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## Aminoxyl radicals bearing a mesogenic core<sup>†</sup>

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Abstract—A series of aminoxyl radicals (nitronyl nitroxide or TEMPO) bearing biphenylcarbonitrile as a mesogenic core (2a-2c and 3a-3c) was prepared. Among them, unusual magnetic transition from the original Curie–Weiss phase to another magnetic phase well expressed by a singlet–triplet model was found in the 4'-undecyloxy-4-biphenylcarbonitrile derivative with oxocarbonyl-TEMPO through the thermal transition. © 2001 Elsevier Science Ltd. All rights reserved.

The development of exotic organic spin systems with multi-properties is a current interest in the field of materials chemistry, and much attention has been paid in recent years to the preparation of such novel spin systems that show synergy with outer stimuli such as heat or light.<sup>1</sup> During the course of our studies for the development of new organomagnetic materials,<sup>2</sup> we have been interested in preparing spin systems with conductivity, photo-functionality or liquid crystalline properties.<sup>3</sup> The preparation of spin systems with 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.<sup>4</sup> We then initiated our study to prepare the spin systems with mesogenic cores and we reported in a previous paper the preparation of the alkyl- or alkoxysubstituted biphenyl derivatives with carboxyamide-TEMPO substituents 1, the liquid crystalline property 4-methylamino-TEMPO (2,2,6,6-tetramethylof piperidinyl-1-oxy) derivative  $[R = CH_3(CH_2)_6, R' = CH_3]$ as well as their magnetic properties.<sup>5</sup> In this communication, we wish to report the preparation and properties of a series of aminoxyl radicals (nitronyl nitroxide or TEMPO) bearing biphenylcarbonitrile as a mesogenic core (2a-2c, 3a-3c) and an unusual magnetic transition behaviour found in the 4'-undecyloxy-4biphenylcarbonitrile derivative with oxocarbonyl-TEMPO **3b** by heating over the thermal transition temperature.

The preparation of the radical compounds 2a-c and 3a-c was carried out as shown in Scheme 1. The alkylation of 4'-hydroxy-4-biphenylcarbonitrile (4) with bromoalkan-1-ols<sup>6</sup> gave alcohols 5a-c in moderate yields. PCC oxidation of the alcohols gave the corresponding aldehydes 6a-c, which were then transformed to the nitronyl nitroxides 2a-c by the conventional method using sodium periodate as an oxidizing reagent.<sup>7</sup> The alcohols 5a-c were also condensed with 4-carboxy-TEMPO by using DCC and DMAP to afford the desired esters 3a-c.<sup>8</sup>

Weak antiferromagnetic interactions based on Curie-Weiss behaviour were observed by SQUID measure-



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Scheme 1. Reagents and conditions:  $Br(CH_2)_nOH$ ,  $K_2CO_3$ , DMF-THF, 120°C, 20 h; (ii) PCC,  $CH_2Cl_2$ , rt, 1.5 h; (iii) (1)  $\{C(CH_3)_2(NHOH)\}_2 H_2SO_4$ ,  $K_2CO_3$ , MeOH-H<sub>2</sub>O, rt, 1 day, (2) NaIO<sub>4</sub>, CHCl<sub>3</sub>, 0°C, 3 min; (iv) 4-carboxy-TEMPO, DCC, DMAP,  $CH_2Cl_2$ , rt, 2 days.

ments in all of the aminoxyls thus prepared (Table 1) and only the thermal transition corresponding to the melting point was found during the temperature range examined by DSC measurement in each compound, except a TEMPO derivative **3b** in which two endothermic peaks appeared at around 84 and 90°C, respectively.<sup>9</sup>

The crystal structure<sup>10</sup> obtained by X-ray analysis of the single crystal of **3b** with Curie–Weiss behaviour revealed a similar packing feature to that of the radical compound **1** [ $R=CH_3(CH_2)_6$ ,  $R'=CH_3$ ].<sup>5</sup> Thus, the molecules stack along the *b*-axis in which TEMPO groups and alkoxycyanobiphenyl groups stack separately to form a columnar structure which appears to be suitable to exhibit a mesogenic-like phase (Fig. 1).

Also, the oxygen–oxygen distance of the spin centers amounts to 5.77 Å, which is apart so weak antiferromagnetic interactions take place between the spins. We then measured the magnetic susceptibility of **3b** with

Table 1. Magnetic data of aminoxyls

Compound	Magnetic interaction	C (emu K mol <sup>-1</sup> )	θ (K)	J (K)
2a	Antiferromagnetica	0.365	-0.83	_
2b	Antiferromagnetic <sup>a</sup>	0.341	-0.40	_
2c	Antiferromagnetica	0.365	-0.63	_
3a	Antiferromagnetic <sup>a</sup>	0.375	-2.37	_
3b	Antiferromagnetica	0.355	-0.19	_
3b	Antiferromagnetic <sup>b</sup>	_	_	-35.3
3c	Antiferromagnetica	0.364	-2.70	_

<sup>a</sup> Fitting for Curie-Weiss law.

<sup>b</sup> Fitting for singlet-triplet model (after phase transition).



Figure 1. Crystal structure of 3b viewed along the *a*-axis.

Curie-Weiss behaviour over 27°C (300 K) up to 100°C (373 K) and the data are shown in Fig. 2.<sup>11</sup> The Curie–Weiss behaviour observed during the heating process was found to change after the thermal transition at ca. 90°C, as shown in Fig. 2, to the behaviour being well expressed by a singlet-triplet (ST) model with antiferromagnetic spin-spin interactions of relatively large J-value  $(J=-35.3 \text{ K})^{12}$  during the cooling process. Thus, the Curie-Weiss behaviour could be changed to another magnetic behaviour by merely heating the radical over the thermal transition temperature, although a reverse change to the original Curie-Weiss behaviour from the latter one was not observed in the further heating/cooling process. Such unusual thermomagnetic behaviour is considered to be derived from the crystal structural change from the former phase to



Figure 2. Temperature dependence of paramagnetic susceptibility ( $\chi_p$ ) for 3b between 2 and 373 K. The inset is the enlarged figure over 300 K.

a new phase, but, no single crystal suitable for X-ray analysis is available so far for the latter phase and the crystal growth of the corresponding phase is currently under study.

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- All aminoxyls described in this paper were characterized by HI-MS data and/or elemental analyses.
- 9. The DSC measurements were carried out between the temperature range 50°C to the temperature ca. 20°C over the melting point of each radical, e.g. 50–110°C for the radical **3b** at a rate of 2°C/min. So far, we have not observed any distinct appearance of a texture in **3b** by polarizing microscope investigation, suggesting that the latter phase of **3b** consists of another polymorphic form.
- 10. Crystal data for **3b** with Curie–Weiss behaviour:  $C_{34}H_{47}N_2O_4$ , FW = 547.77, triclinic (*P*1), *a* = 5.768(1), *b* = 14.89(2), *c* = 18.637(3) Å, *α* = 84.860(3), *β* = 86.644(3), *γ* = 85.737(3)°, *V* = 1583.9(4) Å<sup>3</sup>, *T* = 295 K, *Z* = 2, *Dc* = 1.199 Mg m<sup>-3</sup>, *R* = 0.119, *wR* = 0.136 [2401 reflections and 361 parameters with  $I_0 > 3\sigma(I)$ ].
- 11. The susceptibility measurement for the radical **3b** with initial Curie–Weiss behaviour was carried out as follows:  $2 \text{ K} \rightarrow 300 \text{ K} \rightarrow 373 \text{ K} \rightarrow 300 \text{ K} \rightarrow 2 \text{ K}$ . Another measurement was studied in a similar manner for a different sample of the same radical with a different magnetic behaviour of ST model. However, the behaviour remained unchanged in this case to show again that of an ST model, suggesting that the above change is the irreversible one (see text).
- 12. The  $\chi_p$ -values are expressed in the following equation of a singlet-triplet model.

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

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  $H=-J\mathbf{S}_1\cdot\mathbf{S}_2$ . Cf. Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, Ser. A* **1952**, 214, 451.