Structures and Magnetic Properties of 4-(9-Anthrylmethylamino)TEMPO and Its Dimer

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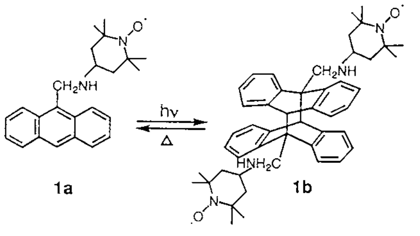
4-(9-Anthrylmethylamino)TEMPO radical (**1a**) and its photo-dimer **1b** have been prepared to show ferromagnetic interactions in the former radical and the variable spin–spin interactions depending on the solvent molecules incorporated in the crystals in the latter biradical.

The development of multi-functional spin systems with synergetic properties is of growing interest and successful studies have recently been carried out in the photo-functional magnetic materials derived from some inorganic compounds[1] and metal complexes[2] with spin cross-over behaviors.[3] Because of the versatility of organic compounds, the development of organic photo-functional spin systems has been awaited and the first experimental results have recently been reported by Iwamura, Matsuda et al. in an azobenzene derivative bearing two aminoxyl radical to observe its UV as well as EPR spectral change upon irradiation in solution.[4] Quite recently, Matsuda and Irie have succeeded to switch the intramolecular magnetic interactions upon irradiation in an elaborated diarylethene derivative bearing two nitronyl nitroxides.[5]

In the course of our studies to develop novel organomagnetic materials,[6] we have been interested in preparing multi-functional spin systems with conductivity, liquid crystalline property or photo-functionality.[7] In this paper, we would like to report on the preparation of a 9-methylanthracene derivative together with the corresponding dimer bearing 4-amino-TEMPO radical, their structures, magnetic properties and the reversibility of the system.



4-(9-Anthrylmethylamino)TEMPO radical (**1a**) has been prepared by the reduction of the Schiff base derived from 9-anthraldehyde and 4-amino-TEMPO and the photo-dimerization of **1a** was carried out by the irradiation with a high pressure Hg lamp (400 W) through a pyrex filter in benzene solution[8] to give **1b** (12%) and which could be reverted to **1a** by heating in xylene (41%) to afford a reversible system in principle. Both forward and backward reaction could be easily monitored by the electronic spectral change with the indication of the presence or the absence of the anthracene chromophore.[9]

The magnetic susceptibility measurement of the monomer **1a** was carried out on the polycrystalline sample by a SQUID susceptometer in the temperature range of 2–300 K and ferromagnetic interactions with relatively large Weiss temperature ($\theta = 0.97$ K) have been observed in the monomer **1a**. The X-ray analysis of the monomer **1a** was carried out by using the single crystal grown from a mixed solution of hexane–chloroform and the molecular/crystal structure is shown in Figure 1.[10] It was found from the molecular structure of **1a** that the six-membered ring of TEMPO moiety protrude in almost perpendicular manner from the anthracene ring (Figure 1, left) and the molecules are stacking almost along the *b*-axis to form the columnar structure (Figure 1, right). The ferromagnetic interactions observed in the spins of **1a** could be rationally understood by considering the spin-polarization mechanism through the intermolecular hydrogen bonds (CH···ON) between the spin centers[11] since the distances between the oxygen atoms of aminoxyls and the methylene carbon atoms on the neighboring heterocycles have been found to be sufficiently short for the hydrogen bonding.

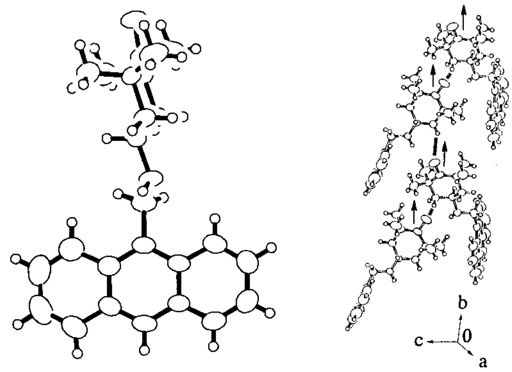


Figure 1. Left: Molecular structure of **1a**. Right: Crystal structure of **1a** with indication of ferromagnetic couplings through hydrogen bonds.

Interestingly, the solvent molecules used for recrystallization have been found to be easily incorporated in the dimer **1b**[12] and the difference of the magnetic behaviors has been observed in the solvated compounds (Table 1). Namely, antiferromagntic interactions have been observed in the compound obtained from benzene for the recrystallization while ferromagnetic interactions have been found in the solvated compounds of **1b** with dichloromethane or chloroform. Single crystals suitable for X-ray analysis have been obtained from the solvated samples of the dimer **1b** with benzene or chloroform and each structure has been analyzed.[13] As shown in Figure 2 (left), anti-configuration of each substituent has been apparent from the analysis of the crystal obtained from a benzene solution and the dissected angle between the planar anthracene ring and the nearly planar four atoms of the six-membered-ring of TEMPO moiety amounts to 58.0˚ being the smaller value than that of **1a**. Coexistence of two crystallographically independent molecules (I and II) has been found in the crystal obtained from a chloroform solution having different dissected angles with the values of 41.2° and 54.8°, respectively (Figure 2, right).

Table 1. Magnetic data of anthracene derivative **1a** and the corresponding dimer **1b**

Compound	Curie constant[a] /emu K mol^{-1}	Weiss temp.[a] /K	Magnetic interaction
1a	0.38	0.97	Ferromagnetic
1b (C_6H_6[b])	0.76	-0.38	Antiferromagnetic
1b (CH_2Cl_2[b])	0.76	0.11	Ferromagnetic
1b ($CHCl_3$[b])	0.70	0.26	Ferromagnetic

[a]Fitting for Curie-Weiss rule. [b]Crystal solvent.

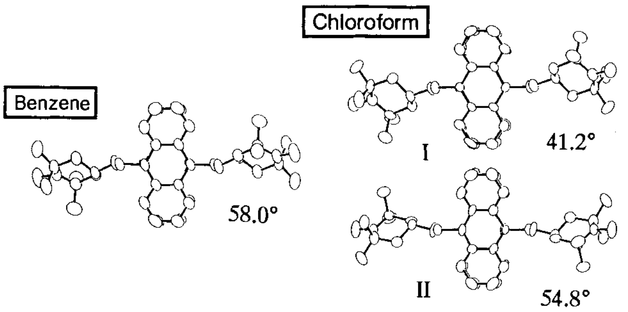


Figure 2. Left: Molecular structure of **1b** formed with benzene. Right: Molecular structure of **1b** formed with chloroform (two independent molecules I and II). Hydrogen atoms are omitted for clarity.

Their crystal structures including solvent molecules (benzene or chloroform solvate) are shown in Figure 3. In spite of the difference of the conformations of the dimer molecules, similar packing features have been found in both crystal structures in which the solvent molecules appear to occupy the cavities or voids formed in the dimer molecules to construct clathrate-like molecular aggregates. At the same time, they tend to prevent the close contact of spin centers of aminoxyl radicals to afford, as the consequence, weak intermolecular spin–spin interactions with antiferromagnetic nature on one hand and ferromagnetic nature on the other hand. Thus, although the efficiency of the reversibility is not so high, it was found to be possible in principle to tune the sign and the magnitude of intermolecular magnetic interactions in the compounds available in this reversible system by choosing light, heat or appropriate solvent.

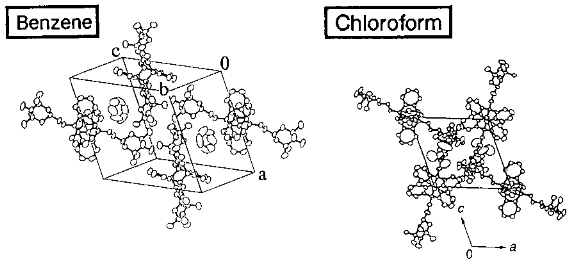


Figure 3. Left: Crystal structure of **1b** formed with benzene. Right: Crystal structure of **1b** formed with chloroform. Hydrogen atoms are omitted for clarity.

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9 The progress of the photo-reaction was monitored by electronic spectral change of the vibronic absorptions in 320–390 nm in benzene and an apparent photo-stationary state was attained after 6 h (50% consumption of **1a**: ca. 4.5 h). The gradual dissociation was observed for the backward reaction to reach a stationary state after 12 h (50% consumption of **1b**: ca. 4 h). No clear isosbestic point was observed due partially to the solvent system used.

10 Crystallographic data for **1a**: $C_{24}H_{17}NO$, FW = 361.51, monoclinic ($P2_1/a$), a = 14.176(2) Å, b = 12.718(3) Å, c = 12.073(2) Å, β = 108.74(1)°, V = 2061.2(6) $Å^3$, T = 295 K, Z = 4, D_c = 1.165 g·cm^{-3}. R = 0.053, wR = 0.041 [3034 observed reflections and 328 parameters, $I > 3\sigma(I)$].

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12 **1b** with benzene: orange rods, mp 225–228 °C (decomp.); **1b** with dichloromethane: orange powder, mp 213–215 °C (decomp); **1b** with chloroform: orange cubes, m.p. 221–223 °C (decomp). From the elemental analyses, their compositions have been estimated as **1b**·2 benzene, **1b**·1.5 dichloromethane and **1b**·2 chloroform, respectively.

13 Crystallographic data for **1b**·2 benzene and **1b**·2 chloroform: $C_{48}H_{58}N_4O_2\cdot(C_6H_6)_2$, FW = 879.24, monoclinic ($P2_1/n$), a = 14.538(2) Å, b = 11.580(1) Å, c = 17.015(5) Å, β = 109.01(2)°, V = 2708.1(9) $Å^3$, T = 295 K, Z = 2, D_c = 1.078 g·cm^{-3}. R = 0.080, wR = 0.081 [3422 observed reflections and 387 parameters, $I > 3\sigma(I)$]; $C_{48}H_{58}N_4O_2\cdot(CHCl_3)_2$, FW = 961.77, triclinic (P-1), a = 12.437(5) Å, b = 19,167(4) Å, c = 11.724(3) Å, α = 101.55(2)°, β = 108.59(2)°, γ = 102.38(2)°, V = 2476(1) $Å^3$, T = 295 K, Z = 2, D_c = 1.290 g·cm^{-3}. R = 0.069, wR = 0.058 [2707 observed reflections and 736 parameters, $I > 3\sigma(I)$].