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Strain, Switching and Fluorescence Behavior of a Nine-Membered Cyclic Azobenzene

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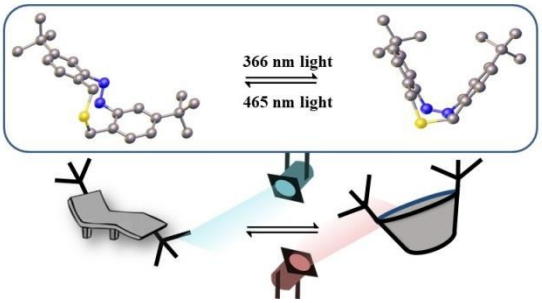

Cyclic azobenzenes with ring strain possess improved photochromic properties in comparison to the acyclic analogs. In this study, we report a nine-membered cyclic azobenzene. This cyclic azobenzene follows the stability of the acyclic systems with the *trans* isomer as the thermally stable form indicating its flexible structure, yet at the same time, it displays the fluorescence properties that is unusual for azobenzenes and requires structural rigidity. The properties of the molecule are thus a result of a balance between the flexibility and rigidity of its structure.

Introduction

Photochromic compounds switch reversibly between two isomeric forms having different colors, structures, and functional properties.[1] They are promising candidates for optical memory and logic devices, molecular motors and machines[2-3] and are currently been used in photochromic glasses and smart windows.[4] Azobenzenes are one of the most widely used photochromic systems that undergo isomerization with light of different wavelengths.[5] Despite its discovery almost two centuries ago by Mitscherlich, excitement with azobenzenes never seem to decline.[6] Usually, for azobenzenes, the *trans* form are the thermally more stable form.[7-9] When the thermodynamically stable *trans* form is exposed to UV light, it is converted to the less stable *cis* form. The *cis* form reverts to the *trans* isomer either upon irradiation with visible light, or thermally.[10] Besides photoisomerization, electrocatalytic cis → trans isomerization has also been demonstrated with azobenzene systems recently.[11] Although, a large number of azobenzene based photochromic systems are reported - the majorities of them have acyclic structures that often suffer from several drawbacks including their non-quantitative interconversion leading to photostationary states, low quantum yields and thermal instability of the *cis* isomers.[12] In contrast, Herges and coworkers have recently demonstrated the superior switching properties of the cyclic azobenzene photochromes[13-14] where the boat-like *cis* form isomerizes to the *trans* isomer with >90% conversion with soft UV light (385 nm), and with 520 nm visible light, the reverse photoreaction is almost quantitative. The faster switching of the cyclic azobenzene systems primarily occurs due to the molecular strain in the cyclic azobenzene molecule. The superior photophysical properties of the cyclic azobenzene compounds make them realistic candidates for applications in photoswitchable drugs and functional materials[15] However, certain cyclic azobenzene systems having enhanced reactivity undergo undesired rearrangement and subsequent cleavage.[16] Cyclic azobenzene molecule containing sulfur with various lengths of methylene chains [$(CH_2)_n$, *n = 3*

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Electronic Supplementary Information (ESI) available: [Procedures for the synthesis, characterization, photo and thermal isomerization studies and crystallographic data CIF file (CCDC 157005). See DOI: 10.1039/x0xx00000x

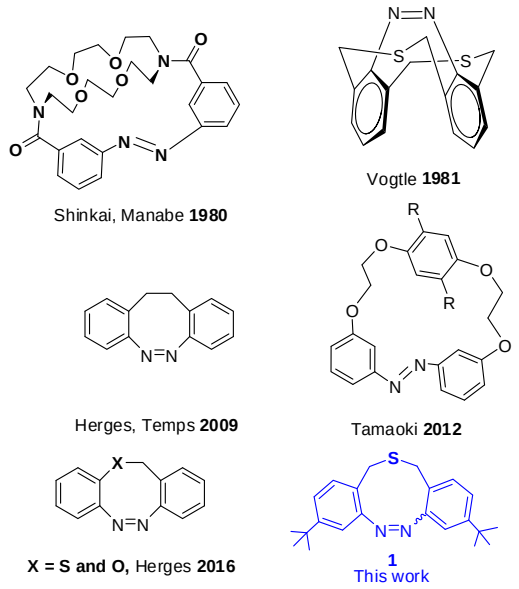


Figure 1: Reported cyclic azobenzenes and our compound **1**.

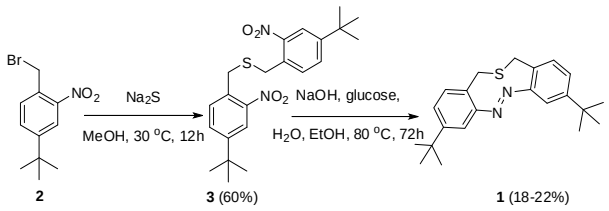
and *4*] have been reported three decades ago.[17] Voegtle's group has reported an intra-annularly azo-substituted [3.2.3](1,2,3)phane although the photochromic properties of the compound was not discussed by the authors (Figure 1).[18] Azobenzene-bridged crown ethers and azacrown ethers were synthesized by Shinkai and Manabe's group (Figure **1).**[19-20] Tamaoki and coworkers have reported the crystal structure of a macrocyclic *cis* azobenzene and systematically studied its thermodynamic parameters for the switching.[21] The same group has reported several cyclic azobenzene molecules with large ring size (>20) and has demonstrated their functions as chiroptical switches, chirality sensors, and molecular brakes.[22-27] The superior switching properties of the cyclic azobenzenes with eight-membered ring systems have sparked tremendous interest for mechanistic investigations primarily by computational methods.[28-33] It was observed that in contrast to Herge's eight membered ring systems, the large ring-size in these molecules were flexible enough to allow the *trans* form to be the thermally stable form, similar to what is observed in case of the acyclic azobenzene switches.

This prompted us to explore the limit of the ring size for obtaining the *cis* form as the thermally stable form over its *trans* isomer. Moreover, the azobenzene compounds are non-fluorescent. Certain structural features such donor–acceptor substitution,[34] hydroxyl substitution,[35] bulky *ortho* substitution, boron-chelated N=N [36] imparts fluorescence properties to these photochromes. Alternatively, self-assembled azobenzene aggregates[37-38] can display aggregation-induced emission properties.[39-44] In general, the fluorescence properties of strained cyclic azobenzene systems that do not have any of the above features have not been studied. We envisaged that if our 9-membered azobenzene is structurally rigid enough, it may display fluorescence properties.

Results and discussion

Synthesis and characterization. We have, therefore, synthesized a cyclic azobenzene system **1** containing a nine-membered ring having a sulfur and methylene-bridges (Figure 1). However, as aptly pointed out by Herges,[45] synthesis of these compounds are notoriously difficult and lack reproducibility. In contrast, the optimized two-step synthesis of **1** containing the nine membered cyclic azobenzene system is reproducible, albeit the low yield (typically <20%). The azobenzene compound **1** was synthesized upon the reduction of the *bis*(nitrobenzyl)sulfane precursor **3** with glucose/NaOH as the reducing agent.[46-47] The product was purified by preparative TLC and was characterized thoroughly by the ^{1}H and ^{13}C NMR, IR spectroscopy and mass spectrometry.

In addition, red crystals of compound **1** were grown by recrystallization of the chromatographed product upon slow evaporation from an acetonitrile solution at room temperature. Single crystal XRD afforded the structure of compound **1** (Figure 5). The precursor **3** was synthesized from the corresponding *o*-nitrobromobenzyl compound **2** upon reaction with sodium sulfide in MeOH at room temperature.[48-49] This synthesis in milligrams to gram scale was repeated twelve times to check the reproducibility. The best yields (22%) were obtained when the reaction was performed in 100 mg scale (with respect to the starting material **3**). In the grams scale, the yields are typically lower (<20%).



Scheme 1. Synthesis of the cyclic azobenzene **1**

In the first step of for the preparation of the precursor compound of **2** from 4-tert butyl toluene (see Scheme S1), the presence of the t-butyl groups forces the nitration exclusively to the ortho position with respect to the methyl groups. In addition, it should be noted that obtaining the cyclic azobenzene product requires the presence of the two nitro groups of the thioether **3** in a close proximity in the intramolecular cyclization step. Thus, it is conceivable that the presence of the two t-butyl groups in the thioether intermediate **3** ensures that the two bulky t-butyl groups are far apart and thereby forces the two $-NO_2$ groups close to each other that probably helps in obtaining a consistent yield of the target cyclic azobenzene **1**. This also minimizes the intermolecular polymeric azobenzene formation.

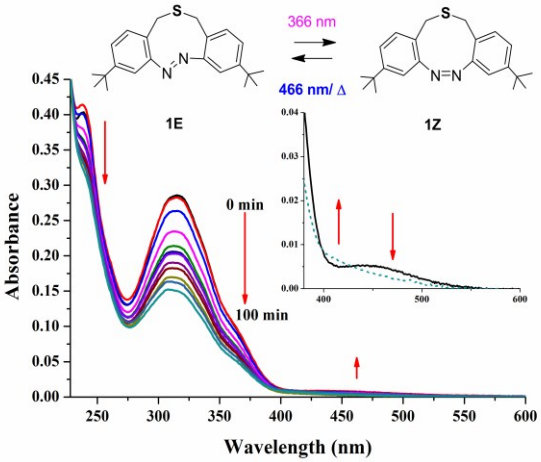


Figure 2: *Trans-cis* isomerization of the cycic azobenzene **1** (*top*); UV–vis spectral changes upon exposure of *trans*-**1** (3 × 10^{-5} M) in acetonitrile with 366 nm UV light (irradiation time: 0 – 100 min); *Inset*: The zoomed-in version of the 450 nm bands of the two isomers.

The *trans* isomer displayed absorption bands at λ_{max} = 238, 316, 360 (sh.) and 444 nm. The band at λ_{max} = 316 nm (ε = 9500 M^{-1} cm^{-1}) corresponds to a π–π* transition and the band at 444 nm is a symmetry forbidden n–π* band (ε = 286 M^{-1} cm^{-1}). Irradiation with UV-light of 366 nm converts the *trans* to the *cis* isomer. It might be noted that exposure to 254 nm UV light also converted the trans form to the cis form. However, when multiple cycles were carried out with the 254 nm light source, partial decomposition of the sample was observed. Hence the 366 nm softer UV was chosen as the light source. The photoisomerization between *trans*-1 and *cis*-1 forms was monitored with UV/Vis spectroscopy in acetonitrile. Upon exposure of a solution (30 μM) of *trans*-**1** in acetonitrile to UV light (λ =366 nm, 8 watts), the thermally stable *trans* **1** form gradually isomerized to *cis*-**1** and reached a saturation in 80 min, which upon exposure to the irradiation for another 20 min did not change the spectra to any significant extent. Upon photoisomerization (Figure 2) from *trans*-**1** to *cis*-**1**, the absorption maxima at 316 and 450 nm gradually decreased and a new peak appeared at 406 nm (ε = 370 M^{-1} cm^{-1}).

The reverse reaction of the thermally less stable *cis*-**1** to the *trans*-**1** form can be achieved by exciting the n-π* band of the cis form in the 450-470 nm range. This was achieved upon the exposure of the sample with blue LED light (λ = 466 nm) (Figure 3). Under continuous irradiation with the blue light, a photostationary state (PSS) consisting of a ~70:30 of the *cis:trans* isomers were obtained. This relative ratio of the two forms was calculated from the UV-vis spectra of the pure trans form and the PSS mixture using Fischer's method at 316 nm. [50] The spectra of the *cis*-rich sample of **1** have been mentioned as the *cis*-form. It might also be noteworthy here to mention that the reversal of the *cis* to the *trans* form were attempted with a 489 nm laser source, although the results were discouraging because of slower and poor conversion to the *trans* form. The *trans*-**1** to *cis*-**1** isomerization with 366 nm light followed a first order kinetics with a rate constant 2.1 × 10^{-2} min^{-1} at 273 K. The reversal of the *cis* to the *trans* form, attained with blue light, also followed a first order kinetics with a rate constant 4.3 × 10^{-2} min^{-1} at 298 K. These values of the rate constants are comparable to the acyclic azobenzene switches reported in the literature.[51]

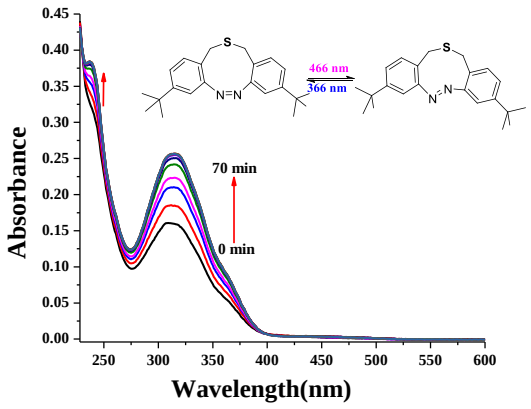


Figure 3: *Cis-trans* isomerization of the cyclic azobenzene 1 (top); UV–vis spectral changes upon exposure of *cis*-**1** (3 × 10^{-5} M) in acetonitrile with 466 nm UV light (irradiation time: 0 - 70 min).

The photoswitching behavior of the compound **1** in CD_3CN was also studied by the NMR spectroscopy. In the presence of 366 nm light, the signals at δ 7.83, 7.34 and 7.20 corresponding to the aromatic protons of the azobenzene unit gradually diminished and growth of three new peaks in the upfield region at δ 7.08, 7.02, 6.60 for the same set of protons were observed (Figure 4). This was consistent with what is normally observed for the *trans* to the *cis* conversion of the acyclic azobenzene systems[52] and distinctly dissimilar to eight-membered azobenzene systems are thermally stable in the *cis* conformation.[53] Therefore, at this point it was apparent that the effect of ring strain responsible for the stability of *cis* form for the smaller ring systems does not extend well to the nine-membered azobenzene ring system. This was further confirmed when the single crystal XRD structure of compound **1** obtained at room temperature was indeed in the *trans* form. The sample did not undergo switching to the *cis* form even upon heating at 50 °C.

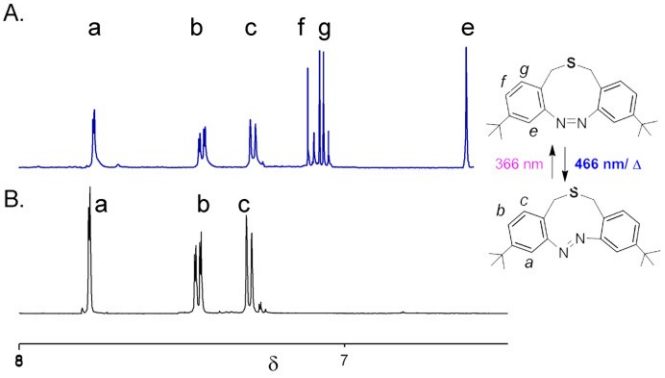


Figure 4: NMR traces of compound **1** in CD_3CN (10^{-2} M) displaying the clear shift in the aromatic protons. (A) after radiation of the *trans* with 366 nm light for 240 min; (B) *trans* form (bottom trace).

Single crystal XRD data confirmed the *trans*-**1** structure. The crystals of **1** were obtained upon slow evaporation of a solution of **1** in acetonitrile at room temperature and were subsequently analyzed by X-ray diffraction crystallography. The solved structure is shown in Figure 5 and Figure S17 clearly shows that the *trans* geometry of the molecule. The X-ray crystallographic analysis data have been summarized in Table 1 and the details are listed in the Supporting Information (Tables S1). The crystal system is monoclinic and space group is P21/c, Z = 4, and the unit cell volume is 2020.6(5) Å^3. The C(9)-N(1)-N(2)-C(14) dihedral angle is 167.015°. This deviation from the ideal dihedral angle of 180°, expected in an acyclic structure, indicates the ring strain. The N=N bond distance of 1.257 Å is close to the ones reported for acyclic azobenzene systems. [CCDC 157005 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.]

It was interesting to note that the (Ar)C-N=N-C(Ar) interplanar angle of 19° between the two phenyl rings in **1** is slightly lower than that of the 21° angle that exists for the calculated *trans* structure of Herge's S-containing an eight-membered ring. The strain energy (ΔH_{strain}) estimated by Pople's computational isodesmic reaction approach[54] indicate that the strain is considerably lower in the case of the *trans* form of compound **1** compared to its *cis* isomer (Figure S7). The combination of a sulfur and two methylene units offers a flexibility that allows the molecule **1** to reside comfortably in the *trans* form under the ambient temperature. This flexibility of our nine-membered ring system is not possible in the eight-membered ring system developed by Herges. There the strain confers it an unusual thermal stability in its *cis* form compared to the *trans*. In our case, compared to the *trans* form, the strain of the *cis* form is 12 kcal/mol higher which makes it thermodynamically less stable.

Table 1: Bond angles and bond lengths of compound-1 observed in crystal structure in acetonitrile solvent.

Bond length (Å)		Bond Angles (°)	
C1-C4	1.446(16)	C1 C4 C2	108.6(12)
C2-C4	1.508(19)	C1 C4 C3	110.0(12)
C3-C4	1.556(19)	C1 C4 C5	117.7(10)
C4 -C5	1.539(11)	C2 C4 C3	99.3(12)
C5 -C6	1.3900	C2 C4 C5	110.5(10)
C5 -C10	1.3900	C9 C8 C11	118.7
C6 -C7	1.3900	C6 C5 C4	119.1(6)
C7 -C8	1.3900	C6 C5 C10	120.0
C8 -C9	1.3900	C10 C5 C4	120.9
C8 -11	1.520(8)	C5 C6 C7	120.0
C9 -C10	1.3900	C8 C7 C6	120.0
C9 -N1	1.358(6)	C7 C8 C9	120.0
C11- S1	1.827(9)	C7 C8 C11	121.2
C12 -C13	1.554		

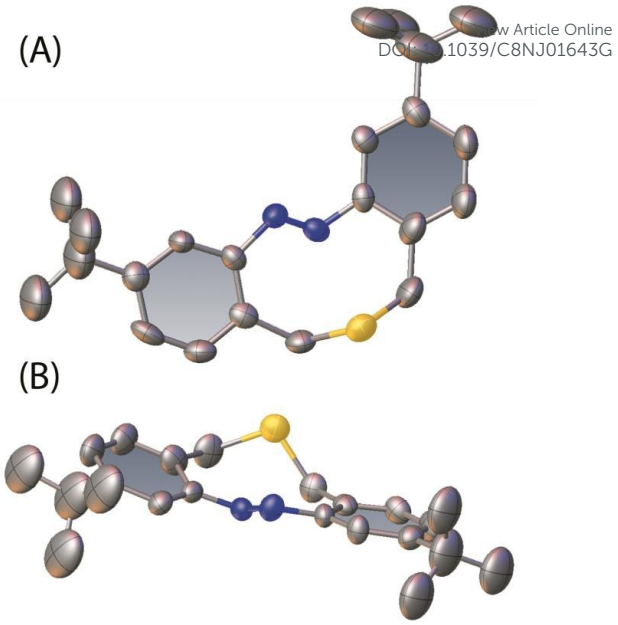


Figure 5: Single crystal X-ray diffraction crystals of compound **1:** (A) top view, (B) side view. The hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

Despite the certain angle strain, akin to the acyclic system, the *trans* form is more stable for compound **1**. We still wondered if there was, at all, any effect of the nine-membered ring on the *cis* to *trans* thermal reversal of the switching of molecule **1**. Thus, the thermal reversibility of compound **1** was studied in six different solvents with varying polarity (see Supporting Information). It was found that the switching rate, measured by the first order kinetics, was slowest in cyclohexane (polarity index of 0.2), and was fastest in DMSO (polarity index of 7.2).

Table 2. Activation energy and half-life of *cis*-**1** in various solvents at 333K.

Solvent	Solvent polarity index	$\Delta E^{\ddagger}$ (kcal/mol)	$t_{1/2}$(min)
DMSO	7.2	17.8	22
Acetonitrile	5.8	18.0	32
MeOH	5.1	18.3	49
Ethyl acetate	4.4	18.5	60
Benzene	3	18.8	78
Cyclohexane	0.2	19.5	366

The correlation of the rate constant for the *cis* to *trans* reversal under the room temperature (25 °C) conditions with the solvent polarity index has been shown in the Figure S9**.** The activation energy ($\Delta E^{\ddagger}$) of the reaction changed significantly as the solvent was altered. This is reflected in the half-life of the *cis* form under the thermal conditions.

Generally, acyclic azobenzenes devoid of any fluorophores are non-fluorescent in either the *cis* or the *trans* forms. This happens as they undergo non-radiative decay through the rotations of the phenyl rings or through photoisomerisation in the photo excited state.[55-56] Interestingly, studies of acyclic azobenzenes have also shown that the *cis* form can display a strong fluorescence on prolonged standing because of the formation of the head-to-tail intermolecular J-aggregates resulting in an aggregation-induced emission where the non-radiative mechanisms are impeded. Kunitake and his coworkers reported azobenzene containing compounds which show strong fluorescence enhancement in the aqueous bilayer system.[57-58] In contrary, compound **1** displays an emission in both the *cis*-rich state (apparent quantum yield of the $PSS_{70/30}$, Φ_{app} = 0.060) and the *trans* (Φ = 0.043) forms upon excitation at 309 nm (excitation spectra, Figure S5) using anthracene as the reference. This unusual emission is as high as that reported for the aggregated *cis* form of the acyclic azobenzenes. It is conceivable that the locked structure of the cyclic compound **1** with restricted degrees of freedom slows down the non-radiative fluorescence deactivation processes. For the reported acyclic azobenzenes which are non-fluorescent, formation of large *J*-aggregates in the *cis* form results in an aggregation induced enhancement of fluorescence. However, here the *cis*-**1** does not form any aggregate even on standing for two days. Molecular modeling studies of the *cis* form reveal a bowl-like structure. Lack of new signals in the larger hydrodynamic volume regime in the dynamic light scattering studies also supports the lack of the formation of the larger aggregates upon standing. It is likely that the *t*-butyl group of cis-1 causes steric repulsion that hinders close approach of the "*cis*-bowls" (**Figure S10**).

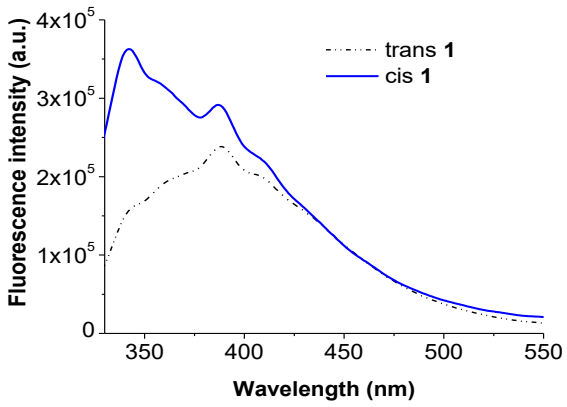


Figure 6: Emission spectra (λ_{ex}= 309 nm, slit 5/5) of *trans*-**1** and *cis*-**1**.

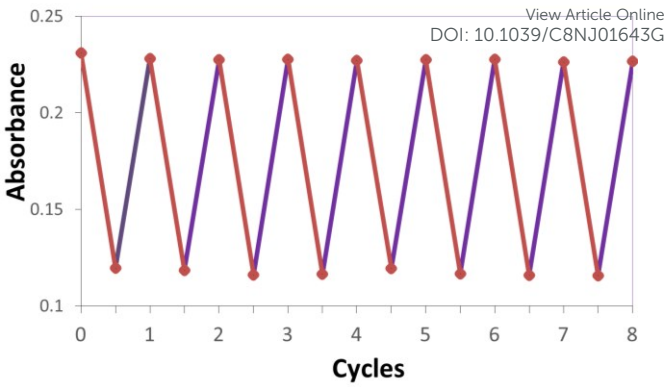
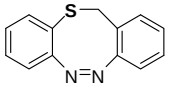
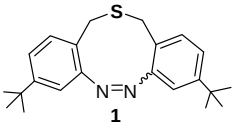


Figure 7: Absorption changes observed of **1** (3×10^{-5} M) at 316 nm after alternating irradiations at 366 nm (half cycles) and 466 nm (full cycles) over eight complete cycles.

The photostability of compound **1** was checked using UV-vis spectroscopy over eight switching cycles in an acetonitrile solution purged with dry nitrogen (Figure 7). Upon alternating irradiation of 366 and 466 nm light and repeating the sequence of the irradiation in multiple cycles, the corresponding absorbance of **1**, peak at 316 nm was used to monitor the switching in cycles. Even after eight cycles, no significant decomposition of the sample was observed.

Table 3. Brief comparison of Herge's compound with compound 1.

Properties		 **1**
Ring size	Eight	Nine
Thermally stable form	*Cis*	*Trans*
$t_{1/2}$ at 298 °K	3.5 d	30 min
Crystal structure	-	Obtained
Ring flexibility	Strained	Flexible and less strain
Color change (Z to E)	Colorless to red	Colorless to faint yellow
Switching rate	Fast	Slower
Synthesis	Difficult	Easy to prepare

Conclusion

To sum up, compound **1** clearly defines the limit of the ring size of the cyclic azobenzenes in terms of its relative stability and photoswitching behavior. The strained 8-membered azobenzene ring systems reported earlier by Herges are thermally stable in the *cis* form. Increasing the chain length merely by one methylene unit shifts the stability towards the *trans* form. The salient different between compound 1with its eight membered analog is presented in Table 3. In addition, it was also revealed in this study that although azobenzenes are

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known to be non-fluorescent, the molecule **1** displays interesting fluorescence behavior in both the *cis* and the *trans* forms with modest quantum yields. This is due to the lack of flexibility, and consequently, restricted non-radiative relaxation of the ring structure which is absent in the acyclic azobenzenes.

Experimental section

Instruments and Reagents: All reactants and reagents were commercially available and were used without further purification unless otherwise indicated. Solvents used were purified and dried by standard methods. Reactions were monitored by thin-layer chromatography (TLC) using Merck plates (TLC Silica Gel 60 F254). Developed TLC plates were visualized with UV light (254 nm). Silica gel (100–200 mesh, Merck) was used for column chromatography. Yields refer to the chromatographically and spectroscopically pure compounds. The structures of the compounds were determined by 1D and 2D NMR spectrometry and other spectroscopic techniques. The ^{1}H and ^{13}C NMR spectra were recorded with 400 MHz Jeol and 500 MHz Bruker instruments. Chemical shifts are reported as δ values relative to an internal reference of tetramethylsilane (TMS) for ^{1}H NMR or the solvent peak. In the case of ^{13}C NMR the solvent peak was used for calibration. The spectroscopic-grade solvents for the spectroscopic experiments were distilled and checked prior to their use to ensure that they were free from any fluorescent impurity. UV–vis spectra were recorded with a Cary 60 UV–vis spectrophotometer. Fluorescence measurements were carried out with a Horiba Jobin Yvon fluorimeter (Fluoromax-3, Xe-150 W, 250–900 nm). Mass spectra were recorded with Melting point was recorded on a Mettler Toledo DSC1 spectrometer. The mass spectrometric data were obtained from an AcquityTM Ultra Performance LC-ESI/quadrupole-TOF MS. Melting point was measured with a Secor, India digital melting point apparatus in melting point tube.

Photoisomerisation studies: *Trans* to *cis* photoisomerisation reaction of compound **1** have been carried out under the UV radiation chamber equipped with cooling fans. A 3 mL UV cuvette was kept under ice cold conditions. A 366 nm UV light (irradiation power 2.3 mW cm^{-2}) was used for the radiation of the sample. The UV-vis absorbance data were recorded subsequently with a Cary 60 UV–vis spectrophotometer at ambient temperature conditions. The *cis* to *trans* isomerization were conducted both thermally and photochemically. For the photochemical reaction, 466 nm LED (irradiation power of 0.5 mW cm^{-2}) light source was used. The *cis* to *trans* isomerization under the thermal conditions were carried out in the spectrophotometer itself using a Peltier heating system accessory with an accuracy of ± 1 °C.

The photoisomerization followed by fluorescence spectroscopy before and after the isomerization was studied in a quartz fluorescence cuvettes (Starna). The photoisomerization conditions are the same as described for the absorption studies. The fluorescence spectra were recorded at 25 °C using a Fluoromax-3, Xe-150 W, 250–900 nm.

Synthesis of compound 1. To a solution of NaOH (1.484 g, 37.10 mmol) in H_2O (5 mL), compound **3** (0.245 g, 0.588 mmol) in EtOH (40 mL) was added. A solution of glucose (1.05 g) in hot water was added to the reaction mixture. The reaction mixture was stirred at 70 °C for 72h. The solution turned red in color. Upon completion of the reaction, concentration in vacuum, the residue was extracted in DCM, washed with brine, dried over Na_2SO_4, filtered, concentrated *in vacuo*, and purified by preparative TLC (100-200 silica gel) using 5% EtOAc in hexane as eluent. The expected compound was obtained as a red solid (41 mg, 19 %;* Varied between 18-22%), m. p. 170 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2 Hz, 2H), 7.34 (dd, *J* = 8 and 2 Hz, 2H), 7.20 (d, *J* = 8 Hz, 2H), 4.13 (s, 4H), 1.40 (s, 18H); 2.1 (Acetone), 1.5 ($CDCl_3$ - Water), 0.88 and 1.256 (Hexane impurity) ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 148.5, 131.5, 130.4, 130.1, 122.1, 33.3, 32.9, 30.9; IR (KBr) 2965 (w), 2908 (w), 1615 (m), 1421 (s), 1362 (s), 1025 (s), 907 (m), 739 (m), 617 (w), 558 (w) cm^{-1}; ESI-MS *m/z* (calc.) 375.2 $[M+Na]^+$, (obtained) 375.2; HRMS (ESI/Q-TOF) *m/z:* $[M + Na]^+$ Calcd for $C_{22}H_{28}N_2NaS$ 375.1871; Found 375.1870**.**

Synthesis of compound 3. To a solution of Na_2S (0.043 g, 0.551 mmol) in MeOH, 4-*t*-butyl-*o*-nitro benzyl bromide (0.1 g, 0.367 mmol) in MeOH (2 mL) was added drop wise under argon atmosphere at room temp. (30 °C). The reaction mixture was stirred at the ambient temperature for 24h. The solution turned yellow in color. Upon completion of the reaction as indicated by the TLC, the reaction mixture upon concentration, extraction with EtOAc ,washing with water, drying over Na_2SO_4, concentration, and purification by flash column chromatography (silica gel) using n-hexane as eluent, the expected compound was obtained as a yellow viscous liquid (0.025 g, 80 %), R_f = 0.4 (5% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2 Hz, 2H), 7.53 (dd, *J* = 8 and 2 Hz, 2H), 7.34 (d, *J* = 8 Hz, 2H), 3.92 (s, 4H), 1.33 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 148.5, 131.5, 130.4, 130.1, 122.1, 33.3, 32.9, 30.9 . ESI-MS *m/z* calculated 455.1401, obtained: 455.1700. HRMS (ESI/ Q-TOF)) *m/z:* $[M + Na]^+$ Calcd for $C_{22}H_{28}KN_2O_4S$ 455.1401; Found 455.1402.

Synthesis of Compound 2: Compound 2 was prepared following the method reported by Rose *et al.* [59] The ^{1}H NMR data matches well with the reported literature. R_f = 0.6 (5% EtOAc in hexane). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.61(d, *J* = 8 Hz, 1H), 7.48 (d, *J* = 8 Hz, 1H), 4.80 (s, 2H), 1.34 (s, 9H); ^{13}C NMR (125MHz, $CDCl_3$) δ 153.7, 147.7, 132.2, 130.7, 129.7, 122.4, 34.9, 30.8, 28.9.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 W. Szymański, J. M. Beierle, H. A. V. Kistemaker, W. A. Velema and B. L. Feringa, *Chem. Rev.*, 2013, **113**, 6114– 6178.
2 E. Merino and M. Ribagorda, *Beilstein J. Org. Chem.*, 2012, **8**, 1071–1090.
3 B. L. Feringa, W. R. Brown, Molecular Switches, 2nd ed.; *Wiley- VC.*
4 R. A. Evans, T. L. Hanley, M. A. Skidmore, T. P. Davis, G. K. Such, L. H. Yee, G. E. Ball and D. A. Lewis, *Nat. Mater.*, 2005, **4**, 249-253.
5 H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.*, 2012, **41**, 1809-1825.
6 E. Mitscherlich, *Ann. Pharm.*, 1834, **12**, 311–314.
7 C. Dugave and L. Demange, *Chem. Rev.*, 2003, **103**, 2475–2532.
8 K. G. Yager, C. J. Barrett, *J. Photochem. Photobiol. A: Chem.* 2006, **182**, 250-261.
9 E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72–191.
10 M. Yamamura, K. Yamakawa, Y. Okazaki and T. Nabeshima, *Chem. – Eur. J.*, 2014, **20**, 16258–16265.
11 A. Goulet-Hanssens, M. Utecht, D. Mutruc, E. Titov, J. Schwarz, L. Grubert, D. Bléger, P. Saalfrank and S. Hecht, *J. Am. Chem. Soc.*, 2017, **139**, 335–341.
12 C. M. Stuart, R. R. Frontiera and R. A. Mathies, *J. Phys. Chem. A*, 2007, **111**, 12072–12080.
13 Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Nather. F. Renth and F. Temps, *J. Am. Chem. Soc.*, 2009, **131**, 15594–15595.
14 M. Hammerich, C. Schütt, C. Stähler, P. Lentes, F. Röhricht, R. Höppner and R. Herges, *J. Am. Chem. Soc.*, 2016, **138**, 13111–13114.
15 D. K. Joshi, M. J, Mitchell, D. Bruce, A. J. Lough and H. Yan, *Tetrahedron*. 2012, **68**, 8670-8676.
16 T. Erich, M. Reinhard *Liehigs. Ann*., 1996**,** 1213-1216.
17 G.Hans-Friedrich and Schmiegel**,** *J. Chem. Ber*. 1989, **122,** 1929-1933.
18 K. Boeckmann and F. Voegtle, *Chemische Berichte*, 1981**,** **114,** 1065 – 1073.
19 S. Shinkai, T. Nakaji, Y. Nishida, T. Ogawa and O. Manabe, *J. Am. Chem. Soc.* 1980, **102***,* 5860-5865.
20 S. Shinkai, T. Ogawa, T. Nakaji, T. Kusano and O. Manabe, *Tetrahedron Lett.* 1979, 4569.
21 Y. Norikane, K. Kitamoto and N. Tamaoki, *Org. Lett.*, 2002, **4**, 3907.
22 K. Rijeesh, P. K. Hashim, S. Noro and N. Tamaoki, *Chem. Sci.*, 2015, **6**, 973–980.
23 R. Thomas, Y. Yoshida, T. Akasaka and N. Tamaoki, *Chem. – Eur. J.*, 2012, **18**, 12337–12348.
24 M. Mathews and N. Tamaoki, *J. Am. Chem. Soc.*, 2008, **130**, 11409–11416.
25 M. C. Basheer, Y. Oka, M. Mathews and N. Tamaoki, *Chem.–Eur. J.*, 2010, **16**, 3489–3496.
26 P. K. Hashim, R. Thomas and N. Tamaoki, *Chem. – Eur. J.*, 2011, **17**, 7304–7312.
27 Y. Oka and N. Tamaoki, *Inorg. Chem.* 2010, **49,** 4765–4767.
28 M. Böckmann, N. L. Dotsinis and D. Marx, *Angew. Chem. Int. Ed.,* 2010, **49,** 3382–3384.
29 R. Siewertsen, J. B. Schönborn, B. Hartke, F. Renth and F. Temps, *Phys. Chem. ChemPhys.* 2011, **13**, 1054–1063
30 L. Liu, S. Yuan, W. Fang and Y. Zhang, *J. Phys. Chem. A* 2011, **115,** 10027–10034.
31 C. W. Jiang, R. H. Xie, F. L. Li and R. E Allen, *Chem. Phys. Lett.* 2012, **521**, 107–112.
32 C. Gao, B. Li, P. Zhang and K. Han, *J. Chem. Phys.* 2012, **137**, 204305.
33 O. Carstensen, *Phys. Chem. Chem. Phys.,* 2013, 15, 15017–15026.
34 M. Nepraš, S. Luňák, R. Hrdina and J. Fabian, *Chem. Phys. Lett.*, 1989, ***159,*** 366-370.
35 G. Gabor, Y. Frei, D. Gegiou, M. Kaganowich and E. Fisher, *Isr. J. Chem.*, 1967, **5**, 193-211.
36 H. Bisle and H. Rau, *Chem. Phys. Lett.*, 1975, **31**, 264-266.
37 K. Tsuda, G. C. Dol, T. Gensch, J. Hofkens, L. Latterini, J. W. Weener, E. W. Meijer and F. C. de Schryver, *J. Am. Chem. Soc.*, 2000, **122**, 3445–3452.
38 M. Han and M. Hara *J. Am. Chem. Soc.*, 2005, ***127,*** 10951-10955.
39 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.*, 2001, 1740 -1741.
40 B. K. An, S. K. Kwon, S. D. Jung and S. Y. Park, *J. Am. Chem. Soc.*, 2002, **124**, 14410-14415.
41 S. S. Babu, K. K. Kartha and A. Ajayaghosh, *J. Phys. Chem. Lett.*, 2010, **1**, 3413-3424.
42 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361-5388.
43 B.-K. An, J. Gierschner and S. Y. Park, *Acc. Chem. Res.*, 2012, **45**, 544.
44 Aggregation –Induced emission, ed. Qin, A and Tang B.Z. Wiley. 2013.
45 R. Siewertsen, H. Neumann, B. Buchheim-Stehn, R. Herges, C. Nather, F. Renth and F. Temps, *J. Am. Chem. Soc.*, 2009, **131**, 15594–15595.
46 S. Ghosh, D. Usharani, A. Paul, S. De, E. D. Jemmis and S. Bhattacharya, *Bioconjugate Chem.*, 2008, **19**, 2332-2345.
47 M. Y. Qiu, J. C Zhang, Y. Wei, Q .C Jia and Y. S. Niu, *Asian J. Chem.* 2012, **24**, 2295.
48 D. H. Marrian, P. B. Russell, B. J. F. Hudson, J. W. Cornforth. R. H. Cornforth, W. J. Dunstand and M. L. Tomilson, *J. Chem. Soc*. 1946, 753-756.
49 D. Rottger and H. Rau, *J. Photochem. Photobiol. A.* 1996, **101**, 205-214.
50 Fischer, *J. Phys. Chem.* 1967, **71**, 3704.
51 J. Hatai and S. Bandyopadhyay. *Chem.-Eur. J.* 2014, **20**, 10020–10026.
52 M. Samanta, V. S. R. Krishna and S. Bandyopadhyay, *Chem. Commun*. 2014, **50**, 10577–10579.
53 M. Hammerich, C. Schütt, C. Stähler, P. Lentes, F. Röhricht, R. Höppner and R. Herges, *J. Am. Chem. Soc.*, 2016, **138**, 13111–13114.
54 W. J. Hehre, R. Ditchfield, L. Radom and J. A. Pople, *J. Am. Chem. Soc*. 1970, **92,** 4796–4801.
55 H. Rau, *Angew. Chem. Int. Ed. Engl*. 1973, **12,** 224-235.
56 A. Cembran, F. Bernardi, M. Garavelli, L. Gagliardi and G. Orlandi, *J. Am. Chem. Soc.*, 2004, **126**, 3234–3243.
57 B.-K. Tsai, C.-H. Chen, C.-H. Hung, V. K. S. Hsiao and C.-C. Chu, *J. Mater. Chem.*, 2012, **22**, 20874.
58 M. Shimomura and T. Kunitake, *J. Am. Chem. Soc.* 1987, **109,** 5175-5183**.**
59 E. Rose, A. Kossanyi, M. Quelquejeu, M. Soleilhavoup, F. Duwavran, N. Bernard and A. Lecas, A. *J. Am. Chem. Soc.* 1996**,** **118**, 1567-1568**.**

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Strain, Switching and Fluorescence Behavior of a Nine-Membered Cyclic Azobenzene

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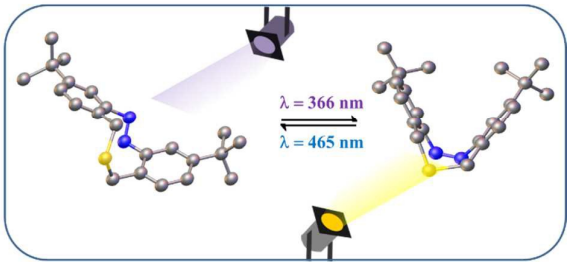

The work defines the smallest ring size for obtaining the trans form of cyclic azobenzene as the thermally stable form.