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Supporting Information

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

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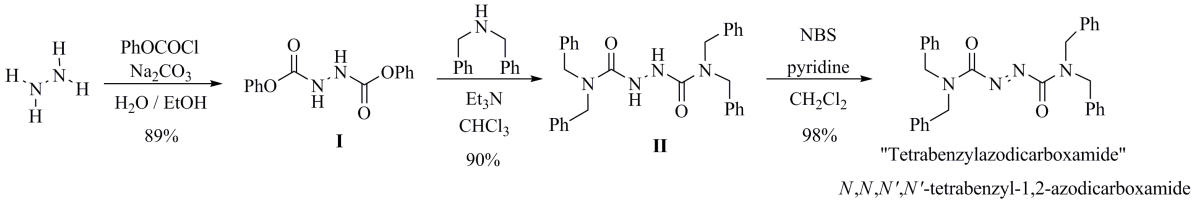
S1. Synthesis of tetrabenzylazodicarboxamide

Tetrabenzylazodicarboxamide was obtained in a 79% overall yield by the following three-step synthetic route:

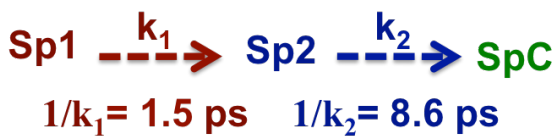


Diphenyl hydrazodicarboxylate (**I**) was synthesized from hydrazine as described in J. M. Harris, R. McDonald, J. C. Vederas, *J. Chem. Soc., Perkin Trans. 1*, **1996**, 2669-2674 and showed identical spectroscopic data as those reported therein. Afterwards *N,N,N',N'*-tetrabenzyl-1,2-hydrazodicarboxamide (**II**) was prepared as described in J. Berna, M. Alajarin, R.-A.Orenes, *J. Am. Chem. Soc.* **2010**, *132*, 10741-10747. Finally, to a solution of **II** (0.76 g, 1.56 mmol) in dichloromethane (20 mL) were added pyridine (135 μL, 1.72 mmol) and *N*-bromosuccinimide (0.28 g, 1.56 mmol). The resulting orange solution was stirred at room temperature for 1 h. Then the reaction mixture was diluted with dichloromethane (20 mL) and sequentially washed with water (40 mL), 5% aqueous solution of $Na_2S_2O_3$ (35 mL) and saturated solution of $NaHCO_3$ (2 x 35 mL). The organic phase was dried with anhydrous $MgSO_4$, and concentrated *in vacuo* to afford a crude material which was purified by column chromatography on silica gel eluting with a $CHCl_3$/MeOH (98/2) mixture as eluent to give the tetrabenzylazodicarboxamide as a yellow solid (0.74 g, 98%). This compound was reported in the last above mentioned paper and showed identical spectroscopic data as those reported therein.

Elemental analysis of tetrabenzylazodicarboxamide: calculated C, 75.61; H, 5.92; N, 11.76; found C, 75.63; H, 5.98; N, 11.53. This analysis was performed on a LECO CHNS-932 Elemental Analyzer from the University of Murcia (Spain).

S2. Spectroscopic details

A detailed description of the setup used for the UV-pump/IR-probe measurements has been given previously.[1] In short, we generated mid-IR probe pulses for our time-resolved experiments by an amplified Ti:sapphire system (Spectra-Physics Hurricane, 600 μJ, repetition rate 1 kHz). By pumping a commercial BBO-based OPA (Spectra-Physics OPA-800C), the signal and idler output were difference-frequency-mixed in an $AgGaS_2$ crystal. The UV pump pulses (400-340 nm, ca.1 μJ) were generated by SHG. The diameter of the UV pump focus was ca. 200 μm; that of the IR probe focus, ca. 150 μm. The delay positions were scanned by mechanically adjusting the beam-path of the UV pump using a Newport ESP300 translation stage. The sample was placed in the IR focus using a IR cell with CaF_2 windows (1 mm spacing). From the full width at half-maximum of the pump probe cross-correlation function a temporal resolution of 200 fs was determined. Transient spectra were recorded by subtracting non-pumped absorption spectra from the pumped absorption spectra, whereas the pump pulse was chopped at 500 Hz. An Oriel MS260i spectrograph was employed and the frequency-dependent IR intensity was measured using a 2×32 HgCdTe detector array (Infrared Associates). All transient IR measurements were done in chloroform and at room temperature. The global data analysis of the transient IR data was performed using a sequential model:



and according to the previous reported scheme.[2]

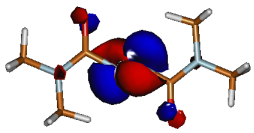
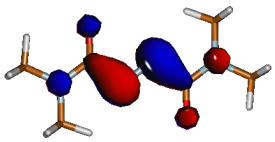
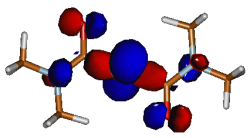
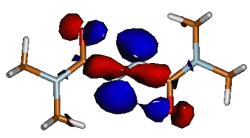
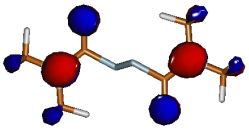
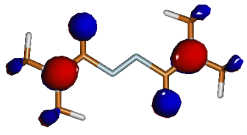
S3. Computational details.

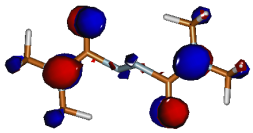
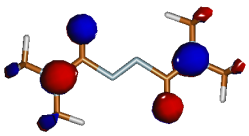
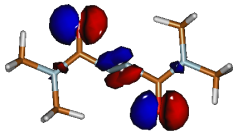
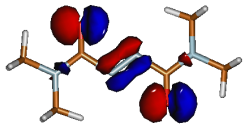
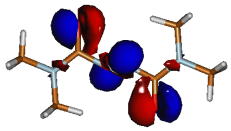
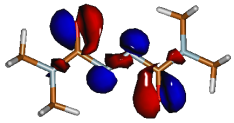
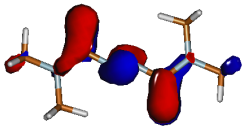
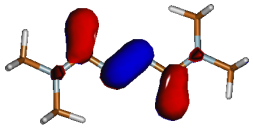
The geometry-optimization and normal-mode calculations of the ground and electronically excited state of the azodicarboxamide-based molecular switch were performed at the (Time-Dependent) Density Functional Theory ((TD)-DFT) level using the B3LYP functional[3] and the 6-31G(d,p) basis sets. The Polarizable Continuum Model (PCM) was employed to implicitly describe solvation effects (solvent: Chloroform).[4] To scan the potential energy surface in the electronic ground state (Figure 2a of the main text), calculations at the MP2/6-31G level were performed.[5] Subsequent calculations along the reaction coordinate of the pedalo-type motion (Figure 2b of the main text) were performed on the CCSD(T)/6-31++G** level using optimized geometries obtained by calculations at the MP2/6-31++G** level. All quantum mechanical calculations have been done using the Gaussian 09 software.[6]

S4. Ground-state geometry

The observed symmetry breaking in the geometry of the tetramethylazodicarboxamide-based molecular switch in the electronic ground-state can be explained by comparing the molecular orbitals of the non-planar molecule with those of the fictitious planar structure (see Table S1) and in particular the (HOMO-5) orbital. This orbital represents the doubly-occupied π-orbital at the azo-group and is stabilized by 0.446 eV for the non-planar structure as compared to the planar structure. In the planar structure the (HOMO-5) orbital shows an anti-bonding character with respect to the C-N bond. In the non-planar case, in contrast, a bonding contribution arises due the twisting of the C-N bond and a constructive overlap of the atomic orbitals.

Table S1: Analysis of the Molecular Orbital: Comparing the molecular orbitals (MO) of the non-planar tetramethylazodicarboxamide-based molecular switch, which represents the minimum in the electronic ground state, with the hypothetical planar structure in order to understand the structural properties of the molecule. MOs are plotted using an isovalue of 0.05 and MO energies are giving in a.u. above each MO.

	Non-planar	planar
LUMO	-0.082460 	-0.100600 
HOMO (MO46)	-0.234320 	-0.234760 
HOMO-1 (MO 45)	-0.254590 	-0.251730 

HOMO-2 (MO 44)	-0.256190 	-0.253880 
HOMO-3 (MO 43)	-0.278820 	-0.268900 
HOMO-4 (MO 42)	-0.310240 	-0.301490 
HOMO-5 (MO 41)	-0.363120 	-0.346730 

S5. Excited-state Geometry

To identify the motion the molecule performs upon photoexcitation, one intuitively would focus on identifying the structure of the molecule after that it has relaxed back to the electronic ground state. However, it should be realized that detection of ground-state conformers upon radiation that are different from the initial conformer only allows one to conclude that *something* has happened but not *along which path*. As an example may serve the photoisomerization pathway of *trans*-azobenzene, one of the working horses of molecular nanotechnology, for which there has been a long-standing debate on whether photoisomerization occurs via an out-of-plane torsional motion along the diazo-bond or an in-plane inversion at the nitrogen atoms.[7] In the case of the presently studied azodicarboxamide-based molecular switch further consideration of isomerization pathways similarly shows that the ground-state conformation generated via the pedalo-type motion can from a structural point of view also be reached by inversion at the two azo-nitrogen atoms, or by a combination of torsion and inversion. Identification of the final photoproducts thus does not shed light on the structure adopted in the electronically excited state.

The IR absorption spectrum of the molecule in the electronically excited state provides important fingerprints to unravel the photoinduced motion. To further support the conclusion on the loss of non-planarity upon photoxcitation, we have therefore performed calculations in which we have studied how the frequency of the IR-active carbonyl stretch mode depends on the planarity of the molecule. In these calculations we find that at the Frank Condon (FC) geometry the frequency of this mode changes from 1715 cm^{-1} in the ground state to 1677 cm^{-1} ($\Delta\nu$=38 cm^{-1}) in the excited state.[1] Upon planarization this frequency difference is almost doubled as the frequency decreases to 1649 cm^{-1}. Experimentally this band is observed at

[1]At this geometry the force field of S_1 contains modes with imaginary frequencies. However, inspection of these modes shows that they do not involve the carbonyl stretch and will thus not influence the frequency of the IR-active carbonyl stretch mode.

1640 cm^{-1}, which is not in line with a scenario in which the molecule would retain its ground-state non-planarity.

References

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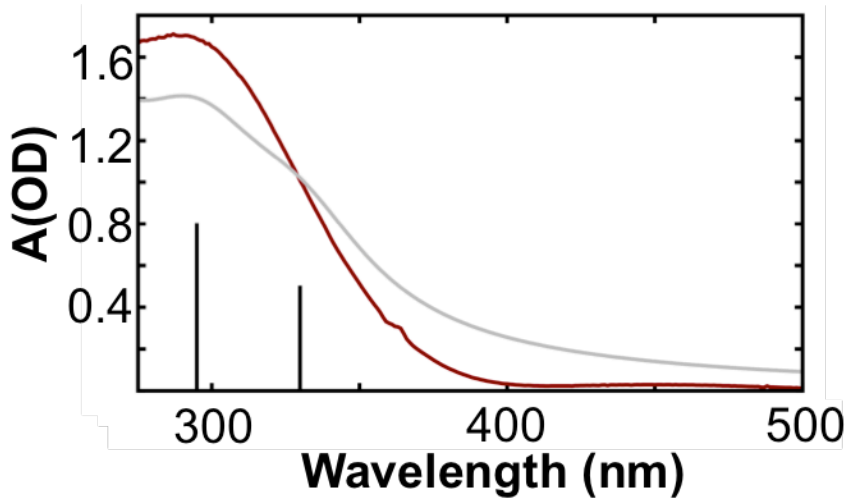

Figure S1. UV/Vis spectra of the azodicarboxamide-based molecular switch: solvent-corrected UV/Vis spectra of the sample dissolved in chloroform (c=6.6mM) (red); calculated spectra of tetramethylazodicarboxamide stick spectra (black); and Lorentzian broadened (half-width: 30 cm^{-1}) (gray) at the B3LYP/ 6-31G(d,p) level (PCM solvent: chloroform).

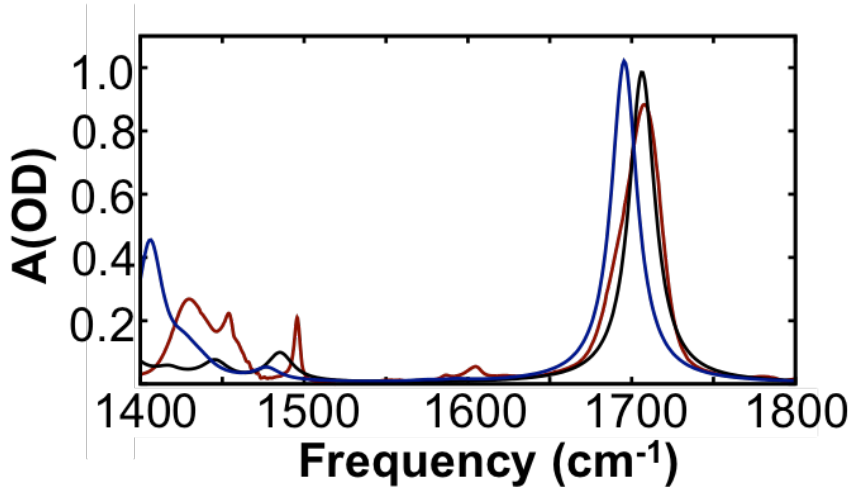

Figure S2. FTIR spectra of the azodicarboxamide-based molecular switch: solvent-corrected FTIR spectra of the sample dissolved in chloroform (c=6.6mM) (red); calculated spectra of tetrabenzylazodicarboxamide (black) and tetramethylazodicarboxamide (blue) at the B3LYP/ 6-31G(d,p) (PCM, solvent: chloroform) level using a scaling factor of 0.965.

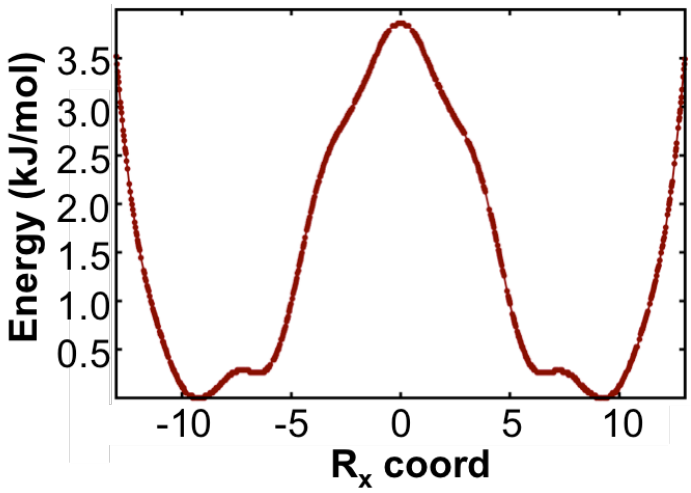

Figure S3. Energy profile along the intrinsic reaction coordinate (IRC) connecting the two ground-state conformers of tetramethylazodicarboxamide at the B3LYP/6-31G(d,p) (PCM solvent: chloroform) level.

Cartesian coordinates of equilibrium geometries S_0 and S_1

Both geometries were optimized at the B3LYP/6-31G(d,p) level and have been confirmed by normal mode analysis to be stable structures.

S_0-Geometry

24			
C	2.657362	-1.654856	0.060548
N	2.751011	-0.197684	0.054889
C	4.073994	0.376235	-0.159894
C	1.680097	0.620878	0.139508
O	1.684434	1.844411	0.093674
N	0.428946	-0.081933	0.442232
N	-0.428951	0.081926	-0.442262
C	-1.680102	-0.620879	-0.139543
O	-1.684448	-1.844414	-0.093769
N	-2.751008	0.197688	-0.05486
C	-2.657349	1.654859	-0.06047
C	-4.073992	-0.376233	0.15992
H	1.647429	-1.969978	0.318593
H	2.913144	-2.06004	-0.925339
H	3.355367	-2.064639	0.79778
H	3.99843	1.461195	-0.118989
H	4.761484	0.02617	0.617495
H	4.468208	0.075047	-1.13693
H	-3.355427	2.064671	-0.797617
H	-2.913028	2.060011	0.925457
H	-1.647442	1.969985	-0.31861
H	-4.761468	-0.026224	-0.617506
H	-3.998414	-1.461194	0.119081
H	-4.46823	-0.074988	1.136928

S_1-Geometry

24			
C	1.574218	-0.168027	1.863975
N	0.232603	-0.148832	1.30129
C	0.125388	0.051569	-0.134827
C	-0.908834	-0.305664	2.034012
O	-2.05452	-0.293583	1.583741
N	-0.645101	-0.489331	3.403041
N	-1.49585	-0.656919	4.30375
C	-1.232117	-0.840594	5.672778
O	-0.08643	-0.852686	6.123047
N	-2.373553	-0.997419	6.405501
C	-3.715169	-0.978211	5.842818
C	-2.266338	-1.197824	7.841618
H	1.528607	-0.324148	2.941549
H	2.162033	-0.976429	1.413725
H	2.081713	0.783144	1.665257
H	-0.92581	0.043814	-0.416323
H	0.571957	1.011595	-0.419887
H	0.652232	-0.746586	-0.67122
H	-4.222673	-1.929377	6.041536
H	-4.302976	-0.169804	6.29307
H	-3.669559	-0.822089	4.765244
H	-2.712916	-2.157847	8.126676
H	-1.21514	-1.190079	8.123112
H	-2.793175	-0.399665	8.378013