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Gas phase cation-π complexation of cyclic and acyclic organosilicon compounds: electrospray mass spectrometry analysis and theoretical investigation by *ab initio* molecular orbital calculations †

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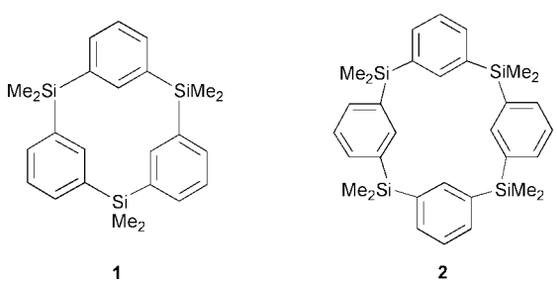
The gas phase cation-π complexation of oligo[(dimethylsilylene)phenylene]s with alkali metal cations was observed by electrospray mass spectrometry for the first time. The cation-π complexes were derived not only from cyclic oligomers but also from acyclic derivatives in spite of the large conformational flexibility. The substituent effect of silyl groups on cation-π interaction was investigated by *ab initio* calculations of the model compounds. The calculation showed that not the silyl (SiH_3) group but the trimethylsilyl ($SiMe_3$) group substantially increased the attraction between the cation and the π system, especially due to the large gain in induction energy. Theoretical calculations for trimethylsilylbenzene and a model compound of silamacrocycles suggested that significant conformational changes occurred due to the complexation. The observed Cs^+ selectivity of the silamacrocycle in the electrospray mass spectrometry was explained by the calculated binding energies of the cation-π complexes, if the solvation of the cations was considered. The results from mass spectrometry can be understood in terms of competition between cation-π complexation and solvation by species in the solvent matrix.

Introduction

In recent years the cation-π interaction has been recognized as an important non-covalent binding force.[1] It plays crucial roles in biological systems such as enzyme regulation,[2] protein structure,[3] and transmembrane channels,[4] and also in molecular recognition processes in artificial supramolecular systems.[5,6]

It is believed that the cation-π interaction found in organometallic compounds[7,8] also plays an important role for the stabilization of thermally unstable compounds.[9] For instance, it has been observed in many organosilicon compounds. The short contact distance between the metal cation and π system was observed in crystals of silylcarbanions,[10] silylamides,[11] silyl thiolate,[12] organosilanides,[13,14] and silylstannides.[14] Therefore the understanding of the cation-π interaction in organosilicon compounds has been a very important issue. The organosilicon compounds in these crystals, however, were negatively charged. Detailed information on the interaction between the metal cation and 'neutral' organosilicon compounds is essential to understand the effects of the silicon atom on the cation-π interaction in organosilicon compounds. Unfortunately, however, no experimental nor theoretical study has been reported on the cation-π interaction between neutral organosilicon compounds and metal cations.

Recently, heterocalixarenes with the bridges replaced by Group 14 elements have received much attention.[15,16] We reported the preparation of silicon-bridged metacyclophanes **1** and **2** (Scheme 1) as silicon analogues of calix[*n*]arenes and found that they formed complexes with Ag^+.[17] The interaction



1 **2**

Scheme 1

between Ag^+ (a transition metal cation) and the π system, however, is not the so-called cation-π interaction because of covalent interactions with d orbitals on the metal.[1] In this paper we report that the silacalixarenes can bind with alkali metal cations. This is the first investigation of the cation-π interaction of silacalixarenes with alkali metal cations using electrospray ionization mass spectrometry (ESI-MS).

It is important to understand the origin of substituent effects on the cation-π interaction. A lot of theoretical calculations have been reported on the geometries and binding energies of cation-π complexes.[4b,18–20] Dougherty[19] and Cubero[20] and coworkers reported calculations of the cation-π interaction of substituted benzenes and found that electron-donating substituents increase the attraction by electrostatic interaction and therefore increase the binding energy, and electron-withdrawing substituents decrease the binding energy. More recently, our group reported calculations of the cation-π interaction of alkylbenzenes and found that a bulky t-butyl group significantly stabilizes the cation-π complex due to the large induction energy.[21] Although many theoretical calculations have been reported, the substituent effects of third-row elements including silicon have not yet been studied. In this paper we calculate the

† Dedicated to Professor Hideki Sakurai on the occasion of his 70th birthday.

Electronic supplementary information (ESI) available: rotatable 3-D diagrams for the calculated structures in CHIME format. See http://www.rsc.org/suppdata/dt/b1/b101282g/

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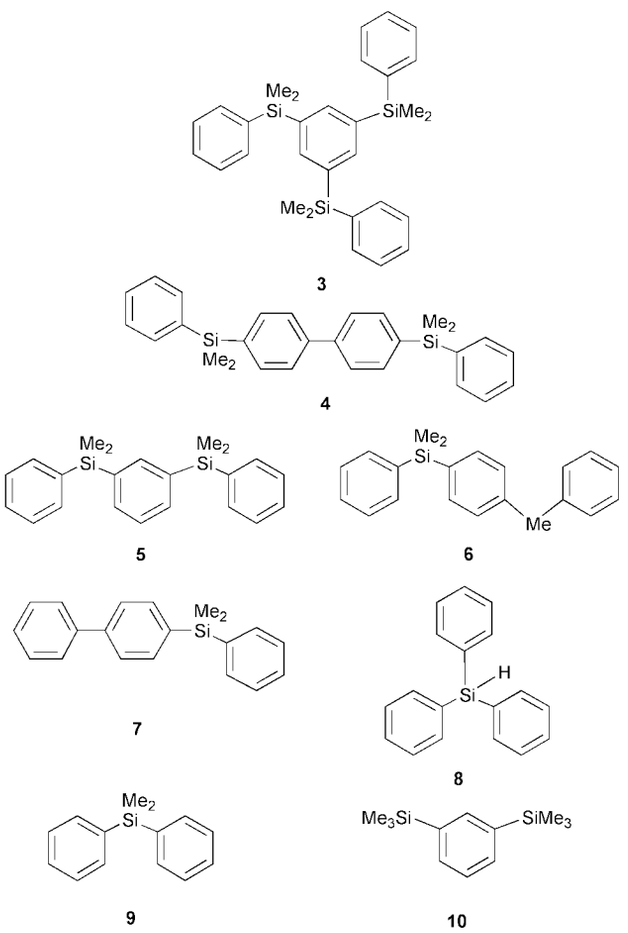
cation-π interaction of benzene, silylbenzene and (trimethylsilyl)benzene by an *ab initio* method to understand the origin of the substituent effects of the silyl groups on the cation-π interaction.

Despite the large number of theoretical calculations reported on the cation-π interaction, only very few studies have been made on the cation-π interaction of large macrocycles.[18f,22] In this paper we also carry out *ab initio* calculations of the cation-π interaction of the silamacrocycle and discuss the cause of the observed Cs^+ selectivity observed by ESI-MS.

Results and discussion

Electrospray mass spectrometry

We prepared acyclic oligo[(dimethylsilylene)phenylene]s along with silamacrocycles in order to examine the effect of molecular size and conformational flexibility on the cation binding properties (Scheme 2). Next, their cation-π complexation behaviour



Scheme 2

with alkali metal cations was assessed by ESI-MS. Recently, an ESI-MS technique has widely been used in studies of supramolecular host–guest chemistry due to the remarkable mildness of the ionization method.[23,24] For example, the ion selectivity of 18-crown-6 ether was examined by ESI-MS, and it was found that, at least for the cases of Na^+ and K^+, the observed peak intensities reproduced the ion selectivity in solution nearly quantitatively within the specified concentration range.[24c] Even for the other alkali metal cations (Li^+, Rb^+ and Cs^+) the trend of the ion selectivity was qualitatively reproduced.[24b] Shinkai and co-workers have reported the application of ESI-MS for the study of cation-π interaction.[25] The cation-π complexes of *meta*- and *para*-cyclophanes without any functional groups were observed by ESI-MS. They found that a large,

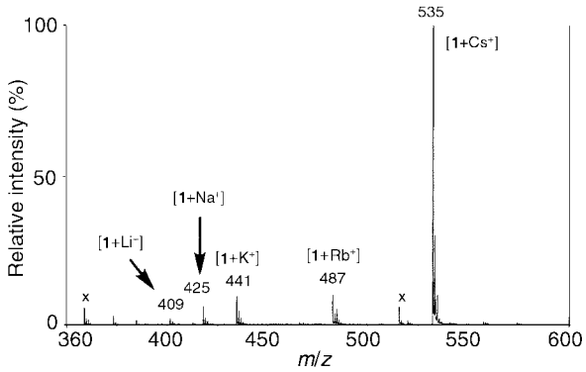


Fig. 1 Electrospray mass spectrum of a 1 : 1 mixture of **1** and alkali metal chlorides MCl (M = Li, Na, K, Rb or Cs) in chloroform–methanol (1 : 1 v/v) solution. [**1**] = [MCl] = 0.5 mM.

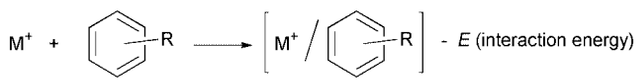
soft Cs^+ bound selectively to the π–basic cavity of the cyclophanes.

All of the acyclic compounds **3**–**10**,[26] that were already known except for 1,3-bis(dimethylphenylsilyl)benzene **5** and 4-(dimethylphenylsilyl)biphenyl **7**, were prepared by dehalogenative coupling between the corresponding bromoarenes and chlorosilanes using magnesium. The compounds with four benzene rings (**3**, **4**) and with three benzene rings (**5**–**8**) are considered as counterparts of tetrasilacalixarene **2** and trisilacalixarene **1**, respectively. Dimethyldiphenylsilane **9** and 1,3-bis(trimethylsilyl)benzene **10** are also regarded as partial fragments of the silacalixarenes **1** and **2**. For the mass spectrometry experiment, we adopted measurement conditions identical with those in the previous Shinkai study.[25] We prepared two solutions: one an organosilicon host solution in chloroform (1 mM) and the other a mixture of alkali metal chlorides in methanol at the same concentration. Then 50 μl portions of both solutions were mixed in a micro tube, and the mixed solution (0.5 mM) was infused into the electrospray mass spectrometer.

A representative mass spectrum obtained for trisilacalix[3]arene **1** is shown in Fig. 1. The strong peak corresponding to the 1 : 1 complex of [Cs^+ + **1**] was dominant. Isotope pattern calculation for the formula $C_{24}H_{30}Si_3Cs$ was in accord with the observed peaks at *m*/*z* 535. Although we carefully examined the higher mass range up to *m*/*z* 2000, the 1 : 2 and 2 : 1 complexes of **1** and alkali metal cations were not observed. We repeated similar experiments for the all of the compounds in the present study, and the absolute intensities of the peaks of the detected complexes were plotted in Fig. 2.

These organosilicon compounds are classified into three groups: the first, including two silacalixarenes **1** and **2**, showed an intense signal corresponding to a Cs^+ complex. The order of the observed relative peak intensities of the metal complexes is $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (*i.e.*, for **1**, 100 : 15 : 12 : 6 : 1; for **2**, 100 : 46 : 25 : 12 : 6). Although we examined the concentration effect of the mixed solution within the range 0.05–0.5 mM, no significant change of the relative intensity was observed. Owing to the absence of functional groups in the two silacalixarenes, the cation-π interaction is expected to be the exclusive attractive force stabilizing the complexes observed in ESI-MS. Since only a few [1.1.1]metacyclophanes (calix[3]arenes) have been prepared so far,[27] this is the first observation of the molecular recognition by [1.1.1]metacyclophane derivatives. Surprisingly, 1,3,5-tris(dimethylphenylsilyl)benzene **3** also selectively forms the Cs^+ complex in spite of the large conformational mobility. In the case of the second group (**4**–**6**), although the π complexation with Cs^+ is still observable, the peak intensities are nearly one-third those of the first group. This result indicates the relatively more fragile property of the π complexes of **4**–**6**. Since there was no significant peak of the π complex, the last group (**7**–**10**) was found to be inert toward

Table 1 Calculated interaction energies of π complexes of the model compounds[a]



Complex	E_{HF}[b]	E_{MP2}[b]	E_{def}[c]	E_{total}[d]	E_{es}[e]	E_{ind}[f]	E_{rep}[g]
Li^+–Benzene	−39.4	−35.6	0.3	−35.4	−18.7	−46.9	30.1
Li^+–**11**	−40.4	−36.6	1.1	−35.5	−17.8	−51.6	32.8
Li^+–**12**	−44.8	−41.1	1.3	−39.8	−20.9	−56.1	35.8
Li^+–**13**[h]	−44.2	−40.2	0.4	−39.7	−20.0	−56.0	35.8
Na^+–Benzene	−24.0	−21.6	0.3	−21.3	−14.8	−21.0	14.1
Na^+–**11**	−24.2	−21.9	0.9	−21.0	−13.8	−24.0	15.9
Na^+–**12**	−27.7	−25.5	1.0	−24.5	−16.2	−28.0	18.7
Na^+–**13**[h]	−27.2	−24.8	0.4	−24.4	−15.6	−27.4	18.2

[a] Energy in kcal mol^{-1}. Geometries are optimized at the MP2/6-311G** level. [b] Calculated interaction energies of complexes using the 6-311G** basis set. [c] Increases of the energies of monomer aromatic molecules by deformation of geometries in complex formation. [d] Total interaction energy of complex. [e] Electrostatic energy. [f] Induction energy. [g] $E_{rep} = E_{total} - (E_{es} + E_{ind})$. E_{rep} is mainly the exchange-repulsion energy. [h] From ref. 21.

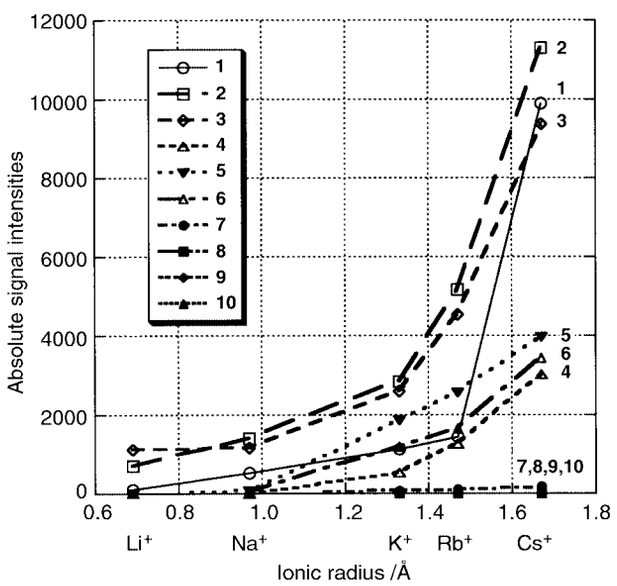


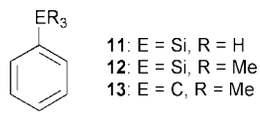
Fig. 2 Absolute intensities of the complexes of **1**–**10** with the alkali metal cations in electrospray mass spectra plotted *versus* the ionic radii of the ions.

any alkali metal ions under identical ESI-MS conditions. We concluded, therefore, that at least three benzene rings are necessary in the neutral organosilicon host molecule to form a stable π complex. In addition, bis(dimethylphenylsilyl)benzenes **5** and **6** form π complexes, while 4-(dimethylphenyl)biphenyl **7** and triphenylsilane **8** consisting of three benzene rings cannot. Therefore, a suitable size of the cavity of the host molecule is crucial for the stability of the π complexes. The strength of the π basicity depends on the number of benzene rings. The strong π basicity of 1,3,5-tris(dimethylphenylsilyl)benzene **3** consisting of four benzene rings would be the cause of the facile Cs^+ complex formation in spite of the large conformational flexibility. The Cs^+ affinity of the silacalixarenes **1** and **2** was further investigated by comparison with the other common host molecule. When compared with 18-crown-6 ether as an internal standard, the relative intensities of Cs^+ complexes of **1** and **2** are one-tenth and one-eighth of that corresponding to [Cs^+ + 18-c-6], respectively. Therefore, even those compounds showing intense peaks of Cs^+ complexes are regarded as very weak cation-acceptor ligands.

It is very difficult to obtain structural information on the π complexes only by ESI-MS. Unfortunately we could not observe any signals of the π complexes in solution by NMR analysis. Similar results were reported by Shinkai and co-workers in their study of the cation-π complexation of cyclophanes without any functional groups.[25] They pointed out two possible reasons: one was the competitive solvation process of metal ions *versus* the cation-π complexation, and the other the entropy loss caused by the organization of the host molecule induced upon guest inclusion. Since the present organosilicon compounds are also conformationally mobile and do not have any functional groups, the difficulty in NMR analysis would be attributed to the same reasons as in their study. The plausible structure of the π complexes of **1** obtained from theoretical calculation will be discussed in the following section.

Theoretical calculations

Substituent effect of silyl groups on the cation-π interaction. Many theoretical studies have been reported on the geometries and binding energies of cation-π complexes.[4b,18–21] However, no study has been done on the substituent effect of third-row elements including silicon atoms on the cation-π interaction. In order to understand the substituent effect of the silyl group, we calculated the interaction energies of cation-π complexes of benzene, silylbenzene **11** and (trimethylsilyl)benzene **12** (Scheme 3) at the MP2/6-311G** level. The results are summarized in Table 1 along with the results for *tert*-butylbenzene **13** calculated in our previous study.[21]



Scheme 3

The E_{HF} and E_{MP2} are the HF and MP2 level intermolecular interaction energies between the cation and the deformed π system, respectively. The cation-π complexation generally induced deformation of the structures of the π system. The E_{def} is the MP2/6-311G** level deformation energy of the π system. E_{total}, which is the sum of E_{MP2} and E_{def}, then corresponds to the binding energy. The E_{total} values of Li^+ complexes of benzene, **11** and **12** are calculated to be −35.4, −35.5 and −39.8 kcal mol^{-1}, respectively. The E_{total} value of [Li^+ + **12**] is 4.4 kcal mol^{-1} larger (more negative) than that of the Li^+–benzene complex, though that of [Li^+ + **11**] is almost comparable. The E_{total} values of Na^+ complexes of benzene, **11** and **12** are also calculated to be −21.3, −21.0 and −24.5 kcal mol^{-1}, respectively. Even in this case, the E_{total} value of [Na^+ + **12**] is 3.2 kcal mol^{-1} larger than that of the Na^+–benzene complex, though that of [Na^+ + **11**] is 0.3 kcal mol^{-1} smaller than that of the benzene complex. Thus, it appears that not the silyl group but the trimethylsilyl group leads to an increase in the binding energy of the cation-π complexes. E_{total} can be divided into three

Table 2 Selected bond lengths (Å) and angles (deg) of trimethylsilylbenzene **12** and its Na^+ complex from MP2/6-311G** calculations

	12	Na^+ + **12**
Si1–C1	1.883	1.911
Si1–C7	1.880	1.885
Si1–C8	1.880	1.868
Si1–C9	1.880	1.868
C1–Si1–C7	108.9	105.5
C7–Si1–C1–C2	59.8	89.2
Si1–C1–C2–C3	180.0	178.6

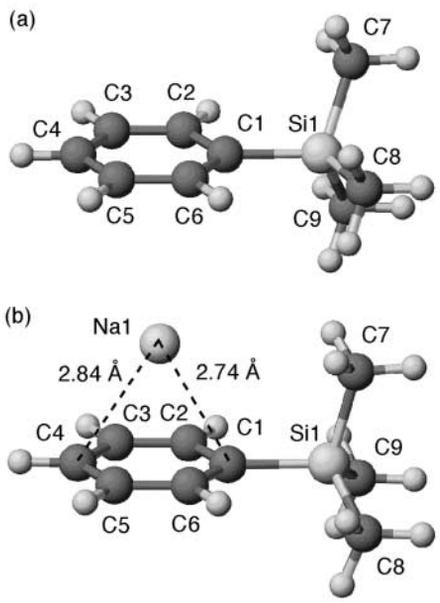


Fig. 3 MP2/6-311G** optimized structures, (a) for (trimethylsilyl)-benzene **12** and (b) for the Na^+ + **12** complex.

major components, which are the electrostatic energy (E_{es}), induction energy (E_{ind}), and repulsion energy ($E_{rep} = E_{total} - (E_{es} + E_{ind})$).[19,21] The E_{es} value of [Li^+ + **12**] is only 2.2 kcal mol^{-1} larger (more negative) than that of the Li^+–benzene complex. However, E_{ind} of [Li^+ + **12**] is 9.2 kcal mol^{-1} larger than that of the Li^+–benzene complex. Similarly, the differences in E_{es} and E_{ind} between the Na^+ complexes of benzene and **12** are 1.4 and 7.0 kcal mol^{-1}, respectively. The trimethylsilyl group significantly increases the attractive induction energy and enhances the cation-π binding as observed in the case of *tert*-butylbenzene.[21]

The optimized geometries of **12** and [Na^+ + **12**] are shown in Fig. 3. Selected geometrical parameters are also shown in Tables 2 and 3. For comparison, the optimized structures and the geometrical parameters of *tert*-butylbenzene and the Na^+–*tert*-butylbenzene complex are shown in Fig. 4, Tables 3 and 4, respectively. The optimized structure of the [Na^+ + **12**] complex suggests a *through-space* attraction between Na^+ and the trimethylsilyl group. The Na^+ in the complex is not located above the center of the benzene ring. The Na^+ moves toward the trimethylsilyl group. The distance between Na^+ and the *ipso*-carbon (C1) connecting the trimethylsilyl group (2.74 Å) is 0.10 Å shorter than that between Na^+ and the carbon at the *para* position (C4) of the benzene ring. In addition, the complexation induces a conformational change in the trimethylsilyl group. In the uncomplexed form of **12** the dihedral angles C*m*–Si1–C1–C2 (*m* = 7–9) are 59.8, 0.0 and −59.8°, respectively, and thus one methyl group (C8) on silicon is coplanar with the benzene ring. However, the dihedral angles C*m*–Si1–C1–C2 (*m* = 7–9) in [Na^+ + **12**] are 89.2, −151.8 and −29.7°, respectively. Eventually, one methyl group (C7) is perpendicular

Table 3 The interatomic distances (Å) between Na^+ and the carbons in the Na^+ complexes of **12** and **13** from MP2/6-311G** calculations[a]

	Na^+ + **12**	Na^+ + **13**[21]
Na1 · · · C1	2.735	2.787
Na1 · · · C2	2.748	2.763
Na1 · · · C3	2.815	2.781
Na1 · · · C4	2.844	2.798
Na1 · · · C5	2.815	2.790
Na1 · · · C6	2.748	2.776
Na1 · · · C7	3.727	3.727

[a] In the Na^+ complex of benzene the Na · · · C distance is calculated to be 2.803 Å in MP2/6-311G** calculation.[21]

Table 4 Selected bond lengths (Å) and angles (deg) of *tert*-butylbenzene **13** and its Na^+ complex from MP2/6-311G** calculations[21]

	13	Na^+ + **13**
C10–C1	1.527	1.526
C10–C7	1.538	1.539
C10–C8	1.533	1.531
C10–C9	1.538	1.539
C1–C10–C7	109.2	109.0
C7–C10–C1–C2	59.9	61.0
C10–C1–C2–C3	180.0	181.8

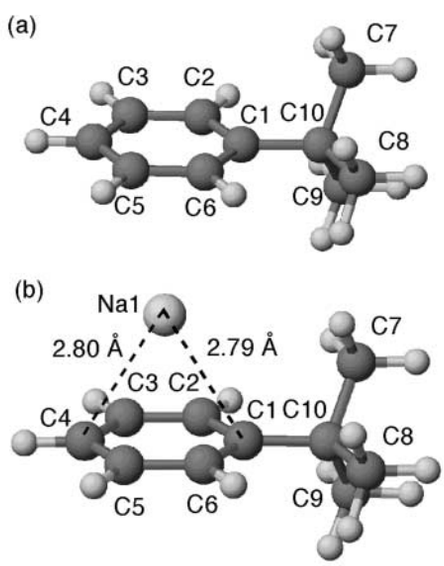
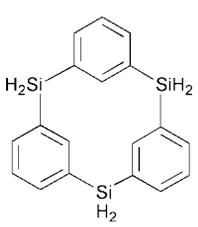


Fig. 4 MP2/6-311G** optimized structures (a) for *tert*-butylbenzene **13** and (b) for the Na^+ + **13** complex (from ref. 17).

to the benzene ring. The C7–Si1–C1 bond angle in the complex (105.5°) was 3.4° smaller than that (108.9°) of **12** in the uncomplexed form. The change in the bond angle indicates that the methyl group bends toward the Na^+ ion. The Si1–C1 bond length (1.91 Å) of [Na^+ + **12**] was 0.03 Å longer than that (1.88 Å) of **12**. The Si1–C7 bond is slightly (0.005 Å) elongated, although the Si1–C8 and Si–C9 bonds are shortened by 0.012 Å. In addition, the Si1–C1–C2–C3 dihedral angle (178.6°) of the complex is smaller than 180°. Therefore, the silicon atom is located *above* (the same side of Na^+) the mean plane of the benzene ring by 0.05 Å and thus moves toward the Na^+ ion. The closest interatomic distance between the Na^+ and the methyl carbon (C7) was found to be 3.73 Å. The interatomic distance was exactly comparable with that (Na1–C7) observed in the Na^+–*tert*-butylbenzene complex, although a silicon–carbon bond is much longer than the carbon–carbon bond. On the other hand, the *tert*-butylbenzene shows only slight geometrical changes due to the complexation as shown in Table 3.

Even in this case the Na^+ in the complex is not located above the center of the benzene ring and the interatomic distances from the Na^+ to all six carbons of the benzene ring are not equivalent. The shortest contact between Na^+ and carbon was observed at the place of the C2 carbon. It seems that there is a slight attractive force between Na^+ and the *tert*-butyl group. However, the C10–C1–C2–C3 dihedral angle (181.8°) of the complex is larger than 180°. The central carbon (C10) of the *tert*-butyl group is located *below* (the opposite side of Na^+) the mean plane of the benzene ring by 0.05 Å. Therefore, the C10 atom moves away from the Na^+ in contrast to the trimethylsilyl group. The observed large deformation of the trimethylsilyl group comes from the intrinsic character of the silicon atom. It is interesting that the existence of such an attractive interaction between alkali metal cations and methyl groups on silicon has often been proposed based on the X-ray crystallography of several organosilicon compounds.[10–14,28] For example, Uhl,[28a] Eaborn[28c,d] and Harder[10b] and their co-workers independently reported the molecular structures of tris- and bis-(trimethylsilyl)methyl metalates. They found that the interatomic distances between the metal cation and the surrounding non-covalent methyl groups were comparable with the distance between the metal cation and a carbanion center. Klinkhammer also observed the intramolecular and intermolecular coordination of methyl groups on silicon toward a metal cation in the molecular structures of tris(trimethylsilyl)-silanides.[14,28b] In order to explain this phenomenon, he proposed two main reasons: one was the dipole–ion interaction between the polarized silicon–carbon bond and metal cations, and the other was the agostic interaction between the C–H bond and the metal cation as observed in other transition metal complexes.[29] The present theoretical calculations also show that the trimethylsilyl group has attraction with the alkali metal cations and increased the binding energy as in the case of electron–donating substituents.

Molecular structures and the ion selectivity of cation-π complexes of the silacalixarene. The structure of compound **14**, in which the methyl groups of **1** were replaced by hydrogens, and the structures of its cation complexes were evaluated by HF/6-31G* level calculations to study the plausible structures of the cation-π complexes of trisilacalix[3]arene **1** (Scheme 4).



14

Scheme 4

In the uncomplexed form of **14** the saddle structure was 2.9 kcal mol^{-1} more stable than the C_3 symmetrical cone structure. This result is in accord with the observed saddle (partial cone) structure of **1** in X-ray crystallography,[17] where one phenylene ring is oriented in the different direction shown in Fig. 5. We have also carried out HF/6-31G* level calculations for **1** in this study. They showed that the saddle structure of **1** was 3.3 kcal mol^{-1} more stable than the cone structure.[30] Our *ab initio* calculations demonstrate that the most stable conformation of trisilacalix[3]arenes **1** and **14** is the saddle one and that the methyl groups of **1** have a negligible effect on its conformational preference.

The calculated interaction energies of the π complexes of **14** are summarized in Table 5. The optimized geometries of Cs^+ complexes with the saddle and cone conformations are also

Table 5 Calculated interaction energies of π complexes of the model compound **14** with alkali metal cations[a]

Cation	Conformation of π complex	E_{HF}[b]	E_{def}[c]	E_{total}[d]	ΔE_{total}[e]
None	Saddle				−2.9[f]
	Cone				0[f]
Li^+	Saddle	−57.7	7.0	−50.7	0
	Cone	−58.9	6.4	−52.6	−1.9
Na^+	Saddle	−41.0	4.2	−36.8	0
	Cone	−46.6	6.3	−40.4	−3.6
K^+	Saddle	−22.0	1.9	−20.1	0
	Cone	−29.9	5.3	−24.6	−4.5
Rb^+	Saddle	−21.1	1.8	−19.3	0
	Cone	−28.7	4.8	−23.9	−4.6
Cs^+	Saddle	−17.2	1.3	−15.9	0
	Cone	−24.1	4.3	−19.9	−4.0

[a] Energy in kcal mol^{-1}. Geometries are optimized at the HF/6-31G* level. [b] Calculated interaction energies of complexes using the 6-31G* basis set. [c] Increases of the energies of monomer aromatic molecules by the deformation of geometries in complex formation. [d] Total interaction energy of the complex. [e] $\Delta E_{total} = E_{total}(cone) - E_{total}(saddle)$. [f] Relative energy difference between the saddle and the cone conformations in the uncomplexed form.

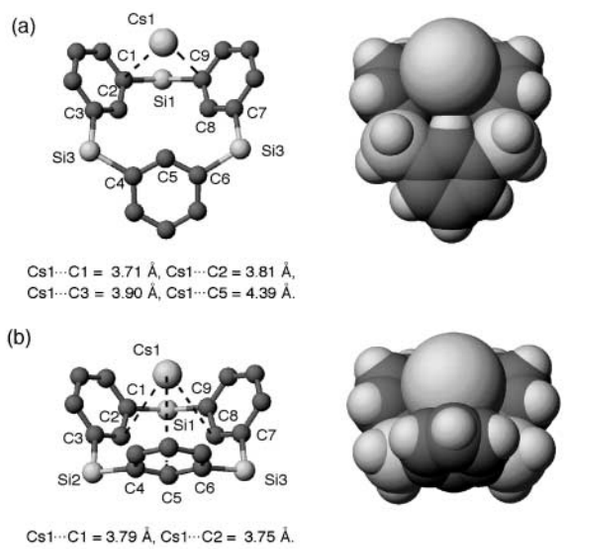


Fig. 5 HF/6-31G* optimized structures of Cs^+ complex of the model compound **14**: (a) for the saddle conformation and (b) for the cone conformation (left, ball and stick model; right, space-filling model). Hydrogens are omitted for clarity in the ball and stick model. Dashed lines indicate the shortest contact between the Cs^+ and the carbon of the benzene rings in **14**.

shown in Fig. 5. Although the cone conformation is less stable than the saddle conformation in the uncomplexed form, the cation-π complexes prefer the cone conformation. In spite of large deformation energies (E_{def}), the interaction energies (E_{HF} and E_{total}) of the alkali metal cations with the cone conformers are much larger (more negative) than those with the saddle one. As shown in Fig. 5, only two benzene rings can have short contacts with the cation in the saddle shaped Cs^+ complex of **14**. The rest of one benzene ring is far from the Cs^+. On the other hand, all three benzene rings can have short contacts with the cation in the cone conformation. The structures suggest that the cone conformation of **14** has greater stabilization with the cation binding.[33] The results can be interpreted by the induced-fit mechanism, the largest gain in the binding energy being obtained during the cation-π complexation.

Shinkai and co-workers reported the 'hole size selectivity' of their π-basic cyclophane compounds. They found a good correlation between the cavity size of the host molecules and ion selectivity.[25] The hole size selectivity can explain the Cs^+

selectivity of **1** under the ESI-MS condition. The flat dish-like surface of the cone structure of **1** (**14**) has a suitable hole size to bind a large Cs^+. However, the calculated binding energies of the cation-π complexes are not consistent with the observed ion selectivity. The HF/6-31G* level calculations of the complexes of **14** show that the Li^+ complex has the largest (most negative) binding energy (−52.6 kcal mol^{-1}), *ca*. 2.6 times as large as that of the Cs^+ complex.[34] As a result, the sequence of binding energy was found to be $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ in contrast to the results of ESI-MS. The calculated binding energy corresponds to reaction (1). Glendening *et al*. reported a similar

$$M^+ + \mathbf{14} \longrightarrow [M^+ + \mathbf{14}] \quad (1)$$

disagreement of the order of the calculated binding energies and the observed ion selectivity of 18-crown-6 ether.[35] They reported that the observed ion selectivity can be explained from the calculated binding energies, if the exchange reaction (2) is

$$[K^+ + \text{18-c-6}] + M^+(H_2O)_n \longrightarrow [M^+ + \text{18-c-6}] + K^+(H_2O)_n \quad (2)$$

considered. Usually, the cation coordination is competitive with solvation. Thus, they suggested that the ion selectivity should be explained by the energy change in reaction (2). In the reaction, the waters ($n = 0$–4), which solvate the cation (M^+), are replaced by the 18-crown-6 ether.

Eventually, they demonstrated that the K^+ selectivity of the 18-crown-6 ether was clearly confirmed by considering the hydration clusters when $n = 3$ and 4. The exchange reaction was calculated to be endothermic for all of the alkali metal cations except for K^+. Previous studies indicate that the K^+ selectivity of 18-crown-6 ether is well reproduced even by ESI-MS.[23,24] These studies show that the solvation process is also crucial for the observed ion selectivity by ESI-MS. In addition, the significant solvation effect on the ion selectivity in the cation-π complexes has been pointed out using MC and MD simulations.[4b,18d,f] Therefore, we also calculated the exchange reaction between the Cs^+ complex of **14** and the hydrated cation clusters eqn. (3). The reaction energies for the exchange

$$[Cs^+ + \mathbf{14}] + M^+(H_2O)_n \longrightarrow [M^+ + \mathbf{14}] + Cs^+(H_2O)_n \quad (3)$$

reactions (3) corresponding to the cation selectivity for a particular cluster size '*n*' are described in Fig. 6. The graph shows that the solvation of the cation gradually changes the reaction energy from exothermic to endothermic for all metal cations. The calculated selectivity was $Cs^+ > Rb^+ > K^+ \gg Na^+ \gg Li^+$ when $n = 3$. This selectivity is consistent with that observed by ESI-MS. Although a 1 : 1 mixture of chloroform and methanol was used as the solvent for the mass spectrometry, the formation of solvated clusters with methanol is expected in the electrospray ionization process, and solvation would result in similar effects. Therefore, we concluded that competition between cation-π complexation and solvation by species in the solvent matrix is essential for understanding the hole-size selectivity of the π-basic host molecules.

Conclusion

We found that several cyclic and acyclic oligo[(dimethylsilylene)phenylene]s were able to form cation-π complexes with alkali metal cations using electrospray mass spectrometry, despite the large conformational flexibility. *Ab initio* calculations of the model compounds demonstrated that not the silyl (SiH_3) group but the trimethylsilyl ($SiMe_3$) group promoted the cation-π interaction, especially by the increase in induction energy. A significant conformational change upon cation-π complexation was also suggested by the calculations of trimethylsilylbenzene and a model compound of the silamacrocycles. The Cs^+ selectivity observed in ESI-MS was explained by the calculated binding energies, if the solvations of the cations are considered. We expect that similar organosilicon fragments can be used in the development of novel organometallic conducting polymers. A study on the cation-π complexation behaviour of high molecular weight poly[(dimethylsilylene)phenylene]s[36] is in progress.

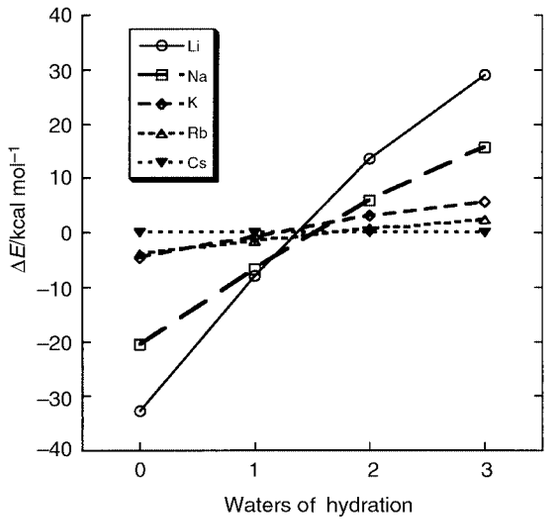


Fig. 6 Energies for the exchange reactions (3) at the HF/6-31G* level of calculation.

Experimental

General methods

^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were measured on a Varian Gemini-300BB NMR spectrometer. Magnesium and anhydrous THF were commercially available.

Materials

All solvents were the best grade commercially available and used without further purification. Triphenylsilane **8** and 18-crown-6 ether were purchased from Tokyo-Kasei and used without further purification.

Preparation

1,1,8,8,15,15-Hexamethyl-1,8,15-trisila[1.1.1]metacyclophane **1** and 1,1,8,8,15,15,22,22-octamethyl-1,8,15,22-tetrasila[1.1.1.1]-metacyclophane **2** were prepared as reported in our previous paper.[17] 1,3,5-Tris(dimethylphenylsilyl)benzene **3**, 4,4′-bis-(dimethylphenylsilyl)biphenyl **4**, 1,4-bis(dimethylphenylsilyl)-benzene **6**, dimethyldiphenylsilane **9** and 1,3-bis(trimethylsilyl)-benzene **10** were prepared as previously reported.[26] 1,3-Bis(dimethylphenylsilyl)benzene **5** was prepared as follows. Under an argon atmosphere, 1,3-dibromobenzene (11.3 g, 47.9 mmol) in dry THF (50 ml) was added slowly to a mixture of magnesium (2.55 g, 105 mmol) and chlorodimethylphenylsilane (18.0 g, 105 mmol) in dry THF (50 ml) at room temperature with rapid stirring. The rate of addition was adjusted to a gentle reflux. The solution was subsequently heated under reflux for 2 h and allowed to stand at room temperature for 1 h. After hydrolysis by adding water (50 ml), the organic layer was extracted with diethyl ether and dried over anhydrous magnesium sulfate. The solvent was removed *in vacuo*, and then 10.3 g (29.7 mmol) of **5** were obtained by distillation from the residue as a colorless oil. Yield 62%. bp = 141 °C/0.1 mmHg. ^1H NMR (300 MHz, $CDCl_3$): δ 0.56 (s, 12H), 7.31–7.40 (m, 7H), 7.50–7.59 (m, 6H), 7.72–7.76 (brs, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.54, 127.23, 127.85, 129.14, 134.24, 135.09, 137.36, 138.34, 139.99. Calc. for $C_{22}H_{26}Si_2$: C, 76.23; H, 7.56. Found: for C, 76.40; H, 7.53%.

4-(Dimethylphenylsilyl)biphenyl **7** was prepared in a similar manner from 4-bromobiphenyl and chlorodimethylphenylsilane. Yield: 58%. Colorless crystals; mp = 51 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.59 (s, 6H), 7.30–7.48 (m, 6H), 7.52–7.64 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ −2.51, 126.63, 127.24, 127.47, 127.93, 128.84, 129.23, 134.28, 134.77, 137.09, 138.26, 141.17, 141.97. Calc. for $C_{20}H_{20}Si$: C, 83.28; H, 6.99. Found: C, 82.96; H, 6.97%; HRMS: calc. for $C_{20}H_{20}Si$ *m*/*z* 288.1334, obs. 288.1346.

Electrospray mass spectrometry

An ESI-TOF mass spectrometer (Applied Biosystems Mariner™) was used for the molecular weight analysis of the cation-π complexes of the oligo[(dimethylsilylene)phenylene]s with alkali metals. A chloroform solution (50 μl) of the host compound (1 mM) and a methanol solution (50 μl) containing a mixture of alkali metal chlorides MCl (M = Li, Na, K, Rb or Cs) (1 mM) were mixed just before the MS measurement. A 50 μl portion of the mixed solution was injected directly into the ESI source by a syringe pump instrument (Harvard Apparatus PHD2000). General instrument settings are as follows: vaporizing temperature, 140 °C; infusion rate, 1 μl min^{-1}; capillary voltage, 3100 V; nozzle potential, 135 V. The signal intensities were averaged over five scans and recorded as the sum of the corresponding isotopic peaks. When compared with the common host compounds, an equimolar amount of 18-crown-6 ether was used as an internal standard in the solution of the silicon host compounds.

Computational method for theoretical calculations

For substituent effect of silyl group. The GAUSSIAN 98 program was used for the *ab initio* molecular orbital calculations.[37] The 6-311G** basis set was used. Electron correlation was corrected by the MP2 method.[38,39] The basis set superposition error (BSSE)[40] was corrected for all calculations using a counterpoise method.[41] The geometries of the complexes were optimized at the MP2/6-311G** level. The distributed multipoles[42,43] of the π systems were obtained from the MP2/6-311G** wavefunctions of monomers using CADPAC version 6.[44] The geometries of monomers in the complexes were used for calculations of the distributed multipoles. The electrostatic and induction energies of the complexes were calculated by ORIENT version 3.2.[45] The electrostatic energy was calculated as the interactions between the distributed multipoles of the π systems and the charge of the cation. The induction energy was calculated as the interaction between the distributed polarizable sites[46] of the π system and the electric field produced by the cation. The anisotropic polarizabilities $\alpha_{xx} = \alpha_{yy} = 14$ and $\alpha_{zz} = 7$ au were put on the carbon atoms of the benzene rings (the *z* axis is parallel to the sixfold axis).[47] The isotropic polarizabilities $\alpha = 17$ and 32 au were put on the other carbon and silicon atoms, respectively.[48,49]

For trisila[1.1.1]metacyclophane model compound 14 and its π complexes. The Mulliken CAChe Satellite program (Ver. 4.1.1)[50,51] was used for the *ab initio* molecular orbital calculations. The 6-31G* basis set was used. For the π complexes of **14** containing heavy alkali metal cations (K^+, Rb^+ and Cs^+) the averaged relativistic effective core potentials with the double zeta polarization function were used.[52] The geometries of the π complexes were optimized at the HF/6-31G* level. The geometries of hydrated metal ion clusters were reported by Glendening and Feller using MP2/6-31+G* level calculations.[53] Using the reported geometries, we also calculated the interaction energy of the clusters at the HF/6-31G* level to examine the exchange reaction.

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