Ring-Opening and -Closure Reaction Dynamics of a Photochromic Dithienylethene Derivative

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The influence of a bulky, strongly coupled substituent (benzoyl−phenyl−ethenyl, BPE) on the dynamics of the photoinduced ring-closure and ring-opening reactions of 1,2-bis[[2−methyl−thien−3−yl]]perfluorocyclopentene (BMTFP) in solution was investigated. UV/vis absorption spectroscopy in combination with chemical actinometry was employed to determine the reaction quantum yields. The relaxation and reaction dynamics were studied by transient absorption spectroscopy, exciting the S_0−S_2 transition of the open isomer with pump pulses at 288 nm, while 657 and 410 nm pulses were used to excite the S_1 and S_2 states of the closed isomer, respectively. Transient absorption spectra in the range of 350−950 nm were recorded using temporally delayed, white-light continuum probe pulses. After structural relaxation in the S_1 excited state, the ring-closure reaction takes place with high quantum yield through a conical intersection. This conical intersection acts also as relaxation funnel for the S_1 excited state of the closed isomer, from which it is separated by an energy barrier. The branching in the conical intersection favors the closed isomer, so that the ring-opening reaction yield is small (10^{-3}−10^{-4}). This yield was found to vary by a factor of 6 for different isomers obtained by rotation around the ethylene bond of the substituent.

1. Introduction

Photochromic 1,2-bis[2-methyl-thien-3-yl]perfluorocyclopentene (BMTFP) derivatives have in recent years received considerable attention because of their high potential for a number of photonic applications.[1−7] In addition, comprehensive spectroscopic investigations of the fundamental photochemical processes have been made.[8−19] Irie and co-workers and, independently, Lehn et al. optimized compounds with respect to reaction quantum yield, resistance to photofatigue, and thermal stability.[1−12] The photochemical, electrocyclic ring-opening and ring-closure reactions occur in the conrotatory mode. For the dithienylethene derivatives, the ground-state isomers are thermally stable because of the low aromatic stabilization energy of the thiophene groups which gives rise to a large potential barrier between the open-isomer and the closed-isomer state.[12] The open isomer is colorless, absorbing in the near UV, whereas the closed isomer has a strong absorption band in the visible range. Previous time-resolved studies of electrocyclic reactions in other dithienylethene derivatives have shown that both ring-opening and ring-closure processes occur on the picosecond time scale.[8−11,13,14,15,18]

Our previous research activities on photochromic BMTFP derivatives were aimed at the characterization of the influence of π conjugated substituents, attached in the 5-position of the thiophene rings, on the reaction dynamics and quantum yields.[13−20] Substituents with various structural and electronic properties, more or less strongly coupled with the photochromic dithienylethene unit, have been introduced, and systems suitable for the use in technologically relevant photochromic materials such as photoswitchable liquid crystals and polymers were prepared. As a result of this work, a more detailed understanding of the various interactions between substituents and the photochromic dithienylethene switch became a central issue. Very recently, we have reported femtosecond transient absorption studies of the ring-opening and ring-closure reaction dynamics of diformyl dithienylethene derivative (1,2-bis[5-formyl-2-methyl-thien-3-yl]perfluorocyclopentene) in solution[14,15] as well as the dianthryl analogue (1,2-bis[5-anthryl-2-methyl-thien-3-yl]perfluorocyclopentene).[18]

The formyl substituent (CHO) is a π-electron donor that interacts very strongly with the dithienylethene switch in the first excited singlet state (S_1). The transients of photoinduced absorption and bleaching have been analyzed in terms of a model potential extracted from calculations of the S_0, S_1, and S_2 potential energy hyperlines.[14] Within the first picosecond after excitation to the S_1 state, the closed isomer is observed to undergo a fast structural relaxation along the S_1 potential energy surface to a precursor state of the ring-opening process. The rather long lifetime of this precursor, $\tau_2 = 13$ ps, is dominated by radiationless deactivation to the ground state, S_0, of the closed isomer, the quantum yield of the ring-opening reaction (3.6%) being rather low. In contrast, the decay of the S_1 state of the open isomer is dominated by the ring-closure reaction with a quantum yield of $\Phi_{RC} = 0.86$.[15] Both the decay of the S_1 state of the open isomer and the generation of the closed isomer are

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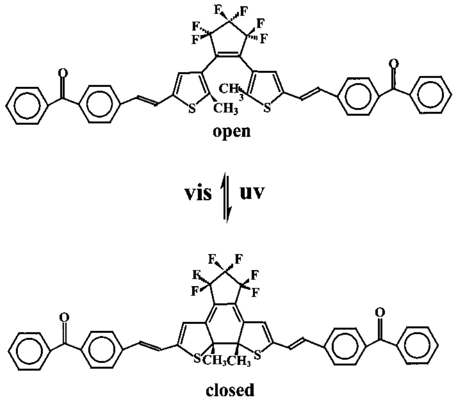


Figure 1. Structure formula of the open (top) and closed (bottom) isomer of bpe-BMTFP.

exponential with a time constant of ca. 2 ps, so that the reaction rate constant for ring-closure is $k_{RC} \approx 4.3 \cdot 10^{11}$ s^{-1}.[15] These results are characteristic for a small π-donating substituent. In contrast, the coupling in the S_1 state between anthracene substituents, attached by a single bond to the 5 position of the thiophene rings, and the dithienylethene switch is significantly smaller because of the nearly perpendicular alignment of the anthracene substituents with respect to the dithienylethene unit. As a result, the S_1 state of the closed isomer is less stabilized, resulting in a relatively smaller ring-closure reaction quantum yield and a larger ring-opening reaction quantum yield when compared to CHO substituent.[18,19]

Here, we present a similar complete study of benzoyl-phenyl-ethinyl substituted 1,2-bis[2-methyl-thien-3-yl]perfluorocyclopentene (bpe-BMTFP, see Figure 1). A preliminary time-resolved study of the closed isomer of this compound had shown relaxation processes on the 1−10 ps time scale.[13] The bpe substituent is rather bulky and has an extended π electron system, which is expected to couple strongly with that of the dithienylethene unit. The reaction quantum yields and the excited-state relaxation dynamics of the closed and open isomer of bpe-BMTFP were investigated. AM1 computations of the optimized geometry and heat of formation of the different equilibrium conformations and isomers of bpe-BMTFP support the analyses of the spectroscopic data.

2. Experimental Section

2.1. Transient Absorption Spectroscopy. Transient absorption spectra with femtosecond time resolution were measured using the pump−probe technique. Pump and probe pulses are generated by a femtosecond laser system described in detail elsewhere.[14] The closed isomer was excited to the S_1 state using 657 nm pulses from the optical parametric amplifier (OPA) or to the S_2 state using frequency-doubled amplified oscillator pulses at 410 nm. The open isomer was excited at 288 nm to the S_2 state with the second harmonics of the 576 nm OPA output. The intensities of the transmitted probe beam with and without pump pulse excitation, I(p) and I(0), respectively, were measured by chopping the pump pulse beam at a frequency of 6 Hz. The ratio I(p)/I(0) equals the pump pulse-induced change of transmittance $\Delta T = T(\mathrm{p})/T(0)$ in the sample. For the small changes recorded here, $1 - \Delta T$ equals the sum of the difference spectra of all species contributing to the signal, weighted by their respective concentrations. Transmission spectra of the sample were obtained by dispersing the probe pulses with a polychromator containing a 400 lines/mm grating in combination with a CCD detector system (LOT, InstaSpec IV). The overall instrumental time resolution is 120 fs for excitation at 410 and 657 nm and is about 630 fs for pump pulses at 288 nm. The time dispersion of 1.4 ps over the spectral range of the white-light continuum probe pulses was determined at spectral intervals of about 80 cm^{-1} from the rise of the bleaching or absorption transients, and all transient spectra shown here have been corrected for this dispersion.

bpe-BMTFP was dissolved in spectrograde dichloromethane at $2.5 \cdot 10^{-5}$ mol/L. The solution was pumped at a velocity of 5 mL/s through a 400 μm flow cell to ensure a complete renewal of the sample from pulse to pulse.

2.2. UV/vis Absorption Spectroscopy and Chemical Actinometry. Commercially (Aldrich) available solvents were used. Absorption spectra were recorded with a Perkin-Elmer lambda 9 spectrometer. Quantum yields were determined from the evolution of the absorption spectra after irradiating the solutions for various intervals of time. The experimental error is estimated as 10%. The intensities of the light sources were calibrated with the furylfulgide actinometer aberchrome 540. The open isomers were irradiated with the UV lines of an Ar$^+$ laser (351−363.5 nm), the closed isomers with laser lines at 514 nm (Ar$^+$ laser), 575 and 690 nm (rhodamine 6G-dye laser), and 632 nm (He−Ne laser).[19]

2.3. Syntheses. *General.* All syntheses, carried out under argon or nitrogen atmosphere, were monitored by TLC using aluminum-backed silica gel (230−400 mesh) or by HPLC using a Hewlett-Packard ChemStation 1040 and 1050 series II instrument and were protected strictly from light. Octafluorocyclopentene was obtained as a donation from Zeon Corporation (Japan). Solvents and other reagents were used as purchased without further purification, unless stated otherwise. Column chromatography was performed on silica gel (230−400 mesh) using nitrogen- or argon-flushed solvents. Melting points: uncorrected and Reichardt THERMOVAR. NMR: Varian VXR 300 and Bruker DRX 500 at frequencies of 300 and 500 MHz for ^{1}H and 470 MHz for ^{19}F, respectively. Reference compounds were TMS (^{1}H) and $CFCl_3$ (^{19}F). UV/visible: Perkin-Elmer lambda 19 spectrophotometer. IR: Perkin-Elmer 1420 spectrometer. EI-MS: Varian MAT 311A and MAT 8000. 1,2-Bis-(2-methyl-5-(2-(4-benzoyl-phenyl-1-yl)ethen-1-yl)-thien-3-yl)-perfluorocyclopentene **6** was synthesized according to Scheme 1. The details of the synthesis are described in the Appendix.

3. Quantum Yields of Ring-Opening and Ring-Closure Reaction

Figure 2 shows stationary absorption spectra of the closed isomer (solid line) and of the open isomer (dashed line) of bpe-BMTFP. The lowest energy absorption band of the open isomer at 355 nm correlates with the S_0−S_1 of the bpe substituents, whereas the S_0−S_2 absorption band, peaking at 245 nm, involves essentially the lowest-energy $\pi\pi^*$ state of the dithienylethene switch. For the closed isomer, the absorption maxima at 620 and 410 nm are assigned to the S_0−S_1 and S_0−S_2 transitions of the dithienylethene unit, respectively. The excitation energy (620 nm) of the S_0−S_1 transition of the closed isomer is fairly low as compared with different substituted dithienylethene derivatives[17] and is a proof of the strong coupling between the π-electron systems of substituent and dithienylethene unit. For example, the closed isomer of the unsubstituted dithienylethene compound has its lowest energy transition at 520 nm and that of the dianthryl derivative is located at 540 nm, while the strong coupling in the closed isomer of formyl substituted compound is responsible for the large redshift of the absorption to 620 nm.[15] The open isomer of bpe-BMFTP may exist as two conformers.[18] The so-called parallel (p) and antiparallel (a−p)

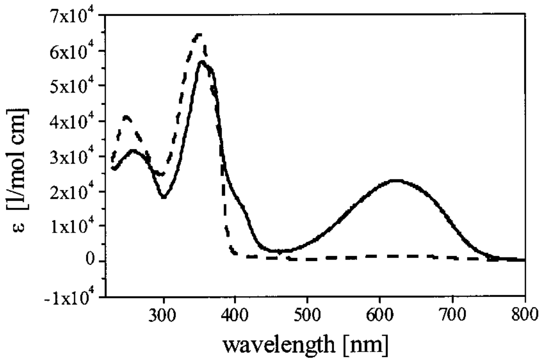
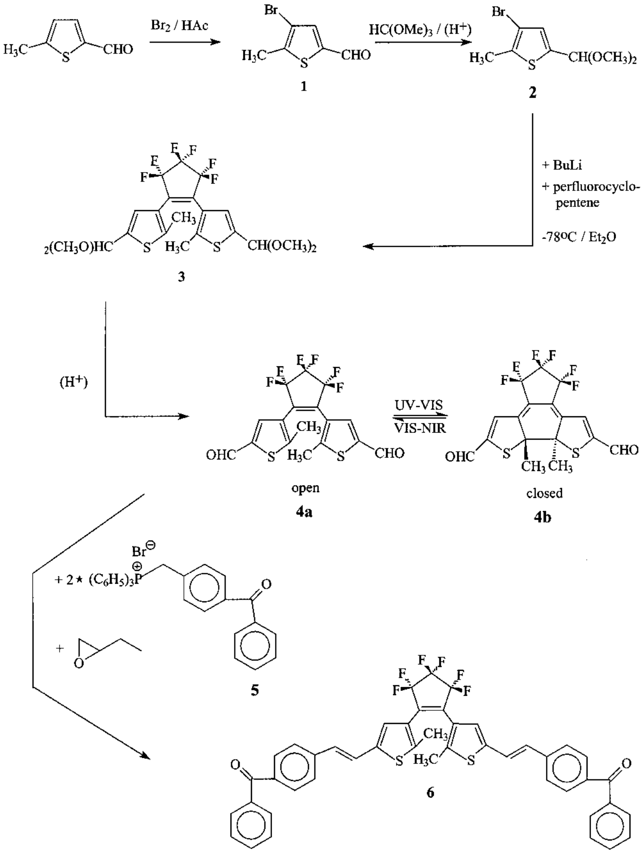


Figure 2. Absorption spectra of the closed isomer (thick solid line) and the open isomer (thick dashed line) of bpe-BMTFP in a 1.1 · 10^{-5} mol/L CH_2Cl_2 solution.

SCHEME 1



conformers are obtained from the planar, closed isomer by con- and disrotatory rotations of the thiophene rings and have the local symmetry of C_s and C_2, respectively.[20] For steric reasons, only the *a*−*p* conformer may undergo the ring-closure reaction. To evaluate the relative populations of the two conformers, the heat of formation, ΔH_F, was calculated using the AM1 procedure of Hyperchem[21] with the following result: $\Delta H_F^{(o:p)} = -587.14$ kJ/mol and $\Delta H_F^{(o:a-p)} = 592.22$ kJ/mol. Neglecting entropy differences and corrections due to differences in solvation energy, the Boltzmann populations of both conformers, ρ_p and ρ_{a-p}, are determined as $\rho_p \approx 12\%$ and $\rho_{a-p} \approx 88\%$. The value of ρ_{a-p} is the upper limit for the overall quantum yield of the ring-closure reaction, consistent with the experimental value of $\Phi_{RC} = 0.76$ (363 nm excitation). Taking the above value of $\rho_{a-p} \approx 88\%$, the quantum yield for the *a*−*p* conformer is $\Phi_{RC}^{(a-p)} = 0.86$.

In contrast, the quantum yield for the ring-opening reaction is rather small, and the measurements expose a more complex behavior, in the sense that the quantum yield depends on both the wavelength of excitation and the doses of irradiation. In addition, the spectrum of the closed isomer was observed to evolve as a function of the doses of irradiation. For example, the quantum yield at the beginning of irradiation decreases from 1.3 · 10^{-3} to 0.41 · 10^{-3} when the wavelength of the irradiation is shifted from 514 to 690 nm. After reduction of the maximum absorption of the closed isomer by irradiation at 514 nm to 10% of its initial value, the resulting spectrum is redshifted by 12 nm. During such an irradiation, the measured quantum yield decreases by a factor of more than 4. The evolution of a solution under irradiation was found to be only dependent on the doses of irradiation and not on the intensity, so that an interruption of the irradiation of the sample for several hours had no influence on the results. All these observations were made in solutions of toluene and are independent of the concentration in the range of 5 · 10^{-4} to 5 · 10^{-5} mol/L.[19] These results clearly indicate the presence of a mixture of different isomers with different reaction quantum yields, which do not interconvert on the time scale of hours. If the minimal presence of just two isomers (i_1 and i_2) is assumed, all observations can be quantitatively analyzed, and the following properties of these isomers are obtained: The initial relative concentrations of the two isomers i_1 and i_2 are 0.6 and 0.4, respectively, and the quantum yield of both isomers is wavelength-dependent and decreases with increasing wavelength. Between 514 and 690 nm, the change is from 1.6 · 10^{-3} to 0.55 · 10^{-3} for i_1 and from 2.5 · 10^{-4} to 0.9 · 10^{-5} for i_2. Analogous wavelength dependence of quantum yields had also been reported by Irie and Mohri[22] and was attributed to the effect of excess vibrational energy. Alternatively, the presence of more isomers or interconverting conformers could also contribute to this behavior. However, because of the increased uncertainty associated with the larger number of parameters, no analysis invoking a greater number of species (isomers or conformers) was made here.

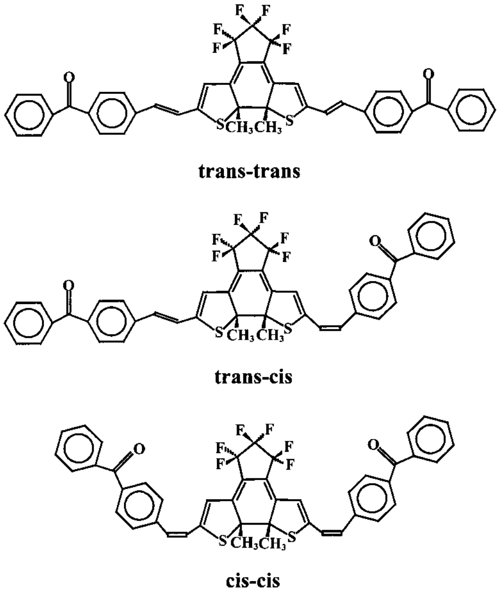


Figure 3. Structure formula of the three cis−trans isomers of bpe-BMTFP.

The most likely isomers are the three different cis−trans isomers of bpe (see Figure 3). To avoid confusion with the open and closed isomers of the dithienylethene unit, these isomers will be referred to in the following as bpe isomers. AM1 computations[21] of the optimized geometries result in different values of the heat of formation, ΔH_F, for the different isomers: $\Delta H_F^{(c:cis-cis)} = -483$ kJ/mol, $\Delta H_F^{(c:cis-trans)} = -497$ kJ/mol with

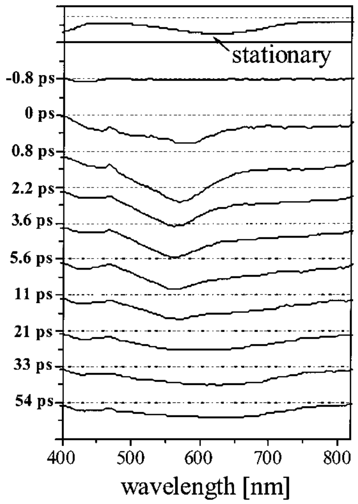


Figure 4. Temporal evolution of the transient absorption spectra of the open isomer excited at 288 nm and recorded at different delay times τ_D as indicated. The S_0-S_1 absorption spectrum of the closed isomer is shown in the top panel.

a statistical weight of 2, and $\Delta H_F^{(c:trans-trans)} = -513$ kJ/mol. We conclude that not only these different isomers may be formed in the course of the chemical synthesis with different probabilities, but also they do differ in their photochemical behavior, and we suggest that these isomers are responsible for the observed dependence of the quantum yield on the irradiation dose and wavelength.

4. Transient Absorption Spectra

To analyze the time evolution of the transient spectroscopic measurements, a decomposition of the spectra into a limited number of components was made in the following way: for each of the two (i.e., open and closed) isomers, the spectra at all delay times were reproduced as the sum of a minimal number of the same spectral components with different amplitudes. The initial unrestricted decomposition clearly exposed, in addition to components that originate from the population of excited state species, components associated with the stable spectra of the two isomers. To reduce the number of free parameters in the final fitting, the position and width of these components were forced to reproduce the stationary spectra. The sum of components with the same time evolution was assumed to be associated with one excited species, generated subsequent to the optical excitation. In this way, the time evolution of the population of all species was extracted.

The quantum yield measurements, presented above, clearly indicate the presence of a mixture of different bpe isomers. While the small ring-opening reaction yield strongly differs for these species, the high ring-closure yield is insensitive and, within the experimental uncertainty, no differences between bpe isomers were found. Not surprisingly, the relaxation dynamics, discussed below, reflects this inhomogeneous composition of the samples.

4.1. Ring-Closure Reaction and Open Isomer Transients. Transient absorption spectra of the open isomer of bpe-BMTFP in dichloromethane, recorded with pump pulses tuned to the S_0–S_2 transition at 288 nm, are shown in Figure 4. The spectrum at $\tau_D = -0.8$ ps provides the baseline with $\Delta T(\lambda) \approx 1$. The stationary absorption spectrum of the closed isomer (top panel) contains the S_0–S_1 absorption band between 570 and 750 nm and the onset of the S_0-S_2 transition below 425 nm. For some of these spectra, the decomposition into five different components, as described above, is indicted in Figure 5a, whereas in Figure 5b the temporal evolution of these species is shown.

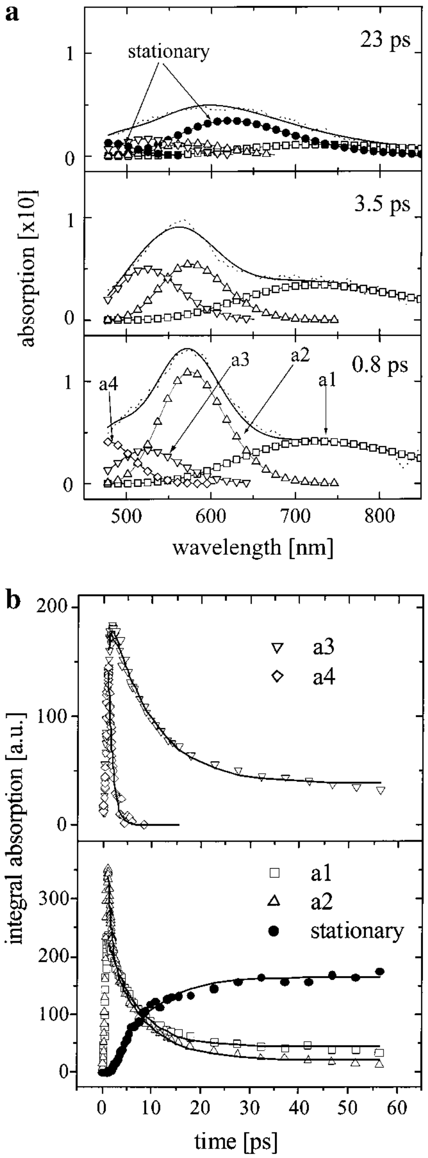


Figure 5. Decomposition of the transient absorption spectra in Figure 4 into the spectral components a1–a4 and the ground-state absorption spectrum of the closed isomer (marked "stationary"). (a) Example of this decomposition at three different delay times. (b) Time evolution of the spectral components.

The temporal evolution of the transient absorption spectra between −0.8 and +54 ps clearly exposes the generation of a long-lived species with a rise time constant of 6 ps. This component is attributed to the S_0-S_1 absorption of the closed isomer generated by the ring-closure reaction (see the ground-state absorption spectrum in Figure 4). In addition, shorter-lived transient absorption bands, peaking at ca. 730 (a1), 580 (a2), and 525 nm (a3) appear within the first picosecond and decay with time constants around 6 ps. The good agreement between these rise and decay times clearly indicates that the ring-closure reaction is the direct relaxation pathway of these excited species. The transient at 470 nm (a4) decays within the first picosecond. In addition, a rise time of ca. 0.4 ps is observed for the 525 nm (a3) transient, whereas the neighboring 580 nm (a2) band has a correspondingly short decay component in addition to the 6 ps lifetime. These subpicosecond evolutions are attributed to a structural relaxation within the S_1 excited state of the open isomer. The observation that the excited-state transients do not

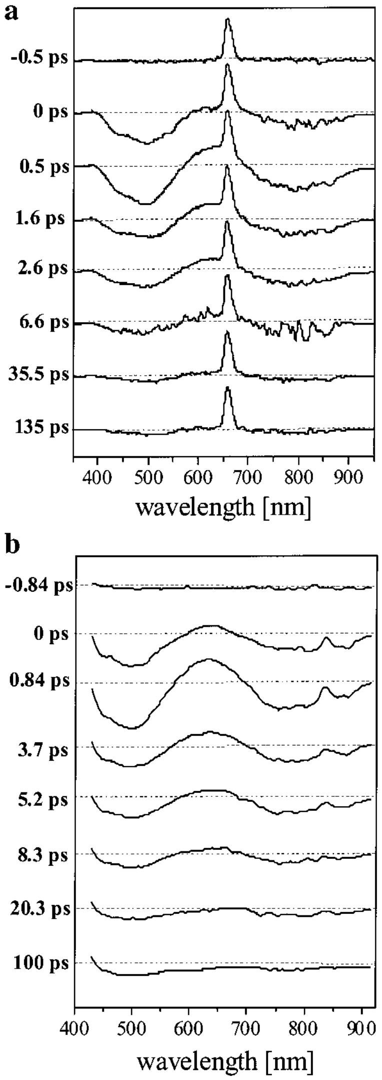


Figure 6. Temporal evolution of the transient absorption spectra of the closed isomer recorded at different delay times τ_D as indicated: excited at (a) 657 and (b) 410 nm.

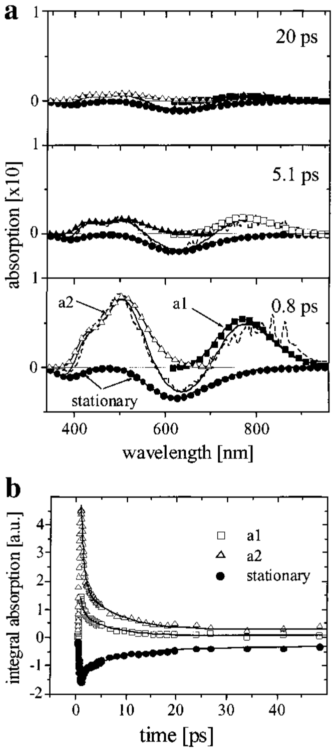


Figure 7. Decomposition of the transient absorption spectra in Figure 6b into spectral components a1, a2, and the ground-state absorption spectrum of the closed isomer (marked "stationary"). (a) Example of this decomposition at three different delay times. (b) Time evolution of the spectral components.

decay to zero is ascribed to the presence of the open isomer in the parallel conformation, which cannot decay via the fast ring-closure reaction, and the decay of which is beyond the time scale of the measurement. As might be expected, the spectra of the different bpe isomers are not separated at the resolution of the experiments, and the relative amplitude of the residual absorption is therefore an indication of the population of the nonreacting *p* conformer, the value obtained here, $\rho_p \approx 15\%$, is consistent with the value of given above in Section 3.

4.2. Closed Isomer Transients. The excited-state dynamics of the closed isomer was studied using pump−pulse excitation wavelengths at 657 and 410 nm, resonant with the S_1 and S_2 excited states, respectively. Typical transient spectra are shown in Figure 6a and b. In fact, aside from the presence of stray light of the pump pulse at 657 nm in Figure 6a, the transient spectra are virtually the same. This observation is consistent with the fact that no rise times are resolved in the spectra of Figure 6b, demonstrating that the S_2 to S_1 relaxation is faster than our instrumental resolution. The decomposition in spectral components, i.e., the ground-state absorption spectrum of the closed isomer and excited-state spectra, a1 and a2, is shown for some of the transient spectra of Figure 6b in Figure 7a, and the corresponding time evolution of these components is shown in Figure 7b. Overall, the picture that emerges is quite simple, as is expected, since the contribution of the ring-opening reaction to the decay dynamics is negligible and only the decay of S_1 to S_0 of the closed isomer is observed. The bleaching of the ground state is clearly identified, as are the components due to excited-state absorption. The decay of all transients can be fitted with biexponential functions of delay time, τ_D, as follows: $\Delta T = 1 + A_1 \cdot \exp(-\tau_D/\tau_1) + A_2 \cdot \exp(-\tau_D/\tau_2)$. The short time constant τ_1 lies between 0.3 and 0.5 ps, and values between 5 and 11 ps are obtained for the long time constant, τ_2. The accuracy of the data does not warrant any fit to sums of more exponentials, even though it is likely that more than just two bpe isomers are present (see above). Nevertheless the inhomogeneous behavior of the sample is obvious from the different values obtained for τ_2, and, more important, the observation of a short as well as a long time constant for each of the spectral components is firmly established.

5. Discussion and Conclusions

The results obtained here for the ring-closure reaction are fully consistent with observations made for other dithienylethene derivatives. Figure 8 summarizes the overall picture of the relaxation and reaction dynamics. After excitation, the open isomer relaxes within less than 1 ps on the S_1 potential energy surface to a state (O_P, "precursor state") with a longer lifetime of about $\tau_P = 6$ ps. Calculations indicate that the S_1 potential energy surface is fairly flat along the reaction coordinate down to about a distance of about 3 Å, after which the descent to the region of the conical intersection becomes steep.[14,15,18] In fact, the excitation energy of the S_1 state of the open isomer is an important factor, this slope becoming smaller for substituents with low excitation energies. It is reasonable to accept that the lifetime of the precursor state is the smaller the higher the slope along the reaction coordinate, and in line with this proposition,

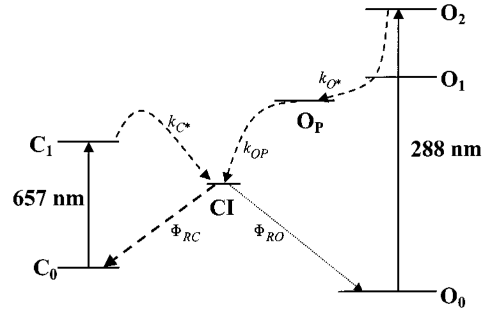


Figure 8. Reaction scheme. The states C_i and O_i denote the states of the closed and open isomers, respectively, the index P referring to the precursor state reached, and CI stands for conical intersection. For simplicity, only the important and dominant rate processes are indicated.

we observe that for the bpe derivative studied here (S_1 at 350 nm) the lifetime of 6 ps is intermediate between that observed for the bianthryl derivative (S_1 at 390 nm, $\tau_P = 10$ ps) and the biformyl derivative (S_1 at 300 nm, $\tau_P = 2$ ps). This picture confirms the view, obtained in studies of other dithienylethene derivatives, that the ring-closure reaction is essentially barrierless and downhill. Noticeable barriers are expected to exist, however, when the excitation energy of the substituent becomes even lower.

For the closed isomer, the transient spectra reflect just the relaxation of the S_1 excited state, because the quantum yield of the ring-opening reaction is negligibly small. The spectrally homogeneous, but temporally at least biexponential decay indicates that an energy barrier exists between the minimum of the S_1 excited state and the relaxation funnel, which we propose to be the conical intersection. This proposition is consistent with the observation that the quantum yield of the ring-opening reaction increases both with temperature and excitation energy.[17,19] The branching between the open and the closed isomers at the conical intersection is then dependent on the excess energy, increasing in favor of the open isomer with increasing energy. The fact that this branching is very sensitive to the geometry of the substituent is a new, important result found here. The change by a factor of 6 of the ring-opening quantum yield, observed for different isomers of the bpe derivative, demonstrates this extreme sensitivity to the structure of the substituent.

The very small overall quantum yield of the ring-opening reaction is consistent with the stabilization of the S_1 excited state of the closed isomer as compared to the unsubstituted dithienylethene and the dianthryl derivatives. This stabilization arises from the delocalization of the π electron system across central unit and the bpe substituents and leads to a shift of the S_0-S_1 absorption to longer wavelength (620 nm).[17] Analogous observations have been made for different polyene- and carotinoid-substituted dithienylethene derivatives.[16,18] The ring-closure reaction yield, on the other hand, benefits from the bpe substituents since the population of the reacting over nonreacting conformers is favored.

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Appendix

3-Bromo-2-methyl-5-thiophenecarboxaldehyde 1. 5-Methyl-thiophene-carboxaldehyde (50.0 g, 0.4 mol) was dissolved in 400 mL icy acetic acid (p.a.). A solution of 25 mL bromine (0.49 mol) in 200 mL icy acetic acid was added at room temperature to the stirred mixture over 9 h. This darkened solution was stirred intensively in the absence of light for a further 16 h at room temperature, and then it was carefully added to a 3.5 L solution of saturated aqueous sodium bicarbonate. The product was extracted with 1.5 L diethyl ether in several small amounts, and the organic phase was washed with aqueous sodium bicarbonate solution (5% w/v, 3 · 500 mL) and with water (2 · 500 mL). Then, the product was dried over Na_2SO_4, filtered, and evaporated in vacuo to give a yellow-brown solid, which was recrystallized in *n*-hexane to yield 61.9 g light yellow crystals. Mp: 57.5 °C (reference mp: 58 °C).[4,5,19] Yield: 76%. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.49$ ppm (s, 3H, $-CH_3$); 7.59 ppm (s, 1H, H-4); 9.78 ppm (s, 1H, $-CHO$).

3-Bromo-2-methyl-5-thiophenecarboxaldehyde-dimethyl-acetal 2. 3-Bromo-2-methyl-5-thiophenecarboxaldehyde (61.7 g, 0.3 mol) **1**, 50 mL trimethyl orthoformiate, and 500 mg *p*-toluoenesulfonic acid were suspended in 100 mL anhydrous methanol. This mixture was refluxed for 8 h under a nitrogen atmosphere. Water (500 mL) was then added, and the product was extracted with 0.75 L diethyl ether and washed with aqueous sodium bicarbonate solution (5% w/v, 2 · 250 mL) and water (3 · 250 mL). Removal of the solvent gave a yellow residue which was triturated in dichloromethane and subsequently purified by CC on silica gel (*n*-hexane/dichloromethane 3:1 (v/v) as eluent). The yielded pale yellow oil was dried in vacuo at 0.1 mbar, yielding 91% (reference yield: 97% yield).[4,5,19] ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.37$ ppm (s, 3H, $-CH_3$); 3.34 ppm (s, 6H, $-(OCH_3)_2$); 5.52 ppm (s, 1H, $-CH(OCH_3)_2$); 6.88 ppm (s, 1H, H-4).

1,2-Bis-(5-formyl-2-methyl-thien-3-yl)perfluorocyclopentene 4. 3-Bromo-2-methyl-5-thiophenecarboxaldehyde-dimethyl-acetal (36.42 g, 0.145 mol) **2** was dissolved in 800 mL anhydrous diethyl ether. This solution was cooled under an argon atmosphere to −78 °C. *n*-Butyllithium (93.75 mL, 0.150 mol, 1.6 M in *n*-hexane solution) was added dropwise over 20 min. The yellow-orange reaction mixture was stirred for further 10 min at −78 °C, before 14.84 g (0.070 mol) perfluorocyclopentene under cooling were added dropwise to the gradually decoloring solution, and the reaction mixture was stirred for 1 h at −78 °C and a further 3 h at room temperature. The reaction was terminated by diluting with 500 mL diethyl ether and washing with dilute hydrochloric acid (1% v/v, 2 · 500 mL), 500 mL saturated sodium bicarbonate solution, and 2 · 500 mL water. The combined aqueous phases were re-extracted with 500 mL diethyl ether, dried over $MgSO_4$, filtered and evaporated in vacuo to yield 33.8 g of the raw dimethylacetal **3.** An analytical sample of the yellow oil was obtained through CC with dichloromethane/*n*-hexane 2:1 (p.v.). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.88$ ppm (s, 6H, $-CH_3$); 3.33 ppm (s, 12H, $-OCH_3$); 5.53 ppm (s, 2H, $-CH(-OCH_3)_2$); 7.00 ppm (s, 2H, H-4).

Dimethylacetal **3** was not isolated. The protecting group was removed by direct acid hydrolysis:

16.9 g of the raw dimethylacetal **3** and 500 mg *p*-toluenesulfonic acid were dissolved in 500 mL diethyl ether. Then 1.5 L water with 1 mL aqueous 43% hydrobromic acid were added to the intensively stirred solution. The resulting yellow suspension was thereafter stirred over 72 h at room temperature. After this period, the complete reaction solution was extracted with diethyl ether (2 · 250 mL), washed with saturated sodium bicarbonate solution (2 · 250 mL) and 750 mL water, dried over Na_2SO_4, and then filtered. Removal of the solvent in vacuo, followed by trituration in dichloromethane and by purification with CC on silica gel (*n*-hexane/dichloromethane 3:1 (p.v.) as eluent) gave 6.7 g bisaldehyde **4** as a pure white powder. Mp: 182 °C. Yield: 45% (reference yield and mp: 52% and 182 °C, respectively.[4,5,19] ^{1}H NMR (300 MHz, CDCl$_3$): open form: $\delta = 2.03$ ppm (s, 6H, $-$CH$_3$); 7.75 ppm (s, 2H, H-4); 9.86 ppm (2H, s, $-$CHO). Closed form: $\delta = 2.18$ ppm (s, 6H, $-$CH$_3$); 7.74 ppm (s, 2H, H-4); 9.86 ppm (s, 2H, $-$CHO). $-$ ^{19}F NMR (200 MHz, CDCl$_3$, ref. CFCl$_3$): open form: $\delta = -109.60$ ppm (t, 4F, CF$_2$ at C-3 und C-5); -131.12 ppm (quint., 2F, CF$_2$ at C-4). Closed form: $\delta = -113.65$ and -114.50 ppm (m, 4F, CF$_2$ at C-3 und C-5); -134.091 ppm (quint., 2F, CF$_2$ at C-4). IR (solid, KBr): $\tilde{\nu}$[cm^{-1}] = 1280 cm^{-1} (C$-$F$-$Val.); 1670 cm^{-1} (CHO$-$Val.); 2870 cm^{-1} (C$-$H$-$Val.(w)). MS (70 eV, EI) *m*/*z* (%) = 424 (100) [M$^+$], 409 (65) [M$^+$-CH$_3$], 404 (8) [M$^+$-HF], 32 (19) [S$^+$]. $C_{17}H_{10}F_6O_2S_2$ (424.38) calcd.: 48.11% C, 2.38% H. Found: 47.80% C, 2.45% H.

1,2-Bis-(2-methyl-5-(2-(4-benzoyl-phenyl-1-yl)ethen-1-yl)-thien-3-yl)perfluorocyclopentene 6. 4-Benzoyl-benzyl-triphenylphosphoniumbromid (3285 mg, 6.0 mmol) **5** and 850 mg (2.0 mmol) bisaldehyde **4** were suspended under an argon atmosphere in 75 mL 1,2-epoxybutane. The initially white suspension was stirred for 5 days at room temperature in the dark, becoming a darkened mixture. Removal of the solvent gave a residue which was triturated in dichloromethane and subsequently purified by CC on silica gel (*n*-hexane/dichloromethane/ethyl acetate 3:2:1 (v/v/v) as eluent). The pale yellow-green solid was dried in vacuo at 0.1 mbar, giving 1187 mg of **6**. Yield: 76%. Mp: 63 °C. ^{1}H NMR (300 MHz, CDCl$_3$ (product contains a mixture of cis/trans isomeres): $\delta = 1.78-1.97$ ppm (s, 6H, $-$CH$_3$); 6.56$-$7.29 ppm (m, 4H, olefinic protons); 6.98 ppm, 7.09 ppm (2H, each d, thiophene-H at C-4_); 7.40$-$7.62 ppm (m, 10H, phenyl protons); 7.78$-$7.83 ppm (m, 8H, benzoyl protons). ^{19}F NMR (200 MHz, CDCl$_3$, Ref. CFCl$_3$) open form: $\delta = -110.54$ ppm (m, 4F, CF$_2$ at C-3 and C-5); -132.24 ppm (m, 2F, CF$_2$ at C-4). Closed form: $\delta = -112.97$ and -115.06 ppm (m, 4F, CF$_2$ at C-3 und C-5); -135.14 ppm (m, 2F, CF$_2$ at C-4). IR (solid, KBr): $\tilde{\nu}$[cm^{-1}] = 710, 750, 800 (phenyl); 990 (C$-$H$-$Val. (conjug.$-$C=C$-$)); 1285 cm^{-1} (C$-$F$-$Val.); 1605 cm^{-1} ($-$C=C$-$Val.(phenyl)); 1660 cm^{-1} ($-$C=O$-$Val.-(aryl)). MS (70 eV, EI) *m*/*z* (%) = 781 (10) [M$^+$], 602 (6) [M^{+-}C$_{13}$H$_9$O], 260 (56) [M$^{3+}{}_{3e-}$], 180 (2) [C$_{13}$H$_9$O$^+$], 105 (66) [C$_7$H$_5$O$^+$], 77 (30) [C$_6$H$_5$$^+$], 44 (100), 32 (58) [S$^+$]. $C_{45}H_{30}F_6O_2S_2$ (780.85) calcd.: 69.22% C, 3.87% H. Found: 69.63% C, 4.08% H.

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