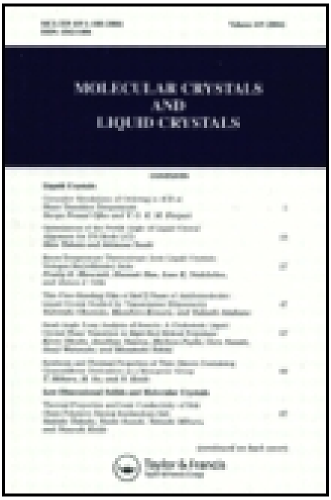

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Shin'ichi Nakatsuji, Soichi Takeuchi, Takeo Ojima, Yuya Ogawa, Hiroki Akutsu & Jun-Ichi Yamada (2001) Preparation and Properties of Photo-Functional Systems with Nitroxide Radicals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 356:1, 23-32, DOI: 10.1080/10587250108023683

To link to this article: http://dx.doi.org/10.1080/10587250108023683

Mol. Cryst. and Liq. Cryst., 2001, Vol. 356, pp. 23-32
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Preparation and Properties of Photo-Functional Systems with Nitroxide Radicals

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Series of TEMPO-substituted norbornadiene, spiropyran and anthracene derivatives have been prepared; their light-induced structural change to the corresponding qudricyclanes, merocyanines or anthracene-dimers and the reverse reactions to the starting materials have been studied. The antiferromagnetic or ferromagnetic behavior observed in norbornadienes/anthracenes was found to be preserved in the corresponding quadricyclanes/anthracene-dimers in spite of the difference of their Weiss temperatures, whereas switching of the intermolecular magnetic interactions was observed in spiropyran/merocyanine systems.

Keywords: Photo-functionality; TEMPO radical; Norbornadiene; Anthracene; Spiropyran; Magnetic property

INTRODUCTION

It is of growing interest to develop photo-tunable molecular-based magnets and successful studies have recently been carried out for the purpose in several inorganic compounds [1] and metal complexes [2] with spin cross-over behavior. Despite the potential versatility of organic compounds to develop such systems as described above, no successful study in purely organic system has been reported until very recently. It is only last year that the first experimental results have been reported by Iwamura et al. in an azobenzene derivative bearing two nitroxide radical to observe its UV as well as EPR spectral change upon irradiation [3]. More recently, Matsuda and Irie have succeeded to switch the intramolecular magnetic interactions upon irradiation in their diarylethene derivative bearing two nitronyl nitroxides although the intermolecular interactions observed in each species are antiferromagnetic [4].

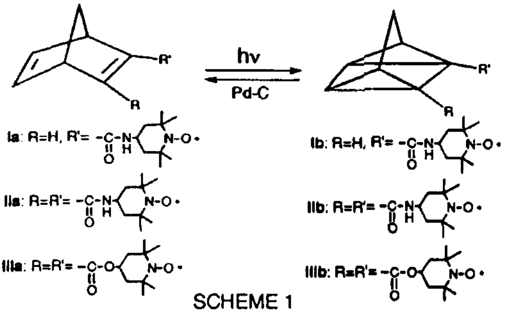
In the course of our studies to develop new organomagnetic materials [5], we have been interested in preparing organomagnetic compounds with multi-functionality, e. g., organomagnetic metals. We have been also interested in developing some photo-functional organomagnets and then tried to prepare such systems as norbornadienes [6], anthracenes [7] or spiropyrans [8] carrying nitroxide radicals for the aim. In this paper, we would like to report on the preparation of three types of photo-functional spin systems with nitroxide radical, i. e., norbornadines, anthracenes and spiropyrans carrying TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) radical, their photo-functional properties affording the corresponding quadricyclenes, anthracene-dimers and merocyanine dyes and their backward reactions, the magnetic behaviors being based on their structural changes.

RESULTS AND DISCUSSION

Norbornadine/Quadricyclane Systems With TEMPO Radicals

At first, we have estimated the molecular structural change based on valence isomerization from a norbornadiene derivative **Ia** to a quadricyclane derivative **Ib** by MM2 calculation [9]. Owing to the valence isomerization, the carbon carrying a substituent changes from sp^2 to sp^3 hybridization and then the bond angle of C(bridge head)-C(with substituent)-C(carbonyl) is estimated to change from 128.2° to 116.1° by the isomerization. The molecular structural change based on the valence isomerization is considered to drive the crystal structural change within the system which may result in the change of their magnetic behaviors.

The preparation of the norbornadiene derivatives has been carried out as follows; norbornadiene carboxylic acid or bis-carboxylic acid [10] prepared by the Diels-Alder reaction of cyclopentadiene and propiolic acid or acetylenedicarboxylic acid have been derivatized with 4-hydroxy-TEMPO or 4-amino-TEMPO by using DCC (1,3-dicyclohexylcarbodiimide) and DMAP (4-dimethylaminopyridine) as the reagents for dehydroxylative condensation to give the norbornadiene derivatives **Ia**, **IIa** or **IIIa** Valence isomerization of **Ia**, **IIa** or **IIIa** were carried out by the irradiation with the light of 254 nm in benzene solution for 3-4 d to give the corresponding quadricyclane derivatives **Ib**, **IIb** or **IIIb** in moderate isolated yield. The quadricyclane derivatives **Ib**, **IIb** or **IIIb** could be reverted to the starting materials in high isolated yield by the treatment of catalytic amount of 5% Pd-C in boiling ethyl acetate (SCHEME 1). Each forward and backward reaction could be easily monitored by UV spectra. For example, the absorption maxima of 243 nm in norbornadine **IIa** shifted to 234 nm in quadricyclane **IIb** and the latter peak turned to the former one by the treatment of the catalyst.



SCHEME 1

The magnetic susceptibility measurement were carried out on the polycrystalline samples by a SQUID susceptometer in the temperature range of 2-300 K. The temperature dependence of χT data for valence isomers **Ia** and **Ib** are rather similar showing Curie-Weiss behavior with antiferromagnetic spin-spin interactions in the lower temperature region and the data suggests that the magnetic interactions are preserved in both isomers on the whole in spite of the difference of their Weiss temperatures. Also, similar magnetic behaviors have been observed in bis-amide derivatives **IIa** and **IIb** with antiferromagnetic interactions in lower temperature region. Rather unusual magnetic behaviors have been found in both bis-esters **IIIa** and **IIIb** showing gradual decrease of χT along with the decrease of temperatures in the higher temperature region while ferromagnetic behaviors have been observed in the lower temperature region (TABLE 1)

Thus, in so far as norbornadiene/quadricylane systems prepared are concerned, the magnetic behaviors tend to be preserved by the intramolecular structural change based on the valence isomerization, although it is not unusual that even slight structural change or modification of certain molecules may sometimes cause serious change of their magnetic behaviors.

TABLE 1 Magnetic data of norbornadiene/quadricyclane systems

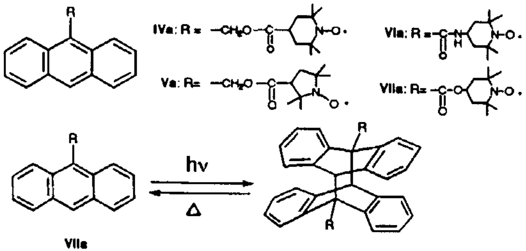
Compound	Magnetic interaction	Weiss temperature/K[a]
Ia	antiferromagnetic	-0.58
Ib	antiferromagnetic	-0.33
IIa	antiferromagnetic	-0.64
IIb	antiferromagnetic	-0.68
IIIa	ferromagnetic[b]	0.13
IIIb	ferromagnetic[b]	0.09

[a] Fitting for Curie-Weiss rule. [b] In the lower temperature region.

Anthracene/Anthracene-dimer Systems with TEMPO Radicals

Along with the valence isomeric system described above, which is concerned with the intramolecular structural change, we have investigated the system in which structural change occurs in intermolecular manner. The anthracene and anthracene-dimer system has been considered to be relevant for the aim and according to the estimation from MM2 calculation for a certain derivative, relatively large structural change is anticipated on going from an anthracene derivative to the corresponding dimer.

Several TEMPO-substituted anthracene derivatives **IVa-VIIa** have been prepared and their light-induced structural changes to the corresponding photo-dimers have been studied (SCHEME 2). So far as



SCHEME 2

we have investigated, any attempts to produce the corresponding photo-dimers upon irradiation of **IVa**, **Va** and **VIa** have not been successful yet. On the contrary, the derivative with a carboxylic ester substituent **VIIa** has been found to give the corresponding photo-dimer **VIIb** upon irradiation in benzene solution using a high-pressure Hg-lamp (400 W) and the latter could be reverted to the former by heating in a toluene solution. The dimer of carboxyamide substituent has been prepared through the known dimer of 9-anthracenecarboxylic acid [11] in indirect manner because of the failure of the direct photo-transformation from the 9-carboxamide derivative **VIa**. The trans-configuration of the dimers has been suggested from the result of point dipole approximation by EPR measurement in 2-Methyl-THF matrix at 123 K. The distances between intramolecular spins is estimated to be 9.60 Å for **VIb** and 9.40 Å for **VIIb**, respectively, and the value is more relevant taking trans-configuration into account.

The data of magnetic measurement for anthracene derivatives and two dimers are summarized in TABLE 2. Curie-Weiss behavior has been observed in each derivatives and ferromagnetic spin-spin interactions have been observed in some of them. Similar magnetic behaviors were observed between anthracene derivative **VIIa** and the corresponding photo-dimer **VIb**, **VIIb**; ferromagnetic behavior observed in **VIa** has

TABLE 2 Magnetic data of anthracenes **IVa**-**VIIa** and anthracene dimers **VIb**-**VIIb**

Compound	Magnetic interaction	Weiss temperature/K[a]
IVa	ferromagnetic	0.08
Va	antiferromagnetic	-0.14
VIa	antiferromagnetic	-0.10
VIb	antiferromagnetic	-0.32
VIIa	ferromagnetic	0.21
VIIb	ferromagnetic	0.28

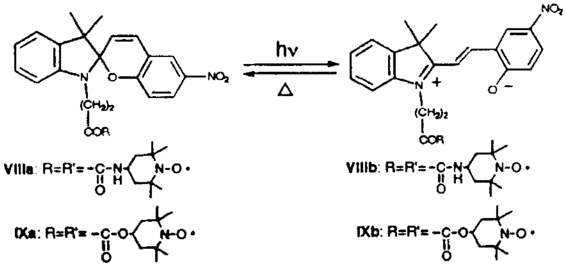
[a] Fitting for Curie-Weiss rule.

been found to be preserved in **VIIb** in spite of the structural difference and the result has been found to be rather similar with the valence isomers described above. It seems to be possible that the packing mode of the molecules might be similar for both anthracene derivative **VIIa** and its dimer **VIIb** although the data of crystal structures for both compounds are not available because of the lack of a suitable crystal for the analysis.

Spiropyran/Merocyanine Systems with TEMPO Radicals

Spiropyran is a well-known class of compounds exhibiting photochromic property being based on the structural change to the corresponding merocyanine dye and we have intended to prepare the derivatives with TEMPO radical to see the magnetic behaviors due to the structural change. Rather large structural change has been anticipated from the foregoing inspection of MM calculation for a certain spiropyran derivative and the corresponding merocyanine.

The spiropyran derivatives **VIIIa**, **IXa** have been prepared for the purpose from the propionic acid derivative of p-nitrospiropyran [12] obtained from 2,3,3-trimethylindolenine. The derivatization reaction of the former compound with 4-amino-TEMPO or 4-hydroxy-TEMPO by using DCC and DMAP to give the spiropyran derivatives **VIIIa** and **IXa** in 62% and 74% yield, respectively. Irradiation of pale yellow solution of **VIIIa** or **IXa** in the non-polar solvent such as carbon tetrachloride with the light of 365 nm afforded reddish colored solution and fortunately dark red precipitates were formed gradually which were filtered by suction as quick as possible to give the zwitterionic merocyanines **VIIIb** or **IXb** as fairly unstable dark red solid. In turn, when **VIIIb** or **IXb** was dissolved in polar solvent as acetonitrile in the dark, the reddish violet color of the solution faded gradually to pale yellow on standing at ambient temperature and thus reversible photochromic behavior between **VIIIa** and **VIIIb** or **IXa** and **IXb** was apparent from the color as well as electronic spectral change (SCHEME 3).



SCHEME 3

In contrast to the norbornadiene/quadricyclane system or anthracene/anthracene-dimer system described above, different magnetic behaviors have been observed in spiropyran systems with TEMPO radical. The spin-spin interactions observed in the low temperature region of **VIIIb** was found to be ferromagnetic with Weiss temperature of 0.27 K, while the interactions in the corresponding open-formed merocyanine derivative **VIIIb** was found to be antiferromagnetic with Weiss temperature of -0.15 K. Similarly, the ferromagnetic interactions found in the spiropyran derivative **IXa** turn to antiferromagnetic in the corresponding merocyanine **IXb** (TABLE 3).

Thus, it is suggested from the results that the switching of the magnetic properties is possible in the spiropyran systems carrying TEMPO radical, although the unstable nature of **VIIIb** and **IXb** in solution as

TABLE 3 Magnetic data of spiropyran/merocyanine systems

Compound	Magnetic interaction	θ^a/K
VIIIa	ferromagnetic	0.27
VIIIb	antiferromagnetic	-0.15
IXa	ferromagnetic	0.38
IXb	antiferromagnetic	-0.82

[a] Fitting for Curie-Weiss rule.

well as in the solid state hampers the further repetition of forward and backward reaction. In spite of such limitation, to our knowledge, these are the first examples in purely organic system in which the magnetic interactions can be switched in intermolecular manner through the structural change invoked by light and heat.

In summary, we have developed three types of photo-functional spin systems with nitroxide radical and studied their structural change to the corresponding isomers and their magnetic behaviors. In the norbornadine/quadricyclane and anthracene/anthracene-dimer systems examined, the magnetic behaviors tend to be preserved within the systems, while in the spiropyran/merocyanine systems, the switching of intermolecular magnetic interactions was found to be possible between the isomers. Further studies to prepare the single crystals of the compounds for X-ray analysis as well as to develop the related photo-functional materials are now underway.

Acknowledgments

We thank to Dr. K. Matsuda of Kyushu University and Prof. A. Naito of this institute for valuable discussion. We are also grateful to Miss K. Sudo and Prof. N. Yasuoka of this institute for the examination of X-ray analysis of some of the compounds described in the text.

Supports of this work 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, Japan are gratefully acknowledged.

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