COMMUNICATION

ChemComm
www.rsc.org/chemcomm

A photochromic thiophenophan-1-ene

Michinori Takeshita,* Miki Nagai and Takehiko Yamato

Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjou 1, Saga 840-8502, Japan. E-mail: michi@ce.saga-u.ac.jp; Fax: 81 952 28 8862; Tel: 81 952 28 8862

Received (in Cambridge, UK) 8th April 2003, Accepted 2nd May 2003
First published as an Advance Article on the web 20th May 2003

A thiophenophan-1-ene, of which two thiophene rings are bridged at 2- and 4-positions, was synthesized and its quantum yield for the photocyclization reaction was increased due to fixation to the photoactive *anti*-conformation.

Recently 1,2-diarylethenes have been attracting much attention as one of the most promising photochromic compounds for organic data storage material, as they are thermally stable and resistant to high fatigue .[1] A feature of diarylethenes is that the aryl group can rotate freely, allowing two conformations to exist in the open-ring form (Fig. 1). Although from the *anti*-parallel conformation the photocyclization reaction can occur indicating that the *anti*-parallel conformation is photoactive, the parallel conformation is photo-inactive. NMR experiments have indicated that up to 50% of the open ring form contains the photo-inactive parallel conformation, therefore the quantum yield for the photocyclization reaction is usually lower than 0.5.[1] As increasing the photoactive *anti*-parallel conformation could result in an increase of quantum yield, several attempts have been studied.[2–5] The conformation of the open-ring form of diarylethene can be controlled by the addition of cyclodextrin to form the inclusion complex. Thus in the presence of large amounts of β- or γ-cyclodextrins, the conformation is almost fixed in the photoactive *anti*-parallel conformation[2] which leads to an increase in the quantum yield for the photocyclization reaction. The inner substituents on the aryl rings also affect the conformational ratio.[3] Large substituents such as isopropyl groups increase the ratio of *anti*-parallel conformation. Other reports show that the aryl groups of the helically locked dithienylethene cannot rotate and the conformation is fixed in the *anti*-parallel conformation.[4] But the quantum yield has not yet been considered. Recently Irie *et al*. reported that diarylethenes in the crystal state, in the photoactive *anti*-parallel conformation, efficiently undergo a ring-closing reaction.[5] These results encouraged us to synthesize a dithienylethene in which the aryl rings were fixed in an *anti*-parallel conformation.

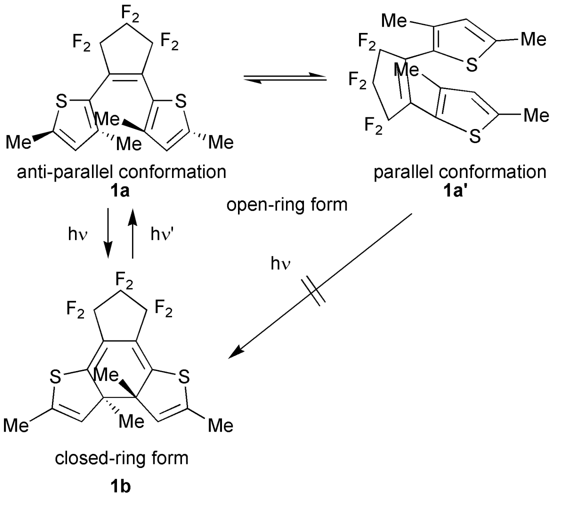
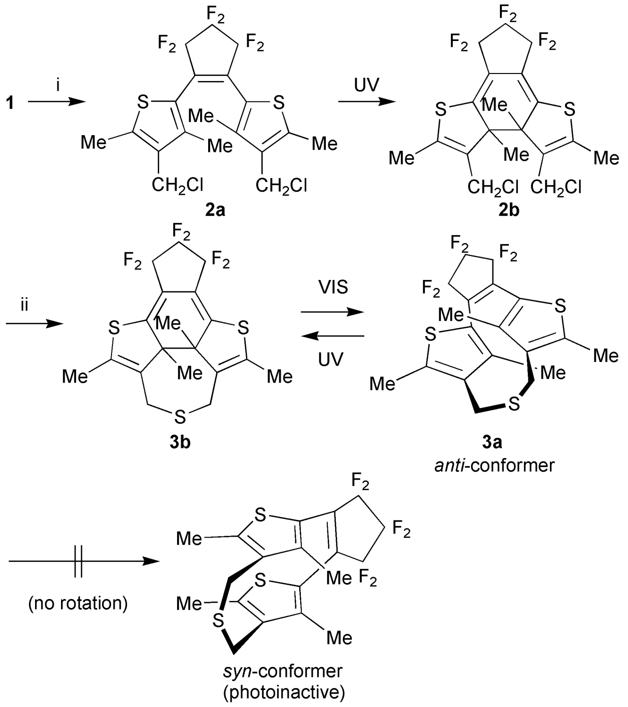


Fig. 1 Photochromic reaction of 1,2-dithienylethene.

We have already reported the synthesis of cyclophanes having thiophene rings[6] and photochromic metacyclophan-1-enes.[7] We have now designed and synthesized a thiophenophan-1-ene in which two positions of the thiophene rings are bridged. When a thiophenophan-1-ene is designed, the thermal stability of both isomers should be considered. A small cyclophan-1-ene has a large distortion energy, indicating that the photo-isomer would have a high energy of formation.[7] Both photo-isomers of dithienylethenes are almost thermally stable, thus the energy of formation of one of the photo-isomers of thiophenophan-1-ene should not be increased when the thermal stability of both isomers is expected. Therefore, we designed thia[2.3](2,4)thiophenophan-1-ene, which is bridged by a considerably long $–CH_2SCH_2–$ linker, and this cyclophane is little distorted.

Scheme 1 shows the synthetic route for a thia[2.3](2,4)-thiophenophan-1-ene **3a**. Chloromethylation of **1**[8] was carried out by chloromethyl methyl ether in the presence of $FeCl_3$ as Lewis acid and the desired bis(chloromethyl)dithienylethene was obtained in 83% yield. Several attempts have been carried out for the intramolecular cyclization of bis(chloromethyl)dithienylethene **2a**, however thiophenophan-1-ene **3a** was not obtained. We considered that the two chloromethyl groups in **2a** were too distant to form any bonds, therefore an intramolecular cyclization of the closed ring form of **2b**, in which the two chloromethyl groups are considerably closer, was carried out.



Scheme 1 *Reagents and conditions*: i, $ClCH_2OCH_3$, $FeCl_3$, CH_2Cl_2, 0 °C; ii, $Na_2S·9H_2O$, EtOH, reflux, high dilution.

DOI: 10.1039/b303916a

Upon UV irradiation the open-ring form **2a** afforded the closed-ring form **2b** since **2** is also a thermally stable photochromic compound. Under high dilution conditions, the intramolecular cyclization occurred in the presence of Na_2S and the closed-form **3b** was obtained in 25% yield. The desired thiophenophan-1-ene **3a** was obtained upon visible light irradiation.†

The ^1H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) of thiophenophan-1-ene **3a** shows the chemical shift of the inner methyl groups at 1.36 ppm, which is shifted 0.34 ppm upfield compared with that of **1a**. Since this upfield shift is due to the shielding effect of the ring current of the opposite thiophene ring, thiophenophan-1-ene **3a** is the photoactive *anti*-conformation as expected. Even when the solution was heated to 70 °C, the spectrum did not change. Therefore, the conformational thiophene ring flipping of thiophenophan-1-ene **3a** is restricted. Also a molecular modelling study indicated that the inner methyl groups are too large to flip the ring to form the *syn*-conformation as shown in Scheme 1.

Fig. 2 shows the absorption spectral change of a hexane solution of thiophenophan-1-ene **3a** upon irradiation with 366 nm light (5.0×10^{-5} mol dm^{-3}). The pale yellow solution of **3a** changed to the yellow solution of a mixture of **3a** and **3b**. The ratio of **3a** and **3b** at a photostationary state of 366 nm was obtained by HPLC analysis and was 30 : 70. Therefore the conversion at the photostationary state of 366 nm was 70%. The absorption spectrum returned to its initial state when it was irradiated with visible light at longer than 450 nm. This reversible photoisomerization indicates that thiophenophan-1-ene **3** is a photochromic compound.

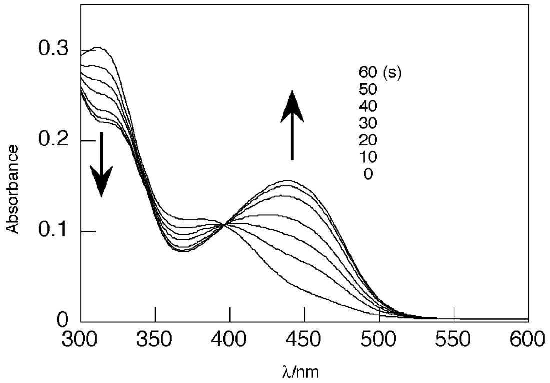


Fig. 2 Absorption spectral change of **3** upon irradiation with 366 nm light. Numbers denote irradiation time (s) (5.0×10^{-5} mol dm^{-3}, in hexane).

The quantum yield for the photocyclization reaction of thiophenophan-1-ene **3a** was estimated and the value was 0.67.[9] It is reported that that of the non-cyclophane dithienylethene **1a** is 0.40.[8] The photocyclization quantum yield of **3a** is 1.6 times larger than that of **1a**. This increase is due to the fixation of the photoactive *anti*-conformation by the bridging, at two positions, of dithienylethene.

The thermal stability of the ring-closed form **3b** was examined at 100 °C. A solution of **3b** in hexane in a sealed tube was stored in a heating oven for 24 h and the initial and the final absorption spectra were measured. The result indicated that 23% of initial **3b** was thermally isolated to give **3a**. From this accelerated examination, the half-life time at ambient temperature in solution is predicted to be more than 2 years.

In conclusion, a thiophenophan-1-ene of which thiophene rings are bridged at two positions undergoes a photocyclization reaction with high efficiency, as fixation of the photoactive *anti*-conformation is possible in the ground state. The half life-time of the ring-closed form was more than 2 years.

Notes and references

† *Selected data* for **3a**: pale yellow prisms (MeOH), mp 163.0–166.0 °C; δ_H (300 MHz, $CDCl_3$) 1.36 (s, 6H), 2.45 (s, 6H), 3.50 (d, J = 14.7 Hz, 2H), 3.98 (d, J = 14.7 Hz, 2H). m/z 454 (M^+), HRMS (EI, 70 eV) calc. for $C_{19}H_{16}F_6S_3$: 454.03181, found: 454 .03155.

1 M. Irie, *Chem. Rev.*, 2000, **100**, 1685; M. Irie and K. Uchida, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 985.

2 M. Takeshita, C. N. Choi and M. Irie, *Chem. Commun.*, 1997, 2265; M. Takeshita, N. Kato, S. Kawauchi, T. Imase, J. Watanabe and M. Irie, *J. Org. Chem.*, 1998, **63**, 9306; M. Takeshita, M. Yamada and M. Irie, *J. Chem. Soc., Perkin Trans. 2*, 2000, 619; M. Yamada, M. Takeshita and M. Irie, *Mol. Cryst. Liq. Cryst.*, 2000, **345**, 431.

3 K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura and M. Irie, *Chem. Lett.*, 1999, 63.

4 L. Dinescu and Z. Y. Wang, *Chem. Commun*, 1999, 2497.

5 *For example*: S. Kobatake, K. Uchida, E. Tsuchida and M. Irie, *Chem. Commun.*, 2002, 2804.

6 M. Takeshita and M. Tashiro, *J. Org. Chem.*, 1991, **56**, 2837; M. Takeshita, M. Tashiro and A. Tsuge, *Chem. Ber.*, 1991, **124**, 1403; M. Takeshita, M. Koike, H. Tsuzuki and M. Tashiro, *J. Org. Chem.*, 1992, **57**, 4654.

7 M. Takeshita and T. Yamato, *Tetrahedron Lett.*, 2001, **42**, 4345; M. Takeshita and T. Yamato, *Angew. Chem., Int. Ed.*, 2002, **41**, 2156.

8 K. Uchida and M. Irie, *Chem. Lett.*, 1995, 969.

9 The quantum yield of the photocyclization reaction of **3a** was obtained by comparing the initial rate for the photocyclization of **3a** with that of bis(2-methyl-1-benzothien-3-yl)hexafluorocyclopentene (ref. 3).