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Diastereoselective Photochromism of Bisbenzothienylethenes with an Oxycarbonyl-Related Functional Group on the Side Chain

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Nine 1-[2-(1-substituted)ethyl-3-benzothienyl]-2-(2-methyl-3-benzothienyl)hexafluorocyclopentenes (4-substituted benzoyloxy, *N*-arylcarbamoyloxy, and aryloxycarbonyloxy) were synthesized. They showed diastereoselective photochromic ring closure upon UV irradiation. Among them, 4-nitrophenoxycarbonyloxy-substituted compound recorded a remarkable 94% diastereomer excess with 91% conversion to the closed form.

Introduction

Photochromic compounds possessing chirality[1] have been paid much attention recently in relation to the development of novel cholesteric and chiral smectic liquid crystalline materials whose properties can be changed reversibly by photoirradiation[2] as well as the photochemical control of their interaction with the biologically important agents.[3]

Diarylethenes are one of the most promising thermally irreversible organic photochromic families for optic/photonic applications.[4] Photochromism of diarylethenes is based on the photochemical electrocyclization−cycloreversion reactions between a 1,3,5-hexatriene (open form) and a 1,3-cyclohexadiene (closed form) (Scheme 1, (1)). When the terminal carbon atoms are fully substituted, the hexatriene of the open form is forced to take one of the two chiral helical structures because of the steric congestion, which usually convert to each other to give a helically racemic mixture at room temperature in solution. On the other hand, the photoproduced cyclohexadiene of the closed form has two new stereogenic carbon atoms as the result of C−C bond formation. When an optically active stereoregulating unit (e.g. A* in Scheme 1, (2) and (3)) is introduced to the peripheral[5,6] or even to the remote part of the hexatriene moiety of the open form,[7] one of the two opposite helically chiral conformers would be more stable than the other, and the diastereoselective ring closure would be observed by photoirradiation, as we have already demonstrated with fulgide derivatives.[8,9]

Recently we have reported a diastereoselective photochromism of diarylethene **1** possessing a methoxymethoxyethyl group, which exhibited 88% diastereomer excess (de) upon UV irradiation at room temperature in solution.[10] The origin of the relatively high diastereoselectivity can be explained by the cooperative combination of (i) allylic strain[11] to anchor the conformation around the stereogenic center on the side chain of the relevant benzothiophene, (ii) stereic repulsion between the methoxymethoxyl group on the stereogenic carbon atom and

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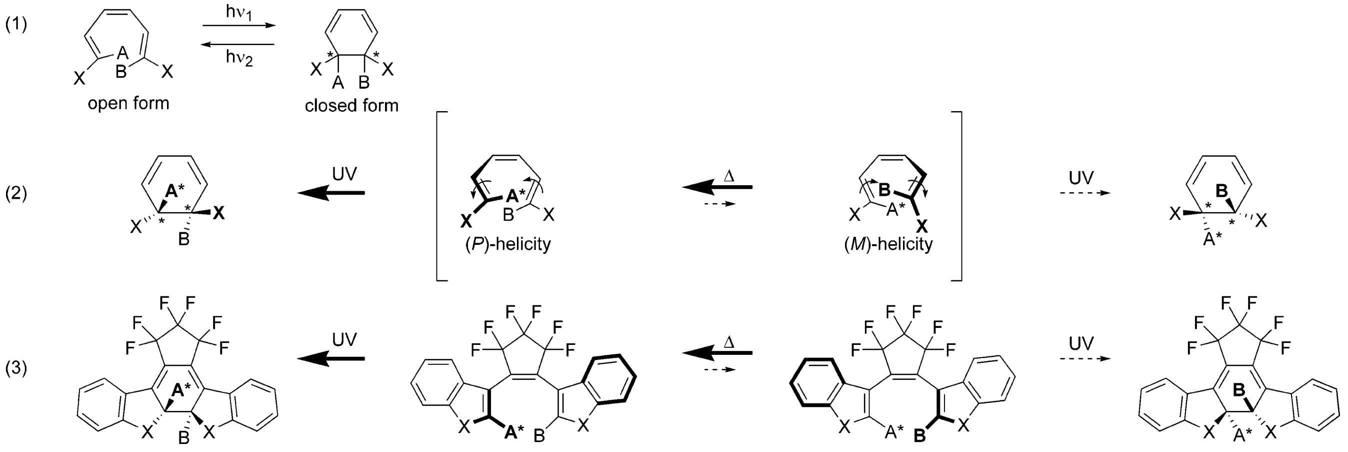
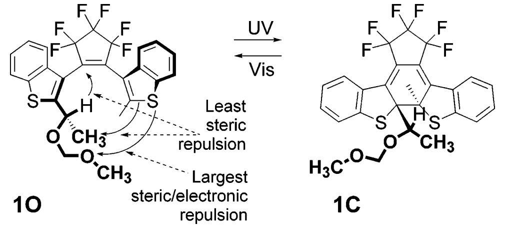
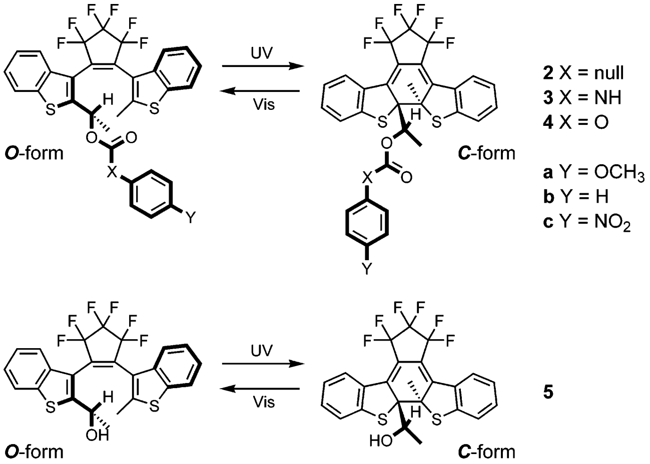
SCHEME 1. Chirality in 6π-Electrocyclization



SCHEME 2. Steric/Electronic Stereoregulation in Bisbenzothienylethene 1



SCHEME 3. Bisbenzothienylethenes Used in This Study



the second benzothiophene, and (iii) electronic repulsion between the oxygen atoms on the side chain and the sulfur atom of the second benzothiophene (Scheme 2).

We here report a more successful example to achieve a remarkable de. It enhanced the steric as well as the electronic repulsion while it maintained the effect of allylic strain.

Results and Discussion

Molecular Design. To design a compound that should exhibit a high de, the increase in steric bulkiness as well as the increase in electronic interaction should be attained. Therefore a compound that has a large substituent with a certain number of electronically negative atoms is preferable. We chose the substituted oxycarbonyl group as the basic atomic array that exerts the electronic repulsion, with a phenyl group at the end of the substituent that wields the steric bulkiness (Scheme 3). The location of two oxygen atoms on the oxycarbonyl moiety followed that of **1**. To tune the electronic properties, we prepared compounds with a methoxyl or a nitro group on the phenyl group attached at the para position, in addition to the plain phenyl compounds. Namely, we synthesized the derivatives of benzoates **2a**–**c**, *N*-phenylcarbamates **3a**–**c**, and phenyl carbonates **4a**–**c** as depicted in Scheme 3.

Synthesis and ^{1}H NMR Behavior. Benzoates were obtained from the diarylethene **5** (prepared from **1**[10]) and the corresponding acyl chloride, carbamates from **5** and the corresponding isocyanates, and carbonates from **5** and the corresponding chloroformates. Their synthetic yields were 45–91% from **5**. There structures were confirmed by ^{1}H NMR, IR, HRMS, and photochemical behaviors.

It is known that conformational isomers of bisbenzothienylethenes can be separately observed by ^{1}H NMR because of the slow conversion relative to the NMR measurement time scale between the conformers. For example, 1,2-bis(2-methyl-3-benzothienyl)hexafluorocyclopentene shows two methyl signals in $CDCl_3$.[12] One, resonating at higher magnetic field (δ 2.21), is that of so-called antiparallel orientation, which suffers strong magnetic shielding from the benzothiophene in opposition so that it appears at higher magnetic field, and the other, at lower magnetic field (δ 2.49), is that of parallel orientation.[12] The former can cyclize to give the C-form upon UV irradiation, while the latter cannot, because of the steric reason for the conrotatory ring closing reaction of photochemical 6π-electrocyclization.[13] For the compounds **1**, **2a**–**4c**, and **5**, introduction of a stereogenic carbon atom made the spectra much more complex. All compounds showed four sets of doublet methyl groups and four sets of singlet methyl groups, corresponding to the sterically favorable/unfavorable conformers α and β (i.e. whether the second benzothiophene lies close to the secondary methyl group or close to the oxygen-containing substituents) for antiparallel/parallel orientations **AP** and **P**, shown in Scheme 4. For **5**, singlet methyl group signals appeared at δ 2.18, 2.20, 2.57, and 2.61 with the ratio of 33:50:6:11 (see the Supporting Information). The

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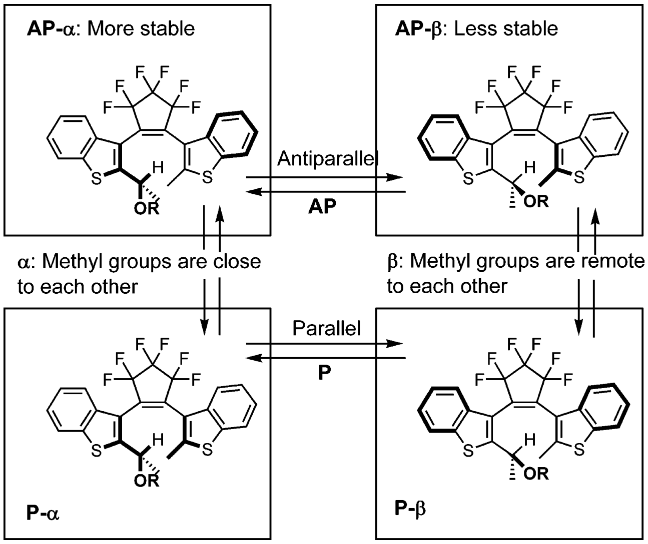
TABLE 1. Spectroscopic Data of C-Forms and the Diastereoselectivity of Bisbenzothienylethenes

	functional group	substituent	λ_{max}/nm (C-form)	$\epsilon_{max}{}^{a}$/cm^{-1} M^{-1} (C-form)	**C/O** at UV−PSS	de/%	ratio of conformers[b]
2a	benzoate	p-OCH$_3$	525	8630	74/26	75	79/21
2b	benzoate	H	525	6990	75/25	76	79/21
2c	benzoate	p-NO$_2$	525	5330	68/32	79	80/20
3a	carbamate	p-OCH$_3$	530	4920	79/21	84	81/19
3b	carbamate	H	530	6850	64/36	84	74/26
3c	carbamate	p-NO$_2$	530	5450	63/37	86	79/21
4a	carbonate	p-OCH$_3$	520	7950	82/18	93	85/15
4b	carbonate	H	520	6600	82/18	91	88/12
4c	carbonate	p-NO$_2$	520	7850	91/9	94	92/8

[a] M = mol dm^{-3}. [b] Ratio of diastereomeric antiparallel conformers of O-form determined by ^{1}H NMR in CDCl$_3$: more stable (**AP**-α)/less stable (**AP**-β).

SCHEME 4. Orientations and Conformers of Side Chain-Substituted Bisbenzothienylethenes



former two signals are attributed to the methyl groups of antiparallel orientations, and the latter two are attributed to parallel orientations. As for the doublet methyl signals of **5**, they appeared at δ 0.68, 1.35, 1.50, and 1.59 with the ratio of 31:8:47:14. Therefore these signals are easily correlated to the conformational isomers of signals of singlet methyl groups.

When we compare the proximity of the C-2 methyl group on the benzothiophene to the other benzothiophene group for **AP-α** and **AP-*β*** conformers of this kind of compounds, that of **AP-α** should be closer because of less steric/electronic repulsion, and therefore suffers stronger shielding from the other benzothiophene. As a result, the singlet methyl group of **AP-α** should appear at the highest magnetic field of all four conformers. In addition, the above discussion leads to the conclusion that the secondary methyl group also suffers a large shielding effect from the opposite benzothiophene because it is close to the C-2 methyl group in the **AP-α** conformation. It can be seen in the ^{1}H NMR data of **5**.

In the case of **5**, as the substituent OH is considerably small, and would be rather attracted by the sulfur atom of the other benzothiophene through a hydrogen bond, the ratio **AP-α/AP-*β*** was 33/50 or 31/47, which is practically equal to 40/60. However, in the cases of **2a**−**4c**, the ratio of **AP-α/AP-*β*** is in the range of 74/26 to 92/8 as the result of steric as well as electrostatic repulsion. Although the spectra were taken in CDCl$_3$, which is different from the solvent of photoreactions, **4c** showed the highest **AP-α/AP-*β*** ratio. It is in good accord that **4c** exhibited the highest diastereomer excess upon photoirradiation (vide infra).

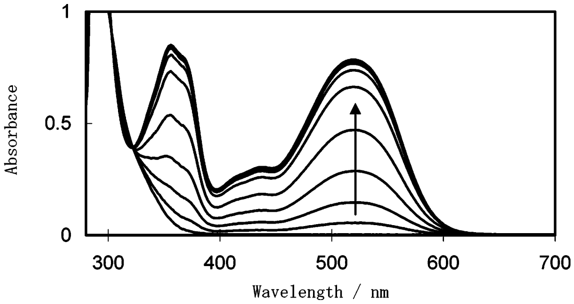


FIGURE 1. UV−vis spectral change during 313-nm irradiation of **4c** (1.0 × 10^{-4} mol dm^{-3}) in toluene. Cell length = 1 cm.

Photochromic Reactions. Photoreactions were carried out in toluene at 10^{-4} mol dm^{-3} concentration with 313-nm light isolated from a 500-W high-pressure mercury lamp by filters. The change in absorption spectra during 313-nm light irradiation to a toluene solution of **4c** is shown in Figure 1.

The concentration of components at the photostationary state was determined by HPLC detected at 519 nm, assuming the molar absorption coefficients of the diastereomers at 519 nm are the same. The ratio of open form and closed form was determined by the change in the concentration of open form by HPLC detected at 313 nm. The results as well as the spectroscopic data are collected in Table 1.

Diastereoselectivity. As shown in Table 1, the order of de is increasing in the order of benzoates, carbamates, and carbonates. In each family of functional groups, the de value is higher for the nitro-substituted derivative. It is noteworthy that **4c**, 4-nitrophenyl carbonate, showed 94% de with 91% conversion to the C-form.

To elucidate the results obtained, the following widely accepted principles of chemistry can be adopted a priori: (i) a larger substituent is sterically more demanding and (ii) atoms more negatively charged are more repulsive toward the heteroatoms. It can be deduced that the larger carbamates/carbonates are sterically more effective than the benzoates, which are in good accordance with premise (i).

To elucidate the differences in electronic properties of the nine compounds which are related to premise (ii), we employed PM3 semiempirical MO calculations,[14] and the

TABLE 2. Results of PM3 MO Calculations

compd	functional group	substituent	C*−O bond order/ bond length/nm	deviation of electron density		
				carbonyl O	ether O	the other heteroatom
2aO	benzoate	*p*-OCH_3	0.9385 0.1440	+0.3895	+0.2541	
2bO	benzoate	H	0.9377 0.1441	+0.3846	+0.2518	
2cO	benzoate	*p*-NO_2	0.9315 0.1443	+0.3677	+0.2488	
3aO	carbamate	*p*-OCH_3	0.9330 0.1441	+0.4097	+0.2642	−0.0910
3bO	carbamate	H	0.9324 0.1441	+0.4074	+0.2642	−0.0868
3cO	carbamate	*p*-NO_2	0.9259 0.1444	+0.3987	+0.2606	−0.0881
4aO	carbonate	*p*-OCH_3	0.9320 0.1446	+0.4120	+0.2218	+0.1621
4bO	carbonate	H	0.9315 0.1447	+0.4112	+0.2210	+0.1672
4cO	carbonate	*p*-NO_2	0.9243 0.1449	+0.4054	+0.2163	+0.1704

results are shown in Table 2. However, we saw little differences for the electron density on the heteroatoms. They are too small to attribute the differences of diastereoselectivity to their differences. In all respects including the bond order/bond length values, the carbamates and carbonates have quite similar properties of substituents irrespective of the substituent on the phenyl group. Therefore the reason for the high diastereoselectivity of carbamates, particularly the nitro-substituted carbamate **4c**, is not rationally elucidated yet.

As shown in Table 1, the de values are not close enough to the **AP-α**/**AP-*β*** ratios. We assume that the quantum yields of coloration of **AP-α** and **AP-*β*** upon UV irradiation and quantum yields of decoloration of major and minor diastereomers upon UV irradiation may be different. Clarification of this subject will be done in due course.

Conclusions

We have succeeded in constructing a new diastereoselective photochromic bisbenzothienylethene system possessing an oxycarbonyl-related functional group on the side chain. Among the compounds synthesized, 4-nitrophenyl carbonate (**4c**) showed remarkable diastereoselectivity. Research to realize a “practically complete” diastereoselective photochromic system (i.e. >99% de) with a simple molecular structure, at ordinary temperature, in media where molecules suffer little steric restriction, and without any special additives, is in progress.

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Supporting Information Available: Detailed synthetic procedures and spectral data for the compounds used in this study (SI-1), ^{1}H NMR spectra of **4cO** (SI-2) and **5O** (SI-3) in $CDCl_3$, and HPLC charts of **4c** during photoirradiation (SI-4−SI-6). This material is available free of charge via the Internet at http://pubs.acs.org.

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