with the general notion that in many reactions higher barriers are observed for annihilation as well as formation of highly delocalized carbanions.[26] However, this is more a classification approach rather than an explanation. It may well be that delocalization induces other phenomena such as enhanced solvation, which could be a major contributor to the observed effect.[9,11c,27]

Experimental Section

Syntheses. The following compounds were prepared according to published procedures. 9-(Nitromethylene)fluorene[28] (1), 9-(dicyanomethylene)fluorene[29] (2), 9-methoxy-9-(nitromethyl)-fluorene[9] (1(HOMe)), 9-cyano-9-(nitromethyl)fluorene[9] (1(HCN)), 9-cyano-9-(dicyanomethyl)fluorene[29b] (2(HCN)), and 9-methyl-9-(dicyanomethyl)fluorene[30] (3). Attempts to prepare 9-methoxy-9-(dicyanomethyl)fluorene (2(HOMe)) were performed under neutral, acidic, and basic conditions. The results were analysed by TLC and UV spectroscopy; 0.1 g of 2 was dissolved in 25 mL of MeOH and refluxed for 2 h. Examination of the reaction mixture after cooling to room temperature showed no reaction of the starting material; 1 g of *p*-toluenesulfonic acid was added to the reaction vessel and the solution was refluxed for two additional hours. Again, only starting material was detected. The reaction under basic condition was performed in a UV cell at ambient temperature. The concentration of MeONa was 1 M. No reaction was observed.

Determination of the pK_a of 1(HCN). The pK_a was determined spectroscopically. Under acidic or neutral condition 1(HCN) showed λ_{max} at 262 nm. In basic solutions the extinction coefficient approximately doubled and the λ_{max} moved to a shorter wavelength, 258.5 nm. These changes are pH dependent and are completely reversible. The spectra were measured in buffered solutions (borax) which were then acidified with minute amounts of concentrated HCl followed by addition of concentrated NaOH. The absorbances at each stage (corrected for dilution) were used in eq 5 to calculate the pK_a of 1(HCN) where A, A_a, and A_b are the observed ODs in the buffered, acidic, and basic solutions, respectively.

Determination of the pK_a of 3. The pK_a was determined by a potentiometric method using a regular combined glass electrode in a 30% sulfolane–70% water solutions (due to the low solubility of 3 in 25% aqueous sulfolane). Four solutions each of ca. 5×10^{-3} M in 3 were partially neutralized with NaOH solutions. From the pH meter reading and a calibration curve, the H^+ concentrations were evaluated and were used to determine the pK_a of 3.

Kinetics. According to the pH ranges, the buffers used were phthalate, NaH_2PO_4, borax Na_2HPO_4, and KOH. The pHs were determined by using a combined glass electrode. The actual H^+ concentration in the reaction medium was calculated from a calibration curve (not shown). Before performing a kinetic run the reactions were followed by repetitive scanning (Perkin-Elmer Model 402 spectrometer) in the 250–510-nm range. The actual kinetics were studied at a single wavelength. (λ_{max} of the olefin, 355 nm for 1 and 350 nm for 2. At pH >13 the reaction of 1(HOMe) was followed at 258 nm, which is λ_{max} of the final product fluorenone.) The reactions were initiated by injection of the substrate in sulfolane solution with a micro syringe to the preincubated UV cell. The data were analyzed on-line via a PDP 11/40 minicomputer.

Registry No. 1 (HOMe), 86120-12-9; 1 (HCN), 86120-11-8; 2 (HOMe), 94620-62-9; 2 (HCN), 7009-36-1; 3, 6235-08-1; $CH_2NO_2^-$, 18137-96-7; CH_2CN^-, 21438-99-3.

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Cationic Cyclocodimerization. 3.[1] Syntheses of [3.3]Paracyclo(1,4)naphthalenophane and [3.3](1,4)Naphthalenophane Derivatives. Stereoselectivity Governed by the Structures of α-Naphthylmethylcarbenium Ion and 1-Vinylnaphthyl Moiety

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The cationic cyclocodimerization of 1-(4-vinylnaphthyl)-3-(*p*-vinylphenyl)propane and 1,3-bis(4-vinylnaphthyl)propane with 2-phenylpropene, indene, 1,1-diphenylethylene, and styrene gave [3.3]paracyclo(1,4)-naphthalenophanes and [3.3](1,4)naphthalenophanes, respectively, in 11.5–53.6% yields. From the structures of carbophanes produced, it is concluded that the stereoselectivity shown in the cationic cyclocodimerization can be attributed to the structures of major conformers of α-naphthylmethylcarbenium ion and its parent 1-vinylnaphthyl moiety. The variable-temperature NMR spectroscopic analysis of some [3.3]paracyclo(1,4)-naphthalenophanes and a [3.3](1,4)naphthalenophane showed that the activation energy for the flipping of the substituted methylene chain is not so affected by the steric hindrance of the peri hydrogens of the naphthalene rings.

Compared with reported methods for [3.3]paracyclo(1,4)naphthalenophanes[2] and [3.3](1,4)-naphthalenophanes,[3,4] the usefulness of the cationic cyclocodimerization[5] was briefly communicated.[1] Further study on the construction of these carbophanes revealed several new aspects, so we would like to report the synthesis, the stereoselectivity of the reaction and its origin,

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Table I. Cationic Cyclocodimerization of St-C3-VN with Some Comonomers[a]

comonomer (mol/L)	St-C3-VN, mol/L	CF_3SO_3H, mmol/L	time, min	yield, % 1	2	3	4	total[b]	VN/St ratio[c]
2-phenylpropene (0.040)	0.020	0.4	25	11.3	10.0	3.8	8.3	33.5	1.8
indene[d] (0.024)	0.012	0.2	25	12.4	10.5	4.2	3.8	30.9	2.9
1,1-diphenylethylene (0.024)	0.012	0.2	25	11.3	7.0	4.1	5.9	28.3	1.8
styrene (0.024)	0.012	0.6	45	10.4	7.3	1.6	1.4	20.7	5.9

[a] Reaction conditions; at 50 °C in dry benzene. [b] Isolated yield. [c] The ratio of VN protonation vs. St protonation in products. [d] Reference 1.

Table II. Physical Properties and Spectroscopic Data of [3.3]Paracyclo(1,4)naphthalenophanes 1

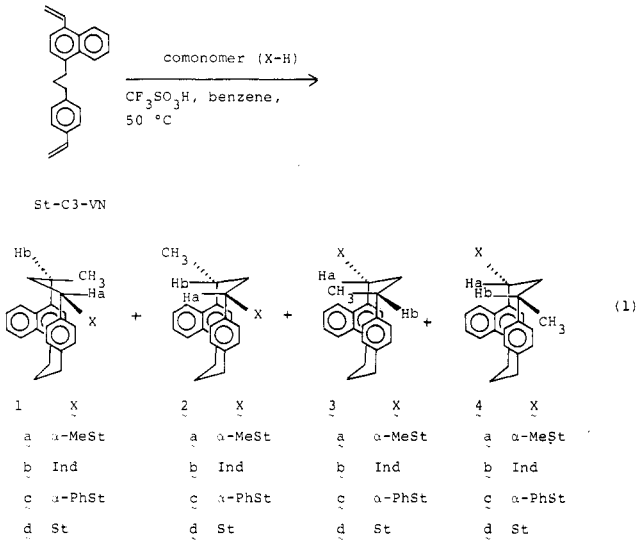
compd	mp, °C	MS ($M^{+\cdot}$, m/z)	vis,[a] nm	FS,[b] nm	IR[c] ($\nu_{C=C}$, cm^{-1})
1a	127–129	416	707 ± 5	368 ± 2	826
1b[d]	105–108	414	697 ± 5	368 ± 2	824
1c	177–179	478	705 ± 5	369 ± 2	821
1d	hl[e]	402	711 ± 5	366 ± 2	960

[a] CT complex with TCNE in dichloromethane. [b] Fluorescence spectroscopy. Taken in nitrogenated cyclohexane. [c] The out-of-plane vibration of the olefinic C–H bond. [d] Reference 1. [e] Heavy liquid.

and static and dynamic structures of phanes produced and also to discuss the mechanism of the cyclocodimerization via α-naphthylmethylcarbenium ion.

Results and Discussion

(1) [3.3]Paracyclo(1,4)naphthalenophanes (eq 1). (a) Cationic Cyclocodimerization of St-C3-VN. Several [3.3]paracyclo(1,4)naphthalenophanes were prepared by the cationic cyclocodimerization of 1-(4-vinylnaphthyl)-3-(*p*-vinylphenyl)propane (St-C3-VN) without any modification to the original procedure.[5] The best comonomer was 2-phenylpropene[5] and gave the desired carbophanes in 33.5% yield. Results are summarized in Table I.



Even if one assumes that each comonomer moiety (X)[6] takes one isomeric form, eight isomers are possible as the products of the reaction.[7] As well as the reported case of the reaction with indene,[1] HPLC analysis of all runs tried showed two major and two minor products.

The isomers in the highest yields, **1**, were isolated and their physical, and spectroscopic data are summarized in Table II. Their structures were determined by variable-temperature NMR (VT NMR) mentioned below, nuclear Overhauser effect (NOE),[1] and other spectroscopies shown in Tables II and III. Compound **1c** showed a different NMR chemical shift of its methyl group from other derivatives **1a**, **b**, and **d**. This different chemical shift was also observed in 1-methyl-3-(α-phenylstyryl)[3.3]paracyclophanes.[5] It is believed that the methyl group is affected by the shielding of one or two phenyl groups of this particular substituent. So the structure was determined by the chemical shifts of H_a and H_b, which are strongly influenced by the cyclophane rings because of the proximity. The chemical shift difference between H_a and H_b of **1c** (0.31 ppm) is similar to those of **1a**, **b**, and **d** (0.11–0.29 ppm) but quite different from that of cis isomer **2b** (0.04 ppm).

Three other kinds of isomers (**2**, **3**, and **4**) in mixtures were designated by the comparison of ^1H NMR spectra with those of phanes (**2b**, **3b**, and **4b**) possessing the indenyl group.[1]

Products **1** and **2** were derived from the initial protonation at the vinylnaphthyl (VN) moiety and **3** and **4** at the styryl (St) moiety. The ratios of VN protonation to St protonation were obtained from the ^1H NMR spectra of the reaction mixture and are summarized in Table I. The

Table III. ^1H NMR Chemical Shifts Selected[a]

compd	chemical shift, ppm H_a	H_b	Me (d, J in Hz)
1a	3.85	3.96	1.58
1b[b]	3.84	4.01	1.59
1c	3.56	3.87	1.31
1d	3.56	3.95	1.58
2b[b]	3.59	3.63	1.41
3b[b]	4.74	3.31	1.35
4b[b]	3.59	ca. 2.4[c]	1.33
5a	4.56	3.62	1.37
5b[b]	4.63	3.62	1.43
5c	4.31	3.53	1.33
5d	4.34	3.72	1.42
6a	4.72	3.94	1.40
6b[b]	4.77	4.05	1.51
6c	4.48	3.93	1.27
6d	4.49	3.96	1.43
7[d]	3.99	3.68	1.37
8[e]	3.90	3.60	1.20

[a] Designation of H_a and H_b is indicated in each of structures 1 to 8. [b] Reference 1. [c] Since the resonance appeared with many other peaks, its precise position could not be determined. The value was obtained by the double irradiation technique. [d] H_c, δ 4.84. [e] H_c, δ 4.45.

(6) Abbreviations: α-MeSt, Ind, α-PhSt, and St mean (*E*)-Ph(CH_3)-C=CH, 2-indenyl, Ph_2C=CH, and (*E*)-PhCH=CH moieties, respectively.

(7) There are two diastereomeric factors (cis–trans and endo–exo) and a constitutionally isomeric factor (VN and St initiation). The endo and exo designation of the bridging methylene group is done for the conformer having the X group (1–6) in a quasi-equatorial position. In an exo isomer, the middle methylene group of the 1,3-disubstituted bridge directs opposite to the peri hydrogen of the naphthyl group nearest to the X group.

Table IV. Cationic Cyclocodimerization of VN-C3-VN with Some Comonomers[a]

comonomer (mol/L)	[VN-C3-VN], mol/L	[CF_3SO_3H], mmol/L	time, min	yield,[b] % 5	6	total	syn/anti ratio
2-phenylpropene (0.118)	0.024	0.2	27	34.4	17.2	51.6	2.0
indene[c] (0.040)	0.024	0.2	20	15.3	4.7	20.0	3.3
1,1-diphenylethylene (0.122)	0.024	0.2	30	7.2	4.3	11.5	1.7
styrene (0.107)	0.003	0.2	33	29.5[d]	24.1	53.6	1.2

[a] Reaction conditions; in dry benzene at 50 °C. [b] Isolated yield. [c] Reference 1. [d] Yields of 7 (9.4%) and 8 (5.0%) were included.

Table V. Physical Properties and Spectroscopic Data of [3.3](1.4)Naphthalenophanes 5–8

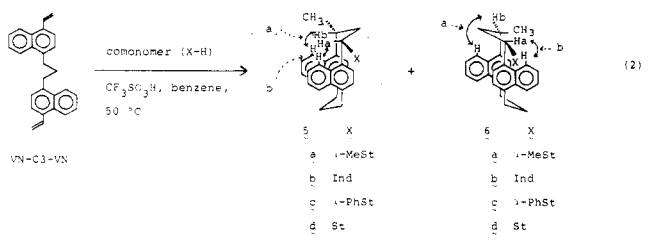
compd	mp, °C	MS ($M^{+\cdot}$, m/z)	vis,[a] nm	FS,[b] nm	IR[c] ($\nu_{C=C}$, cm^{-1})
5a	80–81.5	466	775 ± 5	464 ± 2	830
6a	125–128	466	720 ± 5	404 ± 2	833
5b[d]	246–247	464	770 ± 5	464 ± 2	833
6b[d]	203–204	464	724 ± 5	complex	833
5c	173–176	528	784 ± 5	464 ± 2	834
6c	235–236	528	736 ± 5	420 ± 2	833
5d	85–96	452	771 ± 5	464 ± 2	962
6d	177–181	452	739 ± 5	407 ± 2	962
7	224–228	452	804 ± 5	465 ± 2	
8	208–212	452	808 ± 5	467 ± 2	

[a] CT complex with TCNE in dichloromethane. [b] Fluorescence spectroscopy. Taken in nitrogenated cyclohexane. [c] The out-of-plane vibration of the olefinic C–H bond. [d] Reference 1.

value can be regarded to the relative reactivity of the protonation to vinylnaphthyl group and styryl group: The monomer reactivity ratio r_1 reported for the cationic copolymerization of 1-vinylnaphthalene (M_1) and styrene was reported as 2.6 ± 0.2,[8] which is near the above ratio. It suggests that the product-forming step (trapping of the cyclic cation by olefin) does not affect the product selectivity significantly.

(b) Flipping of the Substituted Methylene Bridge in [3.3]Paracyclo(1,4)naphthalenophanes. Products **1a** and **1b** were analyzed by ^1H NMR spectroscopy (200 MHz) at various temperatures from −90 to 23 °C, the flipping of the substituted methylene bridge was analyzed by using the CLATAX program,[9] and the activation free energy of the motion at 273 K, $\Delta G^{\ddagger}_{273}$, was calculated to be 12.0 ± 1.5 (the major/minor conformer ratio at −90 °C was 88/12) and 11.6 ± 2.1 kcal/mol (the major/minor conformer ratio at −90 °C was 96/4), respectively. The values are almost the same as those of the flipping of [3.3]paracyclophanes ($\Delta G^{\ddagger}_{273}$ = 11.2–11.9 kcal/mol).[5] It can be concluded that the flipping motion can evade the steric hindrance of the peri hydrogen of the naphthyl group in this [3.3]paracyclo(1,4)naphthalenophane skeleton, although the ratio of major/minor was affected much by the presence of the peri hydrogen (Figure 1).

(2) [3.3](1,4)Naphthalenophanes (eq 2). (a) Cationic Cyclocodimerization of VN-C3-VN. The preparation of the carbophanes was the same as the above cases and those of [3.3]paracyclophanes.[5] Again, 2-phenylpropene



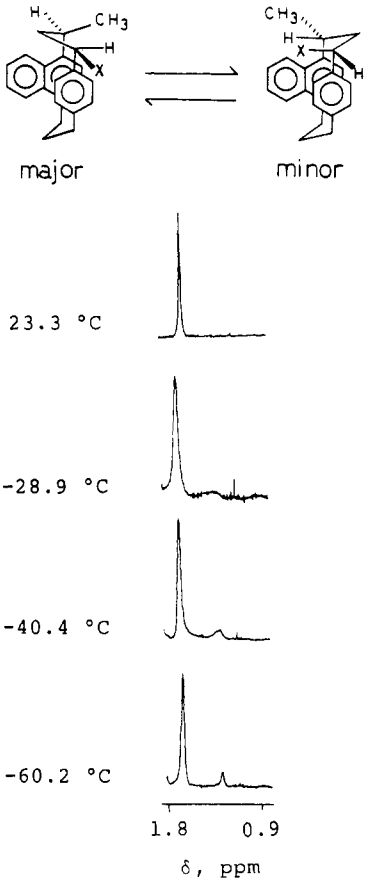


Figure 1. VT NMR spectra of *endo*-[*trans*-1-methyl-3-(α-methylstyryl)][3.3]paracyclo(1,4)naphthalenophane (**1a**). Taken in $(CD_3)_2CO$ on a Varian XL 200 NMR spectrometer. The methyl group was observed as a singlet by the irradiation at the methine group.

gave the highest yield among the comonomers tried. Results are summarized in Table IV.[10]

The spectroscopic data of the products are listed in Tables III and V. Fluorescence and visible[11] spectrosco-

(8) Bunel, C.; Cohen, S.; Laguerre, J. P.; Marechal, E. *Polym. J.* **1975**, *7*, 320–325. Although the r_1 values for 1-methyl-4-vinylnaphthalene and *p*-methylstyrene are necessary for a precise consideration, the qualitative discussion here may be allowed with the data.

(9) Binsch, G. In "Topics of Stereochemistry"; Eliel, E. L., Allinger, N. L., Eds.; Interscience Publisher: New York, 1968; Vol 3, pp 97–192.

(10) This is the first case where the yield of the cyclization to a [3.3](1,4)naphthalenophane skeleton exceeded 50%, so far as we searched in literatures.

Table VI. NOE of [3.3](1,4)Naphthalenophanes (5 and 6)[a]

compd	NOE, % a	b
5a	24	18
6a	21	22
5b[b]	20	31
6b[b]	24	17
5c	31	24
6c	16	11
5d	13	13
6d	9	4

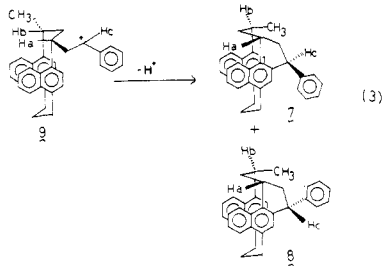
[a] Designation of a and b is illustrated in eq 2. [b] Reference 1.

pies gave evidence for syn/anti configuration,[12] and NOE between peri hydrogens and the bridge chain hydrogens (H_a, H_b) offered definite evidences on the cis/trans and exo/endo configurations[7] as reported.[1] These NOE data are listed in Table VI.

Generally speaking, exo,trans,anti isomers (**6**) showed less NOE than the others, since peri hydrogens suffer less steric hindrance in anti isomers (**6**) than in syn isomers (**5**).

The cationic cyclocodimerization of 1,3-bis(4-vinylnaphthyl)propane (VN-C3-VN) with a monomer showed the selectivity that only two isomers were formed from eight possible ones, except the reaction with styrene (vide infra). All runs tried gave more syn isomers than anti ones. This result suggests that a syn cation is generated predominantly, because this cation is more stabilized than an anti one, by the wider overlapping between the electron-deficient naphthalene ring and the electron-rich ring.

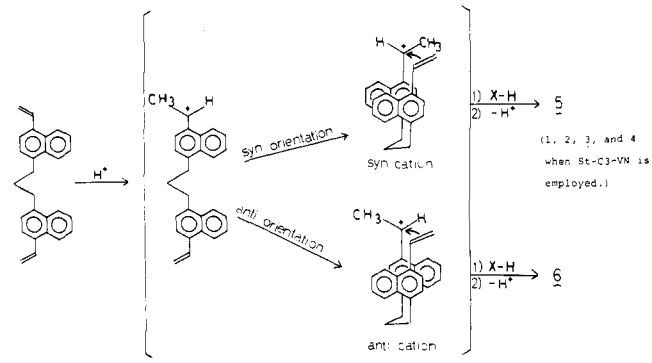
The cationic cyclocodimerization with styrene gave two interesting products (**7** and **8**) in addition to the expected ones (**5d** and **6d**). They are the products formed by the intramolecular naphthalene ring attack of intermediate dimer cation **9** (eq 3). They are concluded to be of syn



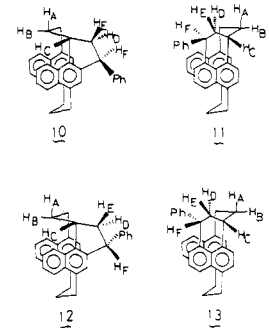
(3)

configuration, because of their highly bathochromic shifts of the CT bands with TCNE (see Table V). There were found none of anti configuration. The syn stereoselectivity is attributed to the fact that only the syn naphthalenophane moiety, which is more susceptible to the attack by a cationic species than the anti one, can react with the α-monosubstituted benzyl cation intramolecularly. Moreover, the result is consistent with those obtained in the cationic cyclocodimerizations of St-C3-St[5] and St-C3-VN where such products were not produced under the conditions employed. Furthermore, the most reactive α-monosubstituted benzyl cation (secondary cation) among the cations (mostly tertiary cations) generated in all cases could only perform this intramolecular indane ring formation. Although the structures of these products could be easily deduced from the mechanism mentioned below and the molecular framework with Dreiding model,[13] they

Scheme I



were finally determined by the spectral simulation by the LAOCOON program[14] installed in a Varian XL-200 NMR spectrometer. Four basic structures, **10**, **11**, **12**, and **13**,



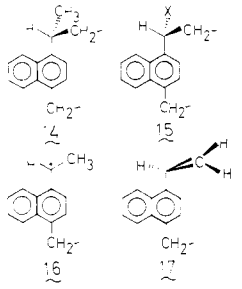
were used and coupling constants of ABCDEF system[15] were calculated by the Karplus equation,[16] using dihedral angles read from each molecular framework using the Dreiding model. Structures **10** and **12** gave the well-fitted simulations of H_a (or H_C in **10** and **12**) and H_c (or H_F) resonances of **7** and **8** with a small deviation from the predicted coupling constants (less than 3 Hz), but models **11** and **13** of peri attack could not produce any fitted spectrum within such a deviation. Thus, ring systems of **7** and **8** were confirmed, including the direction of the phenyl group.

With the assumption that each methyl group is located as shown in structures **7** and **8**, the ^1H NMR chemical shift difference observed between these methyl groups (see Table III) can be reasonably interpreted by the anisotropic shielding effect of the phenyl group attached to the indane moiety. Thus, the structures of compounds **7** and **8** are determined.

(b) Flipping of the Substituted Methylene Bridge in [3.3](1,4)Naphthalenophanes. The flipping of the substituted methylene bridge in compound **6d** was investigated by VT NMR spectroscopy (270 MHz) together with comparison with simulation as mentioned above. The activation free energy at 273 K, $\Delta G^{\ddagger}_{273}$, was calculated 12.0 ± 1.4 kcal/mol (the major/minor conformer ratio at −60 °C, was 68/32). Again any severe retardation of the flipping motion in **6d** was not recognized (Figure 2).

(3) Mechanism of Cationic Cyclocodimerization via α-Naphthylmethylcarbenium Ion. All compounds derived from the initial protonation at the vinylnaphthyl moiety possess structural unit **14** in their skeletons.

(11) CT band of the donor–acceptor complex with TCNE in CH_2Cl_2.
(12) These spectroscopies are very sensitive to the overlapping mode of the aromatic rings, because of excimer formation in fluorescence spectroscopy and CT complex with TCNE by their donor nature.
(13) The framework for a peri-attacked hypothetical product suggests that the product is sterically too crowded to be formed.
(14) For a review, see: Abraham, R. J. "The Analysis of High Resolution NMR Spectra"; Elsevier Publishing Company: New York, 1971.
(15) The $CH_3C(H)<$ moiety was ignored because the program capacity was not enough.
(16) Karplus, M. *J. Am. Chem. Soc.* **1963**, *85*, 2870–2871.



Moreover, all compounds derived from the intramolecular cyclization of the 1-vinylnaphthyl moiety do have structural unit **15**. These findings can be rationalized when the α-naphthylmethylcarbenium ion and 1-vinylnaphthyl group exist in exo conformation like **16** and **17**.[17] If **16** and **17** are arranged in the syn orientation, exo,cis,syn isomer **5** can be formed as a sole product, and if they are done in the anti orientation, only exo,trans,anti isomer **6** can be obtained. This is the origin of the stereoselectivity observed in the cationic cyclocodimerization via the α-naphthylmethylcarbenium ion (Scheme I).

In conclusion, the usefulness of the cationic cyclocodimerization for the preparation of these naphthalenophanes was again stressed. The stereoselectivity caused by the conformation of the intermediate cation and the vinylnaphthyl moiety was made clear, and the static and dynamic structures of products were clarified by several NMR spectroscopic methods.

Experimental Section

General Methods. Elemental analysis was done at the Microanalysis Center of Kyoto University at Uji. Melting points were not corrected. UV and visible spectra were recorded on a Shimadzu UV-190 double beam spectrophotometer. Fluorescence spectra were taken on a Hitachi MPF-4 spectrophotometer. NMR spectra were recorded on a Varian XL-200 NMR spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard, unless otherwise noted. VT NMR technique was the same as reported.[5] The VT NMR data were analyzed in the Data Processing Center of Kyoto Institute of Technology. NOE spectra were measured in nitrogenated $CDCl_3$. Parameters for NMR simulation are available.[18] IR spectra were taken on a JASCO IRA-1 spectrophotometer. Mass spectra were recorded on a Hitachi M80A mass spectrometer. HPLC analysis was carried out by using an Altex Model 110A pump and a Hitachi 635T wavelength tunable effluent monitor.[1,5]

Materials. CF_3SO_3H was purified by distillation. Benzene was distilled over CaH_2 after a prolonged reflux. Comonomers were dried and purified by distillation over CaH_2.

Preparation of St-C3-VN. The Grignard reaction of [2-(α-naphthyl)ethyl]magnesium bromide and benzaldehyde in ether gave 3-(α-naphthyl)-1-phenylpropanol, which was oxidized with Jones reagent and then reduced by Wolff–Kishner–Huang–Minglon procedure to afford 1-(α-naphthyl)-3-phenylpropane (mp 49–51 °C, 51.1% yield for the three steps). The compound was treated in $(CH_2Cl)_2$ by AcCl and $AlCl_3$ to give 1-[1-(4-acetylnaphthyl)]-3-(*p*-acetylphenyl)propane quantitatively. The diketone was reduced by $LiAlH_4$ to afford 1-[1-[4-(1-hydroxyethyl)naphthyl]]-3-[*p*-(1-hydroxyethyl)phenyl]propane in 98.5% yield. The alcohol was treated in Me_2SO at 170 °C for 10 min with $ZnCl_2$–CCl_3COOH.[19] The reaction mixture was poured into ice–water and extracted by cyclohexane. The cyclohexane extract was washed with water, dried over Na_2SO_4, and concentrated by evaporation. The desired olefin St-C3-VN was isolated in 59% yield by column chromatography (SiO_2, benzene/cyclohexane). The olefin was an easily polymerizable, viscous oil so that it was used without further purification.

The preparation of VN-C3-VN was already reported.[19]

Cationic Cyclocodimerization (General Procedure). VN-C3-VN (0.967 g, 2.78 mmol) and 2-phenylpropene (1.77 mL, 13.7 mmol) were dissolved in 116 mL of dry benzene under a nitrogen atmosphere. To the mixture was added all at once at 50 °C with vigorous stirring 0.4 mL of CF_3SO_3H–benzene solution (68.6 mM/L). After the mixture had stirred for 27 min, 10 mL of 5% aqueous NaOH was added to stop the reaction. The reaction mixture was washed 3 times with water, dried over Na_2SO_4, and concentrated by evaporation. 1-Methyl-3-(α-methylstyryl)-[3.3](1,4)naphthalenophane (**5a** and **6a**, 0.669 g, 51.6% yield) was isolated as a mixture of syn (**5a**) and anti (**6a**) isomers by column

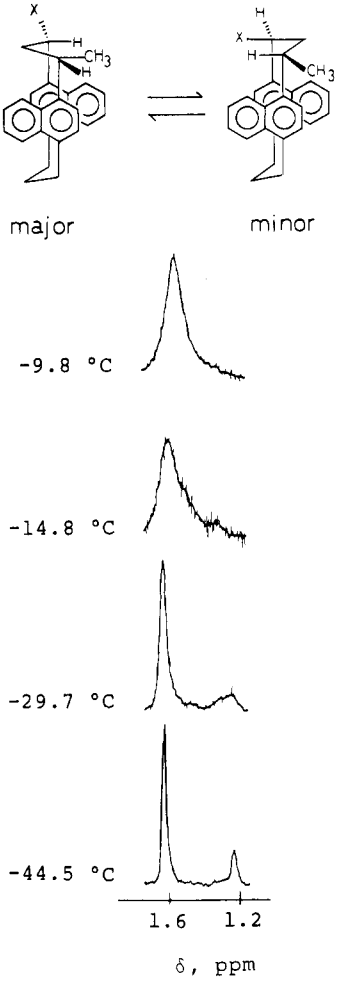


Figure 2. VT NMR spectra of *exo*-(*trans*-1-methyl-3-styryl)-*anti*-[3.3](1,4)naphthalenophane (**6d**). Taken in $(CD_3)_2CO$ on a JOEL FX 270 NMR spectrometer. The methyl group was observed as a singlet by the irradiation at the methine group.

Table VII. Analytical Data of Products

compd	MS ($M^{+\cdot}$, m/z) calcd (found)	elemental anal. calcd (found) C	H
1a	416.2502 (416.2500)		
1c	478.2659 (478.2659)		
1d	402.2346 (402.2344)		
5a		92.66 (92.57)	7.34 (7.40)
5c	528.2815 (528.2797)		
5d	452.2502 (452.2498)		
6a		92.66 (92.83)	7.34 (7.42)
6c	528.2815 (528.2826)		
6d		92.87 (92.63)	7.13 (6.96)
7	452.2502 (452.2508)		
8	452.2502 (452.2497)		

(17) Staley et al. (Staley, S. W.; Dustman, C. K.; Linkowski, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1069–1073) suggested a twisted exo form like **17** as a major conformer by NMR spectroscopy. In the present paper, the exo VN form means this twisted form. There was, however, no evidence led from any reaction so far as we searched in literatures.

(18) In supplementary material section.

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chromatography (SiO_2, cyclohexane/benzene). The isomer ratio was determined by the comparison of methyl signals in the 200-MHz ^1H NMR spectrum of the mixture. Both isomers were separated by HPLC (Cosmosil C-18, methanol, 30 °C), in which generally the anti isomer **6** was eluted more slowly than the syn isomer **5**. These products throughout the work were recrystallized from methanol.

Cyclophanes derived from St-C3-VN were prepared in the same manner as above, but they were isolated by HPLC, using Develosil-PYE instead of Cosmosil C-18, because the latter gave rather poor separation.

The analytical data of naphthalenophanes are summarized in Table VII and their ^1H NMR spectroscopic data are available.[18]

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Registry No. **1a**, 94645-41-7; **1b**, 91922-63-3; **1c**, 94730-81-1; **1d**, 94645-45-1; **2a**, 94730-09-3; **2b**, 92008-74-7; **2c**, 94645-43-9; **2d**, 94730-12-8; **3a**, 94645-42-8; **3b**, 91922-64-4; **3c**, 94645-44-0; **3d**, 94645-46-2; **4a**, 94730-10-6; **4b**, 92008-75-8; **4c**, 94730-11-7; **4d**, 94730-13-9; **5a**, 94645-47-3; **5b**, 91922-62-2; **5c**, 94645-48-4; **5d**, 94645-49-5; **6a**, 94730-14-0; **6b**, 92008-73-6; **6c**, 94730-15-1; **6d**, 94730-16-2; **7**, 94645-50-8; **8**, 94730-17-3; St-C3-VN, 91922-65-5; VN-C3-VN, 79541-70-1; 1-(α-naphthyl)-3-phenylpropane, 29908-29-0; 1-[1-(4-acetylnaphthyl)]-3-(*p*-acetylphenyl)propane, 94645-39-3; 1-[1-(4-(1-hydroxyethyl)naphthyl]-3-[*p*-(1-hydroxyethyl)phenyl]propane, 94645-40-6; 2-phenylpropene, 98-83-9; indene, 95-13-6; 1,1-diphenylethylene, 530-48-3; styrene, 100-42-5.

Supplementary Material Available: Tables of parameters for ^1H NMR simulation and of ^1H NMR spectroscopic data of naphthalenophanes (5 pages). Ordering information is given on any current masthead page.

Synthesis of 5-(Dihydroxyboryl)-2′-deoxyuridine and Related Boron-Containing Pyrimidines[1a]

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Organoboron derivatives of pyrimidines and of 2′-deoxyribonucleosides have been synthesized as potential antiviral and anticancer agents. The first 5-boron-substituted pyrimidine nucleoside, 5-(dihydroxyboryl)-2′-deoxyuridine, has been prepared via a metal–halogen exchange at −50 °C in tetrahydrofuran on 5-bromo-3′,5′-bis(*O*-trimethylsilyl)-2′-deoxyuridine using *n*-butyllithium followed by boronation at −65 °C with tri-*n*-butyl borate in the presence of HMPT. After hydrolysis, the product was purified by column chromatography and repeated fractional crystallization and the purity determined by HPLC. This hydrolytically stable compound showed no activity against Sarcoma 180 (S-180) but inhibited herpes simplex virus type 1 at a nontoxic concentration. The compound sensitized hamster V-79 cells to neutrons and could be of potential use in boron neutron capture therapy. 5-(Dihydroxyboryl)uracil and 6-(dihydroxyboryl)uracil were prepared also by a similar route from the corresponding 5- or 6-bromo-2,4-bis(benzyloxy)pyrimidine. However, the mixture was maintained at −85 °C during the whole reaction sequence and the product was obtained by hydrolysis followed by catalytic hydrogenation. The physical characteristics of these analogues, as well as those of their iminodiethanol esters, are described.

There is an increased interest in the preparation of boron compounds for their potential medicinal and biochemical applications. Numerous organoboron compounds have been investigated in the past with respect to their possible use in cancer therapy based on the ability of the ^{10}B isotope to absorb thermal neutrons thereby producing a cell-destroying nuclear reaction.[2] In addition, the utility of boron as a tool for providing insight into structure and reaction mechanisms rests on its close relationship to carbon. The fact that boron has a vacant p orbital is the origin of the strong electron acceptor properties of tricoordinate boron compounds and the ease with which tetracoordinated boron structures are formed. This unusual property has led to the synthesis of a host of boron-containing compounds as effective transition-state analogues for enzymes-catalyzing acyl-transfer reactions.[3,4] Many other organoborons have been reported to be of potential pharmaceutical importance as diuretics, anticoagulants, or tranquilizers.[2,5] Recently, synthetic models containing boron have been prepared for betaine,[6] glycine[7,8] and phenylalanine,[9-12] and acetylcholine.[13] Models for copper-blue proteins,[14] oxygen transporting proteins such

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