

Synthesis and photochromic mechanism of 3,4-bis[2,5-dimethylthiophene-3-yl]-2,5-dihydrothiophene

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Abstract

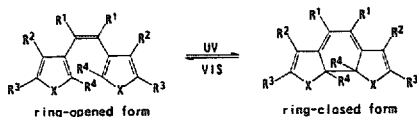
A novel photochromic compound, 3,4-bis[2,5-dimethylthiophene-3-yl]-2,5-dihydrothiophene (BT), has been synthesized. The photochromic reactions of BT in a polar solvent (acetonitrile) and a non-polar solvent (cyclohexane) were investigated by means of steady state absorption spectra and time-resolved transient absorption spectra. The maximum absorption wavelengths of BT in acetonitrile and cyclohexane are at 232 and 233 nm, respectively, and the maximum absorption wavelengths of the photocyclization product (CBT) in acetonitrile and cyclohexane are 445 and 453 nm, respectively. Upon irradiation with ultraviolet light, BT is first excited to the excited singlet state, and then to the excited triplet state via inter-system crossing. Only the excited singlet state generates CBT. The excited triplet state, which has a maximum absorption wavelength at 390 nm, decays rapidly to the starting compound (BT) alone. © 1997 Elsevier Science S.A.

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1. Introduction

Photochromism is defined as the reversible process of a single chemical species between two states having distinguishably different absorption spectra. The reversible reactions are carried out in at least one direction by the action of electromagnetic radiation. Over the last few years, organic photochromic compounds have increasingly attracted the attention and interest of chemists and engineers due to their potential applications in optical information storage [1,2]. Diarylethene derivatives are one kind of important photochromic compounds, which have the excellent properties of fatigue resistance and thermal stability. Upon irradiation with UV light, diarylethene derivatives (ring-opened form) undergo a cyclization reaction, and the photoproduct (ring-closed form), possessing absorption in the visible region, can return reversibly to the starting material after exposure to visible light. The typical photochromic reaction of diarylethene derivatives is shown in Scheme 1.

Recently, Irie et al. [3–8] and Fan et al. [9,10] have synthesized a series of photochromic diarylethene derivatives as mentioned above, and studied their photochromic behaviours from the point of view of their application. Their results



Scheme 1. Photochromism of diarylethenes.

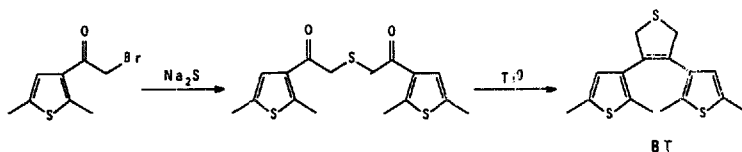
show that perfluorocycloalkene and maleric derivatives have excellent fatigue resistance and thermal stability. In the present work, we synthesized successfully a novel photochromic diarylethene derivative, 3,4-bis[2,5-dimethylthiophene-3-yl]-2,5-dihydrothiophene (BT). The photochromic behaviour and reaction mechanism of BT were studied by means of steady state absorption spectra and laser-induced transient absorption spectra, as well as by decay kinetics.

2. Experimental details

2.1. Synthesis of BT

The synthesis of 3,4-bis[2,5-dimethylthiophene-3-yl]-2,5-dihydrothiophene (BT) is shown in Scheme 2. 3-Bromoacetyl-2,5-dimethyl-thiophene was prepared from

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Scheme 2. Synthetic routine of BT.

2,5-dimethyl-thiophene (Aldrich Chemicals Co.) according to the literature [11].

2.1.1. 1,1'-Bis[2,5-dimethyl-3-thiophenecarbonyl]-methylsulphide

Anhydrous sodium sulphide (1.56 g, 20 mmol) was reacted with 3-bromoacetyl-2,5-dimethyl-thiophene (2.33 g, 10 mmol) in 30 ml ethanol for 0.5 h, with stirring. The crude product was filtered, washed with water (20 ml \times 4) and dried, then purified by recrystallization from ethanol. Colourless crystals, 1.36 g (yield 80%), were obtained: m.p., 117–119 °C; MS (m/z): 338 (M^+), 139. $^1\text{H NMR}$ (CDCl_3) (δ , ppm): 2.40 (s, 6H, CH_3), 2.68 (s, 6H, CH_3), 3.79 (s, 4H, CH_2), 7.00 (s, 2H, Ar-H). Element analysis: calcd. for $\text{C}_{16}\text{H}_{18}\text{O}_2\text{S}_3$: C, 56.77%; H, 5.36%; S, 28.41%. Found: C, 56.87%; H, 5.26%; S, 28.31%.

2.1.2. 3,4-Bis[2,5-dimethylthiophene-3-yl]-2,5-dithiophene (BT)

TiCl_4 (1.26 g, 0.66 mmol) was added to a mixture of zinc dust (0.87 g, 13.3 mmol) and 50 ml THF with ice cooling under nitrogen atmosphere. After removing the ice-bath, the mixture was refluxed for 1 hour. A solution of 1,1'-bis[2,5-dimethyl-3-thiophenecarbonyl]-methylsulphide (1.02 g, 3 mmol) in 50 ml THF was slowly added over 8 h. The reaction mixture was refluxed overnight. After cooling, the reaction was quenched with a solution of K_2CO_3 (1.5 g) in 5 ml water. The product was extracted with ether (50 ml \times 2). The extract was washed with water, dried over anhydrous Na_2SO_4 , filtered and concentrated under vacuum. The residue was isolated by column chromatography on silica gel using petroleum (60–90 °C) as eluent. Colourless crystals, 0.1 g (yield 11%), were obtained: m.p. 89–91 °C. MS (m/z): 306 (M^+), 291, 173, 258, 245. $^1\text{H NMR}$ (CDCl_3) (δ , ppm): 2.41 (s, 6H, CH_3), 2.65 (s, 6H, CH_3), 2.82 (s, 4H, CH_2), 6.99 (s, 2H, Ar-H). Elements analysis: calcd. for $\text{C}_{16}\text{H}_{18}\text{S}_3$: C, 62.70%; H, 5.92%. Found: C, 62.74%; H, 5.85%.

2.2. Solvents and sample preparation

Acetonitrile (spectroscopic grade) and cyclohexane (A.R.) were used without further purification. Sample solutions (approximately 1.0×10^{-4} mol l^{-1}) were contained in $1 \times 1 \times 4$ cm 3 quartz cells, bubbled with high purity nitrogen or oxygen for 20 min before measuring. As a control experimental, the result of bubbling with high purity nitrogen for

30 min was the same as bubbling for 20 min. All measurements were carried out at room temperature (about 20 °C).

2.3. Apparatus

The laser flash photolysis apparatus was manufactured and installed by the Laboratory of Radiation Chemistry, Shanghai Institute of Nuclear Research, Academia Sinica. A KrF excimer laser (248 nm) was used as the excitation source (pulse width, 20 ns; maximum energy per pulse, about 50 mJ). For details, see Ref. [12]. Steady state absorption spectra were

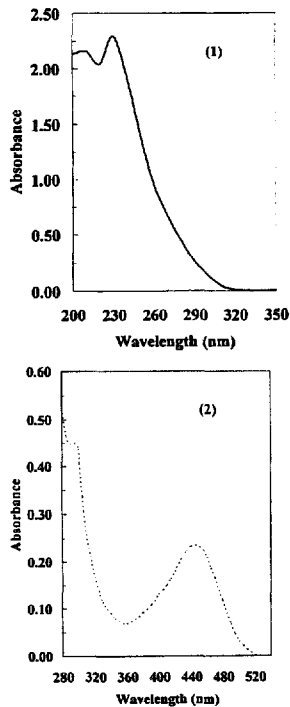
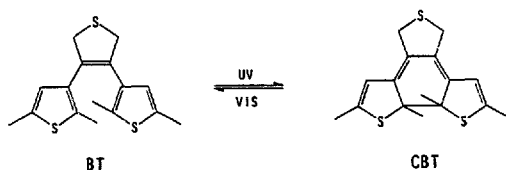


Fig. 1. Absorption spectra of BT (1.0×10^{-4} mol l^{-1}) in acetonitrile (1) and in the photostationary state under irradiation with 254 nm light (2).



Scheme 3. Photochromic reaction of BT and CBT.

measured with a Shimadzu UV-265 FW spectrophotometer. Mass spectra were recorded with an API MS-50 mass spectrometer. ^1H NMR measurements were carried out with a Varian UNITY 200 NMR spectrometer (200 MHz).

3. Results and discussion

3.1. Steady state absorption spectra of BT

Irradiating a solution of BT in acetonitrile or cyclohexane with 254 nm UV light led to a yellow solution which did not bleach in the dark but returned to colourless on exposure to visible light. The absorption spectra of BT in acetonitrile and in the photostationary state under irradiation with 254 nm light are shown in Fig. 1.

The maximum absorption of BT in acetonitrile (Fig. 1(1)) was in the UV region ($\lambda_{\text{max}} = 232$ nm, $\epsilon = 2.3 \times 10^4$ l mol $^{-1}$ cm $^{-1}$). Upon irradiation with 254 nm UV light, a new absorption band appeared (Fig. 1(2)) in the visible region ($\lambda_{\text{max}} = 445$ nm). The new absorption belongs to the stable photochromic product, 2,7,7a-trimethyl-[4,5-e]-3',4'- (2',5'-2H-thiopho)-[6,7-g]-2',3'- (5'-methylthiopho)-7,7a-2H-benzothiophene (CBT), as shown in Scheme 3. In the non-polar solvent cyclohexane (1.1×10^{-4} mol l $^{-1}$), the observation was similar. The maximum absorption (λ_{max}) of BT was at 233 nm ($\epsilon = 3.2 \times 10^4$ l mol $^{-1}$ cm $^{-1}$) and a new absorption band centred at 453 nm appeared upon irradiation with 254 nm light. The polarity of solvents had no clear effect on the absorption spectra of BT. In the photostationary state, another absorption band of CBT was observed at shorter wavelength, but we cannot determine the exact position of the absorption peak because it overlapped with the absorption of BT.

The reversible process between BT and CBT forms a typical photochromic system, with both the forward and back reactions being carried out by the action of a photon.

3.2. Transient absorption spectra of BT upon irradiation by an excimer laser

Up to now, there have been many studies on the synthesis and photochromic behaviour of diarylethene derivatives, but few studies on their photochromic mechanisms have been reported [9]. In order to investigate the photochromic mechanism of BT, we carried out laser flash photolysis. The time-

resolved transient absorption spectra and the decay kinetics of the photoproducts of BT in acetonitrile and cyclohexane were studied. The results are shown in Figs. 2–6 and Table 1.

Fig. 2(1) is the time-resolved transient absorption spectra of BT in cyclohexane deoxygenated by bubbling nitrogen. It shows that on excitation by a 248 nm laser pulse, the absorption maxima of the photolysis products of BT were at 320, 390 and 460 nm, respectively. With the increase in the delay time, the absorption intensities at 320 and 460 nm did not change. By comparing the transient absorption spectrum at 5 μs delay with the absorption spectrum in the photostationary state (Fig. 1(2)), it can be found that the transient absorptions at 320 and 460 nm are the absorptions of one photochromic product (CBT). However, the transient absorption at 390 nm decayed rapidly with the increase in the delay time. Analysis of the decay curve of absorption at 390 nm (Fig. 3) suggests that there are two species at 390 nm, one short-lived and the other long-lived. Because the absorption of the long-lived species at 390 nm was weak and constant, we fitted the decay process of the short-lived species with a first-order kinetic equation, and a lifetime of 3.3 μs was obtained (Fig. 4). It was observed that the decrease in the transient absorption at 390 nm did not lead to an increase in the transient absorptions at 320 and 460 nm. This suggests that the short-lived species was not a precursor intermediate of the long-lived species. The long-lived species at 390 nm was the photochromic product CBT. The absorption of CBT at 390 nm is weak, but can still be detected. In order to determine the nature of the short-lived species, we carried out a comparative experiment in oxygen-bubbled cyclohexane (Fig. 2(2)). The result showed that oxygen did not affect the transient absorptions at 320 and 460 nm, but that the transient absorption at 390 nm decreased and the lifetime of the short-lived species was shorter ($\tau = 1.4$ μs). This can be seen more clearly by comparing the decay curves of the transient species in each case (Fig. 5). The decay of the transient absorption at 390 nm of BT in the high-purity nitrogen-bubbled cyclohexane (Fig. 5(1)) was slower than that in oxygen-bubbled cyclohexane (Fig. 5(2)).

The results of flash photolysis of BT in acetonitrile were similar to that in cyclohexane. In all cases, the kinetic decay processes of the short-lived species could be fitted with a first-order kinetic equation. The lifetimes of the short-lived species are listed in Table 1. The decay of the transient short-lived species in oxygen-bubbled solution was faster than that in nitrogen-bubbled solution for both acetonitrile and cyclo-

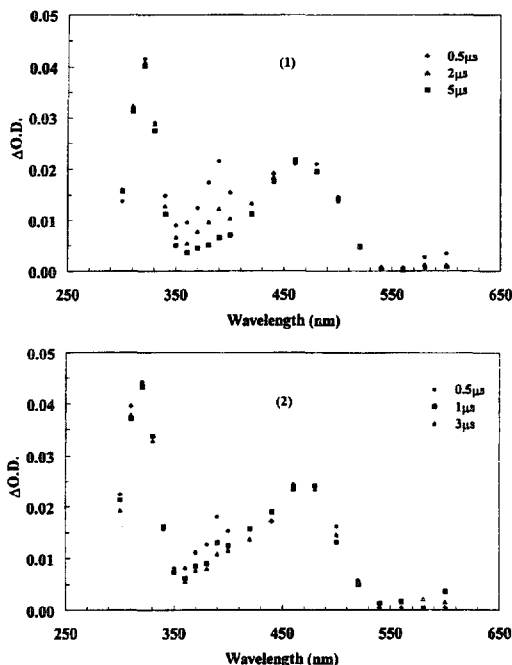


Fig. 2. Time-resolved absorption spectra of BT in cyclohexane (1.2×10^{-4} mol l^{-1}) after a 248 nm laser pulse. (1) Nitrogen-bubbled; (2) oxygen-bubbled.

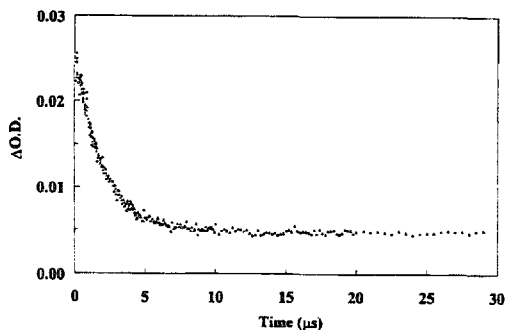


Fig. 3. Decay curve of the transient absorption at 390 nm of BT in nitrogen-bubbled cyclohexane after excitation by a 248 nm laser pulse.

hexane. This suggests that the short-lived species is an excited triplet state which can be quenched by oxygen.

3.3. Generation of transient species

As discussed in Section 3.2, there were two transient species obtained after laser photolysis of BT, the long-lived

photochromic product CBT and a short-lived excited triplet state. In order to determine whether the excited triplet state was $^3BT^*$ or $^3CBT^*$, we examined the risetime of the transient absorption at 390 and 460 nm respectively. The generation of the transient absorptions at 390 and 460 nm are shown in Fig. 6.

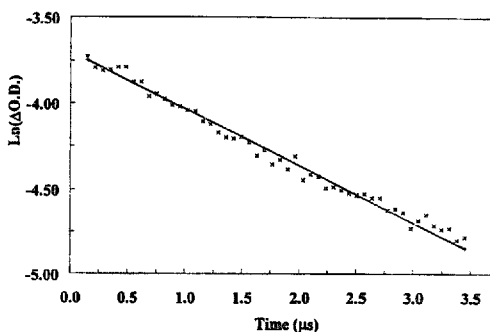


Fig. 4. First-order kinetic decay process of the transient short-lived species in nitrogen-bubbled cyclohexane (monitor wavelength at 390 nm).

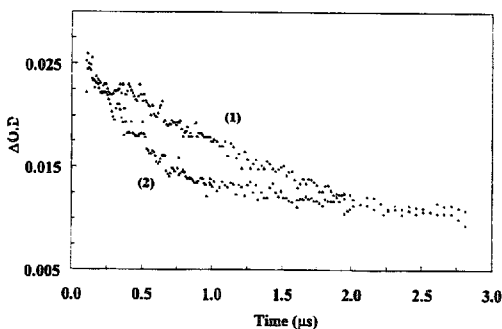


Fig. 5. Decay curve of the transient short-lived species in nitrogen-bubbled (1) and oxygen-bubbled (2) cyclohexane.

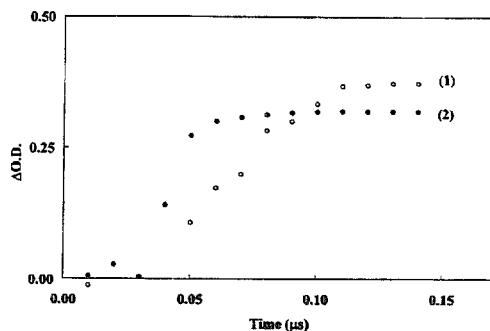


Fig. 5. Optical density change at 390 nm (1) and 460 nm (2) with delay time after laser pulse.

From Fig. 6, it can be seen that the optical density at 460 nm rose faster than that at 390 nm after a 248 nm laser pulse. The time reaching the maximum optical density was about 110 and 60 ns, corresponding to the monitor wavelengths 390

and 460 nm respectively. It was also clearly found that the optical density at 460 nm did not change after rising. In other words, CBT was a long-lived and stable species. However, the optical density at 390 nm decayed rapidly after rising.

Table 1
The lifetime τ of the short-lived species ($A_{max} = 390$ nm)

Solvent	Experimental condition	Lifetime $\tau/\mu\text{s}$
Acetonitrile	Nitrogen-bubbled	4.4
	Oxygen-bubbled	2.9
Cyclohexane	Nitrogen-bubbled	3.3
	Oxygen-bubbled	1.4

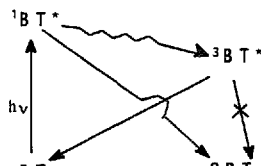
This suggests that the transient species with absorption at 390 nm was short-lived and unstable, the decay of which did not affect the absorption of CBT. It was an excited triplet state. Because the risetime (~ 60 ns) of the transient absorption at 460 nm was longer than the laser pulse width (20 ns), the CBT could not be excited by the laser pulse. Thus it is possible that the transient absorption at 390 nm came from $^1\text{BT}^*$, not $^3\text{CBT}^*$.

It is concluded that the short-lived species ($^3\text{BT}^*$) and the long-lived species (CBT) are independent of each other and that they did not convert to each other. Both of them were generated from the same precursor, the excited singlet state of BT, which was formed by irradiation of a laser pulse.

3.4. Photochromic mechanism of BT

The diarylethene derivatives have the basic molecular framework of 1,3,5-hexatriene. According to the Woodward–Hoffman rule, the reversible cyclization reaction of 1,3,5-hexatriene is allowed, both photochemically and thermally. The conrotatory cyclization reaction to cyclohexadiene is brought about by light, and the disrotatory cyclization reaction of BT when it was heated to a high temperature (200 °C), possibly due to the large potential energy needed for the disrotatory cyclization reaction. This is the reason why both the ring-opened form (BT) and the ring-closed form (CBT) are thermally stable.

By analysis of the results of the steady state absorption spectra of BT, the time-resolved transient absorption after 248 nm laser photolysis and the generation of transient species, we can conclude that one photochromic product, the cyclohexadiene derivative CBT, originates from the excited singlet state $^1\text{BT}^*$, not from the excited triplet state $^3\text{BT}^*$. The photochromic mechanism of BT is shown in Scheme 4. Upon irradiation with UV light, the excited singlet state $^1\text{BT}^*$



Scheme 4. Photochromic mechanism of BT.

is formed first. Then two competitive reactions occur: one reaction pathway of $^1\text{BT}^*$ is to generate CBT, another to form an excited triplet state $^3\text{BT}^*$ through inter-system crossing. In other words, the stable photochromic product CBT only derives from the excited singlet state $^1\text{BT}^*$. The excited triplet state $^3\text{BT}^*$ cannot generate CBT, but rapidly decays to the starting compound (BT).

Acknowledgements

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