New Thermally Irreversible and Fluorescent Photochromic Diarylethenes

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A photokinetic investigation is here carried out on four newly synthesized diarylethenes with the aim to test their performance as photoreversible chromogenic and light emitting materials. The pentatomic ring, which fixes these diarylethenes in the *cis* conformation, contains a Si atom or a PO group. The 1,2 positions at the ethenic bond are symmetrically substituted with thienyl or benzothienyl groups. The results are compared with those for the structurally related and widely studied 1,2-bis(2-methyl-benzo[b]thiophen-3-yl)perfluorocyclopentene (BTF6), investigated here under the same experimental conditions. Spectra of the colorless and colored forms and photoreaction quantum yields were determined; temperature, excitation wavelength and viscosity effects were explored. Compounds containing benzothienyl substituents were found to be good bistable photochromes, with high photochemical yields of both the cyclization and cycloreversion reactions, and to display appreciable fluorescence emission from the colored forms, which is a rare and desirable property for photochromes. In contrast, the molecules not bearing the benzene condensed rings were found unsuitable as photochromes because of side degradation processes occurring in competition with cyclization.

1. Introduction

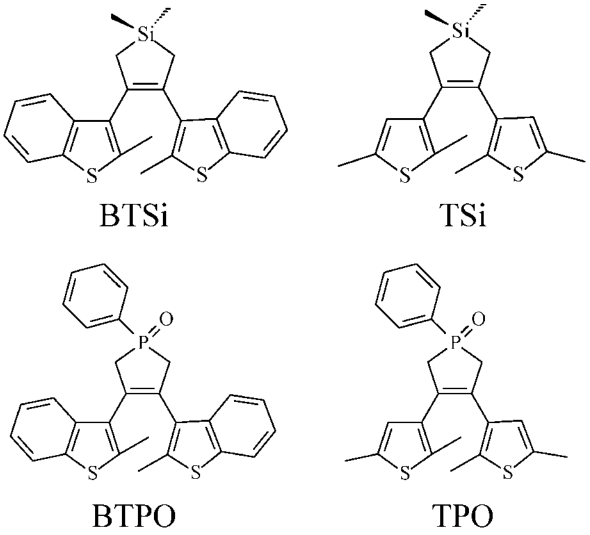
Interest toward photochromic diarylethenes has largely developed in the last decades due to their thermal irreversibility, sensitivity and fatigue resistance.[1] These properties make diarylethenes highly promising for the preparation of light-triggered switching devices.[2–4] Their photochromic process consists of a ring closure/opening electrocyclic isomerization. The open-ring form is colorless, absorbing in the UV region, and the closed-ring form is colored. The open ring form exists in two, parallel (p) and antiparallel (a-p), conformations, only the latter being photoreactive.[2] Because the relative abundance of conformers, and therefore the photochromic performance, highly depends on structure, a great number of variously structured diarylethenes have been synthesized and photochemically studied.[1,2] Also, methods have been developed to correlate the experimental quantum yields with calculated properties, which could be used as guidelines for molecular design.[5]

Additional potentialities for technological applications could be offered by compounds that emit fluorescence.[4] Generally, the closed colored forms do not emit significantly. Therefore, efforts have being done to develop photochromic diarylethenes which exhibit fluorescence emission in the closed form to be used as fluorophores in readout systems.[6,7]

Among the various diarylethenes that have been synthesized, bis(thienyl)perfluorocyclopentenes have been found very promising as bistable photochromic systems; their performance can be extended and tuned by changing the substituents.

In this paper, a photokinetic investigation has been carried out on four new diarylethenes. The structurally related and widely studied 1,2-bis(2-methyl-benzo[*b*]thiophen-3-yl)-perfluorocyclopentene (BTF6) has also been investigated under the same experimental conditions for the sake of comparison. In the new compounds, structural changes were introduced into the cycle that stabilizes the ethenic double bond in the *cis* configuration: perfluorocyclopentene was replaced by different pentaatomic rings containing a Si atom or a PO group. The newly synthesized molecules are the 3,4-bis(2-methylbenzo[*b*]thiophen-3-yl)-1,1-dimethyl-2,5-dihydro-1*H*-silole (BTSi), 3,4-bis(2,5-dimethylthien-3-yl)-1,1-dimethyl-2,5-dihydro-1*H*-silole (TSi), 3,4-bis(2-methylbenzo[*b*]thiophen-3-yl)-1-phenyl-2,5-dihydrophosphole 1-oxide (BTPO) and 3,4-bis(2,5-dimethylthien-3-yl)-1-phenyl-2,5-dihydrophosphole 1-oxide (TPO), Scheme 1.

SCHEME 1: Molecules Investigated



With the aim to test their performance as photoreversible photochromic compounds, the spectra of the colorless and colored forms, the quantum yields of the cyclization and cycloreversion photoreactions and the quantum yields of

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fluorescence were determined. Temperature and exciting wavelength (λ_{exc}) effects were also investigated. Nanosecond laser flash photolysis was used to detect photochemical paths competing with the photocyclization reaction.

2. Experimental Methods

2.1. Materials. The compounds BTSi, BTPO, TSi and TPO were synthesized according to an already described procedure.[8] All samples were accurately checked for purity by HPLC. The reference compound BTF6 was purchased from TCI Europe nv and was used without further purification.

Generally, measurements were carried out in 3-methylpentane (3MP) (Acros Organics, 99%), distilled before use. Other solvents, heptane and decane (Aldrich, 99%), were used as received.

The fluorescence standard, 9,10-diphenylanthracene (Baker), was used as received.

2.2. Photokinetic Measurements. A 125 W Xe lamp, coupled with a Jobin-Yvon H10 UV monochromator, was used for irradiation and an Oxford Instruments cryostat for temperature control. The absorption spectra of the sample solutions were recorded before, under, and after irradiation in a 1 cm cell-path using a HP 8453 diode-array spectrophotometer. For measurements in a rigid matrix, a 0.85 cm path cell was used. A gray filter (10% transmittance) was inserted between the sample cell and the spectrophotometer source to avoid that a fraction of the UV light intensity might reach the sample, thus inducing photochemistry.

The solution concentrations were on the order of $(1-5) \times 10^{-5}$ mol dm^{-3}, corresponding to absorbances in the range 0.1−0.3 at λ_{exc}.

For the chromatographic separation of the compounds at the photostationary state, an HPLC system, equipped with Waters 600 pump and controller, 2487 dual λ absorbance and 996 photodiode array detector, was used. The quantum yields of the open → closed photocoloration ($\Phi_{O\rightarrow C}$) and the back photobleaching ($\Phi_{C\rightarrow O}$) were determined by spectrophotometry from absorbance−time data sets. Potassium ferrioxalate actinometry was used to measure the radiation intensity, which was typically on the order of 1×10^{-7} mol of photons dm^{-3} s^{-1} in the UV region and $(7-8) \times 10^{-7}$ mol of photons dm^{-3} s^{-1} in the visible region. The uncertainty in the quantum yield determinations was estimated to be within 10%.

2.3. Fluorescence Measurements. The corrected fluorescence emission and excitation spectra were obtained using a Spex Fluorolog-21680/1 spectrofluorometer, controlled by the Spex Datamax spectroscopy software. The emission quantum yields were determined by measuring and comparing corrected areas of the sample and the standard (9,10-diphenylanthracene in cyclohexane).

2.4. Laser Flash Photolysis Measurements. For laser flash photolysis measurements, the fourth harmonic (λ = 267 nm) from a Continuum Surelite Nd:YAG laser with fluency less than 10^6 J cm^{-2} s^{-1} per pulse and time resolution of about 30 ns was used. Q-switch delays were used to reduce the laser intensity. For the spectrophotometric analysis, 150 W xenon source, Baird-Tatlock monochromator blazed at 500 nm, Hamamatsu R928 photomultiplier and Tektronix DSA 602 digitized analyzer were used. The data were processed by a Tektronix PEP 301 computer.

2.5. NMR Measurements. NMR experiments were carried out in $CDCl_3$ at 298 K using a Bruker Avance DRX 400 spectrometer. Chemical shifts for ^1H spectra were referred to the residual resonance of the deuterated solvent (δ = 7.27) and were reported as parts per million relative to tetramethylsilane. Standard integration of signals in a single-scan experiment was used to calculate the relative percentage of the p (parallel) and a-p (antiparallel) conformations.

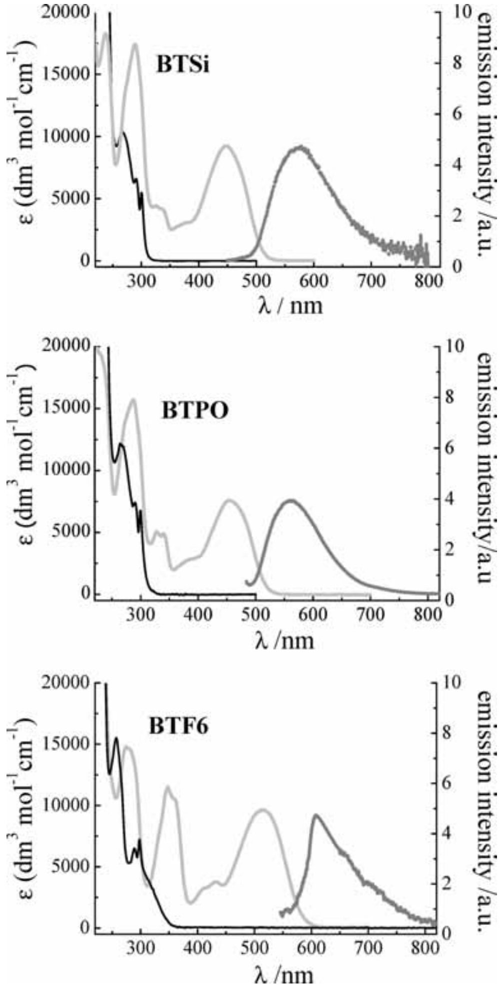


Figure 1. Absorption (black, ring-open form; light gray, ring-closed form) and fluorescence (dark gray) spectra of BTSi (a), BTPO (b) and BTF6 (c) in 3MP at room temperature. Due to its weakness, the fluorescence spectrum of BTF6 (c) is slightly distorted by a Raman peak.

3. Results

Results for the dibenzothienyl (BTSi and BTPO, compared with BTF6) and the dithienyl (TSi and TPO) compounds, are presented separately because their photobehavior was rather different and the photokinetic parameters could be determined for the dibenzothienyl derivatives only.

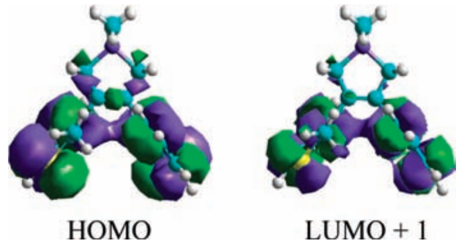
3.1. Spectra of the Colorless and Colored Forms of BTSi and BTPO. Irradiation of 3MP solutions of BTSi and BTPO with UV light partially converted the uncolored open form into the cyclized colored isomer. The photoproduct was thermally stable and could be isolated by HPLC. The spectra of the pure colorless and colored forms of BTSi and BTPO in 3MP are shown in Figure 1, along with those of the reference compound, BTF6. The two new molecules exhibited similar spectral features. The maximum of the color band was observed around 450 nm and the molar absorption coefficients were on the order of 10^4 dm^3 mol^{-1} cm^{-1}. The spectra of the open forms were well reproduced by calculations performed using the AM1 procedure of Hyperchem, whereas the agreement was less

TABLE 1: Absorption (Experimental and Calculated λ_{max}/nm, Absorption Coefficients, ε_{max}/dm^3 mol^{-1} cm^{-1}, and Oscillator Strengths, f) and Emission (λ_{max} and Quantum Yields, Φ_F) Characteristics of the Open and Closed Forms of the Diarylethenes in 3MP at Room Temperature

	open-ring isomer			closed-ring isomer		
	absorption			absorption		
	exp	calc		exp	calc	
compounds	ε_{max} (λ_{max})	f (λ_{max})	fluorescence λ_{max} (Φ_F)	ε_{max}(λ_{max})	f (λ_{max})	fluorescence λ_{max} (Φ_F)
BTSi	10360 (267 nm)	0.59 (263 nm)	not observed	9230 (447 nm)	0.34 (440 nm)	575 nm (3×10^{-3})
BTPO	12170 (264 nm)	0.50 (272 nm)	not observed	7590 (455 nm)	0.33 (430 nm)	570 nm (2×10^{-3})
BTF6	15520 (257 nm)	0.79 (250 nm)	423 nm (6×10^{-3})	9630 (514 nm)	0.37 (457 nm)	625 nm ($\sim 10^{-4}$)
(from literature)	14000 (258 nm)^a			9100 (517 nm)^a		630 nm^b
	16000 (258 nm)^c		436 nm (1.2×10^{-2})^c	10000 (523 nm)^c		

^{a} In hexane, refs 9 and 10. ^{b} In hexane, ref 11. ^{c} In ethyl acetate, ref 6.

SCHEME 2: Orbitals Involved in the Lowest Energy Transition of BTSi



satisfactory for the closed forms (Table 1). The molecular orbitals involved in the lowest spectrally detectable transition (HOMO → LUMO + 1 for BTSi, Scheme 2) do not include the pentatomic ring. This explains the similarity of the absorption spectra of the new compounds and that of the reference compound, BTF6, which is shifted toward the red, for both the open and closed forms. Spectral features of the three molecules are reported in Table 1. Those for BTF6 are compared with literature data in different solvents.[6,9,10]

Fluorescence emission was detectable only for the colored forms of BTSi and BTPO ($\lambda_{max} = 575$ and 570 nm, respectively, Figure 1); the fluorescence−excitation spectra well reproduced the absorption ones. The quantum yields are $>10^{-3}$, Table 1. For the reference compound, fluorescence was observed in both the open and closed forms (see Table 1), in agreement with a literature report.[11] The fluorescence of the closed form is very weak ($\Phi_F \sim 10^{-4}$); therefore, only the maximum, but no quantum yield, had been previously reported for this isomer.[11]

3.2. Photochemistry of BTSi and BTPO. Photocoloration was carried out in diluted 3MP solutions (10^{-5} mol dm^{-3}) by irradiating at isosbestic points between the colored and uncolored forms (266 nm for BTSi, 267 nm for BTPO and 316 nm for BTF6). The kinetics were followed at the absorption maximum of the colored form. Photobleaching was excited and analyzed at 445 nm, a wavelength which is absorbed by all three compounds. An example of the spectral time evolution under UV irradiation up to photostationary state achievement and subsequent decoloration using Visible light is shown in Figure 2 for BTSi, along with kinetics followed on the color band: maintenance of isosbestic points demonstrates that the photoreaction is clean and that cycloreversion to the starting molecule is complete.

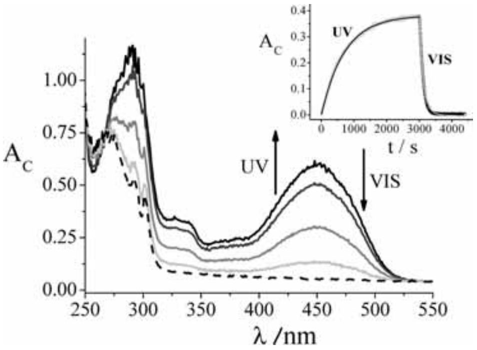


Figure 2. Time evolution of the spectrum of 7×10^{-5} mol dm^{-3} BTSi in 3MP upon UV ($\lambda_{exc} = 266$ nm) and visible ($\lambda_{exc} = 445$ nm) irradiation. Inset: photocoloration and photobleaching kinetics ($\lambda_{analysis} = 445$ nm).

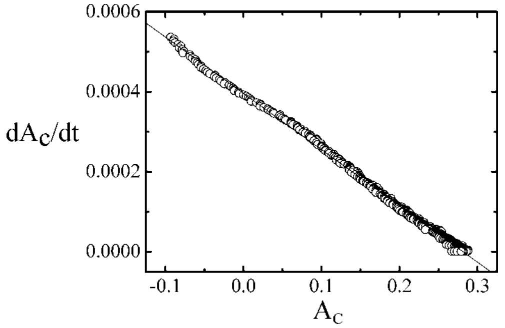


Figure 3. Absorption−time data treatment according to eq 3 for BTSi in 3MP.

The kinetics of the photoreversible process is described by eq 1, where the rate of accumulation of the ring-closed colored form, d[C]/dt, is expressed in terms of the monochromatic light intensity (number of photons dm^{-3} s^{-1}) absorbed by the open (I_O) and closed (I_C) forms and the quantum yields of the forth ($\Phi_{O\to C}$) and back ($\Phi_{C\to O}$) photoprocesses.

$$d[C]/dt = I_O\Phi_{O\to C} - I_C\Phi_{C\to O} \qquad (1)$$

At the photostationary state, attained under irradiation with I^0 intensity (isosbestic point), eq 2 holds:

$$[C]\Phi_{C\to O} = [O]\Phi_{O\to C} \qquad (2)$$

from where the degree of O → C conversion at the photostationary state can be derived from the ratio, $\Phi_{O\to C}/(\Phi_{O\to C} + \Phi_{C\to O})$.

TABLE 2: Quantum Yields and Degree of Conversion at the Photostationary State of the New and Reference Compounds in 3MP at Room Temperature (290 K)

compound	$\Phi_{O\to C}$	conversion	$\Phi_{C\to O}$	
BTSi	0.37 $\lambda_{exc} = 266$ nm	0.50	0.37 $\lambda_{exc} = 266$ nm	0.56 $\lambda_{exc} = 445$ nm
BTPO	0.31 $\lambda_{exc} = 267$ nm	0.48	0.34 $\lambda_{exc} = 267$ nm	0.76 $\lambda_{exc} = 445$ nm
BTF6	0.29 $\lambda_{exc} = 316$	0.40	0.44 $\lambda_{exc} = 316$	0.42 $\lambda_{exc} = 445$ nm
(from literature)	(0.35)[a] (0.31)[b]	(0.45)[a] (0.43)[b]		(0.35)[a] (0.28)[b] (0.28)[c] (0.9)[d] (0.3)[e]

[a] In hexane, refs 10 and 16. [b] In ethyl acetate, ref 17 [c] In hexane, ref 18 at $\lambda_{exc} = 437$ nm. [d] In hexane, ref 11. [e] In hexane, ref 19.

To determine the quantum yields, eq 1 was rearranged into eq 3, for a 1 cm cell-path,[12]

$$dA_C/dt = \varepsilon_C \Phi_{O\to C} I^0 F A^0 - A_C[I^0 F \varepsilon_{iso}(\Phi_{O\to C} + \Phi_{C\to O})] \quad (3)$$

where the color forming rate is expressed in terms of the absorbance, A_C, and molar absorption coefficient, ε_C, of the closed colored form at the analysis wavelength, $F = A_{total}/(1 - 10^{-A_{total}})$ is the photokinetic factor[13,14] and A^0 is the initial absorbance at the irradiation wavelength. From eq 3, by plotting dA_C/dt vs A_C, a straight line is obtained, which gives ($\Phi_{O\to C} + \Phi_{C\to O}$) from the slope and $\Phi_{O\to C}$ from the intercept (see Figure 3). The photobleaching quantum yield can also be obtained by irradiating the photostationary solution (or even the solution of the pure colored form) with visible light and following the color fading, based on eq 4,[15]

$$-dA_C/dt = \varepsilon_C \Phi_{C\to O} I^0 (1 - 10^{-A_C'}) \quad (4)$$

where A_C' is the absorbance of the colored form at the irradiation wavelength. A plot of - dA_C/dt vs $10^{-A_C'}$ gives a straight line with equal slope and intercept from where the quantum yield of the closed → open photodecoloration ($\Phi_{C\to O}$) is obtained. These values are reported in Table 2 along with the conversion degree at the photostationary state. Values from literature for BTF6 in different solvents, reported in parentheses,[11,16–19] are generally in line with our data.

Quantum yield measurements were also carried out as a function of temperature. The $\Phi_{O\to C}$ appeared to be independent of temperature, within the experimental uncertainty, in the 260−300 K temperature range, whereas a more severe temperature increase (315 K) caused an appreciable increase of quantum yield especially for BTSi (from 0.37 at 290 K to 0.57 at 315 K).

The $\Phi_{C\to O}$ of all three compounds was found to regularly decrease with decreasing temperature, as illustrated for BTPO in Figure 4. The effect of the temperature on the photochemical yield in 3MP is shown in Table 3.

The reaction yields as a function of temperature were treated according to the Arrhenius-type eq 5, which was deduced by assuming that the reaction proceeds through the activated path only and that other relaxation paths are temperature independent.

$$\ln(1/\Phi_{C\to O} - 1) = E_a/RT + \text{const} \quad (5)$$

Activation energies and "limit" yields ($\Phi_{C\to O}^{lim}$) reported in Table 4 were determined from the slope and intercept, respectively, of linear plots of $\ln(1/\Phi_{C\to O} - 1)$ vs T^{-1}. An example of graphical treatment for BTPO is shown in Figure 5.

To understand whether the temperature effect was due to an intrinsic barrier or to a viscosity barrier to the ring-opening reaction, measurements of quantum yields of BTSi were carried out in different hydrocarbons with similar dielectric constant to that of 3MP but rather different viscosity. Table 5 provides $\Phi_{C\to O}$ of BTSi as a function of viscosity in some aliphatic hydrocarbons at 298 and 280 K. From the data reported in Table 5, showing that the photochemical yield is substantially independent of viscosity, it can be deduced that the temperature effect is not due to a change of viscosity but rather to some changes in the intramolecular dynamics.

Further increasing viscosity, in a 3MP rigid matrix at 80 K, led to very surprising viscosity/temperature effects. The $\Phi_{O\to C}$ of BTSi became almost unity, whereas that of cycloreversion was reduced to 10% upon UV excitation and to 1% using visible light. For BTPO the matrix/temperature effect was not so dramatic at $\lambda_{exc} = 267$ nm, but with visible light $\Phi_{C\to O}$ was reduced to a very low value (0.04). For the reference, BTF6, $\Phi_{O\to C}$ was much lower than in fluid solution and $\Phi_{C\to O}$ was less than 0.1% at both $\lambda_{exc} = 316$ and 445 nm (Table 6).

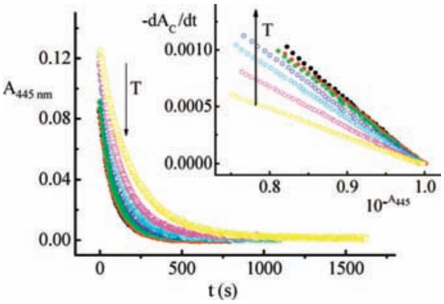


Figure 4. Temperature effect on the photobleaching kinetics of BTPO in 3MP ($\lambda_{exc} = 445$ nm). Inset: data treated according to eq 4.

TABLE 3: Temperature Effect on $\Phi_{C\to O}$ for BTSi, BTPO and BTF6 in 3MP, $\lambda_{exc} = 445$ nm

	$\Phi_{C\to O}$		
T/K	BTSi	BTPO	BTF6
200	0.31	0.45	0.19
220	0.39	0.47	0.25
240	0.50	0.56	0.31
260	0.52	0.63	0.35
280	0.56	0.72	0.37
300	0.58	0.75	0.38
315	0.80	0.80	0.40

TABLE 4: Parameters Obtained from the Graphical Treatment of Eq 5

	BTSi	BTPO	BTF6
E_a/kJ mol^{-1}	6.5	8.5	5.0
$\Phi_{C\to O}^{lim}$	0.95	0.99	0.85

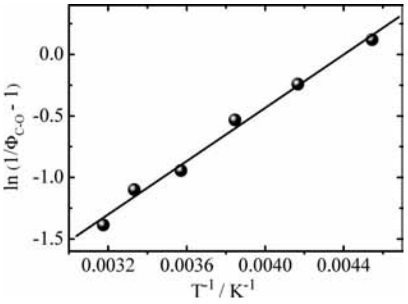


Figure 5. Photobleaching quantum yields of BTPO in 3MP as a function of temperature, treated according to eq 5.

TABLE 5: Solvent Effect on $\Phi_{C\to O}$ of BTSi (λ_{exc} = 445 nm)[a]

solvent	η/cp	$\Phi_{C\to O}$
3MP 298 K	0.306	0.58
Heptane 298 K	0.390	0.56
Heptane 280 K	0.488	0.57
Decane 280 K	1.143	0.58

[a] viscosities at different temperatures were calculated using the relationship: $\eta_T = \eta_0\ e^{-\ \Delta E/RT}$).

TABLE 6: $\Phi_{O\to C}$ and $\Phi_{C\to O}$ (UV and Visibile Excitation, Respectively) Obtained in a 3MP Rigid Matrix at 80 K

	UV excitation		visibile excitation
compound	$\Phi_{O\to C}$	$\Phi_{C\to O}$	$\Phi_{C\to O}$
BTSi	0.99	0.1	0.001
BTPO	0.35	0.52	0.04
BTF6	0.1	$\leq 10^{-3}$	$\leq 10^{-3}$

3.3. Photobehavior of TSi and TPO. The compounds not bearing the condensed benzene rings, TSi and TPO, showed a different photobehavior. They were not promising from the point of view of potential applications because their phoreactions were not sufficiently clean. This can be seen from Figure 6 where two consecutive UV-coloration ↔ visible-bleaching cycles, carried out with TSi, did not give reproducible results (room temperature). From the spectra before irradiation and after UV and visible irradiation it could be seen that the system is not reversible. HPLC analysis of the irradiated solutions showed the presence of several unidentified products.

Also TPO showed a similar behavior. In this situation, quantum yield determinations were not expected to give reliable results and therefore were not done.

From laser flash photolysis experiments (nanosecond resolution), which only allowed the colored form to be detected for BTSi and BTPO, a transient with triplet characteristics, λ_{max} = 380 nm, was observed for TSi. It decayed with a lifetime of 0.26 μs, leaving the colored form, and was quenched by oxygen.

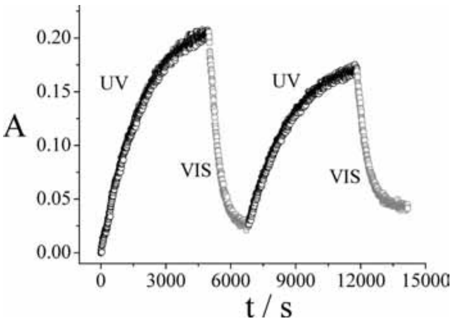


Figure 6. Consecutive kinetics of photocoloration and photobleaching of TSi in 3MP.

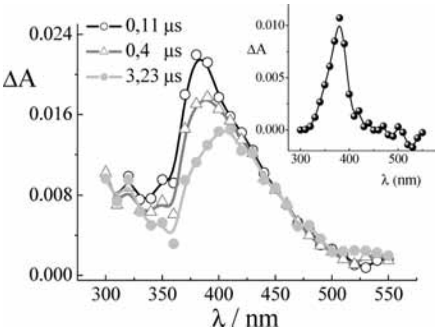


Figure 7. Spectral evolution of TSi in 3MP upon laser flash photolysis. Inset: spectrum of the transient obtained by subtracting the spectrum of the colored closed form (3.23 μs) to the initial signal (0.11 μs).

The spectral time evolution and kinetics are shown in Figure 7. This transient was not the precursor of the colored form but could be that of the photodegradation products.

For an analogous compound, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (TF6), $\Phi_{O\to C}$ = 0.40 and $\Phi_{C\to O}$ = 0.58 have been reported in *n*-hexane, with the absorption maximum of the color band at 425 nm (ε = 5800 dm^3 mol^{-1} cm^{-1}).[20] Moreover, for another structurally related compound, 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene, byproducts were found that were separated by chromatography and a photofatigue mechanism was also proposed.[21]

4. Discussion

The foregoing results show that replacement of thiophene rings with benzothiophene rings remarkably increases the fatigue resistance of photochromic diarylethenes, in agreement with previous literature data.[1] Absence of nanosecond living intermediates by flashing the benzothiophene derivatives and triplet detection in the thiophene derivatives suggest that the byproduct derives from the triplet state, whereas the ring-closing reaction occurs from the singlet state on a picosecond time scale.[22]

For the benzothiophene derivatives there are several salient observations that are of particular significance regarding the dependence of photochemistry on temperature and excitation wavelength.

4.1. Color-Forming Photoreaction. Literature information about the temperature effect on the photochemistry of this kind of photochromic diarylethenes is scarce and random. From ^{1}H NMR measurements, it was demonstrated[23] for some 1,2-bis(benzo[*b*]thiophen-3yl)ethene derivatives that the antiparallel/parallel ratio slightly increases as the temperature decreases (from +20 to −60 °C), whereas the NMR signals of the two conformers collapse at higher temperature ($T \geq 45$ °C) due to interconversion of the two conformers. Therefore, the yield should increase with decreasing temperature. However, the change in rate that has been experimentally found[23] on decreasing temperature did not allow any conclusion to be drawn, being on the order of the experimental uncertainty. For such type of molecules, the activation energy for the p ↔ a-p interconversion has been estimated to be about 70 kJ mol^{-1}, independent of substituents at the ethene moiety.[23] A theoretical investigation on a structurally related diarylethene, 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anidride,[24] has demonstrated that a rather high energy barrier (54 kJ mol^{-1}) separates p and a-p conformations, even in that case. Interconversion between the two conformations is therefore considered to be hampered. The barrier is much lower in the S$_1$ state,[22] but the ring-closure reaction is so fast (picosecond scale) as not to allow interconversion to occur in S$_1$. The ground state energy barrier could inhibit intercorversion at low temperature but not at higher temperature where the antiparallel form can be replaced as it is consumed in the photoclosing reaction. This would result in an increase of $\Phi_{O\to C}$ on increasing the temperature, as observed. NMR measurements, carried out on BTSi have shown that the a-p/p ratio is 69/31 at room temperature and that the rate of p ↔ a-p interconversion is 440 s^{-1}. These NMR data are in agreement with the high experimental yield of photocoloration and the undetectable effect of the interconversion on the yield at moderate temperature.

Very interestingly, for some diarylethenes in the solid crystalline state, it was found that the $\Phi_{O\to C}$ yield increases even up to 1, compared with solution, because inclusion in the crystal lattice allows only the a-p reactive form to be present.[25,26] Other kinds of constriction were found to favor the a-p conformation: it has been reported that the reaction yield of some diarylperfluorocyclopentenes dramatically increases when the photochrome is enclosed in cyclodextrine cavities.[27] By analogy, it is conceivable that BTSi molecules are constrained to the a-p conformation in a 3MP rigid matrix where we measured an almost unit $\Phi_{O\to C}$. Occurrence of the photoreaction with very high yield in matrix at low temperature is also in agreement with the statement that the ring-closure reaction of diarylethenes "is essentially barrierless and downhill".[22]

4.2. Photobleaching. Concerning the cycloreversion process, an important question is what are the causes for the temperature and wavelength dependence of $\Phi_{C\to O}$. Both effects were previously observed in photochromic diarylethenes but not much attention has been devoted to these aspects. For some phenyl-substituted diarylperfluorocyclopentenes, the ring opening reaction was found to be more than doubled with increasing temperature (from 22 to 80 °C); this increase has been attributed to destabilization of the excited state due to partial suppression of the π-conjugation consequent to rotation of the phenyl groups.[28] This hypothesis was also supported by a consistent blue shift of the absorption maximum, observed with increasing temperature. In the present cases, free rotating aryls are not present. A viscosity effect can be also excluded on the basis of our experimental findings (see Table 5). Therefore, the effect of temperature is reasonably a direct result of its impact on the molecule undergoing photochemistry. The activation energies for the reaction in the excited state here determined are of the same order of magnitude as those previously found for the 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in a single-crystalline phase.[29] Very significantly, the $\Phi^{\lim}_{C\to O} \to 1$, extrapolated at $T \to \infty$ from the plots obtained applying eq 5, shows that the reaction is only hampered by the energy barrier for the two new compounds, whereas for BTF6 ($\Phi^{\lim}_{C\to O} = 0.85$), about 15% of the absorbed quanta are wasted by different ways than the reactive one.

The quantum yield of the cycloreversion process depends on the probability that the ring closed molecule, excited at the Franck–Condon (FC) level, has to pass over the transition state (TS) to the conical intersection (CI).[5,30] The origin of the barrier, which strongly depends on structural factors, has been interpreted in terms of "diabatization" by Nakamura et al. in a recent theoretical work.[31] The authors have demonstrated that the ground state of the closed form correlates with the higher excited state of the open form, thereby originating the barrier. The temperature effect observed in our molecules is in agreement with this interpretation, whereas the exceptionally high quantum yield is unexpected on the basis of the theoretical model.

If an energy barrier to the ring opening exists, it should be overcome by increasing the excitation energy. This has been found in other cases,[24] but, for our molecules, just the opposite occurred: an increase in the excitation energy caused a decrease in the reaction yield. The ring-opening reaction yield determined by exciting with UV light was lower than that obtained by exciting with visible light, despite the large increase in energy. For example, for BTPO at 290 K, we found $\Phi_{C\to O} = 0.76$ ($\lambda_{exc} = 445$ nm) and $\Phi_{C\to O} = 0.34$ ($\lambda_{exc} = 267$ nm), despite the enormous excitation energy increase, about 180 kJ mol^{-1}, for the second excitation. Such wavelength effect was not observed for the reference molecule. We do not have a definite explanation of this finding. However, when we excite the colored form with UV light, a different electronic transition is excited and this may open competitive relaxation pathways, thus reducing the number of the absorbed quanta that reach the reactive lower lying state. This was also found to occur in the ring-opening reaction of some naphthopyrans.[32]

4.3. Fluorescence. Concerning the presence of fluorescence, it was surprising, but very interesting, to find that the new compounds were fluorescent only in the closed form, whereas fluorescence has been more frequently found for the open forms. For BTF6 the presence of fluorescence for both isomers, previously reported by others,[6] was confirmed in the present work, but with a very low quantum yield ($\Phi_F \sim 10^{-4}$) for the ring-closed form. Rare cases of fluorescence emission from both isomers are found in the literature. For example, for an asymmetric diarylethene, in an EPA matrix, fluorescence from both isomers was observed, the Φ_F of the open and closed forms being 0.27 and 0.1, respectively.[33]

The fluorescence bands of the new molecules in the colored form exhibit larger Stokes shifts (4500–5000 cm^{-1}) than BTF6 (~3500 cm^{-1}), which indicates that emission occurs from a relaxed excited state with a greater change in geometry.

Compared with the reference compound, BTSi and BTPO are more suitable for applying the fluorescence signal as a switch, because the emission intensities of their colored forms are greater by more than 1 order of magnitude.

5. Conclusions

The results of this work show that the new compounds, BTSi and BTPO, are photoreversible photochromic molecules that exhibit fairly high quantum yields for both the UV-stimulated photocoloration ($\Phi_{O\to C} \approx 0.37-0.31$) and the visible-stimulated photobleaching ($\Phi_{C\to O} \approx 0.76-0.56$), with a photoconversion percentage of 48–50% at the photostationary state (UV excitation). The $\Phi_{O\to C}$ is affected by the temperature, this dependence essentially reflects the percentage of the reactive a-p conformation which is actually present in the system. At high temperature, the a-p concentration is maintained at the equilibrium value because the thermal barrier to interconversion can be overcome; therefore, the $\Phi_{O\to C}$ increases. At low temperature, the equilibrium a-p concentration also increases and becomes almost 100% for BTSi in a rigid matrix at 80 K, where $\Phi_{O\to C}$ is ~1. There exists a wide temperature interval, around room temperature, in which both temperature effects are small and cannot be detected by quantum yield measurements. Also $\Phi_{C\to O}$ is temperature dependent, due to an energy barrier (7–9 kJ mol^{-1}) in the excited state. A similar behavior is also exhibited by the reference molecule BTF6. Unexpectedly, $\Phi_{C\to O}$ decreases with increasing the excitation energy, probably due to competing relaxation pathways in the upper electronic states. This λ_{exc} effect was not observed for BTF6.

The new molecules exhibit appreciably intense fluorescence emission ($\Phi_F > 10^{-3}$) in the visible region, originating from the closed form, that could be used as a switching signal alternative to absorbance changes in readout systems.

The study carried out on TSi and TPO showed that their photoreactions are not clean, originating several byproducts besides the colored form; therefore, they are not interesting from the point of view of applications.

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