

Supplementary information for:

Unconventional Thermodynamically Stable *Cis* Isomer and *Trans* to *Cis* Thermal Isomerization in Reversibly Photoresponsive [0.0](3,3')-Azobenzophane

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1. Material and general methods.

[0.0](3,3')-Azobenzophane (1) was synthesized by the reported procedure.¹ 1 was characterized by ¹H NMR, ¹³C NMR and mass spectroscopies. The crystals of 1 suitable for X-ray analyses was obtained the recrystallization from CCl₄/hexane.

Solvents for the spectroscopic measurements (acetonitrile) were spectroscopic grade and used as received. Highly deuterated solvent (benzene-d₆, 99.95%D) was used for the ¹H NMR experiment with photoirradiation (Hg lamp and laser). All experiments were carried out in acetonitrile except for the ¹H NMR experiment.

UV-vis absorption spectra were measured on a JASCO V-570 spectrophotometer. ¹H NMR and ¹³C NMR spectra were recorded on a Varian 300 and 75 MHz spectrometer, respectively.

Photoirradiation was carried out with a 500 W high pressure mercury lamp with appropriate glass filters. Laser irradiation was carried out with 430- or 450-nm laser pulses from an optical parametric oscillator (OPO) system (Spectra Physics, MOPO-SL) excited by a Nd³⁺:YAG laser (Spectra Physics, Pro-230-10). The duration of the laser pulse was about 10 ns and intensity was 20 and 200 mJ / cm² per pulse. All irradiations were carried out until the photostationary state was established. Instantaneous photon number (*N*) of single laser pulse (20 mJ / cm² per pulse, 10 ns duration) is 10⁸ times more intense than the continuous Hg lamp (at 20 mW / cm²) during 10 ns (2×10⁻⁷ mJ / cm²). However, in terms of the total photon numbers per second, the laser ((20 mJ / cm²) × (10 pulses) = 200 mJ / cm²) is only 10 times more intense than that of the Hg lamp (20 mW / cm² × 1 s = 20 mJ / cm²).

2. Transient absorption measurement.

450 nm laser pulses (10 Hz, 18 mJ / cm²) from an optical parametric oscillator (OPO) system (Spectra Physics, MOPO-SL) excited by a Nd³⁺:YAG laser (Spectra Physics, Pro-230-10) were used for pumping light. The duration of the laser pulse was about 10 ns. Continuous light at 330 nm from a Xe lamp was used as a probe light. During irradiation, intensity of transmitted probe light decreased due to formation of *trans-cis* isomer and reached equilibrium after ca. 10 sec irradiation. Then, the laser irradiation was stopped and temporal change of probe light intensity was recorded. Laser power and irradiation time were adjusted to minimize the formation of the *trans-trans* isomer. The diameter of both pumping and probe light were 5 mm. The experimental time sequence for the transient absorption measurement is shown in Fig. 1S.

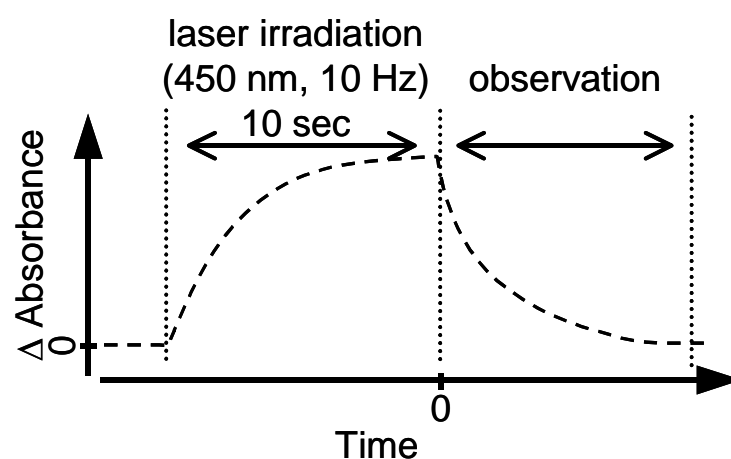


Fig. 1S Experimental time sequence for the transient absorption measurement.

3. DFT calculation.

DFT calculation was carried out with the GAUSSIAN03 program package² on a workstation (Fujitsu Celsius X630, Xeon 3.8 GHz x 2 processors). The B3LYP method³ was employed with a 6-31G(d,p) basis set. Zero-point energy corrections were calculated using computed harmonic frequencies. We applied simple DFT calculations and did not consider solvent effect (e.g. PCM approach) for the simplicity of discussion, because we have not observed considerable solvent effect so far in the experiment.

The optimized structure and energies of isomers of 1 is shown in Fig. 2S and selected bond length, bond angle, and dihedral angle along with those in the crystal are listed in Table 1S. We found another stable form in *cis-cis* isomer that has highly symmetric structure (*cis-cis* (twist)) in Fig. 2S). The energy is slightly higher than the bowl conformer that was observed by the X-ray analysis. Experimentally we could not observe this conformation by X-ray or NMR. Interconversion between two conformers maybe very fast because we were able to convert back and forth in a simple molecular model.

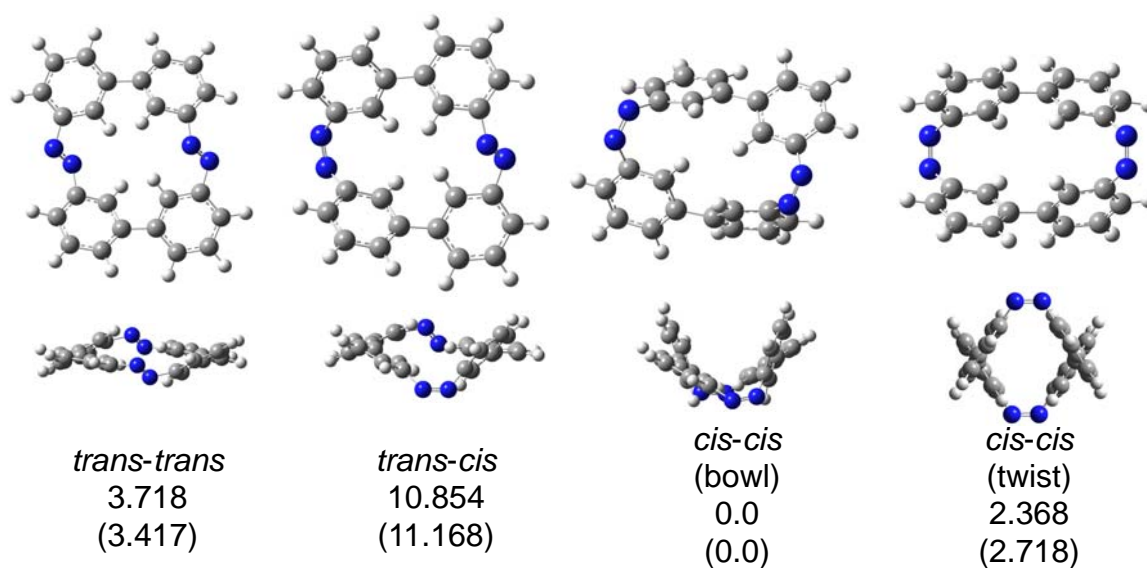


Fig. 2S Optimized structure of isomers of 1. Values are relative calculated energy with and without (in parentheses) zero-point energy correction.

4. Molecular structure.

Selected bond length, bond angle, and dihedral angle of DFT calculation and crystal structure are listed in Table 1S. The origin of stability of the *cis-cis* form is attributed to the highly strained geometry in the *trans* isomers. The destabilization of molecules can be deduced qualitatively from the bond angles and dihedral angles by comparing the values of azobenzene in the literature.^{4,5} For example, one of the C–N=N bonds in *trans-trans* isomer is compressed about 4 degrees, and the other is unbent about 5 degrees. The C–N=N–C dihedral angle is twisted ca. 27 degrees from the planar configuration. The distortion is even larger in the *trans* azo moiety in *trans-cis* isomer. The dihedral angle is twisted by as much as 33 degrees. On the other hand, the *cis-cis* isomer does not seem to be highly distorted both in bowl and twist forms. Thus, the already highly "twisted" geometry of *trans* azobenzene moiety plays an important role in the unusual *trans*-to-*cis* thermal isomerization. One might expect that these steric distortion may affect the N=N bond lengths, however, we could not find significant difference in these values among isomers.

Table 1S Selected bond length, bond angle, and dihedral angle of isomers of 1 calculated by DFT calculation and *cis-cis* isomer of 1 by X-ray crystallography.

Sample	Azo group	bond length / Å		bond angle / degree		dihedral angle / degree
		N=N		C–N=N		C–N=N–C
<i>trans-trans</i>	I	1.260		110.3	119.0	153.2
	II	1.260		110.3	119.0	–153.2
<i>trans-cis</i>	I (<i>trans</i>)	1.261		107.6	118.9	–146.8
	II (<i>cis</i>)	1.243		128.1	128.3	6.5
<i>cis-cis</i> (bowl)	I	1.249		122.9	123.8	5.6
	II	1.249		122.9	123.8	5.6
<i>cis-cis</i> (twist)	I	1.250		121.0	121.0	0.0
	II	1.250		121.0	121.0	0.0
<i>cis-cis</i> (bowl) crystal	I	1.246(6)		121.4(4)	120.4(4)	2.5(6)
	II	1.272(5)		122.3(3)	119.9(3)	5.8(5)
<i>trans</i> -azobenzene ^a		1.247(2)		114.1(1)	114.1(1)	180.0
<i>cis</i> -azobenzene ^b		1.253		121.9	121.9	8.0

a) Structure in the crystal reported in Ref. 4

b) Structure in the crystal reported in Ref. 5

5. Thermal isomerization from trans-trans isomer.

The sample solution was irradiated by Hg lamp (436 nm) for 10 min. The absorption at 320 nm was monitored at different temperatures. The time profile of the thermal isomerization is shown in Fig. 3S.

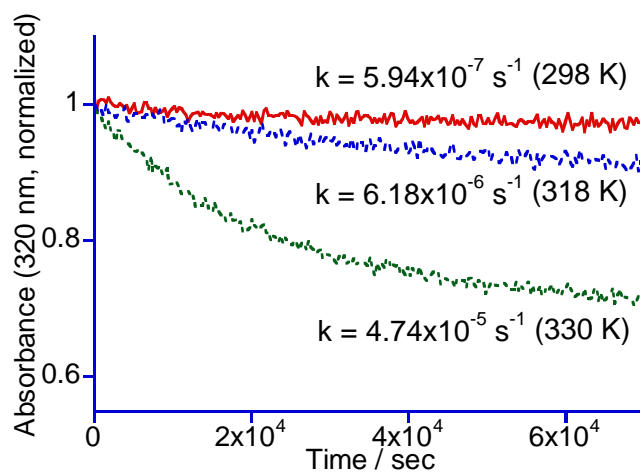
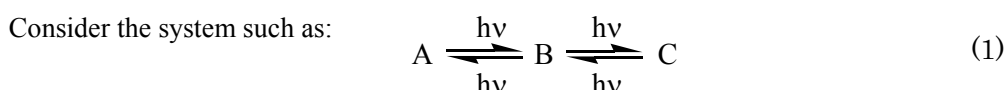


Fig. 3S Time profile of the absorption at 320 nm at 298, 318 and 330 K after the irradiation at 436 nm.

5. Considerations on light intensity dependence of the isomer ratio at the photostationary state.

The purpose of this section is to explain mathematically the light intensity dependence on the isomer ratio at the photostationary state, observed in this study. Let us consider a photoswitching system that contains three isomers such as A, B, and C. Photoisomerization can occur either in forward or backward directions and isomer B is an intermediate state. Firstly, we consider the system without thermal isomerization for simplicity. Then, we discuss the system with thermal isomerization.

a) three state system without thermal isomerization



In this system only photoisomerization can take place and thermal isomerizations are neglected. On light irradiation, the rate of isomerization can be written as:

$$\frac{d[A]}{dt} = -I(1-10^{-D}) \times \frac{\varepsilon_A[A]l}{D} \times \frac{1}{V} \times \Phi_{AB} + I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BA} \quad (2)$$

$$\begin{aligned} \frac{d[B]}{dt} = & I(1-10^{-D}) \times \frac{\varepsilon_A[A]l}{D} \times \frac{1}{V} \times \Phi_{AB} - I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BA} \quad (3) \\ & - I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BC} + I(1-10^{-D}) \times \frac{\varepsilon_C[C]l}{D} \times \frac{1}{V} \times \Phi_{CB} \end{aligned}$$

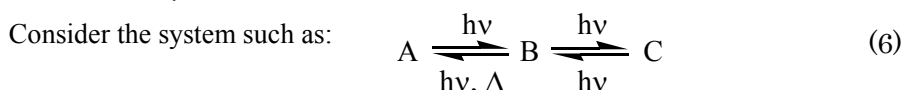
$$\frac{d[C]}{dt} = I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BC} - I(1-10^{-D}) \times \frac{\varepsilon_C[C]l}{D} \times \frac{1}{V} \times \Phi_{CB} \quad (4)$$

where [A], [B] and [C] are concentration of A, B and C, I , ε , D , l , V and Φ are light intensity, molar extinction coefficient, absorption value, optical length, volume of sample solution, and quantum yield for isomerization, respectively. At the photostationary state, $d[A]/dt = d[B]/dt = d[C]/dt = 0$ and from equations 2 and 4, we can obtain:

$$\frac{[C]}{[A]} = \frac{\varepsilon_A \Phi_{AB} \Phi_{BC}}{\varepsilon_C \Phi_{BA} \Phi_{CB}} \quad (5)$$

Therefore, the isomer ratio of initial (A) and final (C) state depends on the absorptivity and the quantum yields. In this case, the isomer ratio does not depend on light intensity.

b) three state system with thermal isomerization



In this system both photoisomerization and thermal isomerization can take place. However, the thermal isomerization from C to B can be neglected if the lifetime of C is long enough (such as 20 days). On light irradiation, the rate of isomerization can be written as:

$$\frac{d[A]}{dt} = -I(1-10^{-D}) \times \frac{\varepsilon_A[A]l}{D} \times \frac{1}{V} \times \Phi_{AB} + I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BA} + k[B] \quad (7)$$

$$\begin{aligned} \frac{d[B]}{dt} = & I(1-10^{-D}) \times \frac{\varepsilon_A[A]l}{D} \times \frac{1}{V} \times \Phi_{AB} - I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BA} \\ & - I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BC} + I(1-10^{-D}) \times \frac{\varepsilon_C[C]l}{D} \times \frac{1}{V} \times \Phi_{CB} - k[B] \end{aligned} \quad (8)$$

$$\frac{d[C]}{dt} = I(1-10^{-D}) \times \frac{\varepsilon_B[B]l}{D} \times \frac{1}{V} \times \Phi_{BC} - I(1-10^{-D}) \times \frac{\varepsilon_C[C]l}{D} \times \frac{1}{V} \times \Phi_{CB} \quad (9)$$

where k is the rate constant for the thermal isomerization from B to A. Similar to the previous case, $d[A]/dt = d[B]/dt = d[C]/dt = 0$ at the photostationary state. From equations 7 and 9, we can obtain:

$$\frac{[C]}{[A]} = \frac{\varepsilon_A \varepsilon_B \Phi_{AB} \Phi_{BC}}{\varepsilon_C \Phi_{CB} (\varepsilon_B \Phi_{BA} + DVk/I(1-10^{-D})l)} \quad (10)$$

From equation 10, it can be realized that the ratio of the isomer C increases when more intense light (higher I value) is applied. Further, the ratio of the isomer C decreases when the thermal isomerization is faster (higher k value). The theoretical upper limit of the $[C]/[A]$ value (when $I \rightarrow \infty$ or $k \rightarrow 0$) is identical to the equation 5.

In the case of the azobenzenophane in this study, isomers A, B, and C correspond to *cis-cis*, *trans-cis*, and *trans-trans* isomers, respectively. The mathematical considerations described above agree well qualitatively to our observations in this study as well as previous results reported in the literature.⁶

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