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Novel Radical Compounds Bearing Mesogenic Cores with Long Alkyl Substituents

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Series of aminoxyl radicals (TEMPO or nitronyl nitroxide radicals) bearing phenyl benzoate, troponoid, or biphenylcarbonitrile as mesogenic cores with long alkyl substituents were prepared. Although most aminoxyl radicals showed only weak antiferromagnetic interactions due probably to the remote spin centers as clarified by the X-ray analysis of **4a** and no appreciable mesogenic phase was observed in each compound, an unusual magnetic transition from an original Curie−Weiss phase to another magnetic phase well-expressed by a singlet−triplet (ST) model was disclosed through the thermal transition in the 4′-undecyloxy-4-biphenylcarbonitrile derivative with oxocarbonyl-TEMPO **12b**.

Introduction

Stable radicals, above all aminoxyl radicals, have been widely used as spin labels,[1] reagents for redox[2] or polymerization reactions,[3] and some other purposes[4] in biological, physicochemical, or synthestic studies and their usage in materials chemistry has emerged in recent years as the building blocks in molecular based-magnetic materials.[5]

During the remarkable progress of chemistry and physics in the field of molecular based-magnetic materials, considerable interest has recently been focused on the development of magnetic materials (spin systems) with multiproperties and several attractive examples of such spin systems that respond to the outer stimuli of *heat* have been reported along this line in the past few years. After the eminent studies of Kahn et al. on spin-transition polymers,[6] Fujita and Awaga found novel room temperature magnetic bistability in 1,3,5-trithia-2,4,6-triazapentalenyl (TTTA).[7] Sugano reported last year on the magnetic phase transition in the 5-carboxy-2-thienyl nitronyl nitroxide radical[8] and Schultz et al. prepared an intriguing biradical showing magnetic bistability with a hysteretic phase transition.[9]

In the course of our studies to develop novel organomagnetic materials,[10] we have been interested in preparing multifunctional spin systems with conductivity, photofunctionality, or liquid crystalline property by using stable radicals, especially aminoxyl radicals, as spin sources.[11] The development of spin systems with the liquid crystalline property is particularly interesting because of the possibility of ordered spin interactions in the oriented molecular aggregates and/or the possibility of the alteration of the magnetic properties through the phase transition. We then have been interested in preparing the spin systems with mesogenic cores such as cholesterol or biphenyl with long alkyl substituents and reported previously on the existence of a liquid crystalline phase and a magnetic phase transition through the phase in a biphenyl derivative with 4-(*N*-methyl)-

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[1] Cf.: (a) *Nitroxide Spin Labels, Reactions in Biology and Chemistry*; Kocherginsky, N., Swartz, H. M., Eds.; CRC Press: Boca Raton, FL, 1995. (b) *Biological Magnetic Resonance, Vol. 14: Spin Labeling*; Berliner, L., Ed.; Plenum Press: New York, 1998.

[2] Cf.: (a) Bobbitt, J. M.; Flores, M. C. L. *Heterocycles*, **1988**, *27*, 509. (b) de Nooy, A. E. J.; Besemer, A. C.; van Bekkum, H. *Synthesis* **1996**, 1153. (c) Naik, N.; Braslau, R. *Tetrahedron* **1998**, *54*, 667.

[3] Cf.: (a) Hawker, C. J. *Acc. Chem. Res.* **1997**, *30*, 373. (b) Malmström, E. E.; Hawker, C. J. *Macromol. Chem. Phys.* **1998**, *199*, 923.

[4] Cf.: (a) Corvaja, C.; Maggini, M.; Prato, M.; Scorrano, G.; Venzin, M. *J. Am. Chem. Soc.* **1995**, *117*, 8857. (b) Ishii, K.; Fujisawa, J.; Ohba, Y.; Yamauchi, S. *J. Am. Chem. Soc.* **1996**, *118*, 13079. (c) Bossmann, S. H.; Ghatlia, N. D.; Ottaviani, M. F.; Turro, C.; Durr, H.; Turro, N. J. *Synthesis* **1996**, 1313. (d) Mizuochi, N.; Ohba, Y.; Yamauchi, S. *J. Phys. Chem. A* **1997**, *101*, 5966. (e) Ishii, K.; Hirose, Y.; Kobayashi, N. *J. Am. Chem. Soc.* **1998**, *120*, 10551. (f) Ishii, K.; Ishizaki, T.; Kobayashi, N. *J. Phys. Chem. A* **1999**, *103*, 6060.

[5] For recent review books on molecular-based magnetic materials, see, for example: (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker, Inc.: New York, Basel, 1999. (b) *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha/Gordon and Breach Science Publishers: Tokyo, Japan, 2000. (c) *Structure and Bonding, Vol. 100, π-Electron Magnetism: From Molecule to Magnetic Materials*; Veciana, J., Ed.; Springer-Verlag: Berlin, Germany, 2001. (d) *Magnetism: Molecules to Materials*; Eds. Miller, J. S.; Drillon, M., Wiley-VCH: Weinheim, 2001−2002; Vols. I−III.

[6] Cf.: Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44.

[7] Fujita, W.; Awaga, K. *Science* **1999**, *286*, 261.

[8] Sugano, T. *Chem. Lett.* **2001**, 32.

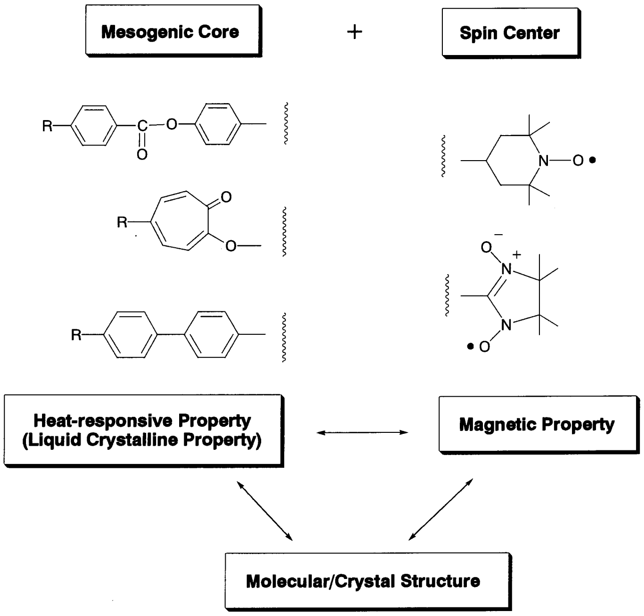
[9] Shultz, D. A.; Fico, R. M., Jr.; Boyle, P. D.; Kampf, J. W. *J. Am. Chem. Soc.* **2001**, *123*, 10403.

[10] Cf.: Natatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161.

[11] Cf.: (a) Nakatsuji, S. *Adv. Mater.* **2001**, *13*, 1719. (b) Nakatsuji, S. In *Recent Research Developments in Organic & Bioorganic Chemistry*; Pandalai, S. G., Ed.; Transworld Research Network: Trivandrum, 2002; Vol. 5, pp 1−26. See also: Nakatsuji, S.; Ojima, T.; Akutsu, H.; Yamada, J. *J. Org. Chem.* **2002**, *67*, 916.

10.1021/jo0206972 CCC: $25.00

CHART 1



amino-TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy)-substituent,[12] although it is known that the sources of organic radicals are unsuitable for the synthesis of liquid crystals in general, due mainly to inappropriate substitution patterns or the geometry and bulkiness of radical-stabilizing substituents, which are detrimental to mesophase stability.[13] Actually, beside the radical mentioned above, only a few organic radicals with less bulky DOXYL (4,4-dimethyl-3-oxazolidinyloxy)-substituent have so far been reported to show the liquid crystalline property.[14] We wish to report in this paper our further search for organic radical compounds consisting of TEMPO or nitronyl nitroxide radical on one hand and bearing phenyl benzoate, troponoid, or biphenylcarbonitrile with long alkyl substituents as mesogenic cores on the other hand toward the development of heat-responsive liquid crystalline radicals and the finding of an unusual magnetic transition from a Curie−Weiss phase to another magnetic phase well expressed by a ST model through the thermal transition in the 4′-undecyloxy-4-biphenylcarbonitrile derivative with oxocarbonyl-TEMPO **12b** despite the absence of a distinct liquid crystalline phase.[15]

Results and Discussion

Preparation of Radical Compounds with Mesogenic Cores. (1) Phenyl Benzoate Derivatives 3a,b and 4a,b. Phenyl benzoate derivatives with long alkyl substituents are known to be possible mesogenic cores exhibiting liquid crystalline phases and we then tried to prepare the derivatives with stable radicals together with long alkyl substituents. At first, phenyl benzoate derivatives (**3a**,**b**) with alkyl substituents as well as the 4-imino-TEMPO-subsitutent were prepared from the corresponding 4-formyl derivatives **2a**,**b** by condensing with 4-amino-TEMPO in toluene solution containing a catalytic amount of acetic acid. The formyl derivatives, in turn, were obtained by the esterification of 4-heptyl- or 4-octylbenzoic acid **1a**,**b** with 4-hydroxybenzaldehyde in moderate yields by using DCC (1,3-dicyclohexylcarbodiimide) and DMAP (4-(dimethyamino)pyridine) as the condensation reagents. The radical compound **4a**,**b** was prepared from the formyl derivative with 2,3-bis(hydroxylamino)-2,3-dimethylbutane sulfate and potassium carbonate in methanol and successive oxidation of the resulting hydroxylamine derivative with sodium periodate,[16] although the yields of the desired radical compounds were very low (Scheme 1).

(2) Troponoid Derivatives 7 and 9. Troponoids with appropriate subsituents have been elucidated to be promising mesogenic cores from the extensive studies of one of the present authors[17] and therefore we next tried to prepare the derivatives with stable radicals. The alkyl troponoid derivative with 4-imino-TEMPO-subsitutent (**7**) was prepared from the corresponding 4-formyl derivative **6** by condensing with 4-amino-TEMPO in a similar manner as for the preparation of phenyl benzoate derivatives **3**. The formyl derivative was obtained by the esterification of dodecyloxy tropolone derivative **5**[18] with 4-formylbenzoic acid by using DCC and DMAP. The formyl derivative, on the other hand, was condensed with benzoic acid derivative with 4-oxocabonyl-TEMPO-substituent to give the troponoid derivative **9** in 46% yield (Scheme 2).

(3) Cyanobiphenyl Derivatives 12 and 14. The preparation of cyanobiphenyl derivatives **12a**−**c** and **14a**−**c** was carried out as shown in Scheme 3. The alkylation of 4′-hydroxy-4-biphenylcarbonitrile (**10**) with bromoalkan-1-ols[19] gave alcohols **11a**−**c** in moderate yields and the corresponding aldehydes **12a**−**c** were obtained after PCC oxidation of the alcohols. TEMPO derivatives with a cyanobiphenyl core (**12a**−**c**) were obtained from the alcohols **11a**−**c** with 4-carboxy-TEMPO by using DCC and DMAP as the condensation reagents and nitronyl nitroxide derivatives with a similar structure (**14a**−**c**) were prepared by the method as described above with sodium periodate as an oxidizing reagent.

Magnetic Properties of 3, 4, 7, and 9 and the Molecular/Crystal Structure of 4a. Typical absorptions due to aminoxyl radicals (TEMPO or nitronyl nitroxide) were observed in the EPR spectra of radicals **3**, **4**, **7**, and **9** in benzene solution. The magnetic susceptibility measurements for the solid samples of each radical were carried out on the polycrystalline sample

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[12] Nakatsuji, S.; Mizumoto, M.; Ikemoto, H.; Akutsu, H.; Yamada, J. *Eur. J. Org. Chem.* **2002**, 1912.

[13] Kaszynski, P. In *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker: New York, Basel, 1999; Chapter 15, p 305.

[14] (a) Dvolaitzky, M.; Billard, J.; Poldy, F. *C. R. Acad. Sci., Ser. C* **1974**, *279*, 533. (b) Dvolaitzky, M.; Billard, J.; Poldy, F. *Tetrahedron* **1976**, *32*, 1835. (c) Allgaier, J.; Finkelmann, H. *Macromol. Chem. Phys.* **1994**, *195*, 1017.

[15] A portion of this work has been reported as a preliminary communication: Ikemoto, H.; Akutsu, H.; Yamada, J.; Nakatsuji, S. *Tetrahedron Lett.* **2001**, *42*, 6873.

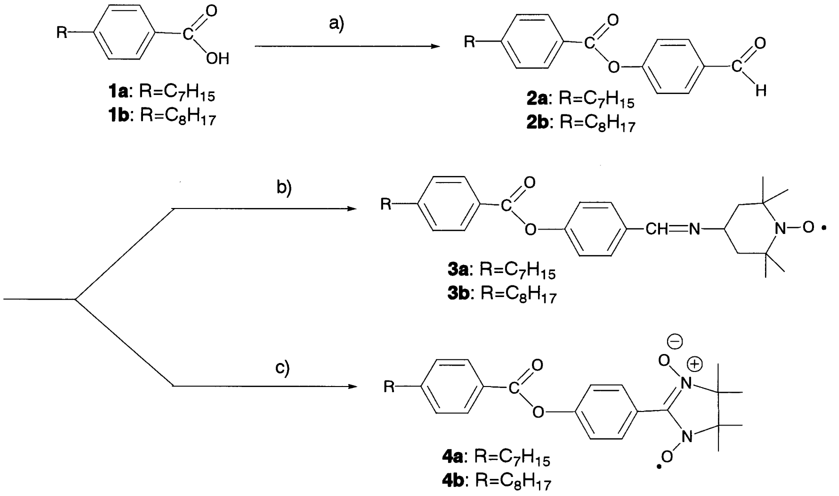
[16] Ullman, E. F.; Osciecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. Am. Chem. Soc.* **1972**, *94*, 7049.

[17] (a) Mori, A.; Takeshita, H. *J. Synth. Org. Chem. Jpn.* **1995**, *53*, 232. (b) Mori, A.; Uno, K.; Takeshita, H.; Kakihara, Y.; Ujiie, S. *Liq. Cryst.* **2002**, *29*, 1539.

[18] (a) Mori, A.; Uchida, M.; Takeshita, H. *Chem. Lett.* **1989**, 591. (b) Mori, A.; Kato, N.; Takeshita, H.; Uchida, M.; Taya, H.; Nimura, R. *J. Mater. Chem.* **1991**, *1*, 799.

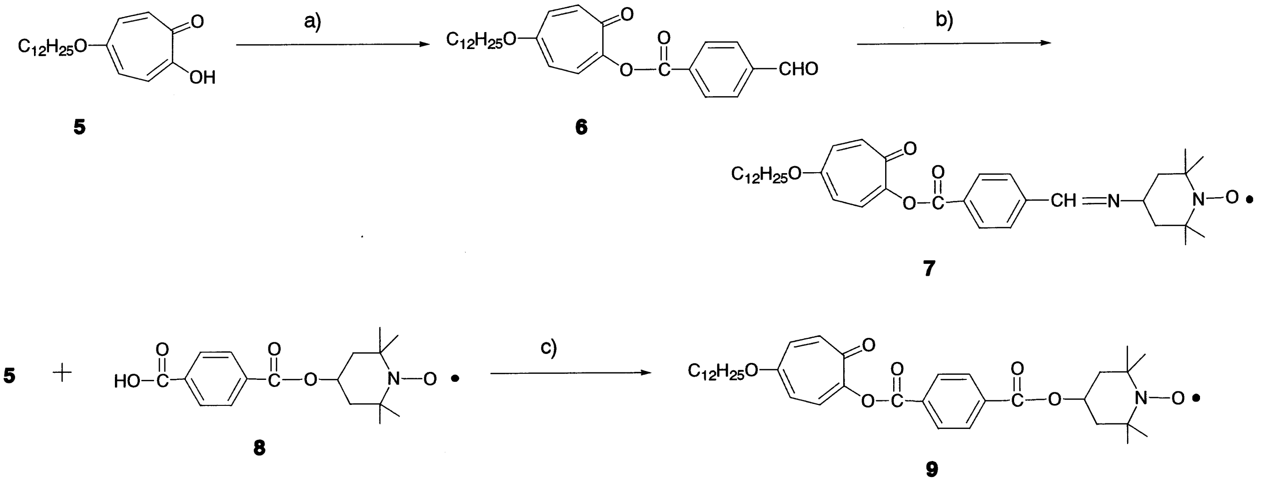
[19] Cf. Chuaed, T.; Deschenaux, R. *Helv. Chim. Acta* **1996**, *79*, 736.

SCHEME 1[a]



[a] Reagents: (a) 4-Hydroxybenzaldehyde, DCC, DMAP. (b) 4-Amino-TEMPO, AcOH. (c) (i) 2,3-Bis(hydroxyamino)-2,3-dimethylbutane sulfate, K_2CO_3; (ii) $NaIO_4$.

SCHEME 2[a]



[a] Reagents: (a) 4-Formylbenzoic acid, DCC, DMAP. (b) 4-Amino-TEMPO, AcOH. (c) DCC, DMAP.

TABLE 1. Magnetic Data for Radicals 3, 4, 7, and 9

compd	magnetic interaction[a]	C^b/emu K mol^{-1}	θ^c/K
3a	antiferromagnetic	0.33 (87)	−2.56
3b	antiferromagnetic	0.37 (97)	−3.58
4a	antiferromagnetic	0.21 (55)	−0.26
4b	antiferromagnetic	0.34 (89)	−0.13
7	antiferromagnetic	0.32 (84)	−1.39
9	antiferromagnetic	0.36 (95)	−0.17

[a] Fitting for the Curie−Weiss law. [b] Curie constant. The numbers in parentheses denote the estimated spin concentration. [c] Weiss temperature.

by a SQUID susceptometer in the temperature range of 2−300 K and the data are summarized in Table 1.

Curie−Weiss behavior with weak antiferromagnetic interactions was observed in each radical compound examined and the tendency of exhibiting slightly larger Weiss temperature was found in TEMPO-substituted derivatives (e.g., **3a**, **3b**) being compared to the corresponding nitronyl nitroxide radicals (e.g., **4a**,[20] **4b**). Such observation of only weak antiferromagnetic interactions between the spins in these radical compounds suggests the absence of significant through space as well as through bond spin−spin interactions between the spin centers. To see the strcture−magnetic property relationship of the radical compounds, the X-ray analysis of radical **4a** was carried out by using a single crystal obtained from methanol solution, its molecular/crystal structure is shown in Figure 1, and the crystal data are summarized in Table 2. As for the molecular structure of **4a**, it is of interest that three important molecular planes are not coplanar (Figure 1, upper). The dihedral angle between the molecular plane of the imidazoline ring and the benzene ring bonding with the ring amounts to 25.3° and that between the two benzene rings connected with the ester group amounts to 103.9°.[21] In the crystal structure, two molecules are dimerized in slipped head-to-tail arrangement and the dimers are stacking almost along the *c*-axis each in a perpendicular manner as shown

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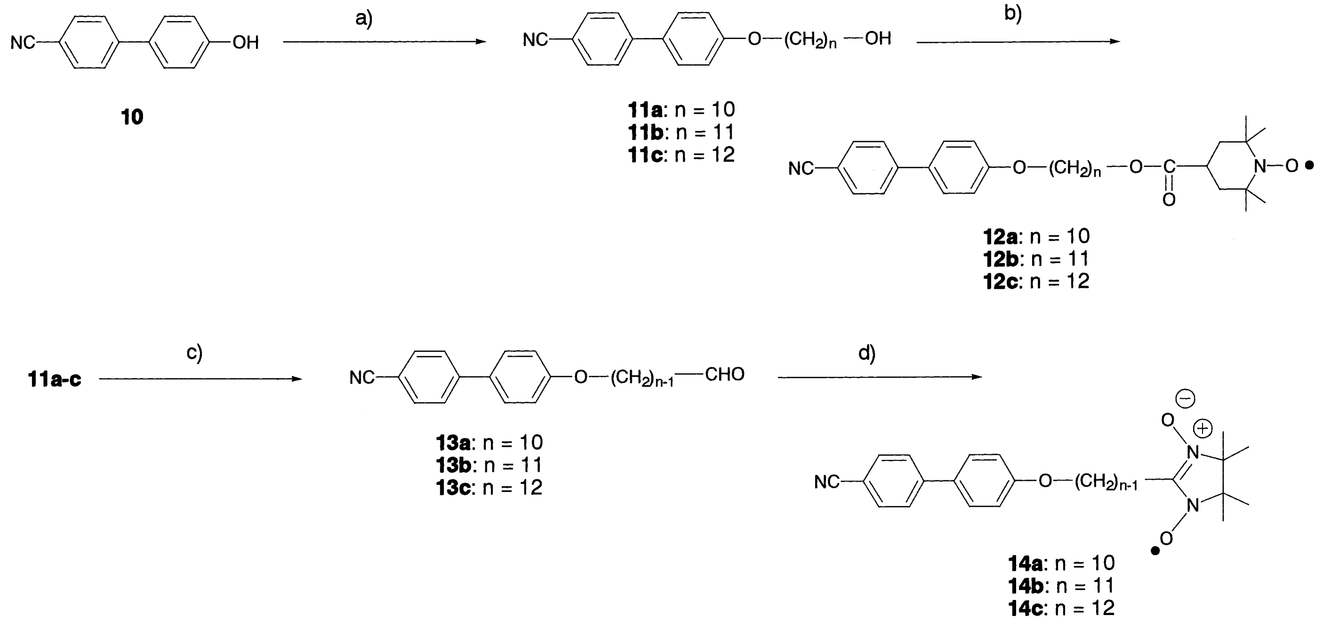
[20] The value of the Curie constant for this radical was found to be rather small owing to its relative instability.

[21] Similar molecular structure has been reported in a Shiff base with the nitronyl nitroxide radical; cf.: Zhang, D.; Zhou, W.; Zhu, D. *J. Mater. Chem.* **1999**, *9*, 1409.

SCHEME 3[a]



[a] Reagents: (a) $Br(CH_2)_nOH$ ($n = 10-12$), K_2CO_3. (b) 4-Carboxy-TEMPO, DCC, DMAP. (c) PCC. (d) (i) 2,3-Bis(hydroxyamino)-2,3-dimethylbutane sulfate, K_2CO_3; (ii) $NaIO_4$.

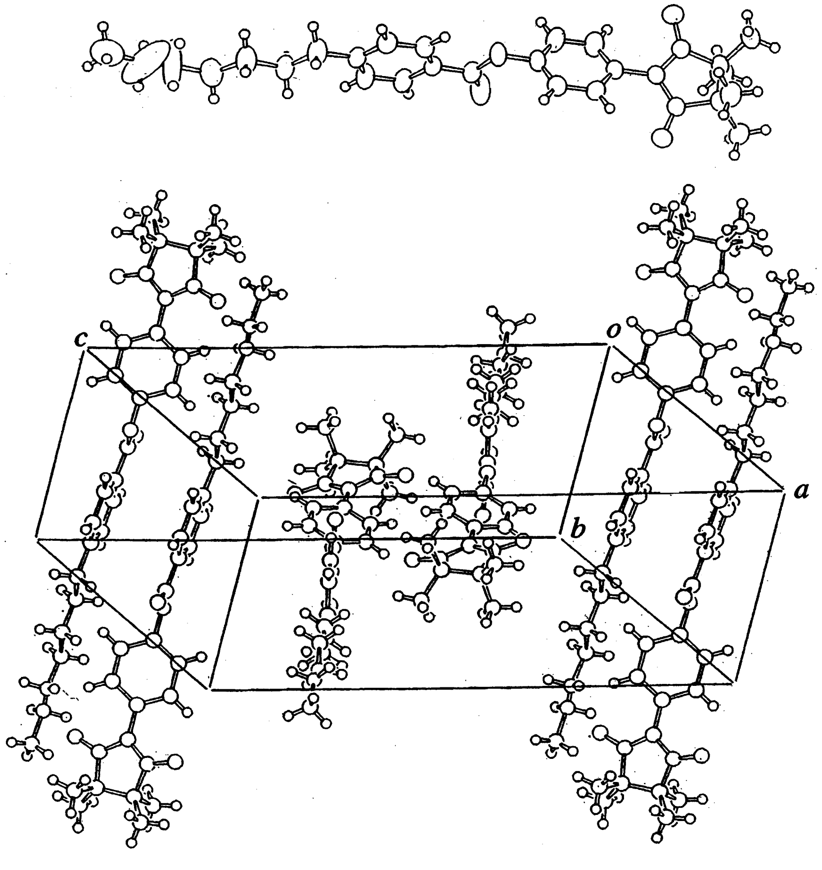


FIGURE 1. (Upper) Molecular structure of **4a**. (Lower) Crystal structure of **4a** with the indication of a unit cell.

in Figure 1 (lower). The shortest O–O distance between the molecules estimated from the analysis is approximately 5.08 Å and no other significant interactions appear to exist between the spin centers to give, as the consequence, only weak spin interactions in the spins of this radical ($\theta = -0.26$ K).

Unfortunately, no phase transition except the melting point was observed in each radical described above by DSC measurements, suggesting the absence of any appreciable mesogenic phase.

Magnetic Properties of 12a–c and 14a–c and the Molecular/Crystal Structure of 12b. The magnetic

TABLE 2. Summary of Crystal Data for 4a and 12b

	4a	**12b**
formula	$C_{27}H_{35}N_2O_4$	$C_{36}H_{47}N_2O_4$
fw	451.58	571.78
cryst syst	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
a/Å	12.008(7)	5.768(1)
b/Å	9.3378(7)	14.891(2)
c/Å	22.958(1)	18.637(3)
α/deg		84.860(3)
β/deg	104.115(5)	84.664(3)
γ/deg		85.737(3)
V/Å^3	2536.7(3)	1583.9(4)
Z	4	2
D(calc)/g cm^{-3}	1.182	1.199
no. of measd reflns	5765	8562
no. of independent reflns	5503	6024
no. of used reflns in refinement $F > 3\sigma$	3183	2401
no. of parameters refined	392	361
R	0.067	0.119
R_w	0.066	0.136

TABLE 3. Magnetic Data of Radicals 12a−c and 14a−c

compd	magnetic interaction[a]	C^b/emu K mol^{-1}	θ^c/K
12a	antiferromagnetic	0.38 (100)	−2.37
12b	antiferromagnetic	0.36 (95)	−0.19
12c	antiferromagnetic	0.36 (95)	−2.70
14a	antiferromagnetic	0.37 (97)	−0.83
14b	antiferromagnetic	0.34 (89)	−0.40
14c	antiferromagnetic	0.37 (97)	−0.63

[a] Fitting for the Curie−Weiss law. [b] Curie constant. The numbers in parentheses denote the estimated spin concentration. [c] Weiss temperature.

properties of 4-cyanobiphenyl derivatives with TEMPO or nitronyl nitroxide substituents and long alkoxyl chains between are summarized in Table 3.

Again, only weak antiferromagnetic interactions obeying Curie−Weiss behavior were observed in each radical prepared and slightly larger Weiss temperatures were clarified in TEMPO-substituted derivatives (**12a**,**12c**) being compared to the corresponding nitronyl nitroxide radicals (**14a**, **14c**) except **12b**, the Weiss temperature of which was as small as −0.19 K. A single crystal suitable for crystal structure analysis was obtained for the radical **12b** grown from methanol solution in a refrigerator and its molecular/crystal structure is shown in Figure 2.

The crystal structure obtained by X-ray analysis for the single crystal of **12b** with Curie−Weiss behavior revealed a similar packing feature to that of the 4-(*N*-methylamino)-TEMPO-substituted 4-heptylbiphenyl-4′-carboxamide derivative, which exhibits mesogenic behavior with the lamellar packing feature.[12] Thus, the molecules stack slantwise along the *b*-axis in which TEMPO groups and undecyloxycyanobiphenyl groups stack separately to form a columnar structure which appears to be suitable to exhibit a mesogenic-like phase (Figure 2, lower). The oxygen−oxygen distances of the spin centers amount to 5.77 Å, which are fairly distant so as to allow only weak antiferromagnetic interaction between the spins.

Thermomagnetic Property of Radical 12b. Only the thermal transition corresponding to the melting point was found in this class of radical compounds (**12a**, **12c**. and **14a−c**) over the temperature range examined by DSC measurement except **12b**, in which two endothermic peaks appeared at around 84 and 90 °C, respectively.[22] However, no distinct appearance of a texture was observed in **12b** by polarizing microscope investigation, suggesting the absence of a mesogenic phase but the existence of another polymorphic form through the thermal phase transition instead. We then measured the magnetic susceptibility of **12b** with Curie−Weiss behavior from 27 (300 K) up to 100 °C (373 K). The Curie−Weiss behavior observed during the heating process was found to change after the thermal transition at ca. 90 °C to another behavior being well expressed by a singlet−triplet (ST) model with antiferromagnetic spin−spin interactions of relatively large J value ($J = -35$ K) during the cooling process as shown in Figure 3.

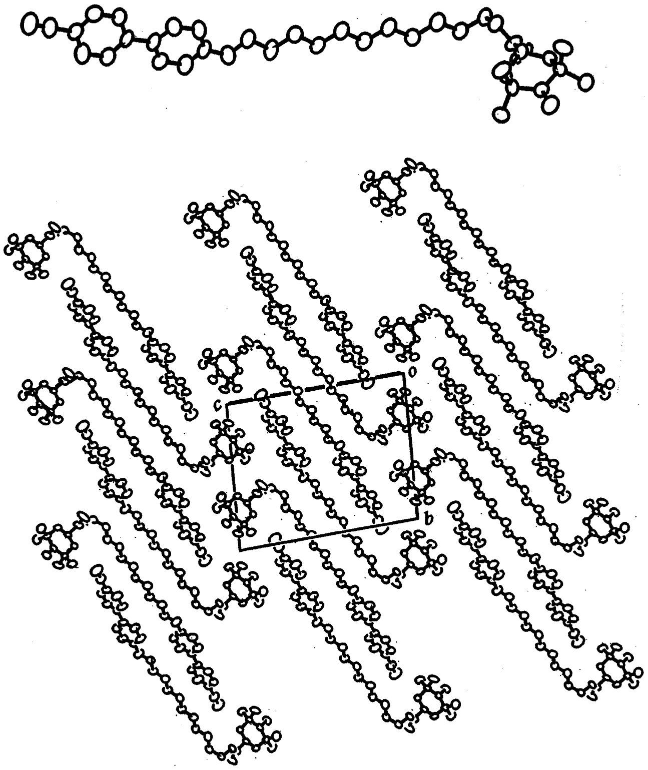


FIGURE 2. (Upper) Molecular structure of **12b**. (Lower) Crystal structure of **12b** viewed almost along the *a*-axis.

Thus, the Curie−Weiss behavior has been found to be changed to another magnetic behavior by merely heating the radical over the thermal transition temperature although a reverse change to the original Curie−Weiss behavior from the latter one was not observed but the behavior of ST model remained unchanged in the further heating/cooling process. Such unusual thermomagnetic behavior is considered to be derived from the crystal structural change from the former phase to a new phase having presumably a more thermally stable structure.[23]

Conclusions

Several organic radical compounds were prepared which consist of TEMPO or nitronyl nitroxide radical as

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[22] The DSC measurements were carried out between 50 and 110 °C for this radical at the rate of 2 °C/min.

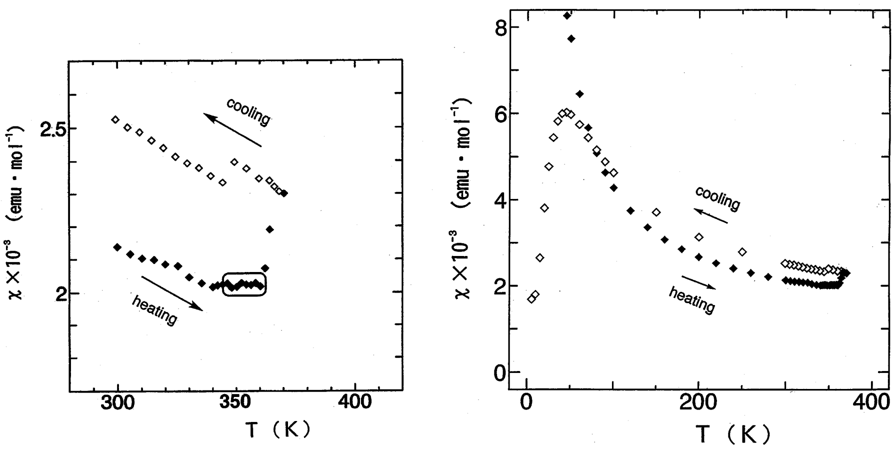

FIGURE 3. (Left) Temperature dependence of magnetic susceptibilities of **12b** between 300 and 370 K measured at 0.5 T. The data for the heating and cooling process are depicted as closed and open squares, respectively. The region between the phase transition temperatures is indicated as an open circle. (Right) Temperature dependence of magnetic susceptibilities of **12b** before and after the phase transition. The data for the heating and cooling process are depicted as closed and open squares, respectively.

spin sources on one hand and phenyl benzoate, troponoid, or biphenylcarbonitrile with long alkyl substituents as mesogenic cores on the other hand to develop heat-responsive liquid crystalline radicals. Although most radicals exhibited only weak antiferromagnetic interactions being based on Curie−Weiss law and the structure−magnetic property relationship could be rationally understood by the crystal structure analysis for radical **4a**, an unusual magnetic transition from a Curie−Weiss phase to another magnetic phase well expressed by a ST model was revealed through the thermal transition in 4′-undecyloxy-4-biphenylcarbonitrile derivative with oxocarbonyl-TEMPO **12b** despite the absence of an appreciable mesogenic phase in the radical.

Experimental Section

Materials. 4-Amino-, 4-hydroxy-, and 4-carboxy-TEMPO radicals used as building blocks in this study are commercially available and were used without further purification.

Instrumentation. Magnetic susceptibility measurements were carried out on a QUNTUM DESIGN MPMS-5 SQUID susceptometer, using ca. 10 mg for each powdered sample in the usual way.[24]

X-ray Structure Determination. X-ray diffraction data were collected on a Nonius (CAD4) with Cu Kα radiation (for **4a**) or Brucker (Mercury CCD) diffractometer with Mo Kα radiation (for **12b**) at room temperature. The structures were solved by direct methods and expanded by using Fourrier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed with use of the teXsan crystallographic software package of Molecular Structure Corporation and detailed crystallographic data (atomic coordinates, hydrogen atom coordinates, anisotropic displacement parameters, bond length and angles) have been deposited with the Cambridge Crystallographic Data Centre. Details are available as Supporting Information.

Preparation of Phenylbenzoate Derivatives with the TEMPO Radical (3a, 3b). To a stirred solution of 4-*n*-heptylbenzoic acid **1a** (0.36 g, 1.6 mmol) and 4-hydroxybenzaldehyde (0.20 g, 1.6 mmol) in dichloromethane (30 mL) was added DCC (0.41 g, 2.0 mmol) and DMAP (0.24 g, 2.0 mmol) and stirring was continued for 1 d at ambient temperature. The resulting reaction mixture was then washed with brine, dried over anhydrous $MgSO_4$, and concentrated in vacuo to give a solid that was purified by column chromatography on silica gel with use of benzene as an eluent. The ester intermediate **2a** was obtained (0.38 g) as a colorless solid that was used without further purification for the successive reaction. The toluene solution (30 mL) of the intermediate **2a** (0.38 g, 1.2 mmol) and 4-amino-TEMPO (0.20 g, 1.2 mmol) with a small amount of acetic acid was heated to reflux and the reaction was continued for 1 h. The reaction mixure was concentrated under reduced pressure to give a crude solid and the recrystallization of the solid from toluene yielded the radical **3a** as a red powdery solid (0.38 g, 48% from **1a**), mp 95−98 °C dec; EPR (benzene) 3 lines, $g = 2.006$, $a = 1.53$ mT; FAB-HRMS calcd for $C_{30}H_{43}N_2O_3$ (M + 2)[25] 479.3220, found *m*/*z* 479.3205. In a similar manner, the radical **3b** was obtained in 24% yield (2 steps), and its data are as follows: mp 105−107 °C; EPR (benzene) 3 lines, $g = 2.006$, $a = 1.50$ mT; FAB-HRMS calcd for $C_{31}H_{45}N_2O_3$ (M + 2) 493.3395, found *m*/*z* 493.3418.

Preparation of Phenylbenzoate Derivatives with Nitronyl Nitroxide Radical (4a, 4b). A mixture of the intermediate **2a** (0.19 g, 0.56 mmol), 2,3-bis(hydroxylamino)-2,3-dimethylbutane sulfate (0.18 g, 0.83 mmol), and potassium carbonate (0.082 g, 0.56 mmol) in a mixed solution of methanol/water (9:1) (50 mL) was stirred for 1d at ambient temperature. After workup of the reaction mixture in the usual manner, the crude product was dissolved in methanol (5 mL) and sodium periodate (0.13 g, 0.56 mmol) was added at 0 °C. The resulting dark blue solution was stirred for 3 min and then extracted with chloroform. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give a solid that was purified by column chromatography on silica gel by using *n*-hexane/ethyl acetate as an eluent and recrystallized from methanol. The radical **4a** was obtained as dark blue needles (10 mg, 4% from **2a**): mp 97−100°C; EPR (benzene) 5 lines, $g = 2.007$, $a = 1.50$ mT; FAB-HRMS calcd for $C_{27}H_{37}N_2O_4$ (M + 2) 453.2714, found *m*/*z* 453.2704. In a similar manner, the radical **4b** was obtained in 4% yield (2 steps), and its data are as follows: mp 95−97 °C; EPR (benzene) 5 lines,

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[23] Such a magnetic switching behavior might allow us to be reminded of, in principle, a write-once recordable memory device by application of an outer stimulus (heat in the present case).

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

[25] The tendency toward appearance of the M + 2 peak as the main peak was observed in the FAB-MS measurements for this class of radical compounds in general and we then adjusted the FAB-HRMS data generally to the main peak.

$g = 2.007$, $a = 1.50$ mT; FAB-HRMS calcd for $C_{28}H_{39}N_2O_4$ (M + 2) 467.2938, found *m*/*z* 467.2915.

Preparation of Troponoid Derivatives with TEMPO Radical (7, 9). Dodecyloxy tropolone derivative **5** was prepared according to the published procedure from 5-hydroxyltropolone with 1-bromododecane[18] and 0.20 g of **5** (0.65 mmol) was condensed with 4-formylbenzoic acid (0.098 g, 0.65 mmol) with use of DCC (0.14 g, 0.69 mmol) and DMAP (0.080 g, 0.69 mmol) in dichloromethane (30 mL) in the usual manner to give the intermediate **6** as a colorless solid. The intermediate **6** (0.20 g, 0.69 mmol) was reacted with 4-amino-TEMPO (0.12 g, 0.69 mmol) with a small amount of acetic acid in toluene solution (40 mL) to give the radical **7** as an orange powdery solid (0.26 g, 50% from **5**): mp ca. 170°C dec; EPR (benzene) 3 lines, $g = 2.007$, $a = 1.60$ mT; FAB-HRMS calcd for $C_{36}H_{52}N_2O_5$ (M + 2) 592.3876, found *m*/*z* 592.3898. The radical **9** was prepared in a similar manner as above from the same compound **6** with TEMPO-substituted terephthalic acid mono-ester **8** which, in turn, was obtained from telephthaloyl chloride with 4-hydroxy-TEMPO and triethylamine in dichloromethane. The data for the radical **9** are as follows: mp 125−128 °C; EPR (benzene) 3 lines, $g = 2.006$, $a = 1.51$ mT; FAB-HRMS calcd for $C_{36}H_{52}NO_7$ (M + 2) 610.3744, found *m*/*z* 610.3729.

Preparation of Cyanobiphenyl Derivatives with TEMPO Radical (12a−c). A stirred mixture of 4-cyano-4′-hydroxybiphenyl **10** (0.20 g, 1.0 mmol), 10-bromodecanol (0.48 g, 2.1 mmol), and potassium carbonate (2.1 g, 3.1 mmol) in DMF/THF (3:1, 30 mL) was refluxed for 20 h. After cooling of the reaction mixture to ambient temperature, the solid material deposited was filtered off and the resulting filtrate was purified by column chromatography on silica gel with use of benzene/diethyl ether (1:1) as an eluent to give the intermediate alcohol **11a**. Alcohol **11a** was then derivatized by using 4-carboxy-TEMPO, DCC, and DMAP in the usual manner to give the ester **12a** in 40% yield (2 steps from 10) as orange needles and its data are as follows: mp 88−91°C; EPR (benzene) 3 lines, $g = 2.007$, $a = 1.55$ mT; FAB-HRMS calcd for $C_{33}H_{47}N_2O_4$ (M + 2) 535.3536, found *m*/*z* 535.3573. The radicals **12b** and **12c** were prepared in a similar manner and the data are as follows: **12b**: mp 82−85 °C; EPR (benzene) 3 lines, $g = 2.007$, $a = 1.49$ mT; FAB-HRMS calcd for $C_{34}H_{49}N_2O_4$ (M + 2) 549.3599, found *m*/*z* 549.3610. Anal. Calcd for $C_{34}H_{47}N_2O_4$: C, 74.55; H, 8.65; N, 5.12. Found: C, 74.57; H, 8.80; N, 5.06. **12c**: mp 86−89 °C; EPR (benzene) 3 lines, $g = 2.006$, $a = 1.58$ mT; FAB-HRMS calcd for $C_{35}H_{51}N_2O_4$ (M + 2) 563.3849, found *m*/*z* 563.3815. Anal. Calcd for $C_{35}H_{49}N_2O_4$: C, 74.83; H, 8.79; N, 4.99. Found: C, 74.91; H, 8.77; N, 4.70.

Preparation of Cyanobiphenyl Derivatives with Nitronyl Nitroxide Radical (14a−c). To a stirred solution of alcohol **11a** (0.20 g, 0.57 mmmol) in dichloromethane (50 mL) was added PCC (0.18 g, 0.85 mmol) and the stirring was continued for 1 h; the resulting solution was filtrated with Celite under reduced pressure. After purification of the filtrate by column chromatography, aldehyde **13a** was obtained as a colorless powdery solid (0.15 g, 76%). Aldehyde **13a** was then derivatized to nitronyl nitroxide derivative **14a** by the two-step sequence as described above. The radical **14a** was obtained as reddish violet microcrystals (49 mg, 19% from **13a**): mp 124−128 °C; EPR (benzene) 5 lines, $g = 2.007$, $a = 1.58$ mT; FAB-HRMS calcd for $C_{29}H_{39}N_3O_3$ (M + 1) 477.2991, found *m*/*z* 477.3036. In a similar manner, the radicals **14b** and **14c** were obtained in 13% and 14% yield, respectively, and the data are as follows: **14b**: mp 126−130 °C; EPR (benzene) 5 lines, $g = 2.007$, $a = 1.63$ mT; FAB-HRMS (M + 2) calcd for $C_{30}H_{42}N_3O_3$ 492.3227, found *m*/*z* 492.3252. **14c**: mp 133−136°C; EPR (benzene) 5 lines, $g = 2.007$, $a = 1.51$ mT; FAB-HRMS calcd for $C_{31}H_{43}N_3O_3$ (M + 1) 505.3304, found *m*/*z* 505.3304.

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Supporting Information Available: X-ray crystallographic data (bond lengths and angles, atomic coordinates, and anisotropic thermal parameters) for **4a** and **12b** (CIF files). This material is available free of charge via the Internet at http://pubs.acs.org.

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