinonoid structure, and there are signs of shortened bond lengths for the bonds connecting the aminoxyl nitrogen atoms with the benzene rings (1.43−1.45 Å is typical of phenylaminoxyls).[9] Compared with the carbon analogue **C** where two *p*-phenylene rings exhibit quinonoidal bond alternation by 0.05 Å, any bond alternation is less than 0.02 Å in the rings of **N**. The dihedral angles between the benzene rings and the central trigonal nitrogen plane are somewhat larger for a quinonoid structure. Triradical **N** exhibits a broad absorption band at 450−800 nm ($\lambda_{\max}$ 534 nm, $\epsilon = 5500$). 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.

2. Diradical C. The X-ray crystal structure shows that two *p*-phenylene rings exhibit bond alternation by 0.05 Å, suggesting a contribution of the quinonoid resonance structure as shown in Scheme 2. This resonance structure corresponds to a *p*-phenylene-extended nitronyl nitroxide structure. A strong absorption characteristic of a quinonoid structure is observed at 554 nm, $\epsilon = 20400$.

3. Triradical B′. The X-ray analysis demonstrates that the molecule lies on a crystallographic 3-fold axis, and therefore the boron and the three carbon atoms bonded to it are coplanar. The aryl groups are tilted by 49.2° with respect to the borane valence plane. The torsion angle is almost the same as that found in the trimesitylborane (51.1° and 49.6°).[15] In **B**, which does not have the six aryl methyl groups, the propeller shape must have been a bit flatter as in triphenylborane (35° and 28°).[16]

Magnitude of the Intramolecular exchange couplings in N, C and B′. 1. Antiferromagnetic Coupling in Triradical N. In stark contrast to the ferromagnetic coupling in **C**, the corresponding amine **N** has now been found to have antiferromagnetic coupling. As a result, the ground state is a doublet with a quartet state lying 559 K above the ground state. There are too many parameters (*J*s) to determine for applying a general triangular coupling model to the experimental temperature dependence of paramagnetic susceptibility. If a regular triangle model is applied, $J/k_B = -135$ K. Note that this antiferromagntic coupling is almost comparable in magnitude to the ferromagnetic coupling of $J/k_B = 205$ K in **C**. A superexchange mechanism has been evoked in organic di- and tricarbenes,[17] but there are 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.

Triradical **N** may be regarded as an organic counterpart of bridged trinuclear metal complexes exhibiting the superexchange

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[14] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1992.

[15] Blount, J. F.; Finocchiaro, P.; Gust, D.; Mislow, K. *J. Am. Chem. Soc.* **1973**, *95*, 7019.

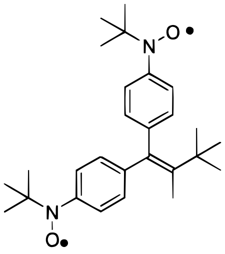
[16] Zettler, F.; Hausen, H. D.; Hess, H. *J. Organomet. Chem.* **1974**, *72*, 157.

[17] (a) Nakamura, T.; Momose, T.; Shida, T.; Sato, K.; Nakazawa, S.; Kinoshita, T.; Takui, T.; Itoh, K.; Okuno, T.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1996**, *118*, 8684. (b) Matsuda, K.; Yamagata, T.; Seta, T.; Iwamura, H.; Hori, K. *J. Am. Chem. Soc.* **1997**, *119*, 8058.

[18] (a) Beckett, R.; Colton, R.; Hoskins, F. F.; Martin, R. L.; Vince, D. G. *Aust. J. Chem.* **1969**, *22*, 2527. (b) Reference 1e, pp 211−228. (c) McCusker, J. K.; Schmitt, E. A.; Hendrickson, D. N. In ref 1c, pp 297−319.

interaction,[18] e.g., $[Cu_3(pao)_3OH]$[18a] and μ^3-oxo-bridged trinuclear Fe(III) acetate complexes.[18c] 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 structure due probably to the crystal field.

2. Strongly Ferromagnetic Coupling in Diradical C. Diradical **C** has a ground triplet state with a singlet state lying by $2J/k_B = 410$ K above the ground state. Matsumoto et al. synthesized 1,1-bis[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]-2-methylpropene **6** similar to **C** and showed that **6** had a small exchange coupling of $2J/k_B = 15.3$ K.[19] Hosokoshi et al. determined much larger exchange coupling of 319 K between nitronyl nitroxide and *tert*-butylaminoxyl radicals in **7**, whereas the exchange coupling between imino nitroxide and *tert*-butylaminoxyl radical in **8** is less than 200 K.[20] A contribution of the quinonoidal resonance forms seems to be important in strengthening the magnitude of the exchange coupling in **C** and **7**. **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.[21]



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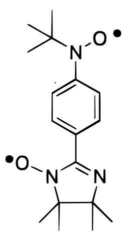

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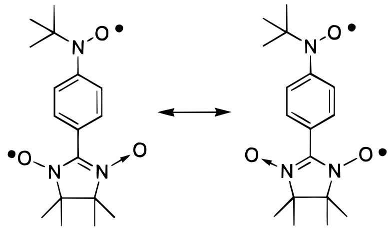

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3. Very Weakly Antiferromagnetic Coupling in Triradical B′. Triradical **B′** has a doubly degenerate ground doublet state which is more stable than a quartet state by $3J/\mathrm{kB} = 9.9$ K. This result is in accord with the expectation based on the Hückel MO calculations. 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 and/or the lack of π electrons on the boron atom. Even though perturbed by six ortho methyl groups, the interaction is through-bonds, and it is likely that the antiferromagnetic interaction would be much stronger in the sterically less-biased **B**.

Conclusions

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 $(\bullet H_2C)_3X$ where X = 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 $CH_2{=}X(CH_2\bullet)_2$ are four for X = C in the carbon analogue, leaving the two electrons for two degenerate orbitals making the triplet electronic configuration most stable (see Figure 1). In the amino analogue, the number of the π-electrons is five, making the two orbitals doubly occupied and leaving only one SOMO. Similarly, in the borane analogue, the π-electron is not supplied by the central atom 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.[22] 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 α spins polarized at the ring carbon atoms attached to the central nitrogen and boron atoms.

The antiferromagnetic coupling in molecular systems is nothing but a partial bonding. The triangular antiferromagnetic coupling among three 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.

Finally let us add some messages pertinent to the design of new molecular based magnets. First, the doublet ground state of the triphenylamine **N** carrying three *N*-*tert*-butylaminoxyl groups on the para positions indicates that not only the topology but also the number of the π-electrons is important in dictating ferromagnetic couplers for molecular-based magnets.[1] Second, if coordinatively doubly unsaturated Lewis-acidic magnetic metal ions having spin *S* form 3:2 polymer complexes with **N** functioning as a bridging ligand, what merit will **N** have over the previously used quartet tris-aminoxyl radicals? Statistically, **N** will behave as a monoradical having three ligating sites. The total number of spins for the *n* units will be $(S - 1/3)_n$ in stead of $(3S - 2/2)_n$ for the equivalent complexes from quartet tris-aminoxyls. For a third, the idea of aligning in parallel the spins of the cation radicals developed by acidic doping of polyarylamines may be in trouble by antiferromagnetic coupling through the unreacted base centers.

Experimental Section

1. Materials. ^1H 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.

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(22) We thank W. T. Borden and E. Brown for disclosing their illuminating results before publication.

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_2O). Powder poly(vinyl chloride) ($n \approx 1100$) used for the preparation of polymer film samples was purchased from Wako Pure Chemical Industries Ltd.

Tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine. To a solution of tris(*p*-bromophenyl)amine (2.0 g, 4.15 mmol) in THF (40 mL) was added *tert*-butyllithium (1.6 M pentane solution, 18.2 mL) at −78 °C. The mixture was warmed to 0 °C over 10 min and then cooled again to −78 °C. 2,2-Dimethylnitrosoethane (1.45 g, 16.6 mmol) was added, and the mixture was warmed to room temperature and stirred for 1 h. Saturated aqueous ammonium chloride and ether were added, the organic layer was separated, washed with water, and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was washed with dichloromethane to afford 0.77 g (37%) of tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine as white powders: mp 153 °C (dec); ^{1}H NMR (270 MHz, DMSO-d_6) $\delta = 8.20$ (s, 3H), 7.92 (d, $J = 8.57$ Hz, 6H), 6.84 (d, $J = 8.57$ Hz, 6H), 1.06 (s, 27H); ^{13}C NMR (67.8 MHz, DMSO-d_6) $\delta = 145.34$, 143.74, 125.29, 122.23, 59.19, 25.99; FAB HRMS: *m*/z calcd for $C_{30}H_{42}N_4O_3$ 506.3257, found 506.3256.

Tris[*p*-(*N*-*tert*-butyl-*N*-oxylamino)phenyl]amine (N). To a solution of tris[*p*-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]amine (100 mg, 0.20 mmol) in dichloromethane (30 mL) was added an excess of freshly prepared Ag_2O (ca. 300 mg), and the mixture was stirred for 2 h. After filtration, the solvent was removed under reduced pressure at ambient temperature. The residue was chromatographed on aluminum oxide using dichloromethane as an eluent and recrystallized from *n*-heptane−dichloromethane (2:1) to give **2** as dark violet plates (86 mg, 87%): mp 190−192 °C; FAB MASS: *m*/*z* 503 [M^+]. Anal. Calcd for $C_{30}H_{39}N_4O_3$: C, 71.54; H, 7.80; N,11.12. Found: C, 7.79; H, 71.44; N, 11.08.

2,5-Dibromo-*m*-xylene (1). To sodium nitrite (9.0 g, 0.130 mole) in concentrated sulfuric acid (100 mL), maintained below 10 °C, was added portionwise a solution of 4-bromo-2,6-dimethylaniline (25.0 g, 0.125 mole) in glacial acetic acid (100 mL). After 1 h, the mixture was added in portions to a vigorously stirred solution of copper(I) bromide (18 g, 0.125 mole) in 48% hydrobromic acid (125 mL) and water (100 mL) at 50 °C. After the addition was complete, the solution was kept at 70 °C for 0.5 h and then diluted with water (1 L). The mixture was extracted with *n*-hexane, washed with water, and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane as an eluent to give **1** as a colorless oil (17.46 g, 53%). ^{1}H NMR (270 MHz, $CDCl_3$) 2.38 (s, 6H), 7.21 (s, 2H).

***N*-(4-Bromo-3,5-dimethylphenyl)-*N*-*tert*-butylhydroxyamine (2).** To the Grignard compound prepared from **1** (17 g, 0.06 mole) and Mg (1.57 g, 0.07 mole) in dry ether (100 mL) was added a solution of 1,1-dimethylnitrosoethane (6.72 g, 0.08 mol) in ether (100 mL) dropwise. After the addition was complete, the mixture was stirred for 0.5 h and then quenched by addition of saturated aqueous ammonium chloride. The mixture was extracted with ether, washed with water, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was washed with *n*-hexane to afford 5.6 g (31%) of **2** as a white powder: mp 117−118 °C (dec).^{1}H NMR (270 MHz, $CDCl_3$) 1.13 (s, 9H), 2.38 (s, 6H), 5.32 (s, 1H), 6.95 (s, 2H).

***N*-(4-Bromo-3,5-dimethylphenyl)-*O*-*tert*-butyldimethylsilyl-*N*-*tert*-butylhydroxyamine (3).** A solution of **2** (5.5 g, 0.02 mol), imidazole (3.2 g, 0.05 mol), and *tert*-butylchlorodimethylsilane (3.0 g, 0.02 mol) in *N*,*N*-dimethylformamide was stirred at 50 °C for 12 h. After dilution with *n*-hexane and water, the organic layer was separated, washed with water, and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane as an eluent to give **3** as a white solid (7.58 g, 97%): mp 53.5−55 °C. ^{1}H NMR (270 MHz, $CDCl_3$) −0.13 (s, 6H), 0.90 (s, 9H), 1.07 (s, 9H), 2.37 (s, 6H), 6.95 (s, 2H).

Tris[2,6-dimethyl-4-(*O*-*tert*-butyldimethylsilyl-*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]borane (4). To a solution of **3** (2.85 g, 7.35 mmol) in ether (15 mL) was added *n*-butyllithium (1.6 M *n*-hexane solution, 4.6 mL) at −78 °C. The mixture was warmed to room temperature over 30 min and then cooled again to −78 °C. A solution of trifluoroboron diethyl ether complex (0.35 g, 2.46 mmol) in ether (10 mL) was added to the mixture, which was then allowed to warm to room temperature and stirred for 1 h. The reaction mixture was quenched by addition of saturated aqueous ammonium chloride, the mixture was extracted with ether, washed with water, and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using *n*-hexane as an eluent to give **4** as a colorless oil (305 mg, 13%). ^{1}H NMR (270 MHz, $CDCl_3$) −0.11 (s, 18H), 0.89 (s, 27H), 1.10 (s, 27H), 1.93 (s, 18H), 6.78 (s, 6H). FAB MASS: *m*/*z* 930 [$M^+ + 1$].

Tris[2,6-dimethyl-4-(*N*-*tert*-butyl-*N*-hydroxyamino)phenyl]borane (5). A mixture of **4** (300 mg, 0.32 mol), glacial acetic acid (2 mL), and THF (10 mL) was stirred at room temperature for 30 min under argon. Dilution with water gave a white precipitate which was collected and washed with water to afford 103 mg (54%) of **5** as a white solid: mp 131−132 °C (dec). ^{1}H NMR (270 MHz, DMSO-d_6) 1.16 (s, 27H), 2.12 (s, 18H), 6.97 (s, 6H), 8.40 (s, 3H). FAB MASS: *m*/*z* 588 [$M^+ + 1$].

Tris[2,6-dimethyl-4-(*N*-*tert*-butyl-*N*-oxyamino)phenyl]borane (B′). To a solution of **5** (103 mg, 0.085 mmol) in dichloromethane (10 mL) was added an excess of freshly prepared Ag_2O (300 mg), and the mixture was stirred for 30 min. After filtration, the solvent was removed under reduced pressure at ambient temperature. The residue was chromatographed on aluminum oxide using dichloromethane as an eluent to give **B′** as a reddish brown powder (100 mg, 98%): mp 180−181 °C (dec). Anal. Calcd for $C_{36}H_{51}B_1N_3O_3$: C, 73.96; H, 8.79; N, 7.19. Found: C, 74.21; H, 9.03; N, 6.87.

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_2Cl_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 Mo Kα radiation ($\lambda = 0.71070$ Å). Indexing was performed from three oscillations which 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 Mo Kα radiation ($\lambda = 0.71070$ Å). The data were collected at a temperature of 23 °C using the $\omega - 2\theta$ 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 non-hydrogen 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′**). The crystal data for these molecules are summarized in Table 2. 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 -3.7×10^{-5} to -6.7×10^{-5} emu G of sample capsules and holding straws used. Contribution of the diamagnetic susceptibility (-1.7×10^{-4} to -2.2×10^{-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.

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.

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Supporting Information Available: X-ray crystal structural data on **C** and **B′**.[7] Computational results: atomic coordinates after structural optimization by B3LYP/6-31G and calculated total energies obtained by B3LYP/6-31G*. This material is available free of charge via the Internet at http://pubs.acs.org.

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