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Ultrafast Bidirectional Dihydroazulene/Vinylheptafulvene (DHA/VHF) Molecular Switches: Photochemical Ring Closure of Vinylheptafulvene Proven by a Two-Pulse Experiment

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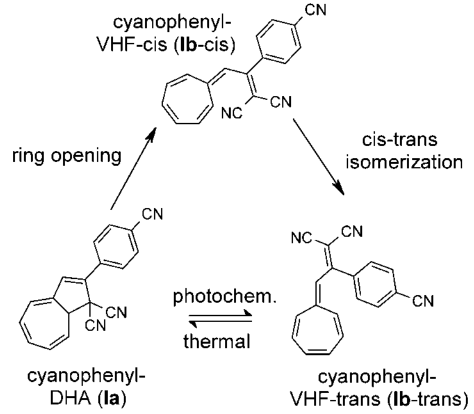
Molecular switches are an active area of research[1] highly motivated by the potential applications in the field of optoelectronics and high repetition rate telecommunication[2] as well as by the essential role that they play in biomolecular systems for the conversion of light into chemical energy, the transport of biochemical information, and signal transmission across biological membranes.[3]

We study the photochromism of dihydroazulene that undergoes upon UV irradiation a ring opening leading to the vinylheptafulvene conformers. Dihydroazulene/vinylheptafulvene constitutes a promising family of photochromic compounds to develop ultrafast molecular devices. Indeed they fulfill a lot of requirements such as a very high quantum yield of conversion, a large shift of the absorption band on going from DHA to VHF, and a singlet state photoreaction path allowing a high fatigue resistance that make them very attractive for developing and studying molecular switches.[4]

The important change of the molecular electronic structure associated with the ring-opening process allows the photoswitching of electronic properties such as fluorescence, redox potentials, charge transfer, or polymer conductivity.[4,5] However, up to now, only the ring opening, i.e., the conversion from DHA to VHF, can be photoinduced, while the back reaction proceeds by thermal activation. According to previous studies of the cyclopentane-DHA derivative,[6] the presence of a conical intersection has been proposed to be responsible for the efficient internal conversion observed after excitation of the VHF conformer, and therefore responsible for the hindrance of the photochemical ring closure of VHF to DHA.

Femtosecond experiments are particularly adapted to study the elementary chemical processes that govern the ultrafast ring opening,[7] but they also provide the possibility of acting on short-lived species[8] and as reported in this communication discovering new photochemical pathways. We investigated in femtosecond pump−probe experiments the ring-opening mechanism of the 2-(4-cyanophenyl)-1,1(8a*H*)-azulenedicarbonitrile (hereafter **Ia**/**Ib** for the DHA and VHF forms, respectively). **Ia** undergoes, under UV irradiation at 360 nm, an efficient photoconversion to **Ib**,[9] the final product has been identified as a trans conformer from X-ray analysis.[10] Therefore, as described in Scheme 1, the conversion from **Ia** to **Ib** must involve a **Ib**-*cis* conformer. In our measurements, we observed after excitation of **Ia** by femtosecond pulses a 100 fs structural relaxation followed by the 1.2 ps ring opening[11] that may be associated with an ultrafast dissociative electron-transfer step from the cycloheptatriene C-8a carbon to the dicarbonitrile substituted C-1. The internal conversion to the **Ib**-*cis* ground state conformer proceeds within 15 ps (see Figure 1b). Figure 1a shows that the transient spectrum after 100 ps[12] is still distinctly different from that of **Ib**-*trans*.[13] The transient species formed within 15 ps is therefore the **Ib**-*cis* isomer, while the cis−trans isomerization must take place on the nano-, micro-, or even millisecond time scale and cannot be investigated with our femtosecond setup.

Scheme 1. 2-(4-Cyanophenyl)-1,1(8a*H*)-azulenedicarbonitrile (**Ia**), Ring-Opening Mechanism



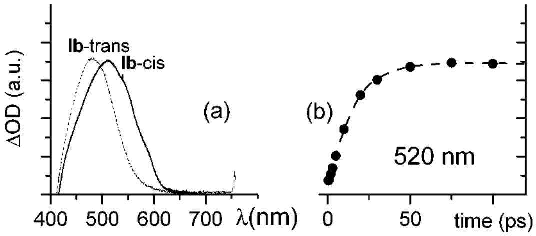


Figure 1. (a) Comparison of the **Ib**-*trans* absorption and the transient spectrum observed 100 ps after femtosecond irradiation at 375 nm (**Ib**-*cis*). (b) Time dependence of the change in optical density at 520 nm after excitation of **Ia** at 375 nm by a 100 fs pulse

Compared to the cyclopentane-DHA, for which the final state is reached in <1 ps, the formation of the **Ib**-*cis* in 15 ps is relatively long, and suggests a strong modification of the topology of the potential energy surface between the two derivatives. On the basis of this observation, the question of a possible photoinduced back reaction from the **Ib**-*cis* isomer is opened, and can be addressed by a femtosecond two pump pulse experiment.

We probed the possibility of a photoinduced formation of **Ia** from **Ib**-*cis* by comparing the result of the irradiation of **Ia** in ethanol in two experiments. In the first one the sample of **Ia** was irradiated at 340 nm by 30 fs pulses with an energy of 110 nJ and a beam diameter of about 100 μm at a repetition rate of 1 kHz for a time $t = 45$ min (corresponding to 2.7×10^6 single pulses) necessary to convert a significant amount of **Ia** to **Ib**. In the second

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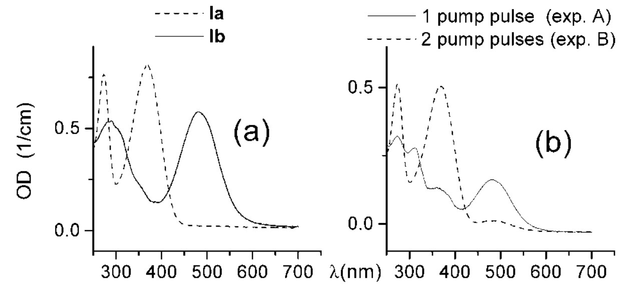

Figure 2. (a) Steady-state UV−vis absorption of **Ia** in ethanol before and after cw irradiation at 340 nm and (b) after the one and two pump experiment.

experiment, a solution of **Ia** (same concentration as the previous one) was irradiated by a sequence of two pulses, at the repetition rate of 1 kHz for the time *t* defined in the previous experiment. The first pulse at 340 nm triggered, as in the previous run and with the same intensity, the photoconversion of **Ia** while the second pump pulse at 530 nm with an energy of 130nJ, beam diameter of about 100 μm and delayed by 25 ps from the first pulse excited the **Ib**-*cis* isomer. The samples were placed in a 1 mm cell that was in translation during the measurement to avoid any thermal effect and to refresh the excited volume. The pump−pump overlap was optimized by maximization of the absorption of the second pump pulse measured with our usual two-color pump−probe transient absorption setup.[14] The pump pulses at 340 and 530 nm were generated by two blue pumped NOPAs.[15]

The resulting absorptions of runs A and B, respectively irradiation by a single and a two-pump sequence, are reported in Figure 2b. They are compared to the **Ia** absorption and to the absorption of a solution of **Ia** irradiated by a cw lamp at 340 nm (Figure 2a). In Figure 2a we observe the usual photoconversion from **Ia** to **Ib**-*trans*, reflected by the disappearance of the **Ia** absorption (280 and 360 nm) and the growing-up of the **Ib**-*trans* absorption at 320 and 480 nm. We can see from Figure 2b that sample A leads after single pump pulse irradiation to the same spectral changes as under cw irradiation. We can therefore conclude that the short pulses induced the same photoreactivity of **Ia**.

By comparing the result of experiments A and B, we see clearly that less **Ib**-*trans* is present in sample B than in A. Consequently there must be more **Ia** molecules in sample B than in A. Moreover no new band, which would indicate a photodegradation of the sample in the two-pump pulse experiment, is observed. The photoinduced back reaction constitutes clearly the main photochemical pathway: After the two experiments, we left the two samples in the dark and observed after 15 h the thermal back reaction to the **Ia** species. The original spectra as measured before the irradiation have been recovered. As a last precaution, we checked the effect of the pump at 530 nm on a solution of **Ia** previously irradiated by a cw lamp at 340 nm. This sample contained the **Ib**-*trans* species. We exposed this solution to the 530 nm laser pulses for the irradiation time *t* used in experiments A and B. No changes in the cw spectrum were observed after this pulsed irradiation. We have therefore established that the specific absorption difference between experiments A and B is due to the two-pump pulse sequence and we conclude that the irradiation at 530 nm of the short-lived **Ib**-*cis* intermediate photoinduced the back reaction to the **Ib** conformation, i.e the ring closure from VHF to DHA.

Thus, we have demonstrated that when manipulated by femtosecond pulses, the cyanophenyl-dihydroazulene derivatives possess the remarkable property of multimode-switching: a very fast photoreversible switch between the DHA and VHF-*cis* conformers, and a thermal switch between the VHF-*cis* and DHA, via the VHF-*trans* conformation. These remarkable features open new promising perspectives for ultrafast logic functions at the molecular level,[16] based on the DHA/VHF photochromic compounds.

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Supporting Information Available: The steady-state spectra of samples A and B after the thermal back reaction, as well as the spectra concerning the pulsed irradiation of the **Ib**-*trans* compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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