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[2.2](4,4')AZOBENZENOPHANE. SYNTHESIS, STRUCTURE, AND CIS-TRANS ISOMERIZATION[1].

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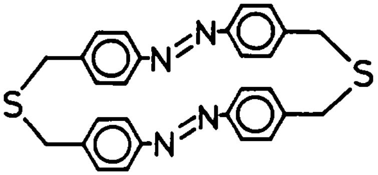
Abstract

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 second 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 photoregurated functions in nature[4]. 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 strain[5]. Grützmacher et al. synthesized a series of dithia-diaza[n.2]paracyclophane-enes[5a] and their metha analogues[5b] 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. sythesized [3.3](4,4')azobenzenophane 1 from 4,4'-

bis(bromomethyl)azobenzene and Na_2S, and first reported that cis-trans thermal isomerization of one azobenzene unit can be controlled by the conformational change of the other azobenzene unit[5c]. 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.



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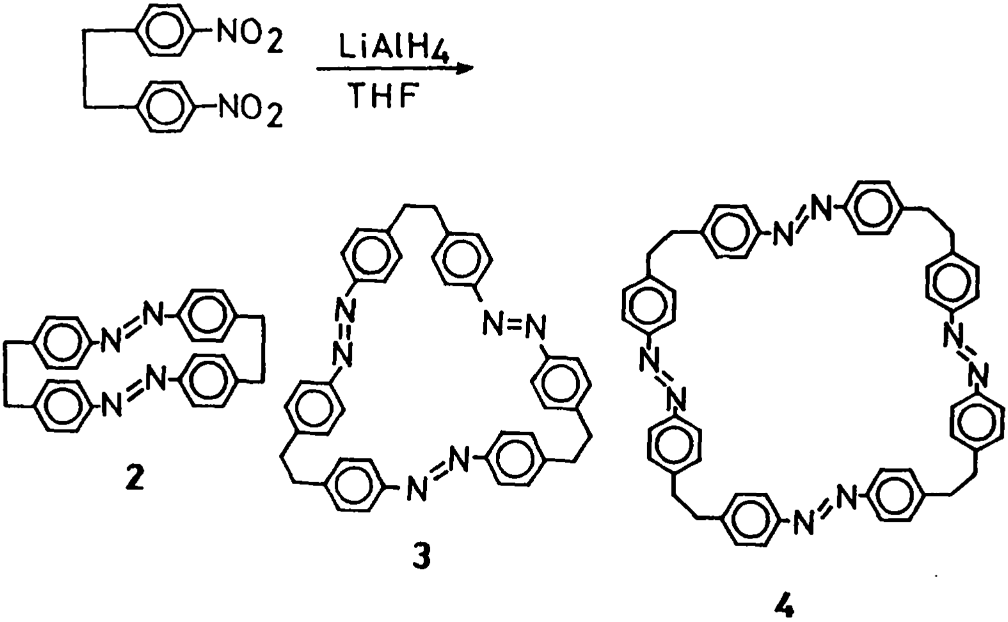
It would be true for [n.n](4,4')azobenzenophane series that the shorter the length of the bridges on both sides of the frame are, the more significant the effect of the other azobenzene unit on the isomerization rate is. In the extreme case, the conformation in which the azobenzene unit on one side is trans and the other is cis (tc) may not exist because of too large ring strain. In this article, we report a simple route to sythesize 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 paper. 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-Hexaaza-[2_4](4,4')cyclophane-1,17-diene 2 and two larger macrocycles 3 and 4 (1,2,17,18,33,34-hexaaza-[2_6](4,4')cyclophane-1,17,33-triene, 1,2,17,18,33,34,48,49-octaaza-[2_8](4,4')cyclophane-1,17,33,48-tetraene, respectively) were synthesized according to scheme 1. A 9.6g(35 mmol) sample of 1,2-bis(4'-nitrophenyl)ethane, which was synthesized by the oxidation of 4-nitrotoluene[6], in 240ml dry THF was added dropwise in 3 h to a suspension of 6.7 g(180 mmol) of $LiAlH_4$ in

Scheme 1.



400ml of dry THF under a nitrogen atmosphere. After the reaction mixture being stirred for 21 h, 200ml 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 ^{1}H-n.m.r., FD-MS and satisfactory elemental analyses. 2: 22mg(0.30%); m.p. above 305°C; mass spectrum, m/e 416(M+). Anal. Calcd. for $C_{28}H_{24}N_4$: C, 80.74; H, 5.80; N, 13.45. Found: C, 80.65; H, 5.69; N, 13.01. 3: 38mg(0.52%); m.p. 286-288°C; mass spectrum, m/e 624(M+). Anal. Calcd. for $C_{42}H_{36}N_6$ 1/2CH_2Cl_2[7]: C, 76.50; H, 5.59; N, 12.59. Found: C, 76.21; H, 5.81; N, 12.38. 4: 17mg(0.23%); m.p. above 305°C; mass spectrum, m/e 832(M+) Anal. Calcd. for $C_{56}H_{24}N_8$ 1/2CH_2Cl_2[7]: 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. $C_{28}H_{24}N_4$, FW=416.5, monoclinic, space group $P2_1/a$, a=10.87(1)Å, b=15.29(1)Å, c=6.831(4)Å, β=99.39(9)°, U=1120(2)$Å^3$, D_x=1.234g cm^{-3}, Z=4(Z=1/2 mol), (Cu K_α)=1.54A. X-ray diffraction data were obtained on a four-circle diffractmeter (Rigaku AFC-5) using Cu K_α 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-78[8] (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 specrophotometrically 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 366nm light with a high-pressure mercury lamp (Ushio-UM-452, 450W) 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 specrophotometer and monitored the changes in absorbance at 328nm as a function of time by a recorder at a chart speed of 48cm/min. A fast change in absorbance ceased in only 15min. at 5°C (this temperature was the lower limit in our experiments). In both isomerization processes (cc→tc and tc→tt), the absorbance against time satisfied a first-order kinetics.

Measurements of light intensity dependence

Photoirradiation was performed at 25±2°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]cyclophanes[9]. 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 $TiCl_4$[10]. 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.

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

compd	$\pi\pi^*$[a]		$n\pi^*$[a]		^1H-NMR[b] δ/ppm	
no.	$\varepsilon(\lambda_{max})$	ε/unit	$\varepsilon(\lambda_{max})$	ε/unit	CH_2	Arom.
2	41300(328)	20700	2400(462)	1200	3.02	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	880(442)	880	2.38	7.24,7.76

[a] In benzene. [b] In $CDCl_3$.

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 sifts 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 transanular distance decreases[11]. The magnitude of change in δ value among the three macrocycles is larger for the protons at metha 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 π 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 seem 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°[12]. 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

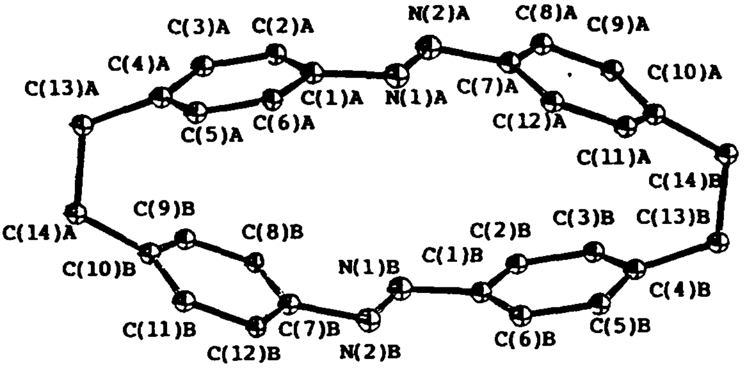


Figure 1 X-ray crystal structure of 2.

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 Tortional 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)

considered for the conformation of the transition state of azobenzene[13],. 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 1.234Å which is not longer than the distances for trans-azobenzene (1.247Å)[14] and 5 (1.244Å)[15]. 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°)[14] and 5 (113.8°)[15].

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 isomerization[13]. 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 366nm light exposure[16]. The absorption spectra of 2 before exposure and at 366nm photostationary state are shown in figure 2. At the photostationary state, 88% of the initial absorbance at 328nm (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 440nm). 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

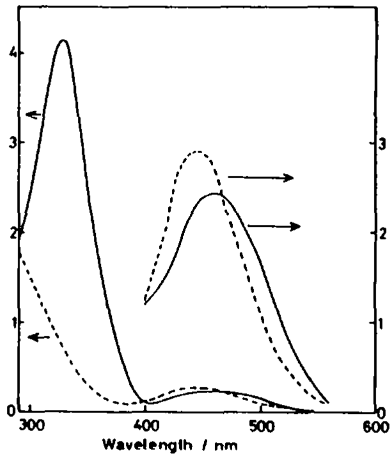


Figure 2 Initial (——) and 366nm photostationary state (----) absorption spectra of 2 in benzene.

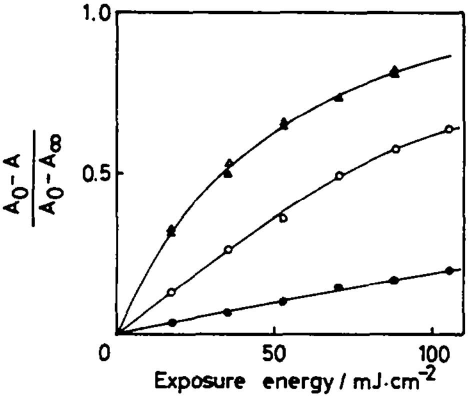


Figure 3 Change of absorbance at $\pi\pi^*$ transition band with exporsure energy using different intensity of light. (○) 2, 882 μW/cm^2; (●) 2, 88.2 μW/cm^2; (△) 5, 882 μW/cm^2; (▲) 5, 88.2 μW/cm^2.

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 366nm by slow thermal isomerization or by 436nm irradiation.

Rau et al. have observed relatively rapid (τ_{298}=6.25min) ct→tt thermal isomerization for [3.3](4,4')azobenzenophane 1[3c]. A similar process of thermal isomerization is expected for [2.2](4,4')azobenzenophane 2, too. Immediately after irradiation by 366nm light at an arbitrary extent, a small amount of rapid thermal recovery of the spectrum is observed for 2. This ct→tt thermal isomerization process is very rapid, but the change of the absorbance at 328nm can be monitored by an usual spectrophotometer below 298K. Spectroscopically determined first-order rate constants and thermodynamic data of cc→tc and tc→tt for 2 are listed with those of c→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→t for ever known azobenzene derivatives without polar substituents[17]. The life time of tc is calculated from the rate constant to be only 22s at 298K , 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 3.5Å longer than that for cis azobenzene[14,18]. To estimate the additional destabilization of the tc conformation, molecular mechanics calculations (MMP2)[19] 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

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/Kcal mol^{-1}	$\Delta S^{\ddagger}_{298}$/cal K^{-1}
2	tc→tt	4.54×10^{-2}	14.0	-19.8
	cc→tc	4.53×10^{-6}	22.2	-10.5
5	c→t	4.53×10^{-6}[a]	21.7[a]	-12.0[a]

[a] From lit. 17.

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 dependent[20]. Figure 3 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→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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