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The Complexing Abilities of Diethyleneoxy- and Xylene-bridged Cryptophanes with Alkanes

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The Syn isomers (3b and 4b) of xylene-bridged cryptophane showed selective complexing abilities for 2,2-dimethylbutane, 3-methylpentane, 3,3-dimethylpentane and 3-ethylpentane among the investigated alkanes, although the Anti isomers (3a, 4a, 5a) did not complex with these alkanes. However, both the Anti- and Syn-isomers (2a and 2b) of the diethyleneoxy-bridged cryptophane showed selective complexing abilities for 2,2-dimethylbutane, 3,3-dimethylpentane, 2,2,3-trimethylbutane and 2,2,3,3-tetramethybutane among the investigated alkanes.

Keywords: Cryptophanes, complexing abilities with alkanes, host–guest

INTRODUCTION

It is well known [1] that during the complexation of host molecules such as cyclophanes, cryptophanes, polands and spherands, having an elliptical hole with various guest molecules, the three-dimensional agreement between the cavity size of the host molecule and the size and shape of the guest molecule, was shown to be important in forming a stable complex. Among these guest molecules, spherical compounds such as cryptands and cryptophanes should be the most favorable for the recognition of spherical guest molecules [1,2]. Collet *et al.* [3–9] reported the syntheses of several kinds of cryptophanes and their complexing abilities with alkylammonium cations and halomethane. For example, cryptophane E can selectively incorporate chloroform and tetramethylammonium cations into the cavity [9,10]. The same behavior is observed with aliphatic hydrocarbons such as isobutane [11], which shows strong binding (*Ka* ca. 100^{-1}) with the trimethylene-bridged cryptophane (**1a**). The cryptophanes, in which the three bridges are relatively short, possess a roughly ridged spherical and lipophilic cavity and the three windows that allow a suitable guest to enter. The size of the cryptophane cavity and the three windows can be changed by varying the length and the structure of the bridge unit. In connection with the above viewpoint, we have already reported the syntheses and the complexing abilities of the diethyleneoxy- and the *o*- and *p*-xylene-bridged cryptophanes with alkyl ammonium cations [12,13]. As described above, the complexing

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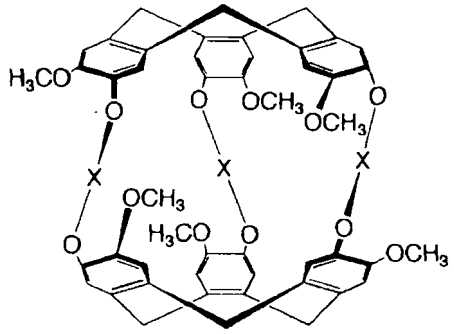
ability of the trimethylene-bridged cryptophanes (**1a**) with isobutane was investigated by Collet *et al.* [11]. However, there is no systematic report on their complexing ability with alkanes. Therefore, we examined the complexing abilities of the diethyleneoxy- and the *o*- and *p*-xylene-bridged cryptophanes with several kinds of alkanes having different carbon numbers and shape, as the guest molecules.

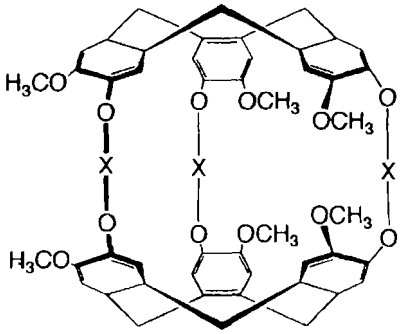
RESULTS AND DISCUSSION

Synthesis of Cryptophanes

The host molecules, **2a** ~ **5a**, **2b** and **4b**, were prepared according to the methods described in the previous papers [12, 13]. In the previous paper [13], we reported the synthesis of **Anti-3a** by the intermolecular cyclization of α,α'-bis[4-hydroxymethyl-2-methoxyphenoxy]-*o*-xylene in formic acid in 3% yield. Also, **Anti-3a** was obtained by the intramolecular cyclization of **rac**-2, 7, 12-tris[2-[4-hydroxymethyl)2-methoxyphenoxymethyl]benzyloxy]-3, 8, 13-trimethoxy-10,15-dihydro-5H-tribenzo [*a*,*d*,*g*]cyclononene in formic acid in 28% yield [13]. However, unfortunately, **Syn-3b** could not isolated in any amount in the above reactions. Therefore, we have tried carefully again to isolate **3b** from the intramolecular cyclization products of **rac-6** as shown in the reaction scheme. The solution of **rac-6** in formic acid was stirred for 24 h at room temperature under a nitrogen atmosphere. After the reaction mixture was treated by the usual procedure, it was chromatographed on silica gel chromatography (dichloromethane-ethyl acetate = 40 : 1) followed by preparative thin layer



Anti-form

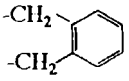


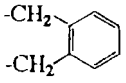
Syn-form

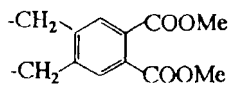
1a: X= $-CH_2CH_2CH_2-$

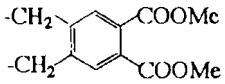
2a: X= $-CH_2CH_2OCH_2CH_2-$

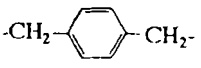
2b: X= $-CH_2CH_2OCH_2CH_2-$

3a: X= 

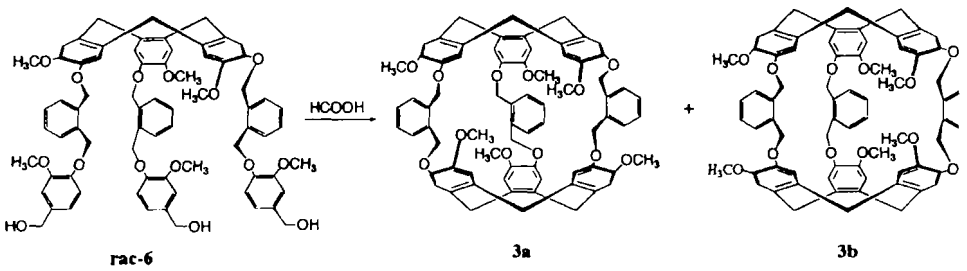
3b: X= 

4a: X= 

4b: X= 

5a: X= 

SCHEME 1



SCHEME 2

chromatography (Wakogel B-5F, dichloromethane: ethyl acetate (40:1) to give crude **3a** (Rf = 0.63) and **3b** (Rf = 0.55). Crude **3a** and **3b** were recrystallized from dichloromethane-methanol to gave **3a** and **3b** in 25 and 31% yields, respectively. The structure of the new compound **3b** was determined using the ^{1}H-NMR and mass spectra, elemental analysis, and high-performance liquid chromatography of **Syn-3b** using an optically active column (CHIRALPAK-OT(+)), showed only one peak, however, compound **Anti-3a** showed two peaks (relative intensity 1:1) due to the presence of optical isomers. As shown in Figure 1, the chemical shifts and coupling constants of the methoxy, the bridging methylene protons and the aromatic protons of the *o*-xylene and the cyclotriveratrylene moieties of **Syn-3b** were slightly different from those of **Anti-3a**, although the ^{1}H NMR spectrum of **Anti-3a** is very similar to that of **Syn-3b**.

These results suggest that **Anti-3a** is a racemic mixture and **Syn-3b** is a meso form.

Complexing Abilities of Cryptophanes with Alkanes

The complexing abilities of a host molecule such as a cryptand and its homologs with a guest ion or molecule depend on several factors: [1] the cavity size of the host molecules, the diameter of the guest ion or molecule, the spatial distribution of the ring binding sites, and the character of the heteroatoms, *etc.* A study of the cryptophanes has also shown that three-dimensional agreement between the hole size of the host molecule and the size of the guest molecule leads to stable inclusion complexes [2,3]. For example, the trimethylene-bridged cryptophane (**1a**) selectively incorporates the match-sized halomethane into the three-dimensional cavity [9,10]. In order to investigate the complexing abilities of cryptophanes with various alkanes, ^{1}H-NMR spectral studies were carried out. As shown in Figure 2, the ^{1}H-NMR spectra of 3,3-dimethylpentane in the solvent (CD_2Cl_2) at 300 K showed the methyl (C1 and C5) and methylene (C2 and C4) proton peaks at δ 0.72(*s*) and 1.12(*q*), respectively, together with the methyl (side chain) proton peak at δ 0.70. Adding 0.5 equivalent of **Syn-3b** in the above solution, the spectral changes in the guest molecule could not be observed. Therefore, in order to determine the inclusion ability, variable temperature ^{1}H-NMR measurements (300 – 210 K, at several intervals) were carried out. At low temperature (210 K), slow exchange on the NMR time scale was observed, and new peaks due to the included guest molecule appeared at δ – 2.13 (*s*, CH_3), – 1.30 (broad *q*, CH_2) and – 0.43 (*t*, CH_3) together with the proton peaks due to the free guest molecule. The huge upfield shifts of the guest molecule protons are in agreement with its inclusion in the cavity of the host molecule (**Syn-3b**). The upfield chemical shift changes in the methyl (C1 and C5), methylene (C2 and C4) and methyl (side chain) protons due to inclusion were 1.15, 2.42 and 2.83 ppm, respectively. A

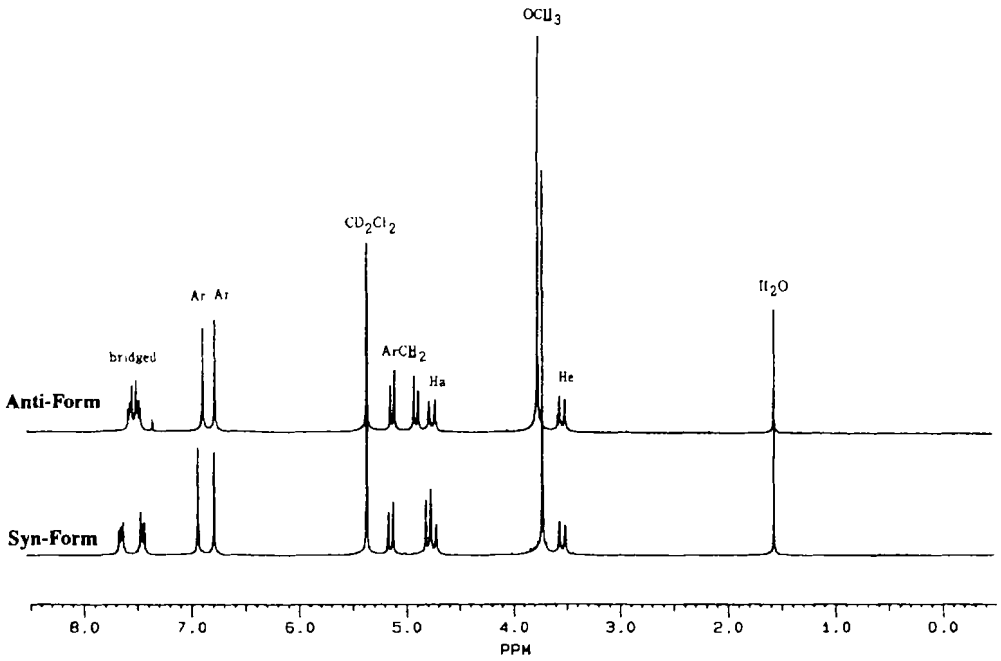


FIGURE 1 ^{1}H-NMR spectra of Anti-3a and Syn-3b in CD_2Cl_2.

similar result was also observed in the complexation of **Syn-3b** with 3-methylpentane. The upfield shifts of the methyl (C1 and C5), methylene (C2 and C4), side chain methyl and methyne (C3) protons of the included guest molecule were 1.45, 1.89, 2.81 and 3.27 ppm, respectively. These results suggest that the upfield chemical shift changes in the protons attached on the near central carbon atom were larger than that of the terminal methyl protons. The apparent equilibrium constant K for the complexation of **Syn-3b** with 3,3-dimethylpentane was estimated by the integral ratio between the free and complexed peak areas of the guest molecule to be $K \sim 58\,M^{-1}$, which was apparently constant in the competition with the solvent, and the free energy change ΔG was calculated to be -1.75 Kcal/mol at 210 K. The results of the temperature dependence ^{1}H-NMR measurements suggested that the complexing ability of **3b** with 3,3-dimethylpentane increased with decreasing temperature. Furthermore, ΔH and ΔS were estimated from the temperature dependence of the ^{1}H-NMR spectra measurements (range 210 to 300 K). A more interesting result was observed in the complexation of **Syn-3b** with 3-ethylpentane. As shown in Figure 3, the ^{1}H-NMR spectra of the mixture of 3-ethylpentane and **Syn-3b** (1:2 ratio) in CD_2Cl_2 at 240 K showed the peaks of the methyl, methylene, and methyne protons due to the included guest molecule at $\delta -0.45$ (t), -1.40 (br. s) and -2.12 (m), respectively. However, the broad methylene peak at $\delta -1.40$ separated into two peaks (at $\delta -1.08$ and -1.82) at 210 K. This seems to be explained as follows: the incorporated guest molecule may be tightly complexed in some direction in the hole of the host molecule, and the two methylene protons attached on the same carbon atom then became magnetically non-equivalent due mainly to the ring current effect of the nine benzene rings of the host molecule. In order to investigate more details of the inclusion manner, the measurement of the NOE ^{1}H-NMR spectra of the solution at 210 K was carried out; however, we

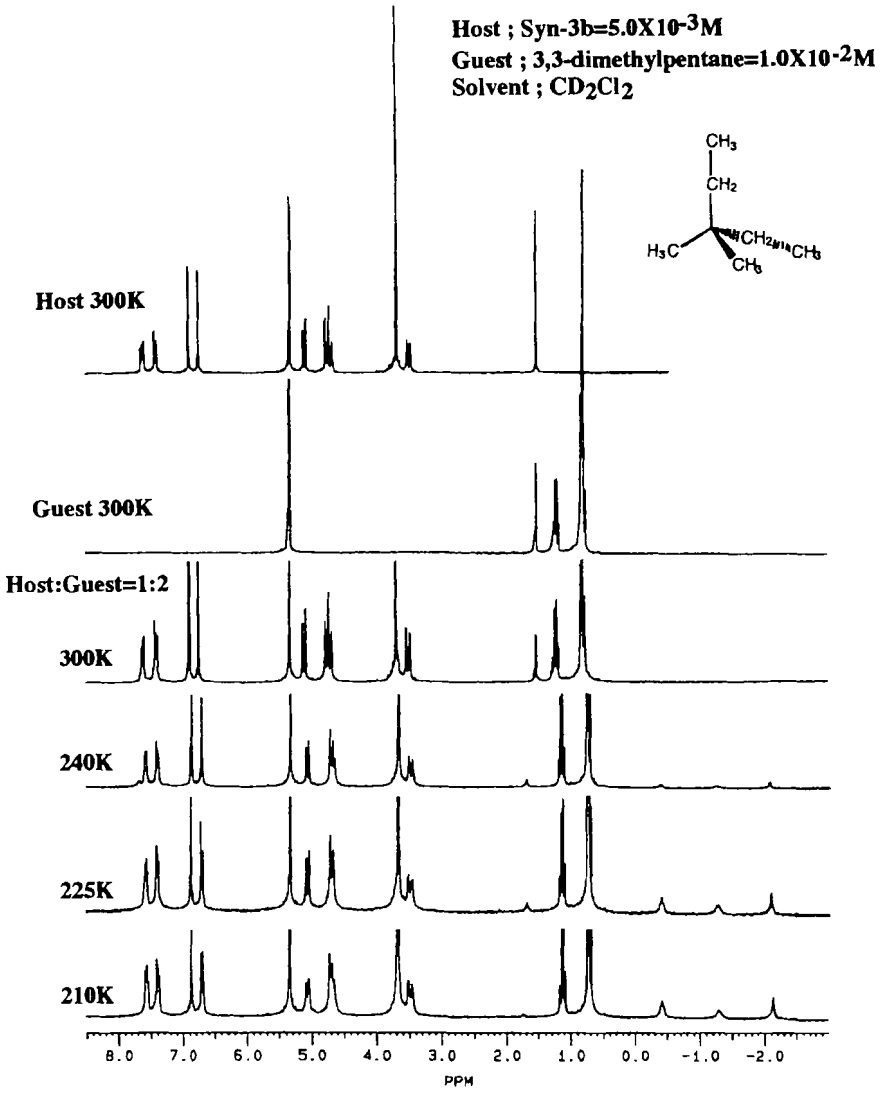


FIGURE 2 ^{1}H-NMR spectra of 3,3-dimethylpentane in the presence of Syn-3b.

could not obtain clear results. As described in the previous paper [12, 13], the effect of the complexing abilities of the cryptophanes with undeuterated solvent (CH_2Cl_2) were investigated by a similar method in the temperature range between 210 to 300 K. However, no complexing phenomena could be observed because the equilibrium of the complexation of the cryptophanes with the solvent is very fast on the time scale of this ^{1}H-NMR due to the mismatch between the hole size of the host molecules and the solvent as the guest molecule. Therefore, the complexing abilities of all cryptophanes with the deuterated solvent (CD_2Cl_2) are neglected in the calculation of the following thermal parameters. The complexing abilities of cryptophanes with other alkanes were investigated by the ^{1}H-NMR spectra using the same method described above. These results are summarized in Table I. The diethyleneoxy bridged-cryptophanes **Anti-2a** and **Syn-2b** were capable of complexing with alkanes containing a quar-

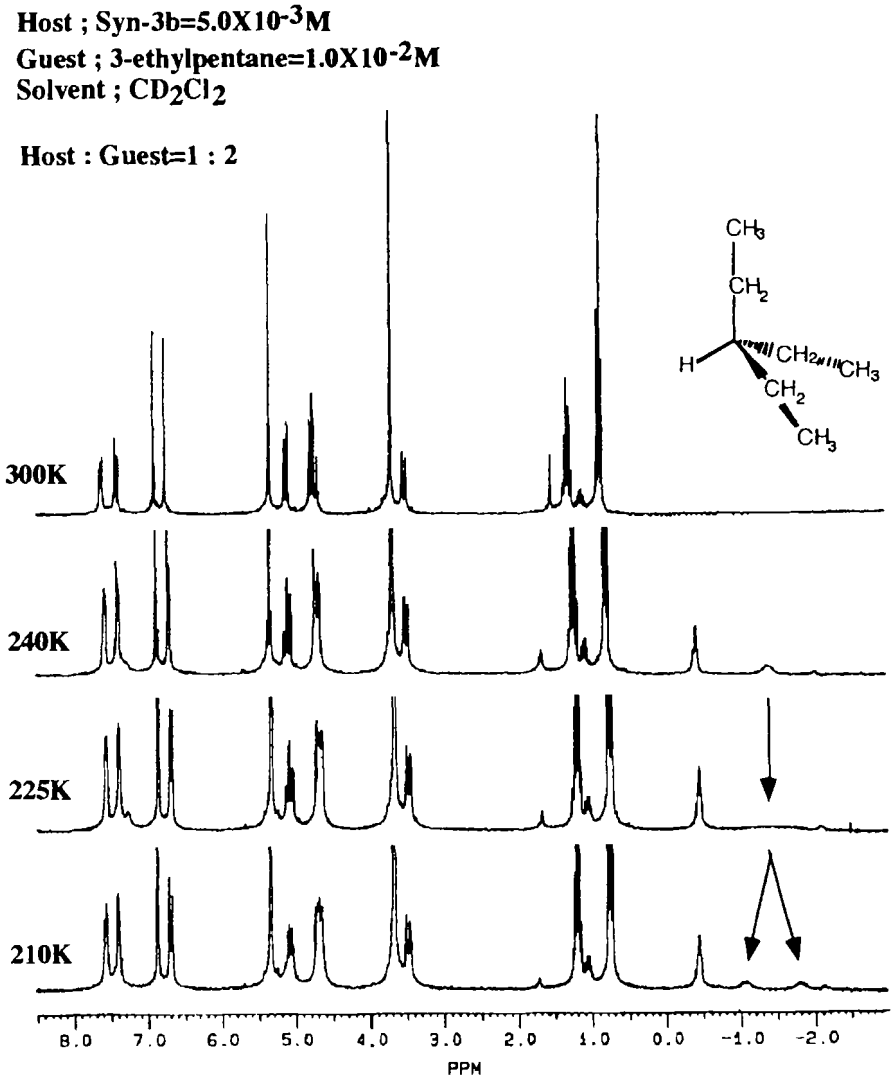


FIGURE 3 ^{1}H-NMR spectra of 3-ethylpentane in the presence of Syn-3b.

ternary carbon atom except 3,3-dimethylhexane among the investigated guest molecules. The cavity of **Syn-2b** appears to be slightly larger due to symmetry than that of **Anti-2a**. The windows between the two bridged chains in **Anti-2a**, through which the guest molecule should go in order to be complexed, are slightly distorted compared to that of **Syn-2b**. However, the inclusion abilities of **Anti-2a** were comparable to those of **Syn-2b**. The results suggest that the ethyleneoxy bridges of **Anti-2a** could twisted to form the complex with the alkane. Therefore, large difference in the complexing abilities of **Syn-2b** and **Anti-2a** with alkanes were not observed. In contrast to the diethyleneoxy-bridged cryptophanes (**Anti-2a** and **Syn-2b**), the **Anti forms** of the xylene-bridged cryptophanes (**Anti-3a**, **Anti-4a** and **Anti-5a**) did not include the alkanes as guest molecule among the investigated alkanes, although both **Syn-3b** and **Syn-4b** showed higher complexing abilities toward 2,2-dimethylbutane, 3-methylpentane,

TABLE I Equilibrium constants (K), the free energy changes (ΔG) and Thermodynamic parameters for the complexation of aromatic bridged cryptophanes with neutral molecules (hydrocarbon)[a, b]

		2a (anti)	**2b** (syn)	**3a** (anti)	**3b** (syn)	**4a** (anti)	**4b** (syn)	**5a** (anti)
C_6H_{14}								
2,2-dimethylbutane	$K(M^{-1})$	5.48	5.63	–	65.5	–	106	–
	ΔG(kcal/mol)	−0.71	−0.72	–	−1.75	–	−1.95	–
	ΔH(kcal/mol)	−2.14 ± 0.08	−2.07 ± 0.45	–	−7.40 ± 1.39	–	−7.45 ± 0.60	–
	ΔS(cal/mol)	−6.81 ± 0.36	−6.37 ± 2.01	–	−26.1 ± 6.0	–	−26.1 ± 2.7	–
3-methylpentane	$K(M^{-1})$	–	–	–	271	–	202	–
	ΔG(kcal/mol)	–	–	–	−2.34	–	−2.21	–
	ΔH(kcal/mol)	–	–	–	−6.70 ± 0.04	–	−7.02 ± 0.63	–
	ΔS(cal/mol)	–	–	–	−20.8 ± 0.2	–	−22.8 ± 2.8	–
2,3-dimethylbutane	$K(M^{-1})$	Δ	Δ	–	3.58	–	2.64	–
	ΔG(kcal/mol)	Δ	Δ	–	−0.53	–	−0.40	–
	ΔH(kcal/mol)	Δ	Δ	–	Δ	–	Δ	–
	ΔS(kcal/mol)	Δ	Δ	–	Δ	–	Δ	–
C_7H_{16}								
3,3-dimethylpentane	$K(M^{-1})$	23.3	21.7	–	58.3	–	67.3	–
	ΔG(kcal/mol)	−1.31	−1.28	–	−1.75	–	−1.76	–
	ΔH(kcal/mol)	−3.28 ± 0.24	−3.11 ± 0.02	–	−6.36 ± 1.75	–	−7.91 ± 1.00	–
	ΔS(cal/mol)	−9.32 ± 1.05	−8.70 ± 0.11	–	−21.9 ± 7.8	–	−29.2 ± 4.5	–
3-ethylpentane	$K(M^{-1})$	–	–	–	66.8	–	189	–
	ΔG(kcal/mol)	–	–	–	−1.75	–	−2.19	–
	ΔH(kcal/mol)	–	–	–	−6.30 ± 1.96	–	−8.83 ± 1.61	–
	ΔS(cal/mol)	–	–	–	−20.6 ± 8.4	–	−30.7 ± 6.9	–
2,2,3-trimethylbutane	$K(M^{-1})$	43.3	56.3	–	–	–	–	–
	ΔG(kcal/mol)	−1.57	−1.68	–	–	–	–	–
	ΔH(kcal/mol)	−3.04 ± 0.39	−3.34 ± 0.88	–		–	–	–
	ΔS(cal/mol)	−7.07 ± 1.76	−7.35 ± 3.79	–	–	–	–	–
2,4-dimethylpentane	$K(M^{-1})$	–	–	–	–	–	–	–
n-heptane	$K(M^{-1})$	–	–	–	–	–	–	–
C_8H_{18}								
2,2,3,3-tetramethylbutane	$K(M^{-1})$	33.7	35.6	–	–			
	ΔG(kcal/mol)	−1.47	−1.49	–	–			
	ΔH(kcal/mol)	−5.17 ± 1.57	−3.41 ± 1.99	–	–	–	–	–
	ΔS(cal/mol)	−15.8 ± 6.5	−7.49 ± 8.18	–	–	–	–	–
3,3-dimethylhexthane	$K(M^{-1})$	Δ	Δ	–	–	–	–	–

[a] K values were estimated by 1H-NMR spectra: Host = 5.0×10^{-3} M and guest molecule = 1.0×10^{-2} M at 210K in CD_2Cl_2. ΔG values were calculated from K ($\Delta G = -RT\ln K$). ΔH and ΔS were estimated from van't Hoff plot (lnK vs 1/T). The errors of ΔH and ΔS were the estimated standard errors calculated from least-squares linear regression by the literature; N. R. Draper and H. Smith, "Applied Regression Analysis" John Wiley & Sons, Inc., New York, (1966).

[b] D means that the complexing abilities were very low to calculate the thermodynamic parameters.

2,3-dimethylbutane, 3,3-dimethylpentane and 3-ethylpentane than those of the diethyleneoxy-bridged cryptophanes (**Anti-2a** and **Syn-2b**). The obvious differences in the complexing abilities of the **Anti-** and **Syn-forms** of the xylene-bridged cryptophanes may be due to the rigidities of the bridged moieties and the shapes of the host molecules which hold tightly compared with those of the ethyleneoxy-bridged cryptophanes (**Anti-2a** and **Syn-2b**). Furthermore, both of the diethyleneoxy-bridged cryptophanes (**Anti-2a** and **Syn-2b**) showed complexing abilities toward 2,2,3-trimethylbutane and 2,2,3,3-tetramethylbutane, although the xylene-bridged cryptophanes (**Anti-3a**, **Syn-3b** **Anti-4a**, **Syn-4b** and **Anti-5a**) do not show any complexing abilities toward these guest molecules.

Also, the complexing abilities of the cryptophanes (**Anti-2a**, **Syn-2b**, **Anti-3a**, **Syn-3b**, **Anti-4a**, **Syn-4b** and **Anti-5a**) with 2,3-dimethylbutane, 2,4-dimethylpentane, *n*-pentane, 3,3-dimethylhexane were investigated; however, no complexation, or very low complexation, was observed.

CONCLUSION

The xylene-bridged cryptophane (**Syn-3b**) was isolated from the intramolecular cyclization products of **rac-6** in 31% yield together with **Anti-3a**. The ethyleneoxy-bridged cryptophanes (**Anti-2a** and **Syn-2b**) showed selective complexing abilities for 2,2-dimethylbutane, 3,3-dimethylpentane, 2,2,3-trimethylbutane and 2,2,3,3-tetramethylbutane; however, the differences in the complexing abilities between **Syn-2b** and **Anti-2a** could not be observed. The **Syn-forms** (**3b** and **4b**) of the xylene bridged-cryptophane showed selective complexing abilities for 2,2-dimethylbutane, 3-methylpentane, 3,3-dimethylpentane and 3-ethylpentane among the investigated alkanes, although the **Anti isomers** (**3a**, **4a** and **5a**) did not complex with these alkanes.

EXPERIMENTAL SECTION

Melting points were determined using a Yazawa micro m.p. apparatus and are uncorrected. ^{1}H-NMR spectra were recorded with a Brucker AC250 spectrometer (250 MHz) with $(CH_3)_4Si$ as the internal standard. Elemental analyzes were carried out using a Perkin-Elmer 2400 instrument. Electron impact (EI) and field desorption (FD) were recorded on Hitachi M-80 and M-2000 spectrometers, respectively. The high-performance liquid chromatography (HPLC) was carried out with a JASCO HPLC system with a Chiralpak-OT(+) column monitored by UV absorption measurements.

MATERIALS

Rac-2,7,12-Tris[2-[4-Hydroxymetyl)-2-Methoxyphenoxymethyl]-3,8,13-Trimethoxy-10,15-Dihydro-5H-Tribenzo[*a*,*d*,*g*]cyclononene (**rac-6**) was prepared according to the procedure described in the previous paper [13]. Diethyleneoxy-and xylene-bridged cryptophanes (**Anti-2a**, **Syn-2b**, **Anti-3a**, **Anti-4a**, **Syn-4b** and **Anti-5a**) were also prepared according to the procedures described in the previous paper [12, 13]. Alkanes as guest molecule were of reagent grade and were used without further purification.

Synthesis of Syn-3b

The solution of **rac-6** (1.0 g, 0.85 mmol) in dichloromethane (5 mL) was added to formic acid (1.2 L) and stirred at room temperature for 24 h under nitrogen atmosphere. Water (1 L) was added to the solution, which was then stirred for 1 h at room temperature. The resulting precipitate was collected by filtration and the residue was dissolved in dichloromethane. The solution was washed with water, dried and concentrated in vacuo. The residue was separated by silica gel chromatography [dichloromethane-ethyl acetate (40:1)] followed by thin layer chromatography

[Wakogel B-5F, dichloromethane:ethyl acetate (40:1)] to give crude **Anti-3a** (Rf = 0.63) and **Syn-3b** (Rf = 0.55). Crude **Anti-3a** was recrystallized from dichloromethane/methanol to produce pure **Anti-3a**, which had already been obtained by this method, as a colorless powder. Yield 25%. m.p. > 220°C (dec.) Lit. [13] > 220°C (dec.).

Crude **Syn-3b** was recrystallized from dichloromethane/methanol to produce pure **Syn-3b** as a colorless powder. Yield 31%. m.p. > 260°C(dec.). MS(FD) m/z 1122 (M^+). Anal. Calcd. for $C_{72}H_{66}O_{12}$ $0.5CH_2Cl_2$: C, 74.70; H, 5.79%. Found: C, 74.99; H, 5.57%. ^{1}H-NMR (250 MHz, CD_2Cl_2): 3.50 (*d*, *J* = 13.7 Hz, 6H, He), 3.69 (*s*, 18H, OCH_3), 4.71 (*d*, *J* = 13.7 Hz, 6H, Ha), 4.76 (*d*, *J* = 11.6 Hz, 6H, OCH_2), 5.11 (*d*, *J* = 11.6 Hz, 6H, OCH_2), 6.75 (*s*, 6H, Ar), 6.90 (*s*, 6H, Ar), 7.39–7.43 (*m*, 6H, Ar), and 7.60–7.65 (*m*, 6H, Ar).

Determination of Anti and Syn Structures

The configurations of **Anti-3a** and **Syn-3b** were determined using HPLC with a Chiralpak-OT (+) column, and they were resolved on this column with good selectivity. The chromatographic conditions were as follows: column temperature, 5°C; wavelength, 230 nm; and flow rate, 1.0 mL/min. The HPLC was carried not using methanol as an eluent, and **Anti-3a** and **Syn-3b** in chloroform solution were injected into the HPLC. The retention times of **Anti-3a** (racemic mixtures) were 34.3 and 110.4 min. The ratio of the two peaks was found to be 1:1, and the retention time of **Syn-3b** (meso form) was 56.9 min as a single peak. Therefore, **Anti-3a** and **Syn-3b** were determined as chiral and an achiral molecules, respectively.

Complexation Studies

All measurements of ^{1}H-NMR spectra were carried out with Brucker AC250 (250 MHz) spectrometer in CD_2Cl_2. The peaks of the complexed guest alkane frequently appeared in the vicinity of TMS, so that the peak of the undeuterated dichloromethane of the solvent at δ 5.33 ppm was employed as the internal standard. All concentrations of guest alkanes were ca. 1.0×10^{-2} M and all concentrations of the cryptophanes as host molecules were ca. 5.0×10^{-3} M. Each equilibrium constant (*K*) and free energy change (ΔG) for the complexations of the host molecules with various alkanes was estimated by the integral ratio between the approximate peak area of the free and included guest alkane. The influence of the solvent on the complexation of the cryptophanes was measured using the undeuterated solvent (CH_2Cl_2) contained ca 20% deuterated (CD_2Cl_2); however, the peaks of CH_2Cl_2 incorporated into the cavity of the host molecule could not be observed at any temperature (210–300 K). Furthermore, when an excess of CH_2Cl_2 as a guest molecule was added to the cryptophanes in CD_2Cl_2, the peak due to the incorporated CH_2Cl_2 in ^{1}H-NMR spectra was not observed. The thermodynamic parameters for the incorporations were calculated using the van't Hoff plots ($\ln K$ *vs.* $1/T$) [14], in which the *K* values were from variable temperature ^{1}H-NMR spectra (300–210 K). Thus, the complexation of the host molecules with deuterated solvent was neglected in the consideration of the complexation of the host molecules with various alkanes. The changes in enthalpy and entropy for the complexation (ΔH and ΔS) were calculated by the plots of ΔG *vs.* *T*, which was given by variable temperature ^{1}H-NMR (mainly at 210, 230, 250, 270 and 300 K), according to the equation $\Delta G = \Delta H - T\Delta S$. The errors in ΔH and ΔS were the estimated standard errors calculated from the least-squares linear regression from the literature [15].

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