Pergamon

Tetrahedron 58 (2002) 5119–5124

TETRAHEDRON

Complex formation between 1-chloro-4-(trifluoromethyl)benzene (guest) and 4-*tert*-butylcalix[4]arenes (host) distally substituted with phosphonic acid or phosphonic ester groups at the lower rim

Sándor Kunsági-Máté,[a,*] Géza Nagy,[a,b] Petr Jurecka[c] and László Kollár[b,d]

[a]*Department of General and Physical Chemistry, University of Pécs, Ifjúság u. 6., H-7624 Pécs, Hungary*
[b]*Research Group for Chemical Sensors of the Hungarian Academy of Sciences, Ifjúság u. 6., H-7624 Pécs, Hungary*
[c]*Department of Inorganic Chemistry, Charles University, Hlavova 2030, Prague 2, Czech Republic*
[d]*Department of Inorganic Chemistry, University of Pécs, Ifjúság u. 6., H-7624 Pécs, Hungary*

Received 23 January 2002; revised 3 April 2002; accepted 25 April 2002

Abstract—The complexation behavior of the distally substituted phosphonic acid and phosphonic ester 4-*tert*-butylcalix[4]arenes (hosts) with 1-chloro-4-(trifluoromethyl)benzene (guest) was examined in chloroform. The complex stability constants (K_s) and the thermodynamic parameters of the complexation were determined by a spectrofluorometric method using Job's method and van't Hoff theory, respectively. A strong dependence of the host–guest interaction on the extent of distortion in the conformation of calixarene host cavity was obtained. The 'pinched cone' conformer of 1,3-substituted calix[4]arenes seems to form a complex with electron-deficient neutral aromatics predominantly through π–π type interaction. © 2002 Elsevier Science Ltd. All rights reserved.

---

1. Introduction

The recognition of neutral organic molecules by synthetic receptors is a topic of current interest in supramolecular- and also in analytical chemistry.[1,2] Calixarenes, cyclic oligomers of phenolic units linked through the *ortho* positions, are a fascinating class of macrocycle, because of the simplicity of their skeleton, which is associated with versatile recognition properties both of metallic or organic ions and of neutral molecules.[3,4] Recent reviews summarize their thermodynamic[5] and redox properties,[6] their applications in analytical and separation chemistry,[7] modeling of their molecular dynamics[8–10] and the extent of their metal ion binding character in solution.[11,12] In the last few years, calixarenes have become very popular compounds in supramolecular chemistry since the OH groups on their lower rim can be selectively functionalized.[13–17]

Among the substituents attached to the lower rim, those containing phosphorus are of considerable practical importance. Calixarene derivatives with phosphorus donor atoms have been reported[18–24] and their coordination to copper,[18] platinum[20,25,26] and gold[24] has been investigated. Calixarene based phosphine and phosphinite ligands were used in platinum-, palladium- and rhodium-catalyzed carbonylation reactions.[27] Calix[*n*]arene phosphine oxides have been used for the inter- and intra-group separation of lanthanides and actinides.[21] Calix[4]arenes containing phosphonate groups either on the upper or on the lower rims were synthesized and used for the extraction of lanthanides into organic solvents.[28]

The molecular recognition properties of calixarene building blocks were recently examined by molecular modeling techniques based on high-level ab initio calculations.[29,30] Arena et al. have also investigated the inclusion of small neutral organic guests (alcohols, ketones and nitriles) with water-soluble calix[4]arene receptors by ^{1}H NMR spectroscopy.[31] They concluded that small polar organic molecules having CH groups, that are usually found inside the apolar cavity of calix[4]arenes in the solid phase[32] are complexed in aqueous solution and the inclusion process is controlled by subtle conformational and electrostatic effects. It is well known, that a CH group can interact in an energetically favorable way with the π system of aromatic compounds.[33,34] It has also been shown that CH–π type interactions play important roles in the supramolecular interactions of some calixarenes.[35,36] A three-component zigzag molecular array was obtained on the inclusion of *p*-xylene by calixarenes,[37] with the array structure being formed by CH–π interactions. Novoa and Mota[38] have found CH–π or OH–π type interactions between compounds having both π-electrons and CH or OH groups (e.g. ethene–ethene, acetylene–ethene, benzene–ethene, acetylene–benzene, benzene–benzene, ethene–water, acetylene–water, benzene–water, etc).

Keywords: calixarenes; neutral guest; recognition; complex stability.

* Corresponding author. Tel.: +36-72-327622(-4208); fax: +36-72-327622(-4680); e-mail: kunsagi@ttk.pte.hu

PII: S0040-4020(02)00474-X

In our previous papers[39,40] the complexation behavior of calix[4]arene and 4-*tert*-butyl-calix[6]arene (hosts) with neutral π-electron deficient 1-trifluoromethyl-benzene derivatives (guests) in chloroform and dimethylformamide was reported. The formation of stable host–guest complexes was examined by the spectrofluorometric method and quantum-chemical model calculations. The solvent effect on the stability of the complex was clearly detected. Results obtained later dealing with the complexation of 1,3-substituted calix[4]arene derivatives with 4-chloro-1-trifluoromethyl-benzene showed the importance of π–π interactions between the phenolic rings of the calixarene host and the neutral guest molecule.[41]

In this paper the complexation behavior of distally substituted phosphonic acid and phosphonic ester derivatives of 4-*tert*-butylcalix[4]arenes (hosts) in the presence of 1-chloro-4-(trifluoromethyl)benzene (guest) was studied by spectrofluorometric and quantum-chemical methods. The complex stability constants (K_s) and the thermodynamic parameters of the complex formation were determined by Job's method and van't Hoff theory, respectively. The experimentally determined thermodynamic data were compared with the host–guest interaction energy derived from quantum-chemical calculations.

2. Results and discussion

The aromatic rings in the calixarene core can form an electron rich cavity due to the electron donating effects of *tert*-butyl-, methylene- and alkoxy groups, therefore electron deficient neutral aromatic guest molecules were chosen for earlier model studies.[39–42] Preliminary experiments indicated that 1-chloro-4-(trifluoromethyl)benzene (BTF) interacts with calix[4]arene and 4-*tert*-butyl-calix[6]arene in chloroform. It was therefore decided to use this molecule as a model guest to study the host–guest interactions with phosphonic acid derivatives of calixarenes. It is expected, that 1,3-substituted calix[4]arenes, unlike the parent calix[4]arene, exist in a distorted 'cone' conformation showing different features in the 'host–guest' interaction. The structures of the molecules investigated are shown in Fig. 1.

(A) (B)

	R
1a	$CH_2P(O)(OH)_2$
2a	$(CH_2)_2P(O)(OH)_2$
3a	$(CH_2)_3P(O)(OH)_2$
1b	$CH_2P(O)(OC_2H_5)_2$
2b	$(CH_2)_2P(O)(OC_2H_5)_2$
3b	$(CH_2)_3P(O)(OC_2H_5)_2$

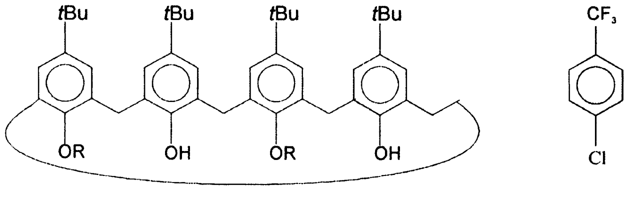

Figure 1. Calixarenes (A) as hosts and 1-chloro-4-(trifluoromethyl)-benzene/BTF (B) as guest chosen for this model study.

2.1. Photoluminescence (PL) spectra

Fig. 2 shows the PL spectra of phosphonic acid (**a**) and phosphonic ester (**b**) derivatives of 4-*tert*-butylcalix[4]arene dissolved in chloroform using 280 nm for excitation. The shape of the PL spectra are very similar, the maximum intensity was obtained at 312 nm in each case. The calixarenes having phosphonic acid substituents show approximately two times higher PL intensity. Both the acid- and ester-like calixarenes show similar changes in the intensity of the PL signal with the chain lengths of 1,3-substituents. **2a** and **2b** derivatives show the highest PL intensity in the **a** and **b** series, respectively.

2.2. Effect of complexation on PL intensity

In order to investigate the interaction of the different 1,3-substituted 4-*tert*-butylcalix[4]arene derivatives with BTF, equimolar 10^{-4} M solutions of calixarene: 1-chloro-4-(trifluoromethyl)benzene were prepared in chloroform and the PL spectra were recorded. Evaluating them it could be seen that the presence of the guest molecules induced changes in the spectra. Whilst there were no major changes in fluorescence wavelength, the change in intensity was significant in each case (see Fig. 3 as representative). The calixarenes showed lower PL intensity in the presence of

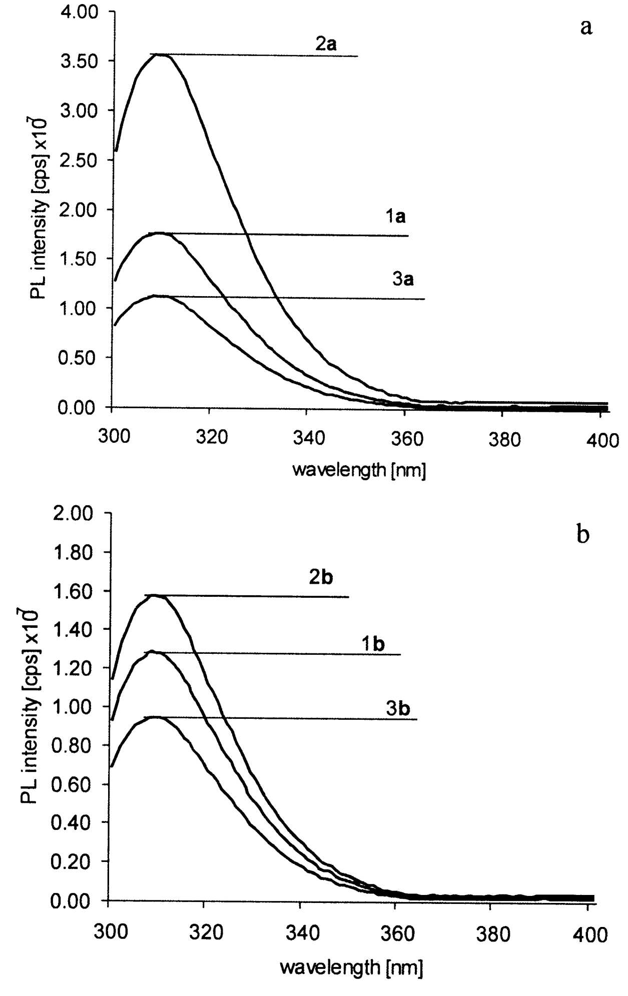

Figure 2. PL spectra of series **a** (top) and **b** (bottom) calixarenes in chloroform.

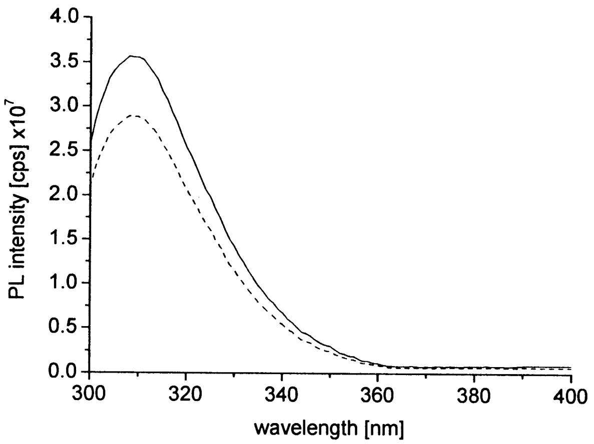

Figure 3. Spectral change of **2a** obtained in the presence of 1-chloro-4-(trifluoromethyl)benzene (solid line: **2a**, dashed line: **2a**–BTF).

1-chloro-4-(trifluoromethyl)benzene. According to our earlier results[39–42] it was supposed that the spectral changes observed were induced by the inclusion interaction of calixarenes with the guest molecules.

2.3. Determination of complex stability

Job's method[43] is a well known, often used approach for determination of the complex stoichiometry with spectroscopic techniques, also in calixarene chemistry.[44–48] The method of Job validated 1:1 stoichiometry in each case (Fig. 4) and the stability constants of the examined host–guest complexes were determined by least squares fitting as described earlier.[44–47,49]

Table 1 summarizes the stability constants of the inclusion complexes of distally substituted **1a**–**3a** and **1b**–**3b** with 1-chloro-4-(trifluoromethyl)benzene in chloroform solvent at temperature of 20°C.

2.4. Thermodynamic description of guest inclusion

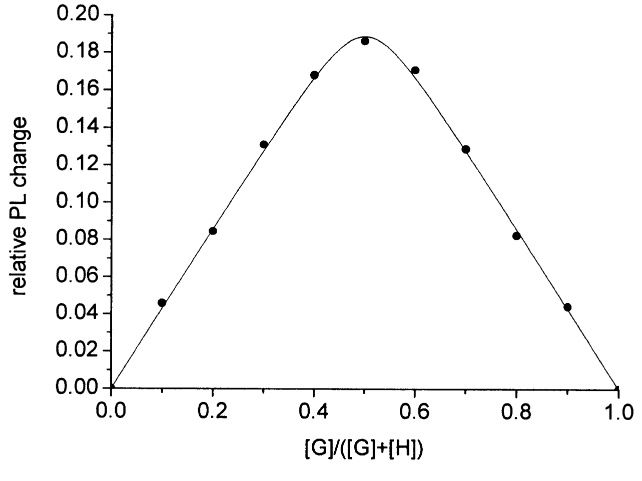

Figure 4. A typical Job's plot of **2a**–BTF complexes.

Table 1. Thermodynamic parameters of complexation of calix[4]arenes (**1a**–**3a** and **1b**–**3b**) with 4-chloro-1-(trifluoromethyl)benzene

Host	log K_s	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J K^{-1} mol^{-1})
1a	1.25±0.05	−6.67±0.14	−27.62±0.04	−70.26±0.02
2a	1.98±0.03	−10.81±0.16	−29.43±0.05	−62.43±0.02
3a	2.89±0.03	−15.94±0.14	−32.42±0.04	−55.26±0.02
1b	2.54±0.04	−13.96±0.14	−31.34±0.04	−58.26±0.02
2b	3.34±0.03	−18.52±0.15	−34.16±0.04	−52.43±0.02
3b	3.96±0.04	−22.02±0.14	−36.43±0.04	−48.32±0.02

The thermodynamic parameters for the individual complexes formed between 1-chloro-4-(trifluoromethyl)benzene (guest) and distally substituted 4-*tert*-butylcalix[4]arenes (host) were determined from the thermal dependencies using the van't Hoff equation:

$$K = \exp\left(-\frac{\Delta G}{RT}\right) = \exp\left(-\frac{\Delta H}{RT}\right)\exp\left(\frac{\Delta S}{R}\right) \qquad (1)$$

and

$$\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \qquad (2)$$

where ΔG is the Gibbs free energy change, ΔS the entropy change and ΔH the enthalpy change associated with the inclusion complex formation. To determine these thermodynamic properties experimentally, the stability constants of the complexes were determined using the Job's method at six different temperatures selected in the 15–40°C range with a step size of 5°C. From the obtained values of the stability constant, the enthalpy and entropy changes of the given inclusion complex formation was determined by least square fitting of Eq. (2) to the experimental data. Fig. 5 shows an example of the thermal dependence of the logarithm of the K_s formation constant for the calixarene **1a**–BTF system.

Table 1 summarizes the thermodynamic parameters for the complexation of **1a**–**3a** and **1b**–**3b** with 4-chloro-1-(trifluoromethyl)benzene. It can clearly be seen that the Gibbs free energy change and the enthalpy change of complexation show a dependence on the chain length of the 1,3-substituents. The phosphonic ester complexes (**1b**–**3b**) have higher stability than the phosphonic acid ones (**1a**–**3a**).

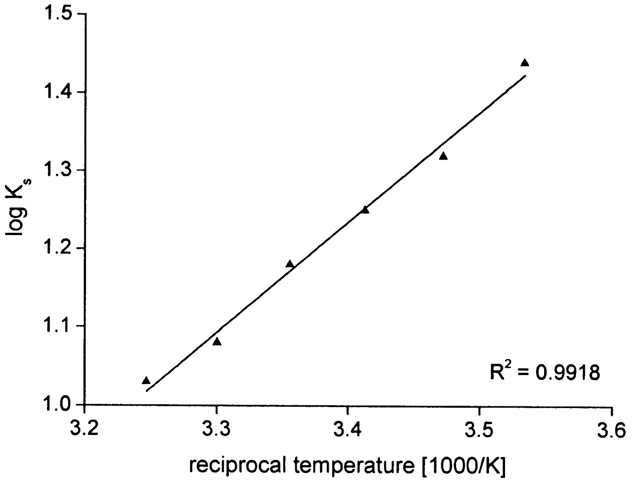

Figure 5. Correlation between the logarithm of measured K_s values of **1a**–BTF complexes and the reciprocal temperature.

In an earlier study[41] we found that the two opposite planes of the phenolic rings derivatized (alkylated) at the lower rim are located closer together than that of the unfunctionalized rings, leading to a 'flattened cone' conformation. Similar findings were recently reported in the case of water soluble calix[4]arenes that contain hydroxyamides attached to their lower rims.[50] Thus, it was possible that the correlation between the energy and enthalpy changes and the stability constants is a result of the fine tuning of the cavity shape caused by the chain lengths of the 1,3-substituents.

2.5. The stabilization energy of the inclusion complexes

To understand the effect of the cavity shape on the complexation, the interaction between the calixarene derivatives (**1a**–**3a**, **1b**–**3b**) and the BTF was also examined by a quantum-chemical method at ab initio level. The interaction energy between the host calixarene and the guest BTF molecules was calculated by the following procedure. The BTF molecule was fixed with its center of gravity on the symmetry axis of calixarene molecule. Beginning from these initial conditions, the free rotation of BTF molecule around its center of gravity was allowed and a geometry optimization was carried out. When the stable conformation of the calixarene–BTF system was found, full geometry optimization was done for the complex. The total energies of the complexes were determined by ab initio calculations. The total energy of the unforced state was used to determine the interaction energy E_{inter} with the following equation:

$$E_{\text{inter}} = E_{\text{system}} - E_{\text{tot,calix}} - E_{\text{tot,BTF}} \tag{3}$$

where E_{system} is the total energy of the calixarene–BTF system, $E_{\text{tot,calix}}$ and $E_{\text{tot,BTF}}$ is the total energy of the separated calixarene and BTF molecules, respectively. All energies were determined in the presence of a solvent cage using TIP3P method i.e. the solvation enthalpies of the species interacted were considered in this way. Only for the case when the BTF molecule is located inside the calixarene cavity (i.e. interacts with calixarene from the side of the upper rim) were stable conformations found. This is in accordance with the results of Brouwer et al., obtained by X-ray and NMR studies.[51]

Fig. 6(a) shows the calculated interaction energy in comparison with the measured enthalpy change of inclusion complex formation of calixarene–BTF system. It can be seen that the interaction energy shows a linear dependence on the chain length of the substituents similar to that which was obtained in the case of distally dialkylated calixarenes.[41] Actually we find a fair correlation between the experimental and theoretical energy values. This provides a supporting evidence that the model used correctly predicts the observed inclusion trends in accordance with the results found in cyclodextrin chemistry.[52–54]

2.6. Cavity shape effect on complexation

It is known that substitution of the OH groups of calix[4]arenes can change the cone conformation to 'partial cone' ('paco') or to 1,2- or 1,3-alternate conformations in vacuo.[55] On the basis of conformational analysis by Langevin dynamic calculations the total energy difference between the cone and paco conformations of **1a** was found to be 37.32 kJ/mol with an energy barrier of 63.26 kJ/mol for cone to paco transition. Therefore it is very likely that the calixarene keeps its cone conformation at room temperature. These results are in agreement with those of Otter and Briels,[56] who used the reactive flux method to consider the solvent effect of chloroform. They could prove the cone stabilization effect of chloroform for calix[4]arene.

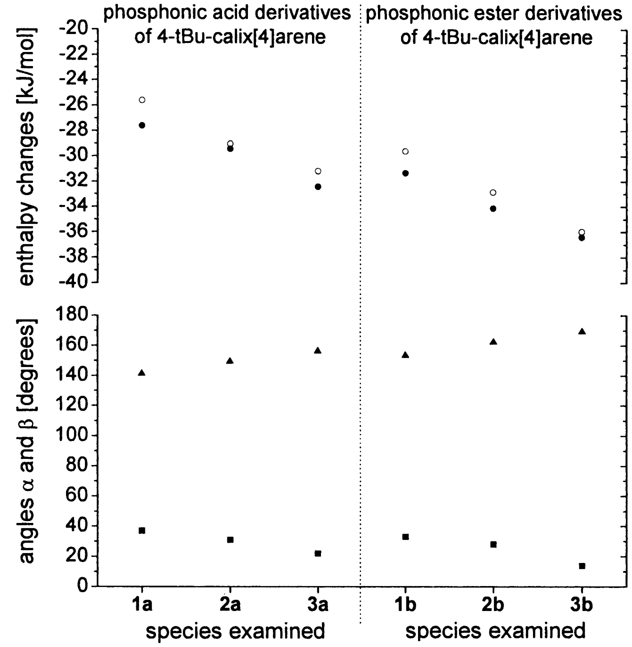

Figure 6. Correlation between the cavity shape of the examined calixarene derivatives (described by α and β angles, represented by ■ and ▲, respectively) and the calculated interaction energy (open circle), measured enthalpy changes (closed circle) during their complexation with BTF.

Calixarenes possess a closed loop of hydrogen bonds at the lower rim.[45] The interaction between the OH groups increases the cavity of calixarene skeleton while the tetragonal distortion on the methylene bridge between the phenolic units counteracts this effect. As a result of these two opposite effects, alternate oscillations of the angles between phenolic rings 1,3 and 2,4 of calixarene skeleton were obtained by molecular dynamic calculations. An oscillation periodicity of approximately 150–180 fs was found in our model calculations.

In the cases of 1,3-substituted calixarenes, there is an interaction between the OH groups of rings 2 and 4 and the O atoms of the phosphonate substituents of rings 1 and 3. This interaction increases the angle β between the rings numbered 2 and 4, while the steric effect on the 1,3-substituents pulls the other two rings (numbered 1 and 3) together. These two effects are influenced by the distortion of tetrahedral methylene bridges. To evaluate this phenomenon, i.e. the interaction of calixarene species with BTF, a geometry optimization was performed for all the examined calixarene derivatives. The angles α and β between the opposite rings of calix[4]arene (Fig. 6) were used to characterize the distortion of calixarenes and were compared with the interaction energy of host–guest complex (Fig. 7).

Fig. 6 (lower curve) shows that with increasing chain length

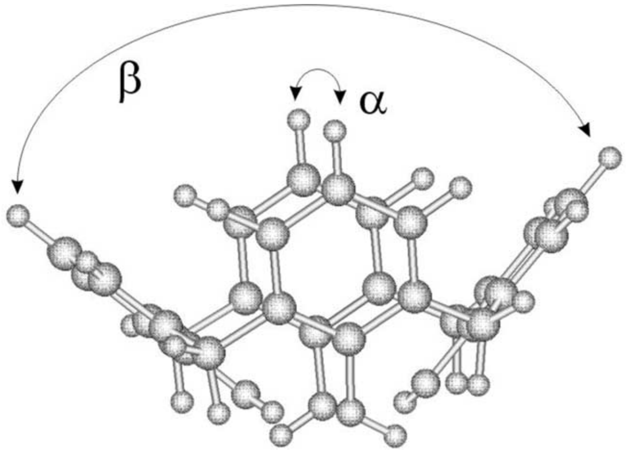

Figure 7. Definition of α and β angles describing the shape of the calixarene cavity.

of the 1,3 substituents, the angle α between the opposite rings 1 and 3 decreases while the angle β between the rings 2 and 4 increases (see Fig. 7). As a consequence of this steric effect, a decrease in the stabilization energy of complex was detected. We mention here that the interaction energy has a negative value, so less interaction energy results in higher complex stability. This means that the optimal complexing sphere is the most flattened cone conformation of the host where the introduction of the guest into the cavity is facilitated by the opening of rings 2 and 4 (high β) and the strong binding site of guest is provided by the nearly coplanar rings 1 and 3 (low α). These results suggest the importance of π–π type interactions between the aromatic ring of BTF and the 1 and 3 rings of calixarene.

3. Conclusion

The inclusion complexation behavior of the distally substituted phosphonic acid and phosphonic ester derivatives of 4-*tert*-butylcalix[4]arenes (hosts) with 1-chloro-4-(trifluoromethyl)benzene (guest) was examined in chloroform. The complex stability constants (K_s) and the thermodynamic parameters of the complexation were determined. A strong dependence of the interaction between the neutral guest molecule and the calixarene on the extent of distortion in the conformation of 'host' cavity was obtained. The pinched cone conformer of 1,3-substituted calix[4]arenes forms a complex with electron-deficient neutral aromatics predominantly through π–π type interactions.

4. Experimental

Parent 4-*tert*-butylcalix[4]arene was obtained from Aldrich. The 1,3-substituted 'lower rim' functionalized calixarenes were prepared as described previously.[28] (For structural details see Fig. 1, series **a** (phosphonic acids): **1a** (M_W=836.38), **2a** (M_W=864.41), **3a** (M_W=892.44), and series **b** (phosphonic esters): **1b** (M_W=948.51); **2b** (M_W=976.55); **3b** (M_W=1004.57).

1-Chloro-4-(trifluoromethyl)benzene (BTF) was obtained from Budapest Chemical Works Co. Ltd. Chloroform obtained from Fluka was freshly distilled before use.

Highly sensitive Fluorolog τ3 spectrofluorometric system (Jobin-Yvon/SPEX) was used to investigate the photoluminescence (PL) spectra of the different solutions. For data collection a photon counting method with 0.2 s integration time was used. Excitation and emission bandwidths were set to 2 nm. 1 mm layer thickness of the fluorescent probes with front face detection was used to eliminate the inner filter effect. A wavelength of 280 nm was chosen for excitation and 312 nm for the emission peak of the spectra. A Grant thermostat (Grant LTD6G, Grant Instruments) was used for temperature controlling. The stoichiometry and stability constants of the complexes were determined by an application of Job's method.[57]

The equilibrium conformation of calixarenes and benzotrifluoride derivative was studied with semi-empirical AM1 (Austin Model) method,[58] followed by ab initio HF/6-31G* calculations. Fletcher–Reeves geometry optimization method was used for the investigation of the conformers. The interaction energy of the studied species was described at an ab initio level using HF/6-31G* calculation. TIP3P method[59] with extension to the solvent used[60] was applied for considering the solvent effect. All types of calculations were carried out with HyperChem Professional 5.1 program package.[61]

Acknowledgements

L. K. thanks I. Lukeŝ (Charles University, Prague) and his group for the generous supply of the phosphorous containing calix[4]arenes. The financial support of Hungarian Scientific Research Fund (OTKA T035047, OTKA T037403), Hungarian National Committee of Technological Development (OMFB 97-20-MU0086) and Francelab Co. (France) are highly appreciated.

References

1. Kuwabara, T.; Nakajima, H.; Nanasawa, M.; Ueno, A. *Anal. Chem.* **1999**, *71*, 2844–2849.
2. Beer, P. D.; Gale, P. A.; Chen, G. Z. *Coord. Chem. Rev.* **1999**, *186*, 3–36.
3. Gutsche, C. D. *Calixarenes*; *Monographs in Supramolecular Chemistry*, Vol. 1; The Royal Society of Chemistry: Cambridge, 1989.
4. Gutsche, C. D. *Calixarenes Revisited*; *Monographs in Supramolecular Chemistry*, Vol. 6; The Royal Society of Chemistry: Cambridge, 1998.
5. de Namor, A. F. D.; Cleverly, R. M.; Zapata-Ormachea, M. L. *Chem. Rev.* **1998**, *98*, 2495–2525.
6. Beer, P. D.; Gale, P. A.; Chen, G. Z. *J. Chem. Soc., Dalton Trans.* **1999**, *12*, 1897–1909.
7. Ludwig, R. *Fresenius J. Anal. Chem.* **2000**, *367*, 103–128.
8. Varnek, A.; Wipff, G. *J. Comput. Chem.* **1996**, *17*, 1520–1531.
9. Lauterbach, M.; Wipff, G. In *Physical Supramolecular Chemistry*, Echegoyen, L., Kaifer, A., Eds.; Kluwer Acadamic: Dordrecht, 1999; pp. 65–102.

10. Varnek, A.; Wipff, G. *J. Mol. Struct. (THEOCHEM)* **1996**, *363*, 67–85.
11. Ikeda, A.; Shinkai, S. *Chem. Rev.* **1997**, *97*, 1713–1734.
12. Yordanov, A. T.; Roundhill, D. M. *Coord. Chem. Rev.* **1998**, *170*, 93–124.
13. Yamamoto, H.; Sakaki, T.; Shinkai, S. *Chem. Lett.* **1994**, *3*, 469–472.
14. Bitter, I.; Grün, A.; Ágai, B.; Tőke, L. *Tetrahedron* **1995**, *51*, 7835–7840.
15. Tóth, K.; Lan, B. T. T.; Jeney, J.; Horváth, M.; Bitter, I.; Grün, A.; Ágai, B.; Tőke, L. *Talanta* **1994**, *41*, 1041–1049.
16. Bitter, I.; Grün, A.; Tóth, G.; Szöllősy, Á.; Horváth, Gy.; Ágai, B.; Tőke, L. *Tetrahedron* **1996**, *52*, 639–646.
17. Bitter, I.; Grün, A.; Tóth, G.; Balázs, B.; Tőke, L. *Tetrahedron* **1997**, *53*, 9799–9812.
18. Floriani, C.; Jacoby, D.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1376–1377.
19. Xu, W.; Rourke, J. P.; Vittal, J. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1993**, *2*, 145–147.
20. Loeber, C.; Matt, D.; Cian, A. D.; Fischer, J. *J. Organomet. Chem.* **1994**, *475*, 297–306.
21. Malone, J. F.; Mars, D. J.; McKervey, M. A.; O'Hagan, P.; Thompson, N.; Walker, A.; Arnaud-Neu, F.; Mauprivez, O.; Schwing-Weill, M.-J.; Dozol, J.-F.; Rouquette, H.; Simon, N. *J. Chem. Soc., Chem. Commun.* **1995**, *20*, 2151–2154.
22. Loeber, C.; Matt, D.; Briard, P.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1996**, *4*, 513–524.
23. Neda, I.; Plinta, H.-J.; Sonnenburg, R.; Fischer, A.; Jones, P. G.; Schmutzler, R. *Chem. Ber.* **1995**, *128*, 267–274.
24. Dieleman, C. B.; Matt, D.; Neda, I.; Schmutzler, R.; Thönnessen, H.; Jones, P. G.; Harriman, A. *J. Chem. Soc., Dalton Trans.* **1998**, *13*, 2115–2121.
25. Wieser, C.; Matt, D.; Toupet, L.; Bourgeois, H.; Kintzinger, J.-P. *J. Chem. Soc., Dalton Trans.* **1996**, *21*, 4041–4044.
26. Cameron, B. R.; van Veggel, F. C. J. M.; Reinhoudt, D. N. *J. Org. Chem.* **1995**, *60*, 2802–2806.
27. Csók, Zs.; Szalontai, G.; Czira, G.; Kollár, L. *J. Organomet. Chem.* **1998**, *570*, 23–29.
28. Jurecka, P.; Vojtisek, P.; Novotny, K.; Rohovec, J.; Lukes, I. *J. Chem. Soc., Perkin Trans. 2* **2002** in press.
29. Quinonero, D.; Frontera, A.; Suner, G. A.; Morey, J.; Costa, A.; Ballester, P.; Deyá, P. M. *Chem. Phys. Lett.* **2000**, *326*, 247–254.
30. Katsyuba, S. A.; Grunenberg, J.; Schmutzler, R. *J. Mol. Struct.* **2001**, *559*, 315–320.
31. Arena, G.; Contino, A.; Giuseppe Gulino, F.; Magrí, A.; Sciotto, D.; Ungaro, R. *Tetrahedron Lett.* **2000**, *41*, 9327–9330.
32. Ugozzoli, F. In *Calixarenes in Action*, Mandolini, L., Ungaro, R., Eds.; Imperial College: London, 2000; pp. 144–171.
33. Steiner, T. *Chem. Commun.* **1997**, *8*, 727–734.
34. Laxmi Madhavi, N. N.; Katz, A. K.; Carrell, H. L.; Nangia, A.; Desiraju, G. R. *Chem. Commun.* **1997**, *20*, 1953–1954.
35. Takahashi, H.; Tsuboyama, S.; Umezawa, Y.; Honda, K.; Nishio, M. *Tetrahedron* **2000**, *56*, 6185–6191.
36. Nishio, M.; Hirota, M.; Umezawa, Y. *The CH/π Interaction*; Wiley–VCH: New York, 1998.
37. Bottino, A.; Cunsolo, F.; Piattelli, M.; Gavuzzo, E.; Neri, P. *Tetrahedron Lett.* **2000**, *41*, 10065–10069.
38. Novoa, J. J.; Mota, F. *Chem. Phys. Lett.* **2000**, *318*, 345–354.
39. Kunsági-Máté, S.; Nagy, G.; Kollár, L. *Anal. Chim. Acta* **2001**, *428*, 301–307.
40. Kunsági-Máté, S.; Nagy, G.; Kollár, L. *Sens. Actuators, B: Chem.* **2001**, *76*, 545–550.
41. Kunsági-Máté, S.; Bitter, I.; Grün, A.; Nagy, G.; Kollár, L. *Anal. Chim. Acta* **2001**, *443*, 227–234.
42. Kunsági-Máté, S.; Bitter, I.; Grün, A.; Nagy, G.; Kollár, L. *J. Biochem. Biophys. Methods* **2002** in press.
43. Rossotti, F. J. C.; Rossotti, H. *The Determination of Stability Constants*; McGraw-Hill: New York, 1961 pp 47–51.
44. Inoue, Y.; Yamamoto, K.; Wada, T.; Everitt, S.; Gao, X.-M.; Hou, Z. J.; Tong, L. H.; Jiang, S. K.; Wu, H. M. *J. Chem. Soc., Perkin Trans. 2* **1998**, *8*, 1807–1816.
45. Liu, Y.; Jin, L.; Sun, S.-X. *Microchem. J.* **2000**, *64*, 59–65.
46. Liu, Y.; Kang, S.-Z.; Zhang, H.-Y. *Microchem. J.* **2001**, *70*, 115–121.
47. Mohammed-Ziegler, I.; Kubinyi, M.; Grofcsik, A.; Grün, A.; Bitter, I. *J. Mol. Struct.* **1999**, *481*, 289–292.
48. Okada, Y.; Mizutani, M.; Ishii, F.; Kasai, Y.; Nishimura, J. *Tetrahedron* **2001**, *57*, 1219–1227.
49. Kunsági-Máté, S.; Bitter, I.; Grün, A.; Nagy, G.; Kollár, L. *Anal. Chim. Acta* **2002**, *461*, 273–279.
50. Smukste, I.; Smithrud, D. B. *Tetrahedron* **2001**, *57*, 9555–9561.
51. Brouwer, E. B.; Enright, G. D.; Ratcliffe, C. I.; Facey, G. A.; Ripmeester, J. A. *J. Phys. Chem. B* **1999**, *103*, 10604–10616.
52. Cai, W.-S.; Xia, B.-Y.; Shao, X.-G.; Guo, Q.-X.; Maigret, B.; Pan, Z.-X. *Chem. Phys. Lett.* **2000**, *319*, 708–712.
53. Liu, L.; Guo, Q.-X. *J. Phys. Chem. B* **1999**, *103*, 3461–3467.
54. Rekharsky, M. V.; Inoue, Y. *Chem. Rev.* **1998**, *98*, 1875–1917.
55. Gutsche, C. D.; Rogers, J. S.; Stewart, D.; See, K.-A. *Pure Appl. Chem.* **1990**, *62*, 485–489.
56. den Otter, W. K.; Briels, W. J. *J. Chem. Phys.* **1997**, *107*, 4968–4978.
57. Connors, K. A. *Binding Constants*; Wiley: New York, 1987.
58. Dewar, M. J. S.; Zoebish, E. G.; Healy, E. F.; Stewart, J. P. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902–3909.
59. Jorgensen, W. L.; Chandrasekhas, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926–935.
60. Bender, T. *Solvent Cage, Excel Macros to HyperChem*, Hypercube, www.hyper.com, 2000.
61. HyperChem Professional 5.1, Hypercube Inc., 1996.