Cationic Cyclocodimerization. 4.[1] Syntheses and Structures of [3.3]Metacyclophane Derivatives. Cyclization Controlled by an Orbital Interaction and a Steric Constraint

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Cationic cyclocodimerizations of α,ω-bis(*m*-vinylphenyl)alkanes and 1-(*m*-vinylphenyl)-3-(*p*-vinylphenyl)propane with some comonomers were carried out. The reactions of α,ω-bis(*m*-vinylphenyl)alkanes gave metacyclophanes in 30–59% yields. The structures of the metacyclophanes were determined by chemical shift differences between intraannular and extraannular protons, VT NMR spectroscopic measurements, and NOE experiments. Cyclocodimerizations of 1,3-bis(*m*-vinylphenyl)propane with several comonomers gave primarily two cyclophanes, although eight isomers are possible. Both 1,4-bis(*m*-vinylphenyl)butane and 1,5-bis(*m*-vinylphenyl)pentane cyclocodimerized with styrene to form *exo,cis*-1-methyl-3-styryl-*anti*-[3.*n*]metacyclophane as the major product. This selectivity is explained by molecular orbital calculation and examination of molecular models. The stabilities of intramolecularly face-to-face associated cations are discussed in relation to the reaction mechanism.

Introduction

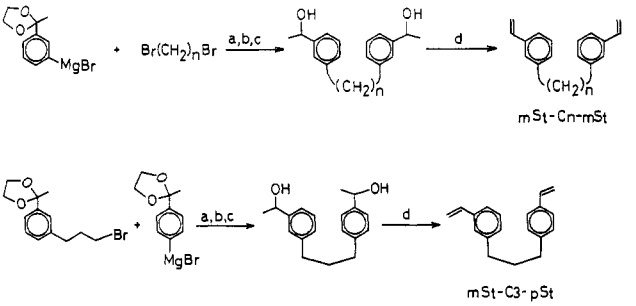
Electrostatic association between cationic species and electron-donating molecules is a general phenomenon.[2] We have been interested in the intramolecular complexation between styrene and styryl cation and have applied the complexation to cyclization, leading to the synthesis of [3.*n*]paracyclophane skeletons.[3] Several reactions that involve only a pseudo-ipso isomer of face-to-face cations have been reported (see Figure 1). These include cyclocodimerizations of 1,3-bis(*p*-vinylphenyl)propane,[3] 1,3-bis(4-vinylnaphthyl)propane,[1,4] and 1-(4-vinylnaphthyl)-3-(*p*-vinylphenyl)propane.[1,4]

Pseudo-ipso, pseudo-ortho, and pseudo-meta complexes between the styryl cation and styrene should have different stabilities. In order to clarify which complex cations can be formed[5] and their distribution in the reaction mixture, cationic cyclocodimerizations were carried out with the monomers α,ω-bis(*m*-vinylphenyl)alkane (*m*St-C*n*-*m*St)[6] and 1-(*m*-vinylphenyl)-3-(*p*-vinylphenyl)propane (*m*St-C3-*p*St), from which complex cations should be generated. We also hoped to develop cyclocodimerization as a widely applicable method for synthesizing cyclophane skeletons. In this paper we report a new synthesis of [3.*n*]metacyclophanes and discuss the mechanism, focusing on the stability of complex cations.

Results

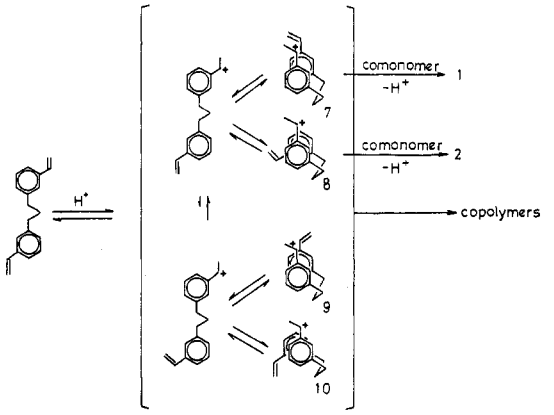
Cationic Cyclocodimerization of *m*St-C*n*-*m*St. Monomers *m*St-C*n*-*m*St (*n* = 3, 4, 5, and 6)[6] and *m*St-C3-*p*St were prepared according to the sequence shown in Scheme I. Pure monomers were obtained in reasonable yields (see Experimental Section) by a Grignard coupling[7] and a conventional dehydration.[8]

Scheme I. Preparation of Monomers[a]



[a] (a) CuBr/THF–HMPA; (b) HCl/DOX–H_2O; (c) $LiAlH_4$/ether; (d) $ZnCl_2$–CCl_3COOH–Me_2SO, 170 °C.

Scheme II. Mechanism



The cationic cyclocodimerizations of these monomers with the comonomers styrene, 2-phenylpropene, and 1,1-diphenylethylene were carried out by the reported procedure.[1,3] Results are listed in Table I. Monomers other than *m*St-C6-*m*St gave metacyclophanes in 30–59% yields. Monomer *m*St-C6-*m*St afforded only linear cooligomers because of the low cyclization tendency due to a longer

(1) Part 3: Nishimura, J.; Yamada, N.; Okuda, T.; Mukai, Y.; Hashiba, H.; Oku, A. *J. Org. Chem.* **1985**, *50*, 836.

(2) For example, see: (a) Williams, J. F. A. *Tetrahedron* **1962**, *18*, 1487. (b) Farnum, D. G. *J. Am. Chem. Soc.* **1967**, *89*, 2970. (c) Meyerson, S.; Leitch, L. C. *J. Am. Chem. Soc.* **1971**, *93*, 2244. (d) Sauvet, G.; Vairon, J. P.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1975**, *52*, 173. (e) Parker, V. D.; Ronlân, A. *J. Am. Chem. Soc.* **1975**, *97*, 4714. (f) Meot-Ner, M.; Hamlet, P.; Hunter, E. P.; Field, F. H. *J. Am. Chem. Soc.* **1978**, *100*, 5466. (g) Kuck, D.; Bäther, W.; Grützmacher, H.-F. *J. Am. Chem. Soc.* **1979**, *101*, 7154. (h) Nishimura, J.; Ishida, Y.; Yamashita, S.; Hasegawa, K.; Sawamoto, M.; Higashimura, T. *Polym. J. (Tokyo)* **1983**, *15*, 303. (i) Schlesener, C. J.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 7472.

(3) Nishimura, J.; Hashimoto, K.; Okuda, T.; Hayami, H.; Mukai, Y.; Oku, A. *J. Am. Chem. Soc.* **1983**, *105*, 4758.

(4) Nishimura, J.; Okuda, T.; Mukai, Y.; Hashiba, H.; Oku, A. *Tetrahedron Lett.* **1984**, *25*, 1495.

(5) The tortional barrier of a trimethylene chain is reported as 3.6 kcal/mol: see, Dale, J. *Tetrahedron* **1974**, *30*, 1683.

(6) Monomers are abbreviated as *m*St-C*n*-*m*St, etc. St and C*n* mean vinylphenyl group and -$(CH_2)_n$-, respectively. Small letters *m* and *p* in front of St's mean meta and para positions of α,ω-diphenylalkanes, where the vinyl groups are located.

(7) Nishimura, J.; Yamada, N.; Horiuchi, Y.; Ueda, E.; Ohbayashi, A.; Oku, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2035.

(8) Nishimura, J.; Ishida, Y.; Hashimoto, K.; Shimizu, Y.; Oku, A.; Yamashita, S. *Polym. J. (Tokyo)* **1981**, *13*, 635.

0022-3263/87/1952-1409$01.50/0

Table I. Cationic Cyclocodimerization of *m*St-C*n*-*m*St with Some Comonomers[a]

comonomer, mM	*m*St-C*n*-*m*St, mM	cat., mM	temp., °C	time, min	total yield, %	isomer distrbn, %
styrene, 61	n = 3, 22	0.22	50	30	59.0[b]	**1a**, 71.7; **2a**, 25.6; unknown, 2.7
2-phenylpropene, 26	n = 3, 13	0.13	50	30	49.8[c]	**1b**, 66.3; **2b**, 20.3; unknown, 13.4
1,1-diphenylethylene, 28	n = 3, 20	0.20	50	30	44.3	**1c**, 73.3; **2c**, 26.7
styrene, 169	n = 4, 27	0.78	50	55	57.1	**3**, 100
styrene, 66	n = 5, 13	3.3	50	40	29.6	**4**, 100

[a] Reaction conditions: ca. 2.5 g of *m*St-C*n*-*m*St; CF_3SO_3H as a catalyst in dry benzene. [b] Including 2.7% of an unknown metacyclophane. [c] Including 8.4% and 5.0% of unknown metacyclophanes, whose ^1H NMR spectra clearly showed upfielded aromatic protons in the range of δ 6.48–6.80.

Table II. Aromatic ^1H NMR Chemical Shifts of [3.*n*]Metacyclophane Derivatives

compd	^1H NMR chemical shift, δ			$\Delta\delta$, ppm
	H_i (fine t)[a]	H_e (sharp t)[a]	H_m (d of fine t)[a]	
1a	6.89 (1 H, 1.2), 6.93 (1 H, 1.2)	6.80 (2 H, 8.0)	6.60 (1 H, br d, 8.0), 6.65 (1 H, br d, 8.0)	0.13
1b	6.89 (1 H, 1.3), 6.95 (1 H, 1.3)	6.78 (1 H, 7.1), 6.81 (1 H, 7.1)	6.64 (m, 4 H)	0.17
1c	6.80 (2 H, br s)	6.76 (1 H, 8.0), 6.78 (1 H, 8.0)	6.52 (2 H, br d, 8.0), 6.62 (2 H, br d, 8.0)	0.02
1d	6.87 (2 H, 1.2)	6.80 (2 H, 7.7)	6.57 (2 H, 7.7 and 1.2), 6.64 (2 H, 7.7 and 1.2)	0.07
2a	6.20 (1 H, br s), 6.25 (1 H, br s)	7.08 (2 H, 8.0)	6.88 (m, 4 H)	−0.88
2b	6.35 (2 H, 1.2)	7.03 (1 H, 6.4), 7.06 (1 H, 6.4)	6.82 (1 H, br d, 6.4), 6.88 (3 H, br d, 6.4)	−0.71
2c	6.14 (1 H, br s), 6.35 (1 H, br s)	6.89 (1 H, 6.4), 7.00 (1 H, 6.4)	6.63 (2 H, br d, 6.4), 6.79 (2 H, br d, 6.4)	−0.86
2d	6.30 (2 H, br s)	7.02 (2 H, dd, 7.0 and 8.4)	6.82 (2 H, dd, 7.0 and 8.4)	−0.72
3	6.41 (2 H)[b]	7.16 (1 H, 7.8), 7.17 (1 H, 7.8)	6.92 (2 H, br d, 7.8), 7.04 (2 H, br d, 7.8)	−0.75
4	6.66 (1 H, 1.3), 6.69 (1 H, 1.3)	7.02 (1 H, 7.5), 7.04 (1 H, 7.5)	6.81 (1 H, 7.5 and 1.3), 6.91 (2 H, 7.5 and 1.3)	−0.38

[a] If spectra show the predicted multiplicities indicated in the parentheses, they are not given repeatedly (J values given in hertz). [b] The proton resonances were not resolved from olefinic ones.

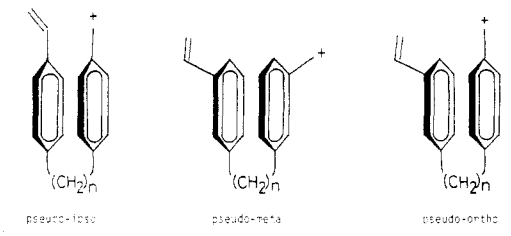


Figure 1. Some face-to-face associated cations.

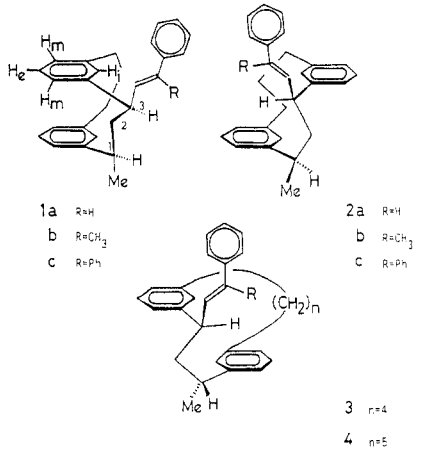
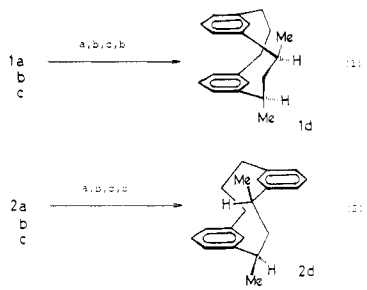


Figure 2. [3.*n*]Metacyclophanes produced by cationic cyclocodimerization.

linkage.[9] Monomer *m*St-C3-*m*St gave two isomeric [3.3]metacyclophanes as major products when it was allowed to react with a comonomer in the presence of CF_3SO_3H (Table I). On the other hand, only one metacyclophane derivative was isolated from the reactions of *m*St-C*n*-*m*St (n = 4 or 5). Chromatographic analyses of the isolated metacyclophanes by reversed-phase HPLC (Comosil C-18, column 10 × 250, MeOH and Develosil PYE,[10] column 8 × 250, MeOH) and by GLC (SE-30 3%, 2 m, 200–300 °C) showed only one peak. Moreover, these products also showed a clear doublet of a methyl group in ^1H NMR spectroscopy, although its chemical shift was affected by different steric circumstances.[1,3] The configuration of the double bonds in **1**–**4** (Figure 2[11]) was determined to be *E* by IR and NMR spectroscopy.[12,13] Metacyclophanes **1** and **2** were transformed into dimethylcyclophanes **1d** and **2d**, respectively, as shown in eq 1 and 2. These dimethylcyclophanes were used for further structural elucidation as described below.



(a) O_3, CCl_4; (b) $LiAlH_4$, ether; (c) TsCl, Py

The cationic cyclocodimerization of *m*St-C3-*p*St with 2-phenylpropene gave no [3.3]metaparacyclophanes but only linear cooligomers, even though the comonomer is considered to be best for the reaction.[1,3,4,14]

(9) Nishimura, J.; Yamada, N.; Ohbayashi, A.; Ueda, E.; Oku, A. *Tetrahedron Lett.* **1986**, *27*, 4331.

(10) Tanaka, N.: Tokuda, Y.; Iwaguchi, K.; Araki, M. *J. Chromatogr.* **1982**, *239*, 761.

(11) In these structures depicted, flippings of the linkages are ignored for simplification.

(12) Compounds **1a**, **2a**, **3**, and **4** have the out-of-plane vibration of olefinic C–H bonds at 966, 967, 967, and 966 cm^{-1}, respectively. Compounds **1b** and **2b** showed olefinic proton (1 H) at δ 5.98 and 6.11, respectively, which are very close to the calculated value δ 6.07 for the *E* configuration but far from δ 5.63 for the *Z* configuration (see ref 13).

(13) Pascual, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164.

(14) Cyclophanes of this sort have usually upfield-shifted aromatic proton signals. Moreover, cyclophanes produced by the cationic cyclocodimerization should have a $CH_3CH(Ar)CH_2$– linkage instead of $CH_3CH(Ar)CH{=}C<$ which was found in a linear codimer. The difference can easily be detected by the double irradiation technique.

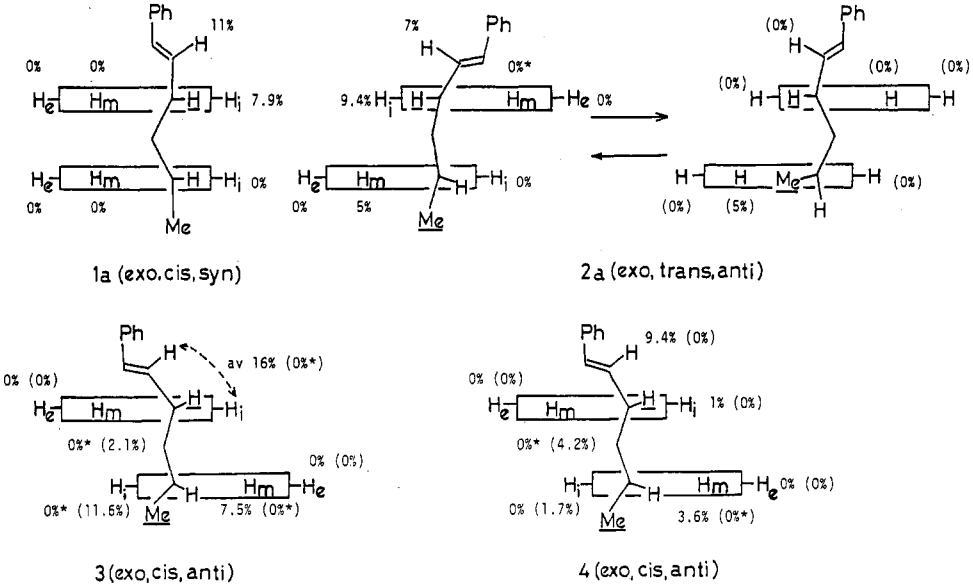
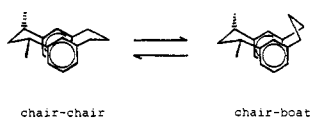


Figure 3. NOE enhancements. Values in parentheses were obtained by irradiations at the methyl protons. Asterisked values are estimated because of unresolved resonances.

Structure Determination.[15] The ^1H NMR chemical shifts of the layered aromatic ring protons of compounds **1–4** are summarized in Table II. Aromatic protons are assigned unequivocally, the intraannular protons (H_i)[16] showing fine couplings ($J \simeq 1$ Hz) with two meta protons appearing as triplets. The extraannular protons (H_e)[16] appear as sharp triplets ($J \simeq 7$ Hz), and other aromatic protons (H_m) are observed mostly as multiplets or doublets of fine triplets due to couplings with H_e, H_i and themselves. The ^1H NMR spectra of **1d** and **2d** are typical.[17] According to Lehner,[16] cyclophanes whose $\Delta\delta$ ($= \delta H_i - \delta H_e$) values are positive but small have a syn conformation, and those with negative but large $\Delta\delta$ values have an anti conformation.[15] Hence compounds **1a–d** are assigned as syn cyclophanes (Table II). The structures of cyclophanes **2–4** are assigned as anti by the negative sign, although their absolute $\Delta\delta$ values are relatively small compared with those reported.[16] Additionally, NOE results described below lead to the same conclusion on the syn/anti conformations of all products.

The cis/trans configuration of 1,3-disubstituted three-carbon chains was based on VT NMR spectroscopy. Generally, cis-1,3-disubstituted three-carbon chains of these ring systems are conformationally stable so that resonances of the methyl groups are not significantly split when the temperature is changed, whereas the methyl groups on a conformationally unstable trans-1,3-disubstituted three-carbon chain give two resonances due to two conformers.

As reported for [3.3]metacyclophane by Semmelhack et al.,[18] the resonance of the intraannular aromatic proton H_i of **1d** is split significantly at temperatures below −69 °C. The methyl resonances of **1d** are also split,[19] but not so much as in *trans*-1,3-dimethyl[3.3]paracyclophane (7 Hz vs. 55 Hz with a 200-MHz NMR spectrometer).[3] The coalescences of H_i and the methyl resonances occur at 231 ± 3 K. The activation free energy of flipping at the coalescence temperature is calculated to be 11.6 ± 0.1 kcal/mol. This value is close to those reported for the flipping motion of three-carbon chains in cyclophanes[1,3,18,20] and cyclohexanes.[21] We attribute the splitting of the methyl resonance to the conformational change (eq 3) between



(3)

chair-chair and chair-boat forms due to the flipping of the unsubstituted three-carbon chain.[18] Consequently, VT NMR evidence indicates that syn isomer **1d** has a cis configuration at the dimethyl-substituted three-carbon chain, and the starting materials **1a–c** for **1d** have a syn,cis configuration.

anti-Dimethylcyclophane **2d** gives two considerably separated methyl proton resonances (76.0 Hz at −94 °C and $\Delta G_c^{\ddagger} = 11.4 \pm 0.3$ kcal/mol in acetone-d_6), so that it is assigned the conformationally unstable trans configuration.[19] VT NMR spectra of **2d** are very broad even at −60 °C, and the methyl proton resonances are widely split.[17] The ratio of the areas under the methyl peaks appearing at δ 1.12 and 1.50 is 72:28.[22] These results are consistent

(15) 1,3-Disubstituted metacyclophanes **1–4** have theoretically eight isomers or three diastereotopic factors; i.e., cis and trans relationships on the two substitutents, syn and anti conformations with regard to the overlapping benzene rings, and finally endo and exo configuration of the disubstituted three-carbon chain. The designation of endo and exo configuration in the disubstituted three-carbon chain is made for the conformers having the styryl or substituted styryl group in a quasi-equatorial position as shown in Figure 2. In the exo isomer, the central methylene group (C2 position) of the chain faces aromatic hydrogen H_m of the layered benzene ring adjacent to the styryl group.

(16) Krois, D.; Lehner, H. *Tetrahedron* **1982**, *38*, 3319.

(17) Spectra are available in the supplementary material section.

(18) Semmelhack, M. F.; Harrison, J. J.; Young, D. C.; Gutiérrez, A.; Rafii, S.; Clardy, J. *J. Am. Chem. Soc.* **1985**, *107*, 7508.

(19) VT NMR spectra are available in the supplementary material section.

(20) Benn, R.; Blank, N. E.; Haenel, M. W.; Klein, J.; Koray, A. R.; Weidenhammer, K.; Ziegler, M. L. *Angew. Chem.* **1980**, *92*, 45.

(21) (a) Jensen, F. R.; Noyce, D. S.; Sederholm, C. H.; Berlin, A. J. *J. Am. Chem. Soc.* **1962**, *84*, 386. (b) Harris, R. K.; Sheppard, N. *Proc. R. Chem. Soc., London* **1961**, 418.

(22) According to molecular models, **2** is a very flexible molecule, so it can have two conformers, as depicted in Figure 3, without a local conformational change around the C3-position. We tentatively believe that this is one of the reasons why the H_i proton shows a relatively high NOE value when the allylic proton is irradiated. Moreover, the fact that **2d** shows two methyl resonances with unequal integrals at −94 °C can be explained by these conformers, i.e., if the same equilibrium of **2a** exists in **2d** and the populations of two conformers are the same, the methyl group lying relatively on the face of aromatic ring and appearing at higher field, δ 1.12, should have an integral three times larger than another methyl group (δ 1.50) sitting at the edge of the aromatic ring, because the population of the former methyl group should be three times that of the latter (see Figure 3). The observed integral ratio between both methyl groups is 2.6:1 (72:28), close to the ratio predicted.

with **2d** having two easily flipping three-carbon chains (see below). Hence **2d** and its starting materials **2a–c** have anti,trans configurations.

The methyl group resonances of **3** and **4** did not change chemical shifts within the temperature range −69 to 23 °C, and these compounds are therefore assigned cis configurations. The spectra of **3** and **4** at −60 °C were much sharper than those of **2d**, suggesting that the former molecules have less mobility than the latter because of their cis configuration.

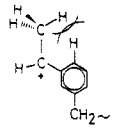
The endo/exo configuration[15] of the disubstituted three-carbon chains in **1–4** was determined by an NOE measurement. When the allylic proton (underlined in Figure 3) of syn,cis isomer **1a** was irradiated, the H_i proton resonance of the benzene ring adjacent to the styryl group was enhanced by 7.9%, indicating that **1a** has the exo configuration. Since **1b** and **1c** gave the same dimethylcyclophane **1d** as did **1a**, we conclude that cyclophanes **1** have the syn,cis,exo configuration.

NOE experiments on **2a**, **3**, and **4** were carried out by the irradiation of both allylic and methyl protons. Results are shown in Figure 3 together with schematic top views. The NOE experiments show that all of **2**,[22] **3**, and **4** have the exo configuration. Moreover, the presence or the absence of transannular NOE interaction between the allylic proton and H_m indicates that **1a** is a syn cyclophane but that **2a**, **3**, and **4** are anti.

Discussion

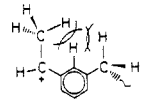
All cationic cyclocodimerizations of the structurally simple styrene derivative *m*St-C3-*m*St gave only two isomeric cyclophanes, although eight isomers are possible in a statistical cyclization.[15] Moreover, monomer *m*St-C3-*p*St, which is structurally similar to *m*St-C3-*m*St and *p*St-C3-*p*St,[3] gave no cyclophanes in this reaction. Therefore, some steric and electronic factors must govern the reaction path or affect the distribution of intermediate cyclic cations.

Protonation of *m*St-C3-*m*St first forms two linear cations. One has an exo methyl group at the cationic center and the other an endo methyl group (see structures **5** and **6**).[23] Taking steric interaction between methyl, methine,



Exo-Me cation (major)

5


Endo-Me cation (minor)

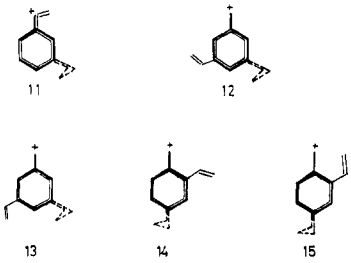
6

and methylene groups into consideration, the exo methyl cation must predominate over the endo methyl cation. This steric effect reflects the yields of isomers. Compounds **1** and **2** are produced from the sterically more favored cation **5**. The same steric effect must also influence the conformation of the vinyl group conjugated with the aromatic ring. Among the four face-to-face cations (**7–10**) of **5**, pseudo-ipso cation **7** and pseudo-meta cation **8** are trapped by the comonomer to afford cyclophanes **1** and **2**. Thus the conformer that is exo to the vinyl group is predominant.[23]

The cationic cyclocodimerization of *m*St-C3-*m*St gave about three times more cyclophane **1** (from cation **7**) than **2** (from **8**), and *m*St-C3-*p*St did not afford any cyclophanes. Since this monomer has no steric factors that should interfere with the cyclization, there must be an electronic effect on the generation of intermediate cation–arene complexes. Using models **11–15** that represent

Table III. Total Delocalization Energy

model	total delocalization energy, kcal/mol
11	10.7
12	9.2
13	8.4
14	7.4
15	6.6



pseudo-ipso (**11** for **7** and **9**), pseudo-meta-exo (**12** for **8**), pseudo-meta-endo (**13** for **10**), pseudo-ortho-endo (**14**), and pseudo-ortho-exo (**15**) complex cations, total delocalization energies were calculated by the CNDO/2 method,[3] assuming that the styrene and benzyl cation are arranged parallel separated by 0.314 nm.[24] The calculated energies, listed in Table III, can be regarded as an index of the orbital interaction between two aromatic groups of the cationic species.

On the basis of the total delocalization energies, the stability of cations decreases in the order **11** > **12** > **13** > **14** > **15**. Although this order parallels the yields of cyclophanes, the yields do not correlate exactly with the total delocalization energies because of approximations in the molecular orbital calculation.[3] But the stabilities of cations represented by models **11** and **12** indicate that the concentrations of cations **7** and **8** in the reaction system must be high, and they undergo predominantly an intramolecular cyclization to afford cyclophanes **1** and **2**. In addition, the different conformational stabilities of the methylene linkages must also influence the concentration of these cations. Thus both the *m*St-Cn-*m*St (n = 4 and 5), which have less favorable linkages than *m*St-C3-*m*St for allowing their aromatic rings into a close, parallel arrangement, gave only one cyclophane from one intermediate cation.

We believe that the formation of *exo,cis*-1-methyl-3-styryl-*anti*-[3.4]- and -[3.5]metacyclophanes from *m*St-C*n*-*m*St (n = 4 and 5) proceeds through pseudo-ipso cations, the homologues of **7**, with subsequent rotation of one of the benzene rings, because *anti*-[3.4]- and -[3.5]metacyclophanes are conformationally more stable than their syn isomers.[16] We are not sure why only the benzene ring adjacent to the methyl group rotates. One possibility is that the benzene ring adjacent to the methyl group, which is relatively smaller than the styryl group, may rotate after the product is formed. Alternatively, it is possible that only this ring can rotate in the cyclic cation because the other ring, adjacent to the cationic sp^2 carbon center, is prevented from rotating by the p,π conjugation.

In summary, the cationic cyclocodimerization of *m*St-C*n*-*m*St affords [3.*n*]metacyclophane derivatives. The intramolecular stabilization of an intermediate cation by a styryl group under steric constraint is essential to this cyclization.

(23) Endo and exo conformations of the methyl group of the cation or methylene group of the vinyl group are designated as follows. When these groups face the outer direction or H_m proton, the conformer is called exo, and when they face H_i proton, it is called endo.

(24) Gantzel et al. (Gantzel, P. K.; Trueblood, K. N. *Acta. Crystallogr.* **1965**, *18*, 958) reported the X-ray crystal structure of [3.3]paracyclophane has a 0.314-nm spacing between the C4 and C16 positions.

Experimental Section

General Methods. Elemental analyses were done at the Microanalysis Center of Kyoto University. ^{1}H NMR spectra were recorded on Varian T-60A and XL-200 NMR spectrometers in $CDCl_3$ with tetramethylsilane as an internal standard. The VT NMR measurement was carried out with a Varian XL-200 NMR spectrometer in acetone-d_6 with tetramethylsilane. Probe temperatures were determined by a digital thermometer in the spectrometer and used as sample temperatures without any calibration.[25] NOE measurement was done in $CDCl_3$ under nitrogen with relatively weak irradiation at allylic or methyl protons and their vicinity three times each with a delay time of 20 s. The NOE enhancement was calculated from two average values of aromatic proton integrals, which were obtained by irradiation at the particular proton and its vicinity. IR spectra were taken on a JASCO IRA-1 spectrometer. Mass spectra were recorded on a Hitachi M-80A mass spectrometer. GC analysis was done on a Shimadzu GC-4CIT gas chromatograph. Reversed-phase HPLC was carried out by using an Altex Model 110A pump, a Hitachi 635 T wavelength tunable effluent monitor, and a Knauer 98.00 differential refractometer. Melting points are not corrected.

Materials. CF_3SO_3H was distilled under a nitrogen atmosphere. Benzene was distilled over CaH_2 after a prolonged reflux. Other materials were all of commercially available highest grade and used without further purification.

Preparation of α,ω-Bis(*m*-vinylphenyl)alkanes *m*St-C*n*-*m*St. The olefins were prepared by the method reported.[7,8] Yields of precursor glycols after three steps (see Scheme I) were as follows: n = 4, 64% (18.4 g); n = 5, 68% (10.6 g). After dehydration and purification by column chromatography (SiO_2, benzene/cyclohexane) the olefins were obtained as oils. Yields and MS data ($M^{\bullet+}$, m/z, calcd (found)) of *m*St-C*n*-*m*St are as follows: n = 4, 78% yield (0.51 g), 262.1723 for $C_{20}H_{22}$ (262.1722); n = 5, 72% yield (2.2 g), 276.1879 for $C_{21}H_{24}$ (276.1876). ^{1}H NMR data[26] (60 MHz, $CDCl_3$): n = 4, δ 1.61 (4 H, m), 2.55 (4 H, br t, 7.1), 5.11 (2 H, dd, 10.8 and 1.9), 5.61 (2 H, dd, 17.8 and 1.9), 6.62 (2 H, dd, 10.8 and 17.8), 7.06 (8 H, m); n = 5, δ 1.56 (6 H, m), 2.57 (4 H, br t, 7.7), 5.14 (2 H, dd, 10.5 and 2.0), 5.62 (2 H, dd, 17.6 and 2.0), 6.64 (2 H, dd, 10.5 and 17.6), 7.06 (8 H, m).

Preparation of 1-(*m*-Vinylphenyl)-3-(*p*-vinylphenyl)propane (*m*St-C3-*p*St). Monomer *m*St-C3-*p*St was prepared as shown in Scheme I from ketalized (*p*-acetylphenyl)magnesium bromide and ketalized 1-acetyl-3-(3-bromopropyl)benzene.[7] The glycol was obtained in 34% yield (4.0 g) after three steps, and its dehydration produced *m*St-C3-*p*St in 37% yield (1.3 g):[8] oil; MS ($M^{\bullet+}$, m/z), calcd (found) 248.1566 for $C_{19}H_{20}$ (248.1558); ^{1}H NMR data[26] (60 MHz, $CDCl_3$) δ 1.91 (2 H, m), 2.61 (4 H, br t), 5.13 (1 H, dd, 10.0 and 2.0), 5.16 (1 H, dd, 10.0 and 1.8), 5.61 (1 H, dd, 18.0 and 1.8), 5.67 (1 H, dd, 18.0 and 1.8), 6.67 (2 H, dd, 10.0 and 18.0), 7.15 (8 H, m).

Cationic Cyclocodimerization. The procedure was the same as reported,[1,3,4] using ca. 2.5 g of a monomer. Products were isolated by column chromatography (SiO_2, benzene/cyclohexane). Isomers were separated by reversed-phase HPLC (Cosmosil C-18, MeOH). Physical properties and analytical data are as follows.

1a: oil; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.28 (3 H, d, 7.0), 2.16 (4 H, m), 2.66 (6 H, m), 3.64 (1 H, m), 6.39 (1 H, d, 8.0), 6.62–6.93 (8 H),[27] 7.28 (5 H, m); MS, m/z calcd ($M^{\bullet+}$) 352.2192, found 352.2161. Anal. Calcd for $C_{27}H_{28}$: C, 91.99; H, 8.01. Found: C, 91.70; H, 8.02.

1b: oil; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.25 (3 H, d, 7.0), 2.04 (4 H, m), 2.06 (3 H, s), 2.76 (5 H, br t, 5.6), 3.62 (1 H, br t, 8.8), 5.98 (1 H, d, 8.8), 6.64–6.91 (8 H),[27] 7.28 (5 H, m); MS, m/z calcd ($M^{\bullet+}$) 366.2349, found 366.2358. Anal. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.68; H, 8.27.

1c: mp 56.5–58.0 °C; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.21 (3 H, d, 7.0), 2.04 (4 H, m), 2.74 (5 H, m), 3.40 (1 H, br t, 8.0), 6.29 (1 H, d, 10.0), 6.33–6.78 (8 H),[27] 7.28 (10 H, m); MS, m/z calcd ($M^{\bullet+}$) 428.2506, found 428.2489. Anal. Calcd for $C_{34}H_{32}$: C, 92.68; H, 7.32. Found: C, 92.50; H, 7.52.

2a: oil; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.30 (3 H, d, 7.0), 2.11 (4 H, m), 2.68 (5 H, m), 3.22 (1 H, br q), 6.45 (2 H, m), 6.22–7.08 (8 H),[27] 7.30 (5 H, m); MS, m/z calcd ($M^{\bullet+}$) 352.2192, found 352.2199. Anal. Calcd for $C_{27}H_{28}$: C, 91.99; H, 8.01. Found: C, 91.78: H, 7.95.

2b: oil; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.31 (3 H, d, 7.0), 2.00 (3 H, s), 2.09 (4 H, m), 2.66 (5 H, m), 3.50 (1 H, m), 6.11 (1 H, br d, 9.6), 6.34–7.00 (8 H),[27] 7.30 (5 H, m); MS, m/z calcd for $C_{28}H_{30}$ ($M^{\bullet+}$) 366.2349, found 366.2378.

2c: mp 41.5–43.5 °C; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.18 (3 H, d, 7.0), 2.04 (4 H, m), 2.70 (5 H, m), 3.32 (1 H, m), 6.44 (1 H, d, 10.0), 6.14–7.00 (8 H),[27] 7.29 (10 H, m); MS, m/z calcd for $C_{33}H_{32}$ ($M^{\bullet+}$) 428.2506, found 428.2522.

3: oil; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.29 (3 H, d, 8.2), 1.62 (4 H, m), 2.09 (2 H, m), 2.56 (1 H, m), 2.65 (4 H, m), 3.33 (1 H, q, 7.0), 6.41 (2 H, d, 6.0), 6.41–7.16 (8 H),[27] 7.35 (5 H, m); MS, m/z calcd ($M^{\bullet+}$) 366.2349, found 366.2346. Anal. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.53; H, 8.21.

4: oil; ^{1}H NMR data[26] (200 MHz, $CDCl_3$) δ 1.08 (2 H, m), 1.28 (3 H, t, 7.4), 1.57 (4 H, m), 2.16 (2 H, m), 2.52 (4 H, m), 2.72 (1 H, m), 3.36 (1 H, m), 6.37 (2 H, d, 5.4), 6.66–7.04 (8 H),[27] 7.25 (5 H, m); MS, m/z calcd ($M^{\bullet+}$) 380.2506, found 380.2493. Anal. Calcd for $C_{29}H_{32}$: C, 91.52; H, 8.48. Found: C, 91.51; H, 8.51.

Ozonolysis of *exo*,*cis*-1-Methyl-3-styryl-*syn*-[3.3]metacyclophane (1a). General Procedure.[3] Into 100 mL of a CCl_4 solution of **1a** (0.945 g, 2.68 mmol) was bubbled O_3. After the complete consumption of the cyclophane (TLC monitor), N_2 was bubbled in order to expel excess of O_3. The reaction mixture was concentrated by evaporation and treated with $LiAlH_4$ (1.01 g, 26.6 mmol) in 200 mL of ether. After the usual workup, the corresponding alcohol was obtained in 61% yield. The analytical and physical data of the syn and anti alcohols are as follows. Syn alcohol: mp 85.0–87.0 °C; MS ($M^{\bullet+}$, m/z calcd (found)), 280.1828 for $C_{20}H_{24}O$ (280.1827); IR ν_{OH} 3390 cm^{-1}. Anti alcohol: oil; MS, ($M^{\bullet+}$, m/z, calcd (found)), 280.1828 for $C_{20}H_{24}O$ (280.1827); IR ν_{OH} 3360 cm^{-1}.

Preparation of *exo*,*cis*-1,3-Dimethyl-*syn*-[3.3]metacyclophane (1d). General Procedure.[3] The syn alcohol obtained above (66.2 mg, 0.236 mmol) was allowed to react with TsCl (89.8 mg, 0.472 mmol) in pyridine (2 mL) at 0 °C for 2 days. The tosylate, which was obtained after workup, was reduced by excess $LiAlH_4$ in ether. After ordinary workup, dimethylmetacyclophane **1d** was obtained in 81% yield. Both **1d** and **2d** were oils. MS ($M^{\bullet+}$, m/z, calcd (found)): **1d**, 264.1879 for $C_{20}H_{24}$ (264.1874); **2d**, 264.1879 for $C_{20}H_{24}$ (264.1877). ^{1}H NMR data[26] (200 MHz, $CDCl_3$): **1d**, δ 1.24 (6 H, d, 7.0), 1.90 (2 H, m), 2.07 (2 H, m), 2.66 (2 H, m), 2.74 (4 H, t, 6.4), 6.57–6.87 (8 H);[27] **2d**, δ 1.26 (6 H, d, 7.0), 1.92 (2 H, t, 6.8), 2.07 (2 H, quin, 6.0), 2.59 (2 H, q, 7.6), 2.73 (4 H, m), 6.30–7.02 (8 H).[27]

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Supplementary Material Available: Three figures showing ^{1}H NMR spectra of **1d** and **2d** and their VT NMR spectra (3 pages). Ordering information is given on any current masthead page.

(25) Whitlock, B. J.; Whitlock, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 1325.

(26) Given in the following format: chemical shift, δ (integral, multiplicity, coupling constant J in Hz).

(27) See Table II for details.