

Studies on Photochromism of
Macrocyclic Azobenzene Derivatives

by
NOBUYUKI TAMAOKI

Doctor's Thesis Submitted

to

Graduate School of Science and Technology

Chiba University

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General Introduction

Since Hirshberg suggested a possibility of the application of photochromism into optical memories in 1956¹⁾, many photochromic compounds have been synthesized²⁾⁻⁴⁾. Photochromism is the phenomenon whereby some compounds change their color reversively (or one way thermally) upon irradiation. As shown in the figure 1, a compound in state A is changed into state B when irradiated by the light which is absorbed by state A. At the same time the absorption spectrum is changed. A compound in state B is, in this time, changed into state A when the compound is irradiated by light at a wavelength which a compound in state B is able to absorb. As the compound is utilized as a media for optical memories, the compound in all parts of a substrate is first turned into state A (initialization), and the compound is partially irradiated with light of λ_A and this changes the structure from state A to state B (writing). The absorbance of light λ_A or λ_B is monitored (reading). Although many spiropyranes, azobenzene derivatives and fulgides have been synthesized for application to such optical memories⁵⁾, there is a fundamental problem to overcome when photochromic compounds are applied to optical memories. That is, the light for the read-out of the memories causes a photochromic reaction of the compound and destroys the memories.

In order to attain non-destructive read-out, some possible solutions are proposed. For example, a method to control the orientation of the liquid crystalline compounds by the isomerization of the photochromic compounds⁶⁾, a method to read out the memories with the change of the optical rotation of the photochromic compounds in the chiral environment⁷⁾, a method to

change thermally the photo-isomerized photochromic molecules into the photo-stable J-aggregates⁸⁾. However, the read-out of the memories is attained, for the examples, not by utilizing the function of a single molecule but by the effect of media or the orientation of the molecules.

If the photochromism of a single molecule is light-intensity dependent, writing of memories would be accomplished with a high enough intensity of light and read-out would be done with a low enough intensity of light so as destruction of memories would not occur. One of the possible systems which may show such light-intensity dependence is a compound that possesses a thermally unstable state X between A and B. The state X should be populated by the excitation of A, and B by the excitation of X. The excitation energy from A to X and that from X to B should be almost the same. It is one way of thinking to use excited states of A as the thermally unstable state X, however, it is not so easy to design a molecular structure where the two excitation energies are the same. In this study I suggest the idea to use macrocyclic compounds, one of whose ground states is thermally destabilized by a ring strain, for the optical memory media. The functions of macrocyclic compounds are briefly described below.

Many macrocyclic compounds are known to show very interesting functions⁹⁾⁻¹⁰⁾. For example, compounds, which have some hydrophobic or hydrophilic parts facing inside arranged circularly with a space by the macrocyclic structure, bind ions or organic compounds inside the space in organic solvent or water, respectively. crown ethers¹¹⁾, cryptands¹²⁾, cyclodextrins¹³⁾ and calixarenes¹⁴⁾ are well-known as such macrocyclic compounds. These examples are the representations in which the static closed figures of macrocyclic compounds are made

good use of.

On the other hand, macrocyclic compounds with the isomerizable units in the frame structure have recently been taken in interest, because the change of the structure due to the isomerization of parts of the molecules causes structural change of other parts and controls the function of the molecules. The binding ability of alkali metal ions for crown ethers with azobenzene units in the frame structure (8) is changed by the structures (cis or trans) of the azobenzene units¹⁵). This phenomenon is explained below. The ether chain can have circular form as is the case of crown ether with cis-azobenzene units, but in the case of trans-azobenzene units the ether chain is straightened and cannot bind any alkali metal ions. A compound, in which a dye unit and a isomerizable stilbene unit are circularly combined with each other (9), has also been synthesized¹⁶). The dye structure is effected by the conformation (cis or trans) of the stilbene unit. Thus, the structure of the dye is lengthened in the case where the dye has a trans form, and the dye absorb light of longer wavelength than the dye with cis-stilbene in the molecule. These second examples represent the utilization of the dynamic structural change of macrocyclic compounds, which is induced by the ring strain. When a part of the structure of macrocyclic compounds is changed by the isomerization, they change their total conformation to minimize their ring strain.

The influence of the ring strain on the structural change of the macrocyclic compounds is the topic of much interest in view, not only of the application to functional materials but also, of molecular mechanics. Theoretical and experimental studies on the stable conformations of macrocyclic compounds have already

carried out by some researchers⁹⁾. However, the number of kinetical studies on the dynamic processes of structural changes of macrocyclic compounds induced by the ring strain is very few¹⁷⁾, much less the studies on the application of the dynamic process to functional materials.

In the present paper, syntheses, conformations and isomerization properties of macrocyclic compounds, in which more than two azobenzene units are circularly connected with short spacers, are studied. I also describe a possibility of the application of the unique isomerization properties induced by the ring strain of the compounds to the optical memory media with a non-destructive read-out property.

Chapter 1 and 2 describe syntheses, structures and isomerizations of [2.2](4,4')azobenzenophanes, (10) and (11), in which two azobenzene units are connected with two carbons at 4,4' positions each. [2.2](4,4')azobenzenophanes are synthesized for the first time by the synthetic route in which formations of azo-linkages are performed as the final cyclization processes. It is described how the photo- and thermal isomerization of three isomers of the compounds, the trans-trans form, trans-cis form, cis-cis form, are influenced by the ring strains of the isomers. Due to the large ring strain of the trans-cis isomers for 10 and 11, efficiency of photoisomerization from the trans-trans isomer to the cis-cis isomer for those compounds is light-intensity dependent.

Chapter 3 describes isomerizations of [2.2](4,4')-azobenzenophane in polycarbonate films and a theoretical analysis of light-intensity dependent photoisomerization of macrocyclic azobenzene dimers. It is demonstrated that an efficiency of photoisomerization of 10 is light-intensity dependent even in a

polymer film. A relation between life times of the trans-cis isomers and light-intensities, at which an efficiency of photoisomerization is depend on an intensity of light, is also described. It is shown that a photochromic memory composed of 10 and polycarbonate possesses a non-destructive read-out property.

In chapter 4 isomerization properties of $[2_3](4,4')$ -azobenzenophane (12), which is composed of three azobenzene units cyclically connected, are described. Relatively stable isomers, trans-trans-trans, trans-trans-cis, trans-cis-cis, cis-cis-cis, exist for this compound. The photo- and thermal isomerization among those isomers are clarified by using the method of liquid chromatography.

In chapter 5 attempts to apply the synthetic method described in chapter 1 and 2 to other macrocyclic azobenzene derivatives are shown. A cis azobenzene is formed via the macrocyclic azobenzene derivative without using light.

References

- (1) Y. Hirshberg, J. Am. Chem. Soc., 78, 2304 (1956).
- (2) G. H. Brown(ED.), Photochromism, Techniques Chem., Wiley Interscience, New York, 1971.
- (3) H. Dürr and H. B.-Laurent(Eds.), Studies in Organic Chemistry 40, Photochromism, Elsevier, Amsterdam, 1990.
- (4) H. Dürr, Angew. Chem. Int. Ed. Engl., 28, 413 (1989).
- (5) G. J. Ashwell, Nature, 347, 617 (1990). And references cited in.
- (6) K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, Langmuire, 4, 1214 (1988).
- (7) Y. Suzuku, K. Ozawa, A. Hosoki and K. Ichimura, Polym. Bull., 17, 285 (1987).
- (8) E. Ando, J. Hibino, T. Hosida and K. Morimoto, Thin Solid Films, 160, 279 (1988).
- (9) R. M. Izatt and J. J. Christensen(Eds.), Synthesis of Macrocycles, The Design of Selective Complexing Agents, Wiley-Interscience, New York, 1987.
- (10) F. Vögtle and E. Weber(Eds.), Host Guest Complex Chemistry, Parts I-III, Top. Curr. Chem., Springer, Berlin, 1981, Vol. 98; 1982, Vol. 101; 1984, Vol. 121.
- (11) C. J. Pedersen, J. Am. Chem. Soc., 89, 2495 (1967).
- (12) J. M. Lehn and J. P. Sauvage, J. Am. Chem. Soc., 97, 6700 (1975).
- (13) F. Cramer, Ber., 92, 1739 (1959).
- (14) C. D. Gutsche, B. Dhawan, K. H. No and Muthukrishnan, J. Am. Chem. Soc., 103, 3782 (1981).
- (15) S. Shinkai, T. Minami, Y. Kusano and O. Manabe, Tetrahedron Lett., 23, 2581 (1982).
- (16) P. Nesvadba and A. Gossauer, J. Am. Chem. Soc., 109, 6545 (1987).
- (17) H. Rau and E. Lüddecke, J. Am. Chem. Soc., 104, 1616 (1982).

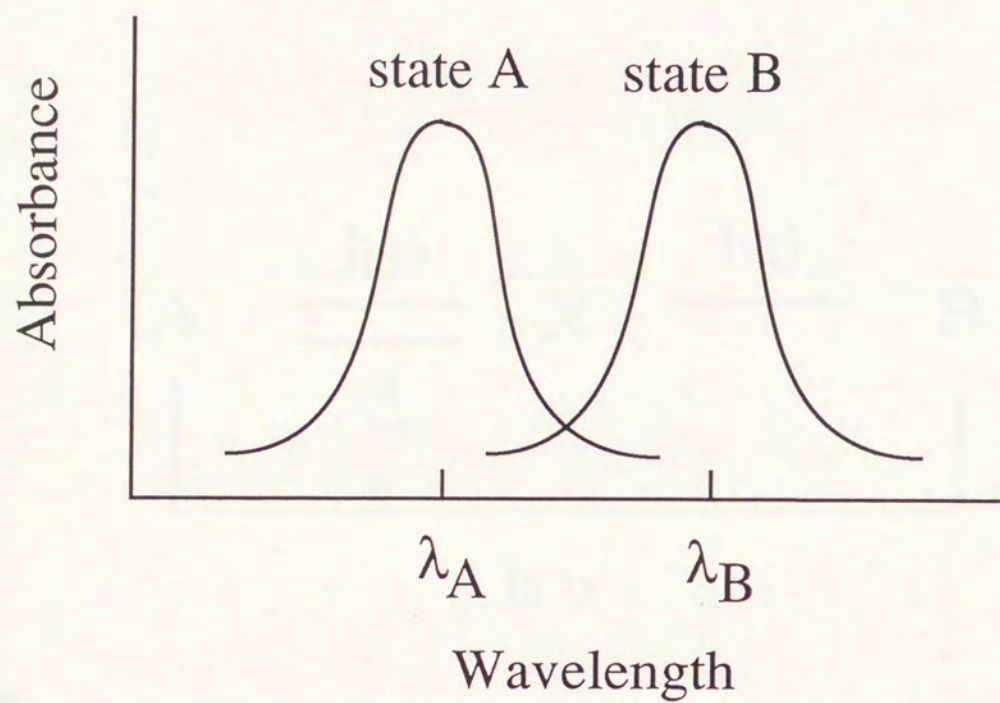


Fig. 1 Absorption spectra of states A and B for a photochromic comound.

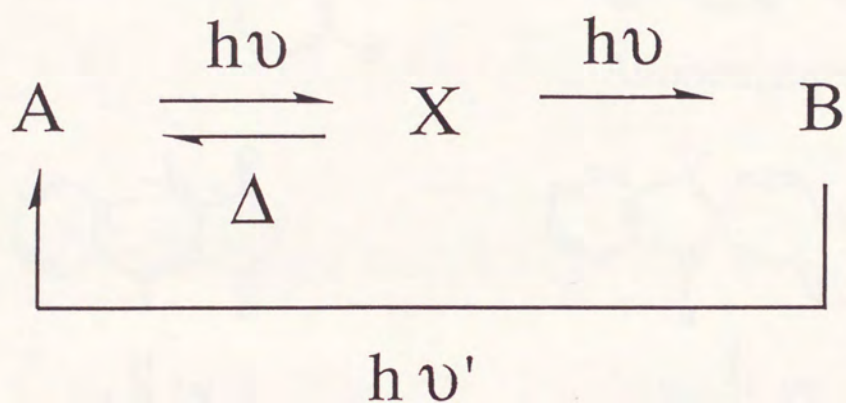


Fig. 2 Reaction scheme of photochromic compounds with a metastable state X.

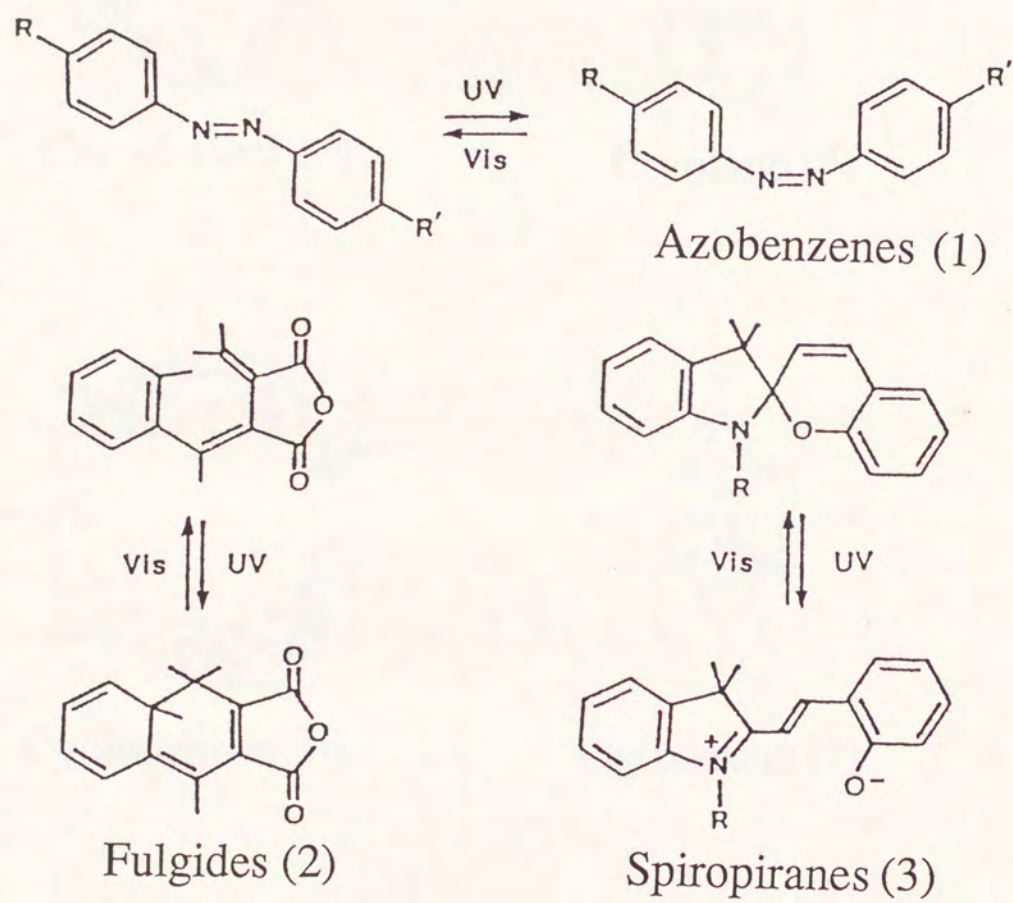
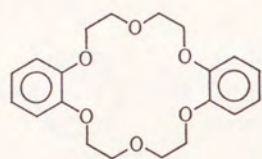
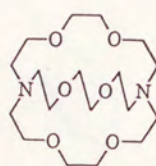


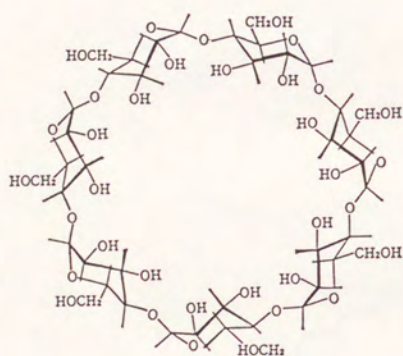
Fig. 3 Structures of typical photochromic compounds.



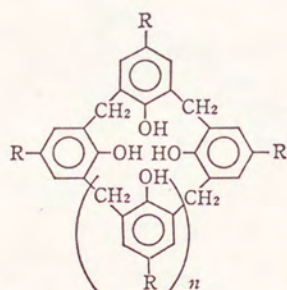
Crown ether (4)



Cryptand (5)

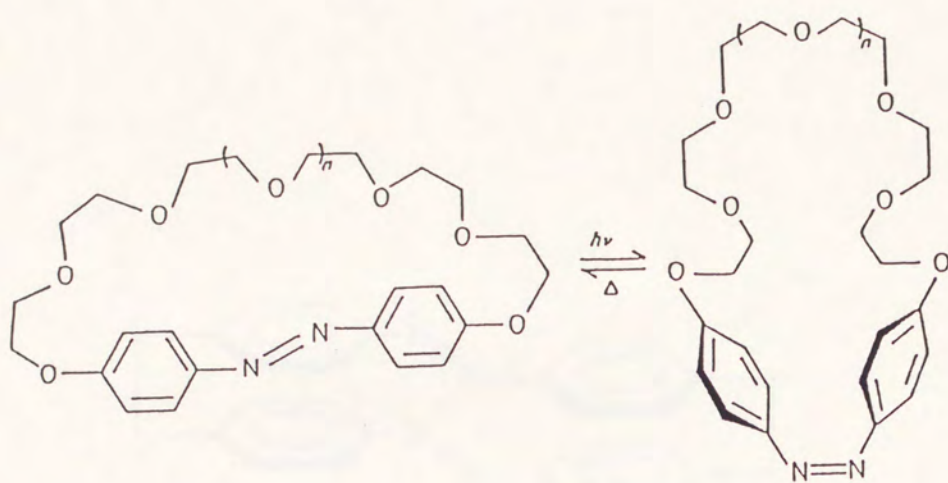


Cyclodextrin (6)

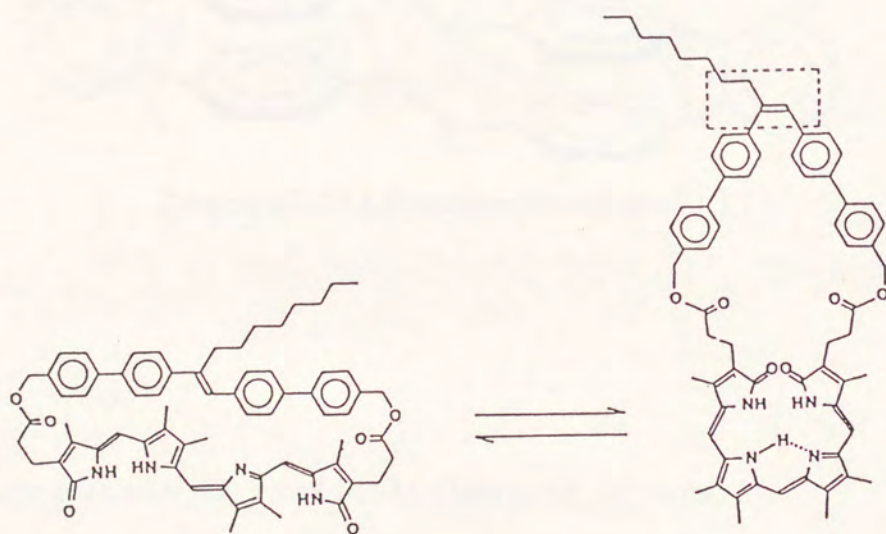


Calixarene (7)

Fig. 4 Structures of typical inclusion compounds.

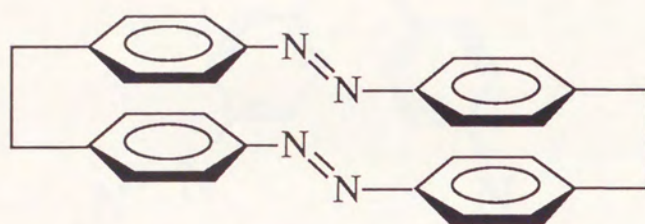


(8)

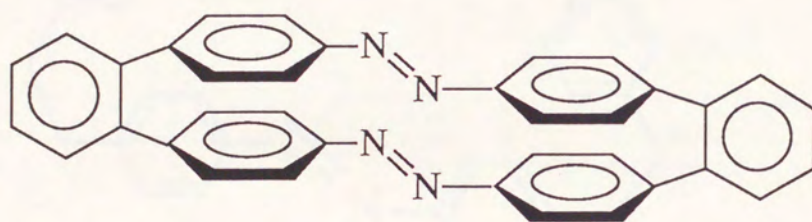


(9)

Fig. 5 Structures of isomerizable macrocyclic compounds.

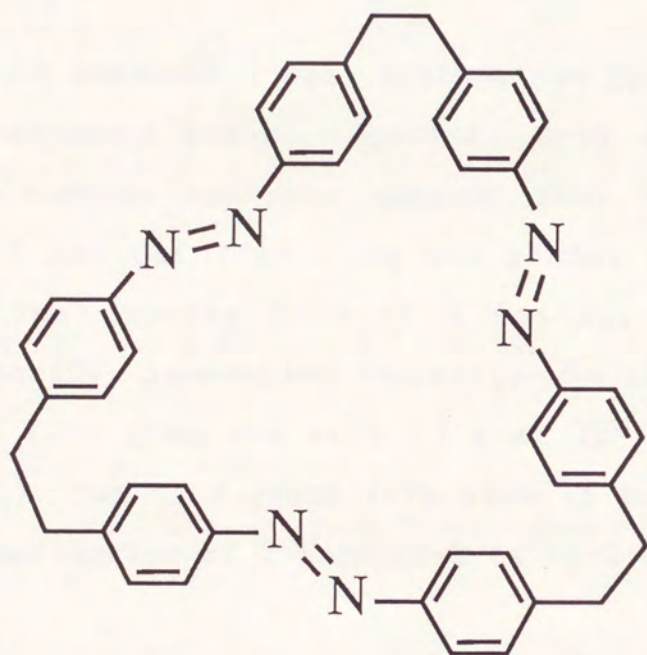


[2.2](4,4')Azobenzenophane (10)



Dibenzo[2.2](4,4')azobenzenophane (11)

Fig. 6 Structures of cyclic azobenzene dimers.



[2 3](4,4')Azobenzenophane (12)

Fig. 7 Structure of cyclic azobenzene trimer.

Chapter 1

[2.2](4,4')Azobenzenophane.

Synthesis, Structure, and Cis-Trans Isomerization.

Abstract

The title compound 2 was synthesized by the reduction of 1,2-bis(4'-nitrophenyl)ethane. Spectral data and results of X-ray crystal structure analyses suggest that facing two azobenzene units in 2 are deformed from the planes both in solution and crystal. The cis-cis form of 2 (cc-2), which was generated photochemically, isomerized thermally via the trans-cis form (tc-2), whose life time was only 22 s at 25°C, to the trans-trans form (tt-2). Due to a short life time of tc-2, the efficiency of photo-isomerization of 2 from tt-2 to cc-2 became light intensity dependent.

Introduction

Macrocyclic compounds which include photoresponsive units as parts of the frame have been extensively studied to mimic photoregulated functions in nature¹. The light induced conformational change of photoresponsive units is efficiently conveyed to other parts of the molecules in such cyclic systems. Consequently, chemical and physical functions of these compounds can be changed in response to photoirradiation. To the contrary, it is also known that the photo- and thermal isomerization of photoresponsive units in some macrocycles is strictly controlled by the size and the conformation of the rest part of the ring due to ring strain². Grützmacher et al. synthesized a series of dithia-diaza[n.2]paracyclophane-enes^{2a} and their metha analogues^{2b} with different ring chain lengths, and reported that the cis/trans ratio in a photostationary state is changed by the length of the alkylene chain. Rau et al. synthesized [3.3](4,4')azobenzenophane **1** from 4,4'-bis(bromomethyl)azobenzene and Na₂S, and first reported that cis-trans thermal isomerization of one azobenzene unit can be controlled by the conformational change of the other azobenzene unit^{2c}. Thus, cis-trans isomerization of an azobenzene unit on one side in **1** occurs 1000 times faster at 25°C when the other azobenzene unit is in the trans form than when in the cis form.

It would be true for [n.n](4,4')azobenzenophane series that the shorter the length of the bridges on both sides of the frame are, the more significant the effect of the other azobenzene unit on the isomerization rate is. In the extreme case, the conformation in which the azobenzene unit on one side is trans and the other is cis (tc) may not exist because of too large ring strain. In this chapter, we report a simple route to synthesize a

novel [2.2](4,4')azobezenophane 2, deformed conformation of 2 and the extremely rapid thermal isomerization from the tc form to the tt form. Photoisomerization, which is seemingly dependent on the light intensity, is another subject of this chapter. We also discuss the mechanism of thermal cis-trans isomerization for azobenzene assuming that the deformed conformation of 2 resembles that of azobenzene in the course of thermal isomerization from cis to trans.

Experimental Section

Materials

1,2,17,18-Tetraaza-[2₄](4,4')cyclophane-1,17-diene 2 and two larger macrocycles 3 and 4 (1,2,17,18,33,34-hexaaza-[2₆](4,4')cyclophane-1,17,33-triene, 1,2,17,18,33,34,48,49-octaaza-[2₈](4,4')cyclophane-1,17,33,48-tetraene, respectively) were synthesized according to scheme 1. A 9.6 g (35 mmol) sample of 1,2-bis(4'-nitrophenyl)ethane, which was synthesized by the oxidation of 4-nitrotoluene³, in 240 ml dry THF was added dropwise in 3 h to a suspension of 6.7 g (180 mmol) of LiAlH₄ in 400 ml of dry THF under a nitrogen atmosphere. After the reaction mixture being stirred for 21 h, 200 ml of water was carefully added to it. Precipitates (inorganic substances and probably insoluble polymer) were filtered off and THF was removed from the water/THF mixture by distillation. Another orange solid precipitated in the water was separated by filtration, and then the solid was extracted with dichloromethane. The dichloromethane solution was washed with water and evaporated. The residue was subjected to isolation by column chromatography (silica gel and dichloromethane-chloroform (1:1 v/v)). The fractions with R_f

values of 0.90, 0.86 and 0.81 were evaporated, recrystallized by slow evaporation of the dichloromethane solution, and identified as 4, 3 and 2, respectively, by ^1H -n.m.r., FD-MS and satisfactory elemental analyses. 2: 22 mg (0.30%); m.p. above 305°C ; mass spectrum, m/e 416(M^+). Anal. Calcd. for $\text{C}_{28}\text{H}_{24}\text{N}_4$: C, 80.74; H, 5.80; N, 13.45. Found: C, 80.65; H, 5.69; N, 13.01. 3: 38 mg (0.52%); m.p. $286\text{--}288^\circ\text{C}$; mass spectrum, m/e 624(M^+). Anal. Calcd. for $\text{C}_{42}\text{H}_{36}\text{N}_6 \cdot 1/2\text{CH}_2\text{Cl}_2$ ⁷: C, 76.50; H, 5.59; N, 12.59. Found: C, 76.21; H, 5.81; N, 12.38. 4: 17 mg (0.23%); m.p. above 305°C ; mass spectrum, m/e 832(M^+) Anal. Calcd. for $\text{C}_{56}\text{H}_{24}\text{N}_8 \cdot 1/2\text{CH}_2\text{Cl}_2$ ⁴: C, 77.53; H, 5.60; N, 12.80. Found: C, 77.41; H, 5.67; N, 12.77.

Crystal data

A crystalline sample of 2 suitable for the X-ray diffraction analysis was obtained from a hexane/dichloromethane (1:2 v/v) solution of 2 by slow evaporation. $\text{C}_{28}\text{H}_{24}\text{N}_4$, FW = 416.5, monoclinic, space group $\text{P}2_1/\text{a}$, $a = 10.87(1) \text{ \AA}$, $b = 15.29(1) \text{ \AA}$, $c = 6.831(4) \text{ \AA}$, $\beta = 99.39(9)^\circ$, $U = 1120(2) \text{ \AA}^3$, $D_x = 1.234 \text{ g cm}^{-3}$, $Z = 4$ ($Z = 1/2 \text{ mol}$), $(\text{Cu K}\alpha) = 1.54 \text{ \AA}$. X-ray diffraction data were obtained on a four-circle diffractometer (Rigaku AFC-5) using $\text{Cu K}\alpha$ radiation. A total of 1970 independent reflections were collected within the range $3^\circ < 2\theta < 120^\circ$ by the $\omega < 30^\circ < \omega - 2\theta$ scan method. An absorption correction was not applied. The structure was solved by the direct methods using MULTAN-78⁵ (UNICS III system, Univ. of Tokyo) and refined by the full-matrix least-squares by using 1592 observed reflections [$|F_o| > 3\sigma(F_o)$]. The final R index was 0.0866 including hydrogen atoms. Even at this final stage the coordinates for one of the hydrogen atoms bound to ethylenic carbon atoms could not be observed. This is probably due to a large thermal vibration.

Photo-isomerization and measurements of thermal isomerization

Kinetic measurements for thermal isomerization of 2 were made spectrophotometrically on a Hitachi 124 by monitoring changes in absorbance at 328nm (λ_{max} of $\pi\pi^*$ transition) of a benzene solution in the dark after sufficient irradiation of 366 nm light 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 ct form to the tt form was monitored by a modified method. Photoirradiation was made in a sealed quartz cell in a thermocontrolled water bath with two quartz windows after equilibration to a desired temperature. Immediately after the photoirradiation, the water bath with the cell was set in a Hitachi Model 200-20 spectrophotometer and monitored the changes in absorbance at 328 nm as a function of time by a recorder at a chart speed of 48 cm/min. A fast change in absorbance ceased in only 15 min at 5°C (this temperature was the lower limit in our experiments). In both isomerization processes ($cc \rightarrow tc$ and $tc \rightarrow tt$), the absorbance against time satisfied a first-order kinetics.

Measurements of light intensity dependence

Photoirradiation was performed at $25 \pm 2^\circ\text{C}$ in a manner almost identical with that described above. The light intensity was changed by filters and changing distances and measured by Eppley Thermopiles (The Eppley Laboratory Ltd.).

Results and discussion

Syntheses and spectral property

There exists a known route to synthesize [2.2]paracyclophanes from dithia[3.3]cyclophanes⁶. We, however, synthesized 2 by the reduction of 1,2-bis(4'-nitrophenyl)ethane using LiAlH_4 , since the synthetic condition from the known 2,19-dithia[3.3](4,4')azobenzenophane 1 to 2 seems to be too harsh for azo linkages. A stilbene analogue of 2, [2.2](4,4')stilbenophane 6, has also been synthesized in a similar manner from 1,2-bis(4'-formylphenyl)ethane by the reduction using Zn and TiCl_4 ⁷. Under the synthetic conditions of the present study, three isolable macrocycles, namely dimer 2, trimer 3 and tetramer 4, were produced in contrast to the result for preparation of 6 where the isolation of no other larger macrocycles was reported. The difference in reaction rate between these reaction systems is probably the most effective factor on the ratio of macrocyclic products and the yields.

The spectroscopic data for compounds 2, 3, 4 and 4,4'-dimethylazobenzene 5 as a model compound are summarized in table 1. Each macrocycle showed one singlet and two doublet ^1H -n.m.r. absorptions due to aliphatic and aromatic protons, respectively. Both of the aromatic δ values were shifted to up-field with the decrease of macrocyclic ring size although the aliphatic δ value did not undergo much change. These n.m.r. chemical shifts are reasonably explained by the shielding effect which works mutually between two benzene rings linked by an ethylenic chain. As the ring size decreases, the angle between the benzene rings decreases and the transannular distance decreases⁸. The magnitude of change in δ value among the three macrocycles is larger for the protons at meta position than those at ortho positions to the ethylene substituent. This trend is also explained by the change in mean distances between the proton and the facing phenyl

ring.

The ring size is also reflected on electronic spectra. The molecular extinction coefficient (ϵ) for $\pi\pi^*$ transition of azobenzene units becomes smaller as a number of the azobenzene units is decreased while ϵ for $n\pi^*$ transition of azobenzene units of 2 is exceptionally enhanced. This spectral behavior is most reasonably attributed to the non-planarity of azo linkages in macrocycles due to ring strain. As the ring becomes smaller the magnitude of non-planarity would become larger and the n orbital of an azo linkage could have a better overlap with the orbital. In order to ensure this explanation of the unusuality of the spectral data for 2, the crystal structure determination was undertaken.

X-ray crystal structure analysis

The final bond lengths, inter bond angles, and dihedral angles of 2 are listed in tables 2, 3, and 4, respectively. Figure 1 shows the crystal structure of 2 without hydrogen atoms. Molecule 2 has C_2 symmetry with a two-fold rotation axis passing through the ring hole. As can be seen in the figure 1, the shape of molecule 2 is ellipsoid which means that the two azobenzene units are not planar. The dihedral angle of C-N=N-C, which is the best index for indication of the planarity, is 168.7° . A deviation of 11.3° from the plane is exceptionally large since the dihedral angles of ever known non-cyclic and cyclic trans-azobenzene derivatives exist in the range of 176.4 - 180° ⁹. The angles between the bonds at the aliphatic carbon atoms are 113.6 and 113.2° . These are larger than usual C-C-C angle, 109° . All these findings are explained by the ring strain, and the bent structure of 2 in solvents, which was postulated to explain the unusual

spectral property of 2, is ensured by the molecular structure of 2 in crystal.

The bent azo linkages in 2 are interesting also in view of the mechanism of cis-trans isomerization for azobenzene, since the conformation of azobenzene units in 2 probably resembles the conformation of azobenzene in the course of isomerization from cis to trans. There should exist two possibilities to make an angle between benzenes connected by azo linkage in the macrocycle 2 in a manner as considered for the conformation of the transition state of azobenzene¹⁰. They are the rotation about a N=N bond with increase of the distance between the two nitrogens and the deformation of the sp_2 atomic orbital of nitrogen retaining the double bond character between the nitrogens. The structural data of the crystal for 2 show that the distance between the nitrogens is 1.234 Å which is not longer than the distances for trans-azobenzene (1.247 Å)¹¹ and 5 (1.244 Å)¹². This result supports that the latter way of the deformation is favored. As explained before in this study by the dihedral angle of C-N=N-C, the deformation of sp_2 atomic orbitals occurred not in a plane, but by the way that the angles of C-N=N are remained, namely, the angle of C-N=N for 2 (113.36 and 113.78°) are almost the same as those for trans-azobenzene (113.6°)¹¹ and 5 (113.8°)¹².

A usual inversion mechanism for cis-trans isomerization of azobenzene has been assumed to occur in a plane. In other words, the sp_2 orbitals of the nitrogen atoms are rehybridized to sp_1 in the course of the thermal isomerization¹⁰. The present results for 2 require to consider another inversion mechanism for azobenzene in which the isomerization occurs not in a plane.

Cis-trans isomerization

Although the conformation of the tt form of 2 (tt-2) is very restricted by the ring strain, 2 in benzene easily photoisomerizes in a manner as observed for usual azobenzene derivatives upon 366 nm light exposure¹³. The absorption spectra of 2 before exposure and at 366 nm photostationary state are shown in figure 2. At the photostationary state, 88% of the initial absorbance at 328 nm (peak of $\pi\pi^*$ transition) is reduced, which means more than 88% of tt-2 is isomerized. The spectral pattern for 2 before and after the UV irradiation in the $\pi\pi^*$ region is almost identical with those for the non-cyclic 5 and other azobenzene derivatives. However, a little difference is found in the region of the $n\pi^*$ transition band (around 440 nm). In contrast with the fact that the absorbance of the $n\pi^*$ transition band in the case of usual azobenzene derivatives is increased after UV irradiation, the one for 2 at the wavelength longer than 470nm is decreased. This novel spectral change is due to the wide and relatively strong absorption of tt-2 in the $n\pi^*$ transition region. These findings again indicate the deformed azo linkages of tt-2 in solution. The initial absorption spectra is recovered from the photostationary state at 366 nm by slow thermal isomerization or by 436 nm irradiation.

Immediately after irradiation by 366 nm light at an arbitrary extent, a small amount of rapid thermal recovery of the spectrum is observed for 2. This thermal isomerization process is very rapid, but the change of the absorption spectra can be monitored by a diode array spectrophotometer with a mercury lamp to irradiate at the cell. Figure 3 shows the change of the spectra detected at an interval of 10 s after irradiation by 366 nm light to an arbitrary extent. This spectral change is mainly occurred

around a $\pi\pi^*$ band, which is similar to the typical cis $\rightarrow$ trans isomerization of azobenzene derivatives. This change of absorbance at 328 nm follows the first order equation as shown in figure 4. On the other hand, the spectra are not changed so much in the range of 0 - 100 s from the photostationary state under 366 nm light as shown in figure 5. Based on these results, the fast thermal spectral change is attributed to tc $\rightarrow$ tt thermal isomerization. Rau et al. have observed relatively rapid ($\tau_{298} = 6.25$ min) ct $\rightarrow$ tt thermal isomerization for [3.3](4,4')azobenzophane **1**^{2c}.

Spectroscopically determined first-order rate constants and thermodynamic data of cc $\rightarrow$ tc and tc $\rightarrow$ tt for **2** are listed with those of c $\rightarrow$ t for **5** in table 5. The thermal isomerization from the ct form to the tt form for **2** is exceptionally fast in comparison with the thermal c $\rightarrow$ t for ever known azobenzene derivatives without polar substituents¹⁴. The life time of tc is calculated from the rate constant to be only 22 s at 298 K, which is 10000 times shorter than that of cc. This unstableness of tc-**2** is easily understood when one remember the distance between 4 and 4' positions for trans azobenzene is 3.5 Å longer than that for cis azobenzene^{11,15}. To estimate the additional destabilization of the tc conformation, molecular mechanics calculations (MMP2)¹⁶ are undertaken for three possible isomers of **2**, namely, tt-**2**, tc-**2** and cc-**2**. The steric energies of tt-**2**, tc-**2** and cc-**2** for the optimized conformations is 10.57, 31.04 and 37.88 Kcal/mol, respectively. The difference of the energy between tt-**2** and tc-**2** is quite larger than that between tc-**2** and cc-**2**. These results of calculations efficiently demonstrate the additional destabilization of the tc conformation due to the difference of sizes of two isomer units in the macrocycle.

The efficiency of photoisomerization for 2 from the tt form to the cc form via the tc form is light intensity dependent¹⁷. Figure 6 shows the change of absorbance for 2 and 5 against the irradiation time with two different powers of light. We measured the absorbance at the peaks of $\pi\pi^*$ for each azobenzene derivatives two minutes after the photoirradiation, in order to rule out the tc $\rightarrow$ tt process and estimate the efficiency of the total process from tt-2 to cc-2. Anyway, the recovery of the absorbance for 2 (the thermal isomerization from tc-2 to tt-2) during the two minutes was small and almost zero for 5. The isomerization of 2 is more efficient with higher light intensity, while 5 is not sensitive to the light intensity. These phenomena are reasonably explained by the fact that tc-2 is not so stable. As the light intensity is lower, the concentration of tc-2 during the photoirradiation would saturate at a lower level. This induces the low efficiency of the photoisomerization from tc-2 to cc-2.

Conclusions

The shorter the bridges which connect two azobenzene units at 4, 4' positions, the shorter the life time of the tc form of the azobenzenophane. This short life time causes the light intensity dependence on the efficiency of the photoisomerization. Although the azo linkages are deformed from the planes in 2, the double bond character of N=N bonds and C-N=N angles are remained. These facts suggest that the thermal isomerization of azobenzene might occur by the deformation of the sp_2 atomic orbitals of the nitrogens not in plane.

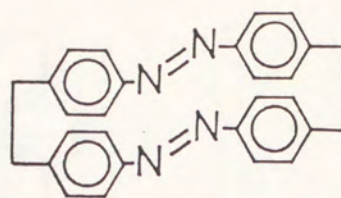
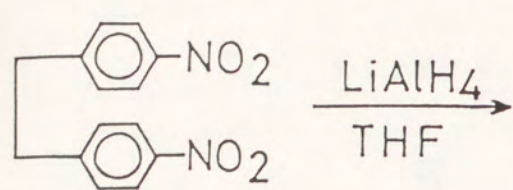
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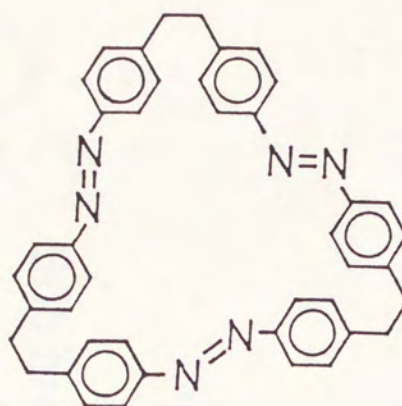
References

- (1) (a) S. Shinkai, T. Nakaji, T. Ogawa and O. Manabe, J. Amer. Chem. Soc., **102**, 5860 (1980). (b) S. Sinkai, T. Minami, Y. Kusano and O. Manabe, *ibid.*, **105**, 1851 (1983). (c) S. Sinkai, Y. Honda, Y. Kusano and O. Manabe, J. Chem. Soc. Chem. Commun., **1982**, 848. (d) A. Ueno, H. Yoshimura, R. Saka and T. Osa, J. Amer. Chem. Soc., **101**, 2779 (1979). (e) P. Nesvadba and A. Gossauer, *ibid.*, **109**, 6545 (1987).
- (2) (a) U. Funke and H.-F. Grützmacher, Tetrahedron, **43**, 3789 (1987). (b) H.-F. Grützmacher and J. Schmiegell, Chem. Ber., **122**, 1929 (1989). (c) H. Rau and E. Lüddecke, J. Amer. Chem. Soc., **104**, 1616 (1982). (d) J. D. Winker and K. Deshayes, *ibid.*, **109**, 2190 (1987). (e) U. Norinder, D. Tanner and O. Wennerström, Tetrahedron Lett., **24**, 5411 (1983).
- (3) Org. Synth. **1943**, Coll. Vol.2, 4.
- (4) Elemental analyses and ^1H -n.m.r. spectra indicate that 3 and 4 include 1 mole of CH_2CCl_2 per 2 moles of 3 and 4, respectively.
- (5) T. Sakurai and K. Kobayashi, Rep. Inst. Phys. & Chem. Res., **55**, 69 (1979).
- (6) (a) R. H. Mitchell and V. J. Boekelheide, J. Amer. Chem. Soc., **92**, 3510 (1970). (b) M. Haenel and H. A. Staab, Chem. Ber., **106**, 2203 (1973).
- (7) D. Tanner and O. Wennerström, Tetrahedron Lett., **22**, 2313 (1981).
- (8) I. Tabushi, H. Yamada and Y. Kuroda, J. Org. Chem., **40**, 1946 (1975).
- (9) (a) J. L. Galigne, Acta Crystallogr., Sect. B, **26**, 1977 (1970). (b) J. S. Parasad, *ibid.*, **35**, 1404 (1979); **35**, 1407 (1979). (c) G. Sawitzki and H. Rau, Liebigs Ann. Chem., **1981**, 993.
- (10) (a) G. Zimmerman, L.-Y. Chow and U.-J. Paik, J. Amer. Chem. Soc., **80**, 3528 (1958). (b) J. P. Otruba III and R. G. Weiss, J. Org. Chem., **48**, 3448 (1983). (c) T. Asano, T. Yano and T. Okada, *ibid.*, **104**, 4900 (1982). (d) T. Asano, T. Okada, S. Shinkai, K. Shigematsu, Y. Kusano and O. Manabe, *ibid.*, **103**, 5161 (1981).
- (11) C. J. Brown, Acta Crystallogr., **21**, 146 (1966).
- (12) C. J. Brown, Acta Crystallogr., **21**, 153 (1966).

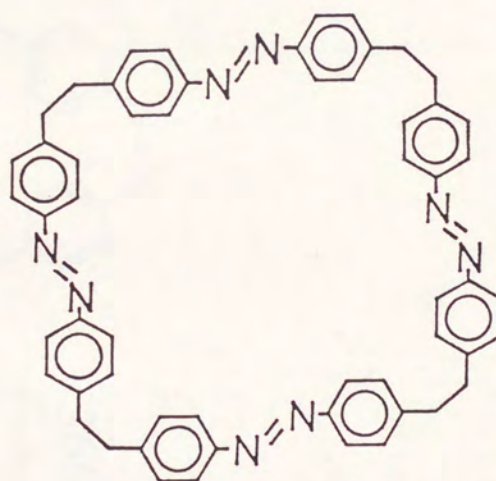
- (13) G. S. Hartley, Nature(London), 140, 281 (1937).
- (14) D. Schulte-Frohlinde, Liebigs Ann. Chem., 612, 138 (1958).
- (15) G. C. Hampson and J. M. Robertson, J. Chem. Soc., 1941, 409.
- (16) Molecular Design Ltd., San Leandro, CA, USA.
- (17) A similar observation has been just qualitatively reported for a four point bridged azobenzenophane; see ref. 2c.



2



3



4

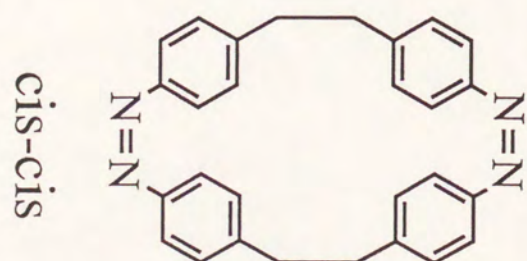
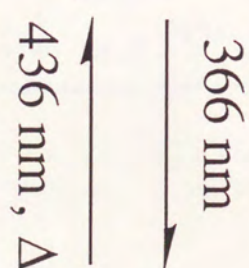
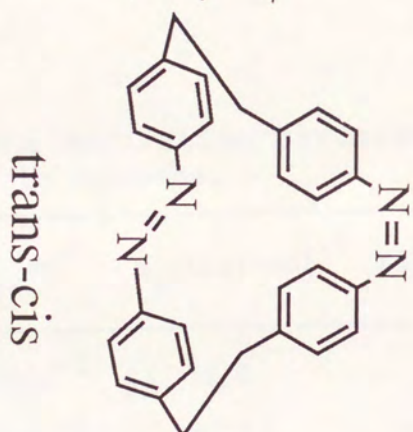
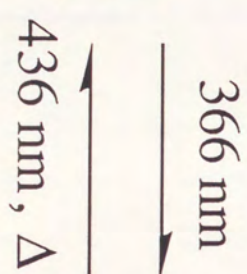
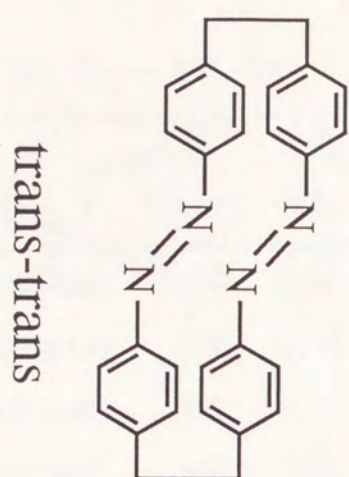


Table 1 Spectral data for 2, 3, 4 and 5.

compd no.	$\pi \pi^*$ [a]		$n \pi^*$ [a]		$^1\text{H-NMR}$ [b] δ /ppm	
	$\epsilon(\lambda_{\text{max}})$	ϵ/unit	$\epsilon(\lambda_{\text{max}})$	ϵ/unit	CH_2	Arom.
2	41300(328)	20700	2400(462)	1200	3.07	6.79, 7.24
3	74600(329)	24900	2200(442)	750	3.08	6.98, 7.53
4	116000(333)	29000	3000(440)	750	3.06	7.03, 7.70
5	24900(339)	24900	800(442)	880	2.38	7.24, 7.76

[a] In benzene

[b] In CDCl_3

Table 5 Rate constants and activation parameters for the thermal isomerization of 2 and 5 in benzene.

compd no.	type of isomerization	k_{298}/s^{-1}	$E_a/\text{Kcal}\cdot\text{mol}^{-1}$	$\Delta S_{298}^\ddagger/\text{cal}\cdot\text{K}^{-1}$
2	tc $\rightarrow$ tt	4.54×10^{-2}	14.0	-19.8
	cc $\rightarrow$ tc	4.53×10^{-6}	22.2	-10.5
5	c $\rightarrow$ t	4.53×10^{-6} [a]	21.7 [a]	-12.0 [a]

[a] from lit. 14

Table 2 Bond distances (Å) of 2.

N(1)A	-	N(2)A	1.234(7)	N(1)A	-	C(1)A	1.452(7)
N(2)A	-	C(7)A	1.437(7)	C(1)A	-	C(2)A	1.376(9)
C(1)A	-	C(6)A	1.382(9)	C(2)A	-	C(3)A	1.398(9)
C(3)A	-	C(4)A	1.388(9)	C(4)A	-	C(5)A	1.395(9)
C(4)A	-	C(13)A	1.527(9)	C(5)A	-	C(6)A	1.390(9)
C(7)A	-	C(8)A	1.388(8)	C(7)A	-	C(12)A	1.381(8)
C(8)A	-	C(9)A	1.376(8)	C(9)A	-	C(10)A	1.389(8)
C(10)A	-	C(11)A	1.397(8)	C(10)A	-	C(14)B	1.529(9)
C(11)A	-	C(12)A	1.385(9)	C(13)A	-	C(14)A	1.551(9)

Table 3 Angles (deg) of 2.

N(2)A	-	N(1)A	-	C(1)A	113.3(4)	N(1)A	-	N(2)A	-	C(7)A	113.7(4)
N(1)A	-	C(1)A	-	C(2)A	116.0(5)	N(1)A	-	C(1)A	-	C(6)A	123.5(5)
C(2)A	-	C(1)A	-	C(6)A	119.9(5)	C(1)A	-	C(2)A	-	C(3)A	120.1(5)
C(2)A	-	C(3)A	-	C(4)A	120.1(5)	C(3)A	-	C(4)A	-	C(5)A	119.1(5)
C(3)A	-	C(4)A	-	C(13)A	121.2(5)	C(5)A	-	C(4)A	-	C(13)A	119.0(5)
C(4)A	-	C(5)A	-	C(6)A	120.0(5)	C(1)A	-	C(6)A	-	C(5)A	120.2(5)
N(2)A	-	C(7)A	-	C(8)A	125.0(4)	N(2)A	-	C(7)A	-	C(12)A	114.8(4)
C(8)A	-	C(7)A	-	C(12)A	119.6(5)	C(7)A	-	C(8)A	-	C(9)A	119.5(5)
C(8)A	-	C(9)A	-	C(10)A	121.0(5)	C(9)A	-	C(10)A	-	C(11)A	118.9(5)
C(9)A	-	C(10)A	-	C(14)B	121.5(5)	C(11)A	-	C(10)A	-	C(14)B	119.3(5)
C(10)A	-	C(11)A	-	C(12)A	119.4(5)	C(7)A	-	C(12)A	-	C(11)A	120.7(5)
C(4)A	-	C(13)A	-	C(14)A	113.6(5)	C(13)A	-	C(14)A	-	C(10)B	113.2(5)

Table 4 Torsional angles (deg) of 2.

C(1)A	-	N(1)A	-	N(2)A	-	C(7)A	168.7(4)
N(2)A	-	N(1)A	-	C(1)A	-	C(2)A	175.9(4)
N(2)A	-	N(1)A	-	C(1)A	-	C(6)A	-11.1(7)
N(1)A	-	N(2)A	-	C(7)A	-	C(8)A	3.6(7)
N(1)A	-	N(2)A	-	C(7)A	-	C(12)A	-168.7(4)
N(1)A	-	C(1)A	-	C(2)A	-	C(3)A	168.4(5)
C(6)A	-	C(1)A	-	C(2)A	-	C(3)A	-4.7(8)
N(1)A	-	C(1)A	-	C(6)A	-	C(5)A	-168.3(5)
C(2)A	-	C(1)A	-	C(6)A	-	C(5)A	4.3(8)
C(1)A	-	C(2)A	-	C(3)A	-	C(4)A	0.7(8)
C(2)A	-	C(3)A	-	C(4)A	-	C(5)A	3.7(8)
C(2)A	-	C(3)A	-	C(4)A	-	C(13)A	-167.5(5)
C(3)A	-	C(4)A	-	C(5)A	-	C(6)A	-4.1(8)
C(13)A	-	C(4)A	-	C(5)A	-	C(6)A	167.2(5)
C(3)A	-	C(4)A	-	C(13)A	-	C(14)A	66.0(6)
C(5)A	-	C(4)A	-	C(13)A	-	C(14)A	-105.2(5)
C(4)A	-	C(5)A	-	C(6)A	-	C(1)A	0.1(8)
N(2)A	-	C(7)A	-	C(8)A	-	C(9)A	-167.1(4)
C(12)A	-	C(7)A	-	C(8)A	-	C(9)A	4.8(7)
N(2)A	-	C(7)A	-	C(12)A	-	C(11)A	166.3(5)
C(8)A	-	C(7)A	-	C(12)A	-	C(11)A	-6.3(8)
C(7)A	-	C(8)A	-	C(9)A	-	C(10)A	2.1(8)
C(8)A	-	C(9)A	-	C(10)A	-	C(11)A	-7.5(8)
C(8)A	-	C(9)A	-	C(10)A	-	C(14)B	167.9(5)
C(9)A	-	C(10)A	-	C(11)A	-	C(12)A	5.9(8)
C(14)B	-	C(10)A	-	C(11)A	-	C(12)A	-169.5(5)
C(9)A	-	C(10)A	-	C(14)B	-	C(13)B	-63.6(6)
C(11)A	-	C(10)A	-	C(14)B	-	C(13)B	111.8(5)
C(10)A	-	C(11)A	-	C(12)A	-	C(7)A	0.9(8)
C(4)A	-	C(13)A	-	C(14)A	-	C(10)B	23.4(6)
C(13)A	-	C(14)A	-	C(10)B	-	C(9)B	63.6(6)
C(13)A	-	C(14)A	-	C(10)B	-	C(11)B	-111.8(5)

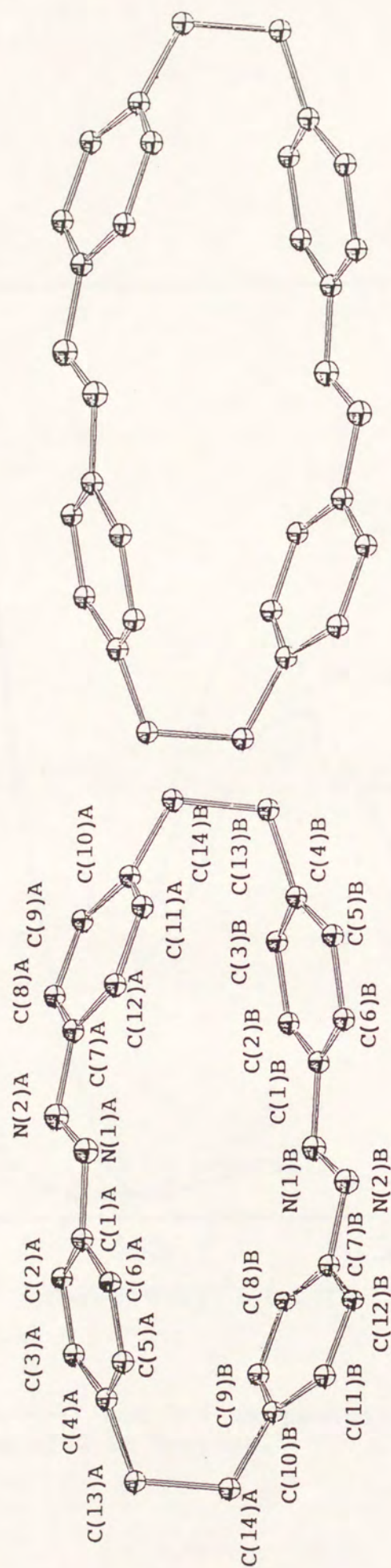


Fig. 1 X-ray crystal structure of 2.

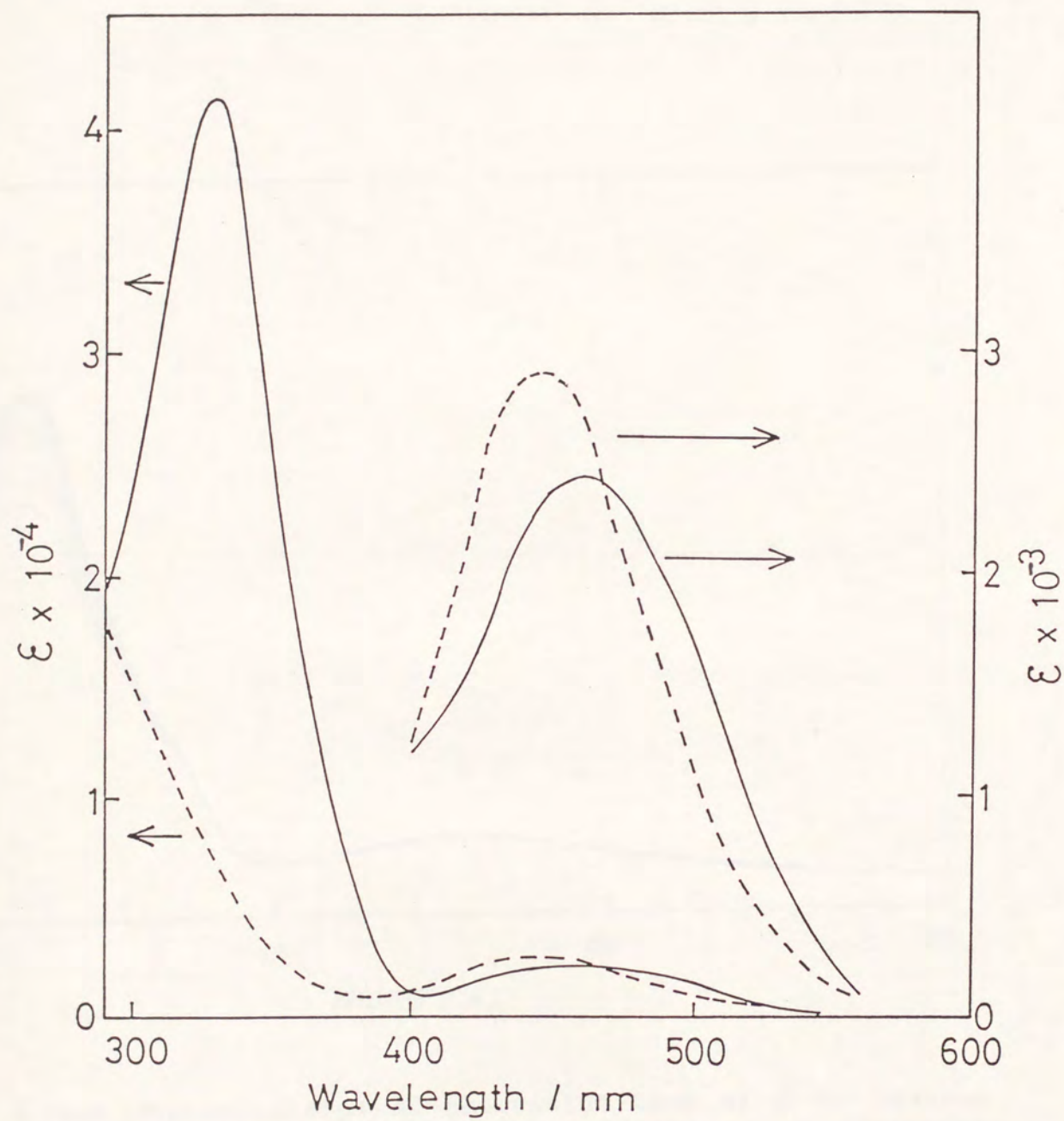


Fig. 2 Initial (—) and 366 nm photostationary state (----) absorption spectra of 2 in benzene.

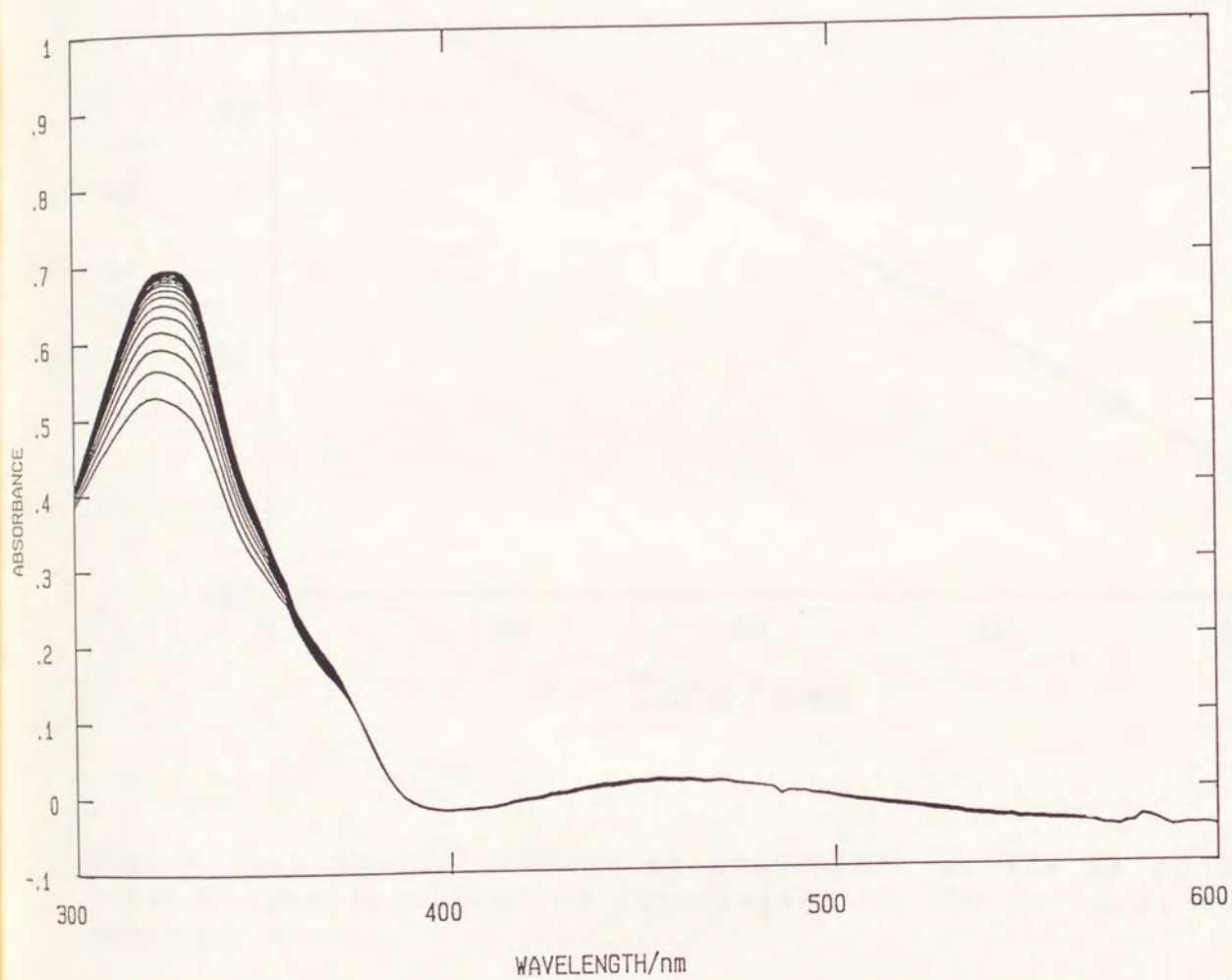


Fig. 3 Fast thermal change of absorption band of 2 in benzene immediately after irradiation by 366 nm light to an arbitrary extent. Each line was recorded at an interval of 10 s.

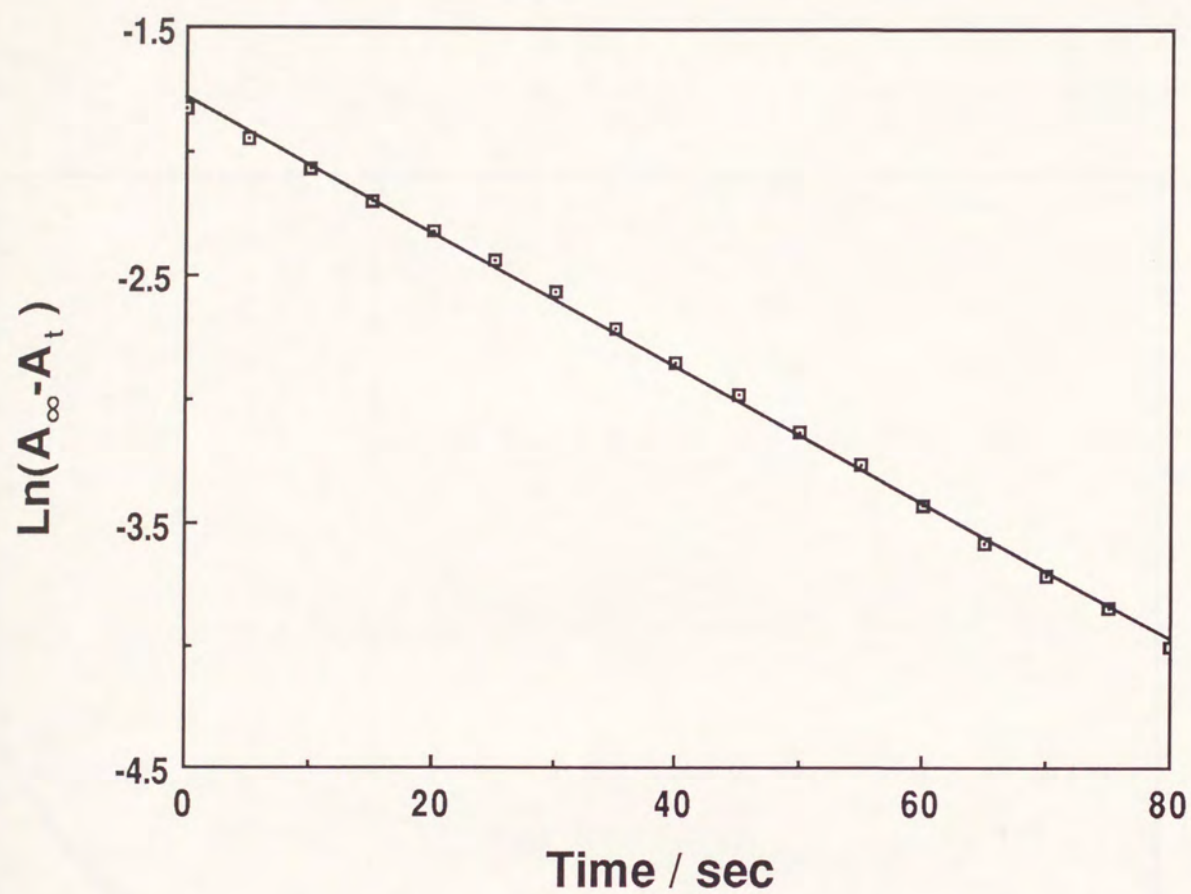


Fig. 4 Fast thermal change of absorbance at 328 nm of 2 in benzene immediately after irradiation by 366 nm light to an arbitrary extent.

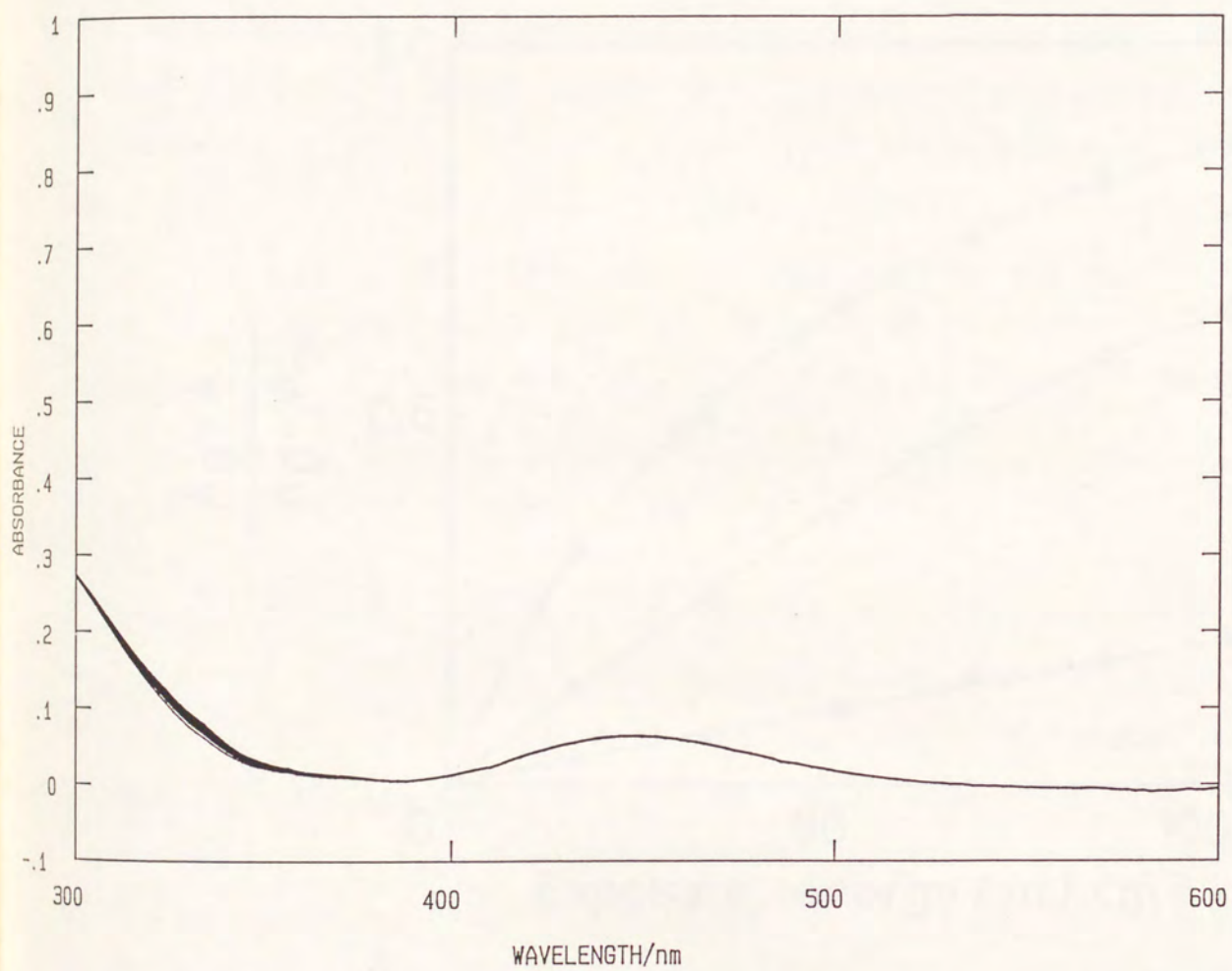


Fig. 5 Fast thermal change of absorption band of 2 in benzene from the photostationary state.

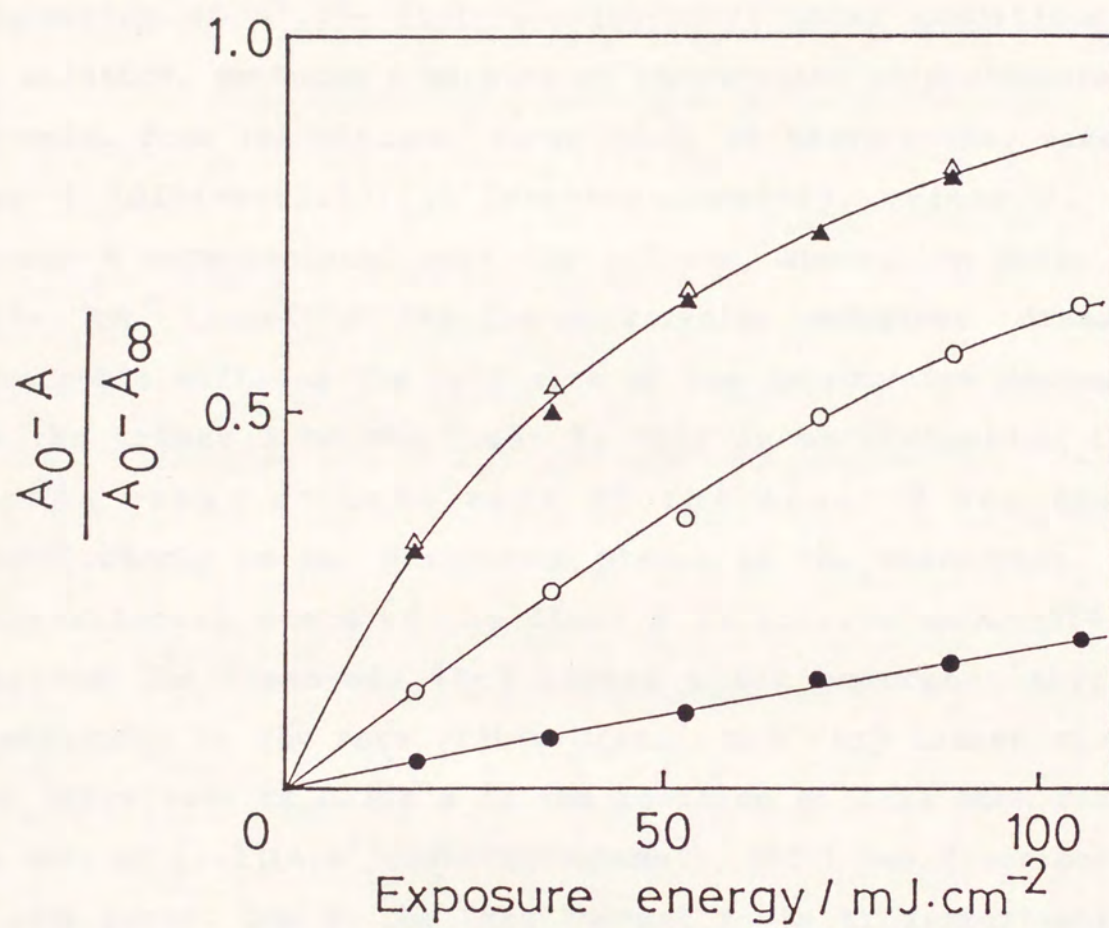


Fig. 6 Change of absorbance at $\pi\pi^*$ transition band with exposure energy using different intensity of light. (○) 2, 882 $\mu\text{W}/\text{cm}^2$; (●) 2, 88.2 $\mu\text{W}/\text{cm}^2$; (△) 5, 882 $\mu\text{W}/\text{cm}^2$; (▲) 5, 88.2 $\mu\text{W}/\text{cm}^2$.

Chapter 2

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

Abstract

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 macrocycles, namely, dimer 2 (dibenzo[2.2](4,4')azobenzenophane), trimer 3, and tetramer 4 were isolated pure. In toluene, absorption peaks due to the $\pi\pi^*$ transition for the macrocycles undergoes 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 $\lambda = 366$ nm contained the trans-cis (tc) isomer which undergoes thermal isomerization to the more stable trans-trans (tt) isomer at the first order rate of 0.768 s^{-1} . The reaction of 2 is much faster than that of [2.2](4,4')azobenzenophane 5, which was described in our last paper. Due to the fast thermal tc to tt isomerization, the efficiency of the photoisomerization from the tt isomer to the cc isomer is light intensity dependent. This dependence is observed at higher light intensities for the dimer 2 than for the dimer 5.

Introduction

It is well known that the absorption spectra of azobenzene derivatives exhibit the reversible changes, when the azobenzenes are irradiated brought about by cis-trans 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 storage²). 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 visualization is possible by use of low intensity light.

We have synthesized 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 trans to cis form is small, and the tc isomer should be stable enough to exist. On the other hand, when the lengths of the bridges is relatively short [scheme 1(b)], the closer proximity between the 4- and 4'-positions of the cis azobenzene units³) produces a large ring strain in the tc isomer. Consequently, the tc isomer becomes unstable and isomerizes very quickly to the tt isomer. The ring strain of the cc isomer is, however, small and the cc isomer is fairly stable. Photoisomerization from the tt isomer to the cc isomer for such

compounds becomes seemingly more efficient as the light intensity is increased, since the concentration of the tc isomer, which is an expected intermediate of the reaction, becomes concomitantly higher. As the lengths of the bridges is reduced further [scheme 1 (C)], it becomes likely that the tc isomer does not exist.

We thought it is of great interest to see whether the two azobenzene units in such compounds could be made to undergo concerted isomerize from a doubly excited $\text{trans}^*-\text{trans}^*$ state to the cc 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 life time of the tc isomer of 5 at 25°C to be 22 s. When the irradiation time exceeded the lifetime of the tc isomer, the amount of the tt isomer which isomerized photochemically to the cc isomer was increased as the irradiation intensity was increased, even though the total amount of the irradiation energy was kept constant⁵⁾.

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 Section

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⁾: ^1H -n.m.r. (CDCl_3) 7.29, 8.12 (2 $\times$ 4H, p-substituted phenyl protons) and 7.47, 7.55

(2×2H, o-substituted phenyl protons).

9,10,25,26,39,40,53,54-Tetrabenzo-1,2,17,18,33,34,49,50-octaaza-[2₈](4,4')cyclophane-1,17,33,49-tetraene 4: 4',4''-dinitro-o-terphenyl (6.0 g, 19 mmol in dry tetrahydrofuran (THF)(100 cm³) was added dropwise over 4.5 h to a suspension of LiAlH₄ (3.5 g, 92 mmol) in dry THF (250 cm³) under a nitrogen atmosphere at room temperature. After an additional hour of stirring water (20 cm³) 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 (silicagel, MERK 5554) using CCl₄ 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 chloroform⁷). Compound 4⁸): 3.0 mg (0.062%); m.p. above 280°C; m/z (EI-MS) 1024 (M+); The ¹H-n.m.r. data are listed in the Results and Discussion section.

9,10,25,26,39,40-Tribenzo-1,2,17,18,33,34-hexaaza-[2₆](4,4')cyclophane-1,17,33-triene 3: 4',4''-dinitro-o-terphenyl (10 g, 31 mmol) in dry THF (1 dm³) was added dropwise by means of an HPLC pump over 53 h to a suspension of LiAlH₄ (6.0 g) in dry THF (200 cm³) under a nitrogen atmosphere at room temperature. After 15 h stirring the reaction was treated as describes 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) (Ultrastyrigel 500 Å, Waters). The second main GPC peak was identified as that of 3.

Compound 3⁸): yield 1.9 mg (0.024%); m.p. above 280°C; m/z (FD-MS) 768 (M⁺). The ¹H-n.m.r. data are listed in the Results and Discussion section.

9,10,25,26-Dibenzo-1,2,17,18,-tetraaza-[2₄](4,4')cyclophane-1,17-diene 2: 4',4''-dinitro-o-terphenyl (7.7 g, 24 mmol) in dry THF (500 cm³) was added dropwise by means of an HPLC pump in 57 h to a suspension of LiAlH₄ (4.6 g) in dry THF (150 cm³) under a nitrogen atmosphere. The reaction mixture was refluxed during the addition of the dinitro compound. Treatment of the reaction mixture as described for 3, afforded 2 as orange crystals.

Compound 2⁸): yield 4.0 mg (0.064%); m.p. above 280°C; m/z (FD-MS) 511 (M⁺-1); The ¹H-n.m.r. data are listed in Results and Discussion section.

Photoisomerization and Measurement of Thermal Isomerization.

Kinetic measurement of thermal isomerization of 2, 3 and 4 were made spectrophotometrically on a Hitachi Model 200-20 spectrophotometer by monitoring changes in absorbance at $\lambda_{\max}$ 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 tc isomer to the tt 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 literature⁵).

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 absorption maximum (λ_{max}) in toluene and ^1H -n.m.r. data for the isolated cyclic compounds 2, 3, and 4 are shown in table 1. The λ_{max} of $\pi\pi^*$ 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 rings in the bridges in 3 and 4; however, in 2 the phenyl rings in the bridges are fixed perpendicularly to the two azobenzene units such that they can no longer conjugate each other.

The fixed conformation of 2 is further supported by the ^1H -n.m.r. 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 ^1H -n.m.r. shifts has been shown for non-benzo azobenzenophanes.⁴⁾

Cis-trans Isomerization.

At $\lambda = 366$ nm light, the absorbance at $\pi\pi^*$ transitions for the cyclic compounds 2, 3 and 4 in toluene are reduced as with other azobenzene derivatives,¹⁾ indicating an trans $\rightarrow$ cis photoisomerization. Figure 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 photoisomerization increases as the ring size becomes larger.

From the spectra it is seen that the macrocycles recover thermally very slowly from the photostationary state. Figure 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 minutes, 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, cis-cis-cis $\rightarrow$ trans-cis-cis, trans-cis-cis $\rightarrow$ trans-trans-cis, trans-trans-cis $\rightarrow$ trans-trans-trans⁹⁾. Although we have not separated the four isomers of 3 and estimated the rates of isomerization rate 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 seconds after photoirradiation (This detection was not possible with the usual spectrophotometer. Figure 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 $7.68 \times 10^{-1} \text{ s}^{-1}$. Similar spectral recovery, just after the photoirradiation have also been observed for non-benzo cyclic dimers, and has been attributed to the thermal isomerization of the tc isomer to the tt isomer^{4,10}). The rapid recovery observed in the spectra of 2 is similarly attributed to the isomerization of the tc isomer to the tt isomer. The slow thermal spectral change in 2 shown in figure 2 should reflect the process $cc \rightarrow tc \rightarrow tt$, however, the transformation $cc \rightarrow tc$ seems to be the rate-determining step, the thermal isomerization $tc \rightarrow tt$ being the isomer is much faster. Hence, rate of the thermal $cc \rightarrow tc$ isomerization was estimated by 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 cis $\rightarrow$ trans isomerization of many azobenzene derivatives have been measured,¹¹) 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.¹²) However, the relationship of E_a and $\Delta S^\ddagger$ for the thermal isomerization of the

tc isomer to the tt isomer of the dimer 2 does not fall on the line. The tc isomer of 2 must therefore isomerize via a transition state which is not the same as that for other known azobenzene derivatives. This unusual phenomena is due to the deformed tc isomer in the ground state and /or as a result of extremely large ring strain. From molecular mechanics calculations (CHARMM) the values of the steric energy for the tt, tc, and cc isomers are estimated to be 41.92, 55.73, 46.08 kcal/mol, respectively. The tc isomer is further destabilized by 9.65 kcal/mol compare with the cc isomer. These calculations support the above isomerization mechanism of the tc isomer of 2 described above.

Generally, in the system of $A \xrightleftharpoons[\Delta]{h\nu} B \xrightleftharpoons{h\nu} C$ the photochemical reaction from A to C is light-intensity dependent when the lifetime of B is short. In addition, the region of the light intensity where the dependence can be seen is dependent on the lifetime of B¹³⁾. That is to say, as the life time of B becomes shorter, the light-intensity dependence becomes apparent at higher light intensities. Figures 4 and 5 show the relationship between exposure energy and the change in absorbance at $\lambda_{\max}$ 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/cm². The change was less in the same range for the non-benzo dimer 5 in contrast with the change observed at light intensities 100-1000 μ W/cm².⁵⁾ This difference in behaviour between 2 and 5 might be attributed to the fact that the lifetime of the tc 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 sec as opposed to 22).

Conclusions

Benzo-[2.2](4,4')azobenzenophane **2** is synthesized by the reduction of 4',4''-dinitro-o-terphenyl under a 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 life time of the tc isomer of **2**, the efficiency of the photoisomerization from the tt isomer to the cc isomer is dependent upon the light intensity in the range 0.76-4.39 mW/cm².

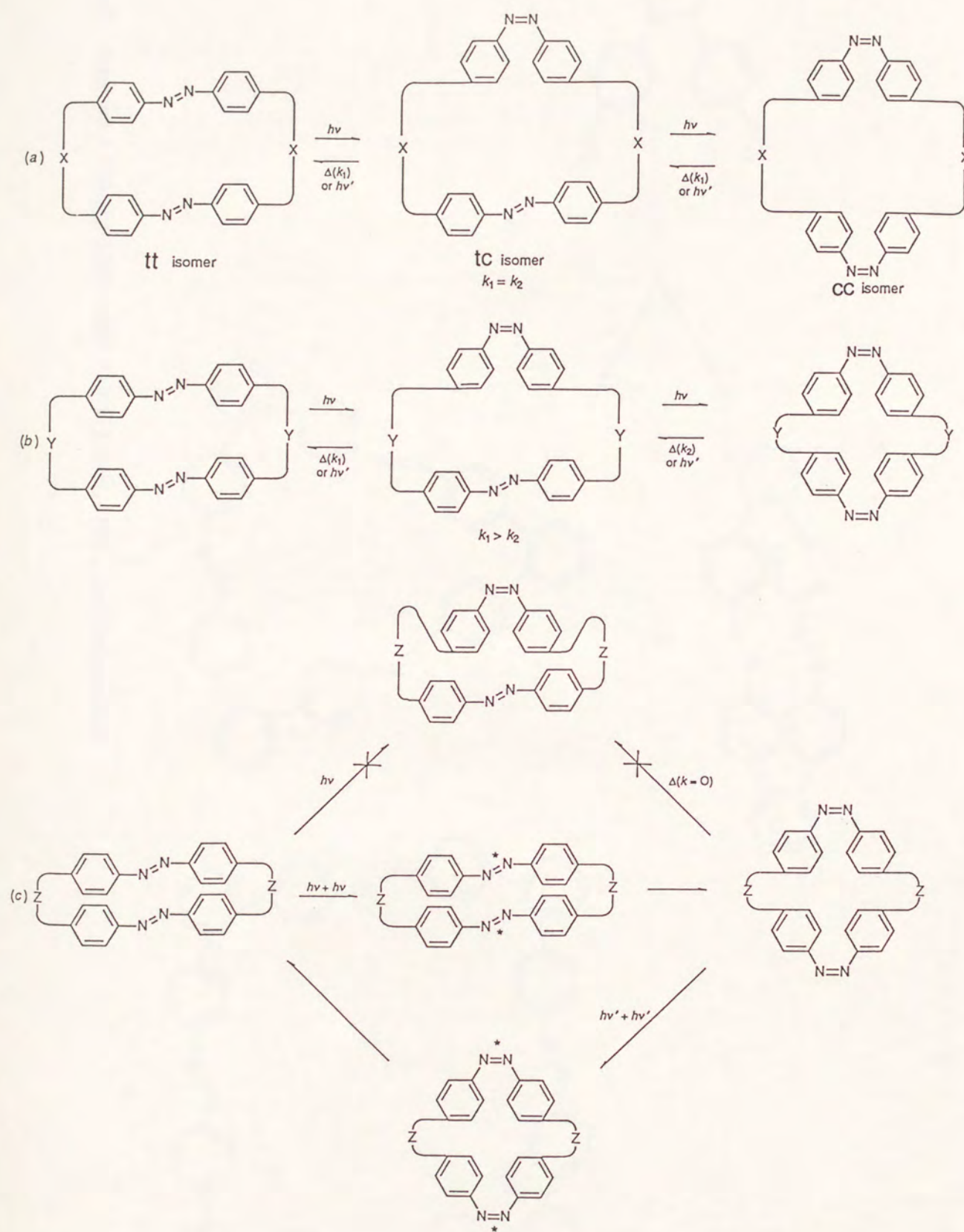
Acknowledgment.

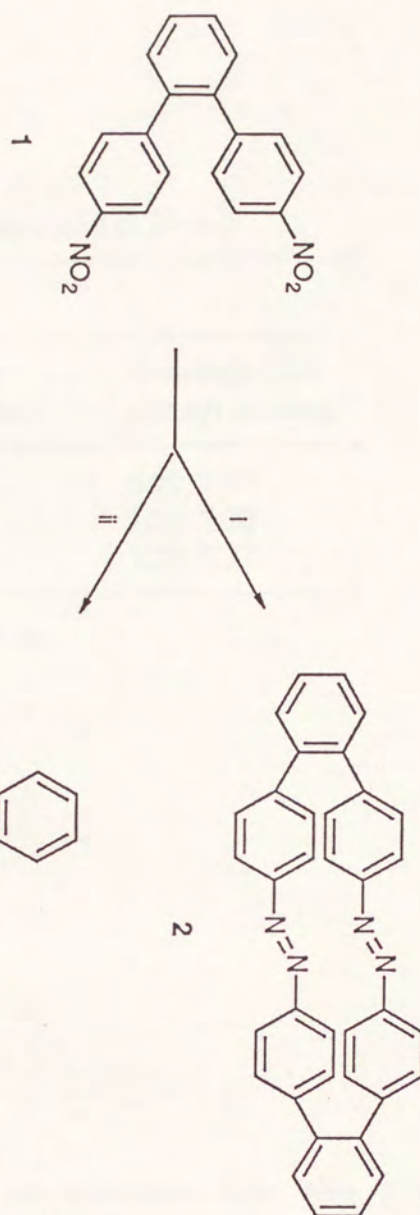
We wish to thank Mr. Madoka Yasuike and Mr. Yasumasa Toba of TOYO INK M.F.D. Co. Ltd., Japan for measuring FD mass spectra and Mr. Kazunari Yamamoto and Dr. Toshihiko Omote of NITTO DENKO CORPORATION, Japan for molecular mechanics calculations. We also thank Dr. Takashi Tamaki of RESEARCH INSTITUTE FOR POLYMERS AND TEXTILES, Japan for providing a diode-array spectrophotometer.

References

- (1)(a) G. S. Hartley, *Nature*, **140**, 281 (1939). (b) D. S.-Frohlind, *Liebigs Ann. Chem.*, **612**, 138 (1958). (c) N. Nishimura, T. Sueyoshi, H. Yamanaka, E. Imai, S. Yamamoto, and S. Hasegawa, *Bull. Chem. Soc. Jpn.*, **49**, 1381 (1976). (d) G. H. Brown, "Photochromism", Wiley-Interscience: New York, 1971.
- (2)(a) Y. Hirshberg, *J. Am. Chem. Soc.*, **78**, 2304 (1956). (b) H. Dürr, *Angew. Chem. Int. Ed. Engl.*, **28**, 413 (1989).
- (3)(a) C. J. Brown, *Acta Crystallogr.*, **21**, 146 (1966). (b) G. C. Hampson and J. M. Robertson, *J. Chem. Soc.*, **1941**, 409.
- (4) N. Tamaoki, K. Koseki, and T. Yamaoka, *Angew. Chem., Int. Ed. Engl.*, **29**, 105 (1990).
- (5) N. Tamaoki, K. Ogata, K. Koseki, and T. Yamaoka, *Tetrahedron*, **46**, 5931 (1990).
- (6) C. F. H. Allen and F. P. Pingert, *J. Am. Chem. Soc.*, **64**, 2639 (1942).
- (7) The third band on the TLC plate contained the macrocyclic heptamer which was detected by FD-MS.
- (8) Elementary analyses for the macrocyclic compounds 2, 3, and 4 do not coincide with the calculated values. This is provably due to the inclusion of solvent or water in the cavity of those macrocyclic ring.
- (9) N. Tamaoki, K. Koseki, and T. Yamaoka, *Tetrahedron Lett.*, **31**, 3309 (1990).
- (10) H. Rau and E. Lüddecke, *J. Am. Chem. Soc.*, **104**, 1616 (1982).
- (11)(a) P. D. Wild, J. G. Pacifici, G. Irick, Jr., and D. G. Whitten, *J. Am. Chem. Soc.*, **93**, 2004 (1971). (b) C. D. Eigenbach, *Macromol. Chem.*, **179**, 2489 (1978). (c) T. Asano, T. Okada, S. Shinkai, K. Shigematsu, Y. Kusano, and O. Manabe, *J. Am. Chem. Soc.*, **103**, 5161 (1981). (d) T. Asano, T. Yano, and T. Okada, *J. Am. Chem. Soc.*, **104**, 4900 (1982). (e) K. S. Schanze, T. F. Mattox, and D. G. Whitten, *J. Org. Chem.*, **48**, 2808 (1983). (f) J. P. Otruba III and R. G. Weiss, *J. Org. Chem.*, **48**, 3448 (1983). (g) K. Itoho, T. Masuda, M. Takei, Y. Sakurai, and M. Nishigami, *J. Chem. Soc., Chem. Commun.*, **1986**, 1028. See also references (1d), (4), and (10).
- (12) L. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley: New York, 1963.

(13) G. C. Bjorklund, Chr. Brauchle, D. M. Burland, and D. C. Alvarez, Opt. Lett., 6, 159 (1981).





Scheme 2 Reagents: i, LiAlH_4 -THF, reflux 57 h; ii, LiAlH_4 -THF, room temperature

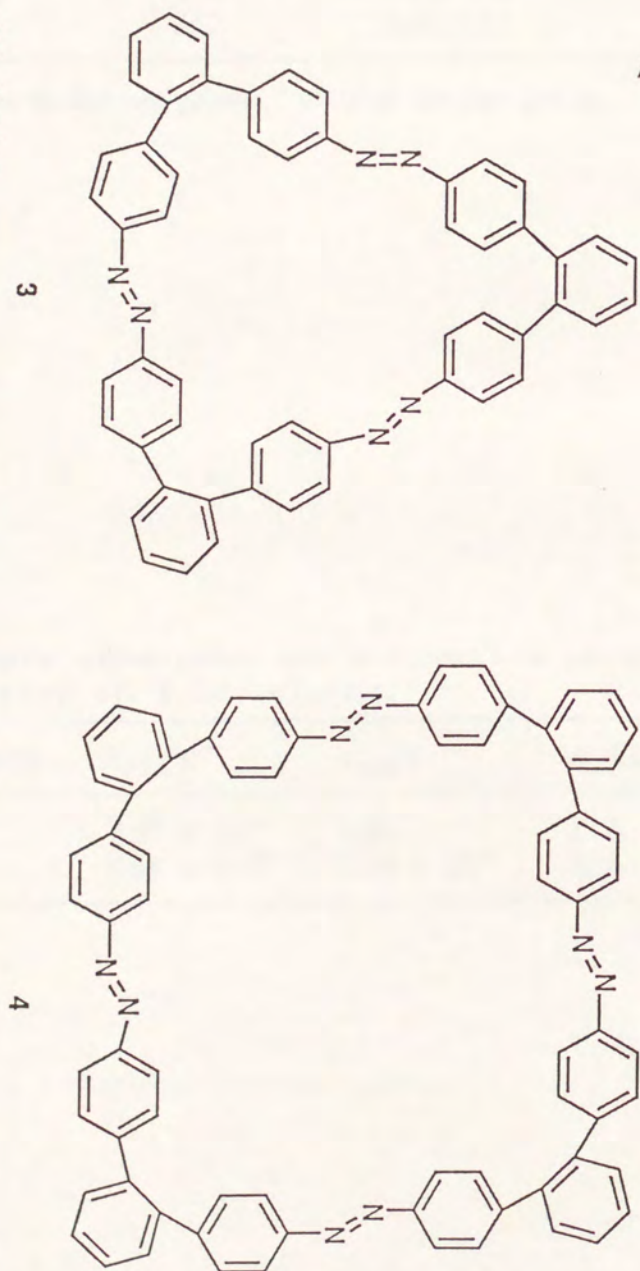


Table 1 Spectroscopic data of compounds 2-4.

Compound	$\lambda_{\max}/\text{nm}$ ($\pi \rightarrow \pi^*$)	$\delta(\text{ppm})$	
		<i>o</i> -substituted phenyl protons ^a	<i>m</i> -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.

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

Transformation	k_{298}/s^{-1}	τ_{298}/s	$E_a/\text{kcal mol}^{-1}$	$\Delta S_{298}^\ddagger/\text{cal K}^{-1} \text{mol}^{-1}$
tc $\longrightarrow$ tt	7.68×10^{-1}	1.30	21.6	11.5
cc $\longrightarrow$ tc	8.62×10^{-5}	1.16×10^4	22.4	-4.08

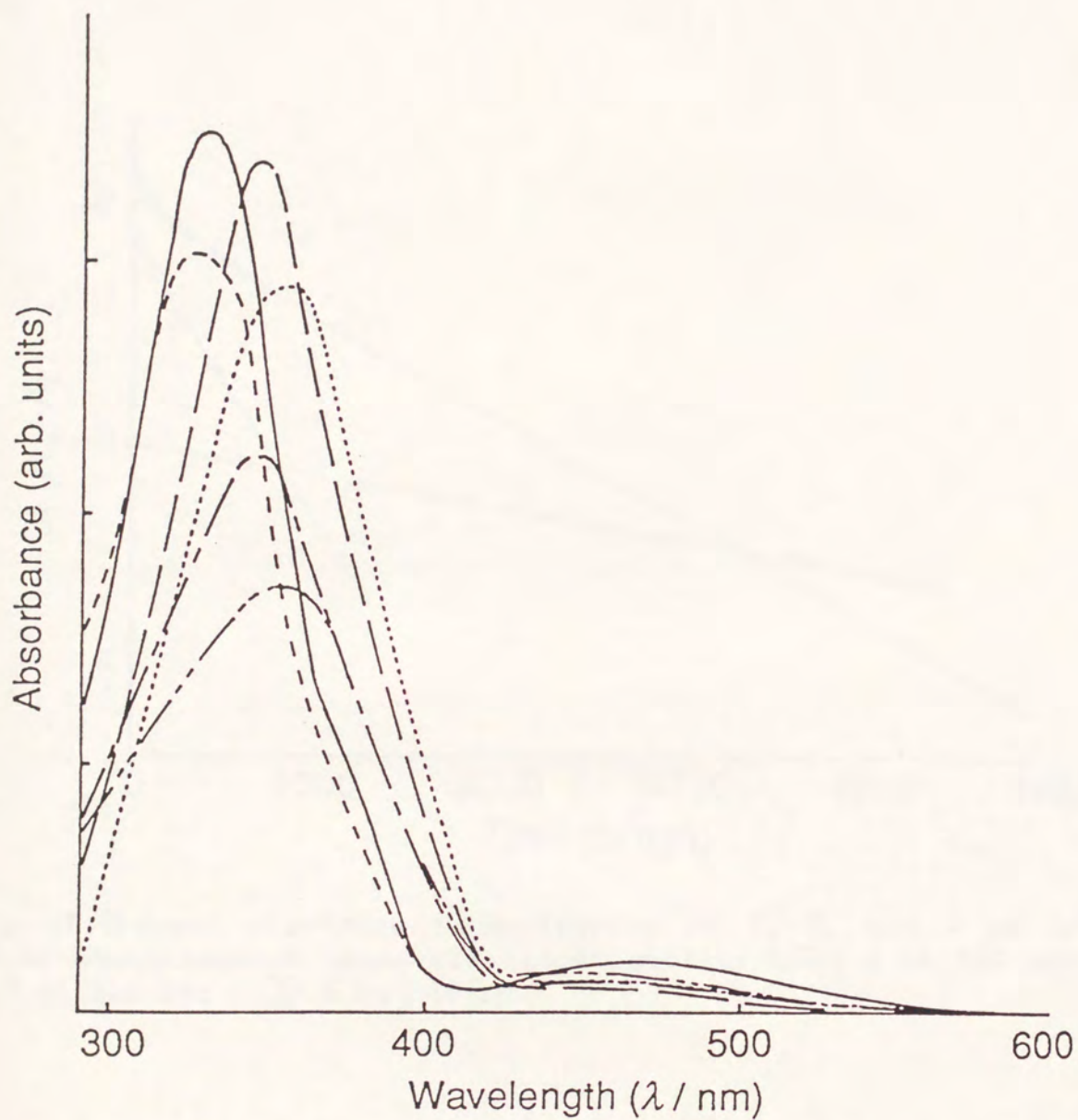


Fig. 1. Absorption spectra in toluene of 2: (—); 3 (— —); and 4 (· · · · ·) before irradiation and 2 (---); 3 (— · —); and 4 (— · · —) at 366 nm photostationary state.

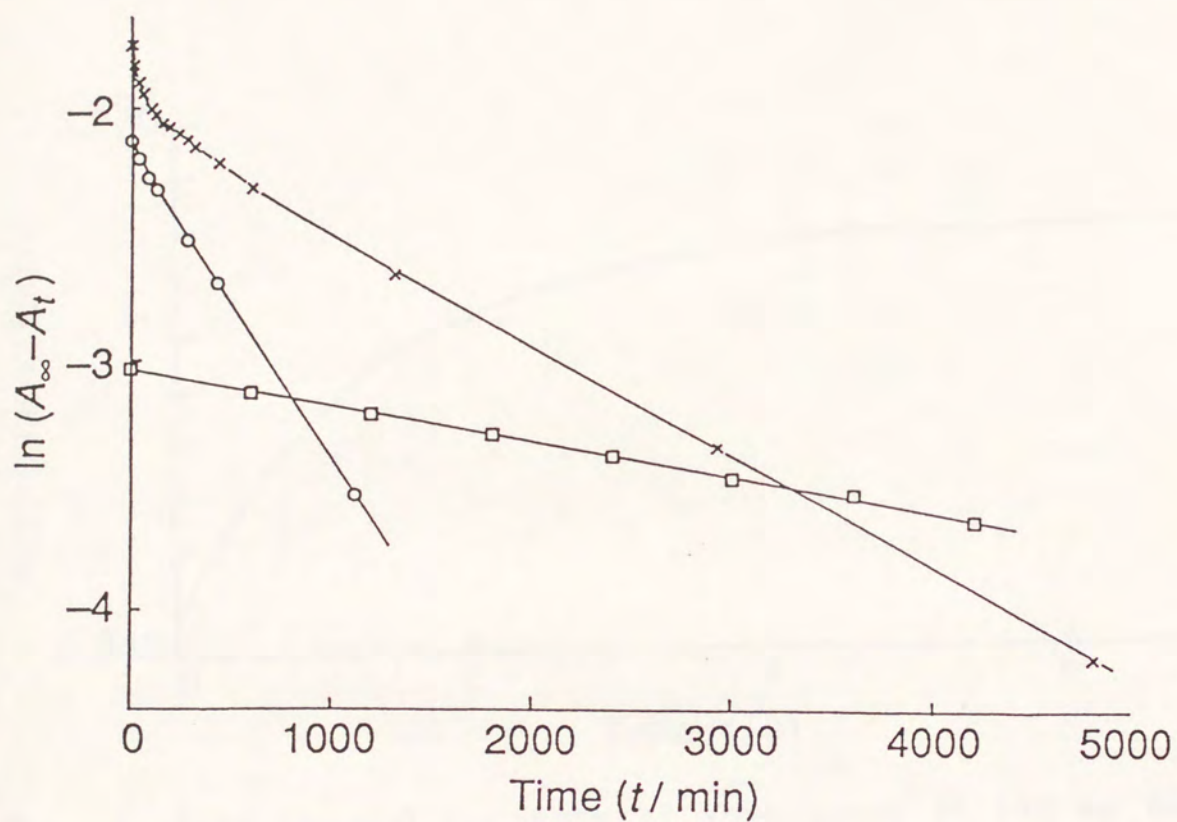


Fig. 2 Thermal cis-trans isomerization of 2, 3, and 4 at 30°C after photochemical trans-cis isomerization: (□) 2 at 330 nm; (X) 3 at 346 nm; (○) 4 at 349 nm.

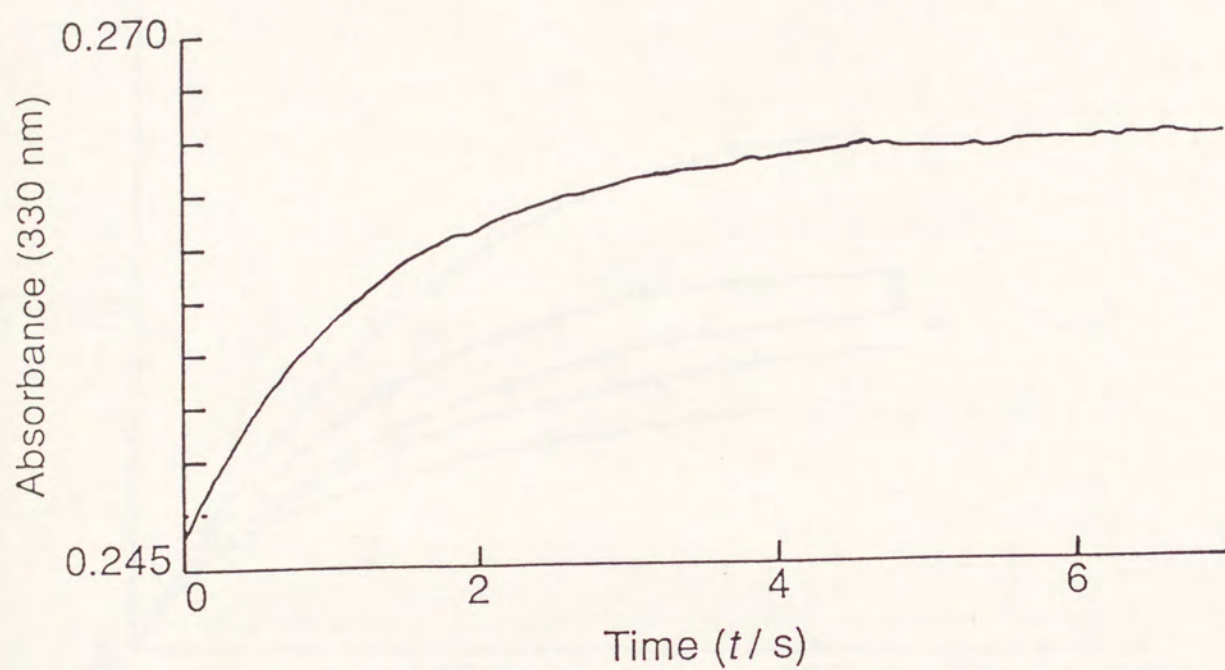


Fig. 3 Fast thermal recovery of absorbance at 330 nm for 2 immediately after irradiation.

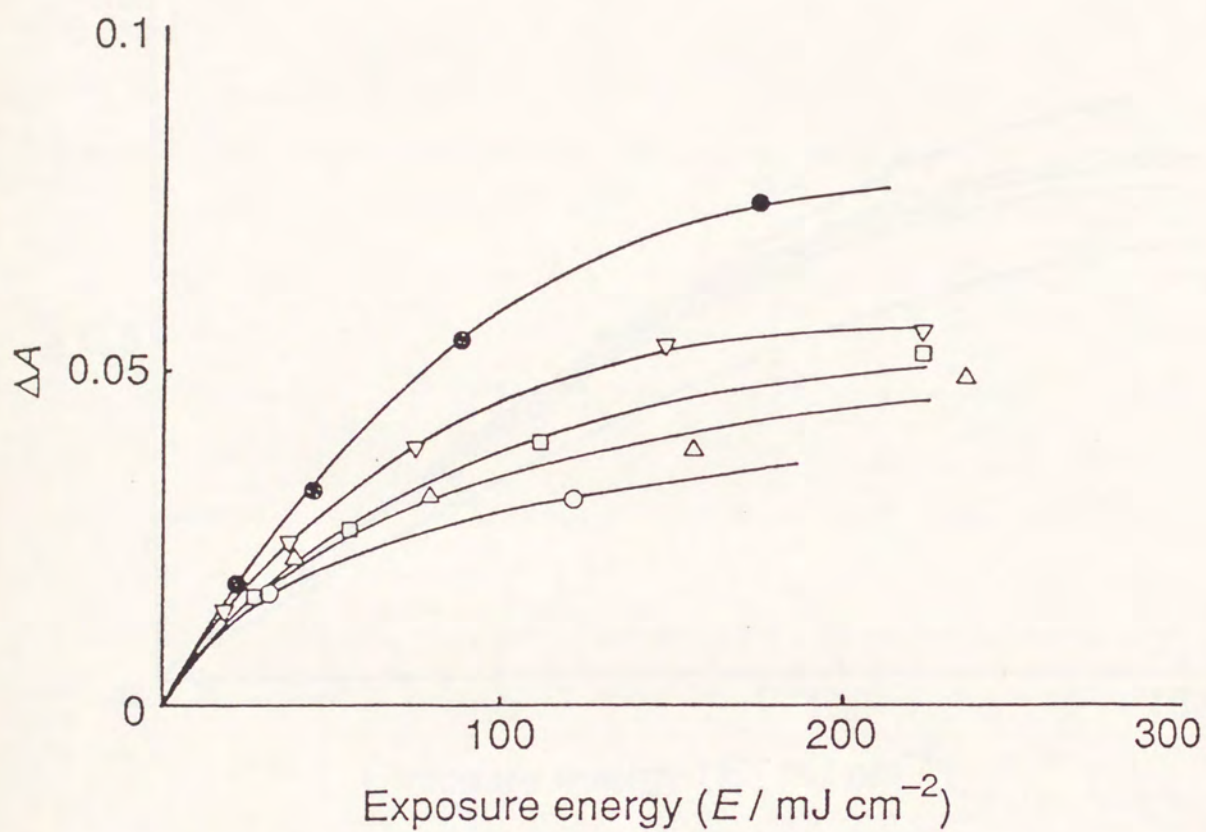


Fig. 4 Changes of absorbance at 330 nm due to the irradiation of 2 in toluene with different light intensities: (●), 4.39 mW/cm²; (▽), 3.71 mW/cm²; (□), 2.77 mW/cm²; (△), 1.96 mW/cm²; (○), 0.76 mW/cm².

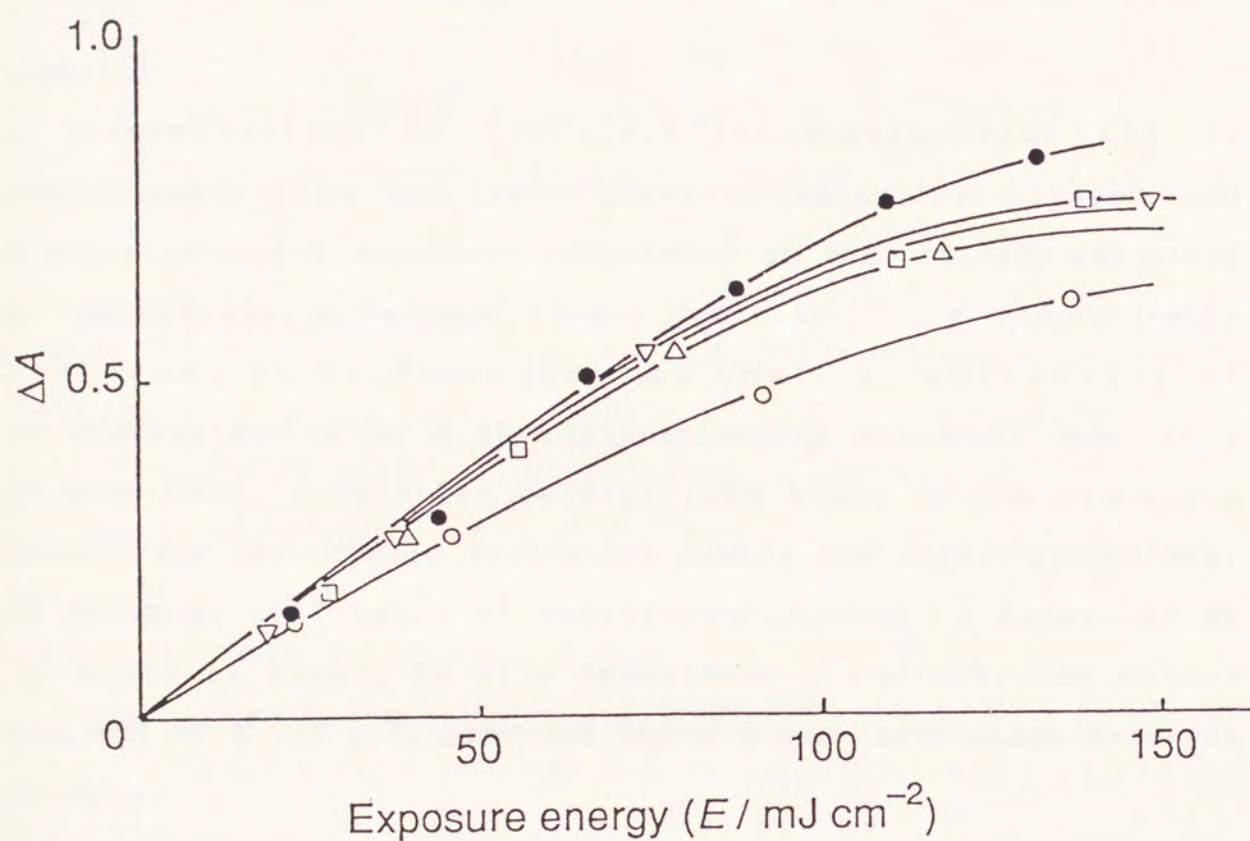


Fig. 5 Changes of absorbance at 328 nm due to the irradiation of 5 in toluene with different light intensities: ($\bullet$), 4.39 mW/cm²; (∇), 3.71 mW/cm²; ($\square$), 2.77 mW/cm²; ($\triangle$), 1.96 mW/cm²; ($\circ$), 0.76 mW/cm².

Chapter 3

Isomerization of [2.2](4,4')Azobenzenophane in Polycarbonate Films and Theoretical Analysis of Light-intensity Dependence of the Photoisomerization.

Abstract

Isomerizations of [2.2](4,4')azobenzenophane (1) in polycarbonate films are spectrophotometrically investigated, and a light-intensity dependent efficiency of the photoisomerization of macrocyclic azobenzene dimers including 1 is theoretically analyzed. It is demonstrated that an efficiency of photoisomerization of 1 is light-intensity dependent even in a polymer film. A relation between life times of the trans-cis isomers for macrocyclic azobenzene dimers and light-intensities, at which an efficiency of photoisomerization is depend on an intensity of light, is also described. A photochromic memory composed of 1 and polycarbonate shows a non-destructive read-out property.

Introduction

There are many studies aiming at applying photochromism to optical memories.¹⁾⁻³⁾ However, those attempts have been impeded by some problems. Among these problems exists a general and fundamental problem. The problem of applying photochromism to optical memories is that memories are destroyed by photoreaction during "read-out" processes. That is, because the wavelengths, λ_A and λ_S , of the light for "writing" and "erasing" of memories are the same as those for "read-out", repetition of "read-out", even with low intensity-light, induces the same reaction for "writing" or "erasing" and destroys the memories. To overcome the problem, some ideas have been proposed.⁴⁾⁻⁷⁾ One promising idea is to synthesize photochromic compounds which show light-intensity dependent photoisomerization. If a quantum yield of the photoisomerization of the compounds is higher as the light-intensity is increased, we can write and erase memories with high intensity light and read out with low intensity light without any serious destruction of memories.

We have synthesized two macrocyclic azobenzene dimers, 1 and 2, and reported that the photoisomerization of those compounds are light-intensity dependent in solvents.^{8),9)} Those compounds have three isomers, namely, the trans-trans (tt), the trans-cis (tc) and the cis-cis (cc). Light-intensity dependent isomerization occurs since the photoisomerization of those compounds from the tt isomer to the cc isomer proceed via the tc isomer, which is thermally unstable and easily isomerizes to the tt isomer.

Now, the unusual properties of the photoisomerization for the macrocyclic azobenzene dimers are theoretically analyzed, and the light-intensity dependent isomerization of [2.2](4,4')-

azobenzenophane, 1, in polymer films is demonstrated. A photochromic memory system which is composed of 1 and polycarbonate shows a non-destructive read-out property.

Experimental section

Materials

Dichloroethane was spectral grade and used without further purification. Bisphenol A type polycarbonate with $M_w = 30000$ was purchased from Teijin Chemical Corporation, Tokyo. 4,4'-Dimethylazobenzene was synthesized by the reduction of nitrobenzene with zinc / NaOH and then purified by recrystallization from ethanol solution.¹⁰⁾ [2.2](4,4')-Azobenzenophane was synthesized according to the method described in an earlier report.⁸⁾

Preparation of polycarbonate films containing azobenzene derivatives for isomerization measurements

1.861 mg of [2.2](4,4')azobenzenophane and 0.1 g of bisphenol A type polycarbonate was dissolved in 1.0 ml of 1,2-dichloroethane, and coated on quartz plates with a wire bar (no. 40). After drying for two hours at room temperature, they were dried completely in an oven at 52°C under vacuum. Similarly, films containing 4,4'-dimethylazobenzene, 3, were obtained by coating quartz plates with the azo compound (0.01056 g) and polycarbonate (0.6 g) dissolved in 6.0 g of dichloroethane. After drying, the film thickness was 2-3 μm , which was calculated from the weight of a certain area and the density of polycarbonate, 1.2.

Preparation of photochromic memory for demonstration of a non-destructive read-out property

The same 1,2-dichloroethane solutions as described above were spread on quartz plates (50 mm $\times$ 50 mm $\times$ 1.5 mm) using a spin-coater (500 r.p.m.). The plates were dried as described above. After drying the film thickness was 4 - 5 μ m.

Measurement of isomerization

A high-pressure mercury lamp (Ushio-UM-452, 450 W) equipped with Toshiba glass filters, UV-34 and UV-D2 was used to expose samples to 366 nm light. Kinetic measurements for thermal isomerization of polycarbonate films containing azobenzene derivatives were made spectrophotometrically on a Hitachi Model 200-20 equipped with a thermo-controlled cell holder by monitoring changes in absorbance at 328 nm (λ_{max} of $\pi\pi^*$ transition) in the dark after sufficient irradiation of 366 nm light. Fast thermal isomerization from the tc form to the tt form was monitored immediately after the photoirradiation. Changes in absorbance at 328 nm as a function of time were recorded with a chart speed of 48 cm/min.

Measurement of light intensity dependence

Photoirradiation was done at $25 \pm 2^\circ\text{C}$ in almost the same manner describe above. The light-intensity was altered by using filters and changing the distance and then measured by Eppley Thermopiles (The Eppley Laboratory Ltd.).

Procedures of writing, reading and erasing memory

The photochromic films on quartz plates were exposed to 366 nm

light (5mW/cm^2) from a super high-pressure mercury lamp with appropriate filters through a mask in contact (figure 1-a). Visualization (read-out) of the patterns were performed by exposure of the plates to 366 nm light ($20\text{ }\mu\text{W/cm}^2$) on a fluorescent sheet. During the visualization process the surface of the photochromic film was in contact with the fluorescent sheet (figure 1-b). The fluorescent sheet used absorbs UV light and emits blue light. The memory was erased with > 450 nm light from a super high pressure mercury lamp with a sharp cut filter.

Results and discussion

Cis-trans isomerization in polycarbonate film

When the light-intensity dependence of photo-isomerization from the tt form to the cc form of [2.2](4,4')azobenzenophane in solution is applied to some functional materials, it is important whether a similar phenomena can be also seen in a polymer matrix. Therefore, the photo- and thermal isomerization properties of [2.2](4,4')azobenzenophane are investigated in a polycarbonate film, which is one of the important polymers as a substrate for optical memories because of its transparency and thermal stability.

Figure 2 shows a spectral change of 1 in polycarbonate upon 366 nm irradiation. Before irradiation 1 show a similar absorption spectrum in a polycarbonate film to that in benzene. The spectrum has two peaks at 328 nm and around 460 nm. These spectral characteristics indicate that this compound exists as trans-trans form in a polycarbonate film. Upon 366 nm irradiation, both of the two peaks at 328 nm and around 460 nm decrease and a new peak around 440 nm increase. A photo-

stationary state is then attained. From this photo-stationary state the initial spectrum is recovered by exposing to light above 420 nm. These spectral changes are similar to that observed in benzene.

Immediately after the irradiation with 366 nm light to an arbitrary extent, a small amount of rapid thermal recovery of the spectrum is observed for 1 in a polycarbonate film. This spectral change is due to a thermal isomerization from the tc isomer to the tt isomer. Spectrally determined life time of the tc isomer at 298 K was about 25 s. This value is almost the same as that for in benzene, 22 s.⁸⁾

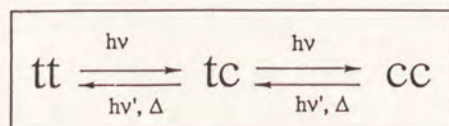
Figure 3 shows an absorption change at several temperatures in long time region, which corresponds to the thermal isomerization from the cc isomer to the tc isomer. Plots of $\ln(A_{\infty} - A_t)$ against time are slightly curved for 1 in polycarbonate films. This means that the isomerization of 1 from the cc isomer to the tc isomer in polycarbonate films does not follow a first-order equation. Similar behaviors have observed for non-cyclic azobenzene derivatives embedded in polymers¹¹⁾ or non-cyclic azobenzene units substituted in a polymer back born or as polymer side chains.¹²⁾

In figures 4 and 5, degrees of the photo-isomerization in Polycarbonate films at two light intensities are plotted against exposure energy for [2.2](4,4')azobenzenophane and 4,4'-dimethylazobenzene, respectively. The light intensities used for the experiments were 2.64 and 0.269 mW/cm². The photo-isomerization of 4,4'-dimethylazobenzene does not depend on the light intensity, but depend only on the exposure energy, as it has been known. On the other hand, the photoisomerization of [2.2](4,4')azobenzenophane is more efficient under the higher

intensity of light. This behavior in Polycarbonate films is coincide with that in benzene.⁸⁾ That is, as expected from the fact that the life time of the tc form of [2.2](4,4')azobenzenophane in a polycarbonate film does not change so much from the value in benzene, the efficiency of the photoisomerization from the tt isomer to the cc isomer of the macrocycle is seemingly light-intensity dependent even in a polycarbonate film.

Theoretical analysis of the light-intensity dependence

Light-intensity dependence on an efficiency of photoisomerization is observed for compounds in which photoisomerization proceeds via a meta stable state like the trans-cis isomer for macrocyclic azobenzene dimers. Light-intensity dependence for such compounds is detected in the range of higher intensities of light as the life time of the meta stable state becomes shorter. When the dependence is applied for the non-destructive read-out, it is important to know the relation between a range, where the efficiency is light-intensity dependent, and the life time of the meta stable states. In order to clarify the relation, calculations are conducted. Based on the reaction scheme for [2.2](4,4')azobenzenophane shown below, the following three differential equations are proposed for the three isomers. Each term in the equations corresponds to one route of the photo- or thermal isomerization.



$$\frac{d[tt]}{dt} = -\frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tt}[tt]L}{D} \phi_{tt \rightarrow tc} + \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tc}[tc]L}{D} \phi_{tc \rightarrow tt} + k_{tc \rightarrow tt}[tc]$$

$$\begin{aligned} \frac{d[tc]}{dt} = & \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tt}[tt]L}{D} \phi_{tt \rightarrow tc} - \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tc}[tc]L}{D} \phi_{tc \rightarrow tt} - k_{tc \rightarrow tt}[tc] \\ & - \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tc}[tc]L}{D} \phi_{tc \rightarrow cc} + \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{cc}[cc]L}{D} \phi_{cc \rightarrow tc} + k_{cc \rightarrow tc}[cc] \end{aligned}$$

$$\frac{d[cc]}{dt} = \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tc}[tc]L}{D} \phi_{tc \rightarrow cc} - \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{cc}[cc]L}{D} \phi_{cc \rightarrow tc} - k_{cc \rightarrow tc}[cc]$$

where [tt] = concentration of tt isomer
[tc] = concentration of tc isomer
[cc] = concentration of cc isomer

I_0 = intensity of light

L = path length of samples

$\phi_{tt \rightarrow tc}$ = quantum yield from tt isomer to tc isomer

$\phi_{tc \rightarrow cc}$ = quantum yield from tc isomer to cc isomer

ϵ_{tt} = molar absorption coeff. of tt isomer

ϵ_{tc} = molar absorption coeff. of tc isomer

ϵ_{cc} = molar absorption coeff. of cc isomer

$k_{cc \rightarrow tc}$ = rate const. of thermal isomerization from cc isomer to tc isomer

$k_{tc \rightarrow tt}$ = rate const. of thermal isomerization from tc isomer to tt isomer

$D = (\epsilon_{tt}[tt] + \epsilon_{tc}[tc] + \epsilon_{cc}[cc])L$

The rate of photoisomerization of cis units at 366 nm is quite low in comparison with trans units because molecular extinction coefficient of cis units is small. Therefore, the photoisomerization, $cc \rightarrow tc$ and $tc \rightarrow tt$, are neglected, and $\epsilon_{tc} = 0.5 \epsilon_{tt}$ is assumed. The equations are then rewritten as follows.

$$\frac{d[tt]}{dt} = -\frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tt}[tt]L}{D} \phi_{tt \rightarrow tc} + k_{tc \rightarrow tt}[tc]$$

$$\frac{d[tc]}{dt} = \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{\epsilon_{tt}[tt]L}{D} \phi_{tt \rightarrow tc} - \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{0.5\epsilon_{tt}[tc]L}{D} \phi_{tc \rightarrow cc} - k_{tc \rightarrow tt}[tc] + k_{cc \rightarrow tc}[cc]$$

$$\frac{d[cc]}{dt} = \frac{1000}{L} I_0 \left(1 - \frac{1}{10D}\right) \frac{0.5\epsilon_{tt}[tc]L}{D} \phi_{tc \rightarrow cc} - k_{cc \rightarrow tc}[cc]$$

With these equations, changes of concentrations of the three isomers under 366 nm light can be calculated by a computer. Using the following data of ϵ_{tt} , thickness of the sample, $k_{cc \rightarrow tc}$ and initial absorbance at 328 nm (A_0) for [2.2](4,4')azobenzophane and assuming quantum yields for $tt \rightarrow tc$ and $tc \rightarrow cc$ as follows, the change of absorbance at 328 nm obtained by the calculations was plotted

$$\left\{ \begin{array}{l} \epsilon_{tt} = 41300 \text{ (366 nm)} \\ \epsilon_{tt} = 13600 \text{ (328 nm)} \\ L = 0.0003 \text{ cm} \\ k_{cc \rightarrow tc} = 5.14 \times 10^{-6} \text{ s}^{-1} \\ \text{Initial Abs} = 0.55 \end{array} \right. \quad \left\{ \begin{array}{l} \phi_{tt \rightarrow tc} = 0.25 \\ \phi_{tc \rightarrow cc} = 0.25 \end{array} \right.$$

against exposure energy. Figures 6, 7, 8 and 9 show results of the calculations in the cases that the life time of the tc isomer were 10, 25, 100 and 1000 s, respectively. Four calculations assuming four different intensity of light, 0.1, 1.0, 10 and 100 mW/cm², for the each life time of the tc isomer were undertaken. Based on these figures, relative initial isomerization rates are plotted against intensity of light in cases of several life time of the tc isomer in figure 10. This figure shows that the light-intensity dependence would be occurred in the region of higher intensities of light as the life time of the tc isomer is decreased. This figure also predicts that the light intensity dependence would be observed in the range of 0.1-10 mW/cm² for compounds, whose life time of the tc isomer is 25 s. These results of the calculations are well coincident with the results obtained for [2.2](4,4')-azobenzenophane in films or in solution.

Tests of a non-destructive read-out property

The absorbance was 0.8 - 1.0 at $\lambda_{\max}$ of $\pi\pi^*$ transition of azobenzene derivatives contained in samples for tests of a non-destructive read-out property. After exposure to 366 nm light (5 mW / cm²) through a mask (writing process), azobenzene derivatives in exposed area are changed from the tt (or trans in the case of 3) form to the cc (or cis in the case of 3) form while those in unexposed area remained unchanged. The patterns were not visible because the difference of absorbance for visible light between tt (or trans)- and cc (or cis)- azobenzene derivatives used are small. Visualization (read-out) of the patterns was accomplished by exposure of samples to 366 nm light (20 μ W / cm²) on a fluorescent sheet, being the surface of the fluorescent sheet in contact with the surface of the photochromic

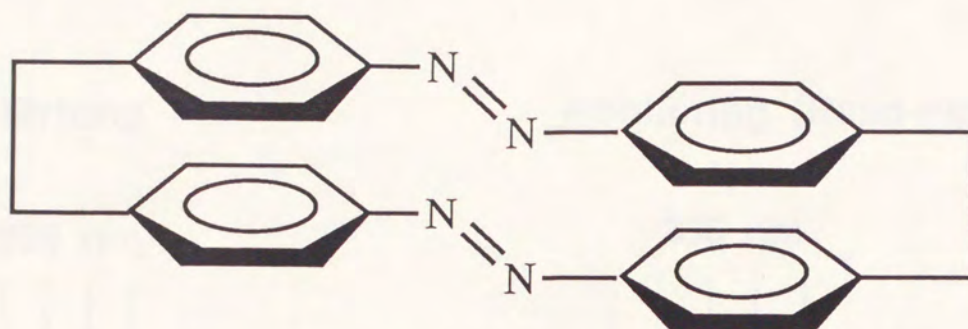
films. In the area of tt (or trans) form 366 nm light doesn't reach to the fluorescent sheet while in the area of cc (or cis) form 366 nm light reach to the sheet and blue light is emitted from the sheet. Figure 11-a and b show the visualized patterns just after the writing process for the photochromic films containing 1 and 3, respectively. Those figures demonstrate that the patterns are successfully visualized with rather high contrast by the visualization procedure described above. Figures 11-c, d, e and f show visualized patterns for the written photochromic films after exposure to a monitor light ($20 \mu\text{W} / \text{cm}^2$). The pattern of the photochromic film containing 3 was almost disappeared after 2 h exposure to the monitor light (figure 11-f). On the other hand the pattern of the photochromic film containing the macrocyclic azobenzene derivative 1 was not changed even after 2 h monitoring. These tests apparently demonstrate that the photochromic memory composed of the macrocyclic azobenzene derivative 1 and polycarbonate have a non-destructive read-out property. Figure 11-g shows Japanese characters which was written by exposure through a new mask to 366 nm light ($5 \text{ mW} / \text{cm}^2$) after an initialization of the sample in the figure 11-e with $>450 \text{ nm}$ light. This test demonstrate the re-writability of the photochromic memory.

Acknowledgment

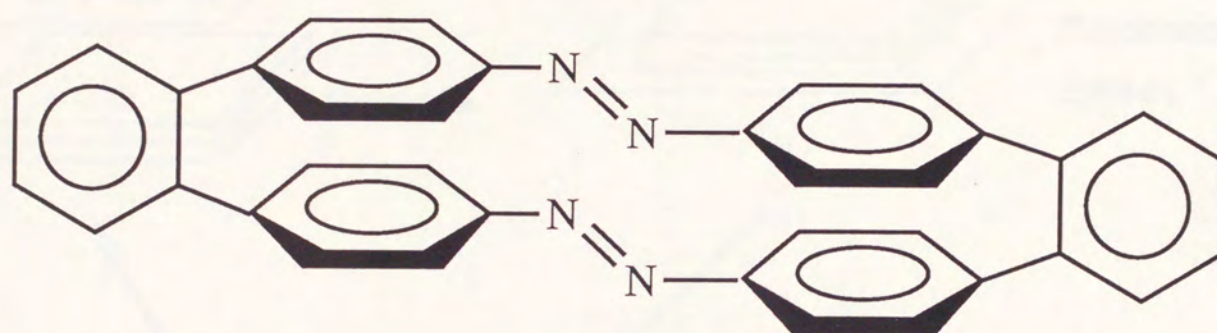
We thank Mr. Toshinao Takahashi for taking photographs of visuarized patterns.

References

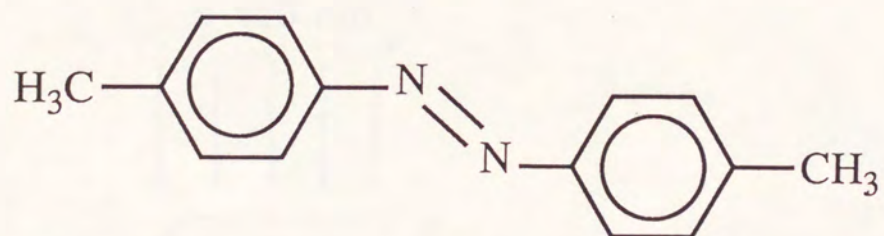
- 1) H. Dürr and H. Bouas-Laurent, Ed., "Photochromism", Elsevier, 1990.
- 2) H. Dürr, Angew. Chem. Int. Ed. Engl., **28**, 413 (1989).
- 3) M. Irie and M. Mohri, J. Org. Chem., **53**, 803 (1988).
- 4) K. Ichimura, Y. Suzuki, T. Seki, A. Hosoki and K. Aoki, Langmuir, **4**, 1214 (1988).
- 5) Y. Suzuki, K. Ozawa, A. Hosoki and K. Ichimura, Polym. Bull., **17**, 285 (1987).
- 6) E. Ando, J. Miyazaki, K. Morimoto, H. Nakahara and K. Fukuda, Thin Solid Films, **133**, 21 (1985).
- 7) Z. F. Liu, K. Hashimoto and A. Fujishima, Nature, **347**, 658 (1990).
- 8) a) N. Tamaoki, K. Koseki and T. Yamaoka, Angew. Chem. Int. Ed. Engl., **29**, 105 (1990); b) N. Tamaoki, K. Ogata, K. Koseki and T. Yamaoka, Tetrahedron, **46**, 5931 (1990).
- 9) N. Tamaoki and T. Yamaoka, J. Chem. Soc., Perkin Trans. 2, **1991**, 873.
- 10) Org. Synth. **1943**, Coll. Vol.2, 4.
- 11) W. Priest and M. M. Sifain, J. Polym. Sci., A-1, **9**, 3161 (1971).
- 12) C. D. Eisenbach, Makromol. Chem., **179**, 2489 (1978).



(1)



(2)



(3)

Scheme Structures of azobenzene derivatives.

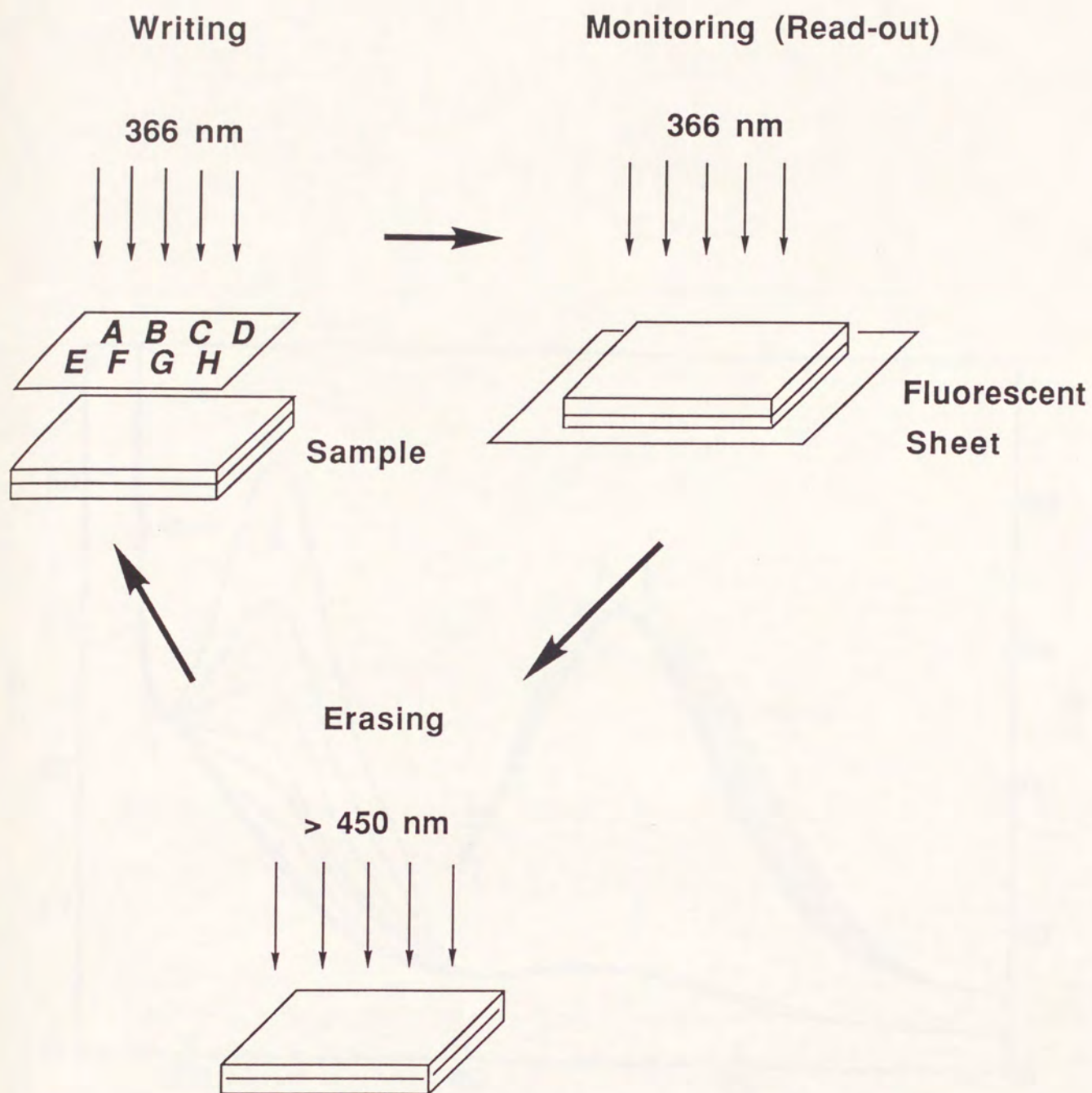


Fig. 1 Procedures of writing, monitoring (read-out) and erasing of memories.

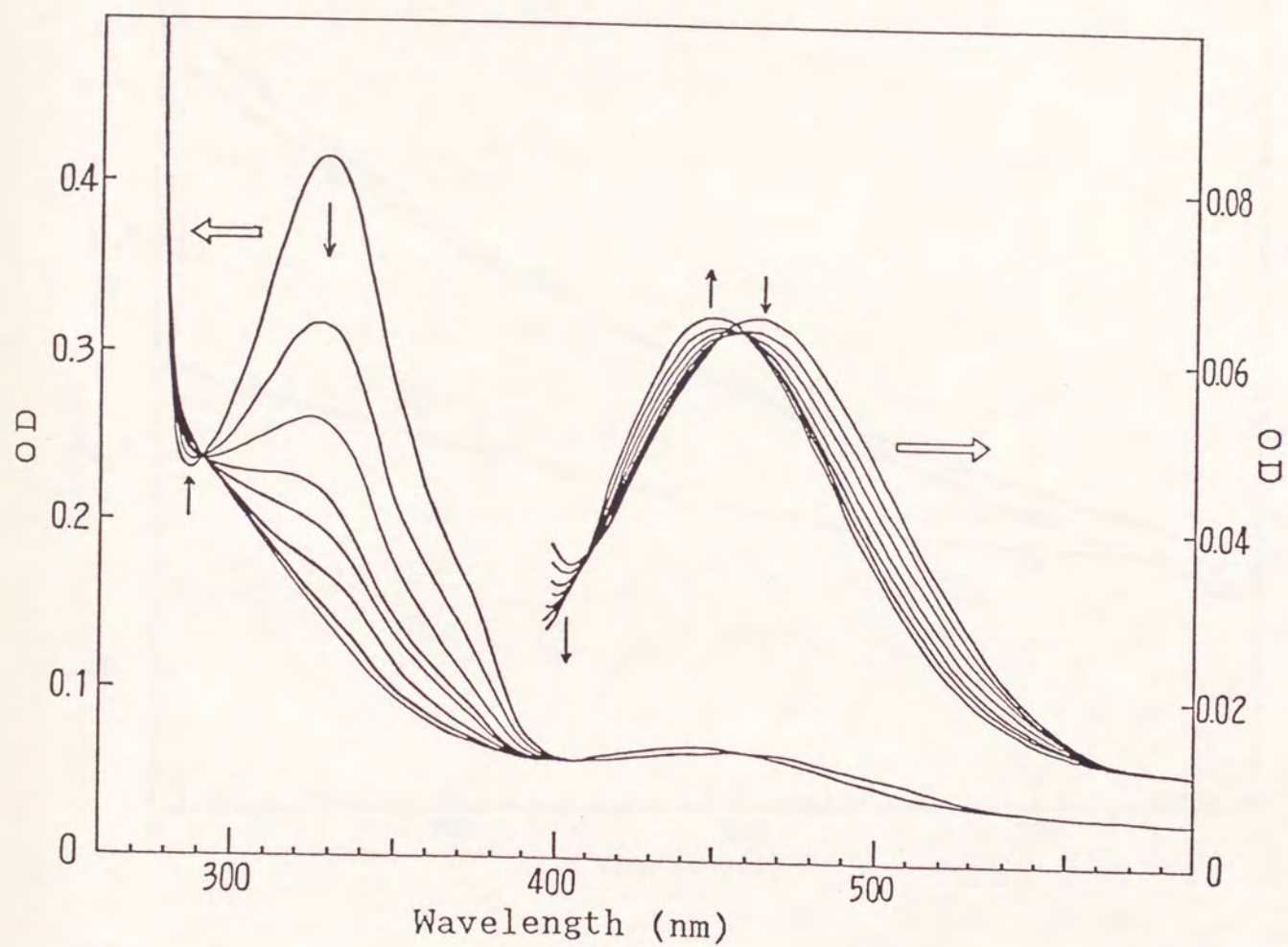


Fig. 2 Changes of absorption spectra of 1 in a polycarbonate film under 366 nm light.

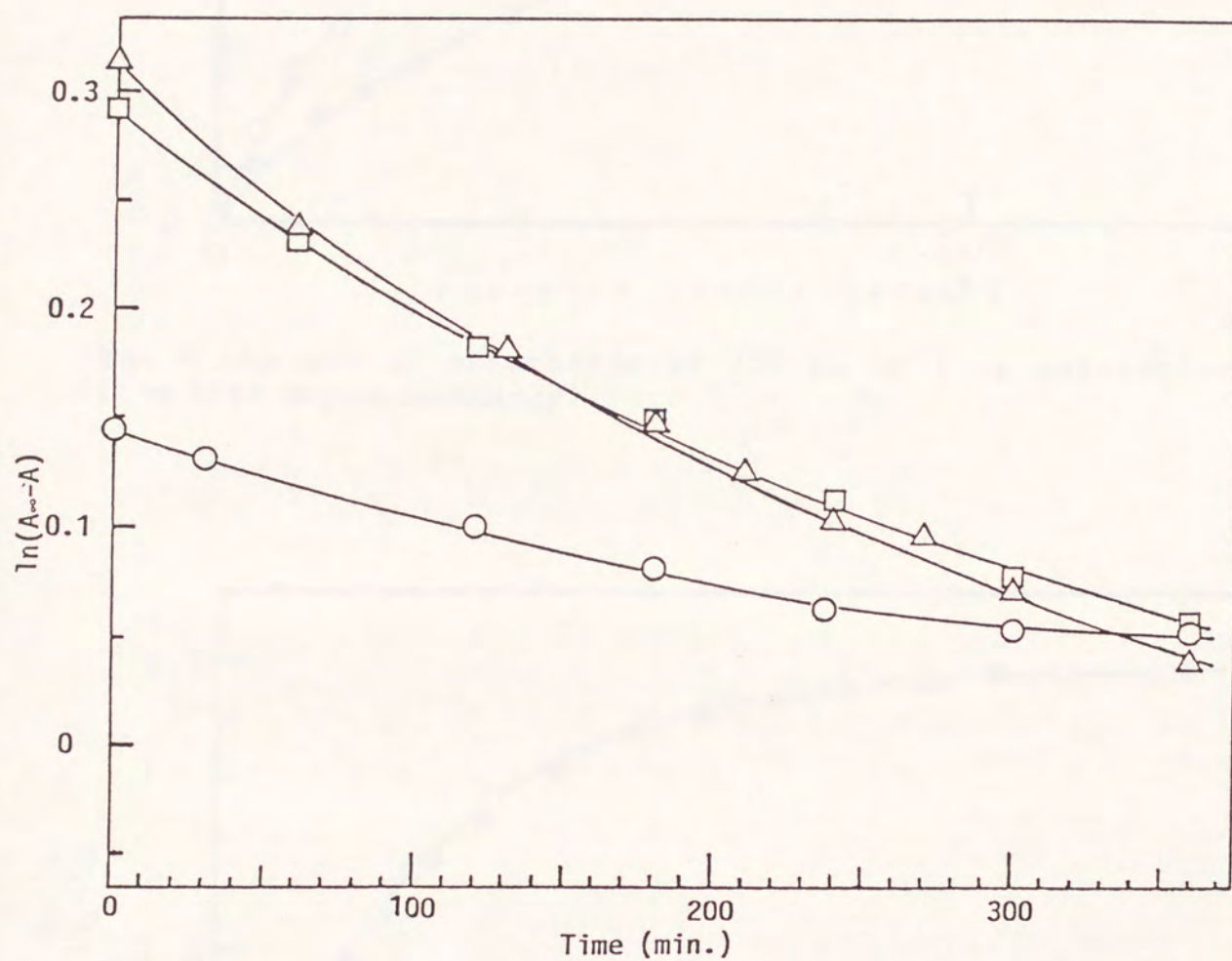


Fig. 3 Thermal isomerization of 1 in polycarbonate films; 38°C, (Δ); 33°C, ($\square$); 25°C, ($\circ$).

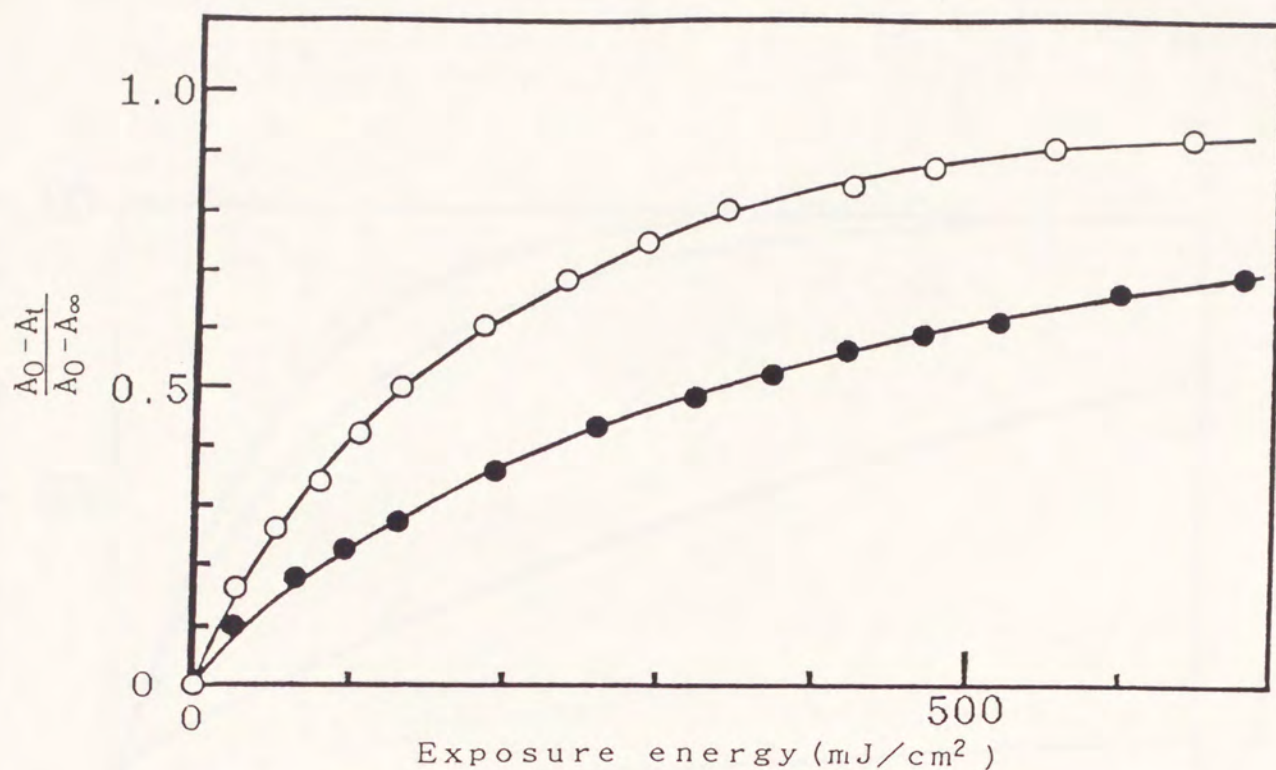


Fig. 4 Changes of absorbance at 328 nm of 1 in polycarbonate films with exposure energy.

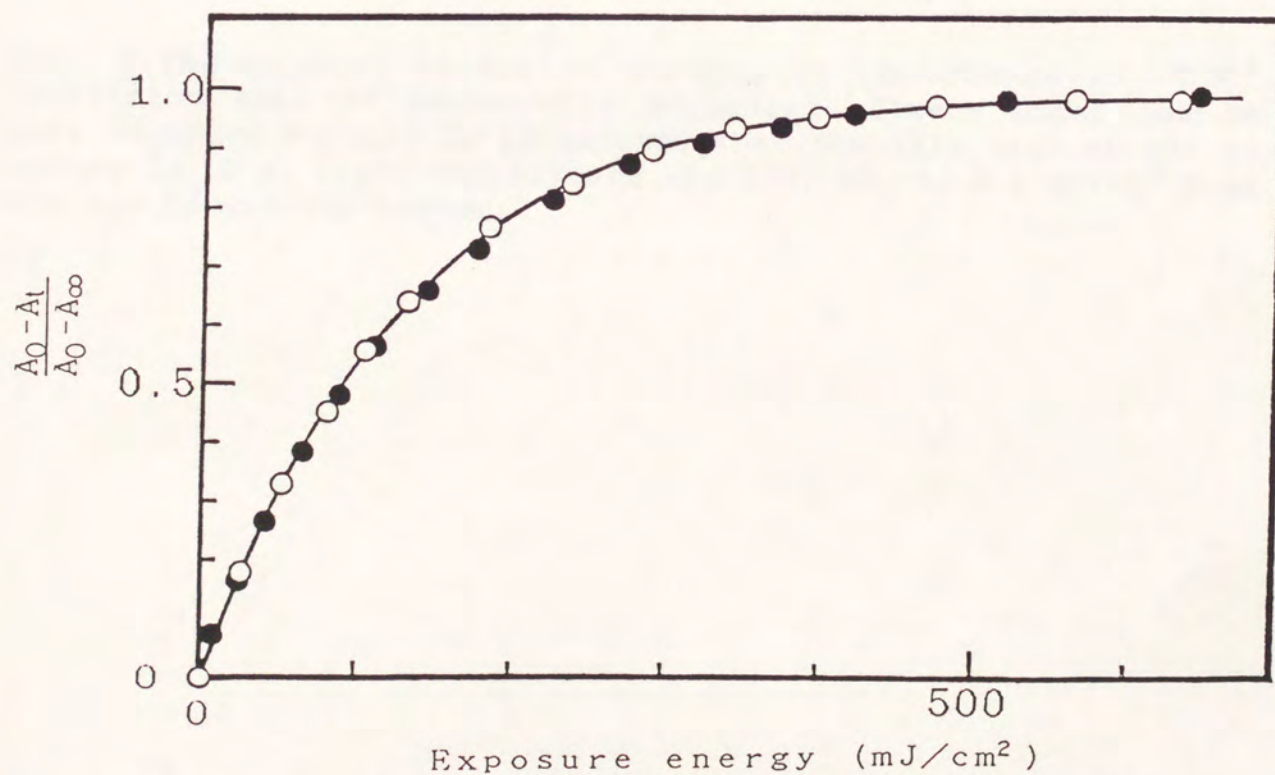


Fig. 5 Changes of absorbance at 339 nm of 4,4'-dimethylazobenzene in polycarbonate films with exposure energy.

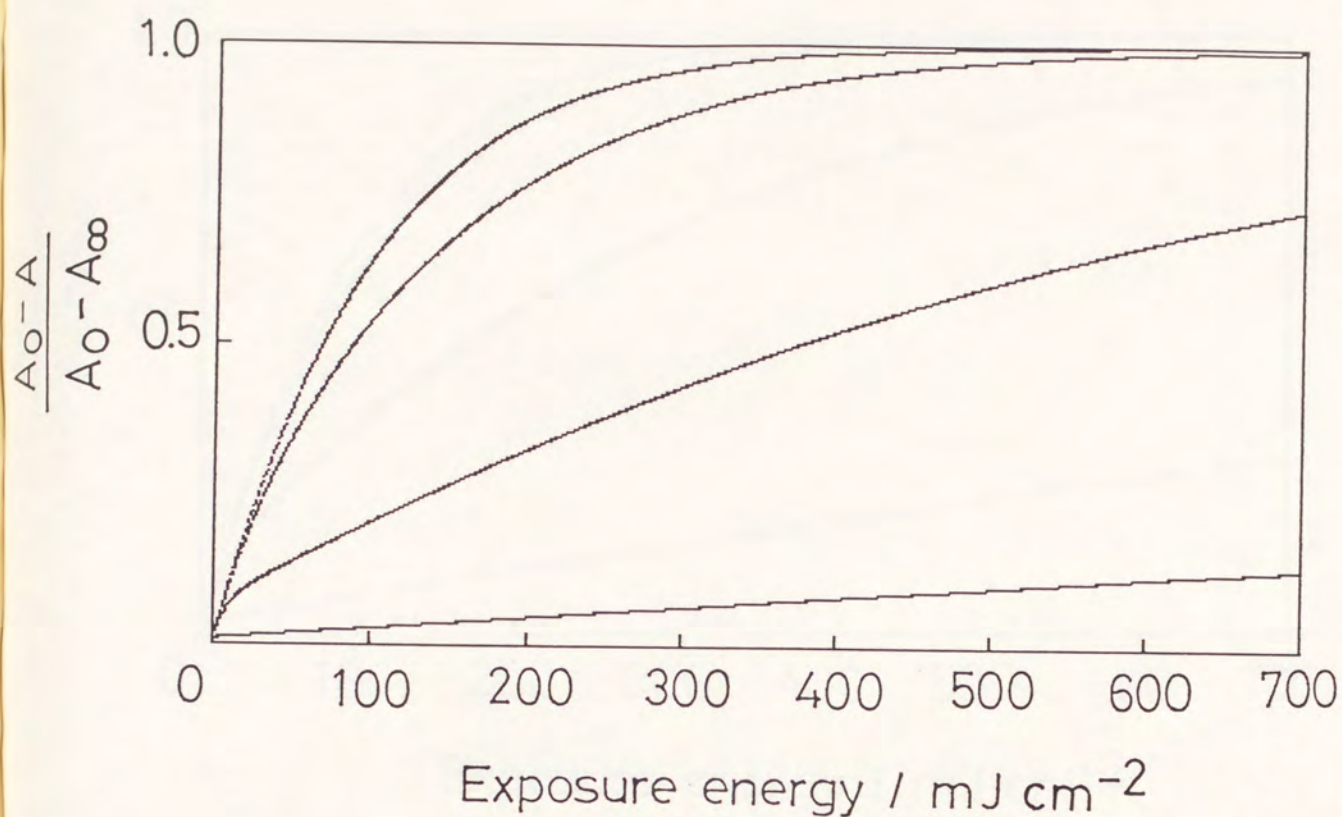


Fig. 6 Theoretical curves of changes of absorbance at $\pi\pi^*$ transition band of macrocyclic azobenzene dimers under 366 nm with exposure energy. It is assumed that the life time of the tc isomer is 10 s. Light intensities are 100, 10, 1, 0.1 mW/cm² from the top toward the bottom.

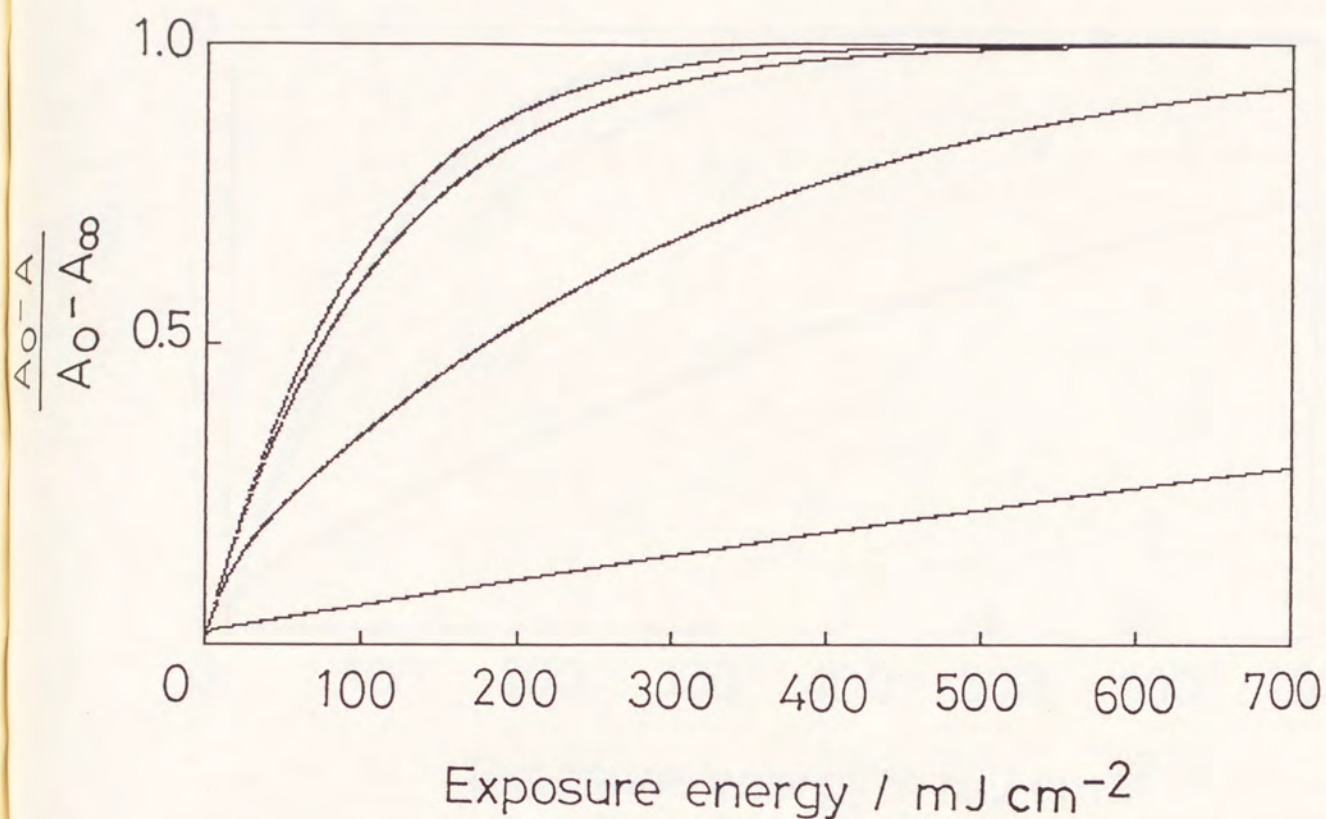


Fig. 7 Theoretical curves of changes of absorbance at $\pi\pi^*$ transition band of macrocyclic azobenzene dimers under 366 nm with exposure energy. It is assumed that the life time of the t_c isomer is 25 s. Light intensities are 100, 10, 1, 0.1 mW/cm² from the top toward the bottom.

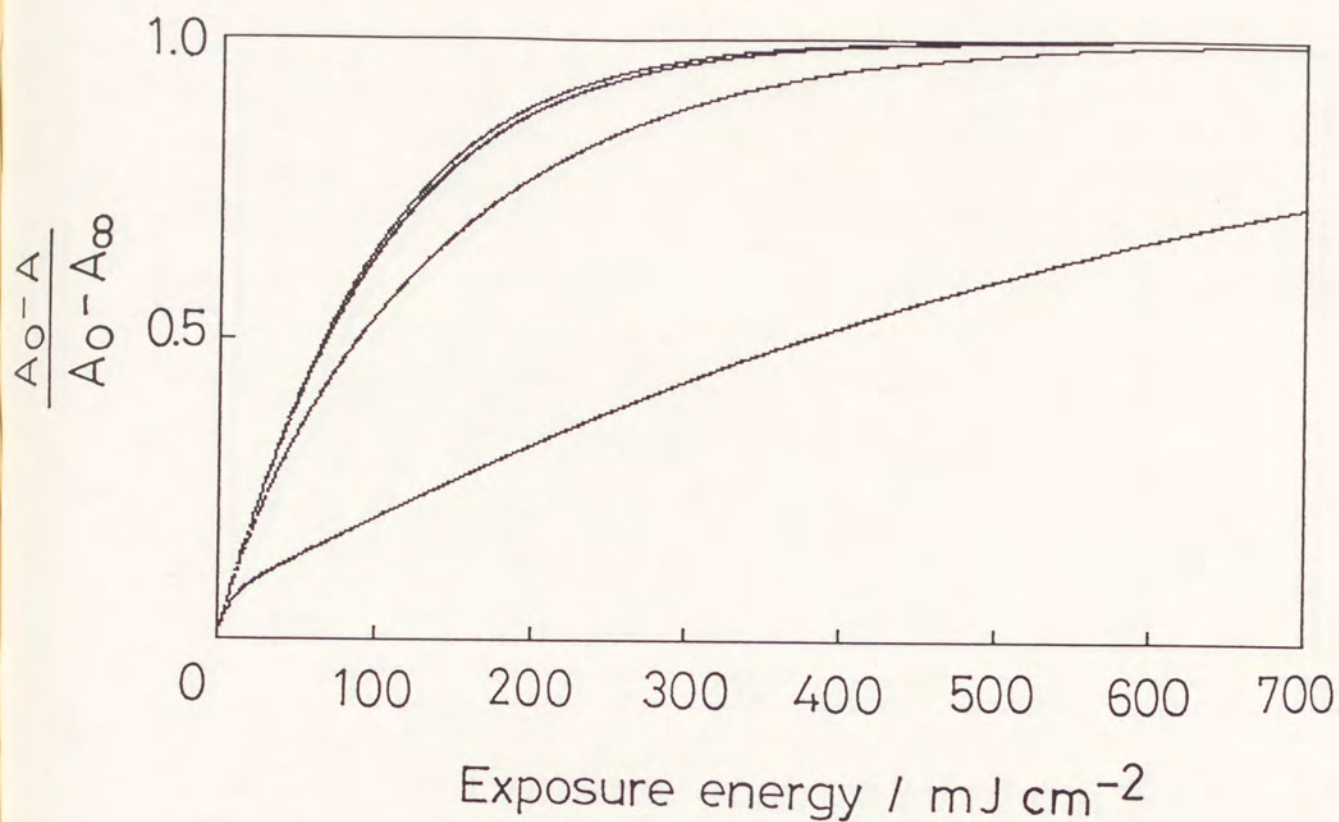


Fig. 8 Theoretical curves of changes of absorbance at $\pi\pi^*$ transition band of macrocyclic azobenzene dimers under 366 nm with exposure energy. It is assumed that the life time of the t_c isomer is 100 s. Light intensities are 100, 10, 1, 0.1 mW/cm^2 from the top toward the bottom.

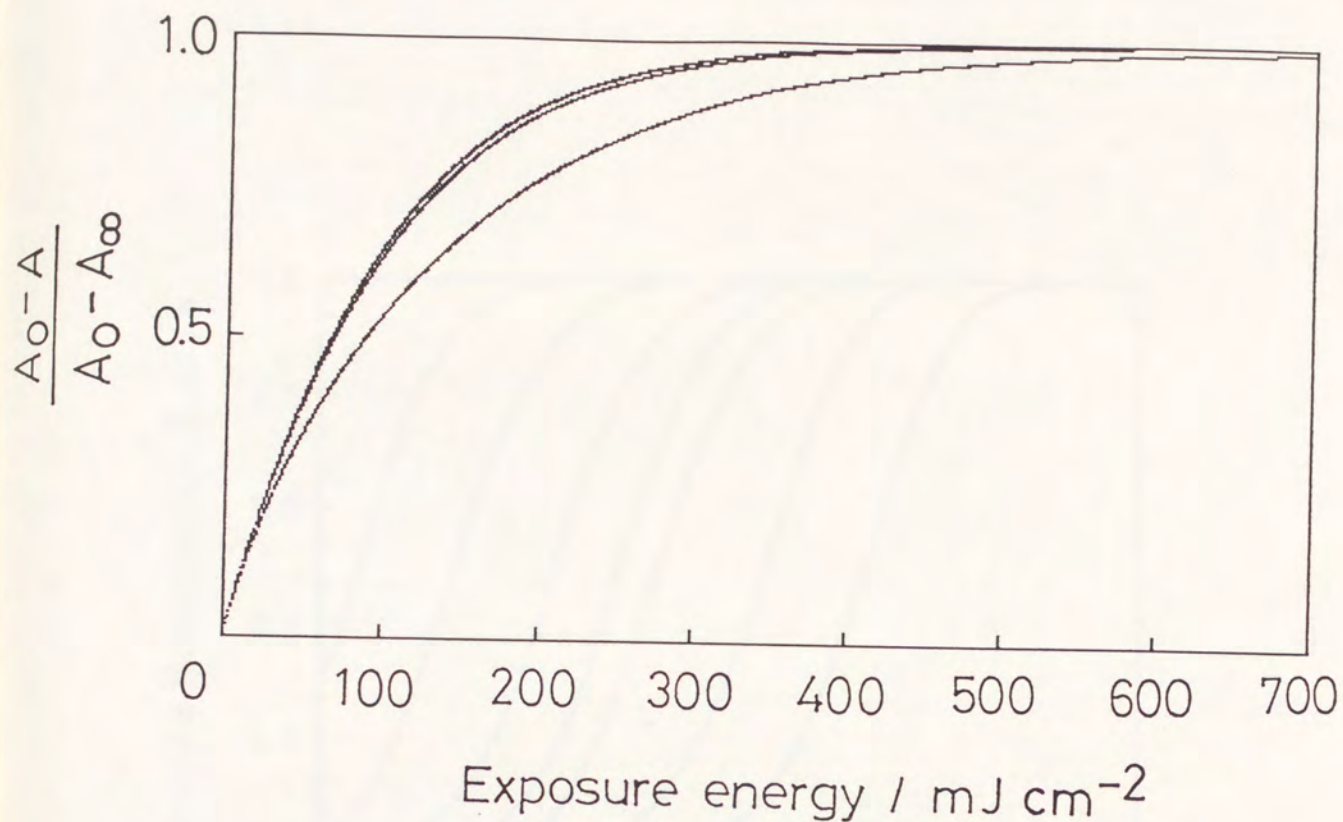


Fig. 9 Theoretical curves of changes of absorbance at $\pi\pi^*$ transition band of macrocyclic azobenzene dimers under 366 nm with exposure energy. It is assumed that the life time of the t_c isomer is 1000 s. Light intensities are 100, 10, 1, 0.1 mW/cm² from top toward bottom.

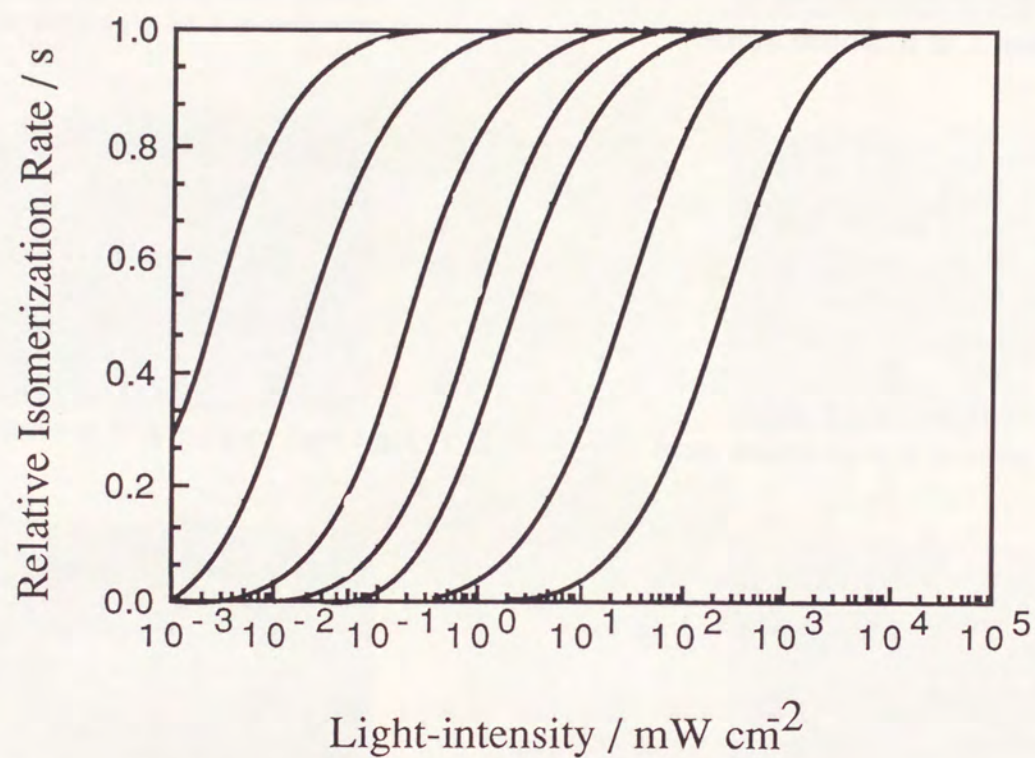


Fig. 10 Theoretical curves of initial photoisomerization rates of macrocyclic azobenzene dimers with different life times of the *tc* isomers against light-intensity. The life times are 10000, 1000, 100, 25, 10, 1, 0.1 s from left to right.

ABCDEFGHIJKL
MNOPQRSTUVWXYZ
WXYZABCDEF
GHIJKLMNOPQ
RSTUVWXYZAB

Before exposure to a monitor light

ABCDEFGHIJKL
MNOPQRSTUVWXYZ
WXYZABCDEF
GHIJKLMNOPQ
RSTUVWXYZAB

After exposure to a monitor light for 1 h

ABCDEFGHIJKL
MNOPQRSTUVWXYZ
WXYZABCDEF
GHIJKLMNOPQ
RSTUVWXYZAB

After exposure to a monitor light for 2 h

あいうえおかき
くけとさしすせ
そたちつてとな
にぬねのはひふ
へほまみむめも

After erasing the image of the alphabets,
Japanese characters were written.

ABCDEFGHIJKL
MNOPQRSTUVWXYZ
WXYZABCDEF
GHIJKLMNOPQ
RSTUVWXYZAB

Before exposure to a monitor light

ABCDEFGHIJKL
MNOPQRSTUVWXYZ
WXYZABCDEF
GHIJKLMNOPQ
RSTUVWXYZAB

After exposure to a monitor light for 1 h

ABCDEFGHIJKL
MNOPQRSTUVWXYZ
WXYZABCDEF
GHIJKLMNOPQ
RSTUVWXYZAB

After exposure to a monitor light for 2 h

Condition of Exposure

Writing	366 nm	5 mW / cm ²	2 min
Erasing	> 450 nm	2 min	
Monitoring (Read-out)	366 nm	20 μ W / cm ²	

Fig. 11 Visualized patterns before and after exposure to light for visualization, and one visualized pattern after re-writing.

Chapter 4

THE PHOTO- AND THERMAL CIS-TRANS ISOMERIZATION OF [2₃](4,4')AZOBENZENOPHANE

Abstract

Four isomers, the trans-trans-trans form, the trans-trans-cis form, the trans-cis-cis form and the cis-cis-cis form, exist for [2₃](4,4')azobenzenophane depending on the degree of the isomerization of three azobenzene units. These isomers are stable enough to be separated by reversed phase liquid chromatography. The compound in methanol exists as the trans-trans-trans form in the dark. Upon 366 nm irradiation the trans-trans-trans form isomerized via the trans-trans-cis form and the trans-cis-cis form to the cis-cis-cis form. At the photostationary state under 366 nm light, 85% of the compound exist as cis-cis-cis form. From the photostationary state the compound thermally isomerized gradually to the trans-trans-trans form. The thermal reaction from the cis-cis-cis form to the trans-trans-trans form also proceeds step by step. The relative values of the quantum yields for the photoisomerization and the absolute value of the rate for the thermal isomerization were determined for each step. Both of the photo- and thermal processes of the direction from cis to trans show the different efficiencies (or rates) depending on the processes. These experimental results can be explained by supposing that the different degree of ring strain works for ground and (or) excited states of each isomer. In this compound, certain isomer can be enriched by the combination of stimuli, like light or heat, from outside. This suggests the possibility

of synthesizing some functional molecules with more than two states of function.

Introduction

Among macrocycles, compounds are included, which show a function to bind alkali metal ions or organic low molecular weight compounds, as exemplified by crown ethers,¹⁾ cyclodextrines²⁾ and calixarenes.³⁾ There are also studies in which a model of the photosynthesis is constructed with electron donative chromophores and electron acceptors by connection in macrocyclic forms.⁴⁾ In the study, a relation of the relative positions of the acceptors and the donors, which are precisely controlled by the macrocyclic figures, and the efficiency of the electron transfer is clarified in detail. These examples represent the utility of the static closed figure of macrocyclic compounds as functions.

On the other hand, macrocyclic compounds including photo-responsive units as parts of the main frame have recently been taken interest in because, it can be possible to change the whole conformation of the macrocyclic compounds by stimuli from outside and to attain more than two kinds of functional states. For example, crown ethers including a azobenzene unit,⁵⁾ cyclodextrene capped with a azobenzene unit⁶⁾ and a compound in which two porphyrin rings are connected circularly with two azobenzene units⁷⁾ have been synthesized. In the former two examples, it is reported that the binding abilities of those compounds to alkali metal ions or toluene etc. can be changed by the isomerization of the azobenzene units. These examples represent the utilization of the dynamic structural change of macrocyclic compounds, which is induced by the ring strain. Although these studies, in which isomerization is utilized as a switch of the whole conformational change of the molecules, are very interesting, there are few studies in which the relation of

kinetical parameters for the dynamic structural change of macrocyclic compounds and the ring strain are discussed.

We have been reported that the synthesis of macrocyclic azobenzene compounds, in which 4,4' positions of two azobenzene units are connected with two carbons each, and that the isomerization at 298 K from the trans-cis form to the trans-trans form is about 10000 times faster than those from the cis-cis form to the trans-cis form.^{8),9)} In these experiments the large differences of the isomerization rates are shown, even though both of the modes are the isomerizations of -N=N- bonds from cis to trans at the same condition except the ring strain. These experimental results demonstrate not only that the ring strain can change the whole conformation of the macrocyclic compounds but also that the degree of the ring strain has influence on the rate of the conformational change.

In this study we have extended the studies to the isomerization of a macrocyclic compound with three azobenzene units in the frame. Four isomers, the trans-trans-trans (ttt), the trans-trans-cis (ttc), the trans-cis-cis (tcc), the cis-cis-cis (ccc), exist for the compound. The rates of photo- and thermal isomerizations among the isomers are determined by the method of liquid chromatography.¹⁰⁾

Experimental

Materials

Methanol used as a solvent for kinetic measurements was spectral grade. 1,2,17,18,33,34-hexaaza-[2₆]paracyclophane-1,17,33-triene (1) was synthesized by the method described previously.⁸⁾

Photo- and thermal isomerization

Photoisomerization of **1** was carried out using 366 nm light produced by a 450 W high-pressure mercury lamp and appropriate combinations of glass filters at $25 \pm 2^\circ\text{C}$. Thermal isomerization was performed in sealed glass tubes equipped in a thermo-controlled bath (kinetic viscosity bath, TV-5S, Thomas Kagaku Co., LTD). The isomerizations were followed by reversed phase liquid chromatography (Merk Hibar LiChrosorb RP-18, Acetonitrile). The absorption spectra of the isomers were measured by a Spectra Multi Channel Photo Detector (Ohtsuka Denshi MCPD 350) after processing by a column of HPLC.

Determination of the concentration of the isomers

Relative concentrations of the isomers were determined by a method of normalization using the peak areas of HPLC monitored by 284 nm light. It was impossible to isolate the isomers of **1** preparatively, however, the response factors to 284 nm light for the isomers were determined by the following equation which should be satisfied for any samples of the same total concentration but different isomer ratio: $A_{ttt}/f_{ttt} + A_{ttc}/f_{ttc} + A_{tcc}/f_{tcc} + A_{ccc}/f_{ccc} = \text{const. } (= K)$ where A_{ttt} , A_{ttc} , A_{tcc} and A_{ccc} are peak areas of isomers shown by subscript; f_{ttt} , f_{ttc} , f_{tcc} and f_{ccc} are response factors of isomers shown by subscript. Thus, the peak areas of HPLC, monitored at 284 nm for 17 solutions whose isomer ratios were changed by changing the irradiation time, were substituted to the equation, and the best fitted values of the response factors were determined. When the response factors have the relation, $f_{ttt} = f_{ttc}/0.99 = f_{tcc}/0.80 = f_{ccc}/0.72$, the coefficient of variation for K was the smallest (3.7 %). This coefficient of variation for the sum of the four

peaks is not so high among the HPLC data obtained by the weighing method¹¹). This fact supports the reliability of this method to obtain the response factors in this study.

Results

Identification of the four isomers

The absorption spectrum in methanol before photo-irradiation has a strong band at 329 nm and a broad band around 440 nm which are characteristics for trans-4,4'-dialkyl substituted azobenzenes. By the reversed phase chromatography, it was confirmed that the solution contains only one kind of compound. Therefore, it is concluded that [2₃](4,4')azobenzenophane exists as the trans-trans-trans form in solution in the dark.

Upon irradiation with UV light, the band at 329 nm is decreased and that around 440 nm is increased. After an arbitrary extent of irradiation, four peaks 1, 2, 3 and 4 ($V_R = 3.6, 5.2, 8.4, 16.4$ ml, respectively) appear on the HPLC chromatograms (Merk Hibar LiChrosorb RP-18, acetonitrile). The absorption spectra of the isomers that give rise to these peaks are measured by a Spectra multi channel photo detector equipped with a data processor (Ohtsuka Denshi MCPD 350). The ratio of absorbance of the isomers at 329 nm (λ_{max} of the spectrum due to $\pi\pi^*$ of the initial solution) to that at 440 nm decreases in the order of the peaks 4, 3, 2, and 1. It is well known for poly azo compounds that the isomers with more cis conformations have a higher dipole moment and thus smaller R_f value on reversed phase HPLC.¹²) The larger absorbance around 440 nm and smaller absorbance around 330 nm in comparison with trans conformers are the characteristics of cis conformers of 4,4'-dialkyl-substituted

azobenzene derivatives. Hence, peaks 1, 2, 3 and 4 can be identified as the ccc, tcc, ttc and ttt, respectively. Figure 1 shows the absorption spectra of the four isomers.

Photoisomerization

Figure 2 shows the change of the relative concentrations against irradiation time. Upon irradiation to 366 nm light the ttt isomer decreases rapidly, and at the same time the ttc isomer increases. The increases of the tcc and the ccc (isomers) follows the change of the ttc. In the early stage the ttc and the tcc attain to the maximum concentrations and decrease gradually. At the photostationary state under 366 nm light, 85% of the compound exists in the ccc form. This concentration change qualitatively demonstrates that the photo-isomerization proceeds consecutively, e.g., $ttt \rightarrow ttc \rightarrow tcc \rightarrow ccc$.

Differential equations for the rate processes of isomers introduced from the scheme 1 are expressed as scheme 2. Each term corresponds to one photo- or thermal process. In the cases of $d[ttt]/dt = 0$ (at $t = 500$ s), $d[ttc]/dt = 0$ (at $t = 30$ and 500 s), $d[tcc]/dt = 0$ (at $t = 60$ and 500 s), and $d[ccc]/dt = 0$ (at $t = 500$ s), respectively, the differential equation for the rate processes gives the equations (1), (2), (3) and (4).

$$\epsilon_{ttt}\Phi_1[ttt] = \epsilon_{ttc}\Phi_4[ttc] \quad (1)$$

$$\epsilon_{ttc}\Phi_2[ttc] + \epsilon_{ttc}\Phi_4[ttc] = \epsilon_{tcc}\Phi_5[tcc] + \epsilon_{ttt}\Phi_1[ttt] \quad (2)$$

$$\epsilon_{tcc}\Phi_5[tcc] + \epsilon_{tcc}\Phi_3[tcc] = \epsilon_{ccc}\Phi_6[ccc] + \epsilon_{ttc}\Phi_2[ttc] \quad (3)$$

$$\epsilon_{ccc}\Phi_6[ccc] = \epsilon_{tcc}\Phi_3[tcc] \quad (4)$$

where $\Phi_1, \Phi_2, \Phi_3, \Phi_4, \Phi_5$ and Φ_6 are the quantum yields for trans-cis photoisomerization(see scheme), ϵ_{ttt} and $[ttt]$, respectively,

are the molar coeff. and the relative concentration of ttt (ϵ and [] for other isomers are defined like ttt).

The fact, that both of ϵ_{ttc} and ϵ_{tcc} are the sum of the molar extinction coeff. originated in the trans parts and the cis parts, makes the calculations of Φ complicated. The assumption, however, that the azobenzene units absorb nearly independently is also a sound one for the isomers. Therefore, we assumed that the trans part of ϵ_{ttc} is $0.75 \epsilon_{ttt}$ and the cis part of ϵ_{ttc} is $0.25 \epsilon_{ccc}$ (similarly the trans part of ϵ_{tcc} is $0.25 \epsilon_{ttt}$ and the cis part of ϵ_{tcc} is $0.75 \epsilon_{ccc}$) and calculated the quantum yields for photons absorbed by the proper part of the molecules. Substituting the relative concentrations, at 500 s to equation (1)-(4), at 30 s to equation (2), and at 60 s to equation (3) from figure 1 and using the relation of molar extinction coeff. mentioned above, gives the relation of $\Phi_1 = \Phi_2 = \Phi_3$ and $0.02 \Phi_4 = 0.3 \Phi_5 = \Phi_6$.

Thermal isomerization

Figure 3 shows the thermal isomerization from the photostationary state at 50°C in the dark. It is noticeable that the concentration of the ttc doesn't increase so much. This fact can be explained by two possibilities. One possibility is that the thermal isomerization rate of $ttc \rightarrow ttt$ is much faster than that of $tcc \rightarrow ttc$, and the other one is that a direct route of $tcc \rightarrow ttt$ exists. By monitoring the thermal concentration change of the isomers after 70 s of irradiation (where the concentration of the ttc isomer is rather high) the first-order disappearance rate of the ttc is determined almost independently ($2.4 \times 10^{-4} \text{ s}^{-1}$ at 50°C) since the rate is fast enough not to be affected by

the thermal reaction of the tcc. The first-order disappearance rate of the tcc in the dark ($1.42 \times 10^{-5} \text{ s}^{-1}$ at 50°C) is also determined independently with the HPLC data after the ccc completely disappears. The fact that the thermal disappearance rate of the ttc is 17 times larger than that of the tcc supports the former possibility, this explains the dull concentration change of the ttc from the photostationary state. The rate constants and the thermodynamic parameters of 1 in methanol are listed in table 1.

Discussion

The cis $\rightarrow$ trans photo- and thermal isomerization rates of one azobenzene unit is dependent on the conformations of the other parts of the macrocycle. We attribute this dependence, in large part, to the differences of the ring strains in the four isomers since the three azobenzene units in the macrocycle are insulated from one another by ethylenic linkages while the distances between 4, 4' positions and the angle of two benzenes in azobenzene are changed from the trans form to the cis form¹³). The variation of the thermodynamic parameters for each isomerization process can be attributed to the different degree of the steric effect in both the cis form and (or) its transition state. The result of the photoisomerization, where the quantum yield of cis $\rightarrow$ trans becomes larger as the number of the trans azobenzene units increases while that of trans $\rightarrow$ cis is not changed, is explained by supposing that the ring strain works in different ways in the excited trans azobenzene unit and the excited cis azobenzene unit¹⁴). We have not yet been able to estimate steric energies for the four isomerization by molecular mechanics calculations because the size of the molecule is too

large to calculate.

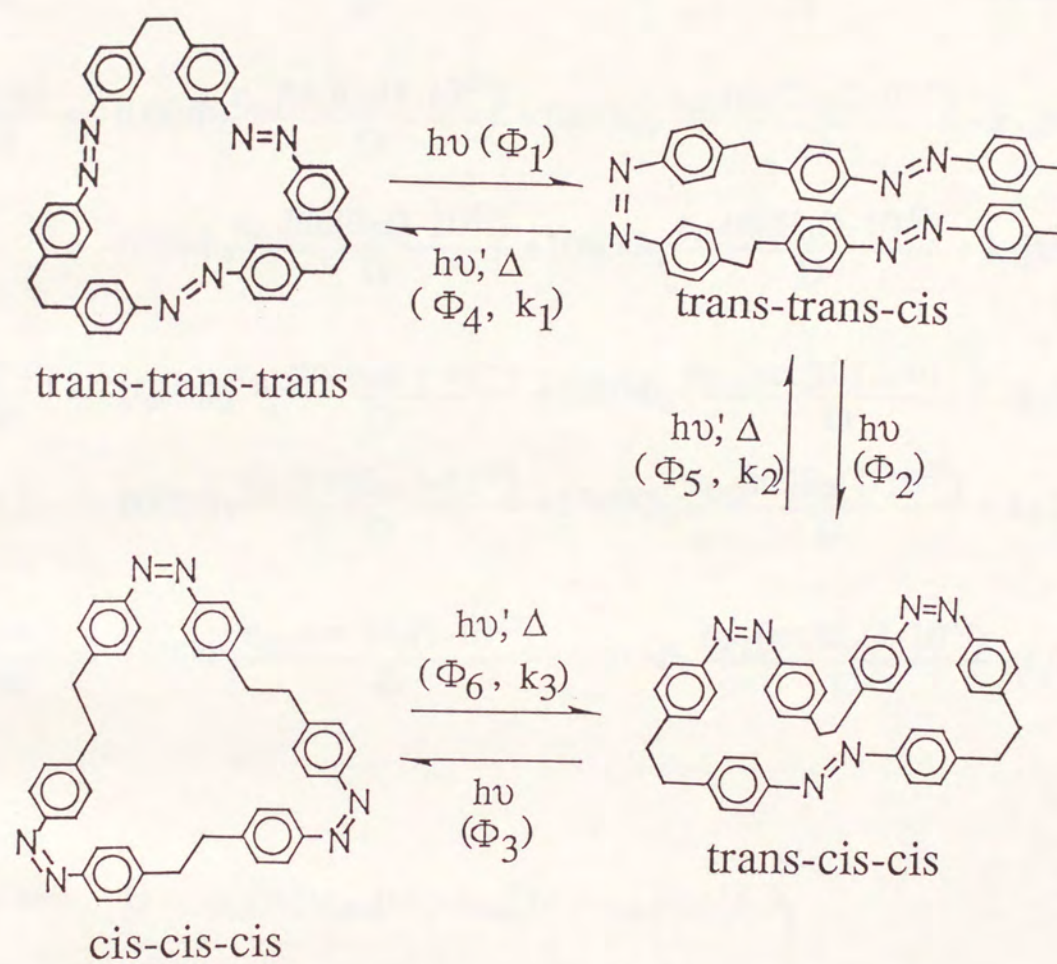
Interestingly, the thermal isomerization of tcc $\rightarrow$ ttc around room temperature is much slower than any of the other thermal processes. So appropriate thermal isomerization from the photostationary state produces a tcc enriched condition (about 70% of isomers exist in the tcc form). Moreover, a ccc enriched (85%) and a ttt enriched (100%) condition is attained by 366nm irradiation and refluxing the solution, respectively. While reports on a tris(azo)macrocylic¹⁵⁾ or a tetra(azo)macrocylic⁷⁾ compound have appeared, we are not aware of any studies that determined their isomerization rates and demonstrated the enrichment of special isomers by external stimuli. Although further efforts to add binding ability are needed, our findings are one of a step towards constructing the enzyme model systems which have more than two different states of binding ability.

Acknowledgement

We thank Mr. Madoka Yasuike of TOYOINK M. F. D. Co. LTD. for providing 3D HPLC systems and for helpful advice.

References and footnotes

- (1) C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 2495 (1967).
- (2) F. Cramer, *Ber.*, **92**, 1739 (1959).
- (3) C. D. Gutsche, B. Dhawan, K. H. No and Muthukrishnan, *J. Am. Chem. Soc.*, **103**, 3782 (1981).
- (4) J. A. Cowan, J. K. M. Sanders, G. S. Beddard and R. J. Harrison, *J. Chem. Soc., Chem. Commun.*, **1987**, 55.
- (5) S. Shinkai, T. Minami, Y. Kusano and O. Manabe, *Tetrahedron Lett.*, **23**, 2581 (1982).
- (6) A. Ueno, H. Yoshimura, R. Saka and T. Osa, *J. Am. Chem. Soc.*, **101**, 2779 (1979).
- (7) K. H. Neumann and F. Vögtle, *J. Chem. Soc., Chem. Commun.*, **1988**, 520.
- (8) (a) N. Tamaoki, K. Koseki and T. Yamaoka, *Angew. Chem. Int. Ed. Engl.*, **29**, 105 (1990); (b) N. Tamaoki, K. Ogata, K. Koseki and T. Yamaoka, *Tetrahedron*, **46**, 5931 (1990).
- (9) N. Tamaoki and T. Yamaoka, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 873.
- (10) Preliminary communication: N. Tamaoki, K. Koseki and T. Yamaoka, *Tetrahedron Lett.*, **31**, 3309 (1990).
- (11) P. R. Brown, "High Pressure Liquid Chromatography", Academic Press, New York, 1973.
- (12) (a) A. H. Cook, and D. G. Jones, *J. Chem. Soc.*, **1939**, 1309; (b) K. Itoh, T. Masuda, M. Takei, Y. Sakurai and M. Nishigami, *J. Chem. Soc., Chem. Commun.*, **1986**, 1028 and also reference 14.
- (13) G. C. Hampson and J. M. Robertson, *J. Chem. Soc.*, **1941**, 409.
- (14) E. Fischer, *J. Am. Chem. Soc.*, **82**, 3249 (1960).
- (15) H.-. W. Losensky, H. Spelthann, A. Ehlen, F. Vögtle and J. Bargon, *Angew. Chem., Int. Ed. Engl.*, **27**, 1189(1988).



Scheme 1

$$\frac{d[ttt]}{dt} = -1000\Phi_1 \frac{\epsilon_{ttt}[ttt]I_0(1-10^{-D})}{D} + 1000\Phi_4 \frac{\epsilon_{ttc}[ttc]I_0(1-10^{-D})}{D} - k_1[ttc]$$

$$\frac{d[ttc]}{dt} = -1000\Phi_2 \frac{\epsilon_{ttc}[ttc]I_0(1-10^{-D})}{D} + 1000\Phi_5 \frac{\epsilon_{tcc}[tcc]I_0(1-10^{-D})}{D} - k_1[ttc]$$

$$-1000\Phi_4 \frac{\epsilon_{ttc}[ttc]I_0(1-10^{-D})}{D} + 1000\Phi_1 \frac{\epsilon_{ttt}[ttt]I_0(1-10^{-D})}{D} + k_2[tcc]$$

$$\frac{d[tcc]}{dt} = -1000\Phi_3 \frac{\epsilon_{tcc}[tcc]I_0(1-10^{-D})}{D} + 1000\Phi_6 \frac{\epsilon_{ccc}[ccc]I_0(1-10^{-D})}{D} - k_2[tcc]$$

$$-1000\Phi_5 \frac{\epsilon_{tcc}[tcc]I_0(1-10^{-D})}{D} + 1000\Phi_2 \frac{\epsilon_{ttc}[ttc]I_0(1-10^{-D})}{D} + k_3[ccc]$$

$$\frac{d[ccc]}{dt} = -1000\Phi_6 \frac{\epsilon_{ccc}[ccc]I_0(1-10^{-D})}{D} + 1000\Phi_3 \frac{\epsilon_{tcc}[tcc]I_0(1-10^{-D})}{D} - k_3[ccc]$$

$$\left(\begin{array}{l} \text{where } D = (\epsilon_{ttt}[ttt] + \epsilon_{ttc}[ttc] + \epsilon_{tcc}[tcc] + \epsilon_{ccc}[ccc])I \\ I_0 = \text{photons / cm}^2 \end{array} \right)$$

scheme 2

Table 1 Rate constants and thermodynamic parameters for the thermal isomerization in the dark of 1 in methanol.

Isomerization mode	$k \times 10^5 / \text{sec}^{-1}$			$\Delta E_a /$	$\Delta S^\ddagger /$
	30°C	40°C	50°C	Kcal·mol ⁻¹	cal·K ⁻¹ ·mol ⁻¹
ccc→tcc	1.02	3.13	9.03	21.2	-13.2
tcc→ttc	0.121	0.442	1.42	23.9	-8.7
ttc→ttt	2.15	7.11	24.0	23.5	-4.4

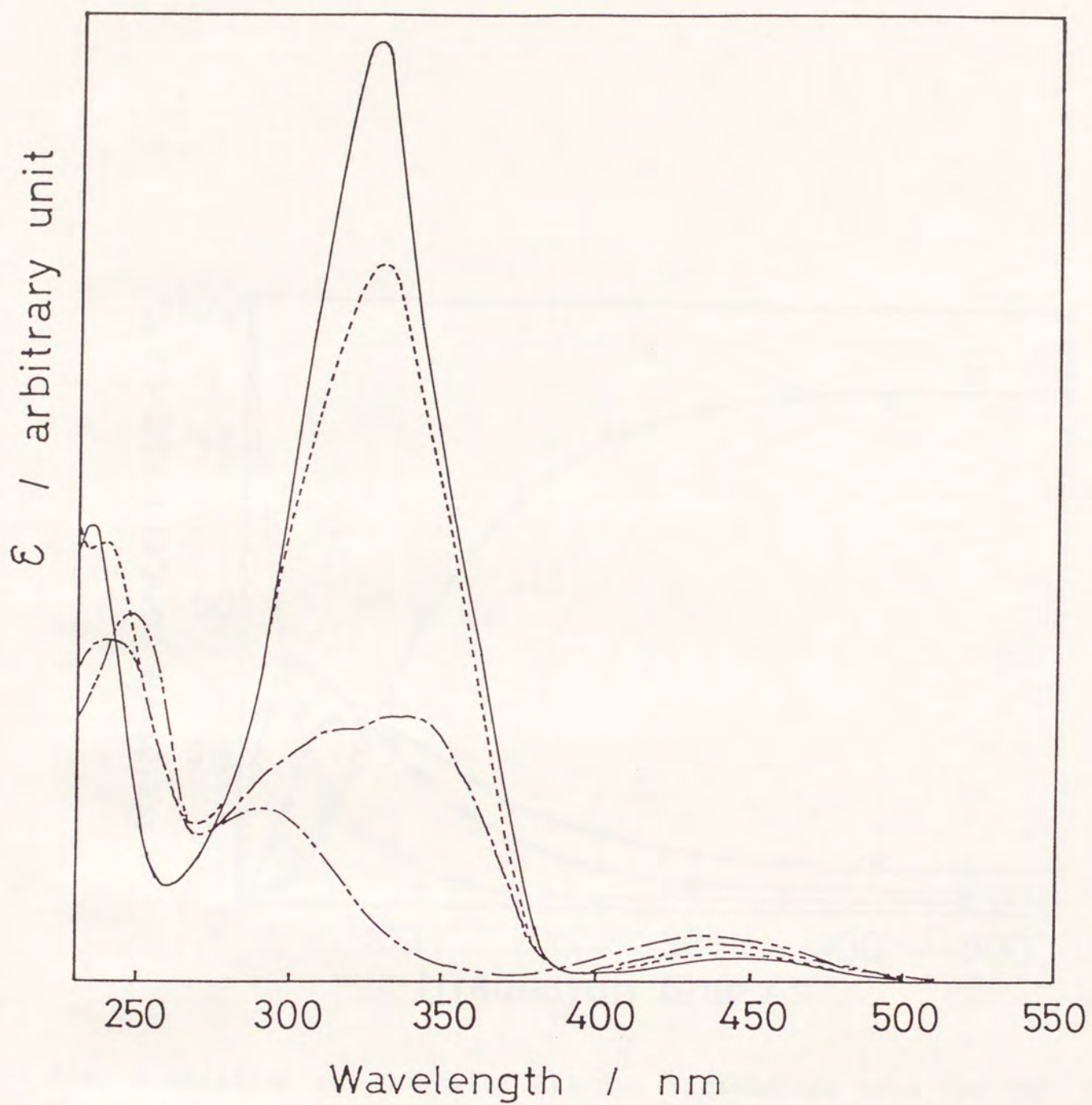


Fig. 1 Absorption spectra of ttt isomer, —; ttc isomer, ----; tcc isomer, —·—; ccc isomer, ···· of (1).

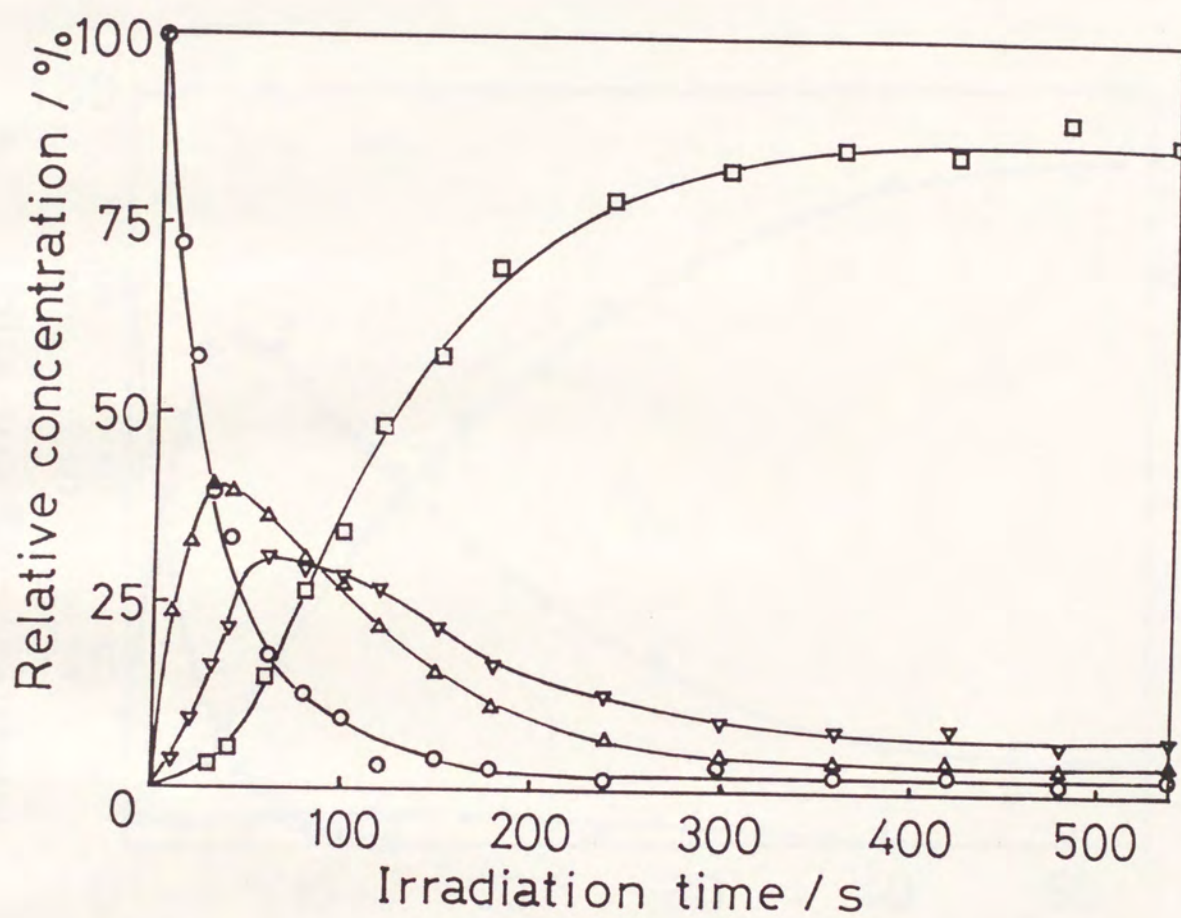


Fig. 2 Relative concentration (%) vs. irradiation time for the photo-isomerization of compound 1 in methanol at 25°C: —○—, ttt; —△—, ttc; —▽—, tcc; —□—, ccc.

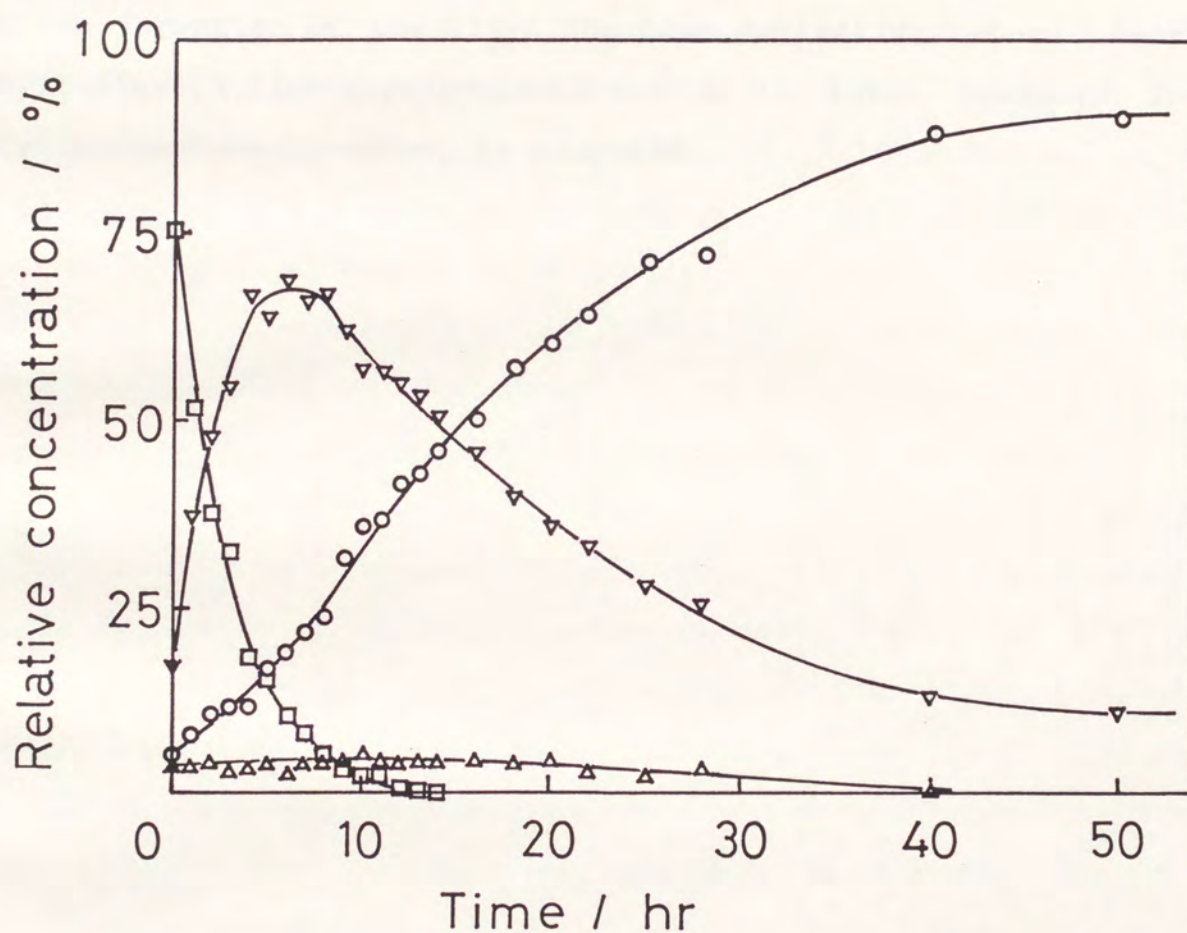


Fig. 3 Relative concentration (%) vs. time for the thermal isomerization in the dark of compound 1 in methanol at 50°C:—○—, ttt; —△—, ttc; —▽—, tcc; —□—, ccc.

Chapter 5

Formation of Acyclic cis-Azobenzene without Light

Abstract

Reduction mixture of bis(4-nitrobenzyl) ether contained a considerable amount of cis-4,4'-dimethylazobenzene. A mechanism of the formation of the cis-azobenzene derivative, where 2-oxa-10,11-diaza[3.2]paracyclophan-10-ene 2 is first produced from bis(4-nitrobenzyl) ether, is proposed.

Although several chemical syntheses of trans-azobenzene derivatives are known¹, chemical syntheses of cis-isomers are known only in the case of cyclic azobenzene derivatives². The only method to synthesize acyclic cis-azobenzene derivatives ever known is a photochemical one, namely, exposing the corresponding trans-azobenzene derivatives to UV light³. This fact is probably due to the fact that intermediates in the chemical formations of azo-linkages energetically favor trans conformations about N-N bonds. In this chapter we describe the one-pot chemical formation of cis-4,4'-dimethylazobenzene, 3, without using light.

Bis(4-nitrobenzyl) ether, 1, was reduced with LiAlH_4 in dry THF by a high dilution method. It was found by TLC that the reaction mixture contained several orange products. The mixture was then separated by column chromatography. Two main orange compounds which eluted together during the early stage of chromatography were further separated by preparative GPC and crystallized by slow evaporation of the solvent under atmospheric pressure at room temperature. One of the fractions was identified as being trans-4,4'-dimethylazobenzene by comparing the ^1H -n.m.r. and retention time on reversed-phase HPLC with an authentic sample* which was synthesized by the reduction of 4-nitrotoluene. Identification of the fraction was further confirmed by FD-MS. The detected mass was 210, which corresponds to 4,4'-dimethylazobenzene. The other fraction of the preparative GPC showed two peaks on reversed-phase HPLC after crystallization. This means that the compound in this fraction of GPC is slowly changed to another compound in the dark. On the ^1H -n.m.r. chart there exist four kinds of doublets (each two peaks of which is coupled) and two kinds of singlets. By a comparison of ^1H -n.m.r. and the retention time on a reversed-phase HPLC with an authentic

mixture* prepared by the UV irradiation of trans-4,4'-dimethylazobenzene in solvent, the second isolated fraction was identified as being a mixture of trans- and cis-4,4'-dimethylazobenzene.

Since we performed the entire process under yellow light (<500 nm), it is certain that cis-4,4'-dimethylazobenzene is formed chemically, not photochemically. This interesting phenomenon is explained as below (scheme). Bis(4-nitrobenzyl) ether was first reduced to form 2-oxa-10,11-diaza[3.2]paracyclophan-10-ene, 2 in which the azo linkage is fixed to the cis form due to a ring restriction. The cyclophane is destabilized by ring strain and is thus very easily further reduced to form an acyclic azobenzene derivative, 3, maintaining the azo configuration in cis form. Another possible route, in which the ether linkage of 1 is first decomposed to form 4-nitrotoluene and then converted to 3, is excluded by the following observation. A reduction of 4-nitrotoluene under similar conditions did not produce cis-4,4'-dimethylazobenzene but produced trans-4,4'-dimethylazobenzene only.

This proposed reaction process to form cis-azobenzene derivative is also interesting fields involving the synthesis of cyclophane which contain hetero atoms. The synthesis of 10,11-diaza[3.2]paracyclophane-10-enes has not yet succeeded, in spite of the intensive efforts by Funke and Grutzmacher⁴. Although we have not yet isolated 10,11-diaza[3.2]paracyclophane-10-enes, we believe that 1,3-bis(4-nitrophenyl)propane will be stably converted to 10,11-diaza[3.2]paracyclophan-10-ene under the same reduction condition as described in this study.

Experimental

Synthesis of Bis(4-nitrobenzyl) Ether, 1

1 was synthesized by a bimolecular condensation of 4-nitrobenzyl alcohol, 4. 6 ml of conc. H_2SO_4 was added to 25 g of 4 in 150 ml of benzene. The solution was heated under reflux for 4 hours. After that, H_2SO_4 was further added until 4 was completely disappeared. After 25 hours the solution was cooled to room temperature and washed four times with 100 ml (each) of water. A small portion of 1 appeared as a white solid two or three days after removing the benzene from the solution by evaporation. Additional 1 appeared after removal of (4-nitrophenyl)phenylmethane⁵ from the remaining solution by distillation. The product was combined and recrystallized from ethanol. 3.82 g (16.2%), m.p. 97-98°C (lit.⁶ 97-98°C), ^1H -n.m.r.(CDCl_3) 4.72 (s, 4H, CH_2OCH_2), 7.55 (d, 4H, Ar), 8.24 (d, 4H, Ar).

Reduction of 1

A solution of 5.0 g of 1 in 100 ml of dry THF was added dropwise for 3 h to a suspension of 3.4 g of LiAlH_4 in 140 ml of dry THF under a nitrogen atmosphere. After 20 h of stirring, a small amount of water was carefully added to the reaction mixture in order to destroy the remaining any LiAlH_4 . O_2 was then passed through the reaction mixture for 4.5 hours in order to oxidize any hydrazo compounds to the corresponding azo compounds. The solid was filtered off and the filtrate evaporated. The residue was extracted by chloroform. A condensed chloroform solution was transferred to a silica gel column and eluted with hexane-chloroform (1:1 v/v). The first eluent was purified by

preparative GPC (Waters, ULTRASTYRAGEL 500 Å + 100 Å / chloroform). cis- and trans-4,4'-Dimethylazobenzene were eluted at retention volume of 95.5 and 99.6 ml, respectively. By slowly evaporating of chloroform parts of the first fraction (8.07 mg, 0.21%) and second fraction (0.196 g, 5.1%) were isolated.

Acknowledgment

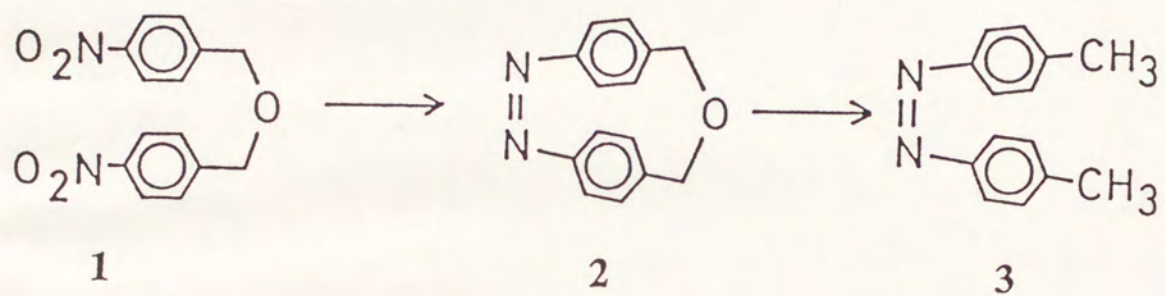
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References

- 1) H. E. Bigelow and D. B. Robinson, *Org. Synth.* III, 103(1955) and references cited in.
- 2) a) H. Dural, *Bull. Soc. chim. France*, 4, 727(1910); b) G. M. Badger, J. H. Seidler, B. Thomson, *J. Chem. Soc.*, 1951, 3207; c) U. Funke and H.-F. Grützmacher, *Tetrahedron*, 43(16), 3787(1987); d) H.-F. Grützmacher and J. Schmieg, *Chem. Ber.*, 122, 1929(1989).
- 3) A. H. Cook, *J. Chem. Soc.*, 1938, 876.
- 4) U. Funke and H.-F. Grützmacher, *Chem. Ber.*, 122, 1503(1989).
- 5) A. Basler, *Ber.*, 16, 2714(1883).
- 6) P. F. G. Praill, *J. Chem. Soc.*, 1957, 3162.

Footnote

* ^1H -n.m.r.(270 MHz): *trans*-4,4'-dimethylazobenzene (CDCl_3), 2.43 (s, 6H), 7.30 (d, J 8.2 Hz, 4H, Ar), 7.81 (d, J 8.2 Hz, 4H, Ar); *cis*-4,4'-dimethylazobenzene (CDCl_3), 2.30 (s, $-\text{CH}_3$), 6.77 (d, J 7.2 Hz, 4H, Ar), 7.05 (d, J 7.2 Hz, 4H, Ar)



Scheme 1

