

# Complexation Properties and Characterization of Four Conformers of a [2.1.2.1]Metacyclophane<sup>\*</sup>

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**Abstract.** Cone, partial cone, 1,2-alternate, and 1,4-alternate conformers of tetrakis[(ethoxycarbonyl)methoxy] [2.1.2.1]metacyclophane (MCP, **2**) were isolated and characterized by <sup>1</sup>H-NMR and an X-ray crystal structure analysis of the 1,4-alternate conformer. Of the four conformers, only the cone conformer **2d** forms a complex with alkali metals. The stability constants of **2d** with alkali metal ions were determined by the direct <sup>1</sup>H-NMR method and UV spectra, and the order observed as potassium ≪ cesium, sodium ions.

**Key words:** Metacyclophane, conformational isomers, ion-selectivity, calixarenes.

## 1. Introduction

Calix[*n*]arenes have attracted great attention as ionophoric receptors [1–4] and potential enzyme mimics [5] in host–guest chemistry. Shinkai *et al.* have reported the preparation and ionophoric properties of four conformers of tetra-*tert*-butyl-tetrakis[(ethoxycarbonyl)methoxy]calix[4]arene [6–8]. Cone and partial-cone conformers are obtained by the metal template effect using sodium and cesium ions, respectively, but the 1,2-alternate and 1,3-alternate conformers were synthesized by the protection–deprotection method [8–10]. They also found that the cone conformer shows a selectivity for sodium [6] and the other conformers show a selectivity for potassium [8].

In our laboratory we have investigated the preparation and reactivities of [2,2]metacyclophanes for two decades. We have developed the sulfur method using the *tert*-butyl group as a positional-protecting group. Using this method we have also prepared [2.*n*.2.*n*]metacyclophanes [11, 12]. These metacyclophanes can be regarded as calixarene homologues and are expected to have larger cavities. Their framework should be more flexible than that of the calix[4]arenes [13–15].

\* This paper is dedicated to the commemorative issue on the 50th anniversary of calixarenes.

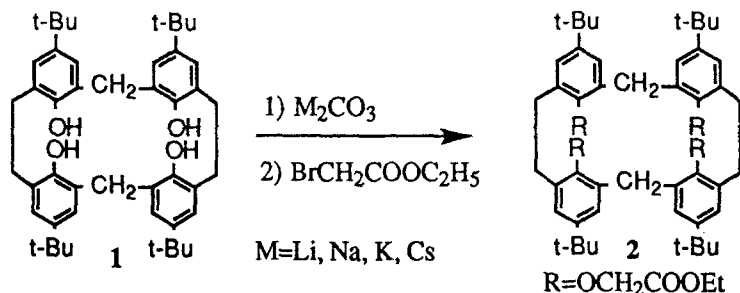
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Here we describe the isolation and the ionophoric properties of the conformers of tetra-*tert*-butyl-tetrakis[(ethoxycarbonyl)methoxy][2.1.2.1]metacyclophane (MCP), a homologue of calix[4]arene.

## 2. Results and Discussion

### 2.1. PREPARATION AND CONFORMATIONAL PROPERTIES

The tetrakis (ethoxycarbonyl)methoxy MCP derivative **2** was obtained as a mixture of conformers in the reaction of tetrahydroxy[2.1.2.1]MCP (**1**) [12] and ethyl bromoacetate in the presence of alkali carbonates in acetone or a mixture of DMF and THF. The ratio of the conformers, **2a**, **2b**, **2c**, and **2d** was determined by HPLC (Megapak Sil-10: 7.5 mm  $\times$  250 mm, a 8.5 : 1.5 mixture of hexane : ethyl acetate as an eluent) (Table I).



Scheme 1.

TABLE I. Reaction conditions and conformer distribution of **2**.

Solvent	Base	Yield of <b>2</b> (%)	Distribution <sup>a</sup> of <b>2</b>	Other (%)
			( <b>2a</b> : <b>2b</b> : <b>2c</b> : <b>2d</b> )	
	Li <sub>2</sub> CO <sub>3</sub>	43	(30 : 28 : 39 : 3)	<b>3</b> <sup>b</sup> 40
DMF-	Na <sub>2</sub> CO <sub>3</sub>	92	(33 : 34 : 17 : 16)	
THF	K <sub>2</sub> CO <sub>3</sub>	83	(43 : 20 : 18 : 19)	
	Cs <sub>2</sub> CO <sub>3</sub>	80	(36 : 35 : 14 : 15)	
	Li <sub>2</sub> CO <sub>3</sub>	0		<b>1</b> 80
Acetone	Na <sub>2</sub> CO <sub>3</sub>	92	(25 : <1 : <1 : 74)	
	K <sub>2</sub> CO <sub>3</sub>	83	(36 : 11 : 13 : 40)	
	Cs <sub>2</sub> CO <sub>3</sub>	80	(35 : 24 : 13 : 28)	

<sup>a</sup>Determined by HPLC (Megapak Sil-10: 7.5 mm  $\times$  250 mm, a 8.5 : 1.5 mixture of hexane : ethyl acetate as eluent).

<sup>b</sup>Bis(ethoxycarbonylmethoxy)dihydroxy[2.1.2.1]MCP **3** was obtained as a by-product, but its region structure cannot be classified. **3** was separated by column chromatography (Wako gel C300, a 9 : 1 mixture of hexane : ethyl acetate as eluent).

In most cases four conformers were obtained but interestingly, when sodium carbonate in acetone was used, only the partial-cone and the cone conformer, **2a** and **2d**, were obtained in 23 and 68% yield. Each conformer could be isolated by careful column chromatography on silica gel (Wako C-300) using an 8.5 : 1.5 mixture of hexane : ethyl acetate as an eluent ( $R_f$  of **2a**: 0.25, **2b**: 0.33, **2c**: 0.37, and **2d**: 0.07).

If we suppose that there is no flipping but some flexibility of the benzene rings, we can expect five conformers of **2**, which can be expressed in terms of calix[4]arene nomenclature. As for the calix[4]arenes, for **2** the cone, partial-cone and 1,3-alternate conformations are possible. Two types of 1,2-alternate conformation, which we call the 1,2-alternate and 1,4-alternate, can be expected. Compound **2** has two alternate bridges with different lengths, an ethylene and a methylene bridge. In the 1,2-alternate conformation, the aromatic rings are reversed at the ethylene bridges, while in the 1,4-alternate, they are reversed at the methylene bridges (Figure 1).

The X-ray crystal structure of **2b** showed it to be the 1,4-alternate conformer (Figure 2); its benzene rings are reversed at the methylene bridges. In the cases of 1,2-alternate conformers of calix[4]arene derivatives, the  $^1\text{H-NMR}$  spectra show the methylene bridges as one singlet and two doublets [8]. The singlet was identified as that of the alternate bridge protons and the two doublets as due to the other bridge protons. Just as for the calix[4]arenes, the methylene protons of **2b** were observed as a broad singlet in the  $^1\text{H-NMR}$  spectrum (Figure 3). These protons are magnetically equivalent and do not show a geminal coupling.

Each of the  $^1\text{H-NMR}$  spectra of **2c** and **2d** showed only one singlet for the *tert*-butyl groups. This result suggests that **2c** and **2d** are either the 1,2-alternate, 1,3-

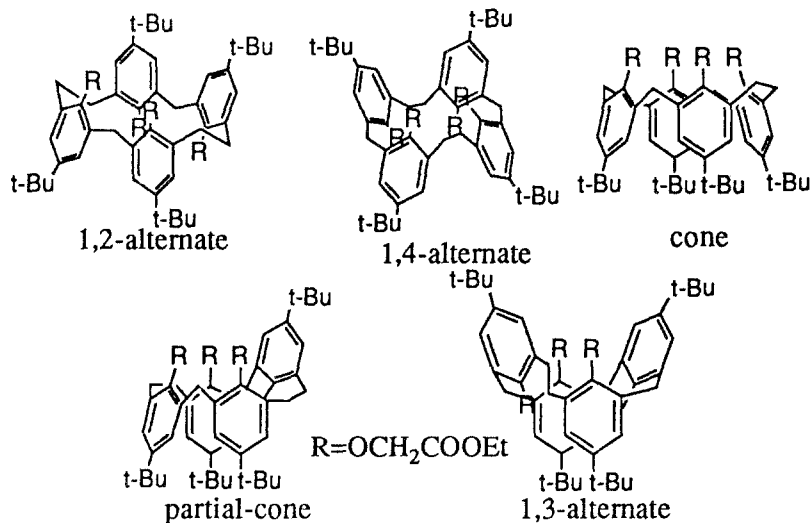
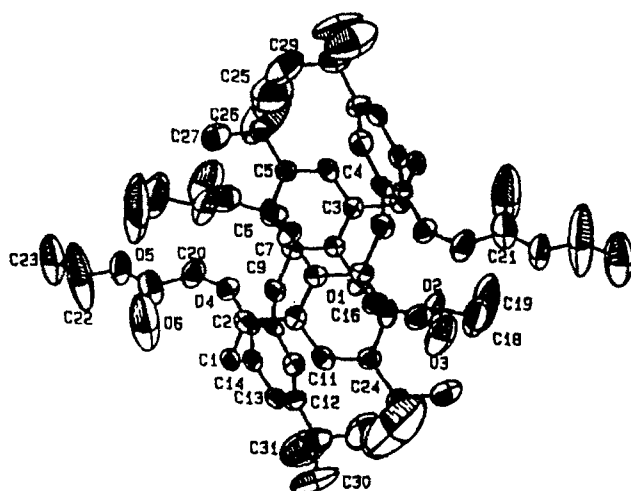
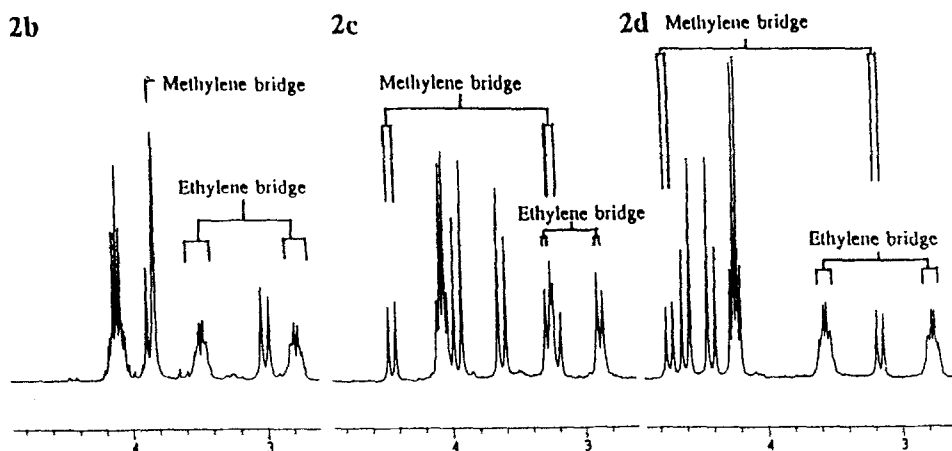


Fig. 1. Conformation of [2.1.2.1]MPC **2**.

Fig. 2. Ortep view of **2b**.Fig. 3. Partial  $^1\text{H-NMR}$  spectra of **2b**, **2c**, and **2d** (270 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ).

alternate, or cone conformers, but neither the partial-cone nor any other conformer such as, for example, the flattened-cone conformer was observed. The partial  $^1\text{H-NMR}$  spectra of **2b**, **2c** and **2d** are shown in Figure 3.  $^1\text{H-NMR}$  spectra of **2c** and **2d** shows their methylene protons as two sets of doublets. This suggests that **2c** and **2d** may adopt the cone or 1,2-alternate conformation of the five conformations expected. Since the shape of the peaks due to the ethylene bridges of **2d** is very similar to that of **2b**, it can be assumed that the two ethylene bridges in **2d** are on the same side of the [2.1.2.1]MCP ring and those of **2c** are on opposite sides. Thus, **2c** adopts the 1,2-alternate conformation and **2d** takes the cone conformation.

The  $^1\text{H-NMR}$  spectrum of **2a** shows the *tert*-butyl protons as four singlet peaks at  $\delta$  1.14, 1.19, 1.27, and 1.32 ppm, indicating that **2a** adopts an asymmetrical conformation. Of the five conformations we expected, only the partial-cone conformation is asymmetrical. Therefore, we can conclude that **2a** takes the partial-cone conformation.

Of the five conformers expected, only the 1,3-alternate type conformer of **2** was not obtained. Presumably, the 1,3-conformer of **2** is less stable than the other conformers, so that we could not obtain the conformer in detectable quantities.

## 2.2. COMPLEXATION PROPERTIES

The complexation properties of the four conformers of **2** were established using  $^1\text{H-NMR}$  spectroscopy [1] and UV spectroscopy [6].  $^1\text{H-NMR}$  spectra were measured for **2** ( $4.9 \times 10^{-3}$  M) in  $\text{CD}_3\text{OD}$  in the presence of alkali thiocyanate ( $0-4.9 \times 10^{-2}$  M), and UV spectra were measured for alkali picrate solutions in THF ( $5.0 \times 10^{-5}$  M) in the presence of **2** ( $0-1.0 \times 10^{-3}$  M).

In the case of **2a**, **2b** and **2c**, we could find no difference in the spectra of **2** with or without alkali ions, but in the case of **2d**, a remarkable difference was observed (Figure 4 and Table II). The stability constants for **2d** were determined by  $^1\text{H-NMR}$  and UV spectroscopy.

The molar ratio plots indicate the formation of a 1 : 1 complex. A typical example is given in Figure 5.

We shall not discuss the  $\Delta\delta$  values of bridge protons, since some of them could not be determined due to overlapping of peaks. For the methoxy protons ( $\text{OCH}_2\text{CO}$ ), high field shifts are observed in the case of potassium and cesium ion, but in the case of sodium ion a low field shift is observed. We assumed that

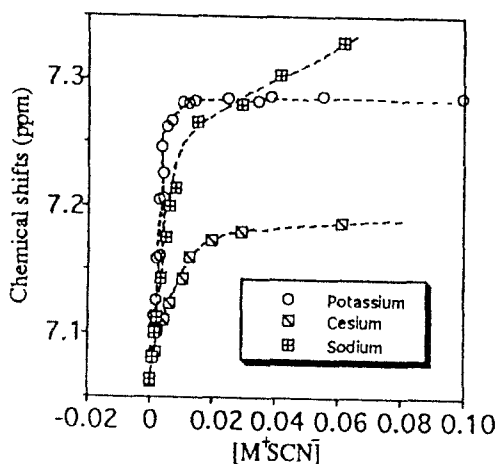


Fig. 4. The observed chemical shifts of aromatic protons of **2d** in the presence of alkali thiocyanate (270 MHz, 25°C,  $\text{CD}_3\text{OD}$ ).

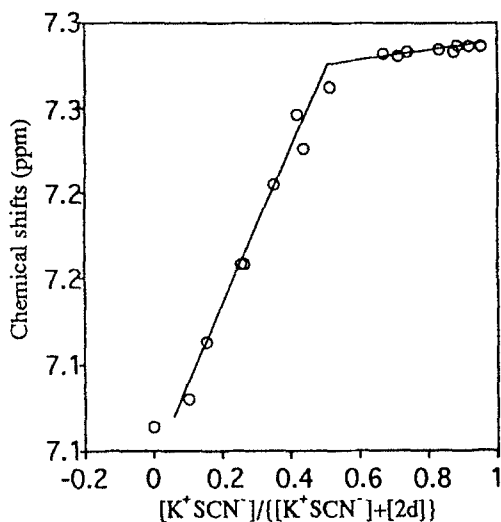


Fig. 5. Molar ratio plot of  $[K^+SCN^-]/([K^+SCN^-] + [2d])$  and chemical shift of aromatic protons (270 MHz, 25°C,  $CD_3OD$ ).

TABLE II.  $\Delta\delta$  Values of **2d** in the presence of alkali cation in  $CD_3OD$ .

Alkali ion	$\Delta\delta$ of methoxy peaks (OCCH <sub>2</sub> CO)	$\Delta\delta$ of bridge peaks (ArCH <sub>2</sub> )	$\Delta\delta$ of aromatic peaks (ArH)
Na <sup>+</sup>	-0.01 <sup>b</sup> , 0.10	- <sup>c</sup> , 0.14	0.23, 0.14
K <sup>+</sup>	-0.07, 0.03	-0.46, 0.18	0.21, 0.13
Cs <sup>+</sup>	-0.11, 0.02	-0.20, - <sup>c</sup>	0.11, 0.07

<sup>a</sup> $\Delta\delta$  Values are the difference of the chemical shift between **2d** and **2d** in the presence of  $M^+SCN^-$  ( $[2d] : [M^+SCN^-] = 1 : 6$ ) in  $CD_3OD$  at 25°C.

<sup>b</sup>The minus values indicate a the high field shift.

<sup>c</sup>These chemical shifts could not be determined due to overlap with other peaks.

potassium and cesium ion coordinates at the carbonyl oxygen and sodium ion coordinates at the phenolic oxygen, since it is expected that the coordination at phenolic oxygen decreases the electron density of methoxy protons.

In all cases of aromatic protons, low field shifts are observed and  $\Delta\delta$  values of the cesium complex are much smaller than those of potassium and sodium complexes. We consider that the aromatic groups come closer to each other on complexation, resulting in the low field shift of the aromatic proton. Therefore, sodium and potassium ion seem to enter into the cavity more deeply than the cesium ion.

Schneider *et al.* [6] have reported the direct <sup>1</sup>H-NMR method used for determining association constants. In the case of a 1 : 1 complex, the stability constant  $K$  can be calculated from Equation 2. The difference of the observed chemical shift  $\delta_{obs}$  and the chemical shift  $\delta_{free}$  of the uncomplexed **2d** is proportional to the

ratio  $[HG] : [H_0]$ , and the proportionally constant is the difference of the chemical shift of the pure complex  $\delta_c$  and  $\delta_{\text{free}}$  (Equation 3). As we can obtain Equation 4 from Equations 3 and 2, we can thus calculate the stability constant  $K$  by a curve fitting calculation (the nonlinear least-squares method) [17].



$$K \text{ (1/mol)} = \frac{[HG]}{[H][G]} = \frac{[HG]}{([H_0] - [HG])([G_0] - [HG])} \quad (2)$$

where  $[H]$  = concentration of free host (**2d**);  $[H_0]$  = total concentration of host (**2d**);  $[G]$  = concentration of free guest ( $M^+R^-$ );  $[G_0]$  = total concentration of guest  $[M^+R^-]$ ; and  $[HG]$  = concentration of complex (**2d** and  $M^+R^-$ ).

$$[HG] = a[H_0] = \frac{\delta_{\text{obs}} - \delta_{\text{free}}}{\delta_c - \delta_{\text{free}}} [H_0] \quad (3)$$

$$[G_0] = \frac{a}{K(1-a)} + a[H_0] : a = \frac{\delta_{\text{obs}} - \delta_{\text{free}}}{\delta_c - \delta_{\text{free}}} \quad (4)$$

where  $a$  = ratio of complex  $HG$  to host (**2d**);  $\delta_{\text{obs}}$  = observed chemical shift of **2d** in the presence of ion;  $\delta_{\text{free}}$  = chemical shift of free **2d**; and  $\delta_c$  = chemical shift of **2d** coordinating with alkali ions.

In UV spectroscopy, the spectra of sodium, potassium and cesium picrate in the presence of **2d** show a red shift of the absorption peak, this being dependent on the separation of the alkali ion from the picrate anion (Figure 6).

The molar ratio plots of **2d** and alkali picrate indicate the formation of a 1 : 1 complex in THF solution (Figure 7), and the stability constants  $K$  in THF are given by a curve fitting calculation (Equations 5, 6).

$$[HG] = b[G_0] = \frac{\text{Abs}_{\text{obs}} - \text{Abs}_{\text{free}}}{\text{Abs}_c - \text{Abs}_{\text{free}}} [G_0] \quad (5)$$

$$[H_0] = \frac{b}{K(1-b)} + a[G_0] : b = \frac{\text{Abs}_{\text{obs}} - \text{Abs}_{\text{free}}}{\text{Abs}_c - \text{Abs}_{\text{free}}} \quad (6)$$

where  $b$  = ratio of complex  $HG$  to guest (alkali picrate);  $\text{Abs}_{\text{obs}}$  = absorbance of alkali picrate in the presence of **2d**;  $\text{Abs}_{\text{free}}$  = absorbance of free alkali picrate; and  $\text{Abs}_c$  = absorbance of alkali picrate coordinating with alkali ions.

The  $\log K$  of the complexes of **2d** and alkali cations in THF and  $CD_3OD$  solution are shown in Table III. The correlation factors of curve fitting calculation are high ( $> 0.99$ ) in all cases. From these results, **2d** prefers potassium ion to sodium or cesium ion in  $CD_3OD$  solution. The difference of  $\log K$  is small in THF solution, although the same order of complexation ability is observed.

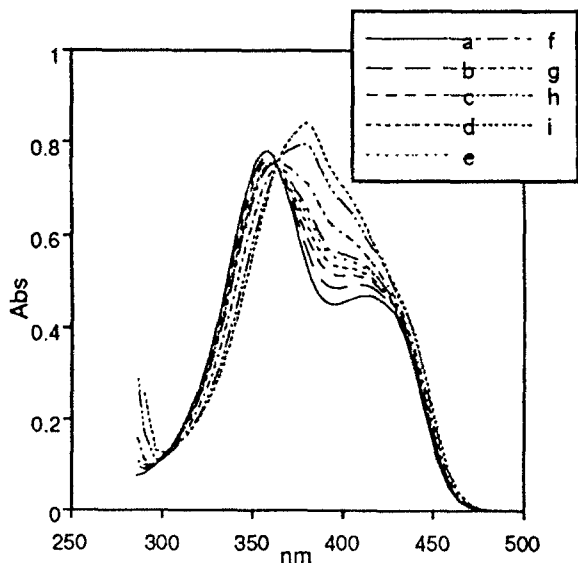


Fig. 6. UV spectra of  $5.0 \times 10^{-5}$  M of potassium picrate in the presence of **2d** in THF. (Potassium picrate: **2d** = a; 1 : 0, b; 1 : 0.2, c; 1 : 0.4, d; 1 : 0.6, e; 1 : 1.08, f; 1 : 1, g; 1 : 2, h; 1 : 5, i; 1 : 10).

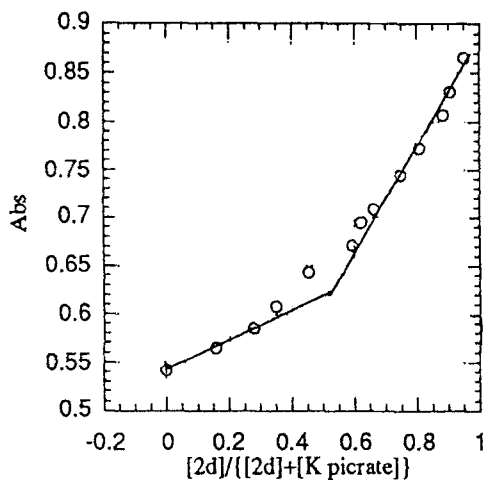


Fig. 7. Molar ratio plot of  $[2d]/([2d] + [K \text{ picrate}])$  and Abs at 380 nm.

Compared with the cone derivatives of calix[4]arene **4** [6], **2d** shows a high affinity for potassium, as the cavity size of **2d** is larger than that of calix[4]arene derivatives. This selectivity seems to be contradictory to the effect of sodium carbonate found in the selective preparation of **2d**, but we presume this difference to be dependent on the coordination site. In the preparation of **2d**, the sodium ion



TABLE III. The stability constants  $K$  of complexes of **2d** and tetra-*tert*-butyl-tetrakis[(ethoxycarbonyl)methoxy]calix[4]arene **4[6]** with sodium, potassium, and cesium ion.

	log $K^a$ of <b>2d</b> (in MeOH- $d_4$ )	log $K^b$ of <b>2d</b> (in THF)	log $K^c$ of <b>4</b> (in THF)
Na	2.42 ± 0.05	3.31 ± 0.13	3.95
K	3.86 ± 0.14	3.92 ± 0.04	3.08
Cs	2.47 ± 0.10	3.72 ± 0.17	1.60

<sup>a</sup>Determined by curve-fitting method of chemical shifts at 25°C.

<sup>b</sup>Determined by curve-fitting method of electron spectra at 23°C.

<sup>c</sup>Determined by Benesi–Hildebrand method of UV spectra in THF at 30°C.

will coordinate to the phenolic oxygen. On the other hand, in the case of complex-formation, the cavity of the lower ethoxycarbonyl groups seems to fit the potassium ion, being too large for the sodium ion.

### 3. Conclusion

As shown above, we could obtain the tetra-*tert*-butyl-tetrakis[(ethoxycarbonyl)methoxy] [2.1.2.1]MCP **2** as four conformers, the partial-cone **2a**, 1,4-alternate **2b**, 1,2-alternate **2c** and cone conformer **2d**. The conformational characterization was determined by <sup>1</sup>H-NMR spectra and an X-ray crystal structure analysis of **2b**. By using sodium carbonate in acetone, we could obtain the cone conformer **2d** selectively and in high yield.

The investigation of the complexation properties of **2** gave some interesting results. In the case of calix[4]arenes, the 1,2-alternate, 1,3-alternate, and partial-cone conformers show an affinity and a selectivity for potassium. The 1,2-alternate 1,4-alternate, and partial-cone conformers of **2**, a homologue of calix[4]arene, do not show any such ionophoric properties. It is assumed that the repulsion of the *tert*-butyl groups in **2** will affect the stability of the complexes to a larger extent than in the calix[4]arenes, since the [2.1.2.1]MCP skeleton is more flexible than that of calix[4]arene derivatives.

In the case of **2d**, the high affinities to alkali cations were observed in CD<sub>3</sub>OD and THF solution. In contrast to the cone conformer of calix[4]arene derivatives **4**, **2d** prefers potassium ion to sodium ion. This difference of selectivity seems to be dependent on the size of cavity of host molecule.

## Appendix: Numerical Data

### X-RAY CRYSTALLOGRAPHIC DATA OF **2b**

Crystal data:  $C_{62}H_{84}O_{12}$ , Formula weight. 1020, triclinic;  $a = 12.05(3)$ ,  $b = 13.40(3)$ ,  $c = 10.82(2)$  Å,  $\alpha = 112.69(2)^\circ$ ,  $\beta = 111.06(2)^\circ$ ,  $\gamma = 92.60(3)^\circ$ ,  $V = 1469.7(7)$  Å<sup>3</sup>,  $Z = 1$  (the special position),  $D_c = 1.153$  g cm<sup>-3</sup>, space group  $P_{\bar{1}}$ ,  $MoK_{\alpha}$  radiation  $\lambda = 0.71073$  Å, colorless prisms. Data were collected on an Enraf-Nonius CAD4 diffractometer,  $\omega$ - $2\theta$  scan type, graphic-monochromatic  $MoK_{\alpha}$  radiation,  $\lambda = 0.71073$  Å. Of 5465 independent reflections collected in the range  $1 < \theta < 35^\circ$  2520 with  $I_0 > 3\sigma(I_0)$  were taken as observed. The crystal did not show any significant decay during the data collection. Positional parameters were determined by direct methods using SIR 88 [18], and were reflected by full-matrix least-squares calculations with all nonhydrogen atoms treated anisotropically and hydrogen atoms treated isotropically using the scheme  $\omega = 4F_0^2/\sigma^2(F_0^2)^2$  to give the final residuals:  $R = 8.88$ ,  $R_w = 10.5$ .

TABLE IV. Bond distances of **2b** (Å).

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
O(1)	C(8)	1.402(5)	C(7)	C(9)	1.501(9)
O(1)	C(6)	1.433(7)	C(9)	C(10)	1.516(7)
O(2)	C(17)	1.34(1)	C(10)	C(11)	1.412(7)
O(2)	C(18)	1.45(1)	C(10)	C(15)	1.389(9)
O(3)	C(17)	1.186(8)	C(11)	C(12)	1.359(7)
O(4)	C(15)	1.390(6)	C(12)	C(13)	1.38(1)
O(4)	C(20)	1.408(8)	C(12)	C(28)	1.517(8)
O(5)	C(21)	1.285(7)	C(13)	C(14)	1.412(7)
O(5)	C(22)	1.33(1)	C(14)	C(15)	1.392(7)
O(6)	C(21)	1.211(9)	C(16)	C(17)	1.476(9)
C(1)	C(14)	1.492(9)	C(18)	C(19)	1.28(2)
C(2)	C(3)	1.511(9)	C(20)	C(21)	1.45(1)
C(3)	C(4)	1.398(6)	C(22)	C(23)	1.33(1)
C(3)	C(8)	1.373(9)	C(24)	C(25)	1.49(2)
C(4)	C(5)	1.398(9)	C(24)	C(26)	1.43(2)
C(5)	C(6)	1.409(9)	C(24)	C(27)	1.44(1)
C(5)	C(24)	1.492(6)	C(28)	C(29)	1.50(2)
C(6)	C(7)	1.381(6)	C(28)	C(30)	1.57(1)
C(7)	C(8)	1.409(9)	C(28)	C(31)	1.46(2)

Numbers in parentheses are estimated standard deviations in the least significant digits.

TABLE V. Fractional atomic coordinate for **2b**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
O(1)	0.9662(3)	0.2036(3)	0.4687(4)	3.5(1)
O(2)	0.9594(5)	0.3662(4)	0.6869(5)	6.6(2)
O(3)	1.0737(7)	0.3181(5)	0.8557(5)	10.2(2)
O(4)	1.1398(4)	-0.0758(3)	0.2848(4)	3.7(1)
O(5)	1.1619(4)	-0.2365(4)	-0.0512(4)	6.0(1)
O(6)	1.3034(7)	-0.1656(9)	0.1721(8)	20.3(4)
C(1)	1.3563(5)	-0.0502(5)	0.5221(6)	3.3(2)
C(2)	0.7328(5)	0.1227(5)	0.4570(5)	3.1(2)
C(3)	0.7790(5)	0.0639(4)	0.3413(5)	2.9(1)
C(4)	0.7026(5)	-0.0270(5)	0.2115(6)	3.3(2)
C(5)	0.7326(5)	-0.0776(5)	0.0917(6)	3.3(2)
C(6)	0.8479(5)	-0.0305(5)	0.1107(5)	3.3(2)
C(7)	0.9273(5)	0.0569(4)	0.3255(5)	2.7(1)
C(8)	0.89001(5)	0.1046(4)	0.3515(5)	2.8(1)
C(9)	1.0417(5)	0.1134(5)	0.2403(5)	3.4(2)
C(10)	1.622(5)	0.1213(5)	0.3586(5)	3.0(1)
C(11)	1.2382(5)	0.2265(4)	0.4585(6)	3.5(2)
C(12)	1.3478(5)	0.2485(5)	0.5700(6)	3.4(2)
C(13)	1.3813(5)	0.1543(5)	0.5891(6)	3.4(2)
C(14)	1.3133(5)	0.0451(4)	0.4951(5)	2.9(1)
C(15)	1.2067(5)	0.0318(4)	0.3768(5)	2.5(1)
C(16)	1.0312(5)	0.2025(5)	0.6078(6)	4.0(2)
C(17)	1.0262(6)	0.2993(6)	0.7299(6)	5.3(2)
C(18)	0.9381(9)	0.4600(8)	0.794(1)	10.4(4)
C(19)	0.862(1)	0.510(1)	0.736(2)	22.8(6)
C(20)	1.1137(6)	-0.1191(6)	0.1341(7)	5.2(2)
C(21)	1.1986(6)	-0.1810(7)	0.0881(7)	6.6(2)
C(22)	1.227(1)	-0.292(1)	-0.120(1)	21.8(5)
C(23)	1.1923(9)	-0.3363(8)	0.264(1)	11.2(3)
C(24)	0.6494(5)	-0.1726(5)	-0.0481(6)	4.0(2)
C(25)	0.574(1)	-0.247(1)	-0.021(1)	19.5(6)
C(26)	0.566(2)	-0.136(1)	-0.145(2)	21.6(8)
C(27)	0.7125(8)	-0.2420(9)	-0.126(1)	11.8(4)
C(28)	1.4224(6)	0.3627(5)	0.6700(7)	5.1(2)
C(29)	1.355(1)	0.4281(9)	0.754(2)	16.5(5)
C(30)	1.5460(9)	0.3651(7)	0.7886(9)	10.0(3)
C(31)	1.435(1)	0.4195(8)	0.528(1)	13.2(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $(4/3) * [\alpha^2 * B(1, 1) + b^2 * B(2, 2) + c^2 * B(3, 3) + ab(\cos \gamma) * B(1, 2) + ac(\cos \beta) * B(1, 3) + bc(\cos \alpha) * B(2, 3)]$ .

TABLE VI. Bond angles of **2b**.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(8)	O(1)	C(16)	118.0(5)	C(1)	C(14)	C(15)	122.6(4)
C(17)	O(2)	C(18)	120.1(6)	C(13)	C(14)	C(15)	116.7(6)
C(15)	O(4)	C(20)	119.3(5)	O(4)	C(15)	C(10)	121.0(4)
C(21)	O(5)	C(22)	125.9(6)	O(4)	C(15)	C(14)	116.5(5)
C(2)	C(3)	C(4)	120.1(5)	C(10)	C(15)	C(14)	122.3(4)
C(2)	C(3)	C(8)	121.7(4)	O(1)	C(16)	C(17)	112.0(6)
C(4)	C(3)	C(8)	117.7(6)	O(2)	C(17)	O(3)	120.9(7)
C(3)	C(4)	C(5)	123.8(6)	O(2)	C(17)	C(16)	113.9(5)
C(4)	C(5)	C(6)	114.9(4)	O(3)	C(17)	C(16)	125.2(8)
C(4)	C(5)	C(24)	123.6(6)	O(2)	C(18)	C(19)	113.6(9)
C(6)	C(5)	C(24)	121.5(6)	O(4)	C(20)	C(21)	116.1(6)
C(5)	C(6)	C(7)	124.3(6)	O(5)	C(21)	O(6)	122.0(8)
C(6)	C(7)	C(8)	117.0(5)	O(5)	C(21)	C(20)	114.9(6)
C(6)	C(7)	C(9)	120.9(5)	O(6)	C(21)	C(20)	121.8(7)
C(8)	C(7)	C(9)	121.8(4)	O(5)	C(22)	C(23)	124.(1)
O(1)	C(8)	C(3)	121.8(5)	C(5)	C(24)	C(25)	111.5(7)
O(1)	C(8)	C(7)	115.2(5)	C(5)	C(24)	C(26)	111.4(7)
C(3)	C(8)	C(7)	122.3(4)	C(5)	C(24)	C(27)	113.5(6)
C(7)	C(9)	C(10)	118.0(6)	C(25)	C(24)	C(26)	107(1)
C(9)	C(10)	C(11)	119.0(6)	C(25)	C(24)	C(27)	105.8(9)
C(9)	C(10)	C(15)	125.1(4)	C(26)	C(24)	C(27)	108.(1)
C(11)	C(10)	C(15)	115.9(4)	C(12)	C(28)	C(29)	109.4(7)
C(10)	C(11)	C(12)	125.2(6)	C(12)	C(28)	C(30)	111.9(6)
C(11)	C(12)	C(13)	115.7(5)	C(12)	C(28)	C(31)	110.1(6)
C(11)	C(12)	C(28)	120.6(6)	C(29)	C(28)	C(30)	105.7(7)
C(13)	C(12)	C(28)	123.6(5)	C(29)	C(28)	C(31)	104.9(9)
C(12)	C(13)	C(14)	123.8(5)	C(30)	C(28)	C(31)	114.5(8)
C(1)	C(14)	C(13)	120.7(4)				

Numbers in parentheses are estimated standard deviations in the least significant digits.

### <sup>1</sup>H-NMR SPECTRUM OF **2a**

$\delta_{\text{H}}$  (270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.14 (s, 9H), 1.19 (s, 9H), 1.27 (s, 9H), 1.32 (s, 9H), 1.15–1.31 (m, 12H), 2.31–4.23 (m, 28H), 6.93 (d, 1H,  $J = 2.2$  Hz), 6.94 (d, 1H,  $J = 2.2$  Hz), 7.00 (d, 2H,  $J = 2.2$  Hz), 7.07 (d, 1H,  $J = 22$  Hz), 7.15 (d, 1H,  $J = 2.2$  Hz), 7.27 (d, 1H,  $J = 2.2$  Hz), 7.39 (d, 1H,  $J = 2.2$  Hz).

### <sup>1</sup>H-NMR SPECTRUM OF **2b**

$\delta_{\text{H}}$  (270 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 1.22 (t, 12H,  $J = 7.3$  Hz), 1.26 (s, 36H), 2.68–2.77 (m, 4H), 3.01 (d, 4H,  $J = 14.7$  Hz), 3.41–3.50 (m, 4H), 3.82 (s, 4H), 3.85 (d, 4H,

$J = 14.7$  Hz), 4.00–4.18 (m, 8H), 7.08 (d,  $J = 2.6$  Hz, 4H), 7.13 (d,  $J = 2.6$  Hz, 4H).

### $^1\text{H-NMR}$ SPECTRUM OF **2c**

$\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.19 (12H, t,  $J = 7.1$  Hz), 1.27 (36H, s), 2.88 (4H, br.d,  $J = 11.5$  Hz), 3.21 (2H, d,  $J = 14.7$  Hz), 3.27 (4H, br.d,  $J = 11.5$  Hz), 3.62 (4H, d,  $J = 15.6$  Hz), 3.95 (4H, d,  $J = 15.6$  Hz), 4.01–4.14 (8H, m), 7.08 (4H, d,  $J = 2.5$  Hz), 7.20 (d, 4H,  $J = 2.5$  Hz).

### $^1\text{H-NMR}$ SPECTRUM OF **2d**

$\delta_{\text{H}}$  (270 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1.11 (s, 36H), 1.31 (12H, t,  $J = 7.1$  Hz), 2.72–2.80 (4H, m), 3.15 (2H, d,  $J = 13.0$  Hz), 3.52–3.61 (4H, m), 4.36 (4H, d,  $J = 15.0$  Hz), 4.60 (4H, d,  $J = 15.0$  Hz), 4.73 (2H, d,  $J = 13.0$  Hz), 4.23 (8H, q,  $J = 7.1$  Hz), 6.85 (4H, d,  $J = 2.3$  Hz), 6.94 (4H, d,  $J = 2.3$  Hz).

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