J. Phys. Chem. A **2005,** *109,* 9437−9442

Ring Closure Dynamics of BTE-Based Photochromic Switches: Perfluoro- versus Perhydrocyclopentene Derivatives

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Received: June 22, 2005; In Final Form: August 26, 2005

The switching behavior of 1,2-bis(5-phenyl-2-methylthien-3-yl)perfluorocyclopentene and its nonfluorinated (perhydro) analogue are compared. For both molecules, the dynamics after optical excitation can be separated into three regimes: preswiching due to excited state mixing; the ring closure itself; postswitching related to vibrational cooling. The fluorinated version switches faster than its nonfluorinated analogue by about a factor of 4.7. This is explained by electronic level shifts near the crossing region between the S_1 and S_0 potential energy surfaces. In the nonfluorinated molecule the various levels involved in the switching have well-separated transition frequencies, which allow for a clear interpretation of experimental data. Thus, the fluorinated molecule makes a better (more efficient and faster) switch, but the nonfluorinated molecule provides a better model system for fundamental studies.

I. Introduction

Recently diarylethenes with heterocyclic aryl groups have been developed as a new class of thermally irreversible photochromic switches.[1,2] For practical applications in optoelectronic and photooptical devices, the photochemical switching process is required to be thermally irreversible, and the photochromic compounds should have a large quantum yield of switching as well as high fatigue resistance. Because reactions in the excited state generally occur in competition with various radiative (fluorescence and phosphorescence) and nonradiative (internal conversion, intersystem crossing) processes, a large rate constant of the photochromic reaction is indispensable to ensure a high quantum yield and avoid photodegradation. Bis(thienyl)*perfluoro*cyclopentene derivatives fulfill all these requirements, and therefore, they are regularly used and studied.[1]

Lately we have developed bis(thienyl)cyclopentenes in which the fluorine substituents on the central cyclopentene ring are replaced by hydrogens.[3,4] The synthesis of these *perhydro*cyclopentene derivatives can be performed on a large scale starting from simple chemicals, and the basic switch can be easily derivatized. In this respect these switching systems possess advantages compared to the perfluorocyclopentenes. In Figure 1 the chemical structures of 1,2-bis(5-phenyl-2-methylthien-3-yl){perfluoro}cyclopentene (B-DT{F}CP) in the open- (**1A**) and closed- (**1B**) ring configurations are presented. Here, the central cyclopentene ring has two phenylthiophene chromophores on both sides.

The photochromic properties of B-DTCP and B-DTFCP are remarkably similar.[5] The quantum yield of the ring closure reaction was found to be 0.6 ± 0.1 for both. However, the photostability of the perfluorinated analogue was found to be roughly 2½ times higher than that of the nonfluorinated compound.[5] The dynamics of the switching behavior of B-DTCP was studied in detail with femtosecond nonlinear optical experiments and density functional calculations.[6] In this paper we present the results of similar time-resolved experiments on B-DTFCP. The differences between the switching dynamics of B-DTCP and B-DTFCP are rationalized using semiempirical calculations. To our knowledge, in the work presented here for the first time an explicit comparison between the ultrafast ring closure dynamics of fluorinated and nonfluorinated bis(thienyl)ethenes is given.

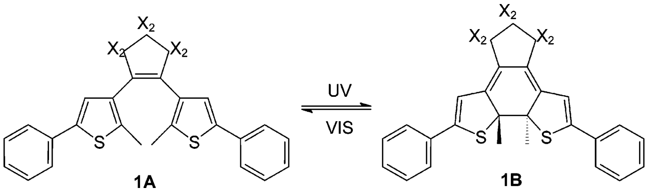

Figure 1. Chemical structures of the bis(thienyl)cyclopentenes B-DTCP (X = H) and B-DTFCP (X = F), in the open (**1A**) and closed (**1B**) form. Interconversion is possible by irradiation with UV (**1A** → **1B**) and with visible (**1B** → **1A**) light.

The paper is organized as follows: in section II the experiments are briefly described. The results of femtosecond pump−probe experiments are presented in section III. The influence of fluorination on the reaction dynamics is discussed in section IV, and conclusions are formulated in section V.

II. Experimental Section

B-DTFCP was synthesized starting from 1,2-bis(5′-chloro-2′-methylthien-3′-yl)perfluorocyclopentene[7] via a Suzuki reaction according to a slightly modified procedure described by Tsivgoulis and Lehn.[8] For the optical experiments, compound **1A** was dissolved in cyclohexane (pa, Merck) at a concentration of 0.7 mM. The solution was circulated at a speed of about 3 mL/s using a peristaltic pump system, to ensure that fresh sample was available for every single measurement. The optical density

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10.1021/jp053386e CCC: $30.25

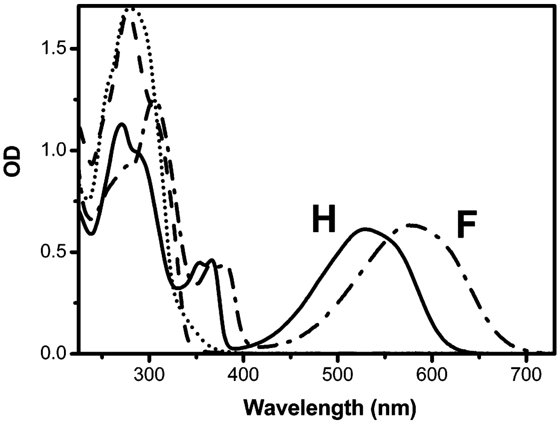

Figure 2. Steady-state absorption spectra of B-DTCP (H) and B-DTFCP (F) in cyclohexane. The spectra of the closed forms of B-DTCP and B-DTFCP are indicated by the solid and dash−dotted lines, respectively. The spectra of the open forms of B-DTCP and B-DTFCP are shown as the dashed and dotted lines.

of the sample did not exceed 0.3, ensuring homogeneous excitation. The experiments were performed at room temperature ($T = 294$ K).

Femtosecond frequency resolved pump−probe experiments were performed as described elsewhere[6] by using a 1 kHz Ti: sapphire laser system (Hurricane, Spectra Physics) and optical parametric amplifiers (Light Conversion). The excitation wavelength was 310 nm, while the probe wavelengths covered the full visible wavelength range (see next section). The cross-correlation function of the pump pulse centered at 310 nm and the probe pulse centered at 600 nm, as measured by monitoring two-color two-photon absorption in a 100-μm glass plate, has a width of about 90 fs fwhm. In the fitting procedures, the finite time resolution was taken into account by convoluting decay functions with the relevant system response function. The measurements were carried out in the magic angle configuration, to avoid artifacts due to rotation of molecules during the dynamics.

III. Results

3.1. Steady-State Absorption Spectra. The photochromic reaction of bis(thienylethene)-based switches is based on a reversible ring closure reaction. The ground-state interconversion between the isomers is prohibited, but upon UV-irradiation **1A** converts to **1B** (see Figure 1). As a consequence, π-conjugation spreads throughout the molecule which results in the appearance of a new red shifted absorption band. Upon visible irradiation of **1B** the ring opens again to yield the initial open form **1A**.

The steady-state absorption spectra of B-DTCP and B-DTFCP in the open and closed form are presented in Figure 2. In the open form, the spectra of the fluorinated and the nonfluorinated analogues of the photochromic switch are rather similar to each other as well as to the spectrum of the phenylthiophene chromophore that is attached on both sides to the central cyclopentene bridge.

It has previously been noted[6,9] that in the open form of these switches the phenylthiophene moieties interact only weakly and that the lowest energy excitation of the switch therefore closely resembles the first excitation of the chromophores. In this light it is not surprising that fluorination of the central cyclopentene ring does not significantly influence the open-form spectrum. Since π-conjugation spreads across the central bridge when the switch closes, fluorination does have a pronounced effect on the excitation energies of the π-electron system of the closed form. Although the absorption spectra are very similar in shape for both analogues, the spectrum of closed-form B-DTFCP features a substantial red shift of about 1500 cm^{-1} (0.19 eV). This red shift can be qualitatively explained by the larger electron affinity of the fluorinated cyclopentene bridge, which lowers the lowest unoccupied molecular orbital (LUMO) and therefore gives a smaller S_0−S_1 energy gap.

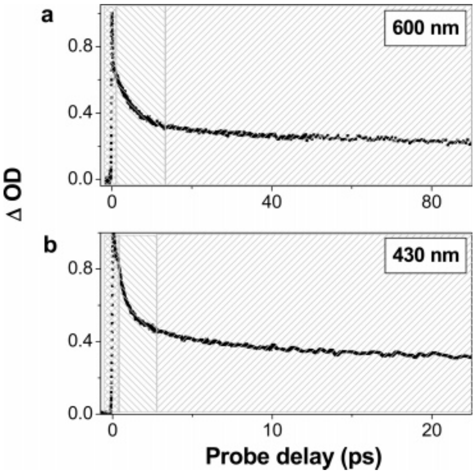

Figure 3. Normalized pump−probe transients for (a) B-DTCP and (b) B-DTFCP. The probe wavelengths are indicated in the panels. Areas corresponding to preswitching, switching and postswitching dynamics are marked by XXX, [\\\], and ///, respectively.

3.2. Dynamics of Switching. In Figure 3, typical pump−probe transients are shown for both B-DTCP and B-DTFCP. In these transients, three distinct time regimes can be distinguished. There is ultrafast response, with a typical time scale of a few tens of femtoseconds, then dynamics in the range of about a picosecond, and finally transient behavior at a few tens of picoseconds. In our previous publication[6] on the ultrafast dynamics of B-DTCP, we referred to these three time windows as preswitching, switching, and postswitching dynamics, being due to ultrafast state mixing, ring closure, and vibrational cooling, respectively. It is clear from Figure 3 and other results, presented below, that a similar distinction in transient behavior can be made for B-DTFCP. Thus, we will discuss the similarities and differences in the ring closure dynamics of B-DTCP and B-DTFCP within this framework.

3.3. Preswitching Dynamics. The contour plots presented in Figure 4 summarize the preswitching dynamics of B-DTCP and its fluorinated analogue B-DTFCP. The spectrum of B-DTCP (plot a) peaks immediately after excitation at about 450 nm. Very rapidly this band relaxes and a new absorption feature appears on the red side that rapidly shifts from about 550 nm when it is formed to about 510 nm at a delay of 200 fs.

At first sight, the dynamics of B-DTFCP looks quite different from that of B-DTCP. The contour plot b of Figure 4, although resembling some aspects of plot a in a general way, displays much less structure. However, it turns out that the basic processes are the same, only less clearly observable. To visualize spectral dynamics a contour plot c of the Figure 4 is constructed from pump−probe transients which are normalized to unity. In this representation of the experimental data, which is not sensitive to decay processes and illustrates how the shape and position of the pump−probe spectrum change in time, it becomes clear that again a precursor−successor dynamics occurs and also a rapid blue shift of the second absorption maximum. The absorption band of the originally excited state is a bit

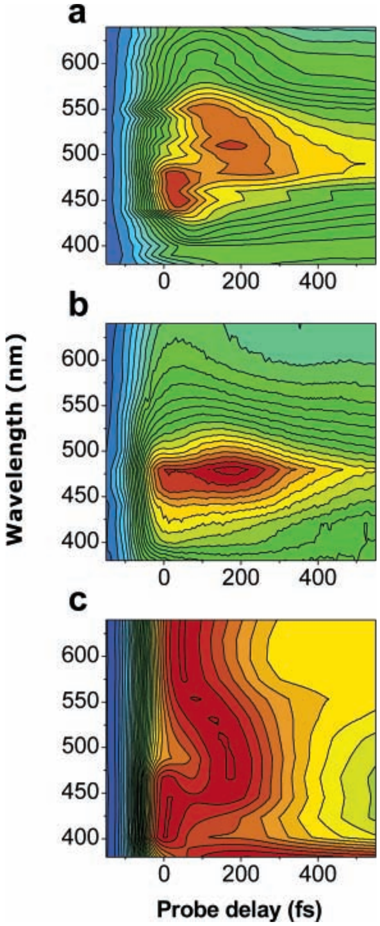

Figure 4. Contour plots representing the subpicosecond dynamics of (a) B-DTCP and (b) B-DTFCP. In contour plot c, the pump−probe transients of B-DTCFP are normalized to get a better view of the subpicosecond dynamics. The shift continues until the absorption maximum reaches about 490 nm. As discussed in our previous publication,[6] the dynamics display a two-state precursor−successor relation: the decay of the initial photoinduced absorption on the blue side of the spectrum occurs with the same time constant as the rise of the signal on the red side. This precursor−successor relation is modified by a rapid spectral shift, during which also line broadening and a small drop in intensity occur. After about 500 fs no spectral changes occur anymore and only an overall decay of the spectrum with a time constant of 4.2 ps is observed.

broader, from 420 to 450 nm, and the blue-shift goes a bit farther, from 550 to 475 nm, but these are relatively minor details.

The absorption spectra of the initially excited states, although somewhat different in detail, resemble for both B-DTCP and B-DTFCP the photoinduced absorption spectrum of the phenylthiophene chromophore. The fact that these three spectra are similar to each other confirms the weak coupling between the chromophores in the initially excited state.[6,9,10] Ring closure does not occur immediately, on a femtosecond time scale, but rather on a (sub)picosecond time scale. The formation of the successor state happens so fast that the nuclear displacements, necessary for ring closure, cannot have taken place yet. Instead, as we argued before,[6] rapid mixing of electronic states, accompanied by motion on the excited-state potential energy surfaces, gives rise to the observed precursor−successor behavior and rapid blue shift.

The B-DTCP transients could be fitted by applying a model[6] that accounts for both the precursor−successor relation (70 ± 15 fs) and for the subpicosecond spectral shift (150 ± 30 fs). Due to the small amplitude of the absorption changes, it is more difficult to extract the corresponding numbers for B-DTFCP from the experimental data. However, if we fit solely in the spectral region 580−640 nm, in the red wing of the absorption spectrum of the successor state, we find a time constant of 50 ± 10 fs for the precursor−successor relation and 120 ± 30 fs for the blue shift in the case of B-DTFCP. Apparently, the fluorination of the central cyclopentene ring speeds up the preswitching dynamics. Since the time scale of the ultrafast dynamics is very close to the time resolution of the experiments, in the fitting procedure the multiexponential functions were convoluted with the cross-correlation function of pump and probe pulses, as measured by sum frequency generation.

The smaller amplitude of the spectral changes found in the case of the fluorinated species is caused by the stronger overlap between the spectra of the precursor and successor states, by the faster dynamics, and maybe by the fact that the successor state is to some extent directly excited by the laser field, so that less population redistribution between the states occurs.

3.4. Ring Closure. Following the preswitching dynamics, the intermediate excited state of B-DTCP was found in ref 6 to relax to the hot ground state of the closed form with a time constant of 4.2 ± 0.6 ps. The decay of the successor state absorption at 490 nm, discussed above, and the formation of the closed-form ground-state absorption at 530 nm (see Figure 2) is evidence for this process. In the case of B-DTFCP multiexponential fits of the transients disclose several processes, which we will discuss one by one. These processes occur with time constants of 170 ± 20 fs, 0.9 ± 0.1 ps, and 7 ± 1 ps.

The dominant time constant is 0.9 ps, which resembles the previously reported values of 1−3 ps that were obtained for different types of bis(thienyl)perfluorocyclopentenes and were ascribed to the ring-closure process in the central part of the molecule.[9,10,11] The assumption that the ring closure is involved is supported by the fact that a decay with this time constant is seen in spectral regions where absorption of the closed-ring conformer is negligible, whereas a rise with this time constant is observed at wavelengths close to the maximum of steady-state absorption of the closed form of B-DTFCP (around 590 nm). Therefore, it can be concluded that the 0.9 ps process is caused by the ring closure, i.e., by the transition from the successor excited state that is populated in the preswitching dynamics to the ground state of the closed form. Consequently, it can be concluded that fluorination of the central cyclopentene ring speeds up the ring closure by about a factor of 4.7 compared to the nonfluorinated molecule in case of this particular photochromic switch.

After switching of B-DTFCP had occurred, the steady-state spectrum of the closed form still was not obtained. Apart from dynamics at tens of picoseconds, to be discussed below, a strong feature is seen at about 475 nm after the 0.9 ps decay has taken place. Figure 5 displays how this band and also some absorption on the far red side at about 690 nm decays with a time constant of 7 ps. In the case of B-DTCP a band with a maximum at around 430 nm was reported,[6] which decayed with a time constant of about 100 ps. It was concluded that this decay channel involves the relaxation of electronically excited open-form molecules that cannot participate in the switching process. NMR data[12,13] on bis(thienyl)cyclopentenes in solution indicate a close to 1:1 ratio between conformers in which the two central CH_3 groups point either in the same (C_s symmetry) or in opposite direction (C_2 symmetry). Only the conformer possessing C_2 symmetry can undergo the ring-closure reaction in the conrotatory fashion prescribed by the Woodward−Hoffmann rules.[14] Consequently, only about half of the total amount of

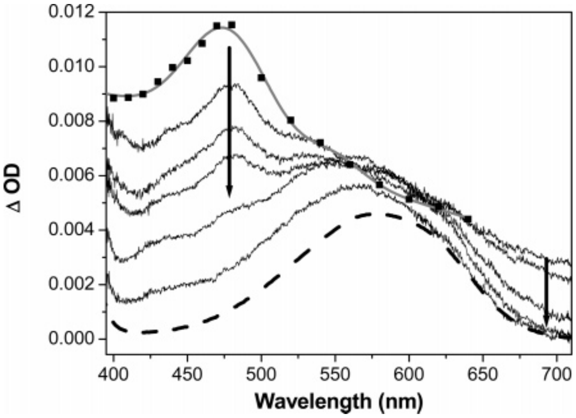

Figure 5. Spectral dynamics of B-DTFCP on a picosecond time scale. The pump−probe spectra are shown from top to bottom at probe delays of 1, 5, 10, 20, 50, and 100 ps, respectively. The arrows indicate the disappearance of the absorption of the nonswitchable conformers with a time constant of 7 ps. The steady-state absorption spectrum of B-DTFCP in the closed form is given by the dashed line.

excited molecules are capable of switching while the other half is expected to eventually relax back to the ground state of the open form. From the analogy between the observations made in the cases of B-DTCP and B-DTFCP we can then identify the band centered at 475 nm as the photoinduced absorption band of the nonswitchable conformers of the fluorinated molecules. Apparently, the fluorination not only speeds up the switching process but also the internal conversion between the S_1 and S_2 potential energy surfaces of nonswitchable molecules, so that the relaxation goes from 100 ps for B-DTCP to 7 ps for B-DTFCP. This may be part of the explanation for the higher photostability of the fluorinated analogues.[5]

Finally, on the blue side of the spectrum a weak process with a time constant of 170 fs is observed. This also resembles the case of B-DTCP, where an extra decay with a time constant of 325 fs had to be added to fit the pump−probe transients in the spectral region where the nonswitchable conformers absorb.[6] The process was attributed to the ultrafast state mixing of the initially excited state of the nonswitchable conformers, similar to the preswitching dynamics of the switchable conformers. In the case of the fluorinated analogue B-DTFCP the 170-fs component possesses the same spectral behavior; i.e., its relative weight follows the photoinduced absorption spectrum of the nonswitchable conformers.

3.5. Postswitching Dynamics. On a few tens of picoseconds time scale, some absorption changes occur in addition to the ones described previously. As can be seen in Figure 5, the maximum of the ground-state absorption band of the closed form undergoes a small red shift under the influence of the 7 ps decay of the 475 nm band. Figure 5 also shows that spectral narrowing proceeds on a much slower time scale. Even at the longest delay the steady-state absorption spectrum has not been fully obtained. A similar situation was observed in the case of the nonfluorinated switch,[6] for which it was concluded that the spectral narrowing indicates vibrational cooling of the closed-form ground state. This occurs for both B-DTCP and B-DTFCP during the first 100 ps after excitation.

IV. Discussion

Recently there have been many discussions in the literature on the pathway of the ring closure reaction. Woodward−Hoffmann rules for electrocyclic reactions[14] predict in the case of 6π-electron ring closure a concerted one-step mechanism through a conrotatory path in the excited state.[15] Indeed, no intermediates in the pathway of the ring closure reaction were found by Ern et al.[11] in the case of 1,2-bis(5-formyl-2-methylthien-3-yl)perfluorocyclopentene, by Ohtaka et al.[16] in the case of diarylethene derivatives with terthiophene, and by Owrutsky et al.[10] in the case of 1,2-bis(5-pyridyl-2-methylthien-3-yl)perfluorocyclopentene. In contrast, Tamai et al.[9] for a diarylethene structure with thiophene oligomers as side groups, Ern et al.[17] for 1,2-bis(5-anthryl-2-methylthien-3-yl)perfluorocyclopentene, and Bens et al.[18] for a di-bpe dithienylethene reported the existence of intermediate states from which the ring closure reaction occurs. Most experimental studies were performed with a time resolution of a few hundreds of femtoseconds.

As shown in the previous section for B-DTCP and B-DTFCP, excited-state preswitching dynamics may occur on ultrafast time scales. This means that in principle a time resolution of a few tens of femtoseconds is necessary to be able to trace these processes. Moreover, the presence of preswitching is not always easily detectable. For B-DTCP a rather clear picture of the ultrafast dynamics could be easily constructed from the experimental data.[6] However, upon fluorination all processes speed up considerably and in addition the preswitching dynamics is obscured by the fact that the photoinduced absorption bands of the initially excited precursor state and the successor state strongly overlap. This leads to relatively small experimental signatures of the dynamics that takes place.

To obtain a better understanding of the observed speeding up of both the preswitching dynamics and the ring closure upon fluorination, a series of semiempirical calculations of the ground and excited states of both B-DTCP and B-DTFCP was performed at different fixed distances between the carbon atoms that produce the σ-bond ring closure. Ground-state structure optimization was performed at each fixed carbon−carbon distance using the AM1 method, while subsequently the manifold of excited states was calculated using the ZINDO/S method with configuration interaction using 10 occupied and 10 unoccupied molecular orbitals. The calculations were performed for conformations that have approximate C_2 symmetry, which are the switchable molecules, but no symmetry restrictions were imposed on the system. The resulting potential energy surfaces are plotted in Figure 6. Similar results were previously obtained by Ern et al.,[11] as well as by Guillaumont et al.[19] and Boggio-Pasqua et al.,[20] using CASSCF methods.

In Figure 6 is shown that the ground-state potential features minima for large (about 3.8 Å) and small (about 1.5 Å) carbon−carbon distances. These can be assigned to the open and closed forms, respectively. Vertical excitation of the open form brings the switch into a region with a high density of electronic states, some of which are dark. Following the excitation we can therefore expect that fast mixing of these close-lying states takes place. This explains the fast precursor−successor relation observed in the pump−probe experiments.[6]

As was found previously by Guillaumont et al.[19] and is shown in Figure 6 for B-DTCP, the first few excited states of the open form come in nearly degenerate pairs, which under strict C_2-symmetry restrictions would closely resemble the symmetric and antisymmetric linear combinations of excitations on the thienyl chromophores. Figure 6 also shows that fluorination of the bridge decreases the energy separation between the first and second excited-state pairs to the extent that they cannot be distinguished anymore. This is reflected in the absorption spectra of the open forms of B-DTCP and B-DTFCP: the two bands that dominate the absorption spectra of the open forms in Figure 2 in the spectral region above 30 000 cm^{-1} are better separated

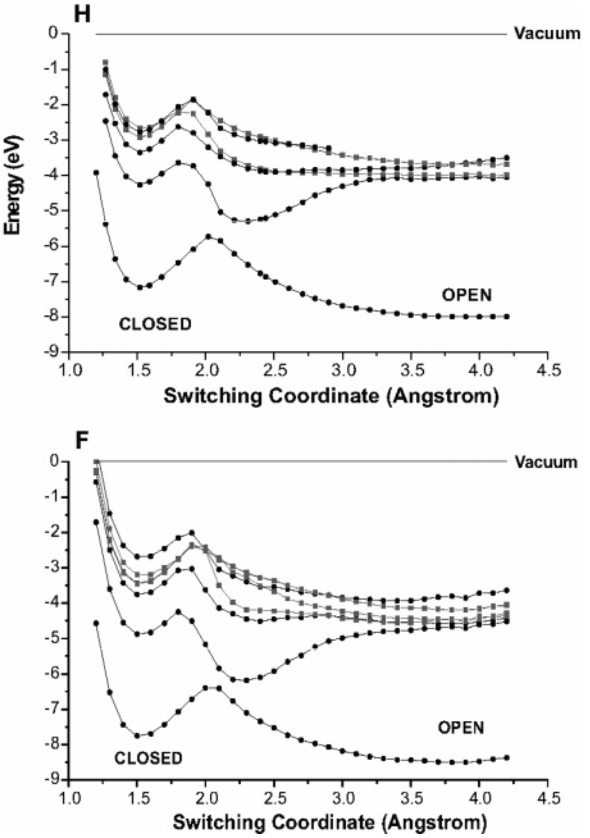

Figure 6. Ground- and excited-state potential energy surfaces of B-DTCP (top) and B-DTFCP (bottom), according to semiempirical calculations (see text). These curves were calculated as a function of the separation between the carbon atoms on the 2-positions of the thienyl chromophores, which approximates the ring closure coordinate. Black lines/dots indicate the ground state and excited states that have high oscillator strength from the ground state. Gray lines/squares denote (nearly) dark states.

in the perhydro case. Also, the smaller separation between the excited-state pairs in the case of the perfluoro switch is expected to result in faster state mixing, which explains the observed speeding up of the precursor−successor relation.

The form of the S_1 excited-state potential in Figure 6 indicates that relaxation will take place, reducing the C−C distance from about 3.8 Å after optical excitation of the open form to about 2.2 Å at the minimum of the excited-state potential. We identify the observed subpicosecond spectral shift with this relaxation. The energy lowering due to this partial ring closure in the excited state is larger in the case of B-DTFCP, and the ground- and excited-state potentials therefore approach each other closer than in B-DTCP. This larger energy relaxation in B-DTFCP is caused by the interaction of the fluorine atoms on the π-electron system. Whereas this interaction is rather weak in the open form, it becomes stronger when the chromophores become more coplanar with the cyclopentene bridge and the π-electrons start to delocalize over the central bridge, i.e. when going to smaller C−C distances. This energy lowering effect was already mentioned in section 3.1, where the red shift was discussed of the absorption spectrum of the closed form of B-DTFCP compared to B-DTCP. As a result of the closer approach of the S_1 and S_0 energy surfaces at a C−C distance of about 2.2 Å, internal conversion to the ground state is faster for B-DTFCP and the formation of the closed form occurs at a substantial higher rate, in accordance with the observations.

It should be mentioned here that the theoretical results, presented in this paper, differ from the ones in our paper on the dynamics of B-DTCP.[6] In that publication, time-dependent density functional theory (TDDFT) in the local adiabatic density approximation (ALDA) was used. Recently, it has become clear that this method often gives poor results in describing $\pi-\pi^*$ excitation energies in extended π-conjugated systems.[21,22]

V. Summary and Conclusions

The switching behavior of the bis(thienyl)cyclopentenes B-DTCP and B-DTFCP was studied in detail with femtosecond frequency resolved pump probe experiments. A comparison of the population dynamics during ring closure revealed similar pathways of the reactions in the two cases. Semiempirical calculations provided a general picture of the reaction pathway: first, the initially excited state rapidly mixes with nearby dark states, which is followed by excited state relaxation to a partially ring-closed state. Second, population transfer to a hot ground state of the closed form takes place; this we term the actual switching process. Third, the vibrationally hot ground state of the closed conformer relaxes to thermal equilibrium. This completes the switching process. Simultaneously, in the relaxation of conformers that are not capable of switching due to symmetry reasons, the conformers experience also preswitching dynamics (state mixing) and population relaxation to the ground state of the open form.

From the comparison of the dynamics of B-DTCP and B-DTFCP it is evident that the fluorination of the central cyclopentene ring causes faster preswitching. Speeding up of the state mixing process from 70 to 50 fs can be rationalized by the fact that the density of states near the initially excited, bright state is higher. The excited-state relaxation occurs somewhat faster, from 150 to 120 fs, due to the slightly larger slope of the excited-state potential.

Fluorination also speeds up the rate of the switching dynamics, from 4.2 to 0.9 ps. The ring closure occurs due to internal conversion from the excited to the ground state in a partially ring-closed configuration at a central carbon−carbon atom distance of about 2.2 Å. The increased rate is explained by the smaller energy separation of the S_1 and S_0 potential energy surfaces of B-DTFCP near the crossing region. The quantum yield is unaffected because in the case of the nonfluorinated compound the reaction already proceeds at near 100% efficiency for the molecules which have a suitable (near C_2) conformation. However, in applications where there are competing processes on a few-picosecond time scale (for instance resonance energy transfer between neighboring chromophores), the ring closure quantum yield of the *perfluoro* switch is predicted to be generally higher.

While the characteristics of the dynamical processes point to the fluorinated switch as being better, i.e., faster and more efficient, than the nonfluorinated switch, the latter provides a clearer experimental picture of the mechanisms that are involved. The analysis of the dynamics in the case of B-DTFCP is rather complicated because the photoinduced absorption spectra of the initially excited state, the successor state, and the excited state of the nonswitching conformers largely overlap. This is in contrast with the case of the nonfluorinated switches where these spectra are fairly clearly separated. This makes the nonfluorinated analogue a better model system for fundamental investigation of the reaction dynamics in bis(thienyl)ethenes.

Acknowledgment. This work was supported by the “Nederlandse organisatie voor Wetenschappelijk Onderzoek” (NWO). The Royal Netherlands Academy of Sciences is gratefully acknowledged for a fellowship for J.H.v.E.

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