

## Azobenzene derivatives with a long alkyl chain and aminoxyls†

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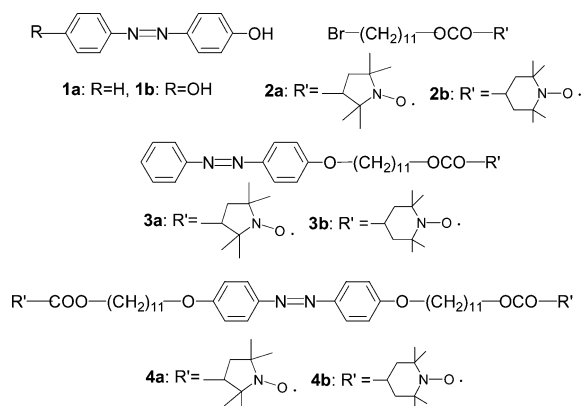
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A *trans*-azobenzene derivative with a long alkyl chain and a TEMPO radical showed photo-induced isomerization to become the corresponding *cis*-isomer with a significant change of its intermolecular magnetic interaction from a weak ferromagnetic one based on the CW model to a relatively strong antiferromagnetic one based on the ST model with the  $J$ -value of 36.7 K.

Considerable interest is currently focused on the development of photo-responsive molecular-based magnetic materials<sup>1</sup> and searches for new organic photo-responsive spin systems have been actively carried out by several research groups along these lines in recent years.<sup>2</sup> In the course of our studies for the development of novel organic spin systems, we have been interested in preparing multifunctional spin systems with conductivity, photo-functionality, liquid crystalline properties or pressure-functionality by using stable radicals, especially aminoxyl radicals, as spin sources.<sup>3</sup> As for the spin systems with photo-functionality, we have so far proposed several photo-responsive spin systems by using such photochromic systems as norbornadiene/quadracyclane, spiropyran/merocyanine, anthracene/dimer, or naphthopyran/merocyanine systems.<sup>4</sup> In this communication, we wish to report our latest results on the development of new photochromic spin systems, azobenzene derivatives with aminoxyl radicals and a long alkoxy as well as an ester group in between. The introduction of a long alkoxy group was initially designed to add a possible heat-responsive property<sup>5</sup> to the photo-functionality expected from the existence of an azobenzene core.

When 4-hydroxyazobenzene **1a** was reacted with bromoundecanoxy-carbonyl-PROXYL (2,2,5,5-tetramethyl-1-pyrrolidinyloxy) **2a**<sup>6</sup> or the corresponding TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) derivative **2b**<sup>6</sup> prepared from bromoundecanol and either 4-carboxy-PROXYL or 4-carboxy-TEMPO in the presence of potassium carbonate (1 equiv.) in THF-DMF (1 : 3) at 130 °C, the corresponding azobenzene derivative with a PROXYL-substituent (**3a**) or with a TEMPO-substituent (**3b**) was obtained in 72 and 71% yield, respectively. In a similar manner, bis-aminoxyl-substituted azobenzene derivatives **4a** and **4b** were obtained when 4,4'-dihydroxyazobenzene **1b**,<sup>7</sup> prepared by the treatment of *p*-hydroxybenzenediazonium chloride with copper sulfate pentahydrate, was used as a substrate and a bimolecular amount of the aminoxyl-substituted-bromide **2a** or **2b** was added as the reagent for the derivatization, though their yields were lower than for the mono-substituted derivatives (29 and 31%).

DSC measurements for each sample thus prepared did not show the appreciable endothermic peak expected for the existence of a mesogenic phase but only the endothermic peaks corresponding to melting points. Next, the temperature dependence data of their magnetic susceptibilities were measured by a SQUID susceptometer between the temperatures of 2 and 300 K. Regarding the magnetic properties of monoradicals, the behavior being well expressed by the singlet-triplet (ST) model with a small  $J$ -value was apparent in the interaction of the PROXYL-based monoradical **3a**, while weak ferromagnetic interaction based on the Curie-Weiss



(CW) model was found in the spins of TEMPO-based monoradical **3b** (Table 1). On the other hand, an antiferromagnetic interaction was observed for both of the biradical compounds (**4a**, **4b**) and while the weak intermolecular magnetic interaction based on the CW model was observed in the PROXYL derivative **4a**, the magnetic behavior based on the ST model and with a notably large  $J$ -value was observed in the spin-spin interaction of the TEMPO derivative **4b**.

Although no single crystal was obtained for each of the biradicals **4a** and **4b** and their structure-property relation could not be recognized as yet, the structure of the TEMPO derivative **4b** is anticipated to have a similar structural motif to the biradicals with naphthalene as well as a biphenyl core because of their similar magnetic behaviors together with the  $J$ -values of *ca.* -40 K.<sup>8</sup> On the other hand, a single crystal of the PROXYL-based monoradical **3a** was obtained by the recrystallization from *n*-hexane-methanol and its structure with a *trans*-configuration in the azobenzene moiety is apparent from the preliminary X-ray analysis† (see also ESI). The oxygen-oxygen distance of the neighboring spin centers amounts to 4.10 Å, which is relevant to the behavior of the ST model with a weak antiferromagnetic interaction of  $J = -4.2$  K. A single crystal suitable for X-ray analysis† could also be obtained by the recrystallization of the corresponding TEMPO derivative **3b** from *n*-hexane-methanol and the crystal structure viewed along the *a*-axis is shown in Fig. 1. Thus, the molecules are forming a sheet-like structure on the *bc*-plane and the nearest oxygen-oxygen distance of the neighboring spin centers is estimated to be 5.97 Å, which is fairly far apart for giving strong intermolecular magnetic interaction and is

**Table 1** Magnetic data of azobenzenes with aminoxyls **3a/3b**, **4a/4b** and **5**

Compound	Magnetic interaction	$C^e/\text{emu K mol}^{-1}$	$\theta^d/\text{K}$	$J^e/\text{K}$
<b>3a</b>	antiferromagnetic <sup>a</sup>	—	—	-4.2
<b>3b</b>	ferromagnetic <sup>b</sup>	0.38	+0.09	—
<b>4a</b>	antiferromagnetic <sup>b</sup>	0.76	-2.72	—
<b>4b</b>	antiferromagnetic <sup>a</sup>	—	—	-38.5
<b>5</b>	antiferromagnetic <sup>a</sup>	—	—	-36.7

<sup>a</sup> Fitting for ST model. <sup>b</sup> Fitting for CW model. <sup>c</sup> Curie constant. <sup>d</sup> Weiss temperature. <sup>e</sup> Exchange interaction.

† Electronic supplementary information (ESI) available: a table with a summary of the crystal data and diagrams of the crystal structures for **3a** and **3b**. See <http://www.rsc.org/suppdata/cc/b4/b408432b/>

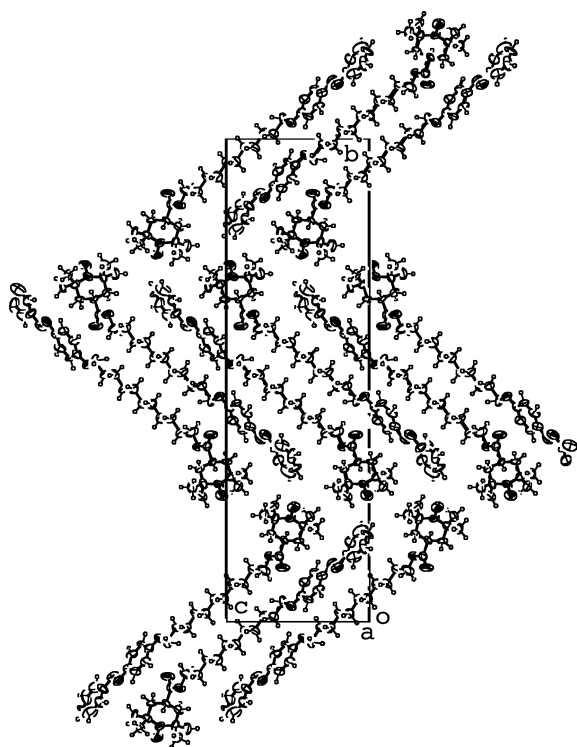
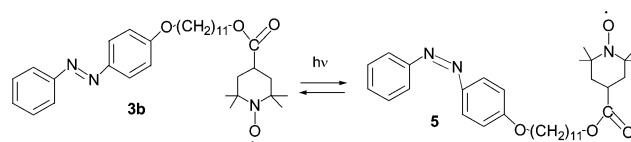


Fig. 1 Crystal structure of **3b** viewed along the *a*-axis.

relevant to the observed magnetic interaction in this radical. The weak ferromagnetic interaction observed in this radical can be understood by considering the spin polarization effect between the spin centers through the hydrogen-bonds between the oxygen atom of a spin center and a hydrogen atom on a methyl group of the neighboring molecule, which amounts to 3.17 Å (see ESI).<sup>8</sup>

While any attempt to isomerize and isolate the PROXYL-based radicals **3a**, **4a** or TEMPO-based biradical **4b** as a stable solid form has so far been unsuccessful, the photochemical isomerization of the TEMPO-based monoradical **3b** was found to proceed efficiently, giving the corresponding *cis*-isomer as a relatively stable solid material. Thus, irradiation of **3b** with light of 365 nm in dichloromethane showed an apparent absorption spectral change and gave after a period of exposure of 4 h the desired *cis*-isomer **5**, which could be purified by a short column chromatography on SiO<sub>2</sub> affording an orange yellow solid in 40% yield which was found to be persistent when kept in the dark and stored in a refrigerator. The reverse reaction was found to occur when the *cis*-isomer **5** ( $\lambda_{\text{max}}$  in the solid-state: 435 and 307 nm) was exposed in the solid-state to diffused sunlight for 1 d to recover the original *trans*-isomer **3b** ( $\lambda_{\text{max}}$  in the solid-state: 350 nm) in 50% yield and thus the reversible system could be constructed in principle (Scheme 1).

At the same time, the distinct change of the intermolecular interaction was disclosed by the structural change, that is, the weak ferromagnetic interaction based on the CW model being observed



Scheme 1

in the spins; the *trans*-isomer **3b** could be changed to the relatively strong antiferromagnetic interaction based on the ST model in the *cis*-isomer **5** with a *J*-value as large as  $-36.7$  K. The successful isolation of the *cis*-isomer **5** as a stable solid material is thought to be due to the formation of an efficient supramolecular structure in the crystal lattice of this isomer enabling it, at the same time, to give the relatively strong spin–spin interaction based on the ST model. In this context, novel organic spin systems with intriguing properties would be developed by using a supramolecular approach as exemplified in this work and therefore related work is still in progress along these lines.

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## Notes and references

‡ Crystal data for **3a**: C<sub>32</sub>H<sub>46</sub>N<sub>3</sub>O<sub>4</sub>, *M* = 536.74, triclinic, space group *P*-1, *a* = 6.6750(7), *b* = 11.850(2), *c* = 20.811(2) Å,  $\alpha$  = 75.756(7),  $\beta$  = 81.813(3),  $\gamma$  = 75.557(2)°, *V* = 1539.3(3) Å<sup>3</sup>, *T* = 296 K, *Z* = 2,  $\mu$ (Mo-K $\alpha$ ) = 0.076 mm<sup>-1</sup>, 8022 reflections measured, 4337 unique, *R* = 0.177, *wR* = 0.081. For **3b**: C<sub>33</sub>H<sub>48</sub>N<sub>3</sub>O<sub>4</sub>, *M* = 550.76, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 5.973(6), *b* = 42.691(9), *c* = 12.856(7) Å,  $\beta$  = 100.52(7)°, *V* = 3223(3) Å<sup>3</sup>, *T* = 303 K, *Z* = 4,  $\mu$ (Mo-K $\alpha$ ) = 0.074 mm<sup>-1</sup>, 6455 reflections measured, 6205 unique, *R* = 0.060, *wR* = 0.056. CCDC numbers 240929 and 240930. See <http://www.rsc.org/suppdata/cc/b4/b408432b/> for crystallographic data in .cif or other electronic format. Crystal data for the compounds are available as ESI.

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