Light-intensity Dependence in the Photochromism of Dibenzo[2.2](4,4′)-azobenzenophane

Nobuyuki Tamaoki * and Tsuguo Yamaoka
Department of Image Science and Technology, Chiba University, 1–33 Yayoi-cho, Chiba 260, Japan

Reduction of 4′,4″-dinitro-*o*-terphenyl under conditions of high dilution, produces a mixture of macrocyclic poly(azobenzene) compounds. From the mixture, three kinds of macrocycle, namely, dimer **2** {dibenzo[2.2](4,4′)azobenzenophane}, trimer **3** and tetramer **4** have been isolated pure. In toluene, absorption peaks due to the $\pi \rightarrow \pi^*$ transition for the macrocycles undergo dramatic hypsochromic shifts as the ring size of the macrocycles decreases from the trimer **3** to the dimer **2**; this is an indication that benzene rings at both ends of the dimer **2** are fixed perpendicularly to two azobenzene planes in the macrocycle. The photostationary state of the dimer **2** in toluene at λ = 366 nm contained the *EZ* isomer which undergoes thermal isomerization to the more stable *EE* isomer at the first-order rate of 0.768 s^{-1}. The reaction of **2** is much faster than that of the dimer **5**, which was described in our last paper. Due to the fast thermal *EZ* to *EE* isomerization, the efficiency of the photoisomerization from the *EE* isomer to the *ZZ* isomer is light-intensity dependent. This dependence is observed at higher light intensities for the dimer **2** than for the dimer **5**.

It is well known that the absorption spectra of azobenzene derivatives exhibit reversible changes, when the azobenzenes are irradiated, brought about by *EZ* isomerization.[1] Such photochromic properties have attracted a significant amount of attention from the viewpoint of possible applications to the control and measurement of radiation intensity, visual contrast effects and information imaging and storage.[2] In some of these applications, light-intensity-dependent photoisomerization (or photochromism), in which quantum yields are increased as the light intensity becomes higher, is necessary. For example, in the case of information storage, non-destructive visualisation is possible by use of low intensity light.

We have synthesized a number of macrocyclic compounds in which two azobenzene units are present within the frame (azobenzenophanes) and investigated their isomerization behaviour, in particular, the dependence of light intensity on the efficiency of the photoisomerization. The basis of these studies are described below.

When bridges that connect the two azobenzene units of azobenzenophanes are of a certain length [Scheme 1(*a*)], the change of ring strain due to the isomerization of one azobenzene unit from *E* to *Z* form is small, and the *EZ* isomer should be stable enough to exist. On the other hand, when the length of the bridges is relatively short [Scheme 1(*b*)], the closer proximity between the 4- and 4′-positions of the *Z* azobenzene unit[3] produces a large ring strain in the *EZ* isomer. Consequently, the *EZ* isomer becomes unstable and isomerizes very quickly to the *EE* isomer. The ring strain of the *ZZ* isomer is, however, small and the *ZZ* isomer is fairly stable. Photoisomerization from the *EE* isomer to the *ZZ* isomer for such compounds becomes seemingly more efficient as the light intensity is increased, since the concentration of the *EZ* isomer, which is an expected intermediate of the reaction, becomes concomitantly higher.

As the length of the bridges is reduced further [Scheme 1(*c*)], it becomes likely that the *EZ* isomer does not exist.

We thought it of great interest to see whether the two azobenzene units in such compounds could be made to undergo concerted isomerization from a doubly excited E^*–E^* state to the *ZZ* isomer; an isomer in which the ring strain is relatively small.

In earlier papers[4,5] we reported the synthesis of [2.2](4,4′)azobenzenophane (**5**) and the lifetime of the *EZ* isomer of **5** at 25 °C to be 22 s. When the irradiation time exceeded the lifetime of the *EZ* isomer, the *EE* isomer, which isomerized photochemically to the *ZZ* isomer, was present in larger amounts as the irradiation intensity was increased, even though the total amount of the irradiation energy was kept constant.[5]

We now report the synthesis, the conformation and the isomerization behaviour of **2** which has shorter and more rigid bridges than **5**. For comparison we also report the properties of compounds **3** and **4**, which have the same component units as compound **2**.

Experimental

Materials.—*4′,4″-Dinitro-*o*-terphenyl* (**1**). This was synthesized by the nitration of *o*-terphenyl (Wako Pure Chemical Industries, Ltd.) according to the method of Allen *et al.*[6] $\delta(CDCl_3)$ 7.29, 8.12 (2 × 4 H, *p*-substituted phenyl protons) and 7.47, 7.55 (2 × 2 H, *o*-substituted phenyl protons).

9,10,25,26,39,40,53,54-*Tetrabenzo*-1,2,17,18,33,34,49,50-*octa-aza*-$[2_8]$(4,4′)*cyclophane*-1,17,33,49,-*tetraene* (**4**). 4′,4″-Dinitro-*o*-terphenyl (6.0 g, 19 mmol) in dry tetrahydrofuran (THF) (100 cm^3) was added dropwise over 4.5 h to a suspension of $LiAlH_4$ (3.5 g, 92 mmol) in dry THF (250 cm^3) under a nitrogen atmosphere at room temperature. After an additional hour of stirring water (20 cm^3) was carefully added to the reaction mixture. The precipitate (inorganic substances and probably insoluble polymer) was filtered off and the THF was removed from the solution by evaporation. The residual orange solid was taken up in dichloromethane and the solution was washed with water and evaporated. The residue was isolated by preparative TLC (silica gel, Merck 5554) using CCl_4 as the eluent. The second and the third orange bands from the top of the plate was separated and taken up in dichloromethane (the first band contained insufficient product to isolate). The fraction from the second band on the TLC plate was almost pure and recrystallized from chloroform.†

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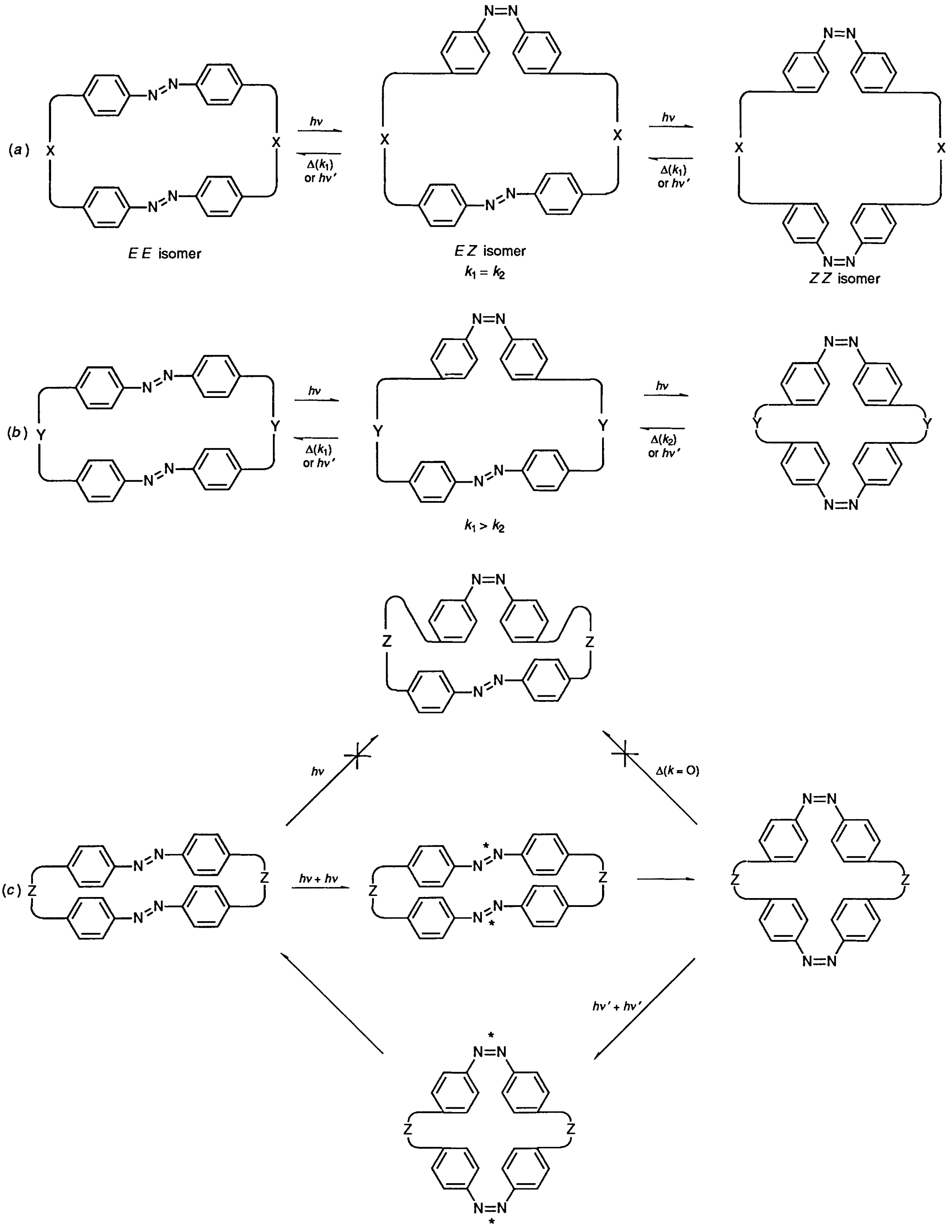
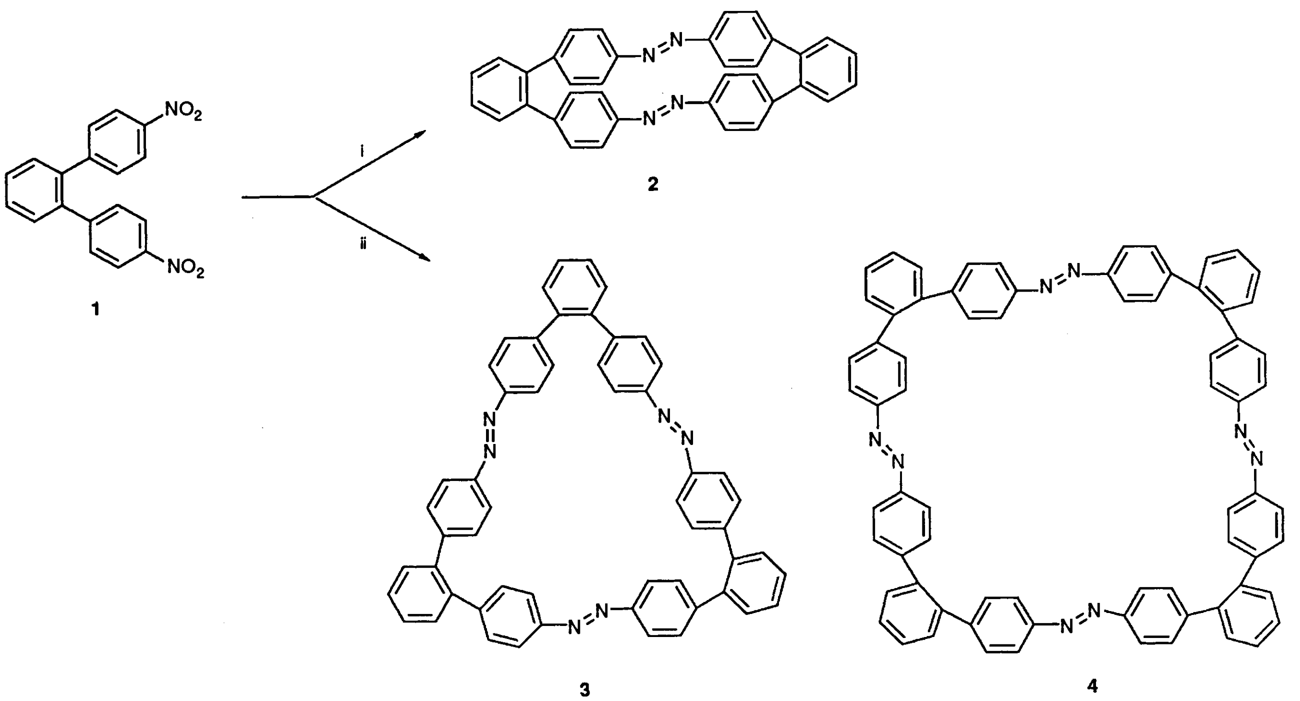
† The third band on the TLC plate contained the macrocyclic heptamer which was detected by FD-MS.


(a)
X
N=N
hν
Δ(k₁) or hν'
E E isomer
E Z isomer
k₁ = k₂
Z Z isomer
(b)
Y
Δ(k₂) or hν'
k₁ > k₂
(c)
Z
hν + hν
Δ(k = O)
hν' + hν'
*

Scheme 1



Scheme 2 *Reagents:* i, $LiAlH_4$–THF, reflux 57 h; ii, $LiAlH_4$–THF, room temperature

Compound **4**[8]*: Yield 3.0 mg (0.062%); m.p. >280 °C; *m/z* (EI-MS) 1024 (M^+), The ^1H NMR data are listed in the Results and Discussion section.

9,10,25,26,39,40-*Tribenzo*-1,2,17,18,33,34-*hexaaza*-$[2_6]$-(4,4′)*cyclophane*-1,17,33-*triene* (**3**). 4′,4″-Dinitro-*o*-terphenyl (10 g, 31 mmol) in dry THF (1 dm^3) was added dropwise by means of an HPLC pump over 53 h to a suspension of $LiAlH_4$ (6.0 g) in dry THF (200 cm^3) under a nitrogen atmosphere at room temperature. After 15 h of stirring the reaction was treated as described for **4** to give an orange solid mixture. The orange solid was isolated by column chromatography (silica gel and chloroform). The first red fraction was further separated by preparative gel permeation chromatography (GPC) (Ultrastyragel 500 Å, Waters). The second main GPC peak was identified as that of **3**.

Compound **3**[8]: yield 1.9 mg (0.024%); m.p. >280 °C; *m/z* (FD-MS) 768 (M^+). The ^1H NMR data is listed in the results and Discussion section.

9,10,25,26-*Dibenzo*-1,2,17,18-*tetraaza*-$[2_4]$(4,4′)*cyclophane*-1,17-*diene* (**2**). 4′,4″-Dinitro-*o*-terphenyl (7.7 g, 24 mmol) in dry THF (500 cm^3) was added dropwise by means of an HPLC pump over 57 h to a suspension of $LiAlH_4$ (4.6 g) in dry THF (150 cm^3) under a nitrogen atmosphere. The reaction mixture refluxed during the addition of the dinitro compound. Treatment of the reaction mixture as described for **3**, afforded **2** as orange crystals.

Compound **2**[8]: yield 4.0 mg (0.064%); m.p. >280 °C; *m/z* FD-MS 511 ($M^+ - 1$). The ^1H NMR data are listed in the Results and Discussion section.

Photoisomerization and Measurement of Thermal Isomerization.—Kinetic measurements of the thermal isomerization of **2**, **3** and **4** were made spectrophotometrically on a Hitachi Model 200-20 spectrophotometer by monitoring changes in absorbance at the λ_{max} of toluene solutions in the dark after irradiation at $\lambda = 366$ nm with a high-pressure mercury lamp (Ushio-UM-452, 450 W) and Toshiba glass filters, UV-34 and UV-D2. Fast thermal isomerization from the *EZ* isomer to the *EE* isomer of **2** was monitored with a diode-array spectrophotometer (Hewlett Packard HP8452A).

Measurement of the Light-intensity Dependence.—The light-intensity dependence was measured as described elsewhere in the literature.[5]

Results and Discussion

Syntheses and Spectral Properties.—In previous papers[4,5] we have reported a method of synthesizing a cyclic azobenzene dimer, in which the azo linkages are assembled in the final cyclization step. We initially applied a similar method to 4′,4″-dinitro-*o*-terphenyl **1**, however, the smallest cyclic compound in the reaction mixture was the cyclic tetramer **4** and neither the cyclic trimer **3** nor the cyclic dimer **2** was produced. The distribution of the cyclic products was dependent on the addition period and the reaction temperature. When a THF solution of **1** was added over 53 h at room temperature, the cyclic dimer and cyclic trimer were produced along with mono- and di-azoxybenzene derivatives of the cyclic dimer, from which they could not be separated. The reaction mixture obtained from addition of a THF solution of **1** to a refluxing THF suspension of $LiAlH_4$ over 57 h contained the cyclic dimer **2** free from any azoxybenzene derivatives. The cyclic dimer **2** could then be isolated (Scheme 2).

The wavelength of the absorption maximum (λ_{max}) in toluene and the ^1H NMR data for the isolated cyclic compounds **2**–**4** are shown in Table 1. The λ_{max} of $\pi \rightarrow \pi^*$ transition is shifted hypsochromically as the size of the macrocycle is reduced; the difference in λ_{max} between **2** and **3** is as large as 21 nm. These observations can be accounted for by the conformations adopted by the three cyclic compounds. Azobenzene units are partly conjugated with the phenyl ring in the bridges in **3** and **4**; however, in **2** the phenyl ring in the bridges are fixed perpendicularly to the two azobenzene units such that they can no longer conjugate with each other.

The fixed conformation of **2** is further supported by the ^1H

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* Elementary analyses for the macrocyclic compounds **2**–**4** do not coincide with the calculated values. This is demonstrably due to the inclusion of solvent or water in the cavity of the macrocyclic ring.

Table 1 Spectroscopic data of compounds **2**–**4**

		δ(ppm)	
Compound	λ_{max}/nm ($\pi \rightarrow \pi^*$)	*o*-substituted phenyl protons[a]	*m*-substituted phenyl protons[b]
2	325	7.50, 7.59	6.99, 7.44
3	346	7.49, 7.52	7.25, 7.70
4	352	7.49, 7.53	7.29, 7.77

[a] *ortho* to the azo group. [b] *meta* to the azo group.

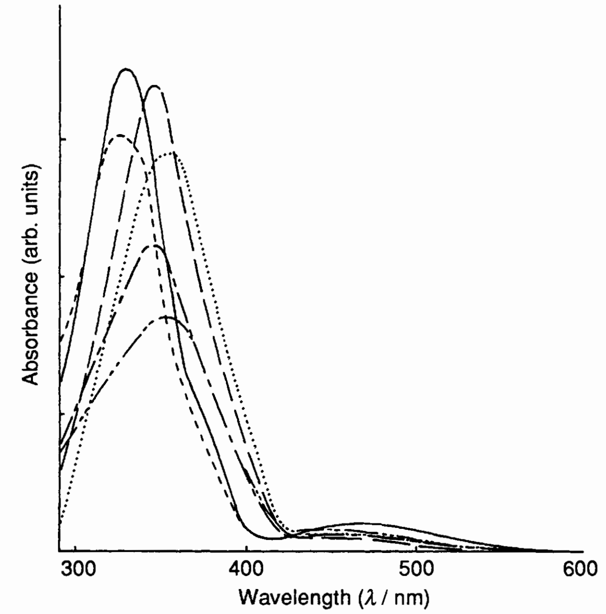

Fig. 1 Absorption spectra in toluene of **2**: (——); **3** (— —); and **4** (- - - - - -) before irradiation and **2** (— — — —); **3** (— - —); and **4** (— - - —) at 366 nm photostationary state

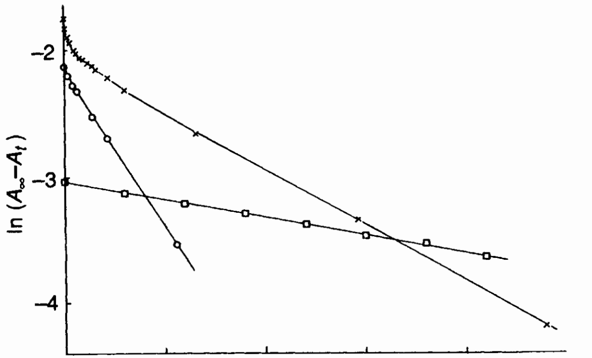

Fig. 2 Thermal *Z*–*E* isomerization of **2**, **3** and **4** at 30 °C after photochemical *E*–*Z* isomerization: □, **2** at 330 nm; ×, **3**, at 346 nm; ○, **4** at 349 nm

NMR spectra. The δ values of the protons on the azobenzene units of **2** appear at higher frequencies compared with those of **3** and **4** owing to the large shielding experienced by the opposing benzene rings of the two azobenzene units. A similar trend of ^{1}H NMR shifts has been shown for non-benzo azobenzenophanes.[4]

Z–E *Isomerization.*—At λ = 366 nm light, the absorbance at $\pi \rightarrow \pi^*$ transitions for the cyclic compounds **2**–**4** in toluene are reduced as with other azobenzene derivatives,[1] indicating an $E \rightarrow Z$ photoisomerization. Fig. 1 shows the absorption spectra for the macrocycles at the initial and at the photostationary states. The macrocycles are not isomerized to any great extent although the degree of photo-isomerization increases as the ring size becomes larger.

From the spectra it is seen that the macrocycles recover thermally very slowly from the photostationary state. Fig. 2 shows the changes of $\ln(A_\infty - A_t)$ plotted against the thermal reaction time. The lines of the tetramer and the dimer are almost straight; however, that for the trimer is curved from 0 to 200 min, the spectral change being faster for the trimer in that period. We have investigated the thermal isomerization reactions of four isomers of the macrocyclic azobenzene trimer **6** and reported that the rates of isomerization are varied for the different processes, namely, *ZZZ* → *EZZ*, *EZZ* → *EEZ* and *EEZ* → *EEE*.[7] Although we have not separated the four isomers of **3** and estimated the rates of isomerization for the three processes in the present study, it is obvious that there exist isomers of **3** which undergo thermally isomerization faster than the others just after the photoirradiation. For the cyclic tetramer **4**, the ring strain is not high in any of the possible isomers, owing to the large ring size, and consequently, the respective rates of thermal isomerization are not so different.

With the diode-array spectrophotometer we were able to detect the changes in the absorption spectra for the cyclic dimer within 10 s of photoirradiation. (This detection was not possible with the usual spectrophotometer.) Fig. 3 shows the change in absorbance at 330 nm just after photoirradiation. The thermal reaction is first order and the rate constant at 25 °C is 7.68×10^{-1} s^{-1}. Similar spectral recovery, just after the photoirradiation, has also been observed for non-benzo cyclic dimers, and has been attributed to the thermal isomerization of the *EZ* isomer to the *EE* isomer.[4,8] The rapid recovery observed in the spectra of **2** is similarly attributed to the isomerization of the *EZ* to the *EE* isomer. The slow thermal spectral change in **2** shown in Fig. 2 should reflect the process *ZZ* → *EZ* → *EE*, however, the transformation *ZZ* → *EZ* seems to be the rate-determining step, the thermal isomerization *EZ* → *EE* being the isomer is much faster. Hence, the rate of the thermal *ZZ* → *EZ* isomerization was estimated from the slow spectral change. In Table 2 are listed the rate constants and the activation parameters for the two steps for the dimer **2**.

E_a and $\Delta S^\ddagger$ for the $Z \rightarrow E$ isomerization of many azobenzene derivatives have been measured,[9] and a compensation relationship (plots of E_a *vs.* $\Delta S^\ddagger$ are reasonably linear), which suggests that the isomerization of all azobenzene derivatives is based on just one mechanism, has become apparent.[10] However, the relationship between E_a and $\Delta S^\ddagger$ for the thermal isomerization of the *EZ* to the *EE* isomer of the dimer **2** does not fall on the line. The *EZ* isomer of **2** must therefore isomerize *via* a transition state which is not the same as that for other known azobenzene derivatives. This unusual phenomenon is due to the deformed *EZ* isomer in the ground state and/or in the transition state as a result of the extremely large ring strain. From molecular mechanics calculations (CHARMM) the values of the steric energy for the *EE*, *EZ* and *ZZ* isomers are estimated to be 41.92, 55.73 an 46.08 kcal mol^{-1},† respectively. The *EZ* isomer is further destabilized by 9.65 kcal mol^{-1} compare with the *ZZ* isomer. These calculations support the above isomerization mechanism of the *EZ* isomer of **2** described above.

Generally, in the system $A \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} B \xrightarrow{h\nu} C$ the photochemical reaction from A → C is light-intensity dependent when the life time of B is short. In addition, the region of the light intensity where the dependence can be seen is dependent upon the lifetime of B.[11] That is to say, as the lifetime of B becomes shorter, the light-intensity dependence becomes apparent at higher light intensities. Figs. 4 and 5 show the relationship between exposure

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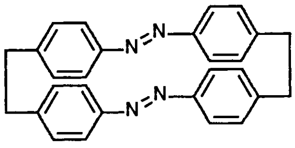
† 1 cal = 4.184 J.

Table 2 Rate constants and activation parameters for the thermal isomerization of 2 in toluene

Transformation	k_{298}/s^{-1}	τ_{298}/s	E_a/kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$/cal k^{-1} mol^{-1}
EZ → *EE*	7.68×10^{-1}	1.30	21.6	11.5
ZZ → *EZ*	8.62×10^{-5}	1.16×10^{4}	22.4	−4.08



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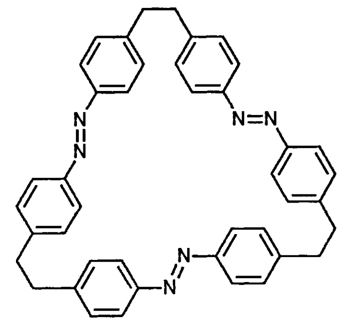

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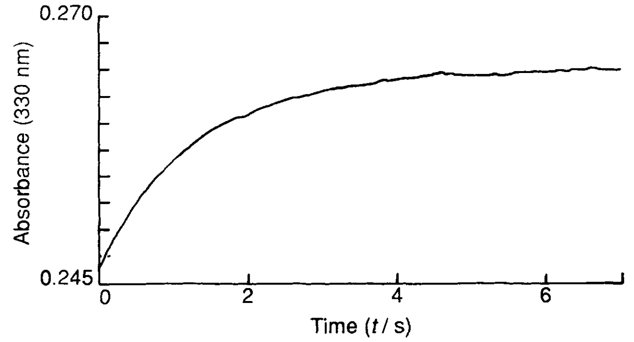

Fig. 3 Fast thermal recovery of absorbance at 330 nm for 2 immediately after irradiation

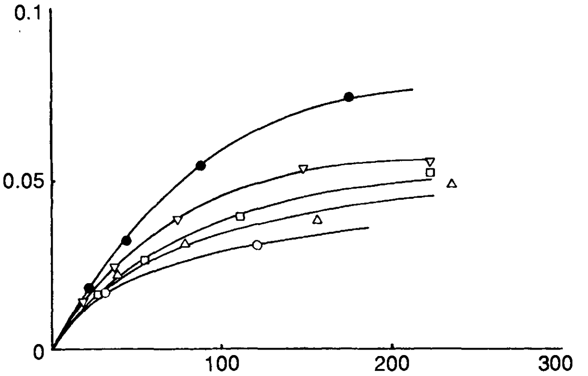

Fig. 4 Changes of absorbance at 330 nm due to the irradiation of 2 in toluene with different light intensities: ●, 4.39 mW cm^{-2}; ▽, 3.71 mW cm^{-2}; □, 2.77 mW cm^{-2}; △, 1.96 mW cm^{-2}; ○, 0.76 mW cm^{-2}

energy and the change in absorbance at λ_{max} for benzo dimer 2 and non-benzo dimer 5, respectively. In the case of benzo dimer 2 the efficiency of photoisomerization is greatly changed when the light intensity is changed from 0.76–4.39 mW cm^{-2}. The change was less in the same range for the non-benzo dimer 5 in contrast with the change observed at light intensities of 100–1000 μW cm^{-2}.[5] This difference in behaviour between 2 and 5 might be attributed to the fact that the lifetime of the *EZ* isomer for the benzo dimer 2 is less, by more than a factor of ten, than that of the non-benzo dimer 5 (1.3 s as opposed to 22).

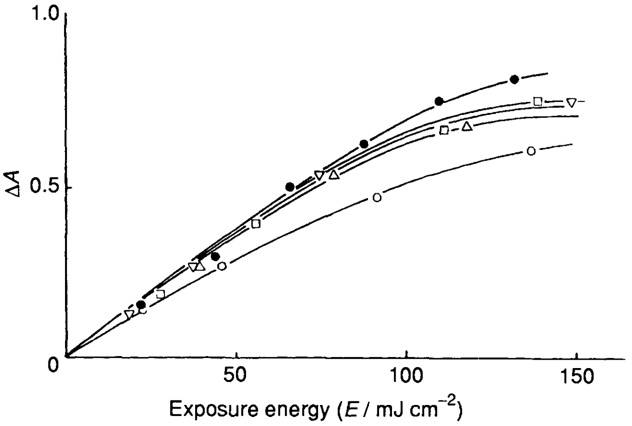

Fig. 5 Changes of absorbance at 328 nm due to the irradiation of 5 in toluene with different light intensities: ●, 4.39 mW cm^{-2}; ▽, 3.71 mW cm^{-2}; □, 2.77 mW cm^{-2}; △, 1.96 mW cm^{-2}; ○, 0.76 mW cm^{-2}

Conclusions

Benzo-[2.2](4,4′)azobenzenophane 2 is synthesized by the reduction of 4′,4″-dinitro-*o*-terphenyl under conditions of high dilution. Two benzo units in 2 are positioned perpendicularly to the planes of the two facing azobenzene units within the same molecule in solution. Owing to the short lifetime of the *EZ* isomer of 2, the efficiency of the photoisomerization from the *EE* isomer to the *ZZ* isomer is dependent upon the light intensity in the range 0.76–4.39 mW cm^{-2}.

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