



A novel Br-substituted diarylethene: Synthesis, crystal structure, and solvent dependent acidochromism



Chunhong Zheng, Congbin Fan, Shouzhi Pu*, Bing Chen, Ben Chen

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang, Jiangxi 330013, PR China

ARTICLE INFO

Article history:

Received 21 December 2015

Received in revised form

13 June 2016

Accepted 13 June 2016

Available online 15 June 2016

Keywords:

Diarylethene

Photochromism

Crystal

Acidochromism

Solvent dependence

ABSTRACT

A novel Br-substituted diarylethene was synthesized, and its structure has been determined by single-crystal X-ray diffraction analysis. Its photochemical property in solution, a PMMA film, and single crystalline phase was studied. In solution, the absorption maximum of its closed-ring isomer shifted dramatically to shorter wavelengths with notable color change from violet to yellow upon the stimulation of trifluoroacetic acid. Moreover, the acidochromism showed obviously solvent-dependence. With enhancement of solvent polarity, the protonation-induced absorption maxima ($\Delta\lambda_{\max}$) and the response time became longer.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Solvents can bring about powerful influence on the rate and equilibrium positions of chemical reactions, as well as the position, intensity, and shape of absorption spectra [1]. Currently, study of the solvent effects on the absorbance and fluorescence spectra has attracted considerable attention in material science from both fundamental and practical points of view [2,3].

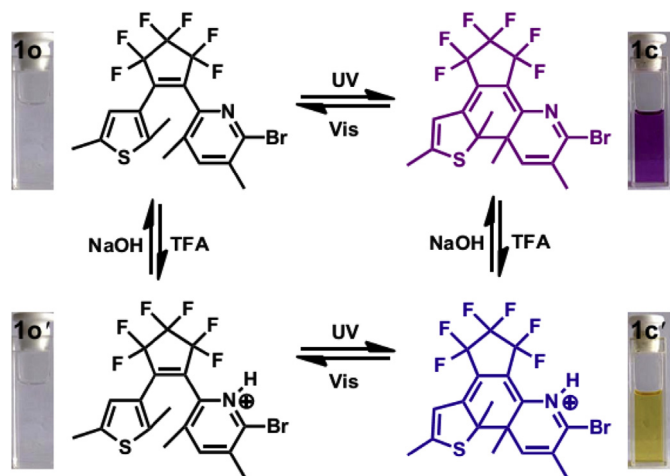
Diarylethenes have attracted remarkable research interests owing to their excellent thermal stability and remarkable fatigue-resistance [4,5]. In the past several decades, significant advancement has been made in the synthesis of novel diarylethene structure with ideal photochromic properties [6–8]. However, these approaches were often accompanied by either post-functionalization or a total new synthesis. More recently, modulation of the photophysical properties by multiple external stimuli, such as acid, solvent, and ions, have been reported [9], which provided simple and efficient approaches to control various chemical and physical properties of diarylethene derivatives [10–13]. Yet, exploring the solvent effects of on the photophysical properties of diarylethene derivatives is much more challenging. Irie et al. found that the solvent polarity may affect the relative

thermal stability as well as the cyclization reaction yield [14,15]. A recent research by Ma et al. [16] observed that the solvent polarity has little influence on the isomerization of open-ring isomers in the ground state, whereas the solvent effects on the electronic structures and absorption spectra of low-lying excited states (S1 and S2) are more significant. Pu et al. reported that a diarylethene with a triazole linkage adjacent to the rhodamine moiety responded to Al^{3+} and Cr^{3+} in neat acetonitrile, but only responded to Cu^{2+} in a mixed solvent of acetonitrile and water (v/v 4:6) [17]. And they recently designed and synthesized an asymmetrical diarylethene with one pyridine moiety. It was observed that solvents could affect the growth of isomeric crystals [18].

In the previous work, the absorption maxima of two Br-substituted diarylethenes shifted to a shorter wavelength based on acid stimulus in hexane [19]. The protonated process occurred fast at room temperature. In the present study, we have found that a newly synthesized Br-substituted diarylethene exhibits a solvent-dependent acidochromism. To the best of our knowledge, the solvent effects on the acidochromism of diarylethenes have been rarely reported [20]. The photochromism and acidochromism of four states was shown in Scheme 1.

* Corresponding author. Tel./fax: +86 791 83831996.

E-mail address: pushouzhi@tsinghua.org.cn (S. Pu).



Scheme 1. Multicolor switching of diarylethene **1**.

2. Experimental

2.1. General methods

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer using CDCl_3 as solvent and tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Mass spectra were measured with an Agilent 1100 ion trap MSD spectrometer. UV–Visible spectra were recorded on an Agilent 8453 spectrometer. Photo-irradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Lights of appropriate wavelengths were isolated using different light filters. Melting points were measured with a WRS-1B melting point apparatus. All solvents used were of spectro-grade and were purified by distillation prior to use. All other reagents were obtained from J&K Scientific Ltd. without further purification.

2.2. 1-(2,5-Dimethyl-3-thienyl)-2-(6-bromo-3,5-dimethyl-2-pyridyl)perfluorocyclopentene (**1o**)

To a stirred solution of **2** (3.15 g, 11.87 mmol) in anhydrous THF (50 mL) was added dropwise a 2.5 M solution of *n*-BuLi in hexane (5.12 mL, 12.80 mmol) at 195 K. The reaction was stirred for 30 min at this temperature, a solution of **3** [21] (3.97 g, 13.06 mmol) in THF (5 mL) was added. The reaction solution was stirred for 1 h at this temperature. The reaction was allowed to warm to room temperature, and quenched with water (15 mL). The product was extracted with diethyl ether. The organic layers were combined, dried over anhydrous Na_2SO_4 , filtered, and concentrated in vacuo. Column chromatography on Al_2O_3 (hexane) afforded diarylethene **1o** (1.62 g, 29%) as a colorless crystal, mp 96–97 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.29 (s, 1H, pyridine-H), 6.64 (s, 1H, thiophene-H), 2.38 (s, 3H, $-\text{CH}_3$), 2.37 (s, 3H, $-\text{CH}_3$), 1.93 (s, 3H, $-\text{CH}_3$), 1.84 (s, 3H, $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3): δ 145.2, 141.7, 141.0, 140.5, 137.9, 136.0, 132.7, 124.5, 123.6, 21.7, 17.4, 15.0, 14.3; ^{19}F NMR (376 MHz, CDCl_3): δ -132.00, -111.26, -110.45; IR (KBr, ν , cm^{-1}): 2923, 1638, 1543, 1444, 1337, 1269, 1187, 1125, 1057, 1004, 895, 825, 735; LRMS, ESI^+ m/z 470.1 (MH^+ , $\text{C}_{18}\text{H}_{14}\text{BrF}_6\text{NS}$ requires 469.0); Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{BrF}_6\text{NS}$: Calcd C, 45.97; H, 3.00; N, 2.98. Found C, 45.91; H, 3.02; N, 2.96.

2.3. Crystallography

Crystal data of **1o** were collected by a Bruker SMART APEX2 CCD

area-detector equipped with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$) at room temperature (294 ± 2 K). The linear absorption coefficients, μ , of the diarylethene for Mo K α radiation was 2.15 and 2.14 cm^{-1} . All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with CAH bond distances of 0.93–0.96 Å according to criteria described in the SHELXTL manual. They were included in the refinement with $\text{Uiso}(\text{H}) = 1.2$ Ueq (C) or 1.5 Ueq (methyl C).

2.4. UV–vis experiment

Spectro-grade solvents were used throughout all experiments. Stock solutions of **1o** (1.0×10^{-3} mol L^{-1}) were prepared in hexane, CHCl_3 , CH_3CN , and DMSO, respectively. They were then diluted to 2.0×10^{-5} mol L^{-1} , respectively. In the dark, a 2.0 mL solution of **1o** (2.0×10^{-5} mol L^{-1}) or its photostationary state (297 nm) was filled in a quartz optical cell of 1 cm optical path length, and TFA/TEA was added into the quartz optical cell gradually by using a micro-pipette. The mixture was shaken vigorously within 10 s, and spectral data were recorded on an Agilent 8453 spectrometer.

3. Results and discussion

3.1. Synthesis of **1o**

As shown in Scheme 2, diarylethene **1o** was obtained by a coupling reaction. 2,6-Dibromo-3,5-dimethylpyridine (**2**) was lithiated and then coupled with (2,5-dimethyl-3-thienyl)perfluorocyclopentene (**3**) to give **1o**. It was characterized by X-ray single-crystal diffraction analysis, elementary analysis, LRMS spectra, ^1H and ^{13}C NMR spectroscopy and IR spectroscopy. Single crystals of **1o** was obtained by slow evaporation of chloroform–hexane cosolvent system and subjected to X-ray analysis. The crystal data was shown in Table 1. Elementary analysis (C, H, N) coincide well with the calculated value for **1o**. LRMS shows a characteristic peak at 470.1 for [**1o** + H^+]. The ^{19}F NMR spectra (Fig. S4) display three distinctly F signals at -132.00 ppm, -111.26 ppm, and -110.45 ppm, respectively, indicating three kinds of F donors on the NMR time scale. The $\nu(\text{C}=\text{C})$ band in the IR spectra occur at 1444 cm^{-1} (Fig. S5).

3.2. Photochromism in solutions and a PMMA film of **1o**

Upon alternative irradiation with UV and visible light, **1o** underwent typical reversible photochromic reactions (Fig. 1A). Irradiation of **1o** with UV light (297 nm) resulted in the emergence of a new absorption band at 532 nm with a color change from colorless to violet due to the formation of closed-ring isomer **1c**. The violet color faded to colorless upon irradiation with visible light (> 510 nm), and the absorption spectrum returned to the initial state of **1o**. The absorption spectral change upon photoirradiation was accompanied by an isosbestic point at 301 nm, which clearly indicated a two-component photochromic reaction, the composition ratio of which changes with light irradiation [22,23]. When the photostationary state was reached, the photoconversion ratio from the open-ring to the closed-ring isomer was analyzed by HPLC analysis with the value of 44% (Fig. 2). Using 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [24] as a reference, the quantum yields of the cyclization and cycloreversion reactions in hexane were calculated to be 0.22 and 0.15, respectively. Similarly, **1o** showed favorable photochromism in a PMMA film (Fig. 1B). Irradiation of **1o**/PMMA film with 297 nm UV light resulted in the appearance of new absorption band at 546 nm, accompanied with a color change from colorless to violet. The violet color was bleached

Download English Version:

<https://daneshyari.com/en/article/1404746>

Download Persian Version:

<https://daneshyari.com/article/1404746>

[Daneshyari.com](https://daneshyari.com)