Unconventional thermodynamically stable *cis* isomer and *trans* to *cis* thermal isomerization in reversibly photoresponsive [0.0](3,3′)-azobenzenophane†

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Sterically hindered [0.0](3,3′)-azobenzenophane exhibits thermal *trans*-to-*cis* isomerization to the thermodynamically stable *cis–cis* isomer, and reversible photochemical isomerization with good fatigue resistance.

It is well known that azobenzene exhibits photochemical *trans* → *cis* and *cis* → *trans* isomerizations upon irradiation of UV and visible light, respectively. Usually the *cis* isomer is thermally less stable, so *cis* → *trans* thermal isomerization takes place in the dark.[1] Utilizing these photo- and thermal properties of azobenzene, numerous photofunctional molecules and photoswithing devices had been designed.[1] Controlling the photo- and thermal reactivity of azobenzene is a prerequisite to optimize the performance of these photofunctional devices. Especially, controlling the volatility of the molecular information generated by light irradiation due to thermal instability of *cis*-azobenzene is of particular interest and is crucial to many proposed practical applications.

In literature, some reports can be found that *cis* isomers of azobenzenes are thermodynamically stable but this is achieved only by compromising its photoresponsive properties.[2,3] Grützmacher *et al.* synthesized macrocyclic azobenzenes in which the 4- and 4′-positions were connected by a covalent chain.[2d] Thermally stable *cis* isomers were isolated when the chain contains four, six and seven atoms, however these compounds were photochemically decomposed upon UV or visible light irradiation. Thermal equilibrium between *trans*- and *cis*-isomers was observed when the chain is longer (eight or nine atoms). Fujita *et al.* showed that thermal and photochemical *cis* → *trans* isomerizations can be suppressed by incorporating *cis*-azobenzene into a supramolecular host molecule.[3]

Azobenzenophanes (macrocyclic azobenzene dimers) are of interest because the photochromic properties of two azobenzene moieties in a molecule often influence each other by the drastic conformational change upon isomerization, resulting in altering stability of isomers and a gate effect on photoisomerization.[4–6] In the course of our studies of azobenzenophanes,[4] we have developed photoresponsive molecular hinges, where two xanthene groups are connected by two azo moieties.[5] It exhibited hinge-like motion between *trans–trans* (open state) and *cis–cis* (closed state) isomers on photoirradiation, with a short-lived intermediate *trans–cis* isomer. Due to the presence of the rigid xanthene bridge, the *cis–cis* isomer was stabilized and its lifetime was 6.4 years at 303 K,[5b] the longest lifetime of a *cis* isomer of azobenzene derivative as far as we know. However, the *cis–cis* isomer was still less stable than the corresponding *trans–trans* isomer and thermal *cis* → *trans* isomerization was inevitable. To the best of our knowledge, there is no report on azobenzene derivatives that exhibit 'reverse' stability, such that a thermal *trans* → *cis* isomerization occurs while its photoresponsive properties are unchanged.

Herein we report the first thermodynamically stable *cis* isomer of an azobenzene derivative, azobenzenophane (**1**), which exhibits thermal *trans* → *cis* isomerization and reversible photochemical isomerization with good fatigue resistance. The azobenzenophane reported here consists of two azobenzenes connected cyclically at 3- and 3′-positions without spacers. The synthesis of **1** was reported recently, however, neither its structure nor photochromic properties has been reported.[7] We have synthesized compound **1** by the reported procedure and obtained crystals suitable for X-ray crystal analysis. Surprisingly, the configuration of both –N=N– bonds are in *cis* forms in the solid state as shown in Fig. 1.‡ Although the molecule has no crystallographically imposed symmetry it does have approximate twofold symmetry, with the geometry at the two azobenzene moieties being slightly different. The dihedral angles of the two C–N=N–C bonds are 2.5(6) and 5.8(5)° with N=N bond lengths of 1.246(6) and 1.272(5) Å, respectively.

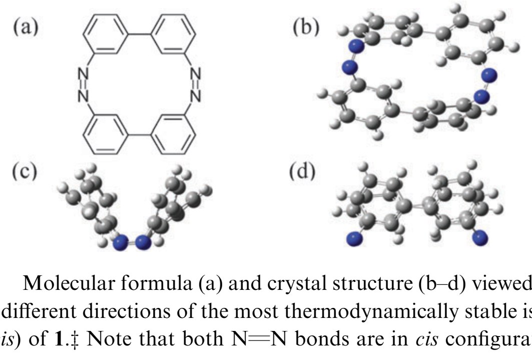

Fig. 1 Molecular formula (a) and crystal structure (b–d) viewed from three different directions of the most thermodynamically stable isomer (*cis–cis*) of **1**.‡ Note that both N=N bonds are in *cis* configuration.

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† Electronic supplementary information (ESI) available: Experimental details for the spectroscopic studies, calculation details and discussion of the light intensity dependence on the isomer ratio at PSS. Crystal data for the *cis–cis* isomer of **1**. CCDC 670051. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718813g

The benzene rings adjacent to each other (biphenyl moiety) are twisted about 28° as estimated by the C(*ortho*)–C(*ipso*)–C(*ipso′*)–C(*ortho′*) dihedral angles. Both the biphenyl moieties are bent towards the inside of the molecular ring by *ca.* 20°.

The UV-Vis absorption spectra of **1** (Fig. 2) gave us the preliminary indication that the *cis–cis* configuration of the molecule is the most stable form even in solution. There was only a single absorption band peaking at 416 nm (ε = 1160 M^{-1} cm^{-1}) in the region between 260 and 600 nm. Generally, *trans*-azobenzene moieties without polar substituents exhibit an intense absorption (π,π^* band) around 300–350 nm.[1a,4,6] However, the observed spectrum lacks this band and the spectrum is rather similar to that of the *cis*-azobenzene moiety.[1a,4,6] Aromatic protons of **1** in the ^{1}H NMR spectrum appeared at higher magnetic field region (6.4–6.8 ppm, Fig. 3(a)) characteristic of *cis* azobenzene.[5,8] These results indicate the configuration in solution is *cis–cis*. Both UV-Vis and NMR samples were kept in the dark for one month at ambient temperature and there was no change in the spectra.

Upon irradiation at 436 nm by a high-pressure mercury lamp, a slight change was observed in the absorption spectrum (Fig. 2(a), dotted line). It reached the photostationary state (PSS) within a few minutes and no further change was observed upon prolonged irradiation. The difference spectra from before and after the 436 nm irradiation showed the absorption maximum at 314 nm, which corresponds well to the π,π^* band of *trans*-azobenzene.[1a,4,6] Thus, the azobenzene moiety in the observed photoproduct is in *trans* configuration, and can be assigned to either the *trans–cis* or *trans–trans* isomer.

We hypothesized that the observed isomer should actually be the *trans–trans* isomer, and the reason for the only slight change in the absorption spectra is due to 'fast' recovery of *cis–cis* isomer from the highly unstable short-lived intermediate *trans–cis* isomer. If so, the absorption change at 314 nm (or the ratio at PSS) must be dependent on the light intensity because the overall photochemical reaction is a stepwise two-photon reaction to generate *trans–trans* from *cis–cis via trans–cis* (for detailed discussion see ESI†). Larger light intensity dependence on the isomer ratio at PSS can be found when the lifetime of *trans–cis* isomer is shorter. Similar light intensity dependences have been observed in some azobenzenophanes,[4b–d,5] although their direction of thermal isomerization (*cis* → *trans*) is opposite to this study (*trans* → *cis*). On the other hand, if the observed photoproduct is the *trans–cis* isomer, the light intensity dependence would not be observed.

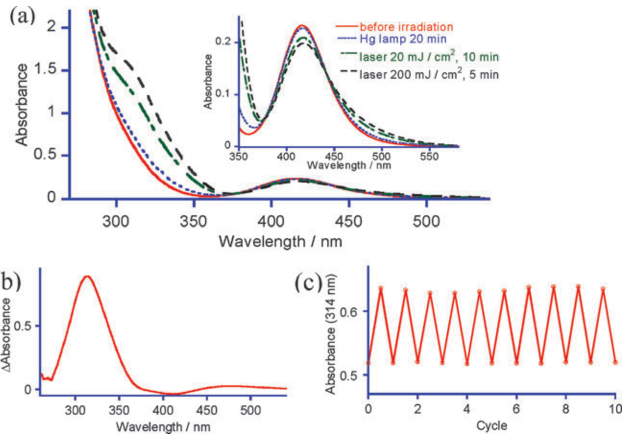

Fig. 2 UV-Vis absorption spectra of **1** upon irradiation with an Hg lamp (436 nm, 20 mW/cm^2, 20 min) or with a laser (430 nm, 10 Hz) (a),§ difference absorption spectrum between before and after the laser irradiation (b), and absorption changes observed at 314 nm after alternating irradiations at 436 and 365 nm over 10 complete cycles (c).

We irradiated the solution for 10 min by 430-nm laser pulses from an optical parametric oscillator (OPO) system excited by a Nd^{3+}:YAG laser. The duration of the laser pulse was about 10 ns and intensity was 20 mJ/cm^2 per pulse. An increase of the 314 nm band at PSS was observed compared to the Hg lamp (Fig. 2(a)). Additional increase of the laser intensity (200 mJ/cm^2 per pulse) by focusing the laser led to a further increase of the 314 nm band.

When a benzene-d$_6$ solution of **1** was irradiated by an Hg lamp small peaks appeared in the lower magnetic field region, where aromatic protons of *trans*-azobenzene generally appear (Fig. 3(b)).[4–6,8] On laser irradiation (170 mJ/cm^2 per pulse) these signals became more intense. These new peaks appeared at 7.59 (dd, J = 7.7 and 2.0 Hz), 7.36 (t, J = 2.0 Hz), 7.30 (dd, J = 7.7 and 2.0 Hz) and 7.09 ppm (t, J = 7.7 Hz) with equal intensity. It can be expected that the signals of the *cis*-azobenzene moiety in the *trans–cis* isomer would be distinguishable form those of *cis–cis* isomer due to the drastic conformational change upon isomerization. However, no new peaks appeared at higher magnetic field (*cis*-azobenzene) region (Fig. 3(c)), indicating that no *trans–cis* isomer was detected. Therefore, the photoproduct observable in the UV-Vis and NMR time scale is assigned as the *trans–trans* isomer, and the ratio of isomer at PSS depends on the light intensity. From the integration of the peaks, the ratio of isomers were 9/100 and 30/100 (*trans–trans*/*cis–cis*) under the conditions of Fig. 3(b) and (c), respectively.

Further, to our surprise, the *trans–trans* isomer was thermodynamically unstable and exhibited *trans*-to-*cis* isomerization. By keeping the photoirradiated solutions in the dark, the *trans–trans* isomer disappeared and the *cis–cis* isomer was regenerated. The *trans–trans* isomer had a lifetime (1/*k*) of 20 days at 298 K and its activation energy was 26.2 kcal mol^{-1}.

As mentioned above, the dependence of light intensity suggests short lifetime of *trans–cis* isomer. To evaluate the lifetime directly, we examined transient absorption measurements. The sample

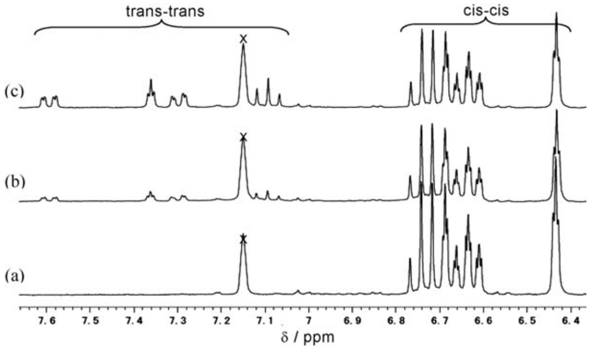

Fig. 3 ^{1}H NMR spectra of benzene-d$_6$ solution of **1** without photoirradiation (a), after 2 h irradiation with a high pressure Hg lamp (436 nm, 30 mW/cm^2) (b), and after 10 min laser irradiation (450 nm, 10 Hz, 170 mJ/cm^2 per pulse) (c).

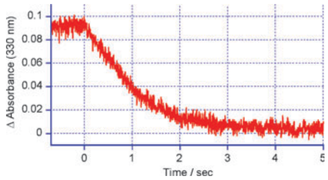

Fig. 4 Time profile of transient absorption of **1** monitored at 330 nm. The sample solution of *cis–cis* isomer of **1** was irradiated by 450 nm laser pulses, and the observation was carried out immediately after cutting off the laser. The Δ absorbance value is based on the sample absorption before the laser irradiation.

solution was excited by 450-nm laser pulses (10 Hz, 18 mJ/cm^2). Continuous light at 330 nm from a Xe lamp was used as a probe light. During irradiation, the intensity of transmitted probe light decreased due to formation of the *trans–cis* isomer and reached equilibrium after *ca.* 10 s irradiation. Then, the laser irradiation was stopped and temporal change of probe light intensity was recorded. The observed time profile of transient absorption due to *trans–cis* isomer is shown in Fig. 4. The signal decayed exponentially and returned to the original baseline after 5 s, indicating that the thermal isomerization direction is *trans–cis* → *cis–cis* and the formation of *trans–trans* isomer by excitation of *trans–cis* isomer is negligible under this condition. The lifetime ($1/k$) of the *trans–cis* isomer can be determined to be 1.0 s.

Photochemically, **1** exhibited reversible isomerization between *cis–cis* and *trans–trans* forms. The *trans–trans* isomer disappeared on irradiation of UV (365 nm) light from Hg lamp. The sample solution became identical to the initial state (*cis–cis*) after UV irradiation, indicating the photoreaction is quantitative. Alternate irradiation of 436 and 365 nm light showed good fatigue resistance (Fig. 2(c)). The overall reaction scheme of **1** is depicted in Fig. 5.

DFT calculations (B3LYP/6-31G(d,p)) were carried out to estimate the relative stability of isomers of **1** (Fig. 5). The most stable isomer was the *cis–cis* form in which the shape of molecule is a bowl-like structure, that matches well to the crystal structure. The *trans–cis* isomer is the most unstable as reflected by its short lifetime. The *trans–trans* isomer is at 3.7 kcal mol^{-1} higher energy than the *cis–cis* isomer. The thermodynamical stability of *cis–cis* isomer is attributed to the relatively higher energies of *trans* isomers caused by highly strained geometry of azobenzene moieties, revealed by the calculated structures (see ESI†for discussion).

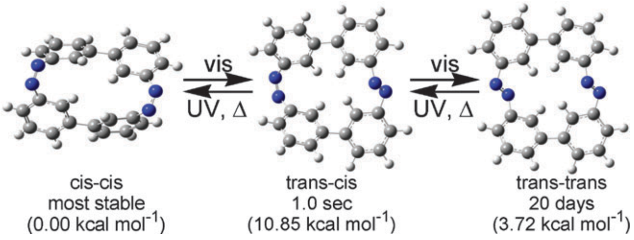

Fig. 5 Reaction scheme of photochemical and thermal isomerization of **1**. Note that thermal *trans*→*cis* isomerizations take place and the *cis–cis* isomer is most stable. Values in parentheses are calculated relative energies (ΔH_f) by B3LYP/6-31G(d,p) with zero-point energy correction. Molecular structures shown are crystal (*cis–cis*) and calculated (*trans–cis* and *trans–trans*) structures.

To date, to the best of our knowledge, this is the first report of thermodynamically stable *cis* isomer of an azobenzene derivative that exhibits unusual thermal *trans*→*cis* isomerization and photochemically reversible isomerization. The lifetime (reaction rate) of thermal *trans*→*cis* isomerization of azobenzene **1** ranges from 20 days (*trans–trans*→*trans–cis*) to 1.0 s (*trans–cis*→*cis–cis*) (1.7 × 10^6 times acceleration!). Our results provide a new insight into the structure–property relationship in azobenzenes such that the relative stability of isomers can be 'reversed' by controlling the steric environment of the azobenzene.

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Notes and references

‡ Crystallographic data for *cis,cis*-[0.0](3,3′)-azobenzenophane: Yellow plate (0.30 × 0.10 × 0.03 mm^3), monoclinic, $P2_1/n$, a = 10.128(3) Å, b = 16.935(5) Å, c = 10.677(3) Å, β = 94.323(7)°, V = 1826.1(10) Å^3, Z = 4, ρ_{calcd} = 1.311 g cm^{-3}, F000 = 752, theta range 2.26–25.00°, Mo$_{K\alpha}$ λ = 0.71073 Å, T = 223(2) K, No. of unique reflections = 3126, GOF = 0.661, $R1$ = 0.0701, $wR2$ = 0.2401.

§ All irradiations were carried out until PSS was established. Instantaneous photon numbers (N) of single laser pulse (20 mJ/cm^2 per pulse, 10 ns duration) is 10^8 times more intense than the continuous Hg lamp (at 20 mW/cm^2) during 10 ns (2 × 10^{-7} mJ/cm^2). However, in terms of the total photon numbers per second, the laser ((20 mJ/cm^2) × (10 pulses) = 200 mJ/cm^2) is only 10 times more intense than that of the Hg lamp (20 mW/cm^2 × 1 s = 20 mJ/cm^2).

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