Structures and Magnetic Properties of Organic Biradical Compounds with an Aromatic Core and Long Alkyl Groups

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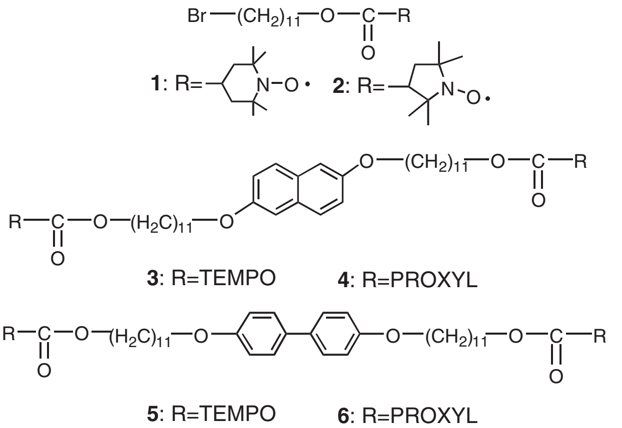
Organic biradical compounds having a biphenyl or naphthalene core and long alkyl groups with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radicals at their ends were found to show moderately strong antiferromagnetic interactions, being based on the singlet-triplet model. The behavior could be understood by considering the structures as being assembled in a "hand-in-hand" fashion.

Aminoxyl radicals have been used in a variety field including biological, physicochemical, and synthetic chemistry and recently as building blocks for molecular-based magnetic materials.[1]

In the course of our studies developing novel organomagnetic materials, we have become interested in preparing multifunctional spin systems with conductivity, photofunctionality, or liquid crystalline property by using stable radicals, especially aminoxyl radicals, as spin sources.[2] The development of spin systems with liquid crystalline property is of interest because of the possibility of ordered spin interactions in the oriented molecular aggregates and the possibility of tuning the magnetic properties through a phase transition. Hence, we have targeted spin systems incorporating mesogenic cores as well as long alkyl substituents and have reported the existence of a liquid crystalline phase in a heptylbiphenyl derivative with 4-(*N*-methyl)amino-TEMPO-substituent, together with the existence of unusal thermomagnetic properties of this derivative and a related spin system.[3] At the same time, it was anticipated during the studies that the specific assemblies of such molecules with supramolecular structures are relevant to the formation of the mesogenic phase and the unusual thermomagnetic properties. We aimed to extend this work and designed several biradical compounds comprised of a mesogenic aromatic core and long alkyl groups with aminoxyl radicals at their ends. We report here the preparation of such biradical compounds and the observation of moderately strong intermolecular interactions in TEMPO-based derivatives (**3** and **5**) resulting from their specific assembly.

11-Bromo-1-undecanol was reacted with an equimolecular amount of either 4-carboxy-TEMPO or 4-carboxy-PROXYL in the usual manner to yield either bromoundecanoxy-carbonyl-TEMPO **1** or the corresponding PROXYL (2,2,5,5-tetramethyl-1-pyrrolidinyloxy) derivative **2**, respectively. Product **1** or **2** was treated with a mixture of 2,6-dihydroxynaphthlene and potassium carbonate in THF/DMF (1:3) at 130 °C to obtain bis-TEMPO-substituted naphthalene **3** or bis-PROXYL-subsitituted naphthalene derivative **4** in 32 and 36% yield, respectively. Addition of 4,4'-biphenol in place of 2,6-dihydroxynaphthlene afforded bis-TEMPO-substituted biphenyl **5** and bis-PROXYL-subsitituted derivative **6** in 37 and 19% yield, respectively.



Experimental data of the temperature dependence of magnetic susceptibility were obtained by the SQUID measurements from 2 to 300 K and the results are summarized in Table 1. Antiferromagnetic interactions were observed in all of the biradical compounds, and the behavior being based on Curie–Weiss law was apparent for the PROXYL-based derivatives, **4** and **6**. In contrast, the TEMPO-based derivatives **3** and **5** showed the behavior consistent with singlet-triplet (ST) model. The *J*-values of **3** and **5** were found to be large (≈40 K for both radicals) compared to those of other TEMPO-based organic radicals.[4]

Table 1. Magnetic data of radical compounds

Compd.	interaction	C^a/emu·K·mol^{-1}	θ^b/K	J/K
3	antiferro[c]	—	—	−38
4	antiferro[d]	0.52[e]	−1.34	—
5	antiferro[c]	—	—	−40
6	antiferro[d]	0.64[e]	−1.11	—

[a]Curie constant. [b]Weiss temperature. [c]Fitting for singlet-triplet model. [d]Fitting for Curie-Weiss law. [e]The estimated spin concentrations of **4** and **6** are 69 and 85%, respectively.

In order to investigate the structure-property relationship[5] we attempted to obtain single crystals suitable for X-ray analysis. Repeated recrystallization from a hexane/dichloromethane solvent mixture produced single crystals of the TEMPO-derivative **3** and **5**, whereas single crystals could not be obtained for the PROXYL-derivatives, presumably because these derivatives exist as a racemic mixture, hindering crystal growth. Single-crystal diffraction data for **3** were recorded using a Quantum CCD area detector on a Rigaku AFC-7R diffractometer at room temperature and the molecular and crystal structure of the biradical **3** was obtained by the analysis as shown in Figure 1.[6]

The molecule **3** has an extended structure of alkyl groups connected to the central aromatic ring like "long arms." The TEMPO groups at both ends are tilted relative to the naphthalene

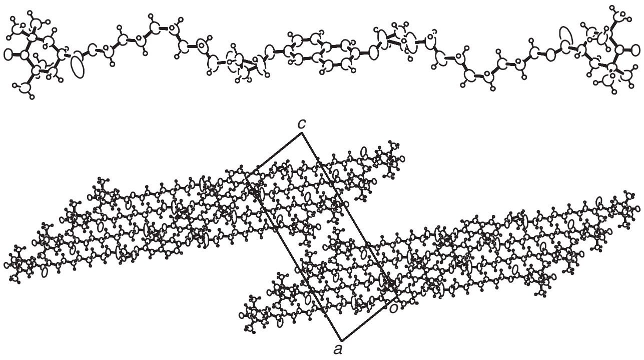


Figure 1. Molecular structure of **3** (upper) and the projected feature of the crystal along the *b* axis (lower).

plane (Figure 1, upper). The molecules are stacked slantwise along the *a* axis to form columnar structures (Figure 1, lower). Fairly close contact is observed between the oxygen atoms of the neighboring molecules as close as 3.50 Å, in which the orientation of both spins is considered to be distorted, with the angle around the central oxygen atom of the O···O–N moiety estimated to be approximately 110°. This distortion presumably occurs to avoid the steric repulsion of the bulky methyl groups around the spin centers. Although several short contacts (3.43–3.54 Å) are observed between the oxygen atom of a spin center and the hydrogen atoms of methyl groups of the neighboring molecules, the short contact between neighboring oxygen atoms is thought to be predominant cause for the magnetic behavior (ST model) in this biradical crystal.[4]

In the columnar structure, TEMPO groups and alkoxynaphthalene moieties are stacked separately. Such an assembly is similar to the stacking observed previously for monoradical crystals of both a heptylbiphenyl derivative and a cyanobiphenyl derivative.[3] Moreover, a “hand-in-hand” (with each “hand” corresponding to a TEMPO group) like assembly is additionally possible in the case of **3**. It is noteworthy that moderately strong antiferromagnetic interactions, being based on ST model[7] are observed in the biradical **3**, even though the molecule appears to be too large for such interactions. The observed behavior is thought to result from the supramolecular packing found in this biradical crystal.

Preliminary X-ray analysis data of the biradical **5** revealed a similar assembly in the crystal structure of the compound. The magnetic property is similar to that of the biradical **3**, which is understandable considering their similar structural features. Thus TEMPO groups, together with the alkyl and aromatic groups appear to affect molecular assembly of the crystals of **3** and **5** and also to allow moderately strong intermolecular spin–spin interactions. Although we can only tentatively predict structure-property relationships for the PROXYL-based biradical compounds **4** and **6** without the information of their crystal structures, it is possible that the decrease of the symmetry from the TEMPO to the PROXYL group together with the existence of a racemic mixture would result in the weak intermolecular spin–spin interactions in these biradicals.

In conclusion, organic biradical compounds incorporating biphenyl or naphthalene cores together with long alkyl groups with ether TEMPO or PROXYL radicals (**3–6**) were prepared and their structure-property relationships were investigated. Moderately strong antiferromagnetic interactions in good agreement with the ST model were observed in the spins of TEMPO-based biradical compounds. These interactions could be understood by considering the structures to be assembled in a hand-in-hand fashion with short contacts between the TEMPO groups of the neighboring molecules. The supramolecular approach enables synthesis of novel spin systems with intriguing properties and, therefore, the related work is still inprogress.

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6 Crystal data for **3**: $C_{52}H_{84}N_2O_8$, fw = 865.24, monoclinic ($P2_1/a$), $a = 10.7581(4)$ Å, $b = 8.4192(9)$ Å, $c = 28.2880(13)$ Å, $\beta = 98.4747(11)°$, $V = 2534.2(3)$ Å^3, $T = 293$ K, $Z = 4$, $D_{\mathrm{calcd}} = 1.13\ \mathrm{g{\cdot}cm^{-3}}$. $R = 0.116$, $wR = 0.056$ [3086 observed reflections and 289 parameters, $I > 2\sigma(I)$].

7 Cf. M. Minguet, D. B. Amabilino, J. Vidal-Gancedo, K. Wurst, and J. Veciana, *J. Mater. Chem.*, **12**, 570 (2002).