

Femtosecond reaction dynamics of a photochromic dithienylethene derivative

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Dedicated to Professor Günter Wulff on the occasion of his 65th birthday

Abstract

The dynamics of the photochromic ring-closure reaction of 1,2-bis[5-formyl-2-methyl-thien-3-yl]perfluorocyclopentene (CHO-BMTFP) in dichloromethane were monitored by fs transient absorption spectroscopy. The open isomer was excited using a 260 fs pump pulse tuned to the S_0 – S_1 absorption transition at 308 nm. A temporally delayed white-light continuum probe pulse measures the rise dynamics of the ground-state absorption spectrum of the closed isomer which exactly displays the monoexponential dynamics of the ring-closure reaction with a time constant of about 2.3 ps. These spectroscopic data are discussed in terms of a model potential calculated in the collective electronic oscillator (CEO) approach. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Photochromic dithienylethene derivatives, constituting molecular optical switches, have motivated intense experimental and theoretical research work [1–7]. The photochromic electrocyclic reactions of these compounds occur photochemically in the conrotatory mode, while the thermally induced ground-state reaction, predicted to take place in the disrotatory mode, is sterically hindered by the two trans-standing methyl groups in the 2' position of the thiophene rings. Fig. 1 shows the absorption spectra of the open isomer (solid line) and closed isomer (dashed line) of 1,2-bis[5-formyl-2-methyl-thien-3-yl]perfluorocyclopentene (CHO-BMTFP). The structure formulas of both isomers are depicted in the inset. The assignment of the absorption bands to the excited singlet states is based on collective electronic

oscillator (CEO) calculations of the respective isomers of CHO-BMTFP, geometry optimized at the AM1 level [6]. Upon UV irradiation, the open isomer undergoes a ring-closure reaction, while the ring-opening reaction may be induced by excitation with visible light. Previous time-resolved studies of electrocyclic reactions in other dithienylethene derivatives have shown that both ring-opening and closure processes occur on the ps time scale [3–6]. Very recently we have reported on fs transient absorption spectroscopy studies of the ring-opening reaction dynamics of CHO-BMTFP in dichloromethane solution [6]. 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 [6], performed in the recently developed collective electronic oscillator (CEO) approach [8,9]. The S_0 , S_1 , and S_2 potential energy hyperlines constitute sections of the potential energy surfaces of the S_0 , S_1 , and S_2 states along the reaction coordinate q , which is defined as the distance between the two C atoms, where the bond breaking takes place (see Fig. 2). Within the first picosecond after excitation to

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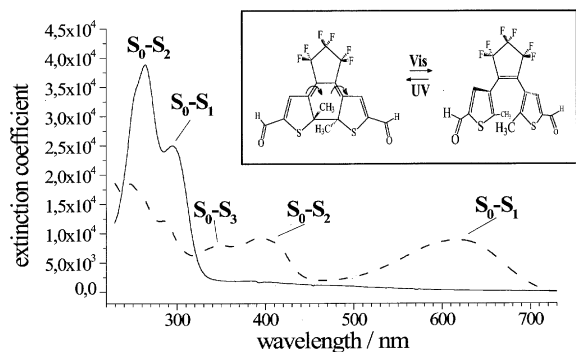


Fig. 1. Absorption spectra of the open (solid line) and closed (dashed line) isomer of CHO-BMTFP in CH_2Cl_2 ; the inset shows the structure formula of the open (right) and closed (left) isomer of CHO-BMTFP.

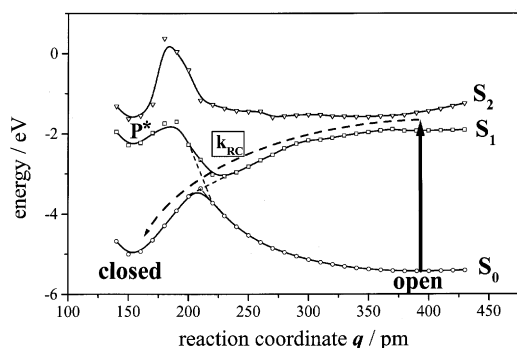


Fig. 2. Schematic illustration of the S_0 , S_1 , and S_2 potential energy surfaces as sections along the reaction coordinate q ; P^* denotes the precursor of the ring-opening reaction.

the S_1 state, the closed isomer CHO-BMTFP is observed to undergo a fast structural relaxation along the S_1 potential energy surface into the minimum P^* constituting a precursor of the ring-opening process. The rather long lifetime of the precursor, $\tau_2 = 13$ ps, is determined by radiationless deactivation to the S_0 -state of the closed isomer, so that the time constant of the ring opening reaction is rather long $\tau_{\text{RO}} \approx 325$ ps. This rationalization is confirmed by the calculated S_1 potential energy hyperline exhibiting a potential barrier in front of the conical intersection with the S_0 state potential energy surface (see Fig. 2).

Here we present fs transient absorption measurements of the ring-closure reaction dynamics of CHO-BMTFP dissolved in dichloromethane. The open isomer CHO-BMTFP has been excited to the S_1 state using 260 fs pump pulses at 308 nm. The temporally delayed white-light probe pulses directly monitor in the range of 400–800 nm the ring-closure reaction dynamics by measuring the rise of the ground-state absorption spectrum of the closed isomer.

2. Experimental

Transient absorption spectra with fs time resolution were measured using the pump–probe technique. Pump and probe pulses are generated by a fs laser system consisting of a passively mode-locked Ti:sapphire laser oscillator (Clark-MXR, NJA-4), a regenerative Ti:sapphire amplifier (Clark-MXR, TRA-1), and an optical parametric amplifier (Clark-MXR, V-GOR). The optical parametric amplifier (OPA) produces, at a repetition rate of 600 Hz, 140-fs pulses with energies between 1 and 30 μJ , which were tuned to 616 nm and converted by a 200 μm -thick BBO crystal, cut at $\theta = 33^\circ$, into its second harmonic at 308 nm with a pulse width of about 260 fs. These frequency-doubled OPA pulses are used as pump pulse beam. White-light continuum probe pulses with a time dispersion of 1.4 ps are generated by focussing the remainder of the fundamental laser pulses (0.2 mJ per pulse), amplified in the OPA, into a 1 cm D_2O flow cuvette. A variable delay line provides a temporal delay (τ_D) for the pump pulses of up to 100 ps with a resolution of 2.4 fs. The polarization of the pump pulse was set by a prism polarizer into the magic angle to that of the probe pulse. The intensity of the transmitted probe beam with and without pump pulse excitation, $I(p)$ and $I(0)$, respectively, was measured by chopping the pump pulse beam at a frequency of 6 Hz. The ratio, $I(p)/I(0)$, corresponding to the pump pulse induced change of the transmission, $\Delta T = T(p)/T(0)$, is determined with a precision of 10^{-3} . The time dispersion of 1.4 ps over the spectral range of the white-light continuum probe pulses has been corrected for by determining the $\tau_D = 0$ point from the rise of the bleaching or transient absorption signals at spectral intervals of about 80 cm^{-1} . 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.

CHO-BMTFP, synthesized and purified as reported by Gilat et al. [2], was dissolved in spectrograde dichloromethane at a concentration of 6.4×10^{-4} mol/l. The solution was pumped at 5 ml/s through a 400 μm flow cell.

3. Results and discussion

The closed isomer of CHO-BMTFP were excited to the S_1 state using 260 fs pump pulses at 308 nm. The excited-state relaxation of the open isomer as well as the rise dynamics of its steady-state absorption spectrum of the closed isomer between 400 and 800 nm were monitored by the temporally delayed white-light probe beam. The time evolution of the transient absorption spectra between -1.4 and $+5.8$ ps is shown in Fig. 3. The spectrum at $\tau_D = -1.4$ ps provides the baseline with $\Delta T(\lambda) \approx 1$. The transmission changes with $\Delta T(\lambda) < 1$ in the spectral ranges 400–450 and

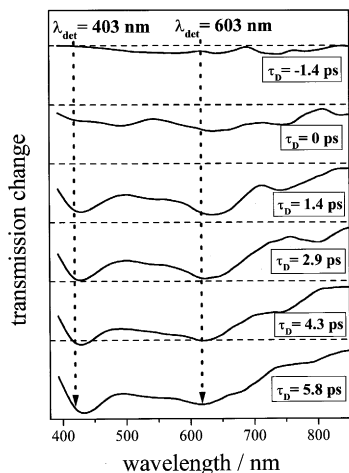


Fig. 3. Temporal evolution of the transient absorption spectra recorded at delay times τ_D between -1.4 and $+5.8$ ps. The pump-pulse wavelength is 308 nm.

470 – 710 nm arise in main from the S_0 – S_2 and S_0 – S_1 absorption transitions of the closed isomer (see Fig. 1), respectively, while the photoinduced transmission changes between 700 and 800 nm are ascribed to S_1 – S_n absorption transitions of the open isomer. The time dependence of the photoinduced transmission changes recorded at a fixed wavelength $\lambda = \lambda_0$ (i.e. $\Delta T(\tau_D)$) is denoted as transient of absorption ($\Delta T(\tau_D) < 1$). Fig. 4 depicts the transients of photoinduced absorption detected at $\lambda_{det} = 403$ nm (top panel) and $\lambda_{det} = 603$ nm (bottom panel) which are representative for the time evolution of the S_0 – S_2 absorption and S_0 – S_1 absorption of the closed isomer, respectively. These decay curves of transmission change (i.e. rise curves of photoinduced absorption) can be described by the exponential decay function $A_0 \times (1 - \exp(-\tau_D/\tau_L))$ with the time constant $\tau_L = 2 \pm 0.2$ ps that is the lifetime of the S_1 state of the open isomer (see Fig. 4: thick solid lines). The rate and time constant of the ring-closure reaction, k_{RC} and τ_{RC} , can be directly obtained from the ring-closure reaction quantum yield of $\Phi_{RC} \approx 86\%$ [7] with $1/k_{RC} = \tau_{RC} = 2.3 \pm 0.2$ ps. This result agrees with the ring-closure reaction time constant of about 1.1 ps, which has been obtained by analogous investigations of the open isomer of an oligothiophene derivative of BMTFP [3]. Moreover, the rather short time constant $\tau_{RC} = 2.3 \pm 0.2$ ps confirms the course of the S_1 potential energy hyperline of the potential model for the ring-closure reaction (see Fig. 2: 260 – 400 pm), which predicts a fast decay of the pump-pulse prepared S_1 state of the open isomer. These decay dynamics are essentially determined by structural relaxation along the barrierless S_1 potential energy hyperline via the conical intersection to the S_0 state of the closed isomer (see Fig. 2: broken-line arrow). This rationalization of the ring-closure reaction

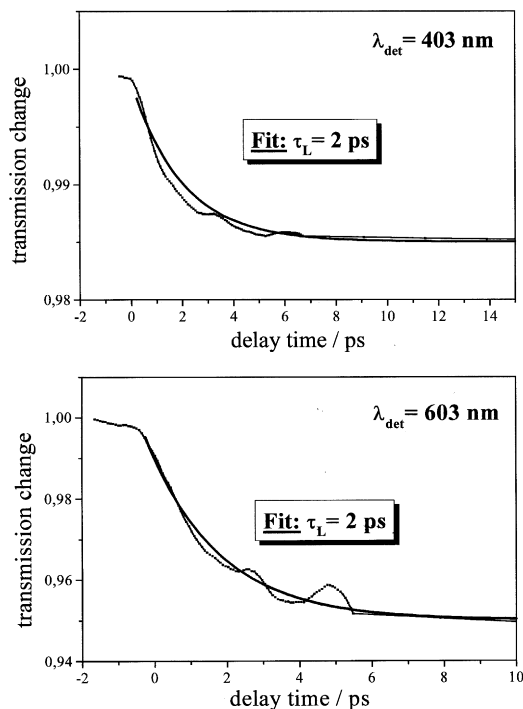


Fig. 4. Transients of photoinduced absorption detected at 403 nm (top) and 603 nm (bottom).

kinetics completes the results which have been recently obtained by analogous investigation of the associated ring-opening reaction dynamics [6], so that the complete elucidation of the photochromic reaction kinetics and mechanism of CHO-BMTFP has been achieved.

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