Photoswitches

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Unraveling a Chemically Enhanced Photoswitch: Bridged Azobenzene**

Marcus Böckmann, Nikos L. Doltsinis, and Dominik Marx*

The possibility to reversibly photoisomerize azobenzene (AB) has made it one of the most ubiquitous light-sensitive molecular switches.[1–10] Opto- and nanomechanical devices[9,10] that convert light to mechanical action, for instance, exploit the considerable stretching of AB on $Z \rightarrow E$ isomerization. In biochemical studies, AB has been integrated into synthetic peptides and foldamers to photocontrol their conformational dynamics.[6,11] Photoaddressable materials such as image-storage media are often based on AB functional units.[12,7] For all of the above applications of the AB photoswitch it is of paramount importance to ensure that the photoisomerization process[13–15] is fast and has a high quantum yield.

Recently, a greatly enhanced $E \rightarrow Z$ quantum yield $\Phi^{\text{AB}-C_2}_{E\rightarrow Z}$ was reported for a bridged azobenzene (AB-C_2 in Figure 1) in the S_1 state compared to the parent molecule AB.[16] This finding may seem surprising at first, as the structural changes involved in isomerization are expected to be hindered by the restriction due to the presence of a bridge interconnecting the phenyl rings. It thus seems remarkable to observe a much larger quantum yield of bridged AB-C_2 compared to AB itself. Herein we demonstrate that, counterintuitively, the bridge does not hinder photoisomerization. On the contrary, it suitably preorients the phenyl rings such that AB-C_2 can more easily undergo $E \rightarrow Z$ isomerization, so that not only an enhanced quantum yield $\Phi^{\text{AB}-C_2}_{E\rightarrow Z}$ but also ultrashort S_1 lifetimes result.

Similar to earlier work[17–19] we investigated the photodynamics of E-AB-C_2 in the S_1 excited state in the gas phase employing nonadiabatic[20,21] ab initio molecular dynamics (AIMD),[22] whereby "on-the-fly" nonadiabaticity is introduced by using Tully's fewest-switches surface hopping[23] to couple S_1 and S_0. In particular, the fewest-switches method has been demonstrated[13–15] to describe satisfactorily, both mechanistically and quantitatively, photoisomerization of the parent compound AB, including the $E \rightarrow Z$ and $Z \rightarrow E$ quantum yields and the timescales involved. Here, all calculations were carried out with the CPMD package[24] by employing a cubic 18 Å periodic box, the PBE functional, and plane waves with dual-space pseudopotentials.[22] A total of 30 nonadiabatic simulations of at least 500 fs were performed microcanonically in the Born–Oppenheimer mode with a time step of 2 a.u., with initial conditions sampled from a canonical ground state run at 300 K.

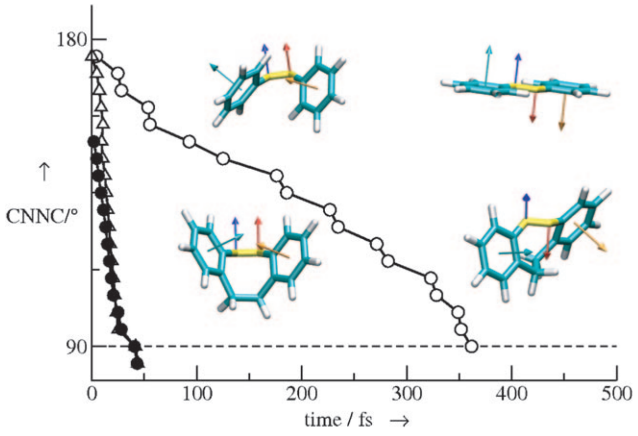

Figure 1. Ensemble average of the CNNC dihedral angle, $\psi^{\text{NN}'}(t)$, during time evolution in the first excited state S_1 at which the specific value $\psi^{\text{NN}'}$ at time t is reached for the first time after vertical photoexcitation from S_0 at $t=0$ for E-AB-C_2 (●), E-AB (○), and Z-AB (△), for which $180° - \psi^{\text{NN}'}$ is plotted; the perpendicular conformation, that is, $\psi^{\text{NN}'} = 90°$, is marked by the dashed line. Insets show optimized Z/E (left/right) plain AB (top) and AB-C_2 (bottom); normal vectors indicate the orientation of the phenyl rings, $\mathbf{n}^{\text{R}}$ and $\mathbf{n}^{\text{R}'}$ (cyan, orange), and of the CNN coordination plane of the N atoms, $\mathbf{n}^{\text{N}}$ and $\mathbf{n}^{\text{N}'}$ (red, blue).

A prerequisite for the dynamics is an extensive validation of the S_0 and S_1 potential energy surfaces, which was done in much detail[18] for the parent compound by comparison with CASPT2 data.[17–19] An analogous analysis for the E-AB-C_2 derivative confirms that the DFT excitation energy (2.59 eV) is again in good agreement with both CASPT2 (2.52 eV) and experiment (2.53 eV). On chemical modification of AB to form AB-C_2 (i.e., addition of a $-CH_2CH_2-$ bridge in *ortho* position of the phenyl rings) the E isomer becomes nonplanar, due to the orientation of the phenyl rings, while only minor structural changes arise for the Z isomer (Figure 1). The mechanical strain introduced into E-AB-C_2 makes it less stable than the Z isomer by 0.31 eV according to DFT (which again compares favorably to the CASPT2 value of 0.35 eV).

When nonadiabatic AIMD simulations are performed after vertical $S_0 \rightarrow S_1$ photoexcitation of E-AB-C_2, roughly half of them result in successful $E \rightarrow Z$ isomerization (quantum yield $\Phi^{\text{AB}-C_2}_{E\rightarrow Z} = (47 \pm 10)\,\%$ including the statistical error of the sample, computed by the blocking method).[25] The

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[*] Dr. N. L. Doltsinis
Department of Physics, King's College London
London, WC2R 2LS (UK)
Fax: (+44) 20-7848-2420
E-mail: nikos.doltsinis@kcl.ac.uk

Dr. M. Böckmann, Prof. Dr. D. Marx
Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum
44780 Bochum (Germany)

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computed value is consistent with the experimental finding[16] of $\Phi_{E\to Z}^{\text{AB}-C_2} = (50\pm10)\,\%$. We note in passing that application of the surface-hopping method here is known to overemphasize coherence,[23,26] which is a potential source of error when extracting quantitative information such as quantum yields or excited-state lifetimes. However, it has been shown[27] to perform rather well when compared to other approximate methods suitable to simulate complex molecular systems; moreover, since it has been demonstrated[14] that surface-hopping quantum yields are only slightly underestimated for bare AB, this approach is validated for this specific case. In stark contrast to E-AB-C_2, the parent compound AB has a much lower experimental value of $\Phi_{E\to Z}^{\text{AB}-C_2} = 24\,\%$,[16] which is again in harmony with nonadiabatic AIMD, in which only roughly 20 % of the trajectories yielded isomerization.[18] Thus, the computational approach reproduces the observed striking difference between AB-C_2 and AB in terms of quantum yields.[16]

Having shown, in a first step, that the simulations yield an overall picture in close accord to available experimental data, we are now in a position to unravel additional dynamical and mechanistic details in subsequent steps. In particular, the calculations demonstrate that photoisomerization of E-AB-C_2 is astonishingly fast according to Figure 1, where $\psi^{\text{NN}'}(t)$ represents the time t at which a specific $\sphericalangle$CNNC value $\psi^{\text{NN}'}$ is reached for the first time during time evolution in the excited state S_1 after vertical excitation from the ground state S_0, averaged over all trajectories of the ensemble. Evidently, the timescale intrinsic to this observable is not strongly dependent on nonadiabaticity but in fact predominantly governed by adiabatic dynamics in the excited state describing the approach from the Franck–Condon region to the nonadiabatic coupling regime. Noteworthily, according to Figure 1 this process is much faster than for unconstrained E-AB (empty circles), while the timescale for E-AB-C_2 (filled circles) is in fact essentially that of plain Z-AB (triangles). In particular, E-AB-C_2 reaches the decisive perpendicular conformation, that is, $\psi^{\text{NN}'} = 90°$ as marked by the dashed line, in only about 40 fs, which is one order of magnitude faster than for the corresponding parent E-AB. Moreover, in contrast to E-AB, E-AB-C_2 rapidly reaches the region beyond the ground-state barrier to $E\to Z$ isomerization along the CNNC coordinate characterized by $\psi^{\text{NN}'} \ll 90°$, and thus enters the Z-AB-C_2 product potential well leading to successful photoisomerization (the optimized value for the Z-AB-C_2 product is $\psi_0{}^{\text{NN}'} = 6.6°$ in S_0). This behavior rationalizes the greatly enhanced isomerization quantum yield consistently found for E-AB-C_2 compared to E-AB both in experiment[16] and in these simulations.

But why is photoisomerization promoted on bridging? Earlier studies on photoisomerization of AB in the bulk[17,18] and suspended between gold electrodes[19] revealed that spatial confinement and mechanical constraints, respectively, only mildly affect $Z\to E$ isomerization, while pronounced slowing down was seen for $E\to Z$. The reason was traced back to ultrafast pedal motion of the N atoms yielding a CNNC angle of $\psi^{\text{NN}'} \approx 90°$ in the S_1 state, which competes with the need to achieve coplanarity of the CNN planes with their adjacent rings ($\psi^{\text{RN}} \approx 0°$). Only for $Z\to E$ does this competition turn out to be a driving force, due to the initial conformation of the phenyl rings, whereas it slows down $E\to Z$ isomerization of the formerly coplanar E-AB.

Based on this scenario the highly efficient photoisomerization of E-AB-C_2 can be understood as follows. Indeed, Figure 2 shows that isomerization of E-AB-C_2 also predominantly proceeds by pedal motion of the CNNC group (since $\psi^{\text{NN}'}(t) \approx \psi^{\text{NN}'}(t{=}0) + \psi^{\text{N}}(t) - \psi^{\text{N}'}(t)$ for all t) in concert with achieving coplanarity of the CNN planes with the rings (since $\psi^{\text{RN}}(t)$ and $\psi^{\text{R}'\text{N}'}(t) \to 0°$ while in the S_1 state). As a result of this correlated dynamics, no large-amplitude motion of the phenyl rings is necessary (i.e., $\psi^{\text{R}}(t) \approx \psi^{\text{R}'}(t) \approx 0°$ initially).

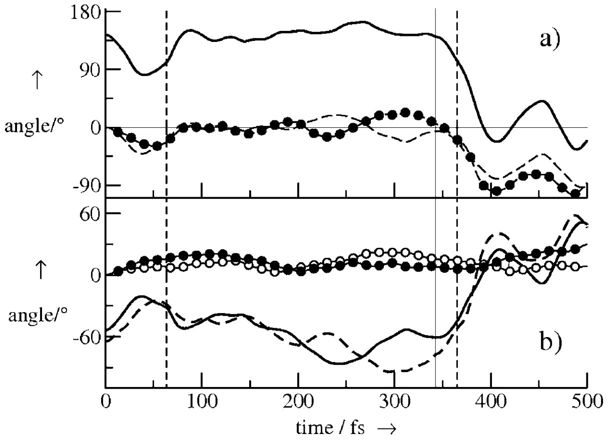

Figure 2. Time evolution for a representative $E\to Z$ trajectory for AB-C_2 of a) $\psi^{\text{NN}'}$ (——), ψ^{N} (-----), and $-\psi^{\text{N}'}$ (●) and b) ψ^{RN} (——), ψ^{R} (○), $\psi^{\text{R}'\text{N}'}$ (-----), and $\psi^{\text{R}'}$ (●), where $\psi^{\alpha\beta}(t) = \sphericalangle[\mathbf{n}^{\alpha}(t), \mathbf{n}^{\beta}(t)]$ and $\psi^{\alpha}(t) = \sphericalangle[\mathbf{n}^{\alpha}(t), \mathbf{n}^{\alpha}(0)]$. Vertical lines indicate $S_1 \to S_0$ (-----) and $S_0 \to S_1$ (——) hops.

This behavior is distinctly different from that of the unbridged E-AB parent, which exhibits slow photoswitching.[18] An analogous scenario to E-AB-C_2, however, has been found for plain Z-AB, which features ultrafast photoisomerization.[17,18] The crucial common aspect of the bridged E-AB compound, E-AB-C_2, and the unbridged Z-AB is a very similar noncoplanar phenyl ring orientation in the S_0 equilibrium structure ($\psi^{\text{RN}} = \psi^{\text{R}'\text{N}'}$) of about 58° for Z-AB and circa 53° for E-AB-C_2 (Figure 1), from which photoisomerization starts after vertical excitation to the S_1 state. Mechanistically speaking the very same driving force as identified for Z-AB is present in E-AB-C_2 and thus leads to ultrafast photoisomerization in both cases, as confirmed by Figure 1. Therefore, in the present case the "bridging" of AB—commonly viewed as a severe steric hindrance to photoisomerization—counterintuitively yields a drastically improved photoswitch which isomerizes on a much shorter timescale with a significantly enhanced quantum yield. By the same reasoning, it is expected that bridging Z-AB to yield Z-AB-C_2 will have only a minor effect on the mechanism, and therefore the $Z\to E$ photoisomerization of AB-C_2 should be as fast as for unbridged AB. This implies that both $Z\to E$ and $E\to Z$ photoswitching of AB-C_2 should be similarly effective.

In summary, in addition to reproducing the enhanced quantum yield found in experiment, our simulations predict that *E*-AB-C_2 photoisomerization should be similar to that of *Z*-AB in many respects, including timescales and its qualitative insensitivity to solvent effects. In particular, analysis of the photoswitching mechanism has revealed that isomerization occurs on a timescale one order of magnitude shorter than for unbridged *E*-AB. This is traced back to a favorable out-of-plane conformational preorientation of the phenyl rings introduced by the bridge that promotes photoswitching. Thus our simulations complement—and go a long way toward explaining—recent experiments[16] which reported a surprising enhancement of the photoswitching qualities of *E*-AB-C_2 relative to *E*-AB. The mechanistic insights into enhancing the switching efficiency of azobenzene by suitable chemical bridging may be exploited as a design principle for optimal engineering of molecular photoswitches in the future.

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