ORGANIC LETTERS

2003
Vol. 5, No. 12
2127−2129

Photochromic Radical Compounds Based on a Naphthopyran System

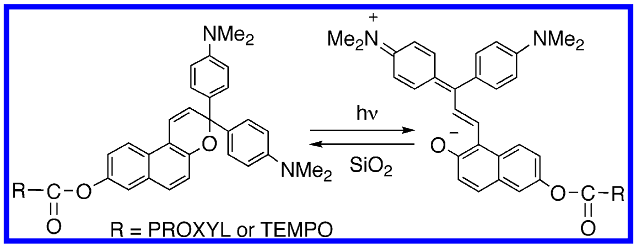
Takashi Kaneko, Hiroki Akutsu, Jun-ichi Yamada, and Shin'ichi Nakatsuji*

Department of Material Science, Graduate School of Science,
Himeji Institute of Technology, 3-2-1 Kouto, Kamigori, Hyogo 678-1297, Japan

nakatuji@sci.himeji-tech.ac.jp

Received April 1, 2003

ABSTRACT



Naphthopyran derivatives with aminoxyl substituents (4a,b) gave the corresponding open-formed isomers (5a,b) by irradiation, which could be changed back to the starting closed-formed naphthopyrans by the treatment with SiO_2 as a catalyst. The tuning of intermolecular magnetic interactions between the isomer couples was found to be possible in these reversible systems.

Aminoxyl radicals have been widely used as spin labeling reagents[1] as impressively exemplified in recent reports on their usage for the elucidation of the helical structure of several oligo(*m*-phenyleme ethynylene)s[2] or as the radical probe for fluorescence imaging.[3] Simultaneously, their usage in the field of materials chemistry as the building blocks for molecular based-magnetic materials has been well recognized in recent years.[1]

In the course of our studies on the development of novel organomagnetic materials,[5] we have been interested in preparing multifunctional spin systems with conductivity, liquid crystalline properties, or photofunctionality by using stable radicals, especially aminoxyl radicals, as spin sources.[6] As for the spin systems with photofunctionality, several organic/organometallic systems have recently been developed by some research groups.[7] So far, we have also proposed our own spin systems with photofunctionality by using such photochromic systems as norbornadiene/quadricyclane, spiropyran/merocyanine, anthracene/dimer, or styrylpyrylium/dimer systems.[8]

In this communication, we wish to report our further approach to the access of new photochromic spin systems, naphthopyran derivatives[9] with aminoxyl radical substituents.

---

[1] Cf. (a) *Nitroxide Spin Labels, Reactions in Biology and Chemistry*; Kocherginsky, N., Swartz, H. M., Eds.; CRC Press: Boca Raton, FL, 1995. (b) *Biological Magnetic Resonance*; Berliner, L., Ed.; Plenum Press: New York, 1998; Vol. 14.

[2] Matsuda, K.; Stone, M. T.; Moore, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 11836−11837.

[3] Coenjarts, C.; Garcia, O.; Llauger, L.; Palfreyman, J.; Vinette, A. L.; Scaiano, J. C. *J. Am. Chem. Soc.* **2003**, *125*, 620−621.

[4] Cf. (a) *Magnetic Properties of Organic Materials*; Lahti, P. M., Ed.; Marcel Dekker, Inc.: New York, 1999. (b) *Molecular Magnetism*; Itoh, K., Kinoshita, M., Eds.; Kodansha/Gordon and Breach Science Publishers: Tokyo, 2000. (c) Veciana, J., Ed. *Structure and Bonding*; Springer-Verlag: Berlin, 2001; Vol. 100. (d) *Magnetism: Molecules to Materials*; Miller, J. S., Drillon, M., Eds.; Wiley-VCH: Weinheim, Germany, 2001−2002; Vols I−IV.

[5] Natatsuji, S.; Anzai, H. *J. Mater. Chem.* **1997**, *7*, 2161−2174.

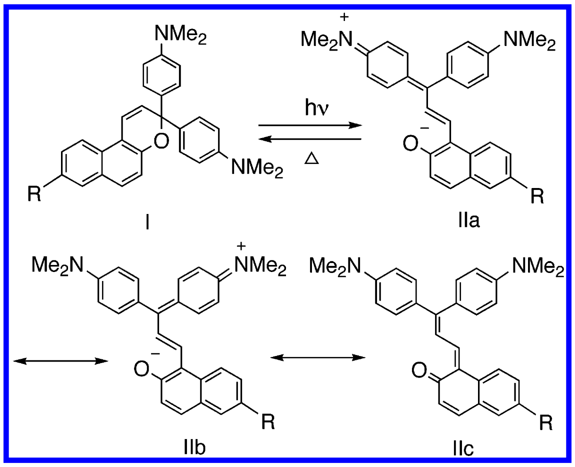
[6] (a) Nakatsuji, S. *Adv. Mater.* **2001**, *13*, 1719−1724. (b) Nakatsuji, S. In *Recent Research Developments in Organic & Bioorganic Chemistry*; Pandalai, S. G., Ed.; Transworld Research Network: Trivandrum, India, 2002; pp 1−26. (c) Nakatsuji, S. *J. Synth. Org. Chem. Jpn*. **2003**, in press.

[7] (a) Hamachi, K.; Matsuda, K.; Itoh, T.; Iwamura, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2937−2943. (b) Matsuda, K.; Irie, M. *J. Am. Chem. Soc.* **2000**, *122*, 7195−7201. (c) Matsuda, K.; Irie, M. *Chem. Eur. J.* **2001**, *7*, 3466−3473. (d) Matsuda, K.; Matsuo, M.; Irie, M. *J. Org. Chem.* **2001**, *66*, 8799−8803. (e) Ratera, I.; Ruiz-Molina, D.; Vidal-Gancedo, J.; Wurst, K.; Daro, N.; Lètard, J.-F.; Rovira, C.; Veciana, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 919−922. (f) Bénard, S.; Rivière, E.; Yu, P.; Nakatani, K.; Delouis, J. F. *Chem. Mater.* **2001**, *13*, 159−162.

[8] (a) Nakatsuji, S.; Ogawa, Y.; Takeuchi, S.; Akutsu, H.; Yamada, J.; Naito, A.; Sudo, K.; Yasuoka, N. *J. Chem. Soc., Perkin Trans. 2* **2000**, 1969−1975. (b) Nakatsuji, S.; Ojima, T.; Akutsu, H.; Yamada, J. *J. Org. Chem.* **2002**, *67*, 916−921. (c) Nakatsuji, S.; Ogawa, Y.; Akutsu, H.; Yamada, J. *Bull. Chem. Soc. Jpn.* **2003**, in press.

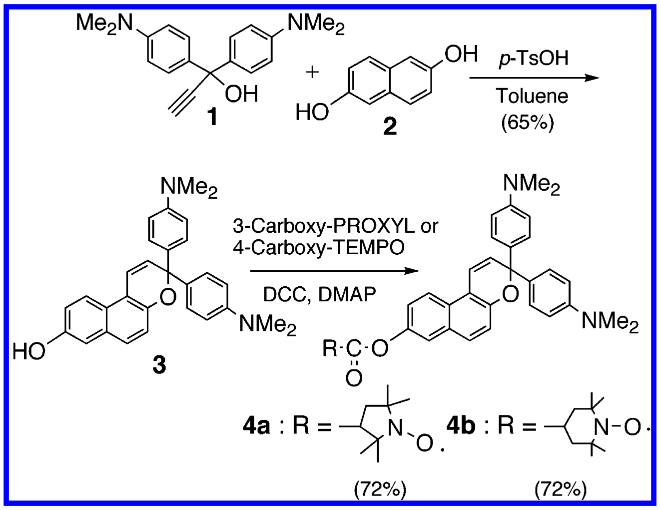
10.1021/ol034574v CCC: $25.00

It was well anticipated that the dimethylamino groups on the *p*-position of two phenyl rings would stabilize the resonance hybrids with a betaine structure in the open-formed species (**IIa** and **IIb**).



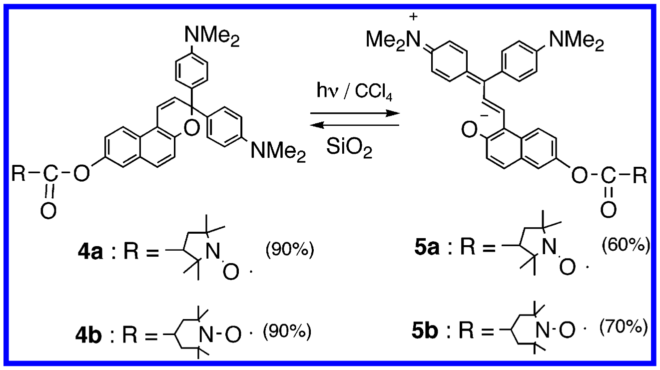
The ethynyl alcohol derivative obtained by the ethynylation of Michler's ketone[10] was heated in toluene with equimolecular amounts of 2,6-dihydroxylnaphthalene in the presence of a catalytic amount of *p*-TsOH to furnish, after Meyer−Schuster/Claisen-type rearrangement and the successive cyclization process, the naphthopyran derivative **3** with a hydroxyl group (Scheme 1).[11] The naphthopyran **3** was then condensed with 3-carboxy-PROXYL (2,2,5,5-tetramethyl-1-pyrrolidinyloxy) or 4-carboxy-TEMPO (2,2,6,6-tetramethyl-1-piperidinylinyloxy) in dichloromethane by using DCC and DMAP to give the desired esters **4a** or **4b**. A single crystal of the latter radical was obtained by the recrystallization from dichloromethane−ethanol solution, and its structure was confirmed by a preliminary X-ray analysis.

Scheme 1



Irradiation of **4a** with light of 365 nm wavelength in carbon tetrachloride gradually gave a reddish precipitate, which was found to be the desired compound **5a**, being elucidated by the spectroscopic measurements together with an elemental analysis (Scheme 2). Similarly, the open-formed compound **5b** was obtained by the irradiation of **4b** in the same solvent. The successful precipitation and isolation of **5a** and **5b** in a nonpolar solvent is thought to be due to the presence of polar structures in the open-formed species, but their unstable nature has prevented further recrystallization in polar solvents such as methanol.

Scheme 2



After several unsuccessful attempts, it was found that the open-formed species (**5a**,**b**) could be changed back to the original naphthopyrans (**4a**,**b**) by the treatment with SiO_2 as a solid-phase catalysis[12] in acetonitrile at ambient temperature. The recovery **4a** and **4b** could be easily monitored by the electronic spectral change to the original spectra, and the yields of these forward and backward reactions are shown in Scheme 2. Consequently, although the efficiency is not so high, reversible systems could be constructed in principle in this case.

To see the magnetic properties of the photochromic couples **4a**/**5a** and **4b**/**5b**, their magnetic susceptibilities were measured by a SQUID susceptometer within the temperature range of 2−300 K, and the data are summarized in Table 1.

Table 1. Magnetic Data of Photochromic Couples **4a**/**5a** and **4b**/**5b**

compd	magnetic interaction[a]	C[b] (emu K mol^{-1})	θ[c] (K)
4a	antiferromagnetic	0.31 (83)	-0.65
5a	antiferromagnetic	0.10 (27)	-0.35
4b	ferromagnetic	0.34 (91)	0.05
5b	antiferromagnetic	0.08 (21)	-0.20

[a] Fitting for Curie−Weiss law. [b] Curie constant. Values in parentheses denote the estimated spin concentration. [c] Weiss temperature.

---

(9) Concerning naphthopyran photochromic systems, see for example: van Gemert, B. In *Organic Photochromic and Thermotropic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum Press: New York, 1999; pp 111−140.

(10) (a) Nakatsuji, S.; Nakashima, K.; Iyoda, M.; Akiyama, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2253−2255. (b) Nakatsuji, S.; Yahiro, T.; Nakashima, K.; Akiyama, S., Nakazumi, H. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 1641−1647.

Although antiferromagnetic interactions have been observed for both **4a** and **5a**, an apparent difference is discerned for their Curie constants as well as Weiss temperatures. Although the reason for the rather low *C* value of **5a** is not clear yet because of the lack of its crystal structure, it is thought to be due, at least partially, to the singlet formation between the spin centers in the solid-state of this radical. A similar but larger difference has been found between the Curie constants of the couple **4b**/**5b**. Moreover, the signs of the Weiss constants are different in this case. Thus, the tuning of their Curie constants together with their Weiss temperatures is apparently possible in these two reversible couples, in principle, by choosing the outer stimuli of light and a catalyst.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (Grant 13440213) from the Ministry of Education, Science, Sports and Culture, Japan, which is gratefully acknowledged.

Supporting Information Available: Figure of the molecular structure obtained by X-ray analysis for **4b**, including a table summarizing the crystal data, and a figure of its magnetic data, tables of FAB−HRMS, and elemental analysis data for the radicals. This material is available free of charge via the Internet at http://pubs.acs.org.

OL034574V

---

(11) Tanaka, K.; Aoki, H.; Hosomi, H.; Ohba, S. *Org. Lett.* **2000**, *2*, 2133−2134. In our case, the reaction in toluene was slightly more efficient than that in the solid state.

(12) It was found to be sufficient for the conversion to pass the solution through a column of SiO_2.