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Primary processes in photochemistry of 2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-enone

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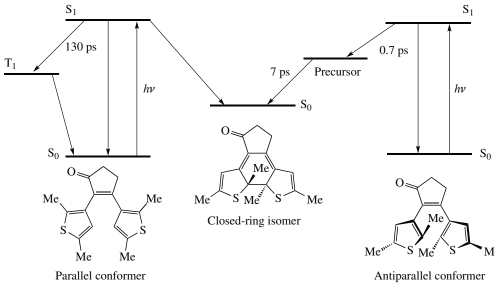
Early processes in photochemistry of 2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-enone were explored using the ultrafast pump-probe spectroscopy. The photocyclization occurs from the antiparallel conformation of an open form on a time scale of 7 ps, while the parallel conformation exhibits an intersystem crossing within 130 ps. The mechanism and timescales were revealed as typical of other thiophene-containing diarylethenes.



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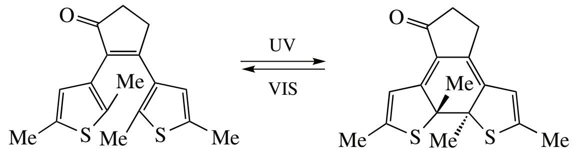
Organic photochromic compounds are of interest as active components in various light-sensitive systems including optical media possessing the nonlinear absorption as well as in optical memory, molecular electronic devices and optical switchers.[1–7] Diarylethenes (DAEs) are among the most promising organic photochromes.[1] Photochromism of DAEs is caused by a light-induced transitions between the colorless open-ring form and the colored closed-ring one. Scheme 1 demonstrates 2,3-bis(2,5-dimethylthiophen-3-yl)cyclopent-2-enone **1** as a typical diarylethene in its colorless (**1A**) and colored (**1B**) forms. Typically, both transitions of DAEs represent photochemical ones with no thermal backward reaction, *i.e.*, they exhibit the P-type photochromism.[8] DAEs are of particular interest due to their breadth of color, absence of thermal reversibility, good resistance to thermal and photochemical fatigue and preservation of photochromic properties in the solid state.[1,9,10]

The scarcity of DAEs originates from the difficulty of their structural modification, which hampers the examination of relationship between their chemical structure and spectral properties.[11,12] 2,3-Diarylcyclopent-2-en-1-ones (DCPs) represent a DAE type that is free of the mentioned deficiency.[13–16] Thus, DCPs provide a useful opportunity for a chemical modification of the cyclopentenone ring, which allows one to synthesize compounds appropriate for specific application areas. For instance, fluorescent switchers based on DCPs were reported.[14,17] In another work,[18] photochemical properties of a typical DCP were improved using its adduct with a metal-organic coordination polymer.



Scheme 1

Despite the synthetic attractiveness of DCPs, the mechanistic aspects of their photochemistry have not been sufficiently explored compared to other DAEs.[2] The mechanism of photolysis for a typical DCP, namely 2,3-bis(2,5-dimethylthiophen-3-yl)-cyclopent-2-enone **1**, has been revealed using stationary and nanosecond laser flash photolysis in our previous work.[19] Herein, we report on the early events in its photochemistry investigated by an ultrafast pump-probe spectroscopy with the time resolution of *ca.* 100 fs. Although the ultrafast[20] photocyclization of particular DAEs was recently reported,[21–25] there is still a lack of data on the early processes in the DCPs photochemistry.

Compound **1** was synthesized according to the known procedure[13] and characterized by elemental analysis, NMR and UV–VIS spectroscopy.† Its open form **1A** does not absorb in the visible spectral range. UV irradiation of **1A** results in the formation of racemic colored closed form **1B**. Electronic absorption spectra of forms **1A** and **1B** (Figure S1, Online Supplementary Materials) coincide with those reported in our previous work.[19] Visible irradiation of **1B** results in a restoration of the open form. Quantum yields of the forward and backward reactions upon excitation at 313 and 530 nm are 0.3 and 0.07, respectively.[19]

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† MeCN of spectrally pure grade (Cryochrom, Russia) was used for the preparation of solutions. Details of the experimental setup[26,27] and data processing[28] are given in Online Supplementary Materials.

Laser flash photolysis experiments[19] have demonstrated that the photocyclization upon the UV irradiation of form **1A** (see Scheme 1) is accompanied by intersystem crossing. The fragment of spectrum of the triplet state **1A**(T) is represented in Figure S1. Photocyclization and intersystem crossing are parallel processes, while the closed isomer **1B** is formed only from the singlet state.[19] The formation of both species **1B** and **1A**(T) is much faster than the resolution time of setup for laser flash photolysis (*ca.* 5 ns).

The photostability of compound **1** is not high. Its UV spectrum changed appear after several cycles of coloration–decoloration.[18,19] This photodegradation is not caused by the reactions of singlet oxygen formed *via* quenching of species **1A**(T) by dissolved oxygen.[19] Therefore, the reason of the photofatigue is the monomolecular photochemical reaction,[18] namely a formal dyotropic rearrangement of the photoinduced isomer.[29,30]

Experiments on the ultrafast kinetic spectroscopy were performed using excitation at 320 nm. An impact of the closed isomer formation during the photolysis was controlled by UV spectra of the photolysed samples and was found to be negligible. Figure 1(*a*) demonstrates intermediate absorption spectra corresponding to different time delays between the pump and probe pulses. Examples of kinetic curves obtained from these spectra are shown in Figure 1(*b*).

The smooth curve [see Figure 1(*a*)] represents the shape of spectrum of the closed form **1B**, and its maximal value is matched to the spectrum of residual in the intermediate absorption spectrum (curve *7*). One can see that the spectrum of the residual corresponds to the long-wavelength wing of spectrum for form **1B**. In the region of 440–520 nm, the residual absorption exceeds the absorption for form **1B**, which could be explained by the absorption of species **1A**(T), whose decay time is an infinity on the time scale of ultrafast experiment. Therefore, we conclude that the residual absorption observed in the ultrafast experiment is the sum of **1B** and **1A**(T) absorptions.

The kinetic curves [see Figure 1(*b*)] were globally fitted using a triexponential function with a residual absorption [equation (1)], since the biexponential fit resulted in a much less satisfactory description. The spectra of amplitudes $A_i(\lambda)$ are shown in Figure S2. The characteristic lifetimes extracted from the global fit were τ_1 = 0.7±0.3, τ_2 = 7.2±1.7 and τ_3 = 130±50 ps.

$$\Delta A(\lambda,t) = A_1(\lambda)\exp\left(-\frac{t}{\tau_1}\right) + A_2(\lambda)\exp\left(-\frac{t}{\tau_2}\right) + A_3(\lambda)\exp\left(-\frac{t}{\tau_3}\right) + A_4(\lambda) \qquad (1)$$

The further analysis of data depends on the model of photochemical processes. We have assumed that the photochemical properties of DCPs are similar to those of other DAEs. There are two conformations, namely parallel and antiparallel denoted as P and AP, respectively of the open form of DAEs, which easily transform into each other in solution.[1,31] For the open form **1A**, these conformations are shown below. The photocyclization can proceed only from the antiparallel conformation.[1]

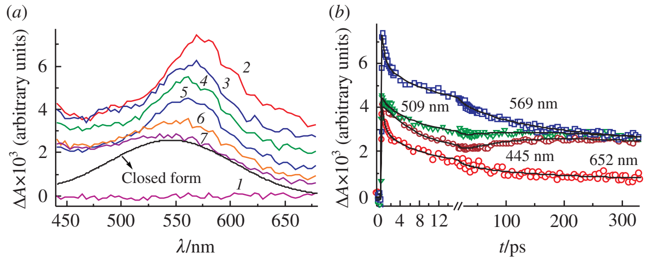
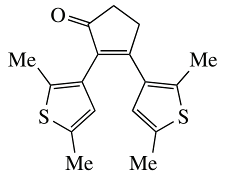
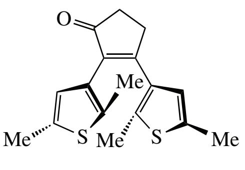


Figure 1 Experimental results for the ultrafast pump-probe spectroscopy (excitation at λ = 320 nm) of form **1A** (7.3×10^{-4} M, 1 mm cell) in MeCN: (*a*) intermediate absorption spectra, curves *1*–*7* correspond to the delays between pump and probe pulses equal to –1.1, 0.3, 1.3, 4.8, 23, 130 and 390 ps, respectively; and the smooth curve is the spectrum of form **1B** and (*b*) kinetic curves at different wavelengths, obtained from the spectra shown in part (*a*). Solid lines represent the best fit approximations according to equation (1).



P conformer



AP conformer

To describe the results of ultrafast pump-probe experiments, we have proposed that the closed form **1B** is formed only from the singlet excited state (^{1}AP*) of form **1A**, while the intersystem crossing is effective only for the singlet excited state ^{1}P*. The similar scheme was earlier assumed for thiophene-substitued DAEs[32,33] and further used for a typical DAE, 1,2-bis(2-methyl-3-benzothienyl)perfluorocyclopentene.[23] The corresponding sequences of reactions are represented in Scheme 2. For clarity, we will further use letters A, B, C, D and E for the designation of five species involved in the process, namely A = ^{1}AP*; B = Pre; C = **1B**; D = ^{1}P*; E = **1A**(T); the nature of species B = Pre (precursor) inserted similarly to the work of Ern *et al.*[33] will be explained below. Constants k_1, k_2, and k_3 are the effective rate constants for the transitions between the species. Note that k_1 and k_3 include the rate constants of internal conversion into the corresponding ground states.

$$^1\mathrm{AP} \xrightarrow{h\nu} {}^1\mathrm{AP^*} \xrightarrow{k_1} \mathrm{Pre} \xrightarrow{k_2} \mathbf{1B} \qquad (a)$$

$$^1\mathrm{P} \xrightarrow{h\nu} {}^1\mathrm{P^*} \xrightarrow{k_3} \mathbf{1A}\mathrm{(T)} \qquad (b)$$

Scheme 2

To calculate the species associated difference spectra (SADS) of the individual components, one needs to know the ratio of absorptions of triplet state (E) and closed form (C) generated during the laser irradiation at 320 nm, $f(\lambda)$ [equation (2); note that $f(\lambda)$ is the ratio of absorptions, but not the ratio of molar absorption coefficients]:

$$f(\lambda) = \frac{S_\mathrm{E}(\lambda)}{S_\mathrm{C}(\lambda)} = \frac{\varepsilon_\mathrm{E}[\mathrm{D}]_0}{\varepsilon_\mathrm{C}[\mathrm{A}]_0}, \qquad (2)$$

where ε_E, ε_C, $[\mathrm{A}]_0$, and $[\mathrm{D}]_0$ are the molar absorption coefficients and initial concentrations of the corresponding species. We have proposed that the $f(\lambda)$ ratio for form **1A** is the same for both the cases of ultrafast laser irradiation at 320 nm and 5 ns laser irradiation at 355 nm (both wavelengths fall into the same absorption band, see Figure S1). This assumption allowed us to extract the function $f(\lambda)$ from the results of laser flash photolysis experiments according to our previous work.[19] Knowing the function $f(\lambda)$, we calculated the SADS according to equations (3)–(7) (note that the formulae for SADS are different from those applied for the commonly occurring case of subsequent formation of intermediates[34]).[‡] Figure 2 shows the calculated values of SADS.

[‡] Their derivation, calculation procedure and graph $f(\lambda)$ are shown in Online Supplementary Materials (Figures S2 and S3).

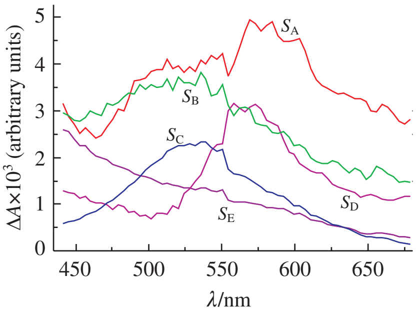


Figure 2 Experimental SADS for the ultrafast pump-probe spectroscopy (excitation at λ = 320 nm) of form **1A** (7.3×10^{-4} M, 1 mm cell) in MeCN derived *via* processing of kinetic curves shown in Figure 1(*b*) by global fit approximation according to equation (1), and calculation of SADS according to equations (3)–(7).

$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_4(\lambda)\frac{1}{1 + f(\lambda)} \quad (3)$$

$$S_B(\lambda) = A_2(\lambda)\frac{k_1 - k_2}{k_1} + A_4(\lambda)\frac{1}{1 + f(\lambda)} \quad (4)$$

$$S_C(\lambda) = A_4(\lambda)\frac{1}{1 + f(\lambda)} \quad (5)$$

$$S_D(\lambda) = A_3(\lambda) + A_4(\lambda)\frac{f(\lambda)}{1 + f(\lambda)} \quad (6)$$

$$S_E(\lambda) = A_4(\lambda)\frac{f(\lambda)}{1 + f(\lambda)} \quad (7)$$

Now let us discuss the reaction pathway (Scheme 2). The transition from the excited AP form to the closed form **1B** was described by a two-step model [Scheme 2(*a*)]. According to this model, the excited ^{1}AP* isomer (see SADS S_A in Figure 2) after excitation of AP to the S_1 state exhibits fast electronic-conformational relaxation on a time scale of 0.7 ps to the precursor (Pre) state (SADS S_B). The transition from ^{1}AP* to Pre consists of moving *via* the reaction coordinate that is the carbon–carbon distance between the methyl group-bearing carbon atoms of two thienyl moieties (see Scheme 1). The precursor transits to the closed form **1B** (SADS S_C) with the characteristic time of 7.2 ps. For a typical DAEs, this transition proceeds *via* conical intersection between S_1 state of the open form and S_0 state of the closed form.[35] Thus, the reaction is essentially downhill and barrierless.[25,32] In this description, the precursor is the excited state of the closed form, where the mentioned C–C distance is less than in the ground AP form. The tentative representation of transition from ^{1}AP* to Precursor is shown in Scheme S1 (Online Supplementary Materials). It should be noted that the transition according to Scheme 2(*a*) is accompanied by vibrational cooling and solvent relaxation. Therefore, our biexponential model is the rough approximation of the real ultrafast process.

The excited S_1 state of the P isomer of form **1A** (SADS S_D) exhibits intersystem crossing to species **1A**(T) (SADS S_E) with the characteristic lifetime of 130 ps. The possible ultrafast relaxation processes for ^{1}P* were not resolved in this work. The lifetime of species **1A**(T) in air-saturated MeCN is *ca.* 0.5 ms.[19]

In conclusion, the mechanism of early photochemical processes for a thiophene-containing DCP was revealed as being similar to that for other thiophene-containing diarylethenes.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.020.

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