Photoinduced Pedalo-Type Motion in an Azodicarboxamide-Based Molecular Switch

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Abstract: Well-defined structural changes of molecular units that can be triggered by light are crucial for the development of photoactive functional materials. Herein, we report on a novel switch that has azodicarboxamide as its photo-triggerable element. Time-resolved UV-pump/IR probe spectroscopy in combination with quantum-chemical calculations shows that the azodicarboxamide functionality, in contrast to other azo-based chromophores, does not undergo trans–cis photoisomerization. Instead, a photoinduced pedalo-type motion occurs, which because of its volume-conserving properties enables the design of functional molecular systems with controllable motion in a confined space.

Switching between two or more states on the molecular level is fundamental for many biological phenomena including regulation of muscle contraction, blood pressure, and vision. In the latter case, a light-triggered conformational change of a molecular chromophore results in a cascade of subsequent processes that enable human sight. Embedded in a protein, the switching of the photoactive molecular unit between two well-defined structural states causes, through specific interactions with the protein environment, a long-range effect that is the basis for the biological activity. Such a level of control of molecular motion on the nanoscale is crucial not only for biological systems but also for the development of new efficient functional materials for a wide range of applications (for example, catalysis, drug delivery, and molecular computers). The functional performance of these materials depends not only on the intrinsic switching properties of the employed molecular units but also, as illustrated by the molecular-level description of human sight, on how switching is transmitted to the macroscopic world. This is done either by coupling the switch to a dynamic molecular environment or by immobilizing it at interfaces or in confined environments such as crystals. In all cases, however, it is clear that coupling inevitably leads to spatial restrictions on the switching process. One of the key challenges is thus the development of externally controllable molecular units with specific volume-conserving motions that are able to influence the local environment. The tuning of the expansion behavior of systems using a thermally induced pedalo-motion in a co-crystal may in this respect serve as an illustrative example of the potential of such an approach. At the same time, the reported photoinduced hula twist or bicycle pedal type of motion further highlights the relevance of volume-conserving dynamics.

In the present study, we aim to transfer this concept to new light-responsive functional materials. For this purpose, we focus on azodicarboxamide-based molecular systems (Figure 1). These systems feature well-defined hydrogen-bond-interaction sites that provide anchor points to the molecular environment and an azo-moiety that might induce light-induced structural changes. Normally, such an azo-moiety is used in conjunction with aromatic substituents that lead to planar geometries around the N–N bond. The conjugation of the same function through carboxamide groups leads one to expect different conformational behavior...
for azodicarboxamide-based systems, potentially resulting in other types of molecular motions.

Apart from one photolysis study,\textsuperscript{[37]} the photodynamic properties of azocarboxamide systems have so far not been studied, and practical applications are largely unexplored. We have therefore combined picosecond time-resolved vibrational spectroscopy of the electronically excited states with quantum-mechanical calculations to elucidate in detail the photodynamics of tetrabenzylazodicarboxamide (Figure 1), which indeed turns out to be completely different from the usually observed trans–cis isomerization in azobenzene-based molecular systems.

To gain insight into the electronic and structural properties of azodicarboxamide derivatives, we have performed quantum-mechanical calculations on tetramethylazodicarboxamide. Detailed investigations of the conformational phase space in the electronic ground-state reveals, in contrast to the parent compound 1,1’-azobisformamide,\textsuperscript{[38,39]} a significantly nonplanar structure of the molecule (Figure 2a). The carbonyl groups are in this case rotated by about 75$^\circ$ with respect to the N=N bond (MP2/6-31G$^*$) and point in opposite directions. Further support for this conclusion is provided by our experimental UV/Vis and IR absorption spectra, which are in excellent agreement with the corresponding results obtained by density functional theory calculations (B3LYP/6-31G(d,p), see Figures S1 and S2 in the Supporting Information). The main path between the two conformers primarily involves the torsion around the C=N bond (see Figure 2 and Figure S3 in the Supporting Information). The resulting dynamics can be described by a pedal-type motion of the central nitrogen atoms. In the context of molecular switches, two unique aspects are associated with this effective motion. First, it is volume-conserving and therefore also possible in confined space. Second, motion along this path changes the direction of the carbonyl groups (Figure 2b) and thus modulates hydrogen bonding with the molecular environment.

To determine the light-triggered properties of the azodicarboxamide functional group, we have performed picosecond time-resolved IR absorption spectroscopy, which has been shown to provide a high temporal resolution and structural sensitivity.\textsuperscript{[40–48]} Figure 3a displays transient IR spectra of tetrabenzylazodicarboxamide in chloroform ($c = 6.6$ mm) in the 1600–1775 cm$^{-1}$ range associated with the carbonyl stretch region after excitation at 350 nm. In agreement with our DFT calculations that show that the first electronic transition with nonzero oscillator strength is expected at around 340 nm, no transient signals could be observed upon excitation at longer wavelengths. This transition corresponds to the $S_1\rightarrow S_0$ transition; the $S_2$ and $S_3$ states have zero oscillator strength and are thus not directly accessible by vertical one-photon excitation.

Before analyzing the vibrational spectra in full detail, we notice that one expects the IR spectrum in the carbonyl stretching range to be quite different for the planar and nonplanar conformations depicted in Figure 2, as is indeed confirmed by our calculations (see below). This part of the spectrum thus is an excellent probe for following a pedal-type motion. The transient IR spectrum at a delay of 0.5 ps shows one intense bleach signal at the position of the carbonyl stretch vibration in the FTIR spectrum of the ground-state conformer (1708 cm$^{-1}$) and an additional induced broader peak at around 1640 cm$^{-1}$ (Figure 3a).\textsuperscript{[49]} For longer delays the induced absorption signal decreases in intensity, while its maximum shifts to higher frequencies. The same is observed for the ground-state bleach signal but on a longer time scale and with a smaller shift of the bleach signal. After about 30 ps,
the transient signal is completely vanished. A full global analysis of the transient data shows that they can be well described by a bi-exponential decay (Figure 3 b). A sequential kinetic model then leads to two species Sp1 and Sp2 with lifetimes of 1.5 ± 0.05 and 8.6 ± 1.1 ps, respectively, and the species-associated difference spectra (SADS) that are shown in the bottom panel of Figure 3a. Our data demonstrate that photoexcitation does not produce any long-lived species. The final species in the kinetic model (SpC) can thus be associated with the system in its electronic ground state.

By combining the derived SADS with the results of DFT calculations, we can elucidate the photodynamics of the system in full detail. As mentioned above, the initially excited state is $S_1$. With our time resolution (ca. 150 fs) we are only able to observe one excited-state species. We thus conclude that, similar to the related fumaramide system, excitation of $S_1$ is followed by ultrafast internal conversion processes that bring the molecule to $S_0$, and it is this state for which we observe the excited-state dynamics. This conclusion finds further support in our calculations on tetramethylazodicarboxamide. Geometry optimization of $S_0$ at the TD-DFT level shows that the molecule initially becomes more planar but never converges, most probably because of the proximity of a conical intersection.

TD-DFT calculations on the lowest electronically excited state $S_1$, on the other hand, find that in this state the molecule adopts a planar structure with a carbonyl stretch frequency that is in perfect agreement with the frequency of the induced absorption band observed in the SADS of Sp1 (Figure 3a). Further support for planarization of the molecule in the excited state is found in frequency calculations at the nonplanar Franck–Condon geometry. In this case, only a small shift of the carbonyl band is predicted ($\Delta \nu = 38 \text{ cm}^{-1}$), which is in line with the measured data but would be consistent with the pedalo-type motion. It is important to realize that one can only decisively conclude which type of motion occurs by identifying the structure of the excited-state species and not by merely considering the initial and final ground-state species (see section S5 in the Supporting Information for further discussion).

We thus associate Sp1 with $S_1$, which decays on a 1.5 ps timescale back to the ground state.$^{[51]}$ The excited-state lifetime of 1.5 ps indicates that internal conversion of the excited state occurs in regions of the potential energy surface of the excited state in which the energy gap with the ground state is relatively small or even absent, as it would be in the case of a conical intersection between the two states. Our computational methodology is not adequate to locate conical intersections; this would require multi-reference methods such as CASSCF with large active spaces (22 $\pi$-electrons), but the fact that our calculations show that there is a stable minimum in the excited state strongly suggests that a barrier needs to be overcome to access such a conical intersection with the ground state.

This excited-state relaxation process results in a vibrationally hot ground-state species, in which the carbonyl-stretch mode is slightly redshifted (causing the Sp2 SADS to look like the first derivative of the FTIR spectrum) because of anharmonic coupling with the hot low-frequency modes. Upon vibrational cooling, the thermally equilibrated ground state is recovered. Remarkably, the overall picture that thus emerges from experiments and calculations (Figure 4) is one in which a nonplanar ground state is excited to an electronically excited state with an equilibrium geometry that corresponds to the transition state between the two equivalent nonplanar ground-state conformers (Figure 2). We therefore conclude that during the photocycle the azodicarboxamide unit effectively performs a pedalo-type motion.

For the considered systems, the two ground-state conformers are fully equivalent. However, because of the nonplanar structure of the molecule, a non-symmetric substitution would lead to axial chirality, potentially providing the
basis for a chiral molecular switch similar to the alkene-based molecular rotary motors.[35] In addition, since azodicarboxamide derivatives have been used in hydrogen-bonded [2]rotaxanes,[32,33] which are known as building units in artificial molecular machines,[53–61] the volume-conserving motion might expand their range of applications.

In conclusion, by combining time-resolved infrared spectroscopy and quantum-mechanical calculation we have investigated an unprecedented light-driven dynamic behavior of azodicarboxamides. Our results demonstrate that in contrast to azobenzene-type molecules, azodicarboxamide switches respond to photoexcitation by means of a pedalo-type motion. This volume-conserving motion makes them ideal candidates for applications under spatially restricted conditions such as occur in the solid state, on surfaces, or upon embedding in photoactive polymers. In addition, the pedalo-type motion combined with the presence of hydrogen-bonding sites allows one to actively modulate the coupling of azodicarboxamide switches to their local environment. Such properties open up fascinating opportunities for tuning macroscopic properties in functional materials by light.

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Conflict of interest

The authors declare no conflict of interest.

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Figure 4. Photodynamics of N,N,N,N-tetrazenylazodicarboxamide molecular switch: Proposed excited-state relaxation pathway for the pedalo-type motion (k1 and k2 referring to the corresponding rate constants).
Because of the strong nonplanarity of the molecule in the ground state, the two carbonyl stretch vibrations are quasi degenerate. In the electronically excited state the molecule is predicted to become planar; but for such a geometry, only the antisymmetric combination of the carbonyl stretch modes is IR active.


It might be argued that the induced absorption band is due to population of the $v = 1$ vibrational level of the carbonyl stretch in the ground state after an ultrafast internal conversion process of the electronically excited state to the ground state occurring within the time resolution of our experiment. However, such a scenario can be firmly ruled out as it is well known that the anharmonic shift of the carbonyl stretch is typically 20 cm$^{-1}$ and thus much smaller than the observed frequency difference between the bleach and induced absorption bands of 65 cm$^{-1}$.


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