

Photochemical and Thermal *cis/trans* Isomerization of Cyclic and Noncyclic Azobenzene Dimers: Effect of a Cyclic Structure on Isomerization

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The effect of ring strain on the photochemical and thermal isomerization of azobenzene dimers was investigated by comparison of macrocyclic (**1**) and noncyclic (**2**) azobenzene dimers. The macrocycle **1** comprises two azobenzene moieties connected at their *meta* positions through two methylene linkers, whereas the noncyclic dimer **2** has only one methylene linker bridging two azobenzenes at the *meta* positions. Upon irradiation of **1** or **2** with UV light, each (*E/E*) (*trans/trans*) isomer exhibited a stepwise photoisomerization to give the corresponding (*E/Z*) (*trans/cis*) isomer, followed by isomerization to yield the (*Z/Z*) (*cis/cis*) isomer. Quantum yields for the isomerization indicated that the photochemical isomerizations of **1** were altered by its cyclic structure. The effect

on the photochemical isomerization process can be explained in terms of the ring strain, causing shifts in the absorption spectra of the azobenzene chromophore and perturbations in molecular motion in the excited state. Thermal (*Z*) → (*E*) isomerization was observed in each **1** and **2**, taking place in stepwise manner as (*Z/Z*) → (*E/Z*) → (*E/E*). The cyclic structure gave higher activation barriers (E_a and $\Delta H^\ddagger$) and activation entropies ($\Delta S^\ddagger$). HF/6-31G** calculations were carried out for **1** and **2** in their ground electronic states in order to estimate the ring strain of each isomer of **1**.

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Introduction

Photochemical (*Z*)/(*E*) (*cis/trans*) isomerization has been employed in photoswitches, in biological photoreceptors, and in various types of artificial molecules and materials.^[1–5] In those systems, regulation of the direction and selectivity of isomerization are major requisites for the display of desired switching properties. Understanding of the relationship between the structures and the behavior of molecules exhibiting photochemical (*Z*)/(*E*) (*cis/trans*) isomerizations can yield significant knowledge and clues for the construction of photoswitching molecules, as well as information about the reaction mechanisms.

Azobenzene exists as (*E*) and (*Z*) isomers. UV and visible light predominantly cause (*E*) → (*Z*) and (*Z*) → (*E*) isomerization, respectively. Typically, the (*Z*) isomer is less stable than the (*E*) isomer, and it thermally converts into the (*E*) isomer in the dark. The azobenzene moiety has been the subject of study for exploration of the reaction mechanisms of photochemical and thermal isomerizations both experimentally^[6] and theoretically,^[7] and has been employed in various types of photoresponsive supramolecular systems and photofunctional materials.^[1,2,4,5]

According to reports on photochemical and thermal isomerizations of azobenzenes, these processes are affected

by intramolecular or intermolecular interactions: bulky substituents at the *ortho* positions alter the photochemical isomerization, for example.^[8] In polymer matrices the photochemical and thermal isomerization of azobenzenes does not follow single-exponential kinetics, due to the widely distributed free volume.^[9] The effect of ring strain in macrocyclic azobenzene dimers has been discussed, several compounds with various type of linkers have been synthesized, their photochemical and thermal isomerizations have been reported,^[6a,10] and the effect of the ring strain on the thermal and photochemical isomerization of the azobenzene moieties in these systems has been discussed. However, the relationship between structure and photochemical/thermal isomerization of azobenzene moieties in macrocyclic azobenzene dimers is not clear, due to the limited information about the structures of azobenzenes.

We have recently reported a new class of molecular hinge that swings between open and closed states.^[4a,4e] Two azo linkers are connected to two xanthene rings. The motion (closed and open forms) can be actuated by alternating irradiation with UV and visible light. The photochemical closure reaction [(*E/E*) → (*Z/Z*) isomer] depends on the intensity of the light used, because of the short-lived intermediate [(*E/Z*) isomer]. The closed form [(*Z/Z*) isomer] is stable in the dark for 2 weeks at 40 °C. These effects were explained by ring strain.

In the course of our exploration of the effect of ring strain on the thermal and photochemical isomerization of azobenzene dimers, we synthesized macrocyclic azoben-

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zenes in which azobenzene units are linked cyclically by $-\text{CH}_2-$ linkers (**1**) and reported the X-ray crystal structures of the (*E/E*) [(*E,E*)-**1**], (*E/Z*) [(*E,Z*)-**1**], and (*Z/Z*) [(*Z,Z*)-**1**] isomers.^[11] Both the thermal and photochemical isomerization processes in solution were different from those of strain-free azobenzenes.^[11] The effect seems to be due to the strain imposed by the cyclic structure.

To investigate the effect of ring structure on the photochemical and thermal isomerization of azobenzene dimers further, it is essential to compare their properties with those of noncyclic azobenzene dimers such as **2**. Here we report the photochemical and thermal isomerization of two compounds, together with ab initio calculations.

Results and Discussion

The macrocycle **1** comprises two azobenzene units connected through two methylene linkers at their *meta* positions. The synthesis of **1** by reduction of the corresponding dinitro compound has been reported previously.^[11] The noncyclic azobenzene dimer **2** consists of two azobenzene units connected through a single methylene bridge at their *meta* positions. The synthesis of **2** was achieved by employing a condensation between bis(3-aminophenyl)methane and 3-nitrosotoluene in acetic acid. Both **1** and **2** can exist in three forms: the (*E/E*) [(*E,E*)-**1** and (*E,E*)-**2**], (*E/Z*) [(*E,Z*)-**1** and (*E,Z*)-**2**], and (*Z/Z*) [(*Z,Z*)-**1** and (*Z,Z*)-**2**] isomers (Scheme 1).

Figure 1 shows the absorption spectra of (*E,E*)-**1** and (*E,E*)-**2** in acetonitrile. The absorption maxima (λ_{max}) of (*E,E*)-**1** are at 451 ($\epsilon = 1150 \text{ M}^{-1} \text{ cm}^{-1}$) and 313 ($\epsilon = 33700 \text{ M}^{-1} \text{ cm}^{-1}$), while those of (*E,E*)-**2** are at 443 ($\epsilon = 1162 \text{ M}^{-1} \text{ cm}^{-1}$) and 322 ($\epsilon = 42800 \text{ M}^{-1} \text{ cm}^{-1}$). The shape of the spectrum of (*E,E*)-**2** is very similar to that of (*E*)-3,3'-dimethylazobenzene, the λ_{max} values of which are 445 ($\epsilon = 518 \text{ M}^{-1} \text{ cm}^{-1}$) and 325 ($\epsilon = 20130 \text{ M}^{-1} \text{ cm}^{-1}$),^[11a] while the molar extinction coefficient (ϵ) of (*E,E*)-**2** is about twice that of (*E*)-3,3'-dimethylazobenzene. This indicates that

there is no electronic communication between the azobenzene moieties in **2**. On comparison of (*E,E*)-**1** and (*E,E*)-**2**, (*E,E*)-**1** exhibits a λ_{max} value for the π, π^* band (the intense absorption band around 315 nm) at lower wavelength, while the λ_{max} value for the n, π^* band (relatively weak absorption band around 450 nm) is at higher wavelength than that in (*E,E*)-**2**.

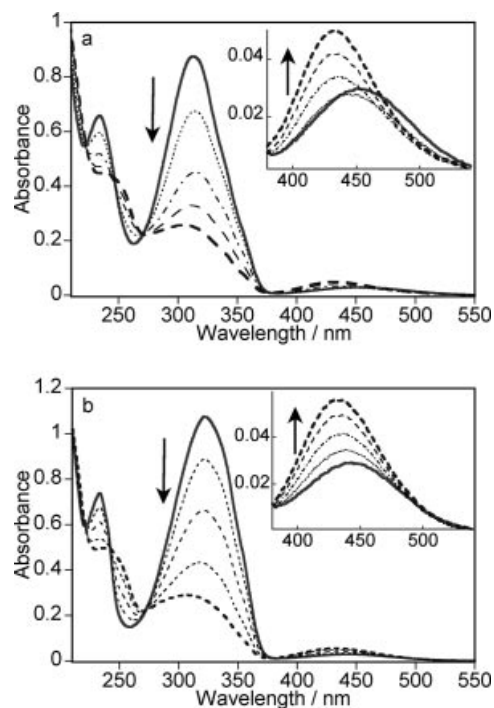
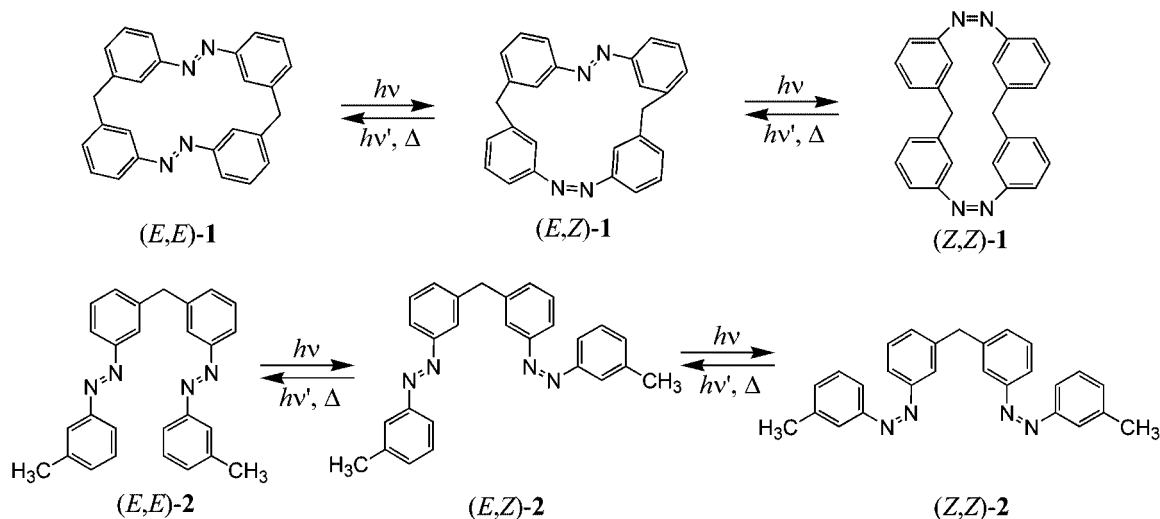


Figure 1. Changes in the absorption spectra of **1** (a) and **2** (b) in acetonitrile upon irradiation at 313 nm. The insets show the n, π^* band spectral range (370–550 nm). Bold lines are the initial (solid) and final (dash) traces.

Upon irradiation, both **1** and **2** exhibited stepwise photoisomerization from (*E/E*) $\rightarrow$ (*Z/Z*) isomers via the (*E/Z*) forms (Scheme 1). Figure 1 shows the changes in the UV



Scheme 1.

spectra of **1** and **2** upon irradiation at 313 nm. Weakening in the π,π^* band and concomitant strengthening in the n,π^* band were observed in both **1** and **2**. In the early stages of the irradiation, the $\lambda_{\max}$ value for the π,π^* band of **1** shifts slightly to a longer wavelength in relation to the initial state, although the $\lambda_{\max}$ ends up at a shorter wavelength in the final spectrum of the photostationary state (Figure 1, a). Furthermore, it should be noted that the intensity of the n,π^* band of **1** slightly decreased during the early stages of isomerization (see the inset of Figure 1, a); this spectral shift is attributable to the presence of (*E,Z*)-**1**. The absorption spectrum of (*E,Z*)-**1** (Figure 2, a) shows the π,π^* band red-shifted in relation to that in (*E,E*)-**1**, whilst the absorption intensity of the n,π^* band in (*E,Z*)-**1** is smaller than that in (*E,E*)-**1**. On the other hand, the π,π^* band in **2** was shifted to a slightly shorter wavelength throughout the irradiation, while the n,π^* band of **2** increased monotonously (Figure 1, b). An isosbestic point was observed at 272 nm

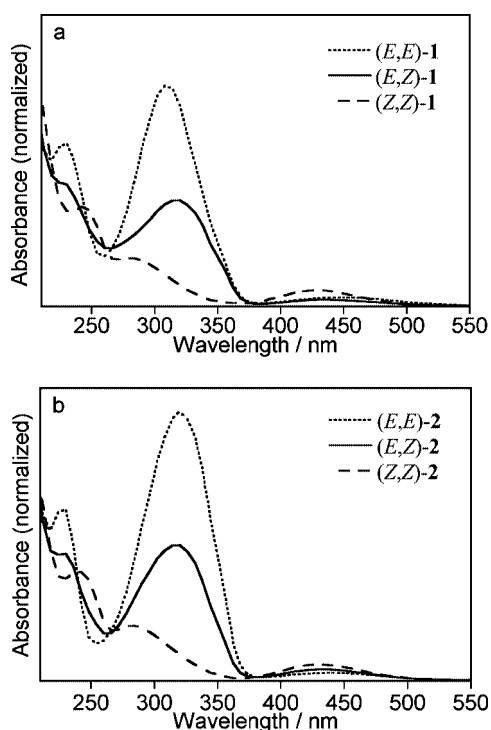


Figure 2. Absorption spectra of each isomer of **1** (a) and **2** (b) measured by use of a photodiode array detector attached to an HPLC system. Spectra are normalized at the isosbestic points (269 and 272 nm for **1** and **2**, respectively).

for compound **2**, while that of **1** shifted slightly from 270 nm to 268 nm during the irradiation at 313 nm.

Comparison of **1** and **2** shows that the intensities of the π,π^* bands of (*E,E*)-**1** and (*E,Z*)-**1** are smaller than those of (*E,E*)-**2** and (*E,Z*)-**2**, respectively. Moreover, the $\lambda_{\max}$ value for the π,π^* band of (*E,E*)-**1** differs markedly from that of (*E,E*)-**2**. On the other hand, there was no significant difference between the absorption spectra of (*Z,Z*)-**1** and (*Z,Z*)-**2**. Those results indicate that the absorption spectra of (*E,E*)-**1** and (*E,Z*)-**1** cannot be expressed as the sums of two individual strain-free azobenzenes, because of the deformed structure of each azobenzene unit, while that of (*Z,Z*)-**1** is almost a simple sum of two (*Z*)-azobenzenes. These observation is consistent with the crystal structures of **1**, which indicated that (*E,E*)-**1** was slightly deformed, (*E,Z*)-**1** was significantly distorted, and (*Z,Z*)-**1** was not deformed.^[11] In (*E,Z*)-**1**, for example, the dihedral angle between the benzene ring and the N=N double bond is nearly 90° in the (*Z*)-azobenzene unit.^[11] This indicates that the transition probability from n to π^* orbitals is reduced by the deformed structure of (*E,Z*)-**1**, resulting in a relatively small molar extinction coefficient of (*E,Z*)-**1**. The small spectral difference between (*Z,Z*)-**1** and (*Z,Z*)-**2** is attributable to the unstrained structure of (*Z,Z*)-**1**, deducible from the crystal structure of (*Z,Z*)-**1**, in which the structure of an azobenzene unit is similar to the crystal structure of (*Z*)-azobenzene.^[11]

In general, upon irradiation at the π,π^* band the photostationary state of azobenzenes lies close to the (*Z*) isomer, while irradiation at the n,π^* band shifts it to the (*E*) isomer. The compounds in this study can each exist as three isomers, and the existence of the intermediate (*E/Z*) isomers makes the systems more complex. Table 1 shows the isomer ratios of **1** and **2** at their photostationary states. Upon irradiation at 366 nm, the proportion of (*Z,Z*)-**1** was as high as 87%, indicating that the absorption of (*Z,Z*)-**1** in this region is very weak. On the other hand, upon irradiation at 436 nm, the proportion of (*E,E*)-**1** did not surpass that of (*E,Z*)-**1**. This is notable because the intermediate state (*E/Z*) dominates among the three isomers at the photostationary state. The noncyclic compound **2** did not show such behavior.

Table 2 shows the quantum yields of isomerization of **1** and **2** on irradiation at 313 and 436 nm. The quantum yields are defined in terms of the ratio of photons producing isomerization/photons absorbed by the molecule over-

Table 1. Isomer ratios at the photostationary states of **1** and **2** in acetonitrile at various irradiation wavelengths.

Wavelength	1 (<i>E,E</i>)- 1	(<i>E,Z</i>)- 1	(<i>Z,Z</i>)- 1	2 (<i>E,E</i>)- 2	(<i>E,Z</i>)- 2	(<i>Z,Z</i>)- 2
269 nm ^[a]	55	37	9			
272 nm ^[b]				45	45	10
313 nm	14	29	57	5	32	63
366 nm	2	11	87	2	22	76
436 nm	44	50	6	59	36	5

[a] The actual isosbestic point shifted from 270 to 268 nm during the isomerization of (*E,E*)-**1** to the photostationary state. [b] Isosbestic point of **2**.

all. For $(E/E) \rightarrow (E/Z)$ isomerization, the following two points should be noted. Firstly, both **1** and **2** exhibited a wavelength dependence on Φ_{EE-EZ} : the Φ_{EE-EZ} values observed on irradiation at 436 nm are higher than those seen on irradiation at 313 nm. This tendency can also be found in azobenzene^[12] and 3,3'-dimethylazobenzene.^[11a] Secondly, macrocycle **1** gave higher Φ_{EE-EZ} values than the noncyclic azobenzene **2** on excitation at both 313 and 436 nm. The first point, which relates to the isomerization mechanism of azobenzene, is discussed in the next paragraph, whilst the second point is discussed in the subsequent paragraph.

Table 2. Quantum yields of isomerization of **1** and **2** on excitation at 313 and 436 nm in acetonitrile.

	Wavelength	Φ_{EE-EZ}	Φ_{EZ-EE}	Φ_{EZ-ZZ}	Φ_{ZZ-EZ}
1	313 nm	0.25	0.26	0.09	0.18
1	436 nm	0.34	0.35	0.15	0.51
2	313 nm	0.19	0.06	0.15	0.30
2	436 nm	0.29	0.31	0.10	0.43

It is well known that the quantum yields of azobenzene isomerization depend on the irradiation wavelength. The quantum yields for $(E) \rightarrow (Z)$ isomerization of azobenzene for irradiation at 313 and 436 nm are 0.10 and 0.28, respectively,^[12] which gave rise to the hypothesis that different mechanisms operate in the two excited states: a rotation mechanism in the $S_2(\pi, \pi^*)$ excited state and an inversion mechanism in the $S_1(n, \pi^*)$ excited state. These mechanisms have been supported by experimental and theoretical results for decades. One powerful piece of experimental evidence has come in the form of an azobenzenophane in which two $-\text{CH}_2-\text{S}-\text{CH}_2-$ bridges connect two azobenzenes cyclically at the *para* positions, for which it was suggested that the rotation pathway is blocked by the ring structure.^[10k] This compound exhibited almost no wavelength dependence of the quantum yields for photoisomerization from the $(E/E) \rightarrow (E/Z)$ isomers: the Φ_{EE-EZ} values for $S_2(\pi, \pi^*)$ and $S_1(n, \pi^*)$ excitations were 0.21 and 0.24, respectively.^[10k] It was concluded that the internal conversion from $S_2(\pi, \pi^*) \rightarrow S_1(n, \pi^*)$ takes place without isomerization, and that the isomerization proceeds through an inversion mechanism along the $S_1(n, \pi^*)$ surface.^[10k] However, stilbenophane, in which two stilbenes are tethered through $-(\text{CH}_2)_2-$ chains at their *para* positions, showed highly efficient photoisomerization around the carbon-carbon double bond ($\Phi_{EE-EZ} = 0.43$).^[13] Stilbene is well known for its isomerization by the rotation mechanism.^[14] In molecular models of azobenzenophanes or stilbenophanes, the $\text{N}=\text{N}$ or $\text{CH}=\text{CH}$ bonds can be readily rotated without breaking any covalent bond of the ring skeleton, and it is therefore doubtful that macrocyclic azobenzene dimers are suitable model compounds for the suppression of the rotation pathway. Furthermore, recent theoretical calculations of the potential energy surface of azobenzene showed that the rotation mechanism is dominant in the $S_1(n, \pi^*)$ excited state.^[7a-c,e] However, to the best of our knowledge, there is little experimental evidence excluding the possibility of the inversion mechanism in the

$S_1(n, \pi^*)$ excited state. In the cyclic system **1**, a multidimensional reaction coordinate rather than simple inversion or rotation reaction coordinates might be required. Although this is rather complicated and makes it difficult to discuss the reaction mechanism, it more closely describes the nature of the reaction.

The Φ_{EE-EZ} value for **1** (0.25) obtained on irradiation at 313 nm is higher than that value for **2** (0.19), although the $(E,E)\text{-1} \rightarrow (E,Z)\text{-1}$ isomerization seems to be less favorable than $(E,E)\text{-2} \rightarrow (E,Z)\text{-2}$, which is free from steric distortion. Since **2** has a higher degree of freedom in intramolecular rotation than **1**, **2** has probably more internal motions, which can compete with the isomerization in the excited states. Some studies have indicated that there is a pathway that competes with the isomerization channel in the $S_2(\pi, \pi^*)$ excitation.^[6b,6d] Thus, in the case of **1**, we assume that the ring strain suppresses the molecular motion, which contributes to the internal conversion without isomerization, and/or enhances the motion towards the isomerization, resulting in a slight increase in the quantum yield (Φ_{EE-EZ}).

Interestingly, for irradiation of **1** at 313 nm, Φ_{EZ-EE} (0.26) is higher than Φ_{EZ-ZZ} (0.09), while Φ_{EZ-EE} and Φ_{EZ-ZZ} in **2** were 0.06 and 0.15, respectively. The excited (Z) -azobenzene unit must be generated in $(E,Z)\text{-1}$ in order for it to undergo $(Z) \rightarrow (E)$ isomerization to give $(E,E)\text{-1}$, although the potential to produce the excited (Z) -azobenzene unit in $(E,Z)\text{-1}$ upon excitation at 313 nm seems to be low because of the relatively low extinction coefficient. Although the absorption spectrum of $(E,Z)\text{-1}$ cannot be divided into two independent (E) - and (Z) -azobenzene chromophores, it can be presumed that the absorption band of each chromophore has been shifted by the deformed structure, resulting in the alteration of the ratio of photon absorption between (E) - and (Z) -azobenzene units and hence in the possible change in quantum yields. The strained structure of the (Z) -azobenzene unit might be more susceptible to isomerization than the (E) -azobenzene unit, since the crystal structure of $(E,Z)\text{-1}$ showed that the (Z) -azobenzene unit is bent to outside of the molecular ring.^[11] One might assume that there is an intramolecular energy transfer from excited (E) - to (Z) -azobenzene chromophore that results in the enhanced overall Φ_{EZ-EE} . However, the singlet energy transfer is less likely to occur, because the excited singlet energies of (E) - and (Z) -azobenzene are very close and the energy transfer is inefficient according to the Forster mechanism.^[15] Moreover, the quantum yields of **2** ($\Phi_{EZ-EE} = 0.06$ and $\Phi_{EZ-ZZ} = 0.15$) suggest that the energy transfer does not take place when two $[(E)\text{-} \text{ and } (Z)\text{-}]$ azobenzene units are covalently attached together with only a single $-\text{CH}_2-$ spacer.

On irradiation at 436 nm, on the other hand, the effects on Φ_{EZ-EE} and Φ_{EZ-ZZ} seen on 313 nm irradiation were not observed between **1** and **2**. There are two possible causes for this wavelength dependence. Firstly, the ratio of the absorption probabilities of (E) - and (Z) -azobenzene units might not change significantly at the irradiation wavelength (436 nm), yielding a similar product distribution to **2**. Sec-

only, the intrinsic isomerization mechanisms might be different for excitation at 313 and at 436 nm. In this case, allowance should be made for a multidimensional reaction coordinate with intramolecular motions that compete with the isomerization pathway.

Thermal isomerizations, with the (Z/Z) forms isomerizing to (E/Z), followed by further isomerization from (E/Z) $\rightarrow$ (E/E), were observed in both **1** and **2**. The thermodynamic parameters (E_a , A , $\Delta H^\ddagger$, and $\Delta S^\ddagger$) as well as the rate constants (k) at room temperature of the (Z) $\rightarrow$ (E) thermal isomerizations of **1** and **2** are compiled in Table 3.

Macrocycle **1** gave higher activation energies (E_a) and activation enthalpies ($\Delta H^\ddagger$) for each process than the corresponding isomerization process in noncyclic compound **2**. In particular, the activation energy of the (E/Z) $\rightarrow$ (E/E) process was increased by 2.5 kcal mol⁻¹ by the presence of the ring structure. The preexponential factor (A) and activation entropy ($\Delta S^\ddagger$) also increased. These effects are larger in the (E/Z) $\rightarrow$ (E/E) process than in the (Z/Z) $\rightarrow$ (E/Z) process. The higher activation enthalpy ($\Delta H^\ddagger$) indicates the existence of a highly deformed transition state. The increase in the activation entropy ($\Delta S^\ddagger$) indicates that the molecular motion contributing to the thermal isomerization (stretching N=N–C bond angle) has been enhanced for some reason, probably ring strain. However, those thermodynamic parameters only represent the difference in the state function between the reactant and transition state. Energy differences between stable isomers are necessary for potential energy curves to be drawn.

Ab initio calculations were performed to estimate the energies of isomers in the ground electronic state. A Gaussian 98^[16] program package with RHF/6-31G** basis set was used. Figure 3 shows the difference between the calculated ground state energies (ΔH_f) of the isomers and the experimentally measured $\Delta H^\ddagger$ values for isomerization. Experimentally, the energy difference between (Z)- and (E)-azobenzene has been reported to be 9.9–11.7 kcal mol⁻¹.^[17] Theoretical calculations gave energy differences of 10–20 kcal mol⁻¹, depending on the calculation method applied.^[7,18] A HF/6-31+G* calculation on azobenzene gave 17.9 kcal mol⁻¹,^[18] which is similar to the energy difference between the isomers (17.0–17.3 kcal mol⁻¹) of **2**. If the energy differences between (E/Z) and (Z/Z) isomers are compared, that in **1** (7.7 kcal mol⁻¹) is smaller than that in **2** (17.3 kcal mol⁻¹) by almost 10 kcal mol⁻¹, due to the highly deformed structure of (E,Z)-**1** and the presence of less strain in (Z,Z)-**1**. On the other hand, the energy difference between (E,E)-**1** and (E,Z)-**1** (14.0 kcal mol⁻¹) was smaller than our expectations (more than 17 kcal mol⁻¹), since

(E,Z)-**1** is highly deformed, and the energy difference between (E,E)-**2** and (E,Z)-**2** is 17 kcal mol⁻¹. Previous reports showed that optimized structures of azobenzene obtained by theoretical calculations are sensitive to the calculation method applied.^[7,18] A MP2 calculation with 6-31+G* gave a distorted structure for (E)-azobenzene, in which the phenyl rings are rotated by 18.5° with respect to the N=N–C plane. On the other hand, HF and DFT calculations resulted in almost planar structures.^[18] Thus, the degree of steric distortion depends on the calculation method. Other calculation methods should be attempted to assist further discussion.

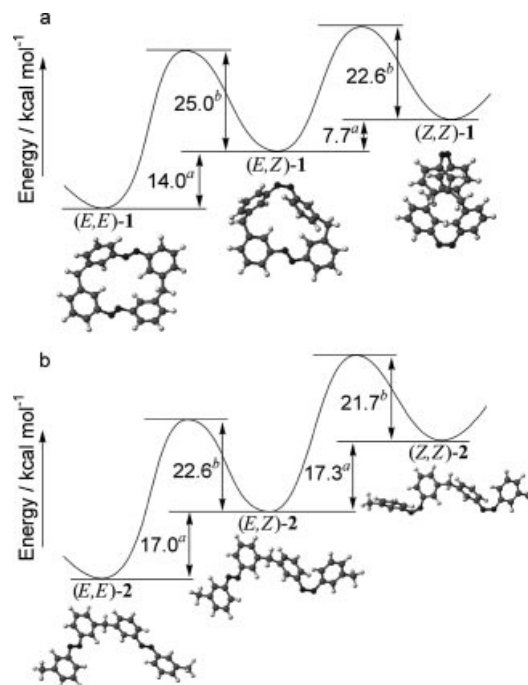


Figure 3. Energy diagram of **1** (a) and **2** (b) estimated from experiment and from theoretical calculations. Structures shown were obtained by RHF/6-31G** calculations. a: calculated values, b: experimentally determined values.

Linear $\Delta H^\ddagger/\Delta S^\ddagger$ relationships have often been used as indications of the reaction mechanisms of thermal (Z) $\rightarrow$ (E) isomerizations in azobenzenes.^[19] Plotting of the $\Delta H^\ddagger$ values against the $\Delta S^\ddagger$ values gives a straight line called the compensation (isokinetic) relationship, which holds when the reaction occurs by a single mechanism.^[19] The values obtained in this study also fall on to the line that has been assigned to the inversion mechanism for various noncyclic azobenzenes,^[19] so the nature of the thermal isomerization

Table 3. Thermodynamic parameters for thermal Z $\rightarrow$ E isomerization of **1** and **2**.

	k_{298} [s ⁻¹]	E_a [kcal mol ⁻¹]	A [10 ¹⁰ s ⁻¹]	$\Delta H^\ddagger$ [kcal mol ⁻¹]	$\Delta S^\ddagger$ [cal K ⁻¹ mol ⁻¹]
(Z,Z)- 1 $\rightarrow$ (E,Z)- 1	5.9×10^{-7}	23.2	5.81	22.6	-11.4
(E,Z)- 1 $\rightarrow$ (E,E)- 1	1.9×10^{-6}	25.8	1290	25.0	-0.6
(Z,Z)- 2 $\rightarrow$ (E,Z)- 2	1.7×10^{-6}	22.3	3.73	21.7	-12.3
(E,Z)- 2 $\rightarrow$ (E,E)- 2	4.9×10^{-7}	23.3	5.80	22.6	-11.4

mechanism does not appear to have been changed significantly by the ring strain.

Conclusion

The effect of a cyclic structure on the photochemical isomerization of azobenzene dimers can be explained in terms of absorption spectra change and the molecular motion in the excited states. A multidimensional potential energy surface should be considered for elucidation of the reaction mechanism. The ring strain in the macrocyclic azobenzene dimer increases the activation energy and activation entropy for the thermal (*Z*) → (*E*) isomerization of the azobenzene moiety. This knowledge of the correlation between structure and reactivity of azobenzene gives significant information for controlling the isomerization to establish photoresponsive functional materials that utilize the isomerization of azobenzene.

Experimental Section

General: ¹H NMR spectra were recorded on JEOL GSX-270 (270 MHz), Varian Gemini-2000/300BB (300 MHz), or JEOL LA600 (600 MHz) instruments. ¹³C NMR spectra were recorded on a Varian Gemini-2000/300BB (75 MHz) machine. UV/Vis absorption spectra were measured with a Shimadzu UV-PC1600 spectrophotometer. Ratios of the isomers were examined by RP-HPLC (ODS-80Ts, TOSO Co./methanol). Photoirradiation was carried out with a 150-W xenon lamp fitted with a monochromator with a bandwidth of ca. 3 nm for all wavelengths used for the experiments. HRMS was measured on a Hitachi M 80B mass spectrometer. Thermodynamic parameters of each thermal isomerization process were determined by measuring the first-order rate constants at different temperatures. Quantum yields for isomerization were determined by the method reported previously.^[11a] Quantum chemical calculations were performed by use of the GAUSSIAN 98 program package.^[16] All optimized structures were obtained by full optimization with a 6-31G** basis set. The atomic coordinates of the corresponding crystal structure were used as the input geometries for (*E,E*)-1, (*E,Z*)-1, and (*Z,Z*)-1. Flat molecular geometries, with all benzene rings on the same plane, were applied for the input geometries for (*E,E*)-2, (*E,Z*)-2, and (*Z,Z*)-2. Solvent for the spectroscopic measurements (acetonitrile) was spectroscopic grade purchased from Dojin Chem. Co. 3-Nitrosotoluene was prepared by a published procedure.^[20]

Synthesis of (*E,E*)-Bis[3-(3-tolylazo)phenyl]methane (2): 3-Nitrosotoluene (411 mg, 3.4 mmol) and bis(3-aminophenyl)methane (347 mg, 1.8 mmol) were dissolved in acetic acid (20 mL) and the system was stirred at room temperature for 18 hours. After addition of saturated Na₂CO₃ solution (10 mL) the reaction mixture was extracted with ethyl acetate. The organic layer was washed with brine and dried with MgSO₄, and the solvent was evaporated under reduced pressure. Repeated chromatography on silica gel (column 1.5 × 25 cm, hexane/AcOEt, 19:1) gave the bis-azo compound (87.9 mg, 13%) as an orange oil in high purity as judged by HPLC and ¹H NMR spectroscopic data. *R*_f = 0.27 (hexane/AcOEt, 19:1). ¹H NMR (300 MHz, CDCl₃): δ = 7.84–7.74 (m, 8 H), 7.47–7.31 (m, 8 H), 4.21 (s, 2 H), 2.46 (s, 6 H) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 153.06, 152.85, 141.85, 139.06, 131.86, 131.60, 129.35,

128.96, 123.55, 122.94, 120.77, 120.58, 41.58, 21.23 ppm. HRMS (*m/z*): calcd. for C₂₇H₂₄N₄: 404.2000; found 404.2034.

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