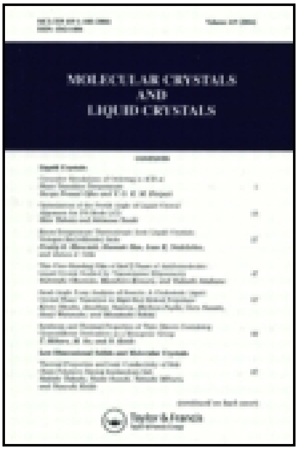

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Structures and Properties of Organic Photo-Responsive Spin Systems

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STRUCTURES AND PROPERTIES OF ORGANIC PHOTO-RESPONSIVE SPIN SYSTEMS

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Organic salts derived from the styrylpyrilium systems as well as anthracene derivatives with TEMPO substituents were prepared and their structures and properties, especially magnetic properties were investigated. Among them, remarkable change of their magnetic properties in the solid-state was found in the styrylpyrilium system with p-methoxy-substituent by changing the counter radical anions or by photo-dimerization.

Keywords: styrylpyrilium; TCNQ radical anion; anthracene; TEMPO radical; photo-responsive property; magnetic property

INTRODUCTION

Considerable interests have recently been focused on the development of molecular-based magnetic materials with multiproperty to see the synergy between magnetic property and other properties such as optical, conducting, or liquid crystalline properties. During the course of our studies for the development of new organomagnetic materials [1], we have been interested in developing organic spin systems with photo-responsive property to see mainly the alteration of intermolecular spin-spin interactions based on the structural change [2]. Several research groups have recently developed their own photo-responsive spin systems having similar aim with ours and among them, Matsuda and Irie have succeeded to switch the intramolecular spin-spin interactions efficiently in their elaborated diarylethene systems [3]. Veciana and his collaborators have reported quite recently on the interesting photo-dimerization in an iminoferrocene derivative with

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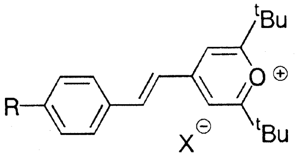
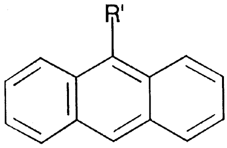
triphenylmethyl radical [4]. In this case, although no backward reaction was reported to occur, photo-induced intramolecular isomerization and the successive dimerization was observed to give this diradical.

We wish to report in this paper on the preparation, the structures and the properties of organic photo-responsive spin systems developed recently in our laboratory. Those include the organic salts derived from the styrylpyrilium systems **3** as well as anthracene derivatives with various TEMPO (2,2,6,6-tetramethylpiperidine-1-oxy) substituents **5**.



3

R: MeO, Me
X: TCNQ(F_4) Radical Anion



5

R': Nitroxide Radicals

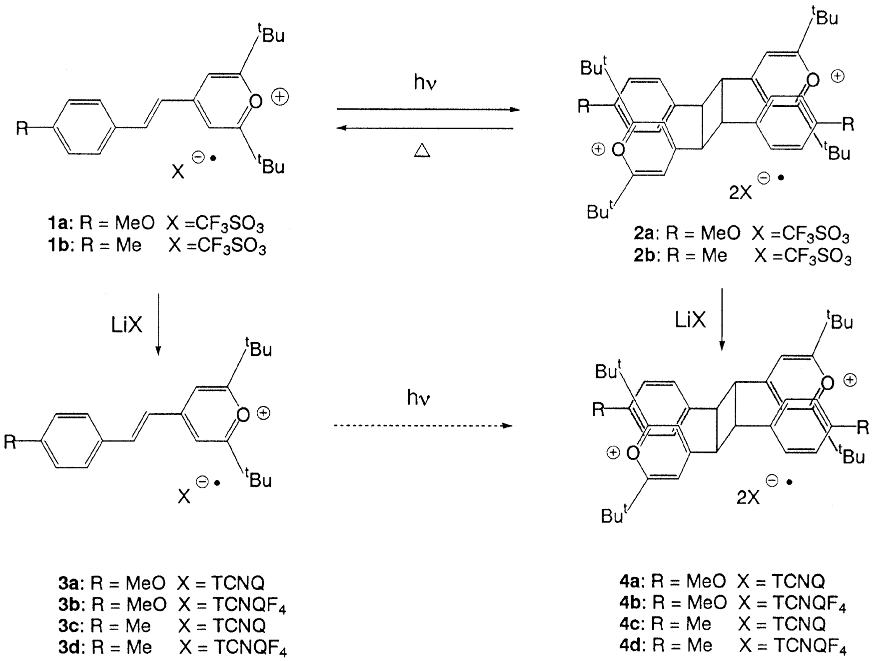
RESULTS AND DISCUSSION

Styrylpyrilium and the Corresponding Dimer Systems with TCNQ or TCNQF$_4$ Radical Anion

It is well known that some strylpyrilium salts [5] dimerize photochemically even in the solid-state and the photo-dimerization of a methanesulfonate salt of *p*-methoxy (**1a**) is reported by Enkelmann *et al.* to be a typical example of single-crystal-to-single-crystal reaction [6] and hence we have been interested in introducing a spin center in this fascinating system to construct a photo-responsive spin system.

At first, we tried to introduce some nitroxide (TEMPO) radicals in this system but the reaction of *p*-methoxy derivative with 4-amino-TEMPO did not proceed well giving deeply colored unknown products. Also, the anion exchange reaction of trifluoromethanesulfonate with an aminosulfonate-TEMPO [7] gave no fruitful result.We then tried to exchange the anion with LiTCNQ or LiTCNQF$_4$ and we could obtain the corresponding radical anion salts in moderate yields (Scheme 1).

The solid-state magnetic data of the salts were obtained by SQUID susceptomer between the temperature region from 2 K to 300 K. The temperature dependence data of the magnetic susceptibility on TCNQ radical salt of *p*-methoxy derivative (**3a**) is shown in Figure 1 (left) and the



1a: R = MeO X = CF_3SO_3
1b: R = Me X = CF_3SO_3

2a: R = MeO X = CF_3SO_3
2b: R = Me X = CF_3SO_3

3a: R = MeO X = TCNQ
3b: R = MeO X = $TCNQF_4$
3c: R = Me X = TCNQ
3d: R = Me X = $TCNQF_4$

4a: R = MeO X = TCNQ
4b: R = MeO X = $TCNQF_4$
4c: R = Me X = TCNQ
4d: R = Me X = $TCNQF_4$

SCHEME 1

behavior was found to be well expressed by one dimensional (1-D) antiferromagnetic Heisenberg model with a relatively large J-value of −5.4 K [8]. The magnetic behavior of $TCNQF_4$ radical salt of *p*-methoxy derivative (**3b**) is rather different from the TCNQ salt as shown in Figure 1 (right), i.e., the behavior based on 1-D ferromagnetic Heisenberg model was observed in the spins of this $TCNQF_4$ salt although the J-value (+0.65 K) is relatively small. Thus, remarkable change of the magnetic behaviors was found in the styrylpyrilium salts by the change of counter radical anion. As summarized in Table 1, the magnetic data of the radical anions of *p*-methyl derivatives (**3c**,**d**) were found to show the behaviors being well expressed by 1-D antiferromagnetic Heisenberg model with similar J-values.

The crystal structure of TCNQ radical anion salt **3a** obtained by X-ray analysis is shown in Figure 2 [9]. Thus, it was evident from the analysis that the strylpyrilium molecules and TCNQ molecules are stacking along the b-axis to form alternate columns. The packing feature is thus largely different from that of the trifluoromethanesulfonate salt in which the strylpyrilium molecules are stacking almost in segregate manner [6]. The 1-D Heisenberg antiferromagnetic behavior found in this salt is considered to be due to the interactions between the spins on TCNQ radical anion along the stacking

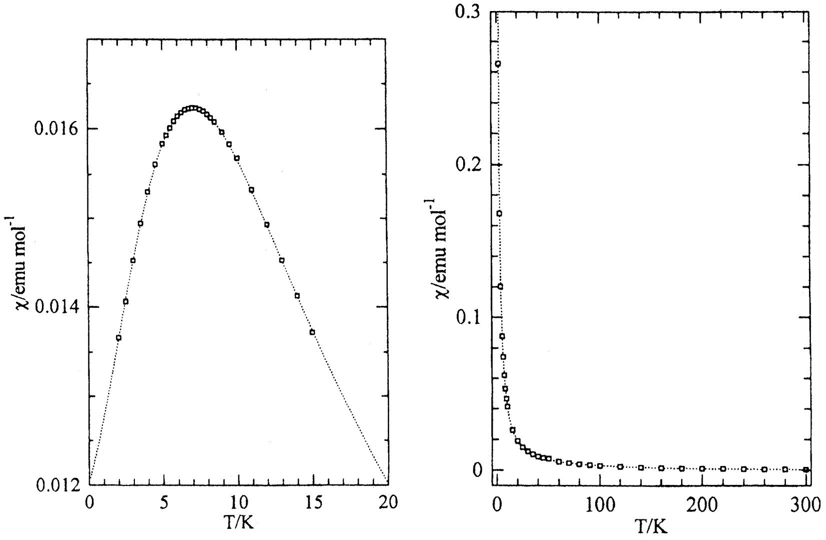


FIGURE 1 (left) Temperature dependence of χ values of **3a**. (right) Temperature dependence of χ values of **3b**.

TABLE 1 Magnetic Data of Styrylryrilium Radical Anion Salts

Compound	Magnetic interaction[a]	J/K
3a	antiferromagnetic	−5.42
3b	ferromagnetic	+0.65
3c	antiferromagnetic	−2.95
3d	antiferromagnetic	−2.80

[a] Fitting for I-D Heisenberg model.

direction. The stacking feature is considered, on the other hand, to be unsuitable for photochemical dimerization in the solid-state (*vide infra*). The alternate stacking feature was also found in TCNQF$_4$ salt as shown in Figure 3 (left). The strylpyrilium molecules and TCNQF$_4$ molecules are stacking along the c-axis to form alternate columns and although the exact reason is not clear yet, the 1-D ferromagnetic interactions observed in the radical anion salt might be caused by the interactions between the spin centers of radical anions through the short contacts between F and N atoms as schematically shown in Figure 3 (right). No single crystal suitable for X-ray analysis has so far been available for the radical anion salts of *p*-methylstyrylpyrilium derivative.

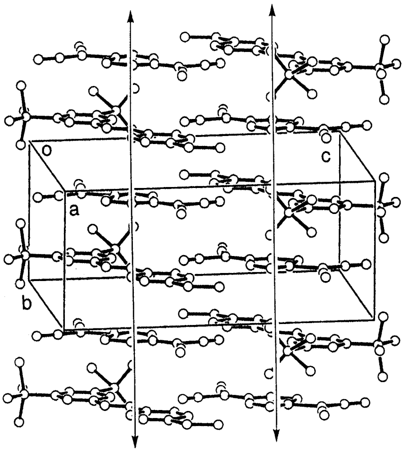


FIGURE 2 Crystal structure of **3a**. The hydrogen atoms are omitted for clarity and the stacking direction is shown by arrows.

We then tried to prepare photo-dimers of the styrylpyrilium radical anion salts (**4**) and we carried out the reaction under various conditions in solution and in the solid-state. But no salts of the dimers have so far been obtained by the direct photo-dimerization reaction. In stead, the dimers of radical anion salts could be obtained by indirect way as shown in Scheme 1. Thus, trifluoromethanesulfonate salts of the dimers (**2a**,**b**) prepared by irradiation were exchanged with LiTCNQ or $TCNQF_4$ to give the corresponding salts of the dimers.

From the magnetic data of radical anion salts of dimers as indicated in Table 2 [10], it is apparent that the Curie constants of the radical anions of the dimers are largely decreased compared with those of the salts of monomers presumably because of the singlet formation between the radical anions. Thus, although the radicals anions could not be directly interchangeable between the monomer/dimer pairs, sharp difference of the magnetic behavior found in each pair attracts us to study the present systems further.

Anthracene and the Corresponding Dimer Systems with TEMPO Radicals

To investigate the photo-responsive system in which structural change occurs in intermolecular manner, anthracene and the corresponding dimer system is considered to be one of the relevant system and we initiated to prepare anthracene derivatives with TEMPO substituents. As some of the

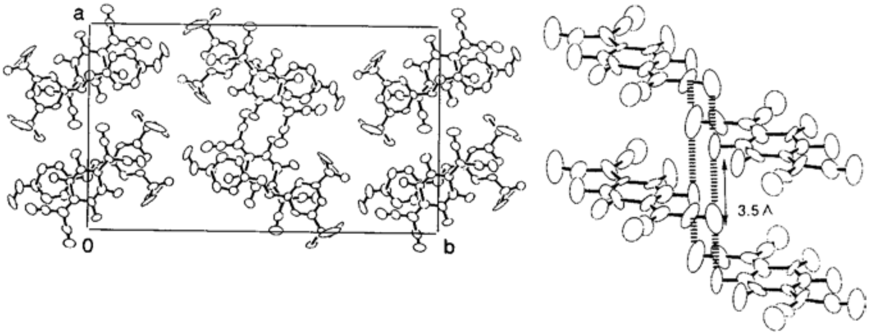


FIGURE 3 (left) Crystal structure of **3b**. The hydrogen atoms are omitted for clarity. (right) $TCNQF_4$ Part of **3b** with indication of short contacts (broken lines) between nitrogen and fluorine atoms.

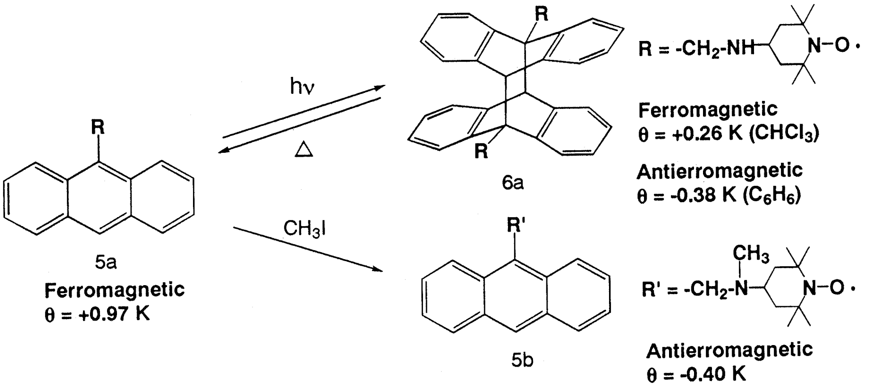
TABLE 2 Magnetic Data of Radical Anion Salts of Dimers

Compound	Magnetic interaction[a]	C/emu K mol^{-1}	θ/K
4a	antiferromagnetic	0.058	−0.83
4b	antiferromagnetic	0.072	−0.11
4c	antiferromagnetic	0.058	−0.15

[a] Fitting for Curie-Weiss law.

earlier efforts were reported previously [11], we wish to report in this paper mainly on 4-amino-TEMPO-substituted as well as 4-(N-methylamino)-TEMPO-substituted methylanthacene derivatives (**5a**,**b**) referring to some earlier results.

4-(N-methylamino)-TEMPO-substituted methylanthacene derivative (**5b**) was prepared from 4-amino-TEMPO-substituted methylanthacene derivative with iodomethane and the latter radical (**5a**) was obtained from 9-anthraldehyde through the Schiff base with 4-amino-TEMPO and its reduction. Being sharp contrast with the radical **5a**, in which the corresponding photo-dimer was obtained by irradiation with the light of high pressure Hg lamp in appropriate solution (Scheme 2), so far, no fruitful result for the photo-dimerization of the radical **5b** was obtained under various conditions. The unexpected difficulty for the photochemical dimerization reaction arose by the replacement of NH group in **5a** to N-CH_3 group in **5b** seems to reflect the difference of the packing features between **5a** and **5b**. Also, apparent difference observed in their magnetic behaviors is undoubtedly based on the difference of their crystal structures.



SCHEME 2

Relatively large ferromagnetic interactions based on Curie-Weiss law (Weiss temperature, $\theta = +0.97\,\mathrm{K}$) were found in the spins of the radical **5a** and the magnetic behavior could be rationally understood taking the spin polarization through the intermolecular hydrogen bonds into consideration. Being different from **5a**, weak antiferromagnetic interactions on Curie-Weiss law ($\theta = -0.40\,\mathrm{K}$) were observed between the spins in the radical **5b** and from the crystal structure obtained by X-ray analysis, the antiferromagnetic interactions observed in the radical are considered to be due to the interactions between the spins centers through the anthracene moiety in between as shown in Figure 4.

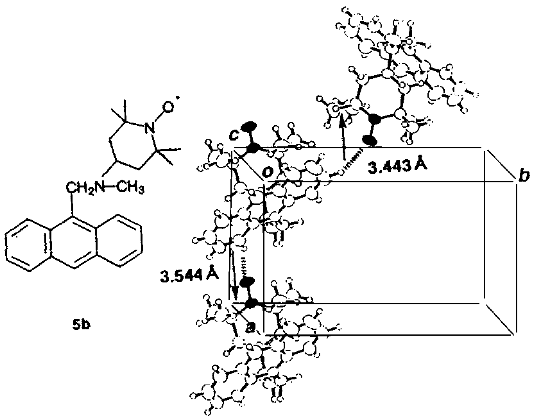


FIGURE 4 Crystal structures of **5b**. The nitrogen atoms as well as oxygen atoms of nitroxide moiety are shown as closed circles.

In the dimer of the radical **5a**, the solvent molecules used for recrystallization were found to be easily incorporated in the crystal of **6a** and the difference of their molecular/crystal structures was observed according to the solvent molecules incorporated to give, as the result, the difference of their magnetic behaviors depending on the solvated molecules. Namely, antiferromagnetic interactions ($\theta = -0.38\,\mathrm{K}$) were observed in the solvated compound with benzene while ferromagnetic interactions ($\theta = +0.26\,\mathrm{K}$) were found in the solvated compound with chloroform to provide an example of photo- as well as solvent-responsive spin system and further studies on such attractive photo-responsive spin systems as described above are still under way together with the related systems.

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