DOI: 10.1002/chem.200901855

Bisthienylethenes Containing a Benzothiadiazole Unit as a Bridge: Photochromic Performance Dependence on Substitution Position

Weihong Zhu,* Xianle Meng, Yuheng Yang, Qiong Zhang, Yongshu Xie, and He Tian*[a]

Abstract: A conveniently synthesized photochromic compound, BTB-1, containing an unprecedented six-membered 2,1,3-benzothiadiazole unit as the center ethene bridge, possesses good photochromic performance, with a high cyclization quantum yield and moderate fatigue resistance in solution or an organogel system. The fluorescence of BTB-1 can be modulated by solvato- and photochromism. However, the analogue BTB-2, in which the dimethylthiophene substituents are relocated to the 5,6-positions of benzothiadiazole, does not show any detectable photochromism. To the best of our knowledge, this is the first example of six-membered bridge bisthienylethenes (BTEs) in which the photochromism can be controlled by the substitution position. The photochromism difference is elucidated by the analysis of resonance structure, the Woodward–Hoffmann rule, and theoretical calculations on the ground-state potential-energy surface. In a well-ordered single-crystal state, BTB-1 adopts a relatively rare parallel conformation, and forms an interesting two-dimensional structure due to the presence of multiple directional intermolecular interactions, including C−H···N and C−H···S hydrogen-bonding interactions, and π–π stacking interactions. This work contributes to several aspects for developing novel photochromic BTE systems with fluorescence modulation and performances controlled by substitution position in different states (solution, organogel, and single crystal).

Keywords: benzothiadiazoles · bisthienylethenes · density functional calculations · fluorescence · photochromism

Introduction

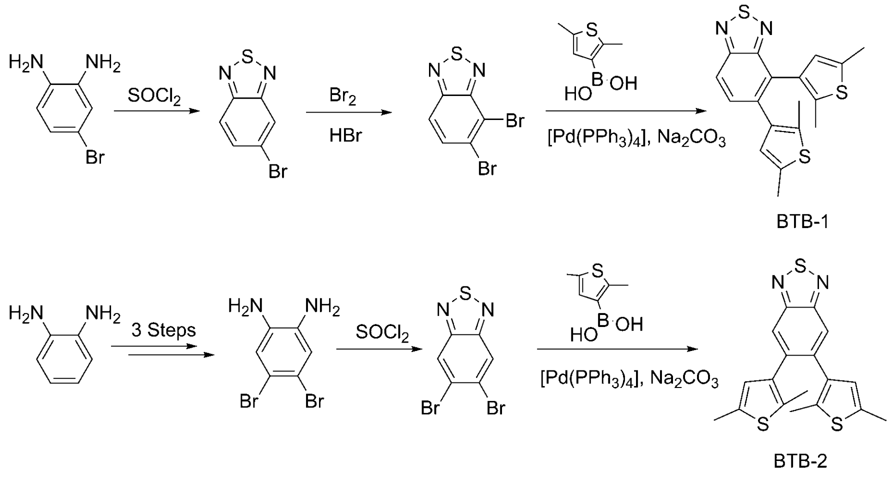
Photochromic compounds are of increasing interest for their potential application in molecular-level devices, such as photoresponsive supramolecular self-assemblies, molecular switches, logic gates, and information storage.[1] Besides extensively developing convenient syntheses of photochromic molecules, one challenging task is to study photochromism in different states, such as in solution, nanoparticles, or single crystals.[2] Recently, Nakatani et al. have successfully demonstrated the application of laser ablation as an efficient technique for nanoparticle fabrication to photochromic molecules.[3] Among various photochromic compounds, bisthienylethenes (BTEs) are known to have excellent thermal stability of two isomers (open and closed-ring isomers) and good fatigue resistance.[4] Generally, the chemical modifications of BTEs are derived from the thiophene units and ethene bridge. Due to the limitations of perfluorocyclopentene, several groups are dedicated to the investigation of novel bridging BTEs.[5,6] Yam et al. have reported a photoactive diarylethene system containing a 1,10-phenanthroline ligand and its metal complexes to perform photochromism.[5] More recently, we have incorporated a naphthalimide chromophore as the center ethene bridge of BTEs, exhibiting a good photochromic performance with fluorescence modulation, even successfully mimicking combined NOR and INHIBIT logic gates.[6b]

In this context, we report a convenient synthesis of two novel bisthienylethenes (BTB-1 and BTB-2 (BTB = 2,5-(bismethylthiophen-3yl)-2,1,3-benzothiadiazole, Scheme 1) containing an unprecedented six-membered aryl ring as the center ethene bridging unit: the 2,1,3-benzothiadiazole chromophore. There are several merits in the design of these BTE derivatives:

---

[a] Prof. Dr. W. Zhu, Dr. X. Meng, Y. Yang, Q. Zhang, Prof. Dr. Y. Xie, Prof. Dr. H. Tian
Key Laboratory for Advanced Materials and
Institute of Fine Chemicals
East China University of Science and Technology
Shanghai 200237 (P.R. China)
Fax: (+86) 21-6425-2758
E-mail: whzhu@ecust.edu.cn
tianhe@ecust.edu.cn

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901855.



Scheme 1. Synthetic routes to BTB-1 and BTB-2.

1) The incorporated ethene bridge of the 2,1,3-benzothiadiazole unit is conjugated to a strong electron-withdrawing group, similar to traditional perfluorocyclopentene, maleic anhydride, or maleic imide bridges, assuring good photochromism with considerable bistability.
2) 2,1,3-Benzothiadiazoles are well-known fluorescent building blocks in the design of functional materials, such as organic light-emitting diodes (OLEDs), nonlinear optical (NLO) materials, and solar cells.[7] The electron-withdrawing group of the 2,1,3-benzothiadiazole unit and the electron-donating thiophene can form an efficient donor–π-acceptor (D-π-A) intramolecular charge-transfer (ICT) system.
3) More importantly, the photochromism is found to be critically dependent upon the substitution position of 2,1,3-benzothiadiazole. BTB-1, with the ethene bridge substituted at the 4,5-positions of 2,1,3-benzothiadiazole, possesses well-defined photochromic properties. In contrast, BTB-2, in which the bridge substitution is located at the 5,6-positions, cannot undergo photocyclization even under prolonged UV irradiation.

Results and Discussion

Synthesis: As illustrated in Scheme 1, intermediates 4,5-dibromo-2,1,3-benzothiadiazole and 5,6-dibromo-2,1,3-benzothiadiazole were prepared according to the reported procedure, in two and four steps respectively.[8] The target molecules BTB-1 and BTB-2 were conveniently prepared from the Suzuki coupling of the appropriate dibromo-substituted 2,1,3-benzothiadiazole and 2,5-dimethylthien-3-yl boronic acid, using $[Pd(PPh_3)_4]$ as a catalyst in a mixture of aqueous Na_2CO_3 (2 M) and 1,4-dioxane under reflux conditions. Their chemical structures were confirmed by ^1H and ^{13}C NMR spectroscopies and HRMS (shown in the Experimental Section).

Optical properties and photochromism: Both BTB-1 and BTB-2 appeared colorless in solution. As shown in Figure 1 and Figure S1 (Supporting Information), they have no absorption band in the visible range. BTB-2 has an identical absorption peak around 370 nm that corresponds to the ICT transition, whereas this peak becomes lower as a shoulder in BTB-1. This might be ascribed to the less efficient ICT from the thiophene group to the electron-withdrawing unit of 2,1,3-benzothiadiazole in BTB-1 (substituted at the 4,5 positions), compared with ICT in BTB-2 (substituted at the 5,6 positions). Additionally, both BTB-1 and BTB-2 have a peak at 310 nm corresponding to

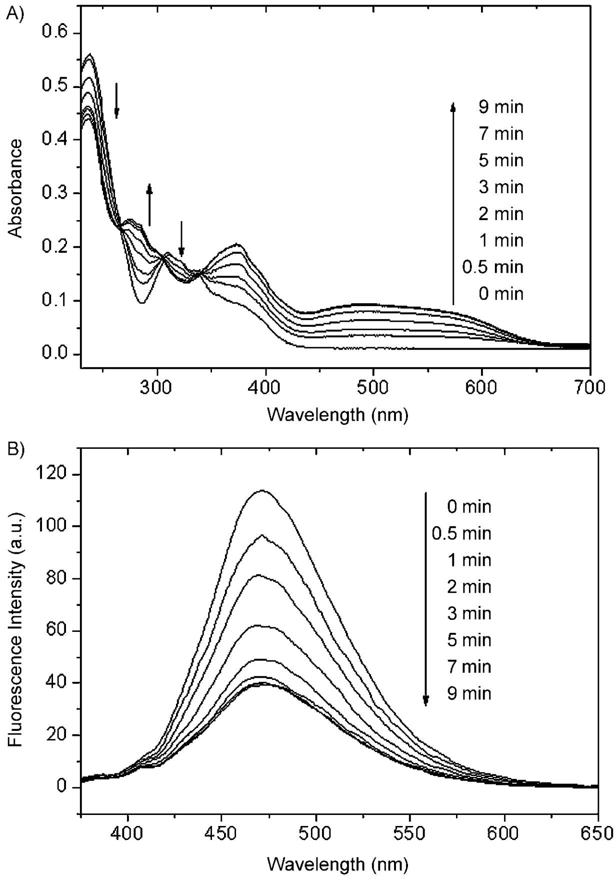


Figure 1. Spectral changes of UV/Vis absorption (A) and fluorescence (B, excited at the isosbestic point of 340 nm) of BTB-1 upon irradiation at 310 nm (in cyclohexane, 2.0×10^{-5} mol L^{-1}). The photostationary states were obtained by irradiating solutions of BTB-1 with 310 nm light until no further spectral changes were observed.

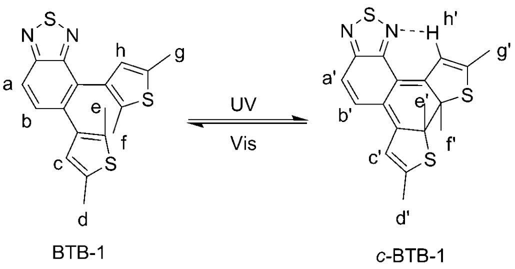
the π–π* transition of the 2,1,3-benzothiadiazole moiety mixed with that of the dimethylthiophene groups.

Table 1. Absorbance data for BTB-1 and BTB-2 before and after UV irradiation in cyclohexane and THF.

Compound (solvent)	Open form (λ_{max} [nm])	Closed form (λ_{max} [nm])	Φ [%][a] Φ_{O-C}	Φ_{C-O}
BTB-1 (cyclohexane)	235, 310, 368 (sh)	230, 368, 486	21.7	18.5
BTB-1 (THF)	217, 312, 370 (sh)	237, 374, 496	24.6	21.3
BTB-2 (cyclohexane)	233, 304, 355	–	–	–
BTB-2 (THF)	239, 305, 355	–	–	–

[a] Quantum yields of cyclization reaction (Φ_{O-C}) and cycloreversion reaction (Φ_{C-O}) were calculated for BTB-1 at 310 and 480 nm, respectively, according to the literature method.[10]

Upon UV irradiation at 310 nm (Figure 1A), the solution of BTB-1 quickly turned to red (Figure S2 in the Supporting Information). Besides an increase in absorption at 390 nm for BTB-1, a new broad absorption band around 500 nm was observed that corresponds to the closed form of BTB-1 (*c*-BTB-1) produced by photocyclization (Scheme 2). It can be evidenced from ^{1}H NMR spectroscopy and HPLC signals that the π-delocalization system was far extended through the photochromic reaction (Figures S3 and S4 in the Supporting Information). Distinct differences in proton NMR signals between the open form (BTB-1) and closed form (*c*-BTB-1) in both the high- and low-field areas were observed. As expected, protons on the benzothiadiazole moiety (H_a and H_b) shifted remarkably to high field upon photocyclization due to great changes (extended π delocalization) in the chemical environment. The four groups of methyl protons on the thiophene moieties of BTB-1 were located at $\delta =$ 2.03, 2.09, 2.18, and 2.22 ppm, respectively. After photocyclization, the signals of these methyl protons were shifted to $\delta = 1.80$, 1.86, 2.43, and 2.45 ppm, respectively. Interestingly, in contrast to the two thiophene protons H_c and H_h ($\delta = 6.47$ and 6.73 ppm) in BTB-1, the $H_{c'}$ shifted upfield to $\delta =$ 5.62 ppm, while $H_{h'}$ shifted downfield to $\delta = 7.65$ ppm in *c*-BTB-1, which can be attributed to the possible formation of an intramolecular hydrogen bond between $H_{h'}$ and the N atom on the benzothiadiazole unit upon photocyclization (Scheme 2). Additionally, HPLC can be used to monitor the closed form on photocyclization. For instance, the ratio between the closed form and the open form in the photostationary state (PSS) of BTB-1 was 54%, obtained from the corresponding integrated areas of the HPLC peaks detected at the isosbestic wavelength, 340 nm (Figure S3 in the Supporting Information).



Scheme 2. Structural change associated with photochromism of BTB-1.

Notably, the color of *c*-BTB-1 can disappear and become completely bleached upon irradiation with visible light ($\lambda >$ 460 nm). The photochromic properties of BTB-1 before and after irradiation are summarized in Table 1. After correction for the active conformer, the quantum yields of the photocyclization for BTB-1 were determined to be about 20–30% in solution. In addition, the fatigue resistance and the thermal stability of the closed form were studied. BTB-1 could reversibly perform the photochromism and revert back by visible-light irradiation with moderate resistance. These coloration and bleaching cycles can be repeated with alternating irradiation by UV (310 nm) and visible light (>460 nm). The irradiation time was long enough for coloration to reach the PSS and for the color to be completely bleached. As shown in Figure S5 in the Supporting Information, the fatigue-resistant characteristics of BTB-1 in solution indicated that about 35% were decreased after 10 repeat cycles. The absorbance of the closed form of BTB-1 in cyclohexane does not show any obvious decrease in the visible range in the dark at room temperature even after one month. Clearly, BTB-1 retains the photochromic properties of parent BTEs when replacing the five-membered cyclopentene ring by a fluorescent benzothiadiazole unit, with a six-membered aryl unit as the center ethene bridge. With strong electron-withdrawing properties similar to perfluorocyclopentene, maleic anhydride, and maleic imide, the benzothiadiazole group might be helpful to ensure such photochromism with considerable bistability.[6] Previously we have found that, due to the strong electron-withdrawing effect, an incorporated naphthalimide unit can remarkably increase the lifetimes of open merocyanine (MC) forms, almost three magnitudes longer than that of unsubstituted spironaphthoxazine.[9]

Fluorescence modulation and solvatochromism: The 2,1,3-benzothiadiazole unit is a well-known fluorescent chromophore with high efficiency and chemical stability.[7] Both BTB-1 and BTB-2 have a typical D-π-A configuration when two electron-donating thiophene groups are attached to the 2,1,3-benzothiadiazole unit. Upon excitation at the isosbestic point of 340 nm, BTB-1 and BTB-2 exhibit intense luminescence with efficiencies of 7.7 and 2.9%, respectively. When irradiated at 310 nm, the solution of BTB-1 underwent photocyclization and exhibited a distinct fluorescence quenching (Figure 1B), in which the fluorescence efficiency dropped by 70% when reaching the PSS. Clearly, this resulted from the closed form as a fluorescence quencher through the possible channel of Förester resonance energy transfer (FRET) from the excited fluorescent chromophore unit to the ring-closed diarylethene unit. Upon irradiation, the resulting closed form, *c*-BTB-1, almost covers the whole visible region with a broad absorption band (Figure 1A), thus resulting in an efficient overlap between the absorption and emission bands. It is the FRET that successfully switches ON and OFF the fluorescence of the incorporated 2,1,3-benzothiadiazole unit. Accordingly, the bistable states of BTB-1 with fluorescence modulation show potential prospects in molecular switches and information storage.[11,12]

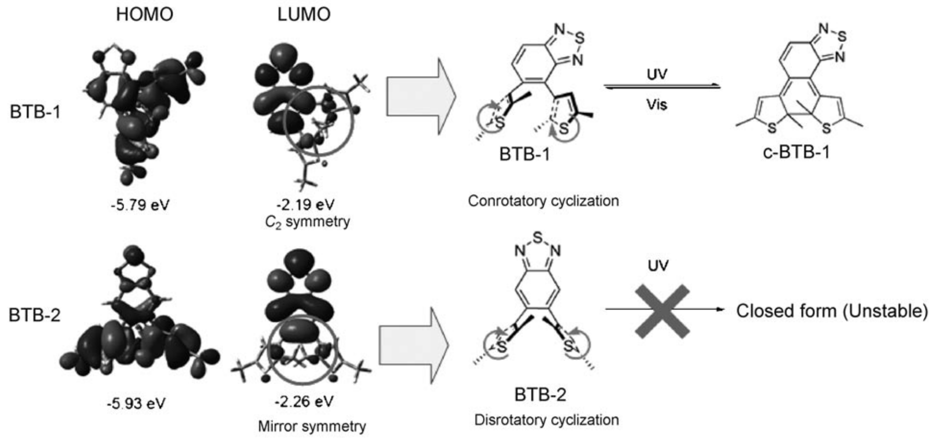


Figure 2. Woodward–Hoffmann rule analysis of BTB-1 and BTB-2.

Interestingly, solvent polarity plays a significant role in the luminescent wavelength of BTB-1 and BTB-2. For BTB-2, the redshift reaches 130 nm from about 420 nm with a dual-exponential decay containing two components of 1.9 ns (36%) and 16.7 ns (64%) with $\chi^2=1.2$ in nonpolar cyclohexane, to around 550 nm containing those of 2.0 ns (72%) and 9.4 ns (28%) with $\chi^2=1.3$ in polar acetonitrile (Figures S6 and S7 in the Supporting Information). However, for BTB-1, a smaller shift by only 50 nm is observed from 470 nm containing two components of 2.1 ns (52%) and 7.0 ns (48%) with $\chi^2=1.3$ in cyclohexane, to 535 nm containing those of 5.3 ns (87%) and 5.8 ns (13%) with $\chi^2=1.2$ in acetonitrile. This might be similarly attributed to the ICT effect in BTB-1 being less efficient than in BTB-2 because the larger difference in dipole moments between the excited and the ground states can result in the larger solvatochromic effect.[13] The increase in the dipole moment ($\Delta\mu$) of BTB-2 can be estimated to be 13 D according to the Lippert plots, whereas for BTB-1 the data appears to be 5 D (shown in the Supporting Information).

Photochromic difference between BTB-1 and BTB-2 in solution: Unexpectedly, in contrast with the good photochromic performance of BTB-1 in solution, there are no obvious changes in the color or the absorption spectra of BTB-2 upon UV-light irradiation (Figure S2 in the Supporting Information). The photochromism is found to be critically dependent upon the substitution position of 2,1,3-benzothiadiazole. To gain an insight into the interesting difference between the photochromic performances of BTB-1 and BTB-2, we first attempt to explain this using the Woodward–Hoffmann rule: a cyclization reaction can take place only if the molecular orbital symmetries of reactants are the same as that of products. Traditionally, according to the Woodward–Hoffmann rule based on the π-orbital symmetries for 1,3,5-hexatriene, a conrotatory cyclization reaction to cyclohexadiene is brought about by light. As can be observed from Figure S9 in the Supporting Information, BTB-1 and BTB-2 have the same total π-electron count and they also have the same simplified hexatriene framework for the π electrons on the benzothiadiazole unit to be both delocalized in the plane. However, the LUMO symmetry of the simplified hexatriene framework in BTB-1 is C_2 symmetry, which is the same as traditional 1,3,5-hexatriene, whereas that of BTB-2 is mirror symmetry (Figure 2). Considering this, photoreaction of BTB-2 could only follow the disrotatory cyclization in accordance with the orbital symmetry conservation theory. This also means that the photoreaction could only occur on the parallel form of BTB-2, resulting in a strained structure with two methyl groups on the same side of the plane, which is certainly unstable given the large steric hindrance of this conformation (Figure 2). As a result, no obvious photochromic changes occur for BTB-2 upon UV-light irradiation.

Second, we roughly estimated and examined the ground-state potential-energy surfaces (PESs) in an effort to further explain the photochromic difference between BTB-1 and BTB-2. On the PES of BTB-1, two minima corresponding to the open- and closed-ring isomers (noted BTB-1 and *c*-BTB-1, respectively, in Figure 3) have been located. The reaction coordinate leading from *c*-BTB-1 to BTB-1 is represented by the value of the distance between the reactive carbon atoms. It shows a high energy barrier of about 52 kcal mol^{-1} for the isomerization from BTB-1 to *c*-BTB-1 in the ground state, indicating that the reaction can only proceed by photoexcitation. The *c*-BTB-1 form is higher in energy only by 7.8 kcal mol^{-1} with respect to BTB-1, corresponding to a high energy barrier of about 44.2 kcal mol^{-1} for the isomerization from *c*-BTB-1 to BTB-1, which is consistent with the experimental thermal stability of *c*-BTB-1. However, on the PES of BTB-2, when the reaction coordinate goes from 3.47 (the distance in BTB-2) to 1.4 Å, no stable isomer has been located. In addition, for the parallel isomer of BTB-2 (noted BTB-2p in Figure 3), in spite of the local minimum found at the shorter distance of 1.56 Å, it would transform to BTB-2 immediately because the energy barrier for this isomerization is low (6.3 kcal mol^{-1}). Therefore, there are no thermally stable closed-ring isomers detected for either BTB-2 or BTB-2p, which is coincident with the analysis based on the Woodward–Hoffmann rule.

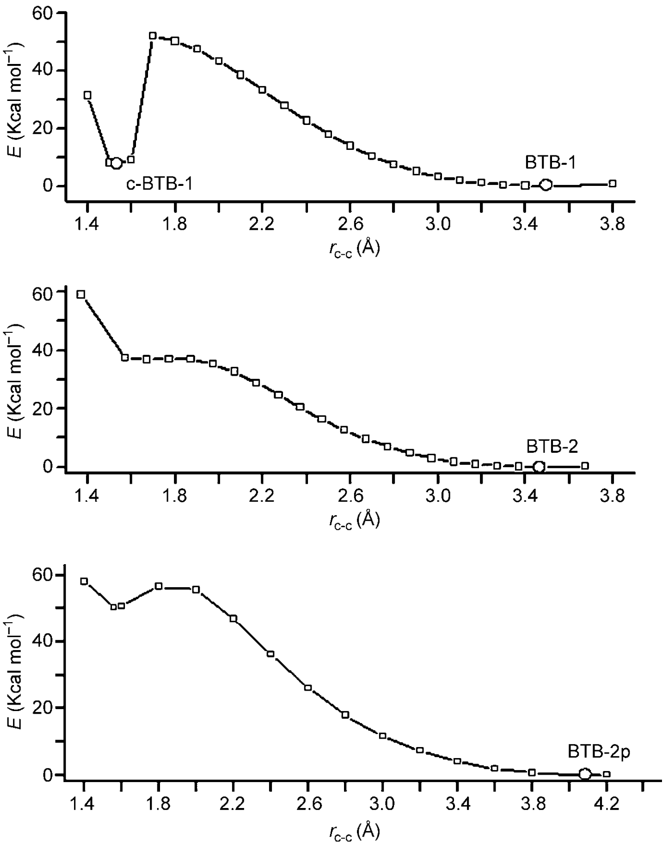


Figure 3. Outline of S_0 PESs calculated at the PBE1PBE/6-31G (d,p) level. r_{c-c} is the distance between the carbon atoms at the 2-position of the two thiophene rings.

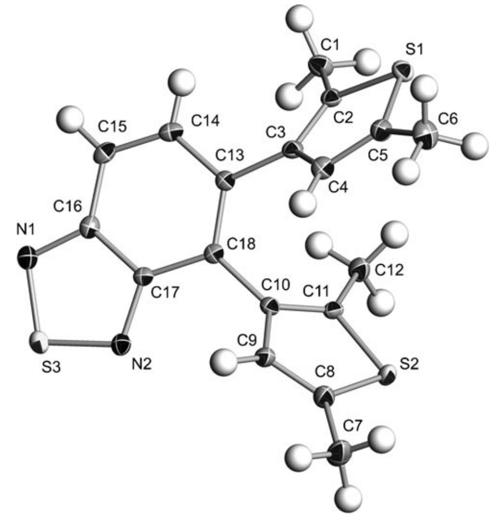


Figure 4. ORTEP representation of the crystal structure of BTB-1 with displacement ellipsoids shown at the 25% probability level. Selected bond lengths [Å]: C13–C14, 1.432(3); C14–C15, 1.361(3); C15–C16, 1.419(3); C16–C17, 1.433(3); C17–C18, 1.435(3); C13–C18, 1.385(3); C2···C11, 3.996(3).

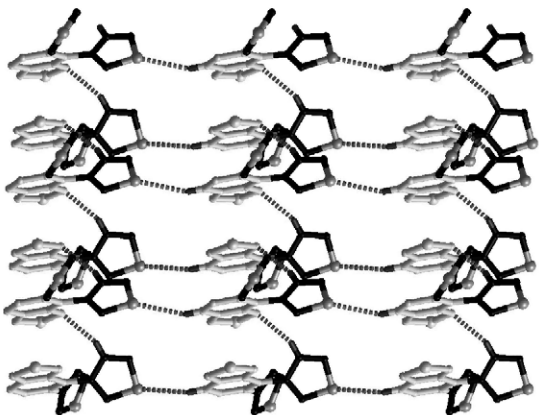


Figure 5. View of the two-dimensional structure of BTB-1 formed by cooperative hydrogen bonding and π–π stacking interactions. Methyl groups are omitted for clarity. Selected distances and angles (Å or °): S···H, 2.92; S···H–C, 155; N···H, 2.44; N···H–C, 149. Interplane (π···π) angle, 1.5; S···centroid (benzene), 3.34 and 3.50.

Photochromic performance of BTB-1 in crystal form and organogel system: Single crystals of BTB-1 and BTB-2 were grown by slow evaporation of their corresponding solutions in MeOH/H_2O. Only the crystallographic data of the open forms is available. X-ray crystal-structure analysis (Figure 4) revealed that in BTB-1 the C13–C18 bond length is 1.385(3) Å, indicative of a double bond. BTB-1 adopts a parallel conformation, in which the potentially photoreactive atoms C2 and C11 are located at the same side of the C13–C18 double bond. In single crystals, most diarylethenes are packed in the antiparallel conformation,[2,3] with only a few examples of parallel conformers.[14] In single crystals BTB-1 molecules were linked by π–π stacking interactions between the benzothiadiazole rings, in addition to C–H···N and C–H···S hydrogen bonds (Figure S11 in the Supporting Information), affording an interesting two-dimensional structure (Figure 5). In the crystalline state BTB-2 also adopts a parallel conformer with π–π stacking interactions between the benzothiadiazole rings (Figure S12 in the Supporting information). However, as illustrated with the single-crystal data for BTB-2 (Figure 6) the C4–C5 bond length is 1.451(2) Å, suggesting a single bond connecting two thiophene units. Accordingly, the resonance structure in BTB-2 that contains the 1,3,5-hexatriene unit forming from the C4–C5 single bond of the six-membered carbon ring and the two thiophene units should be highly unstable; a possible reason why the closed form of the BTB-2 is very unstable relative to the open form.[15] From the strong evidence of both the parallel conformer and essentially a single bond (C4–C5) connecting two thiophene units, it is unsurprising that BTB-2 does not show any color change with photochromic performance. This is in further accordance with the aforementioned PESs and Woodward–Hoffmann rule analysis based on frontier orbital theory.

In the single-crystalline phase, diarylethenes exhibit photochromism only when the molecules adopt an antiparallel conformation and the distance between the potentially reactive carbon atoms is short enough.[2] When the distance is

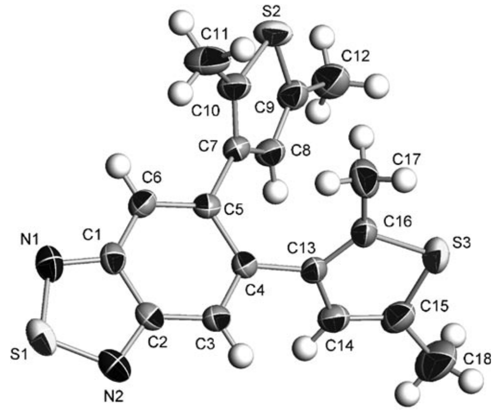


Figure 6. ORTEP representation of the crystal structure of BTB-2 with displacement ellipsoids shown at the 50 % probability level. Selected bond lengths [Å]: C1−C2, 1.422(3); C2−C3, 1.414(3); C3−C4, 1.363(3); C4−C5, 1.451(2); C6−C1, 1.405(3); C5−C6, 1.365(3); C10···C16, 4.018(3).

larger than 4.2 Å, the photocyclization reaction in crystals is suppressed.[2a] Although the distance between two photoreactive carbon atoms in a BTB-1 single crystal is 3.99 Å (shorter than the expected possible photochromic range), the lack of color change upon irradiation with UV light can be attributed to the parallel arrangement observed in the single crystal of BTB-1. This observation provides further evidence that the antiparallel conformation might be a precondition for BTE derivatives to undergo photocyclization in the single crystal state. However, considering the good photochromic performance of BTB-1 in cyclohexane, it is expected that the parallel arrangement in the single-crystal state can shift to the antiparallel conformation in solution due to the loss of the above-mentioned cooperative hydrogen-bonding and π–π stacking interactions in the well-ordered crystal state. In the crystal state, intermolecular interactions are rather strong, which is different from those in dilute solutions, in which intramolecular interactions are predominant. Therefore, it is reasonable that the photochromic behavior can be distinctively different between the crystalline and solution phases.[2,14b] As a further case, illustrated with Figures S13 and S14 in the Supporting information, BTB-1 also exhibits excellent photochromic properties and defined thermoreversible properties in an organogel system (Figure 7). A stable gel with BTB-1 dopant (6.5×10^{-3} wt %) was formed around 20 % w/w Poloxamer 407 (Boluoshamu 407 with the molecular distribution of 9840–14600) in water, and showed an extraordinary sol–gel phase-transition temperature around 28 °C (Figure 7). Irradiation of the thermoreversible organogel of BTB-1 with UV light (310 nm) leads to the appearance of a new absorbance band around 500 nm, which could be bleached by irradiating with visible light ($\lambda > 460$ nm).

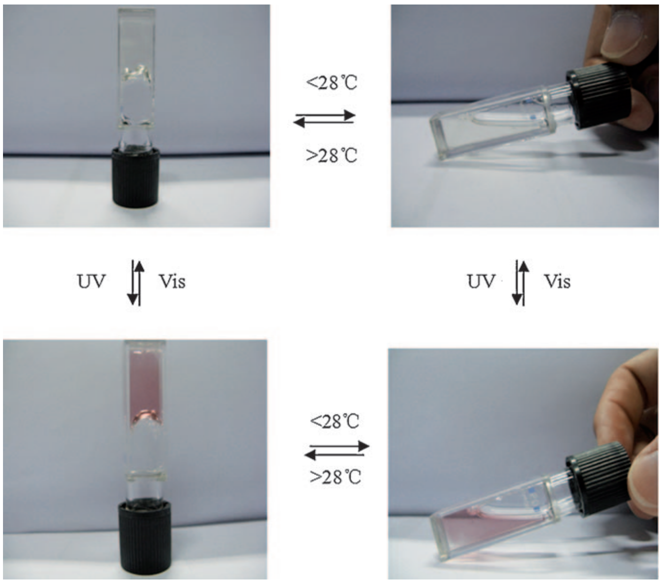


Figure 7. Color changes and sol–gel phase transition of BTB-1 doped in thermosensitive organogel (6.5×10^{-3} wt %) upon irradiation with UV (310 nm) and visible light (>460 nm).

Conclusion

In summary, a conveniently synthesized photochromic compound BTB-1, containing an unprecedented six-membered aryl ring as the center bridging unit with the electron-withdrawing unit of the 2,1,3-benzothiadiazole chromophore, possesses good photochromic performance with high cyclization quantum yield and moderate fatigue resistance in solution or an organogel system. Interestingly, when the center bridge substitution is located at the 5,6-positions of 2,1,3-benzothiadiazole in the analogue BTB-2, no photochromism is detectable. To the best of our knowledge, this is the first example of six-membered bridge BTEs in which photochromism can be controlled by the substitution position. The photochromism difference is interpreted by the resonance structures, theoretical calculations of the ground-state PESs and the Woodward–Hoffmann rule. In the well-ordered single-crystal state, BTB-1 adopts a relatively rare parallel conformation and forms an interesting two-dimensional structure due to the presence of multiple directional intermolecular interactions, including C−H···N and C−H···S hydrogen-bonding interactions and π–π stacking interactions. Furthermore, the fluorescence of BTB-1 could be modulated by solvatochromism and photochromism. This work contributes to several aspects for the development of novel BTE systems with fluorescence modulation and photochromic performances controlled by substitution position.

Experimental Section

General information: ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM-400 or 500 spectrometers. Mass spectra were recorded on an ESI mass spectrometer. Absorption and fluorescence spectra were recorded on Varian Cary 500 and Varian Cary Eclipse spectrophotometers, respectively. Fluorescence lifetimes were measured on an Edinburgh LifeSpecps spectrofluorometer (FL920). HPLC analyses were performed by using an Agilent 1100 instrument, eluting with CH_3CN at a flow rate of $0.6\,mL\,min^{-1}$, detected at the isosbestic wavelength of 340 nm. The optical switch experiments were carried out by using a photochemical reaction apparatus with a 200 W Hg lamp or a Xe lamp (Beijing 7-S Optical Instrument Co. Ltd., 71PX5002) equipped with specific filter set. 5,6-Dibromo-2,1,3-benzothiadiazole, 4,5-dibromo-2,1,3-benzothiadiazole, and 2,5-dimethylthiophen-3-yl boronic acid were prepared according to established methods.[8] All other reagents were of analytical purity and were used without further treatment.

Synthesis of BTB-1: 4,5-Dibromo-2,1,3-benzothiadiazole (0.2 g, 0.68 mmol) and $[Pd(PPh_3)_4]$ (0.1 g, 0.087 mmol) were dissolved in dioxane (10 mL) and the resulting mixture was stirred for 15 min at room temperature before an aqueous solution of Na_2CO_3 (10 mL, $2.0\,mol\,L^{-1}$) was added. The reaction mixture was heated to reflux, then a solution of 2,5-dimethylthiophen-3-yl boronic acid (0.12 g, 0.77 mmol) was added dropwise by syringe. Subsequently, the mixture was heated at reflux for 24 h and cooled to room temperature. The reaction mixture was poured into H_2O and extracted with diethyl ether and the organic layer was separated and dried (Na_2SO_4). After concentration, the compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1 v/v) to yield a white solid (0.15 g, 62%). ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 1.95$ (s, 3H; $-CH_3$), 2.13 (s, 3H; $-CH_3$), 2.39 (s, 3H; $-CH_3$), 2.45 (s, 3H; $-CH_3$), 6.37 (s, 1H; thiophene-H), 6.59 (s, 1H; thiophene-H), 7.63 (d, $J = 8.8$ Hz, 1H; Ph-H), 7.97 ppm (d, $J = 8.8$ Hz, 1H; Ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 14.0$, 14.2, 15.1, 15.3, 119.5, 127.3, 127.8, 128.4, 132.5, 133.5, 133.8, 135.3, 135.4, 135.5, 136.5, 136.8, 154.2, 155.4 ppm; HRMS (TOF EI): m/z: calcd for $C_{18}H_{16}N_2S_3^+$: 356.0476; found 356.0475.

Synthesis of BTB-2: BTB-2 was prepared by a similar procedure to BTB-1 from 5,6-dibromo-2,1,3-benzothiadiazole. Yield: 58%; ^1H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 2.19$ (s, 6H; $-CH_3$), 2.36 (s, 6H; $-CH_3$), 6.27 (s, 2H; thiophene-H), 7.92 ppm (s, 2H; Ph-H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 13.7$, 15.0, 121.8, 127.5, 133.8, 135.1, 136.4, 139.4, 154.1 ppm; HRMS (TOF EI): m/z: calcd for $C_{18}H_{16}N_2S_3^+$: 356.0476; found: 356.0467.

Photochromism of BTB-1 doped in thermosensitive organogel: The sol–gel system was based on commercially available Poloxamer 407 (Boluoshamu 407) with the molecular distribution of 9840–14600. The thermosensitive organogel with a dopant of BTB-1 was prepared as follows: A solution of BTB-1 in methanol (6.5×10^{-3} wt%; 200 μL) was added to Poloxamer 407 aqueous solution (20% w/w; 3.0 g). The viscous solution was cooled to 5 °C and sonicated until the solution became transparent without obvious bubbles. The phase transition for the thermosensitive organogel system was about 28 °C. When keeping the temperature above 28 °C, the aqueous solution of Poloxamer 407 (20% w/w) became an organogel.

Computational details (PBE1PBE-optimized geometries of BTB-1, BTB-2, and *c*-BTB-1): The theoretical calculations were carried out using Gaussian 03 software package.[16] The ground-state geometries of the open forms (BTB-1 and BTB-2) and closed form (*c*-BTB-1) were optimized in the gas phase using density functional theory (DFT) with the hybrid Perdew, Burke, and Ernzerhof functional (PBE1PBE).[17] The 6-31G(d, p) basis set[18] was employed through all the calculations. Vibrational frequencies were calculated in order to check the absence of imaginary-frequency modes for all stationary points.

X-ray crystallography: BTB-1: $C_{18}H_{16}N_2S_3$; $M_w = 356.51\,g\,mol^{-1}$; light yellow block; $0.24 \times 0.08 \times 0.06$ mm; orthorhombic; $Pna21$; $a = 6.8294(2)$, $b = 23.4914(5)$, $c = 10.5186(3)$ Å; $U = 1687.52(8)$ Å^3; $F(000) = 744$; $\rho_{calcd} = 1.403\,g\,mol^{-1}$; $Mo_K = 0.439\,mm^{-1}$; $T = 100$ K; 11147 data were measured on a Bruker SMART Apex diffractometer, of which 3801 were unique ($R_{int} = 0.0391$); 212 parameters were refined against F_o^2 (all data), final $wR_2 = 0.0821$, $S = 1.023$, R_1 (3483 data with $I > 2$ $(I)) = 0.0338$, largest final difference peak/hole = +0.328/−0.208 e Å^3. BTB-2: $C_{18}H_{16}N_2S_3$; FW = $356.51\,g\,mol^{-1}$; light yellow block; 0.42 ×0.37 ×0.32 mm; orthorhombic; $P2_12_12_1$; $a = 6.7369(5)$, $b = 16.0514(12)$, $c = 16.1610(12)$ Å; $U = 1747.6(2)$ Å^3; $F(000) = 744$; $\rho_{calcd} = 1.355\,g\,mol^{-1}$; $Mo_K = 0.424\,mm^{-1}$; $T = 293(2)$ K; 9580 data were measured on a Bruker SMART Apex diffractometer, of which 3442 were unique ($R_{int} = 0.0493$); 212 parameters were refined against F_o^2 (all data), final $wR_2 = 0.0876$, $S = 1.008$, R_1 (3142 data with $I > 2$ $(I)) = 0.0354$, largest final difference peak/hole = +0.198/−0.269 e Å^3. Structures of BTB-1 and BTB-2 were solved by direct methods and refined with full-matrix least-squares technique against F^2 (all data) using SHELXTL.[19] H atoms bound to C were placed at calculated positions. CCDC-734062 (BTB-1) and 735611 (BTB-2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

This work was financially supported by NSFC/China, National Basic Research 973 Program (2006CB806200), grants for New Century Excellent Talents in University (NCET), SRFDP (200802510011), and Shanghai Shuguang Project (07SG34). We also appreciate the assistance of Prof. Seik Weng Ng (University of Malaya, Malaysia) for the single crystal determination of BTB-1.

---

[1] a) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716; b) F. M. Raymo, M. Tomasulo, *J. Phys. Chem. A* **2005**, *109*, 7343–7352; c) H. Tian, Y. L. Feng, *J. Mater. Chem.* **2008**, *18*, 1617–1622; d) S. Yagai, A. Kitamura, *Chem. Soc. Rev.* **2008**, *37*, 1520–1529; e) H. D. Samachetty, N. R. Branda, *Pure Appl. Chem.* **2006**, *78*, 2351–2359; f) H. Tian, S. J. Yang, *Chem. Soc. Rev.* **2004**, *33*, 85–97; g) M. Morimoto, H. Miyasaka, M. Yamashita, M. Irie, *J. Am. Chem. Soc.* **2009**, *131*, 9823–9835.

[2] a) S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, *Chem. Commun.* **2002**, 2804–2805; b) S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778; c) M. Morimoto, M. Irie, *Chem. Commun.* **2005**, 3895–3905; d) H. Koshima, N. Ojima, H. Uchimoto, *J. Am. Chem. Soc.* **2009**, *131*, 6890–6891.

[3] A. Spangenberg, R. Métivier, J. Gonzalez, K. Nakatani, P. Yu, M. Giraud, A. Léaustic, R. Guillot, T. Uwada, T. Asahi, *Adv. Mater.* **2009**, *21*, 309–313.

[4] a) H. Tian, S. Wang, *Chem. Commun.* **2007**, 781–792; b) V. Lemieux, N. R. Branda, *Org. Lett.* **2005**, *7*, 2969–2972; c) J. Andreasson, S. D. Straight, T. A. Moore, A. L. Moore, D. Gust, *J. Am. Chem. Soc.* **2008**, *130*, 11122–11128; d) B. Gorodetsky, N. R. Branda, *Adv. Funct. Mater.* **2007**, *17*, 786–796; e) J. Areephong, T. Kudernac, J. J. D. de Jong, G. T. Carroll, D. Pantorott, J. Hjelm, W. R. Browne, B. L. Feringa, *J. Am. Chem. Soc.* **2008**, *130*, 12850–12851; f) R. Arai, S. Uemura, M. Irie, K. Matsuda, *J. Am. Chem. Soc.* **2008**, *130*, 9371–9379; g) Z. G. Zhou, S. Z. Xiao, J. Xu, Z. G. Liu, M. Shi, F. Y. Li, T. Yi, C. H. Huang, *Org. Lett.* **2006**, *8*, 3911–3914; h) V. Aubert, V. Guerchais, E. Ishow, K. Hoang-Thi, I. Ledoux, K. Nakatani, H. L. Bozec, *Angew. Chem.* **2008**, *120*, 587–590; *Angew. Chem. Int. Ed.* **2008**, *47*, 577–580; i) N. Xie, D. X. Zeng, Y. Chen, *J. Electroanal. Chem.* **2007**, *609*, 27–30.

[5] a) V. W. W. Yam, C. C. Ko, N. Y. Zhu, *J. Am. Chem. Soc.* **2004**, *126*, 12734–12735; b) C. C. Ko, W. M. Kwok, V. W. W. Yam, D. L. Phillips, *Chem. Eur. J.* **2006**, *12*, 5840–5848.

[6] a) Y. C. Jeong, C. J. Gao, I. S. Lee, S. I. Yang, K. H. Ahn, *Tetrahedron Lett.* **2009**, *50*, 5288–5290; b) X. L. Meng, W. H. Zhu, Q. Zhang, Y. L. Feng, W. J. Tan, H. Tian, *J. Phys. Chem. B* **2008**, *112*, 15636–15645.

[7] a) J. Liu, S. Y. Shao, L. Chen, Z. Y. Xie, Y. X. Cheng, Y. H. Geng, L. X. Wang, X. B. Jing, F. S. Wang, *Adv. Mater.* **2007**, *19*, 1859–1863; b) J. Luo, X. Z. Li, Q. Hou, J. B. Peng, W. Yang, Y. Cao, *Adv. Mater.* **2007**, *19*, 1113–1117; c) X. M. Ma, J. L. Hua, W. J. Wu, Y. H. Jin, F. S. Meng, W. H. Zhan, H. Tian, *Tetrahedron* **2008**, *64*, 345–350; d) J. P. Du, E. J. Xu, H. L. Zhong, F. Yu, C. Liu, H. R. Wu, D. L.

Zeng, S. J. Ren, J. Sun, Y. C. Liu, A. M. Cao, Q. Fang, *J. Polym. Sci. Polym. Chem. Ed.* **2008**, *46*, 1376–1387.

[8] a) K. Pilgram, M. Zupan, R. Skiles, *J. Heterocycl. Chem.* **1970**, *7*, 629–633; b) S. Vagin, A. Frickenschmidt, B. Kammerer, M. Hanack, *Eur. J. Org. Chem.* **2005**, 3271–3278.

[9] X. L. Meng, W. H. Zhu, Z. Q. Guo, J. Q. Wang, H. Tian, *Tetrahedron* **2006**, *62*, 9840–9845.

[10] H. Tian, B. Z. Chen, H. Y. Tu, K. Müllen, *Adv. Mater.* **2002**, *14*, 918–923.

[11] a) G. Y. Jiang, S. Wang, W. F. Yuan, L. Jiang, Y. L. Song, H. Tian, D. B. Zhu, *Chem. Mater.* **2006**, *18*, 235–237; b) K. Matsuda, M. Irie, *J. Photochem. Photobiol. C* **2004**, *5*, 169–182.

[12] a) X. F. Guo, D. Q. Zhang, D. B. Zhu, *Adv. Mater.* **2004**, *16*, 125–130; b) M. Berberich, A.-M. Krause, M. Orlandi, F. Scandola, F. Würthner, *Angew. Chem.* **2008**, *120*, 6718–6721; *Angew. Chem. Int. Ed.* **2008**, *47*, 6616–6619; c) H. J. Kim, J. H. Jang, H. Choi, T. Lee, J. Ko, M. Yoon, H. J. Kim, *Inorg. Chem.* **2008**, *47*, 2411–2415.

[13] a) B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, **2001**, pp. 200–225; b) M. E. Vázquez, J. B. Blanco, B. Imperiali, *J. Am. Chem. Soc.* **2005**, *127*, 1300–1306.

[14] a) W. J. Tan, Q. Zhang, J. J. Zhang, H. Tian, *Org. Lett.* **2009**, *11*, 161–164; b) X. C. Li, Y. Z. Ma, B. C. Wang, G. A. Li, *Org. Lett.* **2008**, *10*, 3639–3642.

[15] We thank the referee who suggested the explanation of the instability of the BTB-2 closed form from the viewpoint of resonance structure.

[16] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

[17] a) M. Ernzerhof, G. E. Scuseria, *J. Chem. Phys.* **1999**, *110*, 5029–5036; b) M. Ernzerhof, J. P. Perdew, K. Burke, *Int. J. Quantum Chem.* **1997**, *64*, 285–295.

[18] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys.* **1982**, *77*, 3654.

[19] SHELXS97 and SHELXL97 Programs for Crystal Structure Solution and Refinement, G. M. Sheldrick, University of Göttingen, Göttingen (Germany), **1997**.

Received: July 4, 2009