Binding of monovalent metal cations by the *p*-sulfonatocalix[4]arene: experimental evidence for cation–π interactions in water

Jean-Pierre Morel and Nicole Morel-Desrosiers*

Received 12th September 2005, Accepted 14th November 2005
First published as an Advance Article on the web 19th December 2005
DOI: 10.1039/b512856k

Gibbs free energies, enthalpies and entropies for the binding of Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Ag$^+$, Tl$^+$ and NH$_4{}^+$ by the *p*-sulfonatocalix[4]arene in water are determined by microcalorimetry. Whereas no significant heat effect is detected with Na$^+$ or Ag$^+$, suggesting that these cations are not complexed, weak but selective binding is observed with the other cations. The whole set of thermodynamic parameters, which demonstrate that the cations bind inside the cavity of the calixarene, evidence the importance of the cation–π interactions for these complexes in water.

Introduction

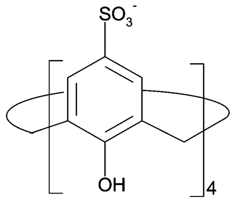
Noncovalent intermolecular interactions play a dominant role in molecular recognition phenomena and supramolecular architectures. Among these interactions those occurring between a cation and a π-system, the so-called cation–π interactions, have generated much interest during the past two decades, particularly because of their contribution to protein stability. Dougherty and coworkers carried out important studies on this type of interaction and, in 1997, published a review providing a detailed overview of the subject.[1]

In numerous theoretical and experimental papers cited in this review or published since then, there was an attempt to estimate the interaction energy for complexes involving different cations and different π-systems in the gas phase but also in a range of solvents.[1–4] This revealed one of the important aspects of the problem: although the energy of the cation–π interaction is notable in the gas phase (for instance, the energy of the K$^+$–benzene interaction, ΔE_K, is of the order of -60 kJ mol^{-1}),[5] it is largely destabilized in solution where the solvent molecules are in competition with the arene for binding to the cation. This is particularly important in water where the cations are strongly solvated. It can also be noted that the metal cation which has the largest Gibbs free energy of hydration is also the one which shows the most energetic interaction with benzene in the gas phase: for instance, Li$^+$ is the alkali-metal cation that binds more strongly to benzene in the gas phase ($\Delta E_\mathrm{Li} \approx -140$ kJ mol^{-1})[5] and that is also the most strongly solvated in water ($\Delta_\mathrm{h}G = -481$ kJ mol^{-1}).[6] This aspect is crucial as regards the role played by the cation–π interactions in biology, as underlined by Diederich and coworkers in a recent review[7] highlighting the energetic features of this type of binding. It also explains why it is experimentally so difficult to evidence without ambiguity this type of interaction in aqueous solution.[8]

The calixarenes constitute a class of macrocyclic receptors that is of great importance in supramolecular chemistry. These hosts, which are composed of phenol units connected by *ortho*-methylene bridges, are able to complex a variety of guests in the solid state and in solution. A tremendous number of articles dealing with the complexation of different ions by numerous calixarene derivatives were published; however, these papers were essentially concerned with the structures of the solid complexes and with the cation extraction efficiency of these ligands in organic solvents. The present work is not concerned by these issues, our purpose being to evidence interactions between cations and π-systems *in the homogeneous aqueous phase*.

The *p*-sulfonatocalixarenes, which have the great advantage of being highly water-soluble, can be used to prepare, under good conditions, complexes in aqueous solutions. Depending on the guest, different types of interactions are involved (ionic, hydrophobic, van der Waals, π–π, cation–π, hydrogen bonding,···). Each of these interactions implies a partial desolvation of the host and guest and also some modification of the degrees of freedom of the species. A complete thermodynamic characterization of the binding process, including not only the association constant but also the enthalpy and entropy of reaction, is one of the key elements in identifying the stabilizing factors.[9–11] Microcalorimetry is a powerful tool for measuring the thermodynamic parameters that characterize interacting molecules because it not only gives the enthalpy changes but can also yield the association constants even in the case of weak interactions.

During the past years, we thus determined by microcalorimetry the thermodynamic properties for the complexation of the *p*-sulfonatocalix[4]arene (SC4) with numerous neutral and charged guests in aqueous solution at 25 °C.[10,11]



p-sulfonatocalix[4]arene
(SC4)

We showed that the inclusion of a hydrocarbon chain into the calixarene cavity is not governed by a favourable entropic contribution, as would be expected for a hydrophobic interaction, but by a favourable enthalpic term ($\Delta_\mathrm{r}H° \ll 0$) which results from the

---

Laboratoire de Thermodynamique des Solutions et des Polymères, UMR CNRS 6003, Université Blaise Pascal (Clermont-Ferrand II), 24 avenue des Landais, 63177 Aubière Cedex, France. E-mail: nicole.morel@univ-bpclermont.fr; Fax: +33 473405328; Tel: +33 473407641

van der Waals interactions between the nearby species. We noticed that the negative enthalpies of reaction vary linearly with the number of methylene groups included into the calixarene cavity, and this was confirmed by molecular dynamics simulations of the SC4 complexes with alkylammonium and tetraalkylammonium cations in water.[12] At the same time, our study of the binding of SC4 with divalent and trivalent metal cations in water gave original results:[10] in spite of an unfavourable enthalpy of reaction ($\Delta_r H^\circ > 0$), this type of complex is relatively strong ($\log K$ varies from 3.3 to 4.2) due to a favourable entropy of reaction ($T\Delta_r S^\circ \gg 0$) that largely controls the binding process. Such a thermodynamic behaviour, which is typical of purely ionic binding and which essentially reflects the desolvation of the species upon binding, clearly indicates that the divalent or trivalent metal cation remains outside the cavity and forms an outer-sphere complex with the SO_3^- groups of the calixarene, as confirmed by the molecular dynamics simulation of the La^{3+}–SC4 complex in water.[12]

During these previous studies[10,11] we also examined the binding of monovalent cations (Na^+, K^+, NH_4^+) in water but, because no significant heat effect was observed, we concluded that there was no specific interaction between SC4 and these ions. These studies were carried out in rather dilute solutions (10^{-3} mol L^{-1}) and the heat effects were indeed very small. However if we more closely examine the thermograms, we notice a very weak endothermic effect for Na^+ and very weak exothermic effects for K^+ and NH_4^+. Being intrigued by this specificity, we decided to repeat the study with more concentrated solutions in order to get more significant heat effects, the high solubility of SC4 in water enabling us to do so. This leads us to report here for the first time the thermodynamic properties for the binding of K^+, Rb^+, Cs^+, Tl^+ and NH_4^+ by the *p*-sulfonatocalix[4]arene in water at 25 °C.

Experimental

Solutions

25,26,27,28-Tetrahydroxy-5,11,17,23-tetrasulfonatocalix[4]arene (SC4), purchased from ACROS, was decolorized by adsorption on active carbon and dried under vacuum at 80 °C. It was checked by NMR spectroscopy and its water content was determined by Karl-Fischer titration. NaCl, KCl, RbCl, CsCl, $AgNO_3$, $TlNO_3$ and NH_4Cl were bought from Merck (suprapur or pro analysi grade); after drying, they were stored in a desiccator and used without further purification.

All the solutions were prepared from triply distilled water. The exact concentration of the calixarene solutions was determined by potentiometric titration. The pH of the calixarene and salt solutions was set at 2.0 with 0.01 mol L^{-1} HCl (Riedel-de Haën). Under such conditions, according to the pK_a values,[13] all the sulfonic acid groups of the SC4 are dissociated whereas all the phenolic hydroxy groups are protonated. This situation remains unchanged upon titration of the calixarene by the cations.

Microcalorimetry

All the measurements were carried out at 298.15 K using a multichannel microcalorimeter (Thermometric 2277 Thermal Activity Monitor) equipped with a 1 mL glass titration-perfusion vessel. Wadsö and coworkers[14] have thoroughly described this twin-thermopile heat-conduction microcalorimeter, specified its working conditions and analysed its performance.

In the present case, each thermogram was obtained by stepwise injection of 8 μL of 0.250 mol L^{-1} salt solution into 0.800 mL of 0.0220 mol L^{-1} calixarene solution. For each titration experiment, 20 injections were made using a Lund syringe pump (Thermometric) equipped with a 250 μL Hamilton syringe fitted with a gold cannula. Separate dilution experiments were performed under the same conditions: since the heat of dilution of the calixarene was found to be negligible, the heat effects observed upon titration were simply corrected for the heats of dilution of the guests. Each experiment was repeated to verify reproducibility. Values for the apparent association constant K' and apparent standard molar enthalpy of reaction $\Delta_r H'^\circ$ in the given medium were calculated by use of the Digitam 4.1 minimization program (Thermometric), all the series of data obtained for each system being treated simultaneously in the regression analysis. Under the present conditions, the apparent values are close to standard values and will thus be designated by K and $\Delta_r H^\circ$ throughout the text.

Results and discussion

The thermograms were fitted by considering the following 1 : 1 binding model:

$$SC4_{(aq)} + M^+_{(aq)} = SC4M^+_{(aq)}$$

The K and $\Delta_r H^\circ$ values deduced from these fits are reported, with the estimated standard errors, in Table 1. As shown by the smallness of the errors, the fit is excellent in all the cases studied here. The calculated $\Delta_r G^\circ$ and $T\Delta_r S^\circ$ values are also listed in Table 1.

No significant heat effect has been detected with Na^+ or Ag^+, and we may thus assume that these two cations are not complexed by SC4 in water. In contrast, the results of Table 1 show that, in water, NH_4^+, K^+, Rb^+ and Cs^+ bind weakly but significantly to SC4. The association constant for the binding of Cs^+ is equal to 14.6 which, although small, is not at all negligible: for instance, in a solution containing 0.01 mole of Cs^+ and 0.01 mole of SC4 per litre, 12% of the species are complexed. The complexation of Tl^+, whose association constant is equal to 460, is much more important since, under the above conditions, 63% of the species are complexed. In all cases, the binding is enthalpy-driven: $\Delta_r H^\circ$ is relatively small for NH_4^+ (-3.7 kJ mol^{-1}) but varies from -10 to -14 kJ mol^{-1} for the other cations. $T\Delta_r S^\circ$ is negative for K^+, Rb^+ and Cs^+ but very weakly positive for NH_4^+ and Tl^+.

Table 1 Thermodynamic properties for the binding of monovalent cations by the *p*-sulfonatocalix[4]arene in water at pH 2 and 25 °C[a,b]

Cations	K	$\Delta_r G^\circ$	$\Delta_r H^\circ$	$T\Delta_r S^\circ$
Ag^+	[c]	[c]	[c]	[c]
Na^+	[c]	[c]	[c]	[c]
K^+	2.9 ± 0.2	−2.6 ± 0.2	−12.3 ± 0.6	−9.7 ± 0.8
Rb^+	5.9 ± 0.2	−4.4 ± 0.1	−10.3 ± 0.2	−5.9 ± 0.3
Cs^+	14.6 ± 0.4	−6.6 ± 0.1	−10.9 ± 0.2	−4.3 ± 0.3
Tl^+	460 ± 30	−15.2 ± 0.2	−14.0 ± 0.3	1.2 ± 0.5
NH_4^+	6.9 ± 0.5	−4.8 ± 0.2	−3.7 ± 0.2	1.1 ± 0.4

[a] Molar scale. [b] $\Delta_r G^\circ$, $\Delta_r H^\circ$, $T\Delta_r S^\circ$ in kJ mol^{-1}. [c] No significant heat effect.

Thus, the first important conclusion that can be drawn from this study is that the binding of these monovalent cations by SC4 in water is enthalpy-driven, in contrast to the binding of the divalent and trivalent metal cations which, as shown previously,[10] is strongly entropy-driven. It can thus be concluded that the monovalent metal cations are included into the calixarene cavity, in contrast to the divalent and trivalent metal cations which remain outside the cavity and bind to SC4 by ionic interactions with the SO_3^- groups of the upper rim. It must be underlined that one cannot interpret the present results by imagining a binding of the alkali metal cations with the phenolic hydroxy groups of the lower rim. To our knowledge, interactions of this type have never been evidenced *in water*; furthermore, such interactions with oxygen atoms would not favour the more polarizable cations, in contradiction with what is observed here.

Binding involves an important desolvation of the cation and ligand, which yields an unfavourable Gibbs free energy that must be compensated by the interactions taking place into the cavity. As expected, within the alkali-metal cations series, the affinity of SC4 is larger for the cation that is less strongly solvated.[6] NH_4^+ cannot be directly compared with the other cations studied here because the entropy of desolvation of a polyatomic cation is relatively more important than that of a monoatomic cation. In contrast, Tl^+ which is more strongly hydrated than the other monoatomic cations studied here is also more strongly complexed: this implies that the interactions of Tl^+ with the host cavity are much more favourable than those of the other monoatomic cations. It can be noted that calix[4]arene tetra(Pr ether) and tetra(allyl ether) used as neutral carriers for ion-selective electrodes showed an important thallium selectivity.[15]

It is possible to quantify very crudely the energy of interaction between a monoatomic cation M^+ and the SC4 cavity by considering a simple model taking K^+, the less strongly complexed cation, as the reference. Let us imagine the following reactions in the gas phase:

$$SC4_{(g)} + M^+_{(g)} = SC4M^+_{(g)} \qquad \Delta E_M$$

$$SC4_{(g)} + K^+_{(g)} = SC4K^+_{(g)} \qquad \Delta E_K$$

$$M^+_{(g)} + SC4K^+_{(g)} = K^+_{(g)} + SC4M^+_{(g)} \qquad \Delta E_M - \Delta E_K$$

The exchange reaction can also be imagined in water:

$$M^+_{(aq)} + SC4K^+_{(aq)} = K^+_{(aq)} + SC4M^+_{(aq)} \qquad \Delta_r G^\circ{}_M - \Delta_r G^\circ{}_K$$

Combining that with the Gibbs free energies of hydration of the species yields

$$\begin{aligned}\Delta E_M - \Delta E_K = \Delta_r G^\circ{}_M - \Delta_r G^\circ{}_K + (\Delta_h G^\circ{}_M - \Delta_h G^\circ{}_K)\\ - (\Delta_h G^\circ{}_{SC4M} - \Delta_h G^\circ{}_{SC4K})\end{aligned}$$

The difference between the Gibbs free energies of hydration of the ions is known.[6] As regards the difference between the Gibbs free energies of the complexes, we will make the assumption that it can be expressed as a fraction of the difference between the Gibbs free energies of hydration of the ions since the included cations are only partially desolvated. If we very crudely assume that the included cations keep about 1/3 of their hydration then

$$\Delta E_M - \Delta E_K = \Delta_r G^\circ{}_M - \Delta_r G^\circ{}_K + 2/3(\Delta_h G^\circ{}_M - \Delta_h G^\circ{}_K)$$

which, to simplify, can be written as

$$\Delta\Delta E_M = \Delta\Delta_r G^\circ{}_M + 2/3\ \Delta\Delta_h G^\circ{}_M$$

Table 2 Parameters of the model described in the text[a]

Cations	$\Delta\Delta_r G^\circ{}_M$	$2/3\Delta\Delta_h G^\circ{}_M$[b]	$\Delta\Delta E_M$
K^+	0	0	0
Rb^+	−1.8	15	13
Cs^+	−4.0	31	27
Tl^+	−12.6	−4	−17
NH_4^+	−2.2	8	6

[a] $\Delta\Delta_r G^\circ{}_M$, $\Delta\Delta_h G^\circ{}_M$, $\Delta\Delta E_M$ in kJ mol^{-1}. [b] Ref. 6.

By combining the results of Table 1 with the Gibbs free energies of hydration of the monovalent cations compiled by Marcus[6] we get the values reported in Table 2.

The $\Delta\Delta E_M$ values, which correspond to the difference between the energies of interaction of SC4 with M^+ and K^+ in the gas phase, show that Tl^+, at the opposite of NH_4^+, Rb^+ and Cs^+, interacts with the benzene rings of the cavity more strongly than K^+. Of course, the value of 1/3 used in the present model for the extent of solvation of the complexed cation is hypothetical: it must be noted, however, that if it is replaced by another reasonable fraction, the $\Delta\Delta E_M$ values are changed but not the sequence. It can also be noted that the conclusion is unchanged if the model is applied to the enthalpies instead of the Gibbs free energies. Now, how is it that Tl^+, although more strongly hydrated than the other monoatomic monovalent cations, forms stronger interactions with the π-system of the SC4 cavity? Because its electronic structure is different, Tl^+ is three times more polarizable than same-size Rb^+ [6] and, as a result, all the polarization-sensitive interactions in which Tl^+ is involved are enhanced. In fact, Tl^+ interacts more strongly with water than the other monoatomic monovalent cations but it is also more strongly complexed by SC4 because the Tl^+–π interaction is much stronger than the other cation–π interactions.

The experimental and computed ΔE_M values for benzene interacting with the alkali-metal cations in the gas phase showed that the cation selectivity is governed by the electrostatic cation–π interactions:[1] the recent experimental ΔE_M values vary indeed from −161 kJ mol^{-1} for Li^+ to −65 kJ mol^{-1} for Cs^+.[16] However, the induction contributions due to the polarizability of the π-system and, depending on the species, the dispersion and charge transfer contributions are also important.[5,17–20] Recent theoretical studies on cation–benzene complexes showed indeed that for Rb^+ and Cs^+ the induction contributions to the binding energies are of the same order of magnitude as the electrostatic contributions, whereas for Li^+, Mg^{2+} and Ca^{2+} they are much more important, which indicates that the cation–π interaction largely depends on the distance between the species.[17,20] Interestingly, Tsuzuki *et al.*'s computed data[17] yield $\Delta\Delta E_M$ values with respect to K^+ ($\Delta\Delta E_{Rb}$ = 4 kJ mol^{-1} and $\Delta\Delta E_{Cs}$ = 12 kJ mol^{-1}) that follow the same trend as the $\Delta\Delta E_M$ values calculated from our experimental data (Table 2).

The binding of benzene with Tl^+ is, as underlined above, very peculiar. Due to its high polarizability, Tl^+ generates, when it interacts at short-distance, an important dispersion energy. Furthermore, its electronic structure exhibits filled 4f and 5d orbitals. In a recent theoretical study,[5] the influence of similar characteristics was quantified for the Ag^+–benzene complex in the gas phase: the calculations showed important induction and dispersion energies. In the present experimental study, no specific interaction between Ag^+ and the π-system of the SC4 cavity is evidenced in water: this is due to the fact that this small cation is much more hydrated ($\Delta_h G = -440$ kJ mol^{-1}) than the other monovalent cations studied here ($\Delta_h G = -304$ kJ mol^{-1} for K^+).[6]

Obviously, the interaction of a monovalent cation with the SC4 cavity cannot be directly compared with the cation–benzene interaction in its optimized geometry. The cation position within the cavity depends on the cation size and on the conformation adopted by the calixarene. It is well-known that SC4 adopts in water cone conformations that are stabilized by intramolecular hydrogen-bonding between the OH groups of the lower rim.[21] Theoretical calculations allowed the prediction of the structures and binding energies of different cation–SC4 complexes.[22,23] It was shown that the structure adopted by the tetraalkoxycalix[4]arenes depends on the nature of the alkoxy group and on the nature of the included cation:[22] in all the privileged structures, the cation interacts both with the benzene rings and the oxygen atoms of the alkoxy groups. The binding of Cs^+, for instance, favours a partial cone conformation with three cation–arene and one cation–oxygen interactions. However, results obtained by computation in the gas phase cannot represent the state of a system in solution, in particular in a very polar medium like water. Experimental NMR studies in mixtures of acetonitrile and chloroform showed[24] that with methyl and *tert*-butyl substituents, the binding of Na^+ favours the cone conformation whereas the binding of Cs^+ involves an exchange between partial cone (80%) and 1,3-alternate (20%) conformations. The MD simulations carried out by Wipff and coworkers[25] on complexes formed between the *p*-*tert*-butylcalix[4]arene anion and alkali metal cations in polar non aqueous solvents showed the existence of various structures depending on the nature of the cation and on the solvent. The complexes studied in the present work, that involve interactions between monoatomic cations and the *p*-sulfonatocalix[4]arene in water, are particularly interesting because they clearly evidence cation–π interactions in a medium into which it is not obvious to demonstrate this type of interactions; for this reason, we intend to further investigate these systems by using other approaches.

Conclusion

We have evidenced by microcalorimetry the formation of weak inclusion complexes between some monovalent monoatomic cations and the *p*-sulfonatocalix[4]arene (SC4) in water. It has been shown that these cations are included into the SC4 cavity due to the favourable enthalpies of cation–π interactions. The affinity of SC4 for the alkali-metal cations in water and the affinity of benzene for the same cations in the gas-phase do vary in reverse order: in aqueous solution, it is thus the cation dehydration that governs the selectivity of SC4 for the alkali-metal cations. What we observe here with monovalent cations is totally different from what was observed previously with multivalent cations. In fact, the divalent and trivalent monoatomic cations, which are more hydrated than the monovalent ones, are not included into the SC4 cavity: they do strongly associate with the ligand but this occurs outside the cavity through ionic interactions with the SO_3^- groups and is totally entropy-controlled. It can be noticed that, although weak, the association of SC4 with Cs^+ in water is not negligible and could possibly be enhanced by changing the solvent. Finally we have shown that the Tl^+–π interaction is particularly favourable due to the cation polarizability.

References

1 J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303.
2 P. C. Kearny, L. S. Mizoue, R. A. Kumpf, J. E. Forman, A. McCurdy and D. A. Dougherty, *J. Am. Chem. Soc.*, 1993, **115**, 9907.
3 R. A. Kumpf and D. A. Dougherty, *Science*, 1993, **261**, 1708.
4 J. P. Gallivan and D. A. Dougherty, *J. Am. Chem. Soc.*, 2000, **122**, 870.
5 D. Kim, S. Hu, P. Tarakeshwar, K. S. Kim and J. M. Lisy, *J. Phys. Chem. A*, 2003, **107**, 1228.
6 Y. Marcus, *Ion Properties*, Marcel Dekker, New York, 1997.
7 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 1210.
8 G. W. Gokel, S. L. De Wall and E. S. Meadows, *Eur. J. Org. Chem.*, 2000, 2967.
9 D. B. Smithrud, T. B. Wyman and F. Diederich, *J. Am. Chem. Soc.*, 1991, **113**, 5420.
10 C. Bonal, J. P. Morel and N. Morel-Desrosiers, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1075.
11 F. Perret, J. P. Morel and N. Morel-Desrosiers, *Supramol. Chem.*, 2003, **15**, 199.
12 A. Mendes, C. Bonal, N. Morel-Desrosiers, J. P. Morel and P. Malfreyt, *J. Phys. Chem. B*, 2002, **106**, 4516; A. Ghoufi, C. Bonal, J. P. Morel, N. Morel-Desrosiers and P. Malfreyt, *J. Phys. Chem. B*, 2004, **108**, 5095; A. Ghoufi, C. Bonal, J. P. Morel, N. Morel-Desrosiers and P. Malfreyt, *J. Phys. Chem. B*, 2004, **108**, 11744.
13 J. P. Scharff, M. Mahjoubi and R. Perrin, *New J. Chem.*, 1991, **15**, 883; G. Arena, R. Cali, G. G. Lombardo, E. Rizzarelli, D. Sciotto, R. Ungaro and A. Casnati, *Supramol. Chem.*, 1992, **1**, 19; I. Yoshida, N. Yamamoto, F. Sagara, D. Ishii, D. Ueno and S. Shinkai, *Bull. Chem. Soc. Jpn.*, 1992, **65**, 1012.
14 J. Suurkuusk and I. Wadsö, *Chem. Scr.*, 1982, **20**, 155; M. Bastos, S. Hägg, P. Lönnbro and I. Wadsö, *J. Biochem. Biophys. Methods*, 1991, **23**, 255; P. Bäckman, M. Bastos, D. Hallén, P. Lönnbro and I. Wadsö, *J. Biochem. Biophys. Methods*, 1994, **28**, 85.
15 K. Kimura, K. Tatsumi, M. Yokoyama, M. Ouchi and M. Mocerino, *Anal. Commun.*, 1999, **36**, 229.
16 J. C. Amicangelo and P. B. Armentrout, *J. Phys. Chem. A*, 2000, **104**, 11420.
17 S. Tsuzuki, M. Yoshida, T. Uchimaru and M. Mikami, *J. Phys. Chem. A*, 2001, **105**, 769.
18 G. K. Fukin, S. V. Lindeman and J. K. Kochi, *J. Am. Chem. Soc.*, 2002, **124**, 8329.
19 R. Amunugama and M. T. Rodgers, *J. Phys. Chem. A*, 2002, **106**, 5529.
20 S. Tsuzuki, T. Uchimaru and M. Mikami, *J. Phys. Chem. A*, 2003, **107**, 10414.
21 S. Shinkai, K. Araki, M. Kubota, T. Arimura and T. Matsuda, *J. Org. Chem.*, 1991, **56**, 295; C. D. Gutsche and L. J. Bauer, *J. Am. Chem. Soc.*, 1985, **107**, 6052.
22 B. P. Hay, J. B. Nicholas and D. Feller, *J. Am. Chem. Soc.*, 2000, **122**, 10083.
23 A. T. Macias, J. E. Norton and J. D. Evanseck, *J. Am. Chem. Soc.*, 2003, **125**, 2351.
24 J. Blixt and C. Detellier, *J. Am. Chem. Soc.*, 1995, **117**, 8536; U. C. Meier and C. Detellier, *J. Phys. Chem. A*, 1998, **102**, 1888.
25 R. Abidi, M. V. Baker, J. M. Harrowfield, D. S. C. Ho, W. R. Richmond, B. W. Skelton, A. H. Whilte, A. Varnek and G. Wipff, *Inorg. Chim. Acta*, 1996, **246**, 275.