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# Preparation and Properties of Novel Mesogenic Spin System

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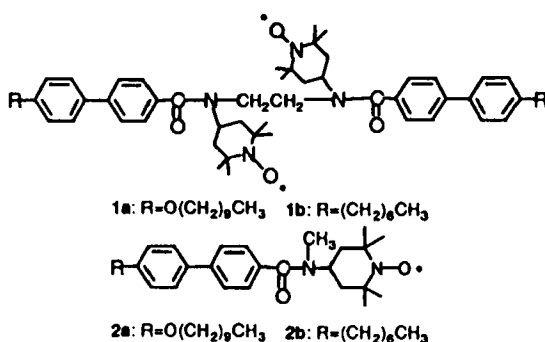
Series of biphenyl derivatives bearing TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)-substituents on one hand and long alkyl- or alkoxy-substituent on the other hand have been prepared. Among them a mesogenic property has been found in a biphenyl derivative with *N*-methyl-amino-TEMPO-carboxamide-substituent having lamellar structure of the molecular arrangement to show local antiferromagnetic spin interactions.

**Keywords:** TEMPO Radical; Magnetic Property; Biphenyl Derivatives; Liquid Crystalline Property; Crystal Structure

In recent years, the search for new molecular-based/organic magnetic materials with multi-functionality is of growing interest in the field of materials chemistry and to construct the novel spin systems that responds to outer stimuli such as heat or light has been paid much attention by research chemists.<sup>[1]</sup> During the course of our studies for the development of new multi-functional organomagnetic materials,<sup>[2]</sup> we have been interested in preparing the spin systems with liquid crystalline property in expectation of occurrence of ordered spin interactions in the oriented molecular aggregates. We then have initiated our study to prepare the spin systems with mesogenic cores,<sup>[3]</sup> 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<sup>[4]</sup> and actually only a few organic radicals with less bulky DOXYL (4,4-dime-

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thyl-3-oxazolidinyloxy)-substituent have been reported to show liquid crystalline property.<sup>[5]</sup> In this communication, we wish to report on the preparation and the magnetic properties of the biphenyl derivatives with 4-substituted-amino-TEMPO-substituents on one hand and the long alkyl- or alkoxy-substituent on the other hand, the liquid crystalline property of 4-methyl-amino-TEMPO derivative **2b** and its molecular/crystal structure together with the structure of non-mesogenic biradical **1a**.



CHART

Since much interest is currently focused on the liquid crystalline dimers (dime-sogens) with two mesogenic units,<sup>[6]</sup> the biradicals with two biphenyl cores (**1a**, **1b**) have been prepared by the condensation of the carboxylic acid derivatives of 4-alkoxy- or 4-alkylbiphenyl with the bis-TEMPO-substituted ethylenedi-amine<sup>[7]</sup> in moderate yields.

However, no liquid crystalline property on these radicals has been observed in the DSC measurement or polarizing microscope and Curie-Weiss behavior with weak antiferromagnetic interactions has been apparent in the magnetic suscepti-bility measurements (TABLE I). It was found from the X-ray analysis of **1a** that the two very similar but crystallographically independent molecules exist in the unit cell (A and B in FIGURE 1) and each six-membered ring of TEMPO moiety in the biradical molecules protrudes from the long and rod-like molecular axis almost in perpendicular manner and in anti-configuration.<sup>[8]</sup> Such TEMPO arrangement is supposed to be inadequate to afford a mesogenic phase by inter-fering the aggregation of the molecules together to result in the absence of such a phase. The nearest intermolecular O-O distance between the radical centers is estimated to be 6.09 Å and which is rather apart for direct and strong spin-spin interactions.

TABLE I Magnetic data of radicals

Compound	Magnetic interaction	$C/\text{emu K mol}^{-1}$	$\theta/\text{K}$	$J/\text{K}$
<b>1a</b>	antiferromagnetic <sup>a</sup>	0.73	-1.14	-
<b>1b</b>	antiferromagnetic <sup>a</sup>	0.73	-0.28	-
<b>2a</b>	antiferromagnetic <sup>b</sup>	-	-	-14.9
<b>2b</b>	antiferromagnetic <sup>b</sup>	-	-	-14.8

- a. Fitting for Curie-Weiss law.  
 b. Fitting for singlet-triplet model. The  $\chi_M$ -values are expressed in the following equation:

$$\chi_M = \frac{2N\beta^2 g^2}{kT \left[ 3 + \exp\left(\frac{-2J}{kT}\right) \right]}$$

where  $\beta$  is the electronic Bohr magneton,  $N$  is Avogadro's number,  $g$  is the Zeeman factor,  $k$  is Boltzmann's constant, and  $J$  is the interaction parameter appearing in the spin Hamiltonian  $H = JS_1 \cdot S_2$ .

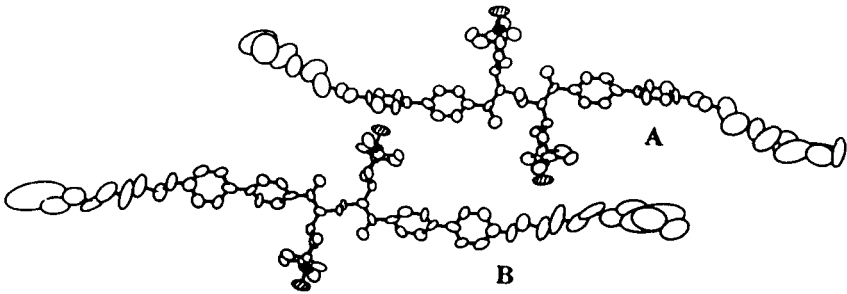


FIGURE 1 Molecular structure of **1a** (two independent molecules). The hydrogen atoms are omitted for clarity. The nitrogen and oxygen of aminoxyl moiety are depicted as closed and hatched circle, respectively

We then turned our attention to the alkoxy- as well as alkylbiphenyl derivatives with 4-methylamino-TEMPO radicals, i.e., **2a** and **2b**. These radical compounds have been prepared by the condensation of the corresponding acids with 4-methylamino-TEMPO derived from 4-oxo-TEMPO and methylamine.<sup>[9]</sup> Investigation of their mesogenic properties revealed the existence of a mesogenic phase only in **2b** among the compounds prepared; Two endothermic profiles during heating process were observed in the DSC measurement of **2b** indicating the existence of mesophase at 374–377 K (101–104 °C) while no reversibility was found during the cooling process. The appearance of schlieren texture in the investigation with polarizing microscope at around 375 K further supported the existence of mesophase in the compound although the range of the phase was found to be rather narrow.

As shown in FIGURE 2, the gradual decrease of the magnetic susceptibilities of **2b** observed in the heating process turned to increase apparently at around 374 K and the temperature corresponds to the phase transition from the crystal phase to the mesophase (not from mesophase to liquid phase). The behavior suggests the change of the contribution of intermolecular interactions around the phase due mainly to the change of molecular alignments. Although the explicit reason for the observed increase of the magnetic susceptibility over the phase transition temperature is not clear yet, it is presumed that the growing strength of the intermolecular antiferromagnetic interactions during the heating process is abruptly released by the phase transition based on the structural change around the TEMPO moieties which are considered to be relatively constrained in the crystal phase (Cf. FIGURE 3, below). Thus, the magnetic behavior observed in the magnetic susceptibility measurement seems to reflect the occurrence of the heat-driven crystal structural change which exhibits the mesophase at around 374 K. However, no appreciable decrease but gradual increase was observed in the measurement during the cooling process indicating the monotropic behavior of the mesogenic phase and the result is also consistent with the DSC measurement.<sup>[10]</sup>

From the measurements of the magnetic susceptibilities of **2a** as well as **2b** (samples without annealing) at lower temperatures down to 2 K, the existence of the local antiferromagnetic spin interactions have been revealed between the spins of the radicals in the lower temperature region. The behaviors are well explained by singlet-triplet (S-T) model with relatively large *J*-values of about -15 K indicating the existence of significant intermolecular spin-spin interactions (FIGURE 3) (TABLE I).<sup>[11]</sup>

It was found from the X-ray analysis of **2b** that there are two crystallographically independent molecules in the crystal (A and B in FIGURE 3, upper): The TEMPO group on molecule A is tilted to come close to piperidine ring of molecule B and the short contact between the oxygen atom in the aminoxyl moiety of the former molecule and the *N*-methyl group as well as C(3) of the piperidine group of the latter molecule (3.36 Å and 3.49 Å, respectively).<sup>[12]</sup> It is suggested from such structural features that the spin-spin interactions occur between the spin centers of the molecules through the hydrogen bond between the oxygen atom of an aminoxyl and the hydrogen on the *N*-methyl group and/or through the oxygen atom and a methylene carbon atom on the heterocyclic ring to afford the local antiferromagnetic interactions.

The crystal structure of the same compound viewed along the *b*-axis is shown in FIGURE 3 (lower) and it is apparent from the figure that the molecules are

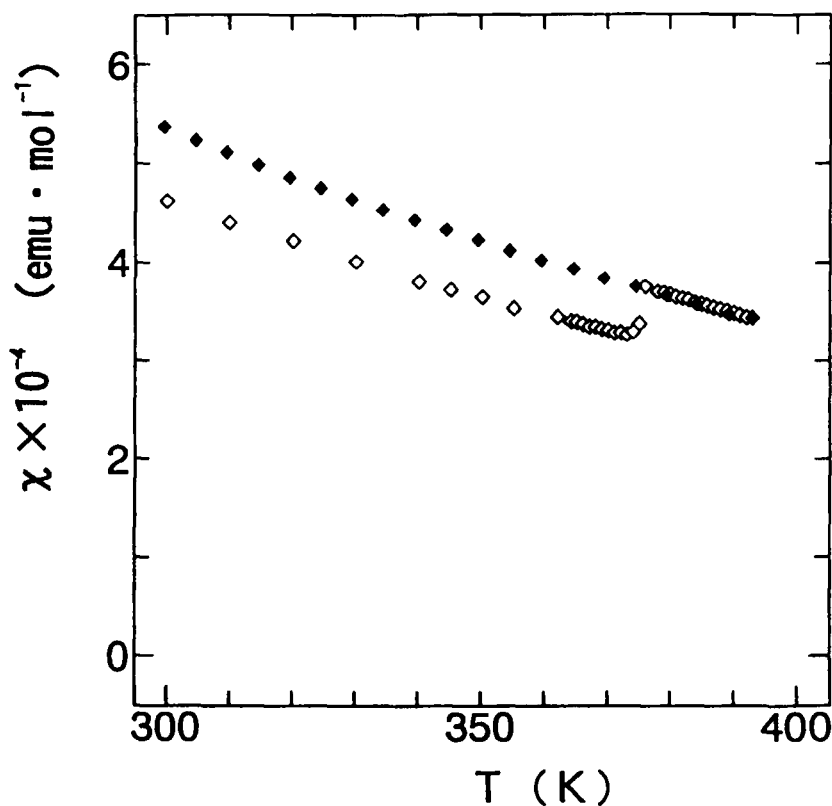


FIGURE 2 Temperature Dependence of Magnetic susceptibilities  $\chi$  of **2b** between 300 – 400 K measured at 0.5 T. The data of heating and cooling process are depicted as open and closed square, respectively

stacking along the c-axis (actually in zig-zag manner along the b-axis) to form the columnar structures in which each alkylbiphenyl group and TEMPO group align separately. The remarkable structural feature reminds us of the lamellar structure of lyotropic liquid crystal or amphiphilic phospholipid bilayer in which the hydrophobic alkyl groups and hydrophilic phosphate groups are stacking separately.<sup>[13]</sup> Such an supramolecular structure found in the crystal of **2b** is considered to be relevant to the formation of mesogenic phase in the compound on one hand and the significant antiferromagnetic interactions on the other hand.

Further studies are now under way to develop related radical compounds with lower transition temperatures to a mesogenic phase and/or with wider mesogenic phase for the better understanding the nature of liquid crystalline radicals.

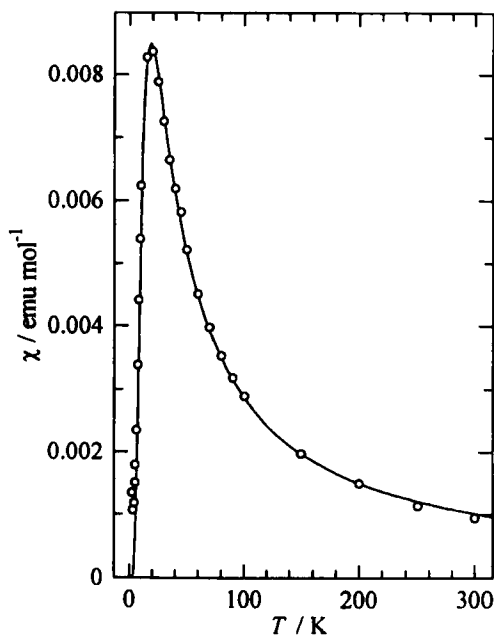


FIGURE 3 Temperature dependence of  $\chi$  for **2b** between 2–300 K. The calculated values for S-T model are shown in the solid line

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### References

1. Cf. O. Kahn and C. J. Martinetz, *Science*, **279**, 44 (1998); W. Fujita and K. Awaga, *Science*, **286**, 261 (1999); K. Hamachi, K. Matsuda, T. Itoh, and H. Iwamura, *Bull. Chem. Soc. Jpn.*, **71**, 2937 (1998); K. Matsuda and M. Irie, *Chem. Lett.*, **2000**, 16; K. Matsuda and M. Irie, *J. Am. Chem. Soc.*, **122**, 7195 (2000).
2. Cf. S. Nakatsuji, M. Mizumoto, A. Takai, H. Akutsu, J. Yamada, S. Schmitt, and K. Hafner, *Mol. Cryst. Liq. Cryst.*, **348**, 1 (2000); S. Nakatsuji, Y. Ogawa, S. Takeuchi, H. Akutsu, J. Yamada, A. Naito, K. Sudo, and N. Yasuoka, *J. Chem. Soc., Perkin Trans. 2*, **2000**, 1969; T. Ojima, H. Akutsu, J. Yamada, and S. Nakatsuji, *Chem. Lett.*, **2000**, 918.



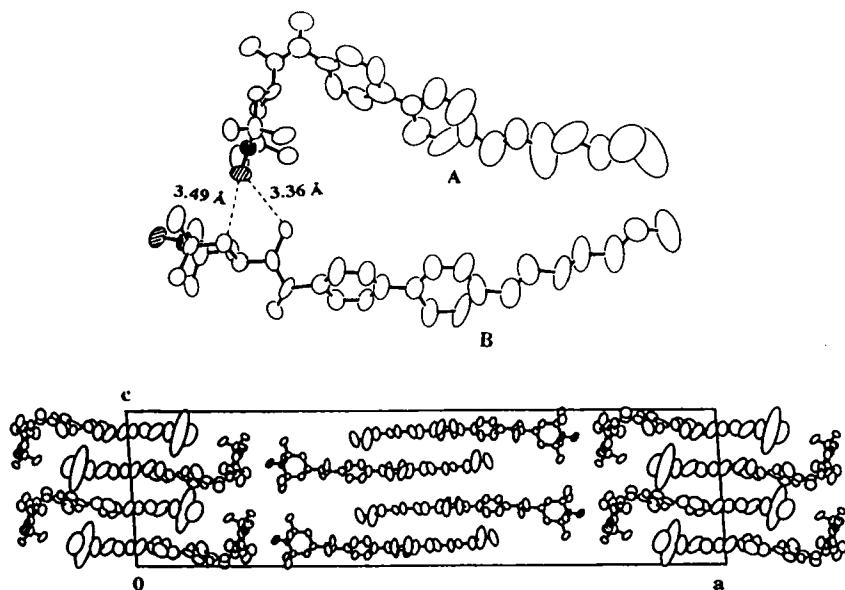


FIGURE 4 Upper: Molecular structure of **2b** (two independent molecules). The hydrogen atoms are omitted for clarity. The nitrogen and oxygen of aminoxyl moiety are depicted as closed and hatched circle, respectively. Lower: Crystal structure of **2b** viewed along the b-axis

3. S. Nakatsuji, M. Mizumoto, K. Kitamura, H. Akutsu, and J. Yamada, *Mol. Cryst. Liq. Cryst.*, in press. Similar studies have been in progress by other workers independently: Cf. R. Tamura et al., presented at the 14th Symposium on Fundamental Organic Chemistry held in Higashi-hiroshima, Japan on November 21–23, 1998, abstract p. 357 and 359; D. Zhang, W. Zhou, and D. Zhu, *J. Mater. Chem.*, **7**, 1409 (1999). See also ref. 4.
4. P. Kaszynski, in "Magnetic Properties of Organic Materials," ed by P. M. Lahti, Marcel Dekker, Inc., New York, Basel (1999), Chapt. 15, p. 305.
5. M. Dvornitzky, J. Billard, and F. Poldy, *C. R. Acad. Sc., Ser. C*, **279**, 533 (1974); M. Dvornitzky, J. Billard, and F. Poldy, *Tetrahedron*, **32**, 1835 (1976).
6. Cf. N. Tamaoki, A. Parfenov, A. Masaki, and H. Matsuda, *Adv. Mater.*, **9**, 1102 (1997); C. T. Imrie and G. R. Luckhurst, in "Handbook of Liquid Crystals," ed by D. Demus, J. Goodby, G. W. Gray, H. -W. Spiess, and V. Vill. Wiley-VCH, Weinheim (1998) vol. 2B, p. 801.
7. S. Nakatsuji, M. Mizumoto, A. Takai, H. Anzai, Y. Teki, and K. Tajima, *Mol. Cryst. Liq. Cryst.*, **334**, 205 (1999).
8. Crystal data for **1a**  $C_{66}H_{96}N_4O_6$ , FW=1041.51, triclinic (P-1),  $a=14.465(7)$  Å,  $b=23.19(1)$  Å,  $c=10.038(2)$  Å.  $\alpha=100.60(2)$ ,  $\beta=94.02(4)$ ,  $\gamma=100.27(3)$ ,  $V=3238(2)$  Å<sup>3</sup>,  $T=295$  K,  $Z=2$ ,  $D_c=1.068$  g·cm<sup>-3</sup>.  $R=0.111$ ,  $wR=0.101$  [2595 observed reflections and 686 parameters,  $I>3\sigma(I)$ ].
9. S. Nakatsuji, A. Takai, K. Nishikawa, Y. Morimoto, N. Yasuoka, K. Suzuki, T. Enoki, and H. Anzai, *J. Mater. Chem.*, **9**, 1747 (1999). See also, S. Nakatsuji and H. Anzai, *J. Mater. Chem.*, **7**, 2161 (1997).
10. Similar magnetic behavior was observed in a preliminary EPR measurement in the heating process around the mesogenic phase, i. e., an apparent increase of the line width was observed around the phase.

11. The spin concentrations of the radicals have been estimated from the calculations to be 65% for **2a** and 83% for **2b**, respectively.
12. Crystal data for **2b** C<sub>30</sub>H<sub>43</sub>N<sub>2</sub>O<sub>2</sub>, FW=436.68, monoclinic (C2/c), a=62.21(1) Å, b=11.206(6) Å, c=16.286(3) Å, β=94.44(2), V=11320(6) Å<sup>3</sup>, T=295 K, Z=16, D<sub>c</sub>=1.088 gcm<sup>-3</sup>, R=0.171, wR=0.145 [3320 observed reflections and 614 parameters, I>3σ(I)]. The high R factors of **1a** and **2b** is due partially to the poor crystallinity of the compounds and also to the fact that the alkyl chains are highly disordered as often seen in liquid crystalline compounds with long alkyl chain. Cf. K. Hori and K. Endo, *Bull. Chem. Soc. Jpn.*, **66**, 46 (1993).
13. Cf. R. H. Pearson and I. Pascher, *Nature*, **281**, 499 (1979).