Structure and Magnetic Property of the Organic Triradical with Triazine Skeleton; 2,4,6-Tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}triazine

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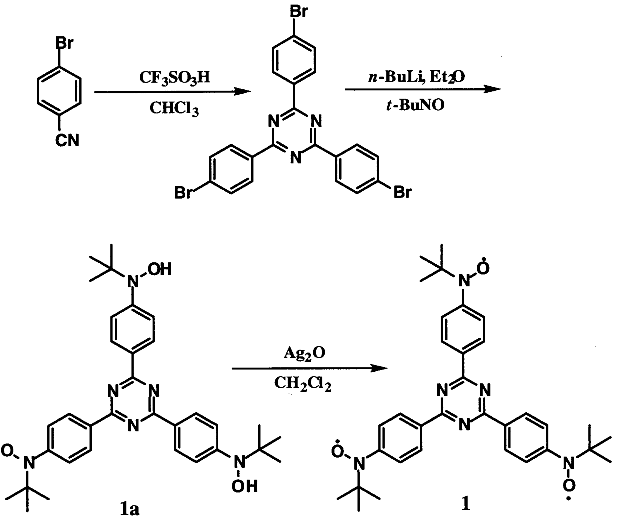
1,3,5-tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}benzene (**2**) is known as a persistent triradical with a quartet ground state. A new triradical with a triazine skeleton was synthesized and characterized. The nitroxide triradical with triazine derivative 2,4,6-tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}-1,3,5-triazine (**1**) exhibited stronger intramolecular ferromagnetic interaction than that with benzene derivative **2**, the magnitude of the interactions depending on the planarity of the structures and/or on the spin density of the center skeletons. The temperature dependence of the magnetic susceptibility values were observed for crystalline **1** in the range of 1.8-350 K. The simulation of an isosceles-triangular exchange coupling model gave 15.3±0.8 K, γ=0.77±0.1.

The design and synthesis of organic molecules with high-spin ground states are current subjects of great importance.[1] When three unpaired electrons are placed in proximity and allowed to interact magnetically, a 1,3,5-Benzenetriyl unit is superior to an *m*-phenylene unit in assembling organic free-radical centers in higher concentrations within a molecule and aligning those spins in parallel for the purpose of designing and constructing very high-spin organic molecules.[1,2] While some 1,3,5-trisubstituted benzene derivatives having nitronyl nitroxides,[3] diarylmethyl radicals,[4] diphenylamine cation radicals,[5] phenylcarbene,[6] and nitrenes[7] as substituents are reported to have high-spin ground states, they are either not persistent under ambient conditions or the intraradical couplings are not strong enough in magnitude. In this paper, 2,4,6-tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}-1,3,5-triazine (**1**) was compared with 1,3,5-tris{*p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl}benzene (**2**), previously reported.[2]

In a dropwise manner, 4.5 g (30 mmol) of CF_3SO_3H was added to a solution of 5.46 g (30 mmol) of 4-bromobenzonitrile in 100 ml $CHCl_3$ at 0 ℃. After stirring for 1 h at 0 ℃, the mixture solution was stirred for 24 h at room temperature. It was then washed with water, and the organic layer was concentrated *in vacuo* to give a colorless solid 2,4,6-tris{*p*-bromophenyl)triazine (85%). Five milliliters (4 equiv.) of 1.6 M *n*-buthyllithium in hexane was added dropwise to a solution of 1.09 g (2 mmol) of 2,4,6-tris{*p*-bromophenyl)triazine in 100 ml THF at -78 °C. After stirring for 1.5 h at -78 ℃, a solution of 697 mg (8 mmol) of 2-methyl-2-nitrosopropane in 10 ml of THF was added to this mixture. Stirring was continued for 4 h at -78 °C and for 1 h at room temperature. The resulting product was 2,4,6-tris{*p*-(*N*-oxy-*N*-*tert*-butylhydroxyamino)phenyl}triazine (**1a**)[8] (a pale-yellow solid, yield: 70%). A mixture of 171 mg (0.3 mmol) of **1a** and 400 mg of Ag_2O in 10 ml of CH_2Cl_2 was stirred for 30 min at room temperature. The filtrate of the reaction mixture was concentrated *in vacuo* to give a red solid which was chromatographed on silica gel with CH_2Cl_2/Et_2O (1:1) as an eluent to give 131 mg (77%) of **1**[9] as red crystals (Scheme 1). The resulting product **1** was a red needle crystal which was stable in air.

An X-ray structure analysis of **1** revealed its space group (tetragonal, $I4_1/a$). The molecular structure[10] is reproduced in Figure 1.



Scheme 1. Synthesis of the triradical **1**.

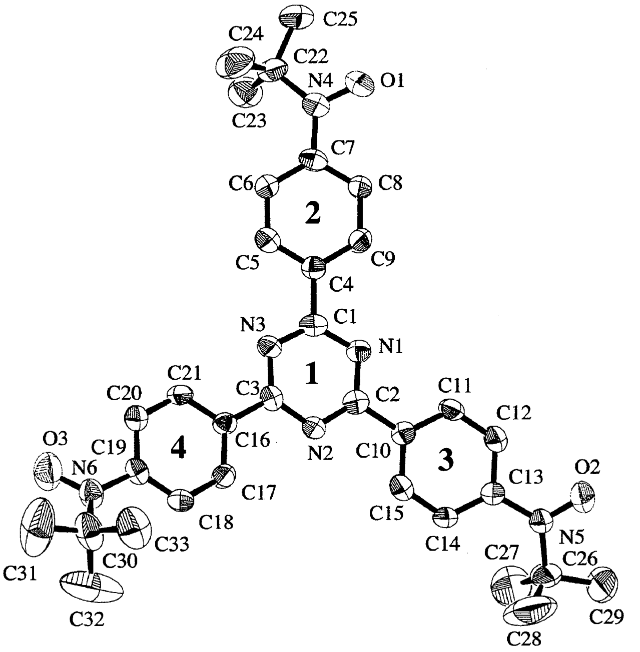


Figure 1. ORTEP drawing of **1** with 50% of probability ellipsoids. All hydrogen atoms are omitted for clality.

The structure of **1** is an isosceles-triangular system. The dihedral angles between the *p*-(*N*-oxy-*N*-*tert*-butylamino)phenyl moieties and the central triazine unit (planes 1 and 2, 1 and 3, and 1 and 4) for **1** are 9.96, 10.29, and 5.37°, respectively. Two nitroxide groups, (N(4)-O(1) and (N(5)-O(2)), for **1** make an additional torsion angle of 22.97 and 24.61°, respectively, out of the peripheral *p*-phenylene rings in the same direction. One nitroxide group (N(6)-O(3)) only makes a torsion angle of -29.51° out of the *p*-phenylene rings in the opposite direction. On the other hand, three nitroxide groups for **2** make an additional torsion angle out of the peripheral *p*-phenylene rings in the same direction. These values (dihedral and torsion angles) are larger than those of **1**, 19.5° and 37.5°, respectively. A planarity of four rings, one triazine and three phenyl, for **1** is better than that of **2**.

A degassed solution of **1** in CH_2Cl_2 at room temperature showed a seven-line EPR hyperfine structure at g = 2.0061, which suggests that the exchange interaction is larger than the hyperfine coupling. A frozen solution of **1** in CH_2Cl_2 gave a singlet at g = 2.0073 and $\Delta m_s = \pm 2$ transition at 1680 G, showing that the dipole-dipole interaction between the three unpaired electrons was rather weak.

The temperature dependence (1.8-350 K) of the magnetic susceptibility of a microcrystalline sample of **1** was measured at 5000 Oe, and the data are expressed by the effective magnetic moment μ_{eff} vs. temperature plot in Figure 2.

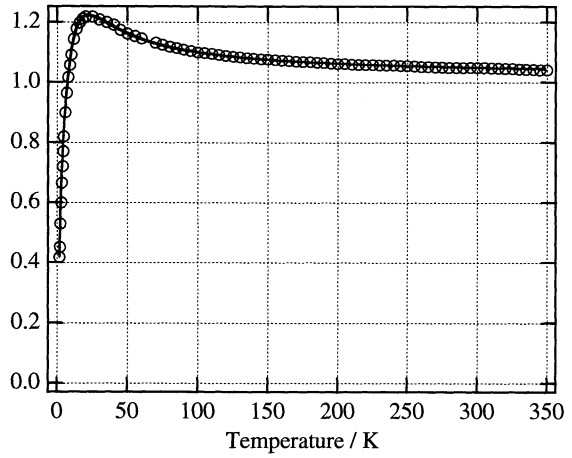


Figure 2. Temperature dependence of $\chi_M T$ values of **1** in neat crystals. Solid curve is a theoretical one. See text for the optimized parameters.

The $\chi_M T$ value of 1.04 emu K mol^{-1} at 350 K was close to a theoretical value of 1.13 emu K mol^{-1} for a three-spin system, increasing gradually as the temperature decreased and reaching 1.22 emu K mol^{-1} at 20 K.

The structure of **1** is closed to isosceles-triangular by X-ray structure. Then, for a system consisting of three spins arranged in an isosceles-triangular model as in trinitroxides, $\chi_M T$ is given as follows:

$$\chi_M T = \frac{N\mu_B^2 g^2}{k_B(T-\theta)}\left[\frac{10+\exp\{-(2\gamma+1)J/k_BT\}+\exp(-3J/k_BT)}{8+4\exp\{-(2\gamma+1)J/k_BT\}+4\exp(-3J/k_BT)}\right],$$

where $\gamma = J_2/J_1$ and J_2 and J_1 are the degrees of spin-exchange interaction between the two spins on the side and the base of the isosceles-triangular (Chart 1) and g value is obtained by EPR.

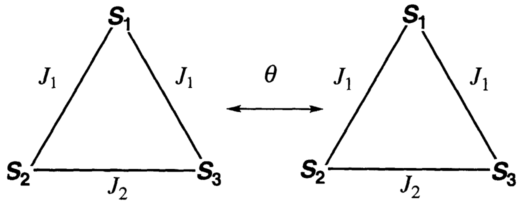


Chart 1.

The best fit of the observed points was reached by J_1/k_B = 15.3±0.8 K, γ=0.77±0.1, and θ=-5.40±0.01 K. As is very often the case, the interaction between molecules is weakly antiferromagnetic. The values of J and θ for **2** were 6.8 and -2.13 K, respectively, and the value of the J of **1** was larger than that of **2**.

We have described the structural and magnetic properties for an organic triradical with triazine skeleton **1** and compared it with **2**. One nitroxide group for **1** only makes the torsion angle out of the *p*-phenylene rings in the opposite direction. In addition, structural studies show that **1** forms better planarity than **2**. The corresponding J value obtained for **1** is +14.7 K, which is larger than that for **2**, and the intramolecular interaction is stronger than that of **2** by replacing with hetero nitrogen atoms instead of homo carbon atoms in the center skeleton. Because of its good planarity, π-electron system scattering appears to be important in intramolecular interaction.

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References and Notes

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8 ^{1}H-NMR ($CDCl_3$): δ 1.25 (s, 9H), 3.75 (s, 1H), 7.05 - 8.60 (d, 4H).
9 Anal. Found: C, 69.64; H, 6.88; N, 14.62%. Calcd. for $C_{33}H_{39}O_3N_6$: C, 69.81; H, 6.92; N, 14.81%. Uv-vis (CH_2Cl_2, λ (ε)) 256 (34200), 282 (28510), 365 (110460), 457 nm (5650). m.p. 213 °C dec.
10 X-Ray crystal structure analysis: A red needle single crystal of **1** was mounted on a glass fiber. $C_{33}H_{39}O_3N_6$, *FW*=567.71, tetragonal, space group $I4_1/a$ (#88), *a*=46.29(1), *c*=6.212(2) Å, *V*=13309(5) Å^3, and D_{calc}=1.133 g/cm^3 for *Z*=16. All non-hydrogen atoms were refined anisotropically. Refinement converged at *R*=0.068 and R_W=0.094 for 1923 reflections [I>2.5σ(I)].