# Anthracene Derivatives and the Corresponding Dimers with TEMPO Radicals

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Anthracene derivatives with several TEMPO radicals (**2**−**4**, **10**) were prepared, and each photodimerization reaction was investigated. Although the photodimerization was unsuccessful in obtaining the dimers of anthracenes **2** and **3**, which could be alternatively prepared in a stepwise manner, the photodimers of anthracenes **4** and **10** were available by the direct photoreaction. The dissociation reaction of the dimers proceeded well by heating them in solution to give the corresponding monomers in each case, and thus the reversible system could be constructed in the latter two systems. While no large difference was observed in their magnetic behaviors between the monomer/dimer pair of **4** and **8**, an intriguing difference was found in the magnetic behaviors for the pair of **10** and **11** from ferromagnetic interactions in **10** to the variable magnetic interactions in **11** depending on the solvent molecules incorporated in the crystals.

## Introduction

Considerable interest is now focused on the development of multifunctional spin systems with synergetic properties, and successful studies have recently been carried out toward the photofunctional magnetic materials derived from some inorganic[1] as well as organometallic compounds.[2] With regard to organic photoresponsive spin systems, Iwamura, Matsuda, et al. reported in 1998 an azobenzene derivative carrying two nitronyl nitroxide radicals and observed its UV as well as EPR spectral change upon irradiation in solution.[3] Quite recently, Matsuda and Irie have succeeded in developing a fascinating series of diarylethene derivatives carrying two nitronyl nitroxides in which a switching behavior of the intramolecular magnetic interactions has been found to occur efficiently by irradiation.[4] A photoinduced trans to cis isomerization was reported recently by Veciana et al. to form a dimerized ferrocene derivative with a Schiff base bridged trityl radical unit in which dimerization is proposed to be favored by the hydrogen bond formation.[5]

In the course of our studies to develop novel organomagnetic materials,[6] we have been interested in preparing multifunctional spin systems with conductivity,[7] liquid crystalline properties,[8] or photofunctionality[9] by using stable radicals, especially aminoxyl radicals as spin sources. For the photoresponsive spin systems, we prepared first norbornadine/quadricyclane as well as spiropyran/merocyanine systems and their magnetic behaviors were based on the intramolecular structural change. Among them, the switching behavior of solid-state magnetic properties was observed in a couple of spiropyran/merocyanine spin systems from ferromagnetic to antiferromagnetic spin−spin interactions and vice versa.

Anthracenes are known to dimerize photochemically in solution and/or in the solid state,[10] and the chromophoric system is therefore a promising system for investigating the change of magnetic properties in a spin system by their structural change upon irradiation. We then planned and initiated preparations of anthacene derivatives carrying some spin centers. In this paper, we report the preparation, structures, and properties, especially magnetic properties, of several anthracene derivatives carrying TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radical substituents as a spin source together with the corresponding photodimers.[11] In this case, we deal with *intermolecular structural change* being different

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[1] (a) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *272*, 704. (b) Gu, Z.-Z.; Sato, O.; Iyoda, T.; Hashimoto, K.; Fujishima, A. *J. Phys. Chem.* **1996**, *100*, 18290.

[2] Nagai, K.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Solid State Commun.* **1997**, *102*, 809.

[3] Hamachi, K.; Matsuda, K.; Itoh, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2937.

[4] (a) Matsuda, K.; Irie, M. *Chem. Lett.* **2000**, 16. (b) Matsuda, K.; Irie, M. *Tetrahedron Lett.* **2001**, *41*, 2577. (c) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195. (d) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 8309. (e) Matsuda, K.; Matsuo, M.; Irie, M. *Chem. Lett.* **2001**, 436. (f) Matsuda, K.; Irie, M. *Chem. Eur. J.* **2001**, *7*, 3466.

[5] Ratera, I.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Wurst, K.; Daro, N.; Létard, J.-F.; Rivira, C.; Veciana, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 919.

[6] Cf. (a) Natatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161. (b) Nakatsuji, S. *Adv. Mater.* **2001**, *13*, 1719. (c) Nakatsuji, S. In *Recent Research Developments in Organic & Bioorganic Chemistry*; Pandalai, S. G., Ed.; Transworld Research Network: Trivandrum, 2001, in press; Vol. 4.

[7] (a) Nakatsuji, S.; Mizumoto, M.; Takai, A.; Akutsu, H.; Yamada, J.; Schmitt, S.; Hafner, K. *Mol. Cryst. Liq. Cryst.* **2000**, *348*, 1. (b) Akutsu, H.; Yamada, J.; Nakatsuji, S. *Chem. Lett.* **2001**, 208. (c) Akutsu, H.; Yamada, J.; Nakatsuji, S. *Synth. Met.* **2001**, *120*, 871.

[8] (a) Nakatsuji, S.; Mizumoto, M.; Kitamura, K.; Akutsu, H.; Yamada, J. *Mol. Cryst. Liq. Cryst.* **2001**, *356*, 33. (b) Mizumoto, M.; Ikemoto, H.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Mol. Cryst. Liq. Cryst.* **2001**, *363*, 149. (c) Ikemoto, H.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Tetrahedron Lett.* **2001**, *42*, 6873.

[9] (a) Takeuchi, S.; Ogawa, Y.; Naito, A.; Sudo, K.; Yasuoka, N.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Mol. Cryst. Liq. Cryst.* **2000**, *345*, 167. (b) Nakatsuji, S.; Ogawa, Y.; Takeuchi, S.; Akutsu, H.; Yamada, J.; Naito, A.; Sudo, K.; Yasuoka, N. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1969. (c) Nakatsuji, S.; Takeuchi, S.; Ojima, T.; Ogawa, Y.; Akutsu, H.; Yamada, J. *Mol. Cryst. Liq. Cryst.* **2001**, *356*, 23.

[10] For a recent review, see: Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2000**, *29*, 43. We thank Dr. Desvergne of Universitè Bordeaux I for kindly sending us a reprint.

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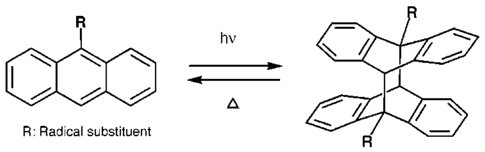
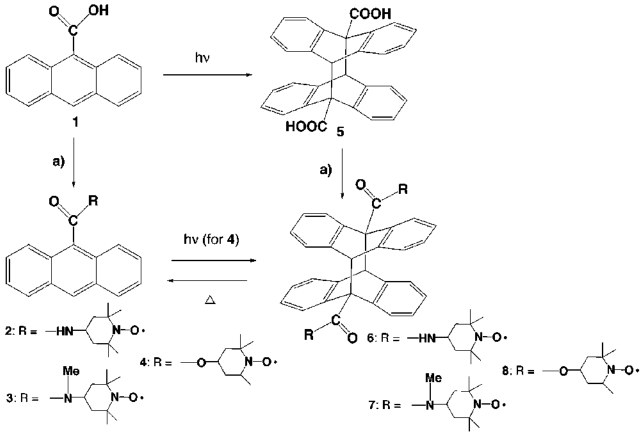
**Chart 1**



**Scheme 1**[a]



[a] (i) $SOCl_2$; (ii) 4-amino-TEMPO, 4-(*N*-methyl)amino-TEMPO, or 4-hydroxy-TEMPO, $Et_3N$.

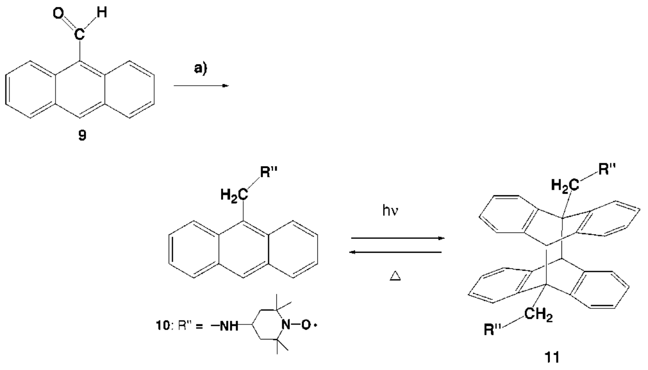
from the previous systems of others[3,4] as well as of ours.[9] The only example that is based on intermolecular structural change is the system developed by Veciana et al.[5]

## Results and Discussion

**Preparation of Anthracenes with TEMPO Radicals and Their Dimers.** Carboxyamide and *N*-methylamide derivatives of anthracene (**2**, **3**) were prepared from 9-anthroic acid **1** by its derivatization with 4-amino-TEMPO as well as 4-methylamino-TEMPO, which was obtained by reductive amination of 4-oxo-TEMPO with methylamine hydrochloride and $NaBH_3CN$.[12] Although all attempts to obtain the corresponding photodimers (**6**, **7**) through the direct photodimerization reaction of **2** and **3** failed, the dimers were prepared by the derivatization of the photodimer of 9-anthroic acid (**5**)[13] with 4-amino-TEMPO or 4-methylamino-TEMPO as shown in Scheme 1. On the contrary, the derivative with a carboxylic ester substituent (**4**) was found to give the corresponding photodimer (**8**) upon irradiation in benzene solution using a high-pressure Hg lamp (400 W) and the latter could be reverted to the former by heating in a toluene solution (Scheme 1).

The methylamino-TEMPO derivative of anthracene (**10**) was prepared by the reduction of the Schiff base derived from 9-anthraldehyde **9** and 4-amino-TEMPO, and the photodimerization of **10** was carried out by irradiation with a 400 W Hg lamp in $CHCl_3$ solution to give the dimer (**11**), which could be reverted to **10** by heating in xylene, affording a reversible system in principle (Scheme 2). The progress of the photoreaction was monitored by the electronic spectral change of the vibronic absorption in 320−390 nm in benzene as shown in Figure 1, and an apparent photostationary state was attained after 6 h (50% consumption of **10** after ca. 4.5 h).[14] Gradual dissociation was observed for the backward reaction by heating **11** in xylene solution to revert half of the dimer **11** after ca. 4 h. Thus, although the efficiency is still limited as described above, two reversible systems could be constructed in principle so far as we have examined.

**Scheme 2**[a]



[a] (i) 4-amino-TEMPO, AcOH; (ii) $NaBH_3CN$.

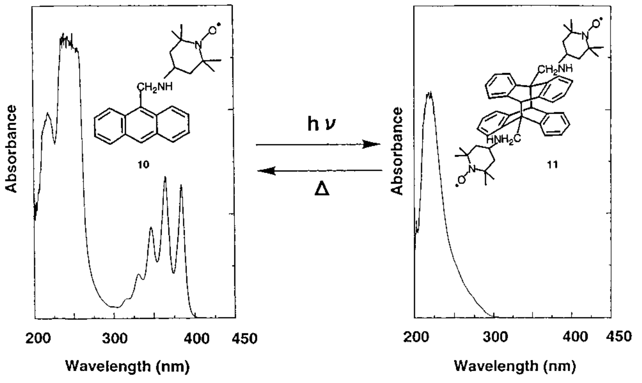


**Figure 1.** Electronic absorption change for the reaction from **10** to **11** and vice versa.

**Magnetic Properties.** Typical absorptions due to the aminoxyl were observed in the EPR spectra of all the monomers, and no appreciable difference was found for those of the corresponding dimers, indicating the absence of significant intramolecular exchange interactions between the spin centers in the dimers. For the estimation of the relative configuration of spin centers for the dimers (biradicals), EPR measurements for the dimers **6** and **8** were carried out in 2-methyltetrahydrofuran at 123 K to give the zerofield splitting parameters of $|D| = 3.36$ mT and $|E| = 0.879$ mT for **6** and $|D| = 3.15$ mT and $|E| = 0.810$ mT for **8**. The distances between the spin centers for each biradical are then estimated by point dipole approximation to be 9.60 Å for **6** and 9.40 Å for **8**. Thus, the trans configuration of the dimers is well suggested from the estimated data.

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(11) Preliminary reports of this paper have appeared portionwise in (a) Ojima, T.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Chem. Lett.* **2000**, 918. (b) Ojima, T.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Polyhedron* **2001**, *20*, 1335.

(12) Cf.: Nakatsuji, S.; Takai, A.; Nishikawa, K.; Morimoto, Y.; Yasuoka, N.; Suzuki, K.; Enoki, T.; Anzai, H. *J. Mater. Chem.* **1999**, *9*, 1747.

(13) Cowan, D. O.; Schmiegel, W. W. *J. Am. Chem. Soc.* **1972**, *94*, 6779.

(14) Since the efficiency of this photochemical reaction was rather low, we tried to characterize byproduct(s). These efforts have not been successful, and no measurement of the quantum yield was carried out for the reaction since that was beyond our initial purpose. For the photochemical reaction of 9-aminomethylanthracene derivatives, see: Mori, Y.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 869.

**Table 1. Magnetic Data of Anthracenes and the Corresponding Dimers**

| compound | magnetic interaction | $C^a$/emu K mol$^{-1}$ | $\theta^b$/K | $J^c$/K |
|---|---|---|---|---|
| **2** | antiferromagnetic | 0.32 (85) | −0.10 | |
| **6** | antiferromagnetic | 0.67 (89) | −0.32 | |
| **3** | antiferromagnetic | | | −3.38 (100) |
| **7** | antiferromagentic | 0.73 (97) | −1.87 | |
| **4** | ferromagnetic | 0.36 (96) | 0.21 | |
| **8** | ferromagnetic | 0.64 (85) | 0.28 | |
| **10** | ferromagnetic | 0.38 (100) | 0.97 | |
| **11** ($C_6H_6{}^d$) | antiferromagnetic | 0.75 (100) | −0.38 | |
| **11** ($CHCl_3{}^d$) | ferromagnetic | 0.70 (93) | 0.26 | |
| **11** ($CH_2Cl_2{}^d$) | ferromagnetic | 0.75 (100) | 0.11 | |

[a] Curie constant. Figures in parentheses denote the estimated spin concentrations. [b] Weiss temperature. [c] Exchange interactions obtained by fitting for a singlet−triplet model. The figure in parentheses denotes the estimated spin concentration. [d] Crystal solvent.

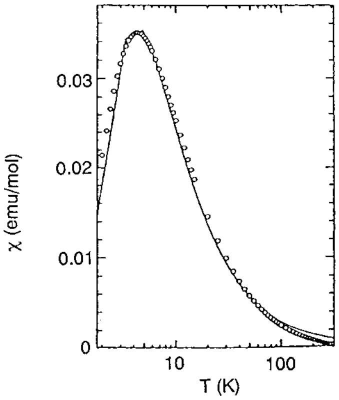

**Figure 2.** Temperature dependence of the magnetic susceptibility (χ) for **3**. The calculated values for the S−T model are shown in the solid line.

The magnetic susceptibility measurements for each monomer/dimer pair were carried out on the polycrystalline sample by a SQUID susceptometer in the temperature range of 2−300 K, and the data are summarized in Table 1.

Similar magnetic behaviors were observed in monomer/dimer pairs of **2** and **6** as well as **4** and **8**, i.e., the antiferromagnetic spin−spin interactions with Curie−Weiss behavior were found in the spin of **2** and tend to be preserved in the spins of **6** despite the difference of Weiss temperatures. Similarly, ferromagnetic interactions proved to exist in the spin centers for both **4** and **8** with slightly different Weiss temperatures. With regard to the monor/dimer pair of **3** and **7**, local antiferromagnetic spin interactions being well expressed by a singlet−triplet model with a *J*-value of ca. −3.4 K were found in the spins of **3** as shown in Figure 2; the Curie−Weiss behavior with antiferromagnetic interactions ($\theta = -1.87$ K) was observed in the spins of the corresponding dimer **7** (Table 1).

Ferromagnetic interactions with relatively large Weiss temperatures ($\theta = +0.97$ K) were observed in the methylamine derivative **10** as shown in Figure 3 (left), and the tendency of the preservation of magnetic interactions was apparent in the corresponding dimer **11** with the smaller Weiss temperature ($\theta = +0.11$ K) being estimated from the data measured on a powdered sample without recrystallization. Interestingly, the solvent molecules used for recrystallization were found to be easily incorporated in the dimer **11** and the difference of the magnetic behaviors of the crystals was observed, i.e., ferromagntic interactions ($\theta = +0.26$ K) when chloroform molecules are incorporated and antiferromagnetic interactions ($\theta = -0.38$ K) when benzene molecules are incorporated (Figure 3, right). Thus, although the efficiency of the reversibility is not so high, it was found to be possible in principle to tune the sign and magnitude of intermolecular magnetic interactions in the compounds available in this reversible system.

**Molecular/Crystal Structures of Monomers 3 and 10 and Dimer 11.** A single crystal of **3** suitable for X-ray analysis was grown from the mixed solvent of *n*-hexane and chloroform, and as shown in Figure 4, the two molecules of **3** are paired and the anthracene moieties are facing each other with each TEMPO moiety protruding in a perpendicular manner and in the anti configuration. It was well anticipated from the viewpoint of its molecular configuration that the photodimerization would proceed even in the crystal phase, but as far as we have examined, no photodimer could be available until now in either the crystal phase or solution. Although the explicit reason for the magnetic behavior observed in this radical (Figure 2) is not clearly understood yet, a couple of short contacts found between the carbon atoms on the anthracene moiety of a molecule and the oxygen atoms of aminoxyls of different molecules might be responsible for the observed magnetic interactions.

The X-ray analysis of the monomer **10** 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 5. It was found from the molecular structure of **10** that the six-membered ring of the TEMPO moiety protrudes in an almost perpendicular manner from the anthracene ring (Figure 5, left), and the molecules are stacked almost along the *b*-axis to form the columnar structure (Figure 5, right). The ferromagnetic interactions observed in the spins of **10** could be rationally understood by considering the spin−polarization mechanism through the intermolecular hydrogen bonds (CH···ON = 3.40 Å) between the spin centers[15] since the distances between the oxygen atoms of aminoxyls and the methylene carbon atoms on the neighboring heterocycles were found to be sufficiently short for the hydrogen bonding.

Interestingly, the solvent molecules used for recrystallization were found to be easily incorporated in the dimer **11** and the difference of the magnetic behaviors was observed in the solvated compounds (Table 1). Namely, antiferromagntic interactions were observed in the compound obtained from benzene for the recrystallization, while ferromagnetic interactions were found in the solvated compounds of **11** with dichloromethane or chloroform. Single crystals suitable for X-ray analysis were obtained from the solvated samples of the dimer **11** with benzene or chloroform, and each structure was analyzed. As shown in Figure 6 (left), the anti configuration of each substituent was apparent from the analysis of the crystal obtained from a benzene solution and the dissected angle between the mean plane of the anthracene ring and that of the six-membered ring of the

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(15) Cf.: (a) Veciana, J.; Cirujeda, J.; Rovira, C.; Vidal-Gancedo, J. *Adv. Mater.* **1995**, *7*, 221. (b) Tagashi, K.; Imachi, R.; Tomioka, K.; Tsuboi, H.; Ishida, T.; Nogami, T.; Takeda, N.; Ishikawa, M. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2821. (c) Matsushita, M. M.; Izuoka, A.; Sugawara, T.; Kobayashi, T.; Wada, T.; Takeda, N.; Ishikawa, M. *J. Am. Chem. Soc.* **1997**, *119*, 4369.

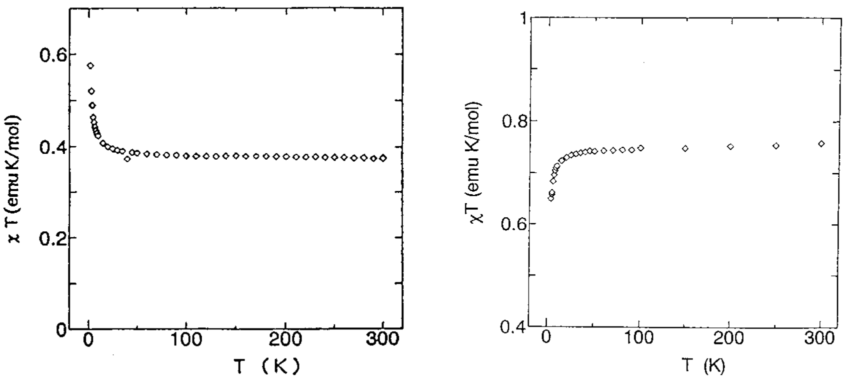

**Figure 3.** (Left) Temperature dependence of $\chi$T for **10**. (Right) Temperature dependence of $\chi$T for **11** solvated with benzene.

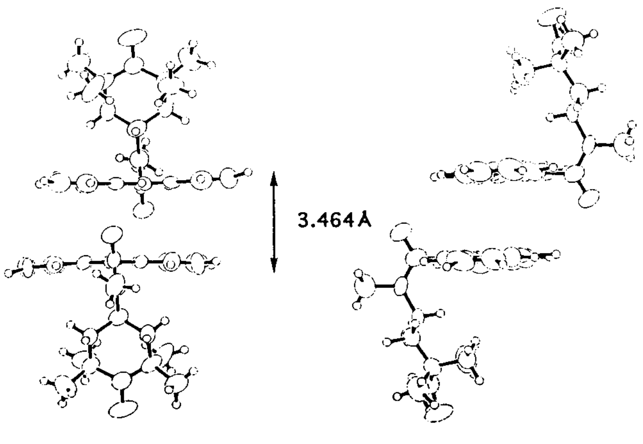

**Figure 4.** Molecular structure of **3** (two molecules are depicted).

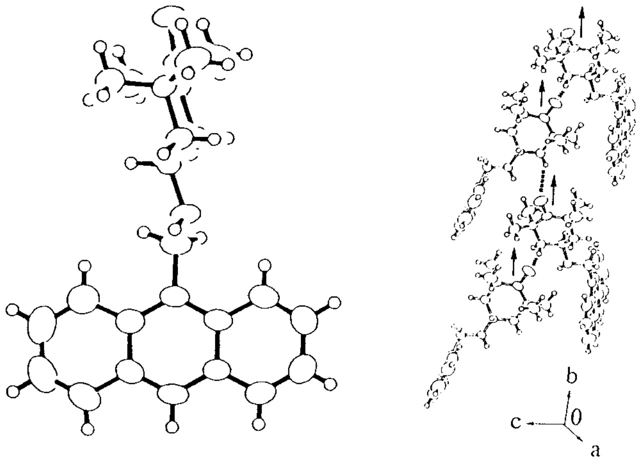

**Figure 5.** (Left) Molecular structure of **10**. (Right) Crystal structure of **10** with indication of ferromagnetic couplings through hydrogen bonds.

TEMPO moiety amounts to 58.0°, a smaller value than that of **10**. On the other hand, a coexistence of two crystallographically independent molecules has been found in the crystal obtained from a chloroform solution having different dissected angles with the values of 41.2 and 54.8°.

The crystal structure of a compound solvated with benzene is shown in Figure 6 (right). Despite the difference of the conformations of the dimer molecules, similar packing features were found in crystal structures of the solvated compounds 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 an antiferromagnetic nature on one hand and a ferromagnetic nature on the other.

## Conclusions

We prepared four anthracene derivatives carrying TEMPO radicals (**2**−**4**, **10**), and although direct photodimerization of two derivatives (**2**, **3**) was not successful, the dimers were prepared in a stepwise manner from dicarboxylic acid derivative of anthracene dimer. On the contrary, the photodimers **8** and **11** could be directly prepared from the corresponding monomers **4** and **10** and the backward reactions, in turn, gave the starting monomers to construct the reversible systems in principle. Whereas the tendency of the preservation of intermolecular spin−spin interactions was observed in the monomer/dimer pairs for **2**/**6** and **4**/**8** from antiferromagnetic to antiferromagnetic in the former pairs and from ferromagnetic to ferromagnetic in the latter despite the difference of their Weiss temperatures, a significant difference was clarified in the pairs for **3**/**7** as well as **10**/**11**. Namely, local antiferromagnetic exchange interactions being well expressed by a singlet−triplet model found in the monomer **3** were turned to antiferromagnetic interactions on the basis of Curie−Weiss behavior in the corresponding dimer **7**. The ferromagnetic interactions found in the spins of monomer **10** were found to be able to tune in the corresponding dimer **11** depending on the solvent molecules incorporated to either antiferromagnetic or ferromagnetic; thus, in principle, the sign and magnitude of intermolecular magnetic interactions was found to be changed by outer stimuli such as *light, heat, or appropriate solvents* in this reversible system.

## Experimental Section

**Materials.** 4-Oxo-, 4-hydroxy-, and 4-amino-TEMPO radicals used as building blocks in this study are commercially available (Tokyo Kasei Kogyo Co.), and these were used without further purification.

**Instrumentation.** Melting points were measured on a YAMATO MP-21 apparatus and are uncorrected. IR spectra were recorded on a JASCO Report-100 spectrometer. UV−vis spectra were obtained on a JASCO Ubest-35 spectrometer. MS spectra were taken using a JEOL JMS-AX 505 mass spectrometer. EPR spectra were obtained on a JEOL JES-FE3XG spectrometer, and each *g*-value was determined using $Mn^{2+}$/

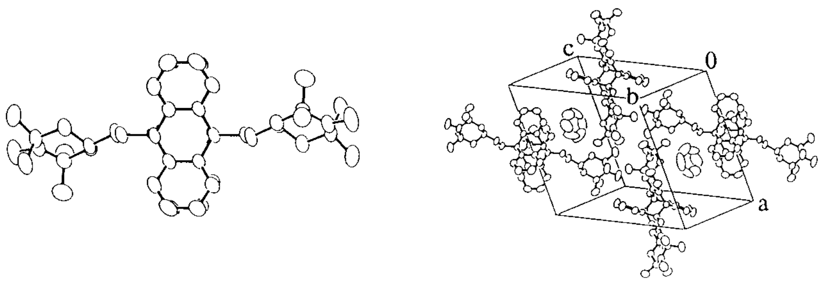

**Figure 6.** (Left) Molecular structure of **11** solvated with benzene. (Right) Crystal structure of **11** solvated with benzene. Hydrogen atoms are omitted for clarity.

MgO maker as the internal standard. Susceptibility measurements were carried out on a QUNTUM DESIGN MPMS-5 SQUID susceptometer using ca. 10 mg of each powdered sample in the usual way.[12]

**X-ray Structure Determination.** X-ray diffraction data were collected on a Nonius CAD4 or Rigaku R-AXIS-4 diffractometer with Mo K$\alpha$ radiation at room temperature. The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation, and detailed crystallographic data (atomic coordinates, hydrogen atom coordinates, anisotropic displacement parameters, and bond lengths and angles) have been deposited with the Cambridge Crystallographic Data Centre.

**Preparation of 4-(*N*-Methylamino)TEMPO.** To a stirred mixture of oxo-TEMPO (1.10 g, 6.20 mmol) and methylamine hydrochloride (2.50 g, 37.0 mmol) in absolute methanol (100 mL) were added $NaBH_3CN$ (0.270 g, 4.30 mmol) and successively 5 N HCl in MeOH to adjust the pH of the solution to ca. 6. After stirring for 2 days at ambient temperature, the reaction mixture was concentrated in vacuo and then aqueous potassium hydroxide solution (4 N) was added to neutralize the resulting reaction product. The mixture was extracted by chloroform, washed well with water and brine, and the organic layer was dried over anhydrous magnesium sulfate. The radical was obtained as pale orange rods (935 mg, 76%) after the solvent was concentrated, purified by column chromatography on silica gel, and recrystallized from the mixed solvent of *n*-hexane and dichloromethane: mp 52−53 °C; EPR (benzene) 3 lines, $g = 2.007$, $a_N = 1.56$ mT; EI-HRMS (*m*/*z*) calcd for $C_{10}H_{21}N_2O$ 185.1653, found 185.1674.

**Preparation of 4-[9-Anthrylcarboxy(*N*-methylamino)]-TEMPO Derivative 3.** 9-Anthracenecarboxylic acid (662 mg, 2.98 mmol) was heated in $SOCl_2$ solution (30 mL) to reflux for 5 h. The resulting solution was concentrated in vacuo to give a solid that was dissolved in $CH_2Cl_2$ (20 mL) and added to a stirred solution of 4-methylamino-TEMPO (552 mg, 2.98 mmol) in $CH_2Cl_2$ (20 mL) with 1 mL of triethylamine. After stirring at 35 °C for 2 days, the reaction mixture was poured into 1 N HCl (50 mL), washed with brine, dried over anhydrous $MgSO_4$, and then concentrated to give a brownish yellow solid, which was purified by column chromatography on silica gel by using the solvent system of *n*-hexane/ethyl acetate and recrystallized from the mixed solvent of *n*-hexane/dichloromethane. The derivative **3** was obtained as orange rods (708 mg, 64%): mp 169−171 °C dec; UV−vis ($CH_3CN$) 242 ($1.26 \times 10^4$), 332 ($2.20 \times 10^3$), 348 ($5.35 \times 10^3$), 366 ($8.71 \times 10^3$), 385 ($7.50 \times 10^3$); EPR (benzene) 3 lines, $g = 2.007$, $a_N = 1.56$ mT; FAB-MS (*m*/*z*) 390 (M + H). Anal. Calcd for $C_{25}H_{29}N_2O_2$: C, 77.09; H, 7.50; N, 7.19%. Found: C, 76.79; H, 7.46; N, 7.08%. In a similar manner, the derivatives **2** and **4** were prepared in 83 and 52%, respectively, and their data are as follows. **2**: orange needles, mp 220−223 °C dec; UV−vis ($CH_3CN$) 256 ($1.46 \times 10^4$), 332 ($2.79 \times 10^3$), 345 ($5.44 \times 10^3$), 363 ($7.81 \times 10^3$), 382 ($6.80 \times 10^3$); EPR (benzene) 3 lines, $g = 2.006$, $a_N = 1.53$ mT; FAB-HRMS (*m*/*z*) calcd for $C_{24}H_{27}N_2O_2$ 375.2073, found 375.2081. **4**: orange needles, mp 203−205 °C dec; UV−vis ($CH_3CN$) 238 ($1.43 \times 10^4$), 329 ($2.60 \times 10^3$), 345 ($5.21 \times 10^3$), 363 ($7.81 \times 10^3$), 382 ($7.22 \times 10^3$); EPR (benzene) 3 lines, $g = 2.007$, $a_N = 1.56$ mT; FAB-HRMS (*m*/*z*) calcd for $C_{24}H_{26}NO_3$ 376.1913, found 376.1947.

**Preparation of 4-(9-Anthrylmethylamino)TEMPO Derivative 10.** A toluene solution (40 mL) of 9-anthraldehyde (1.20 g, 5.84 mmol) and 4-amino-TEMPO (1.00 g, 5.84 mmol) with 2 mL of AcOH was stirred under nitrogen at 65 °C for 12 h. The reaction mixture was concentrated under reduced pressure and then recrystallized from the mixed solvent of *n*-hexane/benzene to give the corresponding imine derivative as yellow needles (1.76 g, 84%): mp 171−173 °C dec; EPR (benzene) 3 lines, $g = 2.006$, $a_N = 1.57$ mT; FAB-MS (*m*/*z*) 359 (M + 1). To the stirred solution of the imine derivative in MeOH (100 mL) was added $NaBH_3CN$ (310 mg, 4.90 mmol) under nitrogen at 0 °C and then 30 mL of MeOH solution with concentrated HCl (0.9 mL) for 20 min. After the reaction mixture was warmed to room temperature, it was concentrated, neutralized with 4 N KOH, and extracted with chloroform. The chloroform layer was dried over anhydrous $MgSO_4$ and then concentrated in vacuo to give a solid that was purified by column chromatography on silica gel by using the solvent system of *n*-hexane/ethyl acetate and recrystallized from the mixed solvent of *n*-hexane/chloroform. The derivative **10** was obtained as orange rods (1.46 g, 82%): mp 123−128 °C dec; UV−vis ($CH_3CN$) 256 ($1.46 \times 10^4$), 331 ($2.59 \times 10^3$), 347 ($5.36 \times 10^3$), 365 ($8.35 \times 10^3$), 385 ($7.85 \times 10^3$); EPR (benzene) 3 lines, $g = 2.007$, $a_N = 1.56$ mT; FAB-MS (*m*/*z*) 361 ($M^+$). Anal. Calcd for $C_{24}H_{29}N_2O$: C, 79.74; H, 8.09; N, 7.75%. Found: C, 79.58; H, 8.09; N, 7.65%.

**Preparation of Photodimer 11.** Into a vessel (200 mL) for photochemical reactions with a Pyrex filter was placed a benzene solution (50 mL) of **10** (1.46 g, 4.04 mmol), and the solution was irradiated with a high-pressure Hg lamp (400 W) under nitrogen at 0 °C. After irradiation of the solution for 11 h, the reaction mixture was concentrated in vacuo and purified by column chromatography on silica gel by using the solvent system of *n*-hexane/dichloromethane to an give orange powdery solid (168 mg, 12%). The solid was then recrystallized from an appropriate solvent (benzene, chloroform, or dichloromethane), and the solvated dimers **11** were obtained as orange crystals in each compound with almost the same melting and spectral data: mp 213−218 °C dec; UV−vis ($CH_3CN$) 218 ($2.28 \times 10^5$); EPR (benzene) 3 lines, $g = 2.007$, $a_N = 1.60$ mT; FAB-MS (*m*/*z*) 723 (M + H). Anal. Calcd for the compound solvated with benzene ($C_{48}H_{58}N_4O_2{\cdot}2C_6H_6$): C, 81.96; H, 8.02; N, 6.37%. Found: C, 81.84; H, 8.01; N, 6.47%. Anal. Calcd for the compound solvated with chloroform ($C_{48}H_{58}N_4O_2{\cdot}2CHCl_3$): C, 62.44; H, 6.29; N, 5.87%. Found: C, 62.75; H, 6.13; N, 5.41%. Anal. Calcd for the compound solvated with dichloromethane ($C_{48}H_{58}N_4O_2{\cdot}1.5CH_2Cl_2$): C, 69.91; H, 7.23; N, 6.59%. Found: C, 69.91; H, 7.29; N, 6.23%. In a similar manner with a shorter irradiation time (3 h), the photodimer **8** was obtained from the corresponding monomer **4** in 34% yield: orange microcrystals; mp 228−230 °C dec; UV−vis ($CH_3CN$) 223 ($2.01 \times 10^5$); EPR (benzene) 3 lines, $g = 2.007$, $a_N = 1.60$ mT; FAB-MS (*m*/*z*) 752 ($M^+$). Anal. Calcd for $C_{48}H_{52}N_2O_6$: C, 76.57; H, 6.96; N, 3.72%. Found: C, 76.41; H, 6.94; N, 3.65%.

**Preparation of Dimer 7.** A stirred solution of the dimer of 9-anthracenecarboxylic acid (528 mg, 1.19 mmol) in $SOCl_2$ (35 mL) with DMF (3 drops) was heated to reflux for 4 h. The resulting solution was concentrated, dissolved in $CH_2Cl_2$ (20 mL), and added to a stirred solution of 4-methylamino-TEMPO (440 mg, 2.38 mmol) in $CH_2Cl_2$ (20 mL) with 3 mL of triethylamine. After stirring at 35 °C for 24 h, the reaction mixture was poured into 1 N HCl (50 mL), washed with brine, dried over anhydrous $MgSO_4$, and then concentrated to give a solid that was purified by column chromatography on silica gel by using the solvent system of *n*-hexane/ethyl acetate. After the recrystallization from the mixed solvent of *n*-hexane/dichloromethane, the dimer **7** was obtained as a pale reddish, powdery solid (113 mg, 43%): mp 168−170 °C dec; UV−vis ($CH_3CN$) 245 ($1.12 \times 10^5$); EPR (benzene) 3 lines, $g = 2.006$, $a_N = 1.56$ mT; FAB-MS (*m*/*z*) 779 (M + H). Anal. Calcd for $C_{50}H_{58}N_4O_4$: C, 77.09; H, 7.50; N, 7.19%. Found: C, 77.46; H, 7.24; N, 7.53%. In a similar manner, the dimer **6** was obtained in 23% yield as a pale reddish, powdery solid: mp 221−223 °C dec; UV−vis ($CH_3CN$) 218 ($3.13 \times 10^5$); EPR (benzene): 3 lines, $g = 2.006$, $a_N = 1.56$ mT; FAB-MS (*m*/*z*) 751 (M + H). Anal. Calcd for $C_{48}H_{54}N_4O_4$: C, 76.77; H, 7.25; N, 7.46%. Found: C, 76.44; H, 7.43; N, 7.18%.

**Dissociation of Dimer 11.** A stirred solution of dimer **11** (100 mg, 0.138 mmol) in xylene (30 mL) was heated to reflux for 24 h, and the solvent was evaporated to dryness to give a solid that was purified by column chromatography on silica gel by using the solvent system of *n*-hexane/ethyl acetate. After the recrystallization from the mixed solvent of *n*-hexane/dichloromethane, the monomer **10** was recovered as orange rods in 45% yield. Similarly, the dissociation reaction of dimers **6**, **7**, and **8** gave the corresponding monomers **2**, **3**, and **4** in 68, 84, and 71%, respectively.

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**Supporting Information Available:** X-ray crystallographic data (crystal structure of **3**, molecular/crystal structure of **11**·$2CHCl_3$, tables of crystal data, bond lengths and angles, atomic coordinates, and anisotropic thermal parameters) for **3**, **10**, and **11** with benzene and **11** with chloroform. This material is available free of charge via the Internet at http://pubs.acs.org.

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