participate in determining the spectrum of the chromophore. It is plausible that a change in distance between the polyene and a protein negative charge which causes the red shift in batho is reversed upon forming BSI. Consistent with this idea are linear dichroism measurements[52] showing that both rho → batho and batho → BSI transitions are associated with major changes in the orientation of the polyene chromophore.

Given its blue-shift, it is interesting that the BSI intermediate lies 3 kcal/mol above the batho intermediate. This calls into question earlier suggestions[6,7,16,18] that the red shift and energy storage are essentially associated with the same mechanism. One might then ask at what stage after formation of the primary photoproduct the energy stored in chromophore–protein interactions is transferred to the protein. One possibility is that energy storage is not associated at all with the chromophore, namely that energy has been channeled into the protein as early as the stage of batho or even photo. Alternatively, energy stored in the chromophore at the batho stage may be transmitted to the protein as batho is converted to BSI. This is consistent with the disappearance of chromophore HOOP modes detected by FTIR and with the blue-shifted absorption of BSI. This may be due to relief of strain in the chromophore. Presumably the relaxation of this strain in BSI would lead to reduction of the large, negative circular dichroism of batho[53] (potentially measurable in the case of the pigments where BSI forms at low temperatures) in keeping with the FTIR data of Gartner et al.[47] Such a model could also provide the moving force for the protein change required to move to the lumi stage. This could be provided directly by the contacts which store the strain energy in BSI. Alternatively, it could result from protein movement into void space potentially opened by distortion of BSI along one wall of the pocket. Either of these mechanisms could plausibly trigger protein change prevented by the presence of the better fitting cis chromophores.

Finally, the fact that the batho ⇄ BSI equilibrium favors BSI is particularly interesting in light of the fact that there is a 3 kcal positive enthalpy difference between these two states. This dictates that this reaction be entropically driven. This situation could arise from protein changes at the BSI stage, but protein changes need not be invoked. Many lines of evidence show that the chromophore is in a twisted strained conformation at the batho stage, and plausibly it is in a more relaxed conformation at the BSI stage. This would give it more degrees of freedom in BSI thus making BSI a higher entropy state. Synthetic chromophore structural changes might then affect the batho enthalpy relative to the transition state and BSI so that the rate of batho to BSI would be accelerated while the back reaction would be less affected. Further work is needed to test these possibilities for spectral and kinetic properties of these intermediates.

Acknowledgment. The authors thank Prof. R. S. H. Liu for the gift of 11-*cis*- and 9-*cis*-13-desmethylretinals. This research was supported by a grant from the Eye Institute of the National Institutes of Health (EY 00983) and by the U.S.-Israel Binational Science Foundation and by the fund for basic research (administered by the Israel Academy of Sciences and Humanities).

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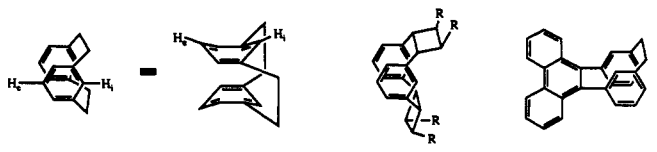
Intramolecular [2 + 2] Photocycloaddition. 10.[1] Conformationally Stable *syn*-[2.2]Metacyclophanes

Jun Nishimura,* Yoichiro Horikoshi, Yasuhiro Wada, Hideo Takahashi, and Mitsuo Sato

Contribution from the Department of Chemistry, Faculty of Engineering, Gunma University, Tenjin-cho, Kiryu 376, Japan. *Received September 20, 1990*

Abstract: Three isomerized 1,2:9,10-diethano-*syn*-[2.2]metacyclophanes **5**, **6**, and **7** were prepared from *cis*-1,2-bis(*m*-vinylphenyl)cyclobutane by photocycloaddition. Their yields were 10, 5, and 3%, respectively. ^{1}H NMR chemical shifts of aromatic protons for cyclophane **5** clearly suggest the syn conformation. It has a rigid structure, according to its VT NMR spectra. The structure was thoroughly analyzed by X-ray crystallography. It became clear that the aromatic nuclei of this syn conformer are not arranged parallel but tilted by ca. 31-34° toward each other. Since the MM2 calculation for parent *syn*-[2.2]metacyclophane (**1**), as well as compounds **5**, **6**, and **7**, gives the tilted structure, the cyclobutane ring systems are not responsible for tilting. Therefore, these cyclobutane-fused compounds are concluded to be good models for *syn*-[2.2]-metacyclophane (**1**), whose structure has not been fully explored in detail yet. Cyclophanes **6** and **7** are also concluded to have syn conformation. Their structures were determined by NMR experiments and UV spectroscopy. Their conformations are stable in a solid state, yet in a solution (in $CDCl_3$, benzene, etc.) they slowly interconverted to each other. The initial rates were 0.29×10^{-6} and 0.44×10^{-6} s^{-1} at 20 °C for **6** and **7**, respectively. At 20 °C, the isomer ratio of **6** to **7** was 60:40 at equilibrium. The conformational change should occur through an unstable, probably short-lived anti conformer that could not have been detected yet. The mechanisms for the interconversion and also for the photocycloaddition are proposed.

syn-[2.2]Metacyclophane (**1**), being unknown for a long time, was finally prepared by Mitchell and his co-workers,[2] using a chromium tricarbonyl complex in the ring-contraction step. The compound was reported to be conformationally stable at low temperatures but to change its conformation to a more stable anti one at higher than 0 °C. Its X-ray crystallographic analysis has not been achieved yet. Naturally, it is not denied that it would be possible at a reduced temperature. Fusing cyclobutane rings at the tethers seems to be one of the ways to make this syn



1 2 3

R=Ph, Napht, COOMe

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Table I. ^{13}C NMR Spectroscopic Data of Diethano[2.2]metacyclophanes[a]

cyclophane	carbon									
	3 (15)	7 (11)	8 (16)	5 (13)	4 (14)	6 (12)	1 (2)	9 (10)	17 (18)	19 (20)
5	139.47	139.42	128.15	131.97	122.83	125.46	49.07	48.05	20.76	20.91
6	139.56	*C3 (15)*	128.26	135.14	122.29	*C4 (14)*	48.03	*C1 (2)*	20.60	*C17 (18)*
7	139.48	*C3 (15)*	127.98	129.09	125.86	*C4 (14)*	48.88	*C1 (2)*	21.15	*C17 (18)*

[a] Peaks were assigned by DEPT and HETEROCOSY experiments. The numbers of identical carbons are indicated in parentheses.

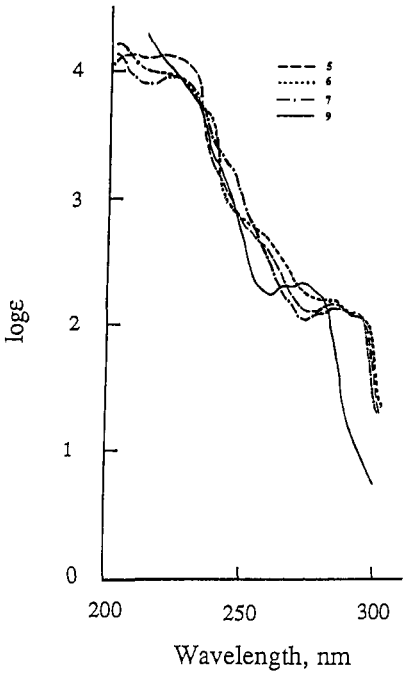


Figure 1. Electronic spectra of cyclophanes **5**, **6**, **7**, and **9**.

conformation more stable than the counterpart, although cyclophanes connected with simple cyclobutane rings had not been reported. Müller and his associates prepared 1,2:9,10-bis(diphenylethano)-*syn*-[2.2]metacyclophane (**2**, R = Ph) by means of [2 + 2] photocycloaddition of *m*-distyrylbenzene.[3] Three isomers obtained were concluded to have syn conformation by the ^1H NMR spectroscopy. Quite recently, Meier and his associates reported the synthesis and properties of several diethano-*syn*-[2.2]metacyclophane derivatives **2** by the same technique.[4] Moreover, Lai and Lee disclosed the route to obtain the elusive *syn*-[2.2]metacyclophan-1-ene by its fusion to a phenanthrene skeleton (**3**).[5] On the other hand, it has been clarified in our laboratories that only one cyclobutane ring fused at a tether of [2.2]metacyclophane is not sufficient to keep the conformation in the syn direction.[6]

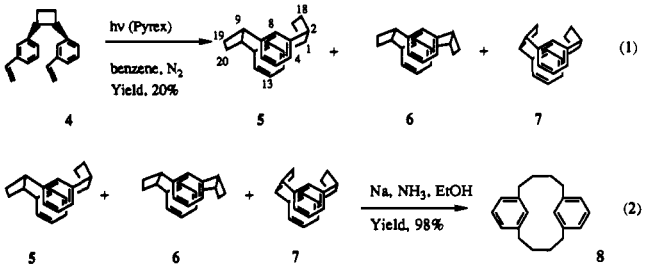
We were prompted by these reports to make more simple, yet conformationally stable, *syn*-[2.2]metacyclophanes by using our photochemical approach[7] and to prove that the simple cyclobutane rings can lock it in the conformation. We found the formation of three isomerized 1,2:9,10-diethano-*syn*-[2.2]metacyclophanes from *cis*-1,2-bis(*m*-vinylphenyl)cyclobutane under photoirradiation, so in this paper we would like to report the synthesis, structural elucidation, and unique properties of these simple *syn*-[2.2]-metacyclophanes obtained.

Results and Discussion

Synthesis of Cyclophanes 5, 6, and 7. The synthesis of olefin **4** has been improved since reported preliminarily.[8] Recently, we could cleave the ether linkage of *cis*-1,2-ethano-11-oxa[2.5]-metacyclophane, which strongly resists the attack of trimethylsilyl cation,[8] using a smaller attacking species (HBr in acetic acid) to give the corresponding bromide in a 66% yield.

The easier route to olefin **4** has been achieved; i.e., the commercially available and purified *m*-divinylbenzene was irradiated in dry benzene under a nitrogen atmosphere by a 400-W high-pressure mercury lamp to smoothly afford olefin **4** and then slowly the final products **5**–**7**. Although the synthesis of cyclophanes **5**–**7** can be carried out directly from *m*-divinylbenzene, the better overall yield was recorded by the stepwise procedure with use of the purified olefin **4**.

Olefin **4** gave the desired metacyclophanes under irradiation as shown in eq 1. Products **5**, **6**, and **7** were isolated by column chromatography (SiO_2, hexane) from the reaction mixture after hydroboration[7] and finally purified by reversed-phase HPLC (C18 reversed-phase, 15 μ, MeOH). Their yields were 10, 5, and 3%, respectively. They are easily and quantitatively converted to [4.4]metacyclophane (**8**) by Birch reduction.[8]



NMR Spectroscopic Analysis. ^1H NMR chemical shifts of aromatic protons of cyclophane **5** clearly suggest the syn conformation, since the $\Delta\delta$ value[9] ($\delta_{H_i} - \delta_{H_e}$; see structure **1** for the proton designation) is 0. It has a rigid skeleton, since its VT NMR spectra show little change in the range of −90 °C to room temperature.[10] Cyclophane **7** shows the $\Delta\delta$ value of 0.62, so it also can be concluded to have syn conformation unambiguously. On the other hand, the $\Delta\delta$ value of cyclophane **6** is negative (−0.57) and appears to suggest its anti conformation at the first glance, which is inconsistent with the symmetrical feature of ^1H and ^{13}C NMR spectra (vide infra) as well as the chemical shifts of the protons H_i and H_e.

According to the ^1H NMR chemical shifts of four cyclobutane methine protons (δ 4.20 and 4.17 for **6** and **7**, respectively), compounds **6** and **7** possess cis cyclobutane rings.[6] Moreover, they should have C_2 axes besides the symmetry plane, because there is only one symmetrical multiplet signal for the methines and there are also only six ^{13}C NMR signals for twenty carbons (see Table I). Therefore, both **6** and **7** are of syn conformation. On the other hand, compound **5**, with two different methine signals (δ 4.31 and 4.12) and ten ^{13}C NMR signals, does not have such a symmetry axis as recognized by the structure depicted in eq 1.

The direction of the cyclobutane rings was determined by NOESY experiments, after all proton signals were assigned by COSY experiments. In these cyclophanes, the NOE interaction is apt to appear clearly between the cyclobutane methine proton and the aromatic proton. Concerning the spectrum of **5**, both methine signals at δ 4.31 and 4.12 have the NOE interactions with

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(10) Available in the supplementary material.

Table II. Isomer Distribution of Cyclophane **2**

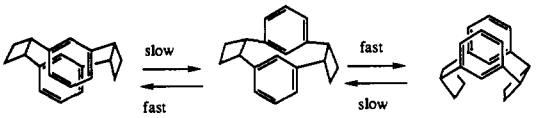
R	yield (%)	isomer distribution (%) exo,endo	endo,endo	exo,exo	ref
H	18	56[a] (56)[b]	28[c] (26)[b]	16[d] (18)[b]	this work
Ph	59	50	45	5	4a,b
2-napht	53	66	31	3	4b
CO_2CH_3	53	64 (64)[e]	16 (27)[e]	20 (9)[e]	4b

[a] For compound **5**. [b] At equilibrium at 20 °C. [c] For compound **6**. [d] For compound **7**. [e] Values in the parentheses were obtained after a chloroform solution of the isomer mixture had stood untouched for a long time.

H8 (H16) and H4 (H14), respectively. The methine signals (δ 4.19) of **6** have the interaction with only H8 (H16) and those of **7** with only H4 (H14). Therefore, compounds **5**, **6**, and **7** are concluded endo,exo, endo,endo, and exo,exo isomers, respectively, as depicted in eq 1.

UV Spectroscopy. Electronic spectra of cyclophanes **5**, **6**, and **7** are depicted in Figure 1, together with that of *anti*-[2.2]-metacyclophane (**9**).[11] Reflecting the better overlapping of the aromatic rings in **5**, **6**, and **7** than in **9**, whole bands become broader and shift remarkably bathochromically. Among the cyclophanes obtained in this work, the shift increases in the order of **6** > **5** > **7**.

Isomerization between Cyclophanes 6 and 7 and the Mechanism of Reaction 1. Their syn conformations are observed to be stable in a solid state and actually did not change their form for a long period (at least for several months under the ordinary conditions). In a solution (in $CDCl_3$, benzene, etc.), however, they slowly interconverted to each other. The phenomenon is just like one observed by Meier and his associates.[4] The initial rates were 0.29×10^{-6} and 0.44×10^{-6} s^{-1} at 20 °C for **6** and **7**, respectively. At 20 °C, equilibrium was attained after 40 days and the isomer ratio of 6 to 7 was 60:40 at equilibrium. The ratio slightly changed to 58:42 and 57:43 at 40 and 60 °C, respectively. In order to avoid the effect of light, the experiments were carried out in the dark. Therefore, a photochemical [2 + 2] cycloreversion is excluded for this conformational conversion. The fact that compound **5** was not detected in the equilibrating mixture of compounds **6** and **7** also supports the conclusion. Accordingly, the conformational change should occur through an unstable, probably short-lived anticonformer **10**, which could not have been detected yet. The mechanism is believed to occur as shown in eq 3.



6 10 7 (3)

anti-Cyclophane **10** was calculated by the MM2 method to have larger steric energies by 1–5 kcal/mole than those of their syn isomers **6** and **7**. As far as the steric energies are concerned, it is quite possible for **10** to participate in the interconversion as an intermediate. According to their structures calculated, the deformation of cyclobutane rings seems to be the major factor for making them unstable, caused by enlarging the dihedral angles at the tethers (for **10**, 33° around H1–C1–C2–H2 and H9–C9–C10–H10; see also Table III for the angles of other syn isomers).

The isomer distribution of cyclophanes **2**, including **5**–**7**, is summarized in Table II. Despite the substituents, all photocyclizations gave exo,endo isomers as major products.

We have already concluded that the photocycloaddition of styrene derivatives in benzene proceeds through excited singlet states.[12] For the analysis of the diastereoselectivity of such a photoreaction in general, the nonequilibration of excited-state rotamers (NEER) principle is commonly used, which was first advanced by Havinga[13] and then studied by Dauben,[14] Baldwin,[15] and others.[16]

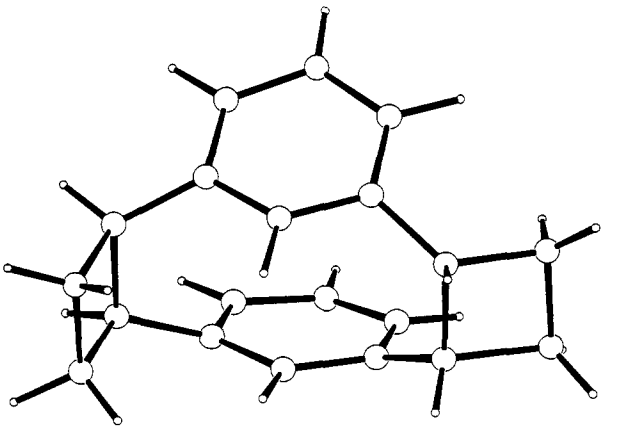


Figure 2. ORTEP drawing of the structure of **5** (R = 0.0705).

Three rotamers of olefin **4**, namely, each for the precursors of **5**, **6**, and **7**, were calculated by the MM2 method to evaluate their steric energies, as well as cyclophanes **5**, **6**, and **7**. The steric energy differences were 0.0, 0.6, and 1.1 kcal/mol for the precursors of **5**, **6**, and **7**, respectively, while they were 2.2, 0.0, 4.2 kcal/mol for cyclophanes **5**, **6**, and **7** themselves, respectively. Accordingly, the product composition analyzed soon after the workup procedure is qualitatively well correlated with the rotamer composition estimated by the MM2 but not with the steric energies of the cyclophanes produced. The tendency is consistent with what is predicted by the NEER principle that the various conformers of the excited singlet of the olefin cannot interconvert within the lifetime of that state. Hence, the mechanism that each excited rotamer fails into a corresponding product cyclophane without the interconversion to other rotamers is proposed for the present reaction, on the basis of above findings.

X-ray Crystallographic Analysis. Since compounds **6** and **7** interconvert to each other and their single crystals have not been obtained yet, only the structure of cyclophane **5** was examined by an X-ray crystallographic method. The single crystal of **5** has two crystallographically independent molecules. Both molecules a and b have almost the same characteristics, but strictly speaking, the former is the more eclipsed one along C1,2 and C9,10 than the latter. The ORTEP drawing of molecule a is depicted in Figure 2 as a representative model. As any crystallographic data of *syn*-[2.2]metacyclophane (**1**) have not been reported, this is the first one examined thoroughly without introducing any large substituents at aromatic nuclei[17] or the complex formation[1c] to decelerate the conformational flipping motion.

As shown in Figure 2, the aromatic nuclei of the syn conformer are not arranged parallel but considerably tilted from each other. Since the MM2 calculation of *syn*-[2.2]metacyclophane (**1**), as well as compounds **5**, **6**, and **7**, gives the tilted structure,[10] the cyclobutane ring systems are not responsible for tilting. Although the small rings should influence the structure to some extent, structure **5** seems to reflect most characteristics of *syn*-[2.2]-metacyclophane (**1**) (vide infra). Selected bond angles, bond

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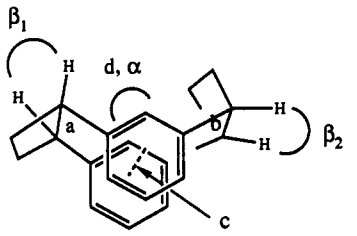
Table III. Dihedral Angles and Bond Lenghts of *syn*-[2.2]Metacyclophane and Other Cyclophanes Prepared[a]

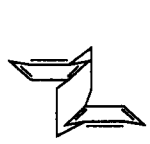


compd	bond length (Å)				dihedral angle (deg)		
	a	*b*	*c*	*d*	α	β_1	β_2
5	1.61[b]	1.60[c]	3.14	2.54	34.0	19.85[b]	9.73[c]
molecule a	(1.60)	(1.62)	(3.27)	(2.69)	(31.5)	(9.97)	(0.67)
molecule b	(1.59)	(1.62)	(3.30)	(2.71)	(33.6)	(23.98)	(9.77)
6	1.61[b]		3.21	2.54	39.5	20.90[b]	20.89[b]
7	1.61[c]		3.07	2.53	31.9	9.74[c]	9.66[c]
1	1.58		3.01	2.52	28.9	11.24	11.03
11[d]	*e*		(3.19)	(2.662)	(28.8)	(35)	(35)

[a] Data from X-ray crystallographic analysis are given in parentheses. Other values were calculated by the MM2 method. [b] For endo cyclobutane ring. [c] For exo cyclobutane ring. [d] Reference 2. [e] See supplementary material of ref 2.

lengths, and interatomic distances of these compounds are listed in Table III.

The interdeck distance between the centers of the two aromatic rings is 3.27 (3.30) Å,[18] which is 0.08 and 0.18 Å longer than those in *syn*-[2.2]metacyclophane–chromium tricarbonyl complex **11**[1c] and [2.2]paracyclophane,[19] respectively. The closest distance



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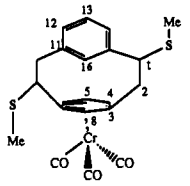
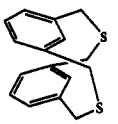


11



12

between the two aromatic rings is recorded between the two internal carbon atoms C8 and C16 and is 2.69 (2.71) Å,[18] which is again longer by 0.03–0.05 Å than that of complex **11** (2.662 Å)[1c] and the C8–C16 distance in *anti*-[2.2]metacyclophane (**9**) (2.633 Å)[20] but shorter by 0.09 Å than the shortest distance between the rings in [2.2]paracyclophane.[21]

As well as the boat-type aromatic rings in **9**[20] and complex **11**,[1c] the characteristic boat-type deformation is observed in the *syn*-cyclophane **5**. The "stern" atoms C8 and C16 are 0.099 (0.13)[18] and 0.12 (0.14)[18] Å outside the plane defined by C3,4,6,7 and C11,12,14,15, respectively. The exterior atoms C5 and C13 are about 0.06 (0.05)[18] Å outside the above planes, respectively. The corresponding values for these four atoms in complex **11** are 0.085, 0.073, 0.06, and 0.06 Å and in *anti*-metacyclophane **9** for C5 and C8 are 0.042 and 0.143 Å, respectively.[20]

One can expect that the donor–acceptor interaction between the electron-deficient aromatic nucleus caused by chromium tricarbonyl complexation and the other aromatic nucleus affects the syn structure of **11**, compared with that of an electronically nonperturbed cyclophane like **5**. This effect actually appears at the deformation around C8 and C16; i.e., they can approach closer in **11** than **5**, and the deformation at C16 is much more in **5** than **11**, because electron-repulsive force working around C8 and C16 is reduced in **11**. Accordingly, cyclophane **5** seems to be a more pertinent model for parent *syn*-[2.2]metacyclophane (**1**) than **11**.

The mean planes of the two aromatic rings of **5** are inclined at an angle of 31.5° (33.6°)[18] to each other, which is greater than those in complex **11** (28.8°)[1c] and *syn*-[3.3]cyclophane **12** (20.6°).[22] The torsional angles about the two ethano bridges of **5** were calculated and listed in Table III. While the dihedral angle between H17 and $H21_{eq}$ in complex **11** was reported to open to 35° wide, those between H1 and H2 and between H9 and H10 are small (10° (24°)[18] and 1° (10°) Å,[18] respectively). As far as the dihedral angles are concerned, the MM2-calculated model fits molecule b more than molecule a. It is believed that molecule a is affected by the lattice energy of the crystal but molecule b is relatively free from the energy in the crystal.

Several X-ray crystallographic analyses of cyclobutane derivatives have been reported.[23] Their conclusions are as follows: When the cyclobutane ring is not centrosymmetrically substituted like the present molecule, the ring is almost always puckered. On the other hand, most, but not all, of the centrosymmetrically substituted rings have the planar forms. The angle, defined between normals to two three-carbon planes with the transannular distance common to both planes in the puckered ring, is reported from 19° to 35°,[23c,d] depending on the substituents at the ring, but most likely is around 22°. The cyclobutane rings of cyclophane **5** have 3° for the exo one and 11° for the endo one of molecule a and 6° for the exo one and 19° for the endo one of molecule b. Endo cyclobutane rings are said to be more puckered than exo ones, although generally they are more planar than other non-centrosymmetrically substituted cyclobutane rings.

Most of ring C–C bond lengths lie in the region of 1.547–1.580 Å, and the reasons for the long bonds were given.[24] Although long bonds are usually the case, an even shorter bond of 1.517 Å has been reported.[25] Interestingly, the cyclophane **5** has a variety of ring C–C bonds from 1.516 to 1.620 Å, which show the tendency of long inner bonds (1.620 Å), common middle bonds, and short outer bonds (1.520 Å), mainly caused by the intrinsic cyclophane strain. The interior angles of cyclobutane rings are around 90° (88.0–92.3°), but of course they are narrower for inner ones than those for outer ones in response to the bond lengths.

Consequently, conformationally stable simple *syn*-[2.2]metacyclophane derivatives were synthesized by intramolecular photocycloaddition, and their conformational stability is due to cyclobutane rings attached at their tethers. X-ray crystallographic analysis of cyclophane **5** shows that the two aromatic rings are

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not parallel but inclined at 31.5–33.6° to each other in the syn conformation, and moreover the aromatic rings are in the boat-form.

Experimental Section

General Methods. Elemental analysis was carried out at the Microanalysis Center of Gunma University. UV spectra were taken on a Shimadzu UV-200S spectrophotometer. NMR spectra were recorded on a Varian Gemini-200 FT NMR spectrometer. Melting points were not corrected.

Materials. Benzene and THF were purified by distillation over Na after prolonged reflux under a nitrogen atmosphere. Other highest grade commercially available reagents were used without further purification, unless otherwise noted.

Synthesis of 1,2-Ethano-11,14-dioxa[2.8]metacyclophanes.[7] 1,8-Bis(*m*-vinylphenyl)-3,6-dioxaoctane[8] (0.53 g, 1.64 mmol) was irradiated in dry benzene (500 mL) under a nitrogen atmosphere for 12 h with a 400-W high-pressure mercury lamp through a Pyrex filter (>280 nm). After evaporation, the reaction mixture was treated with 10 mL of 1 M BH_3–THF solution, stirred for 10 h, and added to 10 mL of methanol. The mixture was condensed by evaporation and dissolved in benzene. The products were purified by column chromatography (SiO_2, benzene).

The desired cyclophanes were isolated by HPLC (C18 reversed-phase, 15 μ, MeOH). *cis*-Dioxametacyclophane[8] (oil, 0.14 g, 26%) and *trans*-dioxametacyclophane (mp 77–78 °C; 0.03 g, 6%) were obtained.

In the same procedure as above, *cis*-1,2-ethano-11-oxa[2.5]metacyclophane was prepared from 1,5-bis(*m*-vinylphenyl)-3-oxapentane in a 56% yield. The reaction gave *cis*-1,2-ethano-11-oxa[2.5]metacyclophane exclusively.[8]

Cleavage of Dioxacyclophanes at the Linkage. *cis*-Dioxametacyclophane mentioned above (0.28 g, 0.87 mmol) was treated with trimethylsilyl iodide[26] (generated in situ from 0.52 g of NaI and 0.38 g of trimethylsilyl chloride) in 20 mL of acetonitrile under a nitrogen atmosphere at 50 °C for 30 h with stirring. The reaction mixture was poured into water and extracted with benzene. The combined organic solution was washed with aqueous $NaHSO_3$ and water, dried over $MgSO_4$, and evaporated in vacuo. The residue on column chromatography (SiO_2, hexane) afforded the corresponding iodide[8] **13** (0.38 g, 82%) as an oil.

cis-1,2-Ethano-11-oxa[2.5]metacyclophane (0.510 g, 1.83 mmol) and 47% HBr (20 mL) were dissolved in 20 mL of acetic acid and stirred at 100 °C for 95 h.[27] After it had cooled, the reaction mixture was extracted by benzene three times. The combined organic solution was neutralized with aqueous $NaHCO_3$, washed with water, and dried over $MgSO_4$. After evaporation, the corresponding bromide **4** was isolated by column chromatography (SiO_2, hexane). Yield was 0.509 g (1.21 mmol, 65.9%).

E2 Elimination of Iodide 13 toward Olefin 4.[28] Sodium metal (0.5 g) was dissolved in the mixed solvent of dry *tert*-butyl alcohol (20 mL) and dry ether (5 mL) under a nitrogen atmosphere. Iodide **13**[8] (0.64 g, 1.24 mmol), dissolved in 2 mL of ether, was added into this sodium *tert*-butoxide solution slowly. The mixture was stirred at 60 °C for 6 h. It was poured into water and extracted with benzene. The combined organic layer was washed with water, dried over $MgSO_4$, and evaporated in vacuo. The residue on column chromatography (SiO_2, hexane) afforded olefin **4** (0.31 g, 97%). Bromide **14** gave the same result as above: ^1H NMR ($CDCl_3$; δ (multiplicity, coupling constant *J* (Hz), intensity)) δ 7.00 (6 H, m), 6.79 (2 H, m), 6.55 (2 H, dd, 17.6, 10.7) 5.53 (2 H, dd, 17.6, 1.1), 5.09 (2 H, dd, 10.8, 1.1), 3.97 (2 H, m), 2.43 (4 H, m); ^{13}C NMR ($CDCl_3$) δ 141.7, 137.2, 137.1, 127.9, 127.6, 125.7, 123.7, 113.3, 45.0, 24.1.

Photocyclodimerization of *m*-Divinylbenzene toward Olefin 4. The commercially available and purified *m*-divinylbenzene (1.0 g, 7.68 mmol) was irradiated in dry benzene (700 mL) under a nitrogen atmosphere by a 400-W high-pressure mercury lamp for 10 h to afford olefin **4** in a 65% conversion and then slowly the final products **5**–**7**. After the irradiation, the reaction mixture was evaporated. On column chromatography (SiO_2, hexane), **4** was obtained as oil in a 42% yield.

Photocycloaddition toward Diethano[2.2]metacyclophanes 5–7. Olefin **4** (0.37 g, 1.42 mmol), dissolved in dry benzene, was irradiated by the high-pressure mercury lamp under a nitrogen atmosphere for 12 h. After evaporation, the reaction mixture was treated with 1 M BH_3–THF solution and stirred for 15 h. Evaporation in vacuo left a residue that, on column chromatography (SiO_2, hexane), afforded the mixture of three diethano[2.2]metacyclophanes. Cyclophanes **5**, **6**, and **7** were isolated by HPLC (C18 reversed-phase, 15 μ, MeOH) in 10% (0.037 g), 5% (0.018 g), and 3% (0.011 g) yield, respectively.

Cyclophane 5: mp 117.1–118.2 °C; ^1H NMR ($CDCl_3$; δ (multiplicity, coupling constant *J* (Hz), intensity)) δ 6.68 (2 H, s), 6.68 (2 H, t, 7.4), 6.62 (2 H, dt, 7.4, 1.5), 6.28 (2 H, dt, 7.4, 1.5), 4.31 (2 H, m), 4.12 (2 H, m), 2.48 (8 H, m). Anal. Calcd (found): C, 92.26 (92.14); H, 7.74 (7.86).

Cyclophane 6: mp 181.1–181.7 °C; ^1H NMR ($CDCl_3$; δ (multiplicity, coupling constant *J* (Hz), intensity)) δ 6.81 (2 H, t, 7.7), 6.57 (4 H, dd, 7.7, 1.7), 6.24 (2 H, t, 1.7), 4.19 (4 H, m), 2.43 (8 H, m). Anal. Calcd (found): C, 92.26 (92.32); H, 7.74 (7.68).

Cyclophane 7: mp 183.2–183.9 °C; ^1H NMR ($CDCl_3$; δ (multiplicity, coupling constant *J* (Hz), intensity)) δ 7.18 (2 H, t, 1.6), 6.53 (2 H, dd, 8.3, 6.8), 6.33 (2 H, dd, 6.8, 1.6), 6.32 (2 H, dd, 8.3, 1.6), 4.17 (4 H, m), 2.64 (8 H, m). Anal. Calcd (found): C, 92.26 (92.48); H, 7.74 (7.52).

Measurement of Equilibrium. Purified cyclophane **6** or **7** (10 mg, 0.038 mmol) was dissolved in 80 mL of MeOH in a 100-mL flask. The flask was sealed, covered with aluminum foil, and maintained in a thermostat. The content of **6** and **7** was determined by HPLC (C18 reversed-phase, 15 μ, MeOH). Data of typical runs are available.[10] At higher temperature (60 °C), little decomposition of the cyclophanes was observed.

X-ray Crystallographic Analysis of Cyclophane 5 ($C_{20}H_{20}$; M = **260.382.** The crystal belongs to the monoclinic system, space group $P2_1/n$, Z = 8. Cell parameters are a = 21.04 (2) Å, b = 8.369 (2) Å, c = 16.296 (6) Å, β = 90.33 (4)°, V = 2869.0 Å^3, d_c = 1.20 g cm^{-3}, and λ (Mo Kα) = 0.71073 Å. Diffractometric intensity data were obtained from a crystal of 0.4 × 0.3 × 0.3 mm. From the 2420 unique reflections collected by the ω–2θ scan technique up to 2θ = 50°, only 2184 reflections were considered as observed having $F_o \geq 3\sigma F_o$ and kept in refinement calculations. The structures were solved by direct methods with use of SHELX[29] and refined by least squares, minimizing the function $\Sigma w(\Delta F)^2$. Most of the hydrogen atoms were located on difference Fourier maps. The final conventional R factor was 0.0705.

Lists of the atomic coordinates, bond distances and angles, and structure factors are available.[10]

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Supplementary Material Available: VT NMR spectra of **5**, figures of typical runs for the isomerization, structures calculated by MM2 for **1**, **5**, **6**, and **7**, and lists of the atomic coordinates, bond distances and angles, and structure numbering designations for X-ray crystallographic analysis of compound **5** (9 pages). Ordering information is given on any current masthead page.

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