

Highly Efficient Reversible *Z*–*E* Photoisomerization of a Bridged Azobenzene with Visible Light through Resolved $S_1(n\pi^*)$ Absorption Bands

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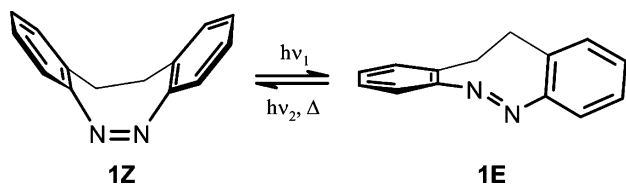
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Photochromic molecules, which can be reversibly switched between two isomeric forms with different colors, structures, or functional properties by light at distinctive wavelengths, attract ubiquitous attention for applications as optical memory and logic devices, or as molecular motors, machines, or manipulators.^{1,2} Azobenzene (AB) and its derivatives enjoy particular interest because of the large-amplitude structural changes between their elongated (*E*) and more compact (*Z*) forms, the reversibility of their transformations, and the high photostabilities which guarantee large numbers of switching cycles. The photochromic properties of AB are, however, far from ideal, because the $S_1(n\pi^*)$ electronic absorption bands of its (*E*) and (*Z*) isomers peak at practically the same wavelength ($\lambda = 450$ – 440 nm) and differ essentially only in their oscillator strengths. Switching AB forth and back therefore requires cycling between irradiation in the $S_1(n\pi^*)$ and $S_2(\pi\pi^*)$ bands, although the latter is located in the less easily accessible UV region, where other molecular moieties attached to the AB unit may suffer photodamage.

Here, we report on the photoswitching behavior of 5,6-dihydrodibenzo[*c,g*][1,2]diazocine (**1**). Although **1** has been first prepared quite some time ago,^{3–5} its high potential as a molecular photoswitch has not previously been recognized and studied in detail to our knowledge.

Scheme 1



Considering its basic functional unit, **1** is a bridged azobenzene derivative but has much more favorable photochromic properties than plain AB. The reversible photoconversion between its **1Z** and **1E** isomers is illustrated in Scheme 1. We show that **1Z** can be switched to **1E** with an efficiency >90% by using blue light at $\lambda \approx 370$ – 400 nm, and **1E** can be switched back to **1Z** with ~100% efficiency by green light with $\lambda \approx 480$ – 550 nm. The calculated ground state structures of both isomers obtained with the B3LYP/def2-TZVP method are displayed in Figure 1a.

We synthesized **1Z** in several batches following a modification of the protocol of Paudler and Zeiler (see Supporting Information).⁴

The product was checked by ¹H NMR spectroscopy and thin layer chromatography, and no traces of impurities were found. The single crystal X-ray diffraction structure (Supporting Information) confirms the calculated slightly disturbed (*Z*) conformation of the central CNNC moiety, which is almost coplanar with a CNNC dihedral angle of only 6.4° and NNC angles of 121° just slightly larger than the ideal sp^2 angle. The ethylenic bridge shows some conformational flexibility. Due to the ring strain, **1Z** and not **1E** is the thermodynamically stable form at room temperature, in complete contrast to normal ABs.

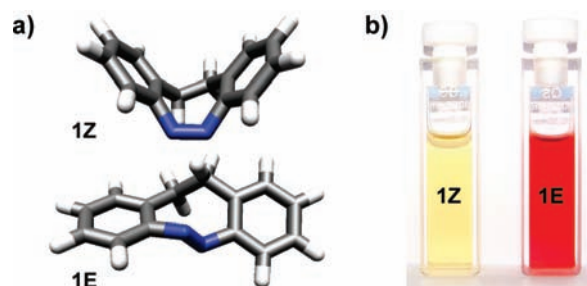


Figure 1. (a) Equilibrium structures of **1Z** and **1E** in the electronic ground states from quantum chemical calculations at the B3LYP/def2-TZVP level of theory using the TURBOMOLE program.⁶ (b) Colors of **1Z** (before irradiation) and **1E** (after irradiation at $\lambda = 385$ nm) in *n*-hexane.

The photoisomerization between **1Z** and **1E** was studied using dilute sample solutions in neat dry *n*-hexane. The UV/vis absorption spectra were monitored on a Shimadzu UV-2401 desktop spectrometer. Conversion of the (*Z*) to the (*E*) isomer was accomplished by irradiating the **1Z** solution using either a broadband UV lamp equipped with a Schott WG360 filter, giving a spectrum with a peak at $\lambda = 370$ nm and width $\Delta\lambda = 33$ nm (fwhm), a 400 mW light-emitting diode at $\lambda = 385$ nm ($\Delta\lambda = 11$ nm), or attenuated second harmonic light pulses at $\lambda = 387$ nm from a 170 fs (fwhm) Ti:Sa laser ($\Delta\lambda = 3$ nm). The (*E*) to (*Z*) back reaction was actively driven using a light emitting diode at $\lambda = 520$ nm or followed under thermal conditions.

The solution of **1Z** stored in the dark before irradiation is light yellow (Figure 1b). On irradiation at $\lambda = 385$ nm, however, the color turns to bright red, due to the photoisomerization to **1E**. The evident photochromic effect is underscored by a corresponding change in the measured near-UV/vis absorption spectrum displayed in Figure 2. As can be seen, **1Z** exhibits a distinctive absorption band with peak at $\lambda = 404$ nm, which we can assign to its $n\pi^*$ excitation. By irradiation at $\lambda = 385$ nm, this band almost disappears, while a new, slightly stronger, and significantly red-shifted absorption grows in. The new band, which is due to the

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$n\pi^*$ transition of the **1E** isomer, has its peak absorption at $\lambda = 490$ nm. Additional spectral changes are seen in the regions of the $\pi\pi^*$ transitions of both isomers at $\lambda < 350$ nm, where the absorption by the (*E*) isomer is again stronger than that of the (*Z*) isomer.

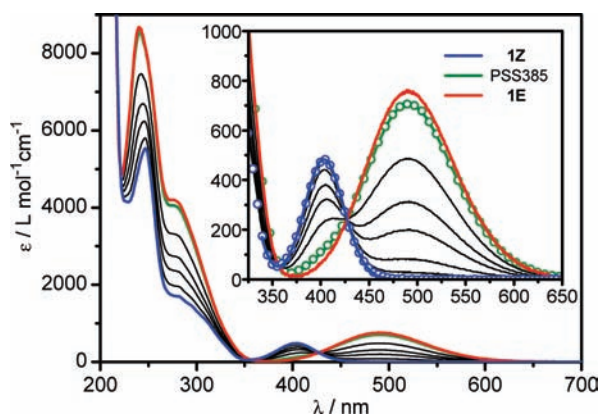


Figure 2. UV/vis absorption spectra of **1Z**, **1E**, and the photostationary state (PSS385) in *n*-hexane (blue, red, and green, respectively). The inset shows the $S_1(n\pi^*)$ region on an enlarged scale, with the recorded spectra (blue and green circles), the fitted log-normal spectra (blue and green lines), and the extracted (*E*) isomer spectrum (red line). The thin black lines show the evolution of the spectrum in the course of the thermal back-isomerization from the PSS385 after $\Delta t = 2, 4, 6, 10,$ and 15 h.

In the observed photostationary state at $\lambda = 385$ nm (PSS385), the (*E*) isomer is clearly predominant. By monitoring the absorption in the dark, its thermal lifetime was found to be $\tau = (4.5 \pm 0.1)$ h at 28.5 °C. To elucidate the spectrum for pure **1E** and to determine the quantitative (*Z*) to (*E*) conversion yield, we fitted the **1Z** spectrum using an appropriate log-normal model function (see Figure 2).⁷ We then fitted the spectrum of the PSS385 using a superposition of the suitably scaled **1Z** spectrum and a second log-normal model function for the **1E** absorption. The resulting spectrum for the pure **1E** isomer is displayed in Figure 2. From the absorption coefficients in the PSS385 compared to the pure isomers, the (*Z*) to (*E*) conversion was derived to be $\Gamma = (92 \pm 3)$ %. Conversely, using light at $\lambda = 520$ nm, the (*E*) isomer was quantitatively ($\sim 100\%$) switched back to the (*Z*) isomer. Moreover, the photoisomerization quantum yields in the forward and back directions, which we investigated using the method of Rau et al.,⁸ are $\Phi_{Z \rightarrow E} = (72 \pm 4)\%$ and $\Phi_{E \rightarrow Z} = (50 \pm 10)\%$. The severe constraints by the ethylenic bridge of our title compound do not appear to hinder its *E*-*Z* photoisomerization.

For a sustainable application as a molecular photoswitch, a compound must have low photochemical fatigue to allow for large numbers of switching cycles. Monitoring the UV/vis absorptions of **1** after many repeated alternating irradiation cycles at $\lambda = 385$ and at $\lambda = 520$ nm, respectively, we were unable to detect any signs for photodegradation (Figure 3). The excellent photostability of the compound is vividly demonstrated moreover by the fact that we could use one and the same batch for all our photoswitching experiments made in the course of half a year.

In conclusion, the bridged AB derivative **1** has much superior spectroscopic properties compared to the parent AB molecule and other commonly used AB derivatives. Most importantly, the respective $S_1(n\pi^*)$ bands of **1Z** and **1E** are well resolved (peak absorptions at $\lambda_Z = 404$ and $\lambda_E = 490$ nm), in striking contrast to AB, where the (*Z*) and (*E*) $n\pi^*$ bands are practically coincident. Efficient switching of **1** in the (*Z*) \rightarrow (*E*) and (*E*) \rightarrow (*Z*) directions can therefore be accomplished with visible light via one or the other $n\pi^*$ band, whereas conversion between the (*E*) and (*Z*) isomers of

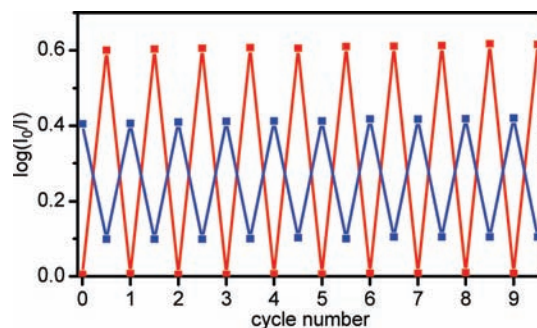


Figure 3. Measured absorbances of a solution of **1** at $\lambda_1 = 400$ nm (blue) and $\lambda_2 = 490$ nm (red) in the photostationary states after alternating irradiation at $\lambda = 385$ and $\lambda = 520$ nm in repeated switching cycles.

AB requires irradiation in the $n\pi^*$ band in the visible in one direction and in the $\pi\pi^*$ band in the UV in the other. The photoisomerization quantum yields of **1** are substantially higher in both directions than in the case of AB, where $\Phi_{Z \rightarrow E} = 53\%$ and $\Phi_{E \rightarrow Z} = 24\%$.⁹ Moreover, a $>90\%$ photoconversion yield cannot be achieved in the case of AB to our knowledge. Unlike AB, the $n\pi^*$ absorption of the (*E*) isomer of **1** is stronger than that of the (*Z*) isomer; this was reconciled by time-dependent density functional calculations on the excited states. The 4.5 h thermal lifetime of **1E** at room temperature is not a drawback especially for applications involving fast repeated forward and backward switching cycles or at lower temperatures.

Cyclic ABs, which attract much attention as shape-switchable molecules,¹⁰ show a tendency for unconventional properties when subject to strain. The ring structures alter the quantum yields,¹¹ and distorted nonplanar geometries shift the $n\pi^*$ bands of the isomers.¹² Except for **1**, however, we are aware of only one cyclic (*Z*)-AB that is thermodynamically favored over its (*E*) isomer without a badly compromised photoresponse, a highly constrained azobenzophane.¹³ Considering its distinctive structural change and the favorable properties of its $n\pi^*$ states, **1** appears to be an ideal functional unit for a molecular tweezer,¹⁴ which would be closed in its off-form (*Z*), opened by photoconversion to the (*E*) isomer, and returned to closed by the reverse photoconversion.

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Supporting Information Available: Experimental protocol, X-ray diffraction results for **1Z**, and calculated electronic ground state structures of **1Z** and **1E**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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