Photokinetics of Two Novel Photochromic Diarylethenes Derived from Benzothiophene

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ABSTRACT: Two new unsymmetrically substituted photochromic diarylethenes, namely 3-[3,3,4,4,5,5-hexafluoro-2-(2-methylbenzothien-3-yl)cyclopent-1-en-1-yl]-2-methyl-6-methoxy-1-benzothiophene and 3-[3,3,4,4,5,5-hexafluoro-2-(2-methylbenzothien-3-yl)cyclopent-1-en-1-yl]-2-methyl-6-methoxy-7-nitro-1-benzothiophene, were synthesized. Their optical properties and kinetics of cyclization and cycloreversion were determined in four solvents and compared with the symmetrical diarylethene (3,3,4,4,5,5-hexafluorocyclopent-1-en-1,2-diyl)bis(2-methyl-1-benzothiophene). While the UV spectra of the three compounds are almost insensitive to solvent changes, the rates of the ring-opening and ring-closure reactions exhibit interesting kinetic behavior that differs from other diarylethenes reported in the literature. The cycloreversion for the three compounds follows first-order kinetics, whereas the cyclization cannot be described by a simple kinetic law. Different approaches were tested, and a complex exponential equation could be derived that fits the experimental data. The unusual presence of two ring-opened conformational isomers, one of them nonphotochromic, is proposed for the ring-opened compounds to explain the derived kinetic law and observed solvent effects. These results are of interest in relation to the application of the novel diarylethenes as potential optical materials. © 2012 Wiley Periodicals, Inc. Int J Chem Kinet 1–9, 2012

INTRODUCTION

The photochromism is an interesting phenomenon that is receiving renewed attention because of their use in optical memories, molecular switches, and holographic optical recording medium [1]. Several materials exhibit a color change when they are exposed to certain types of radiation; when the color change is reversible, the phenomenon is called "photochromism" [2]. Diarylethenes are an important type of photochromic compounds; they change the conformation by effect of the ultraviolet (UV) light: Both isomers of the diarylethene are different not only in their absorption spectra but also in various physical and chemical properties [3,4]. Diarylethenes-bearing heteroaryl rings are among the most promising photochromics for

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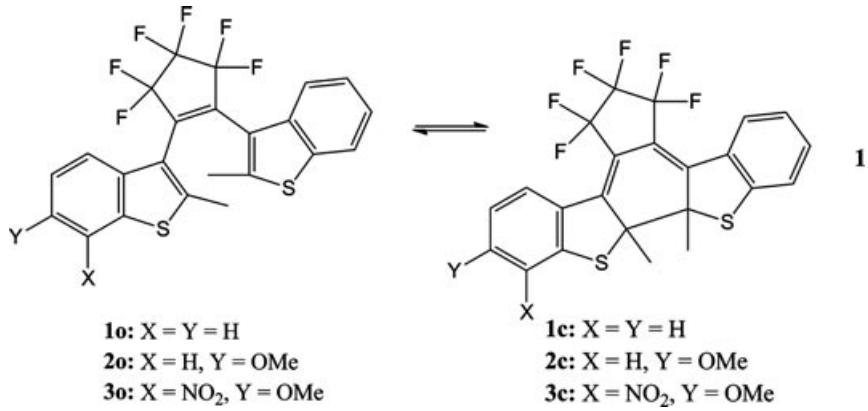


Scheme 1

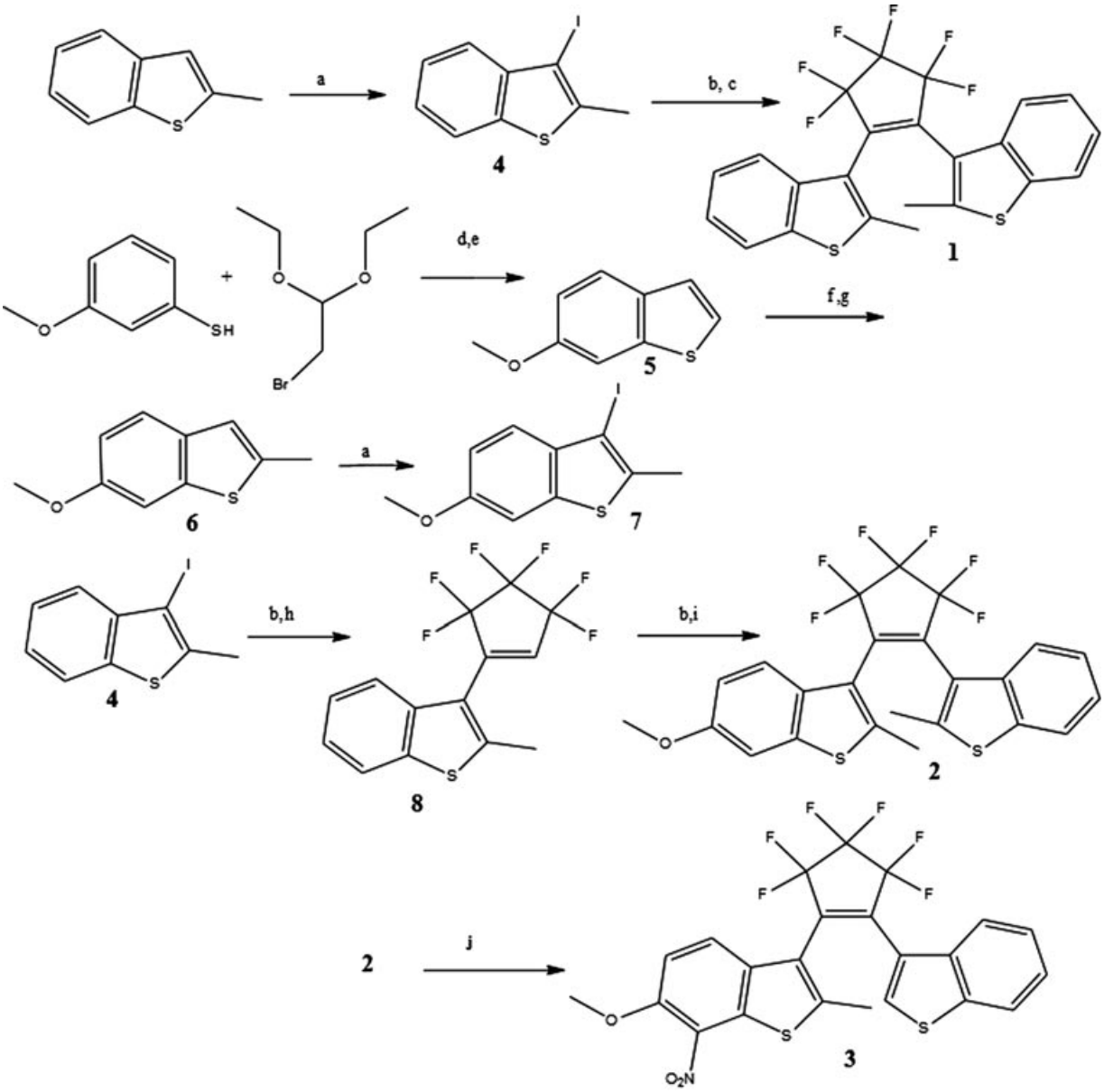
various photoelectronic applications [5,6], because of their fatigue-resistant and their thermally irreversible properties [7–9].

These attractive features turn the study of the physicochemical properties of diarylethenes, and particularly their photokinetic behavior in a very relevant question. Because of its importance, some kinetic studies of diarylethenes are appearing in the recent literature [10]. Wang and coworkers [11] have described a study of an unsymmetrical diarylethene, 1-(2,5-dimethyl-3-thienyl)-2-(2-methyl-5-(2,4-difluorophenyl))-perfluorocyclopentene and found a kinetics of zero order for the UV-induced photocyclization process, whereas the visible-induced photoreversion process exhibits first-order kinetics. Likewise, Liu and coworkers [12] have determined similar kinetic behavior for the thienyl diarylethene 1-[2-methyl-5-(4-cyanophenyl)-3-thienyl]-2-[2-methyl-5-(4-chlorophenyl)-3-thienyl]-perfluorocyclopentene. Kobeleva et al. [13] have described the photochromism of some diarylethenes with sulfur-containing substituents in DMSO with and without silver nanoparticles. The photobleaching of solutions is well described by straight lines, whereas the photocoloration kinetics required complex equations. On the other hand, Nagakawa and coworkers [14] have investigated the thermal bleaching of the ring-closed isomer of an angular terthiazole photochromic diarylethene induced by acid in acetonitrile and have determined a sigmoid shape in the absorbance versus time plot.

Owing to their potential applications, the search for new photochromics is a very active area. In this work, we describe the synthesis of three diarylethenes derived from benzothiophene, namely (3,3,4,4,5,5-hexafluorocyclopent-1-en-1,2-diyl)bis(2-methyl-1-benzothiophene), **1**; 3-[3,3,4,4,5,5-hexafluoro-2-(2-methylbenzothien-3-yl)cyclopent-1-en-1-yl]-2-methyl-6-methoxy-1-benzothiophene, **2**; and 3-[3,3,4,4,5,5-hexafluoro-2-(2-methylbenzothien-3-yl)cyclopent-1-en-1-yl]-2-methyl-6-methoxy-7-nitro-1-benzothiophene,**3** (Scheme 1). We selected a perfluorocyclopentene as the central bridging structure because of its demonstrated high fatigue resistance [15]. To determine the relevance of the substitution in one of the phenyl rings, we selected two substituents of opposite electronic effects and H-bonding characteristics. The spectroscopic properties of the three compounds in solvents of different properties (toluene, hexane, acetonitrile, and methanol), as well as the kinetics of the photochemical cyclization and cycloreversion processes. The purpose of this study was to examine the photokinetic properties of the three compounds as potentially suitable materials for memory storage and other applications.

EXPERIMENTAL

General. All solvents used were of spectroscopic grade and were purified by distillation before use. The synthesis of photochromic compounds **1–3** was carried out by the synthetic route as shown in Scheme 2, adapting procedures that were previously applied to the synthesis of related compounds [16,17]. Essentially, 2-methyl-3-iodobenzothiophene, **4** (obtained from iodination of 2-methyl-benzothiophene), was lithiated at −78°C and coupled with C_5F_8 rendering symmetric compound **1o** (throughout this study, "**o**" is used to indicate the "ring-opened" isomer). For the methoxy-substituted derivatives, a more complex synthetic route was designed. Starting from *m*-methoxy-benzenethiol, 6-methoxybenzothiophene, **5**, was obtained and was then methylated (**6**), iodinated (**7**), lithiated at −78°C, and coupled with 3-(3,3,4,4,5,5-heptafluorocyclopent-1-en-1-yl)-2-methyl-1-benzothiophene, **8**, rendering asymmetric compound



a: I_2, H_5IO_6, HAcO:H_2O:H_2SO_4 100:20:3; b: BuLi, THF, -78°C; c: C_5F_8, -78°C..r. t. ; d: bromoacetaldehide diethyldiacetal, PhSH, K_2CO_3, acetone; e: CH_2Cl_2, BF_3-Et_2O; f:BuLi, -20°C, THF; g: MeI, -20°C..r.t.; h: C_5F_8, Et_2O, -78°C; i: 4, THF, -78°C..r. t.;j: HNO_3 (f), HAcO, Ac_2O, 8°C.

Scheme 2

2o. By nitration of compound **2** at 8°C compound **3o** was obtained. A more detailed description for the synthesis of each one of the compounds presented in Scheme 2 is available in the Supporting Information.

The identity of compounds**1–3** was fully confirmed by ^{1}H and ^{13}C NMR and by HRMS spectroscopic determinations. NMR spectra were recorded on a Brucker 200 spectrometer, with a ^{1}H frequency of 200 MHz, and a ^{13}C frequency of 50 MHz. The absorption spectra were measured at room temperature (ca. 24°C) using a Varian Cary 50 diode array spectrophotometer. Photoirradiation was carried out using a Lumatec SUV-DC lamp, with a monochromator. The required wavelength was monitored by the use of the appropriate filters. For UV irradiations, a 1-mm passband filter Schott UG1 of 290–300 nm was used. For visible irradiations, a 3-mm-long pass filter Schott OG of 515 nm was used. Upon irradiation, a clear shift to the red was

observed in all cases and two new bands appeared in the UV–visible (UV–vis) spectra. For the kinetic determinations, an aliquot of 2.5 mL of a solution of the compound in the desired solvent was placed in a quartz cell and irradiated during 10-s cycle periods, alternating with spectrophotometric determinations, until the stationary state was achieved.

Spectroscopic Data

NMR and high resolution-electrospray ionization mass spectra (HR-ESIMS) of the three synthesized compounds are given below. The HR-ESIMS are fully consistent with the structures of **1o–3o** as shown in Scheme 1 as well as the NMR data. The full spectroscopic data for each compound follow.

***(3,3,4,4,5,5-Hexafluorocyclopent-1-en-1,2-diyl)bis (2-methyl-1-benzothiophene),* 1o.** ^{1}H NMR ($CDCl_3$, 200 MHz): 7.68 (m), 7.34 (m), 7.19 (m), 2.50 (s, CH_3 p isomer, 3H), 2.22 (s, ap isomer, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz): 142.6, 141.1, 138.3, 138.2, 138.0, 124.6, 124.4, 124.3, 122.1, 121.8, 119.4, 119.1, 15.2, 15.1; HR-ESIMS: Calcd. for $C_{23}H_{14}F_6NaS_2$ $(M + Na)^+ =$ 491.03333. Found = 491.03292.

***3-[3,3,4,4,5,5-Hexafluoro-2-(2-metilbenzothien-3-yl)cyclopent-1-en-1-yl]-2-methyl-6-methoxy-1-benzothiophene,* 2o.** ^{1}H NMR ($CDCl_3$, 200 MHz): 7.69 (t), 7.54 (d), 7.34 (m), 7.22 (m), 7.07(d), 7.00 (dd), 6.80 (dd), 3.85 (s, OCH_3 ap isomer, 2.8H), 3.77 (s, OCH_3p isomer, 1.3H), 2.49 (s, CH_3 p isomer, 1.7H), 2.44 (s, CH_3 p isomer, 1.7H), 2.21 (s, CH_3 ap isomer, 3H), 2.15 (s, CH_3 ap isomer, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): 157.3, 157.2, 142.6, 142.2, 139.8, 139.6, 139.4, 139.3, 138.3, 138.1, 138.1, 132.2, 124.6, 124.5, 124.3, 122.8, 122.6, 122.2, 122.1, 122.0, 121.8, 119.4, 119.2, 118.9, 118.7, 114.4, 114.2, 104.7, 104.4, 55.6, 55.5, 15.3, 15.2, 15.1, 15.0; HR-ESIMS: Calcd. for $C_{24}H_{16}F_6NaOS_2$ $(M + Na)^+ =$ 521.04390. Found = 521.04553.

***3-[3,3,4,4,5,5-Hexafluoro-2-(2-methylbenzothien-3-yl)cyclopent-1-en-1-yl]-2-methyl-6-methoxy-7-nitro-1-benzothiophene,* 3o.** ^{1}H NMR ($CDCl_3$, 200 MHz): 7.82 (d), 7.67 (m), 7.62 (m), 7.35 (t), 7.25 (d), 6.96 (d), 4.09 (s, OCH_3 ap isomer, 3H), 3.99 (s, OCH_3 p isomer, 2.1H), 2.50 (s, CH_3 p isomer, 2.2H), 2.47 (s, CH_3 p isomer, 2.2H), 2.21 (s, CH_3 ap isomer, 3H), 2.19 (s, CH_3 ap isomer, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz): 138.3, 128.1, 128.0, 124.8, 124.6, 122.2, 121.5, 111.8, 111.5, 77.7, 77.0, 29.7, 26.8, 15.0, 14.5; HR-ESIMS: Calcd. for $C_{24}H_{15}F_6NNaO_3S_2$ $(M + Na)^+ =$ 566.02898. Found = 566.02709.

RESULTS AND DISCUSSION

The UV–vis spectra of diarylethenes **1**–**3** were registered selecting four solvents, of different properties and polarity, namely *n*-hexane (aliphatic), toluene (aromatic), acetonitrile (dipolar, aprotic), and methanol (dipolar, proton donor). Figure 1 shows the spectra of the ring-opened isomer of compound **2** (the complete set of spectra for compounds **1–3** is given in the Supporting Information). It could be observed that no

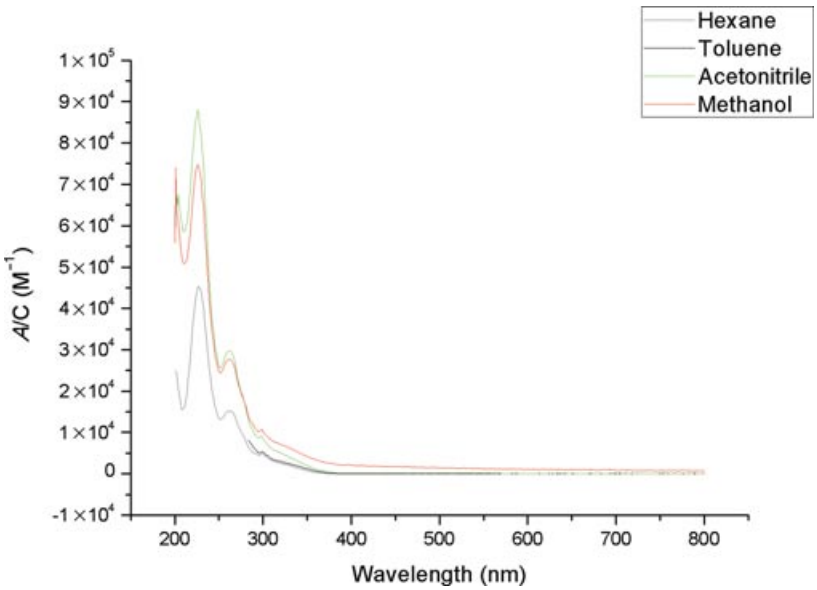


Figure 1 UV–Vis spectra of compound **2**, before irradiation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

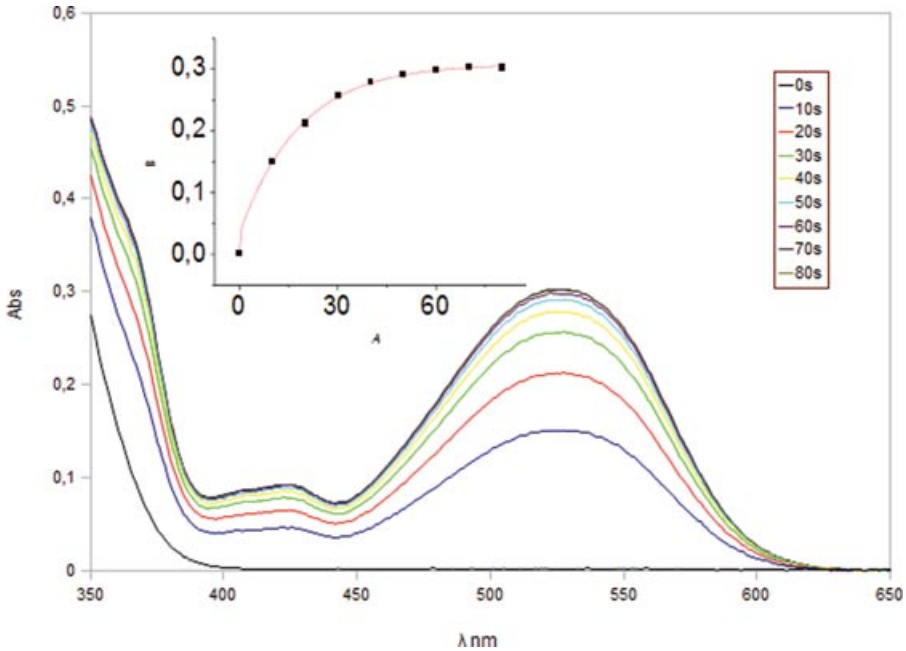


Figure 2 Kinetics of cyclization of compound **2** in toluene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

absorption peaks are found in the visible region (400–700 nm), as expected for colorless solutions. However, upon exposure at UV radiation (~ 300 nm) the solutions turn to red and the compounds exhibit marked absorptions in the visible region. Figure 2 shows the spectra of compounds **2** in toluene, at different times of irradiation. Two new maxima could be observed, the first one near to 430 nm and the second at approximately 520 nm. Table I shows the observed maxima for the three compounds in the four solvents. While examining the substitution pattern of compounds **1–3**, little substituent effect is observed: Thus in the case of the presence of the methoxy group (compound **2**), a slight bathochromic effect is observed for the first maxima, whereas for compound **3** the introduction of the electron-withdrawing nitro group balances the effect. On the other hand, it could be observed that, for the same compounds, the effect associated with the change of solvent is very small.

Figure 3 shows the spectra of compound **2** in toluene, for different exposure times at visible light (near 500 nm). It could be observed that the cyclization process is completely reversible; in less than 2 min the spectra are similar to that before UV irradiation, and a complete decoloration of the solutions is observed.

Kinetics of Closure and Reversion Cycles

The kinetics of cyclization and cycloreversion was studied. Cyclization was achieved by irradiation of the solutions in a quartz cell at UV = 290–300 nm using a filter, in periods of 10 s of irradiation, followed by determinations of the UV–vis spectra of the solutions using a diode array spectrophotometer (see Fig. 2). The cycloreversion (aperture) cycle was achieved by exposure at visible (nearly green) light (using a high-pass filter), in periods of 10 s of irradiation, followed by spectrophotometric determinations (see Fig. 3).

The plot of the absorbance at 525 nm versus time for the cyclization process of compounds **1–3** does not agree with a simple order. This result is unusual, since in most of the kinetic studies on diarylethenes recently reported, linear trends are observed in

Table I Absorption Maxima of Photochromic Compounds

Compound	Solvent	Maxima (nm)	Maxima (nm)
1	Hexane	418	518
	Toluene	425	525
	Acetonitrile	420	525
	Methanol	419	523
2	Hexane	436	515
	Toluene	438	525
	Acetonitrile	436	526
	Methanol	436	523
3	Hexane	421	515
	Toluene	425[a]	525
	Acetonitrile	Not observed	516
	Methanol	Not observed	517

[a] A third maxima at ca. 400 nm is observed.

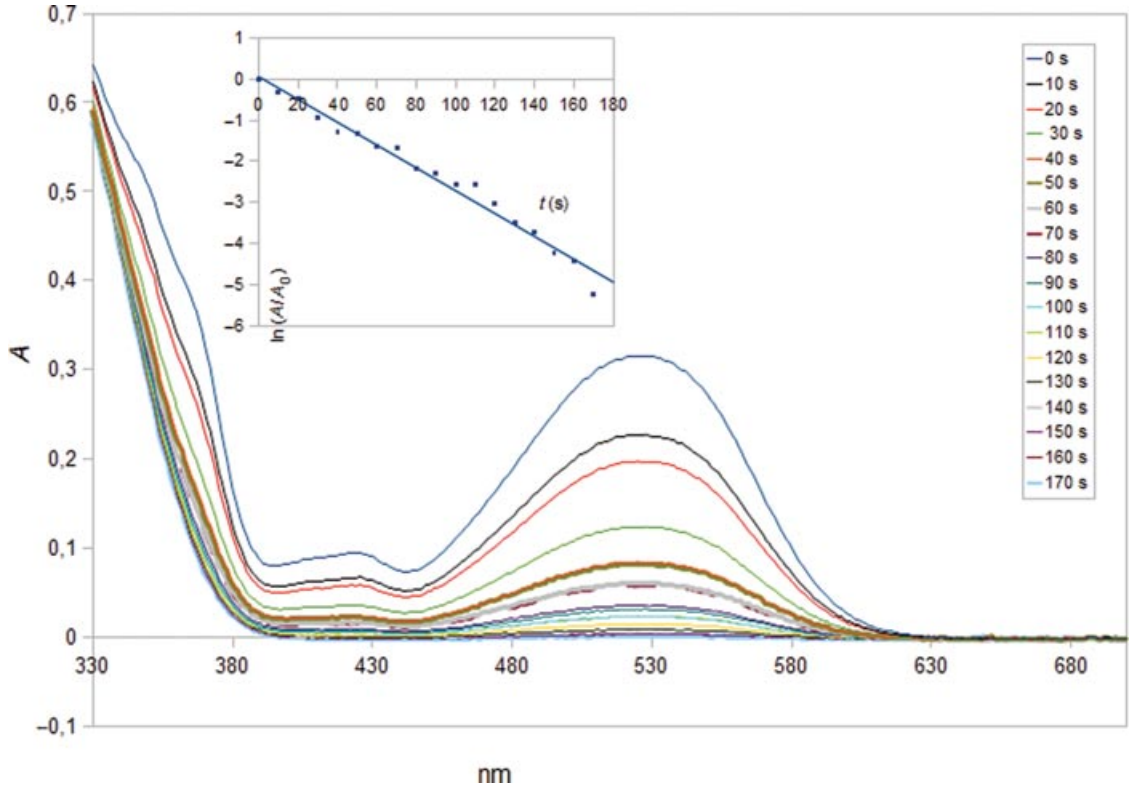


Figure 3 Kinetics of ring opening of compound **2** in toluene. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the plot of $(\ln(A/A_0))$ versus time. Thus, the cyclization of [1-(2-methyl-5-(3-methoxyphenyl)-3-thienyl) and 2-(2-methyl-3-benzothienyl)] perfluorocyclopentene exhibits first-order kinetics [18]; 1-(2-methyl-benzothiophenyl)-2-(2-methyl-5-(4-chlorophenyl))-perfluorocyclopentene shows similar kinetic trends [19]; and similarly, the kinetics of cyclization of 1-[(2-methyl-5-(2-cyanophenyl)-3-thienyl)]-2-[(2-trifluoromethylphenyl)] perfluorocyclopentene is also of first order [20].

However, in the present case, the data for the cyclization can be well fitted by using an exponential function of the type of Eq. (1), where A is the absorbance at the maxima wavelength, t is the time, and Y_0, D, and k' are fitting constants (see Fig. 2, inset).

$$A = Y_0 + D\,e^{k't} \tag{1}$$

It could be observed that in all the cases $Y_0 \approx -D$; thus Eq. (1) could be simplified to Eq. (2).

$$A \approx Y_0(1 - e^{k't}) \tag{2}$$

Table II shows the fitting parameters for **1–3** in the four solvents; the correlation coefficients are good in all the cases. A mechanistic proposal is given below to explain the exponential kinetic law.

Table II Fitting Values for the Cyclization of Compounds **1o**, **2o**, and **3o**[a]

Compound	Solvent	$10^2\,k'$ (s^{-1})	Y_0	$-D$
1	Hexane	6.24	0.243	0.241
	Toluene	6.23	0.305	0.301
	Acetonitrile	4.61	0.487	0.481
	Methanol	5.35	0.193	0.180
2	Hexane	7.15	0.063	0.054
	Toluene	5.08	0.186	0.174
	Acetonitrile	5.49	0.163	0.163
	Methanol	5.36	0.050	0.056
3	Hexane	5.44	0.213	0.210
	Toluene	6.79	0.183	0.175
	Acetonitrile	1.84	0.554	0.543
	Methanol	5.93	0.217	0.214

[a] $R^2 > 0.99$ in all the cases. Concentrations in the range of (0.35–3.85) $\times\ 10^{-4}$ M.

On the contrary, for the case of the cycloreversion process, the data could be fitted into the function $(\ln(A/A_0))$ versus time (see Fig. 3, inset). A straight line is obtained, showing that the reversion process exhibits first-order kinetics, following Eq. (3):

$$v = -\mathrm{d}[\mathrm{C}]\,/\,\mathrm{d}t = k''A \tag{3}$$

Table III Linear Regression for the Reversion Process of **1c**, **2c**, and **3c**[a]

Compound	Solvent	$10^2\ k\ (s^{-1})$	R^2
1	Hexane	5.30	1.00
	Toluene	2.77	0.98
	Acetonitrile	4.38	0.99
	Methanol	3.27	0.97
2	Hexane	2.80	0.89
	Toluene	3.13	1.00
	Acetonitrile	2.89	1.00
	Methanol	1.98	0.95
3	Hexane	4.90	1.00
	Toluene	2.86	1.00
	Acetonitrile	3.09	1.00
	Methanol	4.11	0.99

[a]Concentrations in the range of (0.35–3.85) × 10^{-4} M.

where [C] is the concentration of the closed isomer and k'' is the pseudo–first-order rate coefficient. In fact, under the conditions used to carry out the cycloreversion experiments, that is, by irradiation with a light of >500 nm, without UV components, only the (closed) C isomer has significant absorbance. Thus, $k_{-1} >> k_1$. Under these conditions, considering that the Lambert–Beer law is obeyed Eq. (4) could be obtained, where ε is the extinction coefficient and l is the cell width.

$$-\mathrm{d[C]}\,/\,\mathrm{d}t = k_{-1}\,[\mathrm{C}] = k_{-1}\,1\,/\,\varepsilon l\,A = k''A \qquad (4)$$

Table III shows the first-order parameters for compounds **1–3**; in all the cases, good correlation coefficients were obtained. The linear trend is consistent with some recent reports of first-order kinetics for other diarylethenes.

To explain the anomalous kinetic behavior of the cyclization process, a more complex mechanism is proposed, where the ring-opened isomer exhibits a two-conformer equilibrium, parallel (P) and antiparallel (Ap), as shown in Scheme 3. This scheme would lead to a complex rate equation; however, some conditions can be considered to simplify the system leading to a more simple kinetic law, as shown by Eq. (2). To justify Eqs. (1) and (2), it is necessary to assume that, under the conditions of the experiment, the isomer equilibration, namely the P–Ap interconversion, is faster than the cyclization/ring-opening process. Thus,

$$[\mathrm{P}] = K_{\mathrm{eq}}\,[\mathrm{Ap}] \qquad (5)$$

Likewise,

$$[\mathrm{Ap}] + [\mathrm{P}] + [\mathrm{C}] = C_0$$

$$[\mathrm{Ap}] = C_0 - A/\varepsilon l - K_{\mathrm{eq}}[\mathrm{Ap}]$$

$$[\mathrm{Ap}] = (C_0 - A/\varepsilon l)/(1 + K_{\mathrm{eq}}) \qquad (6)$$

where C_0 is the analytical concentration of photochromic compound.

Being the rate of cyclization given by Eq. (7):

$$v = \mathrm{d[C]}/\mathrm{d}t = k_1[\mathrm{Ap}] - k_{-1}[\mathrm{C}] \qquad (7)$$

replacing Ap with the expression of Eq. (6) and applying the Lambert–Beer law in Eq. (7), Eq. (8) is obtained:

$$\begin{aligned} 1/\varepsilon l\,\mathrm{d}A/\mathrm{d}t &= k_1(C_0 - A/\varepsilon l)/(1 + K_{\mathrm{eq}}) - k_{-1}A/\varepsilon l \\ &= k_1C_0(1 + K_{\mathrm{eq}}) - 1/el\ [k1/(1 + K_{\mathrm{eq}}) \\ &\quad + k_{-1}]A \qquad (8) \end{aligned}$$

$$\int \mathrm{d}A/p - uA = \int \mathrm{d}t$$

where

$$p = \varepsilon l k_1 C_0/(1 + K_{\mathrm{eq}})\,u = k_1/(1 + K_{\mathrm{eq}}) + k_{-1}$$

Integration of the preceding equation renders

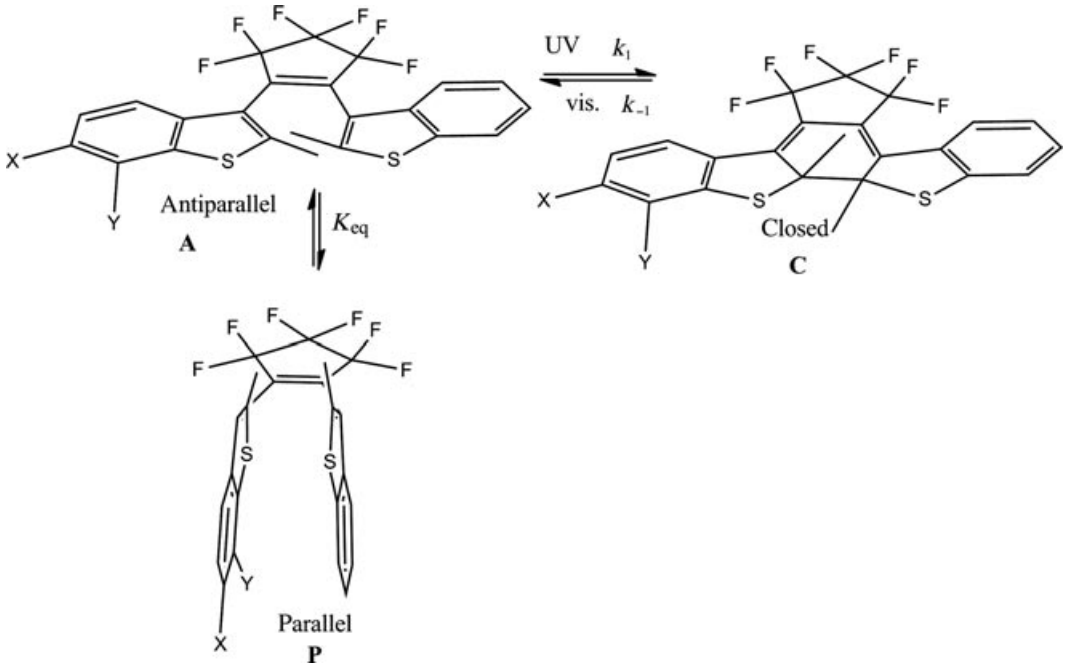
$$-1/u\,\ln[(\mathrm{p} - u\mathrm{A})/p] = t$$

$$A = p/u(1 - e^{-ut}) \qquad (9)$$

This expression has the form of Eq. (2), where $Y_0 = p/u$ and $u = k'$.

Therefore, according to the overall experimental results, if the proposal of the two conformers applies, the fast component could be assigned to the direct ring closure reaction, whereas the slow component is assigned to the reaction through a previous conformational change. Thus, the present results are consistent with a conformational inhomogeneity model, in which a broad distribution of conformations of the ring-opened isomers in the ground state is projected into two minima in the excited electronic potential surface leading to the slow and the fast reaction pathways.

To the best of our knowledge, this is the first time that two conformational isomers are proposed for the ring-opened structure of aprotic diarylethenes; nevertheless, it is worthwhile mentioning that it has been previously proposed for the symmetrical (3,3,4,4,5,5-hexafluorocyclopent-1-en-1,2-diyl)bis(2-methyl-6-(ethylcarboxylic)-1-benzothiophene) [21]. In that case, the H bond that can be established between the carboxylic acid units at both 6-positions of the benzothiophene rings when the compound is in cyclohexane or decalin, firmly maintains the P form and the cyclization is completely inhibited. Adding EtOH disrupts the intramolecular H bonds and allows



Scheme 3

the conrotatory photocyclization from the Ap form to occur, since the Ap conformer is able to undergo the cyclization process, whereas the P conformer is not [22]. This property could be used in the so-called "gated photochromism," a special type of photochromism in which one or both forms of the photochromic system are transformed (chemically or electrochemically) reversibly into a nonphotochromic form [23].

To find out whether the ring-opened isomers of the present compounds actually exist in two conformations, two additional evidences were looked for. A careful examination of the ^{1}H NMR spectra of the three ring-opened compounds shows some interesting features. For the symmetric compound **1o**, two signals of different area could be recognized corresponding to the methyl protons. Similarly, for compounds **2o** and **3o**, two pairs of methyl signals of different area can be observed and likewise two signals for the methoxy protons. This fact can be interpreted as due to the presence of two conformers of the ring-opened diarylethenes, that we call P and Ap isomers. In base to the integration areas of methyl protons of each compound ($area_p/area_{ap}$), it is possible to estimate the percentage of each conformer of the ring-opened isomer. This affords the following results: compound **1o**: 33% P, 67% Ap; compound **2o**: 36% P, 64% Ap; compound **3o**: 42% P, 58% Ap. The second evidence is related to the kinetic parameters presented in Table II. The cyclization process for compounds **1** and **2** is slightly faster in hexane than in polar solvents. Nevertheless, when a nitro group is present at the ortho position, the rate of cyclization is very slow in the dipolar acetonitrile but the rate spectacularly increases in methanol. Since MeOH is a very good H donor, it is probably that the steric requirements of the intramolecular H bonds with the nitro group hinder the P conformation and preferably move the equilibrium to the Ap isomer, which is ready to react.

All of the above results indicate that the novel diarylethenes exhibit interesting properties, their UV–vis spectra are almost insensitive to solvent effects making them suitable to be used in different media; the cyclization/ring opening cycles could be repeated more than 50 times in the four solvents keeping adequate photochromic performance; the ring-opened structures exist in two conformations differing as to whether the two rings are in mirror symmetry (P) or in $C2$ symmetry (Ap), a phenomenon that could be used in "gated photochromism"; the kinetic results show that the rate of the process can be tuned up by an appropriate choice of the solvent.

CONCLUSIONS

The photochemical properties and the kinetics of photochromic compounds **1–3** were examined; these novel diarylethenes exhibit interesting photochromic properties, and they can be activated and deactivated reversibly by switching on and off the closed form

as demonstrated by the synchronous change induced by the UV–vis irradiation cycles. The cyclization/ring opening cycles could be repeated more than 50 times in the four solvents keeping adequate photochromic performance. A complex exponential kinetics for the cyclization was derived, which is consistent with a model that considers the existence of a P and an Ap isomer of the ring-opened compound. This P–Ap equilibrium is reported for the first time in aprotic diarylethenes, though it has been previously reported in carboxylic–benzothiophene diarylethenes where the P form is maintained by intramolecular H bonds. The sensitivity of the cyclization rate to solvent effects for the nitro-substituted compound makes it possible to tune up the photochromic process by suitably chosen substituent and solvent.

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