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Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl19>

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Version of record first published: 24 Sep 2006

To cite this article: Soichi Takeuchi, Yuya Ogawa, Akira Naito, Kyoko Sudo, Noritake Yasuoka, Hiroki Akutsu, Jun-Ichi Yamada & Shin'ichi Nakatsuji (2000): Preparation and Properties of Some Photo-Responsive Compounds with TEMPO Radical, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 167-172

To link to this article: <http://dx.doi.org/10.1080/10587250008023913>

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Preparation and Properties of Some Photo-Responsive Compounds with TEMPO Radical

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A couple of spin systems with photo-responsive property have been developed, i. e., norbornadiene and spiropyran derivatives carrying TEMPO-substituent and their light-induced structural changes to the corresponding quadricyclane or merocyanine derivatives have been investigated together with the changes of their properties in solution as well as in the solid state.

Keywords: Photo-response; Norbornadiene; Spiropyran; TEMPO radical; Magnetic property

INTRODUCTION

In the field of molecular-based magnetic materials, much attention has recently been focused on the development of molecular-based magnetic materials with photo-tunable property and interesting spin systems with such property have been reported in several inorganic, organometallic or organic compounds [1].

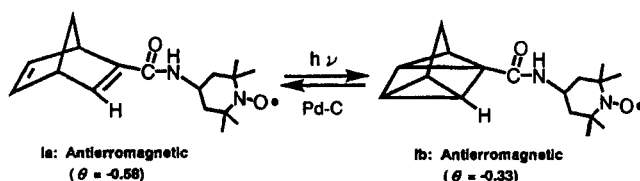
During the course of our studies to develop novel organomagnetic materials [2], we have been interested in preparing new spin systems with multi-functionality including conductivity, liquid crystalline property and so forth. In this paper, we would like to report on the preparation and properties of some photo-responsive compounds, i. e., norbornadiene and spiropyran derivatives with TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radical using the substituent as a spin probe for magnetic interactions. Since we have already reported some of the related results previously [3], we concentrate our discussion on a few of the compounds possibly in detail.

RESULTS AND DISCUSSION

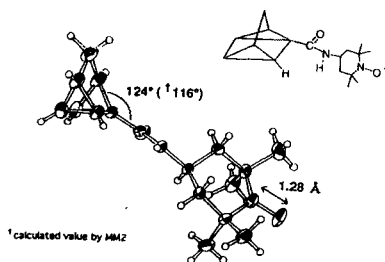
As magnetism is generally known to be very sensitive to the molecular structural change, we have been interested in alternating the *intermolecular* magnetic interactions triggered by the photo-induced structural change of organic spin systems and hence we initiated our study to prepare photo-responsive compounds with stable radical substituents, i. e., norbornadiene/quadricyclane as well as spiropyran/merocyanine system with TEMPO radical. Relatively large change of the molecular structure was anticipated from the MM2 calculation on the valence isomers or photochromic compounds to drive

the crystal structural change within the system and to result in the change of their magnetic behaviors.

The norbornadiene derivative **Ia** has been prepared from norbornadiene carboxylic acid by the treatment with 4-amino-TEMPO, DCC and 4-dimethylaminopyridine. Irradiation of **Ia** with the light of 254 nm in benzene solution gave the corresponding quadricyclane derivative **Ib** in moderate yield. The quadricyclane derivatives **Ib** could be reverted to **Ia** in high isolated yield by the treatment of catalytic amount of 5% Pd-C in ethyl acetate (SCHEME 1). The valence



isomerization reaction could be easily monitored by UV spectra. A single crystals of **Ib** suitable for X-ray analysis was obtained by the recrystallization from n-hexane/benzene and the molecular structure of **Ib** determined by X-ray analysis is shown in FIG. 1. The N-O bond



distance of radical center has been found to be 1.28Å showing the normal value for an aminoxyl radical. The bond angle between bridge-head carbon, the carbon atom carrying substituent and carbonyl carbon

amounts to 124° and the value is about 8° larger than the estimated angle being calculated by MM2.

The solid state magnetic properties of the valence isomers measured by SQUID susceptometer have been found to show Curie-Weiss behavior in **1a** with weak antiferromagnetic intermolecular spin-spin interactions. From the inspection of its crystal structure, the behavior could be rationally understood. Thus, as shown in FIG. 2, the

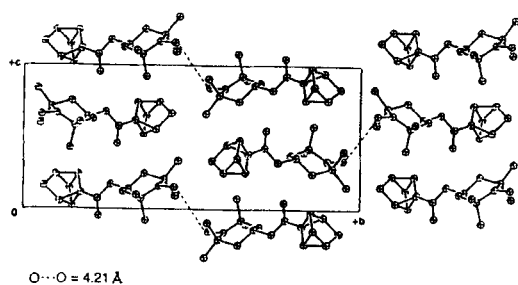
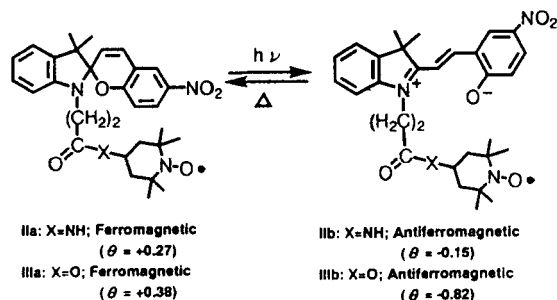


FIGURE 2 Crystal structure of **1b** viewed along the *a*-axis.

molecules have been found to stack along the *c*-Axis in head-to-tail and staggered manner and the nearest intermolecular O-O distances shown in

dotted lines amount to 4.21 Å., which are rather apart for strong spin-spin interactions but are relevant to the antiferromagnetic behavior found in this compound. In spite of the earlier expectation, a similar antiferromagnetic magnetic behavior has been observed in the corresponding quadricyclane derivative **1b** despite the difference of its Weiss temperature and hence, so far as the valence isomers are concerned, the intermolecular magnetic interactions have been found to be preserved by the intramolecular structural change based on the valence isomerization.

Spiropyran derivatives **IIa** as well as **IIIa** were prepared from the propionic acid derivative of *p*-nitrospiropyran and the derivatization reaction of the acid with 4-amino-TEMPO or 4-hydroxy-TEMPO by using DCC and 4-dimethylaminopyridine gave the desired spiropyran derivatives. Irradiation of **IIa** or **IIIa** in CCl₄ with the light of 365 nm afforded dark red precipitates of merocyanines **IIb** or **IIIb** as relatively unstable dark red solid and, in turn, the corresponding starting materials could be recovered when **IIb** or **IIIb** was dissolved in



SCHEME 2

acetonitrile in the dark to give the starting materials and thus reversible photochromic behavior was apparent (SCHEME 2). As summarized in TABLE 1, the hypsochromic effect was observed in MeOH compared with in acetonitrile for both merocyanines and larger stability was found in the former solvent being estimated from the values of their half lives and the first-order reaction rates. As regards the relative stability between **IIb** and **IIIb**, the amide derivative **IIb** was found to have the larger stability compared with the ester derivative **IIIb**.

TABLE I. Photochromic property of **IIb** and **IIIb**

Compound	Solvent	λ_{\max}/nm	$t_{1/2}/\text{min}$	k^a/sec^{-1}
IIb	CH ₃ CN	554	35	3.30×10^{-4}
IIb	MeOH	540	150	7.70×10^{-5}
IIIb	CH ₃ CN	564	25	4.62×10^{-4}
IIIb	MeOH	537	137	8.43×10^{-5}

^aFirst-order reaction rate from **IIb** to **IIa** or **IIIb** to **IIIa**.

In this system, in contrast to the norbornadiene/quadracyclane system described above, difference of the magnetic behaviors has been observed, i. e., ferromagnetic intermolecular spin-spin interactions observed in the low temperature region of **IIa** was found to change to antiferromagnetic interactions in **IIb** accompanying with their photochromic behavior and similar change has also been observed in **IIIa/IIIb** couple (SCHEME 2). Although further repetition of forward

and backward reaction was hampered owing to the unstable nature of **IIb** or **IIIb**, the system was found to provide an example of switching behavior of *intermolecular* magnetic interactions in combination with the photochromic property.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (A) (No. 10146250) and by a Grant-in-Aid for Scientific Research (No. 09640644) from the Ministry of Education, Science, Sports and Culture which are gratefully acknowledged.

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- [2] Cf. S. Nakatsuji and H. Anzai, *J. Mater. Chem.*, **7**, 2161 (1997).
- [3] A related paper has been presented at 14th International Conference on the Chemistry of the Organic Solid State, held in Cambridge in July 25th-30th, 1999 and the proceeding will be published in another volume of Mol. Cryst. Liq. Cryst.