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

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Experimental details. Experiments on the ultrafast pump-probe spectroscopy with the registration in visible spectral region were performed using the experimental setup described earlier.[S1,S2] The initial source of light was a Ti–sapphire laser. Samples were excited by *ca.* 100 fs pulses at 320 nm (4th harmonic of the signal wave of TOPAS parametric amplifier). Energy of the exciting pulses was *ca.* 1 μJ at the repetition frequency of 1 kHz. A portion of exciting laser beam was focused on a cell with heavy water to generate a probe radiation (continuum). The studied solution (total volume of 20 ml) was pumped through a 1 mm optical cell. Flow system allowed us to minimize the formation of closed form **1B** during the photolysis. Experimental kinetic curves were globally fitted using the PyGSpec program.[S3]

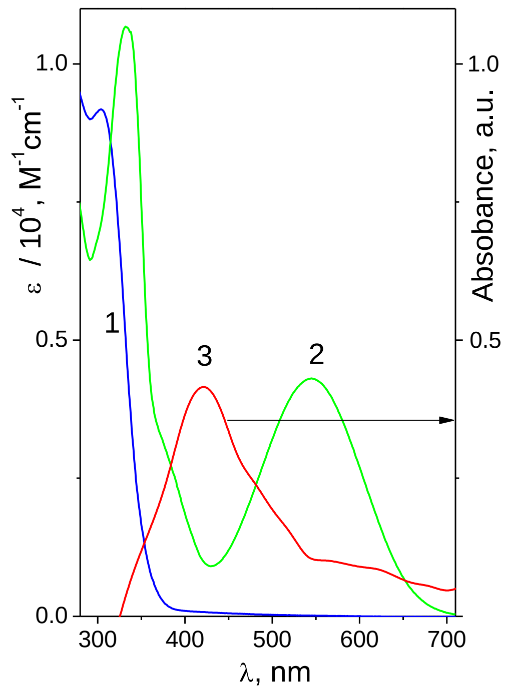


Figure S1 Electronic absorption spectra of compounds **1A** and **1B** (curves *1* and *2*, respectively) and the shape of **1A** T–T absorption spectrum obtained in the laser flash photolysis experiment (curve *3* plotted in arbitrary units). Figure is based on laser flash photolysis data reported in ref. S4. © 2015 Pleiades Publishing, Ltd. Reproduced with the permission.

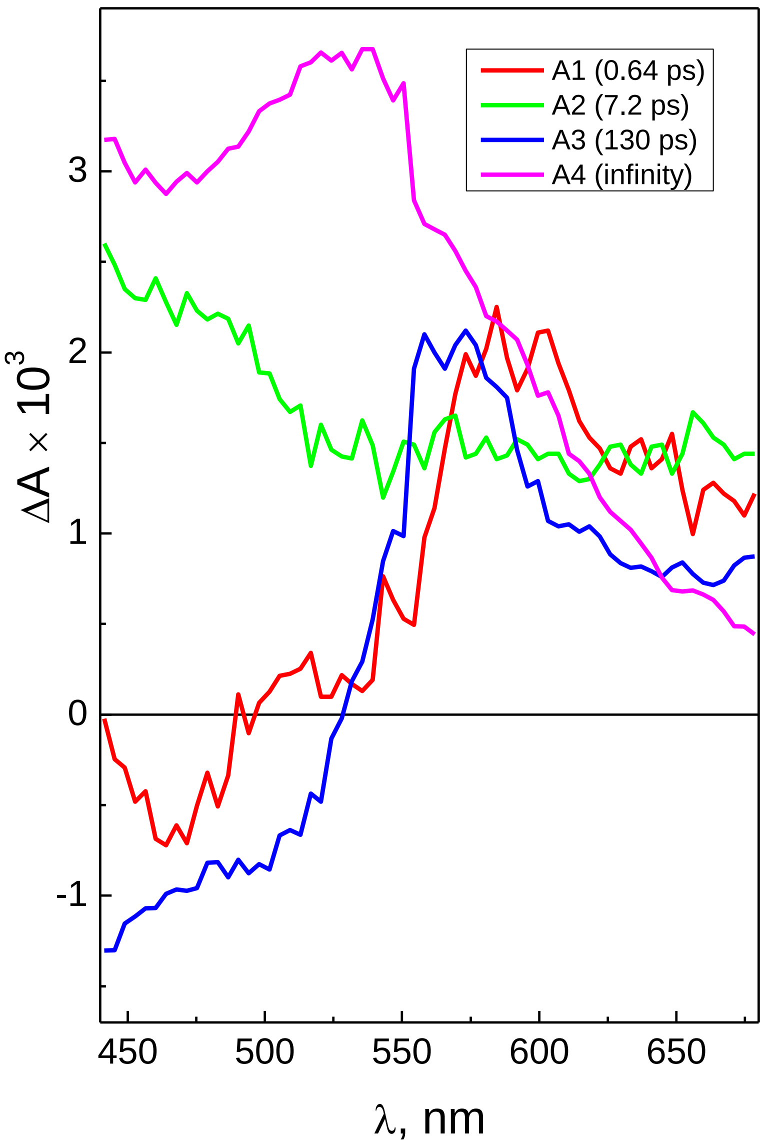


Figure S2 Results of the experiment on the ultrafast kinetic spectroscopy (320 nm) of **1A** (7.3×10^{-4} M, 1 mm cell) in MeCN. Amplitudes of the 3-exponential global fit with the residual (Equation 1 given on page S5).

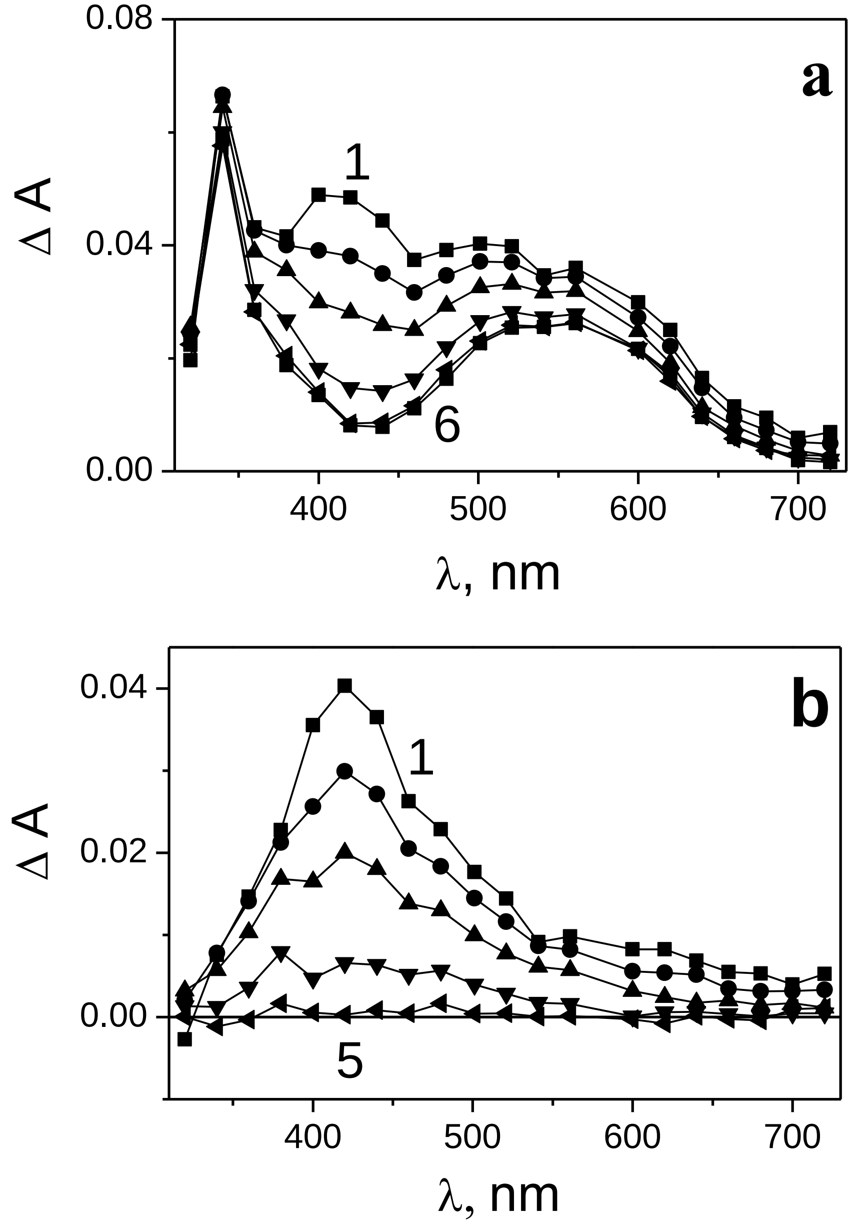


Figure S3 Differential absorption of closed form **1B** and the triplet state of open form **1A**(T)**.** Laser flash photolysis (355 nm) of compound **1A** (2×10^{-4} M in MeCN, 1 cm cell, deaerated solution). (*a*) Intermediate absorption spectra. Curves *1–6* correspond to time delays of 0.4, 1.6, 3.2, 8, 18 and 40 μs after the laser pulse (where curve 6 represents the residual absorption after the complete decay of the triplet state, *i.e.* **1B** spectrum). (*b*) Differential spectra obtained from curves *1–5* by subtraction of spectrum *6* (curve *1* represents the **1A**(T) spectrum. Figure from ref. S4.

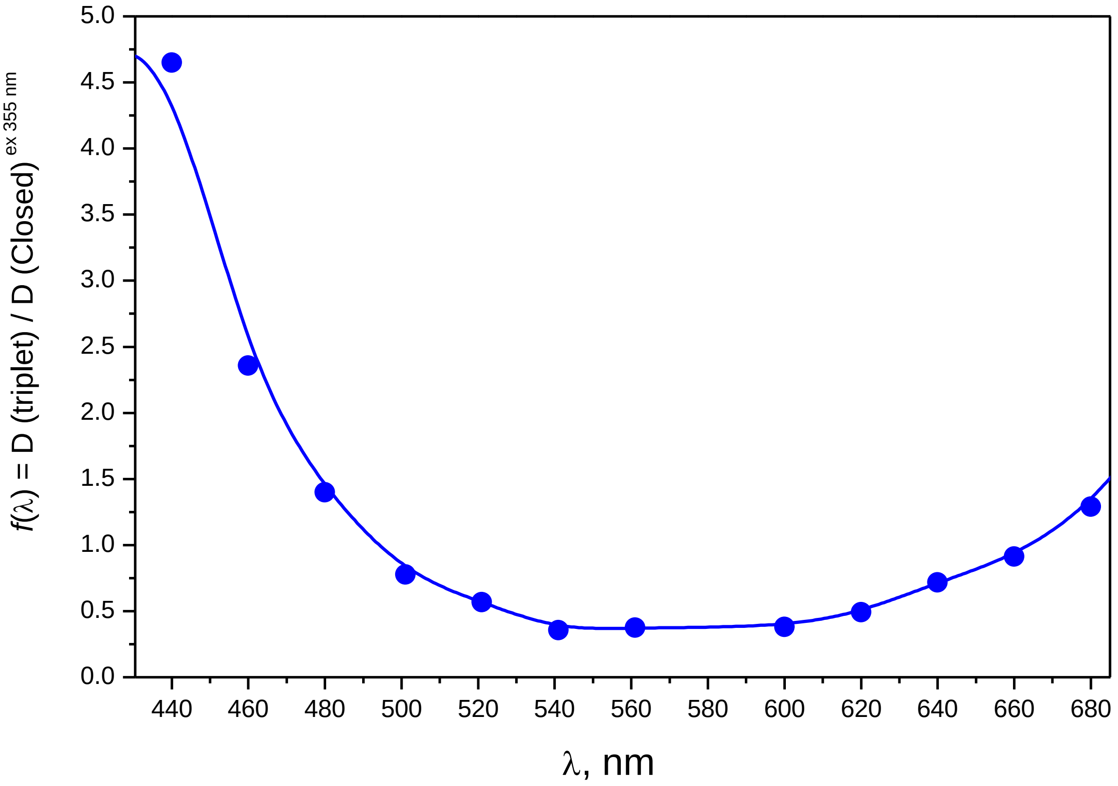


Figure S4 Ratio of absorption of triplet state **1A**(T) and closed form **1B** $f(\lambda) = D(1(T))/D(1B)$ formed by irradiation of **1A** at 355 nm in MeCN. Processing of data shown in Figure 2(*b*). Experimental points and 4 order polynomial regression:

$$f(\lambda) = 1212.24 - 8.925\lambda + 0.0213\lambda^2 - 2.42\cdot10^{-5}\lambda^3 + 1.03\cdot10^{-8}\lambda^4$$

Derivation of Formulae for SADS

Numbering of Equations 1–10 corresponds to those in the main text of paper. Equations *i*–*ix* are used to derive Equations 6–10.

Experimental kinetic curves were globally fitted by function (1).

$$\Delta A(\lambda,t) = A_1(\lambda)e^{-\frac{t}{\tau_1}} + A_2(\lambda)e^{-\frac{t}{\tau_2}} + A_3(\lambda)e^{-\frac{t}{\tau_3}} + A_4(\lambda) \quad (1)$$

The following sequence of reactions was proposed:

$$^1AP \xrightarrow{h\nu} {}^1AP^* \xrightarrow{k_1} Suc \xrightarrow{k_2} 1B\,(Closed) \quad (2)$$

$$^1P \xrightarrow{h\nu} {}^1P^* \xrightarrow{k_3} 1A(T) \quad (3)$$

For clarity we will use letters (A, B, C, D, E) for designation of the five species involved in the process (Eqation 4).

$$A = {}^1AP^*;\;\; B = Pre;\; C = 1B\,(Closed);\; D = {}^1P^*;\; E = 1A(T) \quad (4)$$

The ratio of absorptions of triplet state (E) and closed form (B) $f(\lambda)$ (Equation 5, Figure S4), where ε_E, ε_C, $[A]_0$ and $[D]_0$ are the molar absorption coefficients and initial concentrations of the corresponding species, was derived known from the laser flash photolysis experiments.[S5]

$$f(\lambda) = \frac{S_E(\lambda)}{S_C(\lambda)} = \frac{\varepsilon_E[D]_0}{\varepsilon_C[A]_0} \quad (5)$$

Using equations 2 and 3, we obtain for absorptions of species A, B, C, D, E:

$$D_A(t) = (\varepsilon_E[A]_0 l)e^{-k_1t} = S_A e^{-k_1t} \quad (i)$$

$$D_B(t) = (\varepsilon_B[A]_0 l)\frac{k_1}{k_2-k_1}(e^{-k_1t} - e^{-k_2t}) = S_B\frac{k_1}{k_2-k_1}(e^{-k_1t} - e^{-k_2t}) \quad (ii)$$

$$D_C(t) = (\varepsilon_C[A]_0 l)(1 + \frac{k_1e^{-k_2t} - k_2e^{-k_1t}}{k_2-k_1}) = S_C(1 + \frac{k_1e^{-k_2t} - k_2e^{-k_1t}}{k_2-k_1}) \quad (iii)$$

$$D_D(t) = (\varepsilon_D[D]_0 l)e^{-k_3t} = S_D e^{-k_3t} \quad (iv)$$

$$D_E(t) = (\varepsilon_E[D]_0 l)(1 - e^{-k_3t}) = S_E(1 - e^{-k_3t}) \quad (v)$$

Summarizing Equations *i*–*v*, we obtain $\Delta A(\lambda,t)$ and compare it with Equation 1 getting $A_i(\lambda)$:

$$A_1 = S_A - \frac{k_1}{k_1-k_2}S_B + \frac{k_2}{k_1-k_2}S_C \quad (vi)$$

$$A_2 = \frac{k_1}{k_1 - k_2}(S_B - S_C) \qquad (vii)$$

$$A_3 = S_D - S_E \qquad (viii)$$

$$A_4 = S_C + S_E \qquad (viii)$$

Now we add the value of $f(\lambda)$ from (5):

$$f(\lambda) = \frac{S_E}{S_C} \qquad (ix)$$

Finally, solving the system of algebraic equations *vi*–*ix*, we obtain formulae for SADS (6–10):

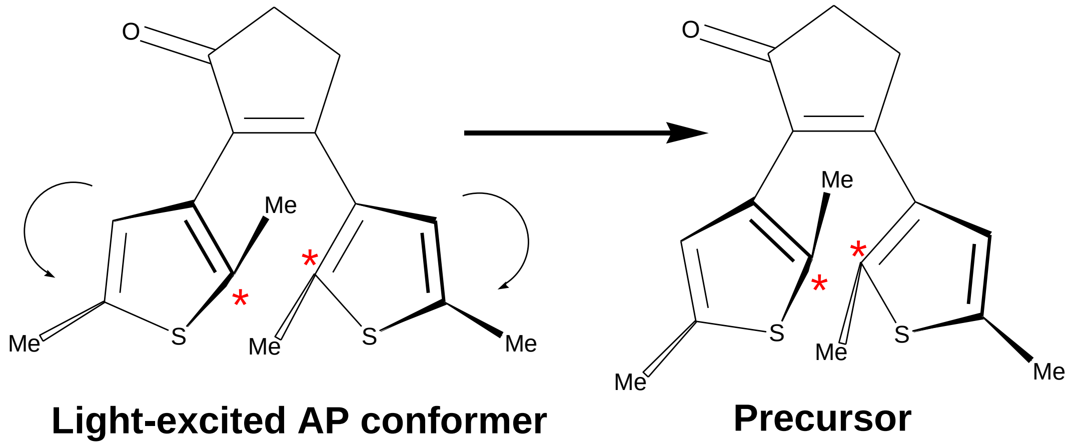
$$S_A(\lambda) = A_1(\lambda) + A_2(\lambda) + A_4(\lambda)\frac{1}{1+f(\lambda)} \qquad (6)$$

$$S_B(\lambda) = A_2(\lambda)\frac{k_1 - k_2}{k_1} + A_4(\lambda)\frac{1}{1+f(\lambda)} \qquad (7)$$

$$S_C(\lambda) = A_4(\lambda)\frac{1}{1+f(\lambda)} \qquad (8)$$

$$S_D(\lambda) = A_3(\lambda) + A_4(\lambda)\frac{f(\lambda)}{1+f(\lambda)} \qquad (9)$$

$$S_E(\lambda) = A_4(\lambda)\frac{f(\lambda)}{1+f(\lambda)} \qquad (10)$$



Scheme S1 Tentative representation of transition from ^{1}AP* to Precursor. At the moment this picture is not supported by the direct ultrafast X-rays measurements.

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