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The allomorphism of a photochromic diarylethene

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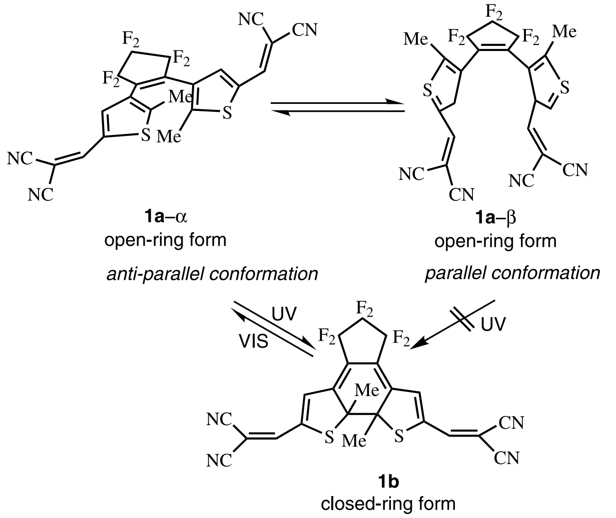
Abstract—The photochromic diarylethene, 1,2-bis(2-methyl-5-(2,2′-dicyanovinyl)-thien-3-yl)perfluorocyclopentene (**1a**), was synthesized by a novel method. Two kinds of single crystals of the compound were obtained depending on the different recrystallization conditions and their structures were determined by X-ray crystallographic analysis. Allomorphism of the photochromic diarylethene was discovered. The compound underwent a photochromic reaction both in solution and in the single crystalline phase of the *anti*-parallel conformer. © 2003 Elsevier Science Ltd. All rights reserved.

Much attention has been devoted to photochromic compounds because of their potential applicability to optical memories and photonic switching devices.[1] Diarylethenes with heterocyclic aryl groups are most promising compounds for such applications due to the good thermal stability of both isomers and their high fatigue resistance and rapid response time.[2–7]

Although many photochromic compounds have been reported so far, compounds which show strong photochromic reactivity in the crystalline phase are very rare.[2,8] Generally, diarylethenes have interconverting parallel and *anti*-parallel conformations in solution, in almost equal amounts. Only *anti*-parallel conformations can undergo effective photocyclization reactions by a conrotatory mechanism, while the parallel conformations are photochemically inactive.[9] However, in crystals, there is no exchange between the two conformers, and the molecules are regularly oriented and packed in fixed conformations depending on the recrystallization solvent.[10] A diarylethene which has two kinds of crystals under normal conditions is very rare. To the best of our knowledge, only a unique example has been reported.[10] The two conformations of a diarylethene can interconvert with each other and achieve an equilibrium state in solution, but, in the crystalline phase, one conformation must transform completely to the other conformation during the course of the recrystallization, and the final conformation in any crystalline phase is determined by the crystallization conditions, such as the recrystallization solvent, concentration, temperature, the velocity of crystallization, and so on. In this letter, it is our goal to report allomorphism of the photochromic compound 1,2-bis(2-methyl-5-(2,2′-dicyanovinyl)-thien-3-yl)perfluorocyclopentene (**1a**), synthesized in very high yield by a novel method. Two types of crystals of the compound were obtained by controlling different recrystallization conditions. Using the X-ray crystallographic analysis method, we found that all molecules of the compound are packed either in an active *anti*-parallel conformation (**1a-α**) or in an inactive parallel conformation (**1a-β**) in the corresponding crystalline phase, therefore,



Scheme 1. Photochromism of the diarylethene.

Keywords: diarylethene; photochromic; allomorphism; X-ray crystallographic analysis.

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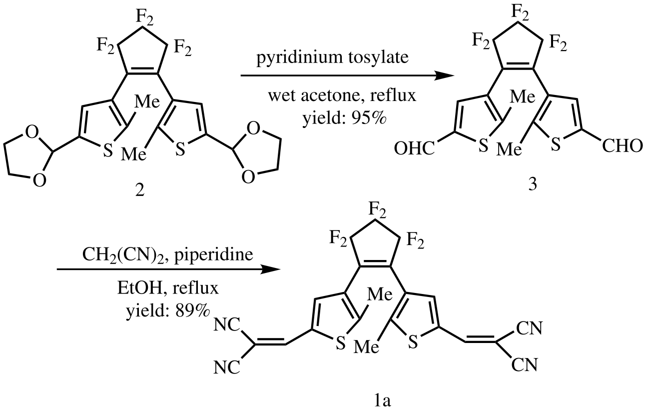
allomorphism of this diarylethene derivative exists. Its photochromism is shown in Scheme 1.

Although the compound was reported by Galit in 1993,[7] we synthesized it by a different method (Scheme 2). Firstly, the compound **3** was prepared by hydrolyzing 1,2-bis[2-methyl-5-(2-(1,3–dioxoane))-thien-3-yl]-perfluorocyclo-pentene **2** in 95% yield.[11] Then, a Knoevenagel[12] condensation was used to convert **3** to the symmetric compound **1a** in 89% yield by employing malonodinitrile, and the structure was confirmed by melting point, NMR and mass spectrometry.[13] Finally, two kinds of yellow crystals were obtained from chloroform by controlling the concentration of the compound, the crystallization temperature and the velocity of crystallization.

Figure 1 shows the absorption spectral changes of alkene **1a** in chloroform solution. Upon irradiation with 365 nm UV light, the colorless solution of **1a** turned green, and absorption maxima of **1b** were observed at 360, 438 and 724 nm. The green colored solution of **1b** returned to colorless on irradiation with visible light (λ>600 nm), and absorption maxima of **1a** were observed at 358 nm.



Scheme 2. Reagents and conditions.

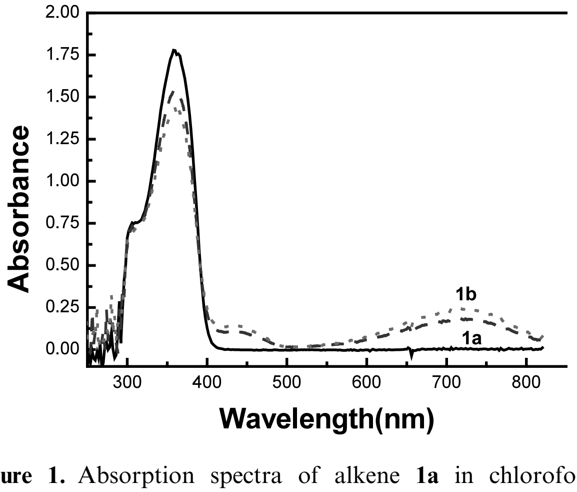


Figure 1. Absorption spectra of alkene **1a** in chloroform solution (4.5×10^{-5}M) open-ring form (solid-line), closed-ring form (dotted-line), and in the photostationary state under irradiation with 365 nm UV light (dashed-line).

The crystal structures were determined by X-ray diffraction. The two types of crystal structures found are shown in Figure 2[14,15] and their packing diagrams are shown in Figure 3. The ORTEP drawing of **1a-α** indicates that **1a-α** is packed in a photoactive *anti*-parallel conformation in the crystal. The ORTEP drawing of **1a-β** in the crystal indicates that **1a-β** is packed in the parallel conformation, which cannot undergo a photocyclization reaction.[16]

For the crystal of **1a-α**, the refinement converged with $R_1=0.0584$ and $wR_2=0.1050$ for all data. The conformation of the cyclopentene is an envelope and one of the five carbon atoms, C(3), is dipositional in disorder. It has two positions located on each side of the plane defined by the other four carbon atoms. The disordered carbon atom and the two fluorine atoms, F(3) and F(4), connecting with it were assigned occupancies to be 0.5 in the refinement which gives the molecule a pseudo-symmetry of a 2-fold axis to meet the requirement of the space group. All non-hydrogen atoms were subjected to anisotropic refinement. The dihedral angles between the cyclopentene ring and the two thiophene rings were both 44.9°. Bond lengths for double and single bonds were within a range of 1.343–1.376 and 1.331–1.718 Å. The distance of C(4)–C(4A) which are the reactive carbon atoms, was estimated to be 0.3589 nm. It is close enough for the reaction theoretically to take place in the crystalline phase.[17] For the crystal of **1a-β**, the hydrogen atoms were generated theoretically and rode on their parent atoms in the final refinement. All non-hydrogen atoms were subjected to anisotropic refinement. The final full-matrix least-square refinement on F^2 converged with $R_1=0.0584$ and $wR_2=0.1050$ for 2380 observed reflections $[I\geq 2\sigma(I)]$. The final difference electron density map showed no features. The dihedral angles between the cyclopentene ring and the two thiophene rings are 55.0 and 60.2°, respectively. Bond lengths for double and single bonds are within the range of 1.336–1.368 and 1.408–1.518 Å. The distance of C(6)–C(15), which should be the reactive carbon atoms, was estimated to be 0.4216 nm, which is far too large for the reaction.[17]

The two types of crystals showed different photochromic reactivity coincident with the theoretical analysis. Table 1 shows the color and $\lambda_{\max}$ changes of the two kinds of crystals on UV light irradiation. On irradiation with 365 nm UV light, the yellow single crystal of **1a-α** turned green. When observed under polarized light, the green color intensity changed on rotation of the crystalline sample. This phenomenon suggested that the closed-ring isomers were regularly packed in the crystal. When the green crystal was dissolved in chloroform, the solution turned to green, and the absorption maximum was observed at 724 nm, which is the same as that of the closed-ring form **1b** shown in Figure 1. The green color disappeared upon irradiation with 700 nm light. However, the yellow single crystals of **1a-β** did not change color on irradiation by UV light. On dissolving the crystal in chloro-

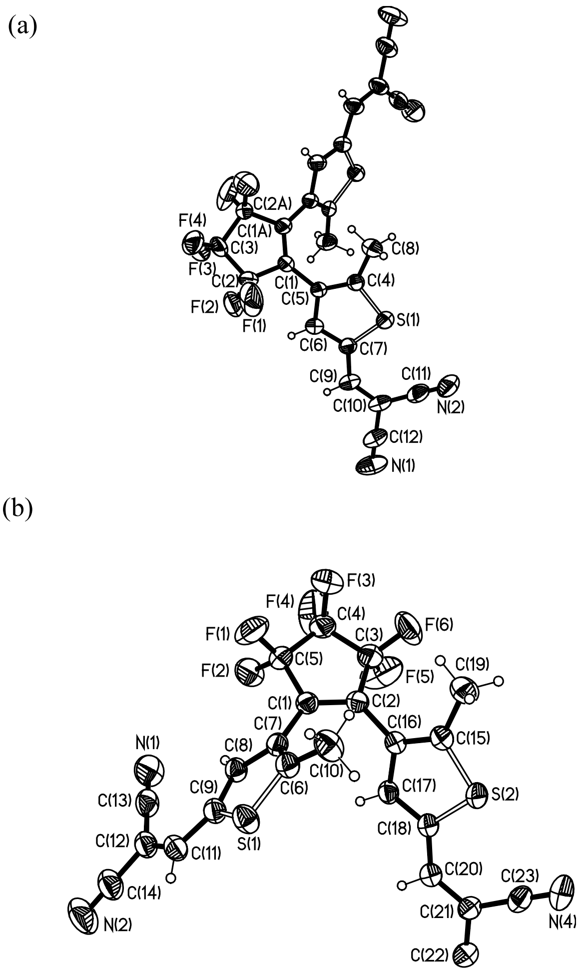


Figure 2. ORTEP drawings for $C_{23}H_{10}F_6N_4S_2$ with 35% probability ellipsoids, showing the atomic numbering scheme. (a) The crystal of **1a-α**—*anti*-parallel conformation. Selected bond distances (Å) and bond angles (°): S(1)–C(4) 1.7177(11), C(1)–C(1A) 1.3428(16), C(1)–C(5) 1.4647(14), C(1)–C(2) 1.4961(16), C(4)–C(5) 1.3612(12), C(4)–C(8) 1.4889(13), C(5)–C(6) 1.4159(13); C(1A)–C(1)–C(5) 130.28(5), C(1A)–C(1)–C(2) 110.55(5), C(5)–C(1)–C(2) 119.16(8), F(1A)–C(2)–C(1) 113.54(8), C(5)–C(4)–C(8) 129.26(10), C(5)–C(4)–S(1) 111.12(7), C(4)–C(5)–C(1) 125.14(8). Symmetry code A: $1+x-y$, $2-y$, $-z$. (b) The crystal of **1a-β**—parallel conformation. Selected bond distances (Å) and bond angles (°): S(1)–C(6) 1.701(3), S(1)–C(9) 1.729(3), S(2)–C(15) 1.709(3), S(2)–C(18) 1.738(3), C(1)–C(2) 1.336(4), C(1)–C(7) 1.473(4), C(1)–C(5) 1.500(4), C(2)–C(16) 1.274(4), C(2)–C(3) 1.502(5), C(6)–C(7) 1.379(4), C(15)–C(16) 1.373(4), C(15)–C(19) 1.504(4), C(16)–C(17) 1.410(4); C(6)–S(1)–C(9) 92.63(16), C(2)–C(1)–C(7) 127.4(3), C(2)–C(1)–C(5) 111.5(3), C(7)–C(1)–C(5) 121.0(3), C(1)–C(2)–C(16) 126.9(3), C(1)–C(2)–C(3) 110.7(3), F(6)–C(3)–C(2) 115.6(3), F(1)–C(5)–C(1) 111.4(3), C(7)–C(6)–C(10) 129.4(3), C(7)–C(6)–S(1) 111.1(2), C(10)–C(6)–S(1) 119.5(3), C(16)–C(15)–S(2) 111.8(2), C(19)–C(15)–S(2) 118.9(2), C(15)–C(16)–C(2) 126.3(3).

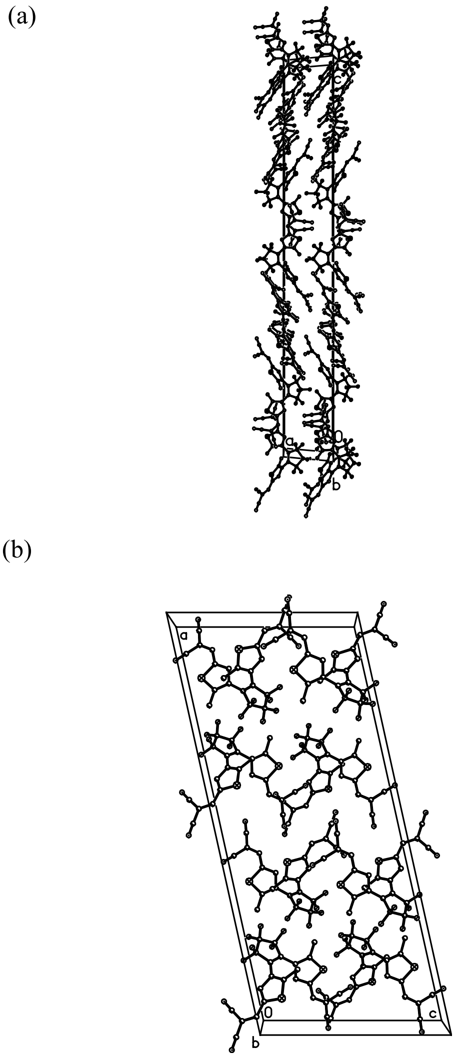


Figure 3. Packing views along the *b* direction. (a) The crystal of **1a-α**—*anti*-parallel conformation; (b) the crystal of **1a-β**—parallel conformation.

Table 1. Color and λ_{max} changes of the two kinds of crystals

Crystal	Before UV irradiation		After UV irradiation	
	Color	$\lambda_{max}{}^{a}$ (nm)	Color	$\lambda_{max}{}^{a}$ (nm)
1a-α	Yellow	358	Green	724
1a-β	Yellow	358	Yellow	358

[a] The maximal wavelength was measured in chloroform.

form after irradiation by UV light, the color in solution did not change, and the maximum absorption was still observed at 358 nm, which is same as that of the open-ring form **1a**. The difference in reactivity between **1a-α** and **1a-β** is ascribed to the different conformations of the compound in the solid state.

In conclusion, the compound described here represents an example of allomorphism within the family of diarylethenes. It demonstrates that diarylethenes can possess two conformations in the crystalline phase, and that only one conformation exists in any crystal. Further utilization of this phenomenon is currently in progress.

Acknowledgements

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13. Selected data for **1a**: yellow solid; mp = 206–208°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14 (s, 6H), δ 7.64 (s, 2H), δ 7.78 (s, 2H); MS m/z (M^+) 520.
14. Crystal data of **1a-α**: $C_{23}H_{10}F_6N_4S_2$, $M = 520.47$, hexagonal, $a = 8.405(3)$, $b = 8.405(3)$, $c = 57.853(16)$ Å, $\alpha = 90.00$, $\beta = 90.00$, $\gamma = 120.00°$, $V = 3539(2)$ Å^3, $T = 295(2)$ K, space group $P6_122$ (no. 178), $Z = 6$, $D_{\mathrm{calcd}} = 1.465$ g cm^{-3}, $F(000) = 1572$, μ(Mo Kα) = 2.92 cm^{-1}, $R_1 = 0.0479$, $wR_2 = 0.0815$. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 191842. Copies of the data can be obtained, free of charge, on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].
15. Crystal data of **1a-β**: $C_{23}H_{10}F_6N_4S_2$, $M = 520.47$, monoclinic, $a = 37.069(10)$, $b = 7.7397(12)$, $c = 16.349(3)$ Å, $\alpha = 90.00$, $\beta = 102.490(14)$, $\gamma = 90.00°$, $V = 4579.5(16)$ Å^3, $T = 295(2)$ K, space group $C2/c$ (no. 15), $Z = 8$, $D_{\mathrm{calcd}} = 1.510$ g cm^{-3}, $F(000) = 2096$, μ(Mo Kα) = 3.01 cm^{-1}, $R_1 = 0.0584$, $wR_2 = 0.1050$. Further details on the crystal structure investigation have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 191843. Copies of the data can be obtained, free of charge, on application to: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk].
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