Available online at www.sciencedirect.com

SCIENCE DIRECT®

Mendeleev Commun., 2007, **17**, 145–147

Mendeleev Communications

Water-soluble tetra(methylviologen)calix[4]resorcinarene: host–guest properties toward aromatic compounds

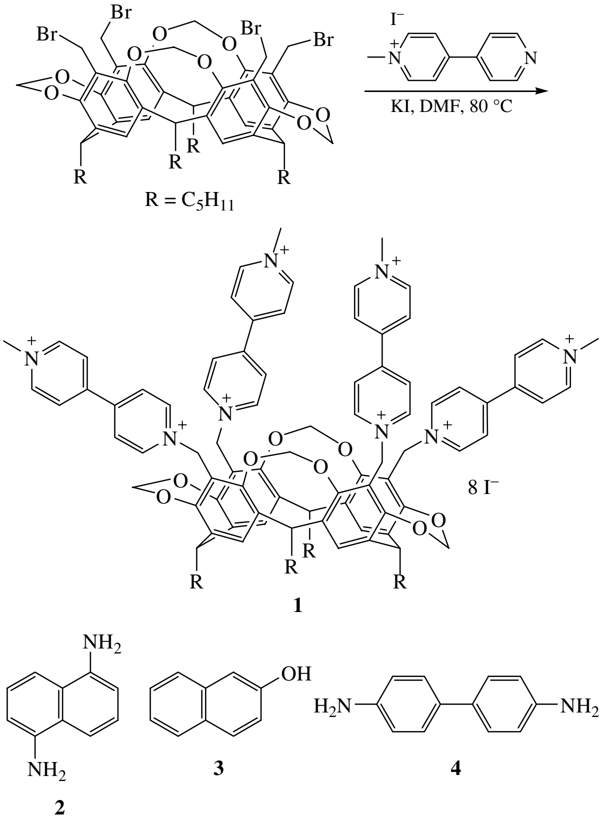
Albina Yu. Ziganshina,* Sergey V. Kharlamov, Ella Kh. Kazakova,
Shamil K. Latypov and Alexander I. Konovalov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 843 273 2253; e-mail: az@iopc.knc.ru

DOI: 10.1016/j.mencom.2007.05.004

The preparation of a water-soluble tetra(methylviologen)calix[4]resorcinarene and its complexation with several aromatic compounds are described.

Viologens are well-known electrochromic compounds, which are widely used in chemistry[1] because of their ability to reversibly change colour upon reduction and oxidation. Viologens in their dicationic form are electron-deficient compounds capable to form charge-transfer (CT) complexes with electron-donating molecules. Usually, the stability of viologen CT complexes is not high in solution and only the incorporation of them into well-organised supramolecular assemblies (pseudorotaxanes, rotaxanes, catenanes and dendrimers) results in the stabilization of the CT structure.[2] The inclusion complexation of viologens with cyclodextrins,[3] cucurbit[*n*]urils ($n = 7, 8$)[4] and calixarenes[5] has been studied. Cyclodextrin derivatives with covalently linked viologen units exhibit an interesting inclusion behaviour, depending on the oxidation states of the viologen moieties.[6] Viologen units were attached onto a resorcinarene platform to synthesise compounds containing resorcinarene building blocks tethered by viologen units. The supramolecular behaviour of the compounds obtained was investigated electrochemically.[7] Here we report the synthesis of water-soluble calixarene **1** consisting of four viologen moieties attached onto a calix[4]-resorcinarene platform and the investigation of its host–guest properties toward aromatic compounds **2**–**4** (Scheme 1). The binding properties of **1** were studied using NMR and UV spectroscopy. In contrast to previous investigations where viologens were tied into rigid molecular system, the use of a calixarene platform allows a much more flexible organization of viologen groups for their future fitting to the structure of a potential guest molecule.



Scheme 1

Calixarene **1** was synthesised using slightly modified published procedure.[7] Calixarene **1** was produced by the reaction of tetra(bromomethyl)calix[4]resorcinarene[8] with monomethylviologen[9] in dimethylformamide (DMF) at 80 °C.[†] Product **1** is well soluble in polar solvents such as water and DMSO. The substitution of anions for the hexafluorophosphate anions results in the solubility of **1** in organic solvents (acetone, acetonitrile, methanol, ethanol and DMF).

The complexation of the host molecule of **1** with aromatic compounds in aqueous solutions with the formation of CT complexes was studied by NMR and UV spectroscopy. When **1** was added to an aqueous solution of **2**–**4**, the colour of the solution became violet and a new absorbance band appeared in the region 350–500 nm in the UV-VIS spectrum indicating the formation of CT complex between guest molecules and host **1** [Figure 1(*a*)]. In the ^{1}H NMR spectra, the addition of **1** to a D$_2$O solution of **2**–**4** causes a significant upfield shift of the proton signals of guest molecules (up to 1.2 ppm) showing inclusion complex formation between **1** and **2**–**4** [Figure 1(*b*)].[‡]

Two methods were used for the investigation of host–guest complexation of **1** toward **2**–**4**: the molar ratio and the con-

---

[†] A mixture of tetra(bromomethyl)calix[4]resorcinarene[7] (0.5 g, 0.42 mmol), monomethylviologen iodide (0.53 g, 1.78 mmol) and potassium iodide (0.3 g, 1.78 mmol) in DMF (20 ml) was stirred at 80 °C overnight. The orange precipitate was filtered, washed with DMF (3 times) and acetone and dried (0.58 g, 53%), mp > 307 °C (decomp.). ^{1}H NMR (600 MHz, D$_2$O) δ: 0.64 (t, 12H, J 7.2 Hz), 1.22 (m, 8H), 1.28 (m, 16H), 2.35 (m, 8H), 4.47 (s, 12H), 4.72 (d, 4H, J 6.5 Hz), 4.77 (m, 4H), 5.83 (s, 8H), 6.36 (d, 4H, J 6.5 Hz), 7.68 (t, 4H), 8.47 (d, 8H, J 6.3 Hz), 8.50 (d, 8H, J 6.3 Hz), 9.02 (d, 8H, J 6.3 Hz), 9.10 (d, 8H, J 6.3 Hz). ^{13}C NMR (150 MHz, D$_2$O) δ: 14.14, 22.20, 27.57, 29.81, 31.16, 37.43, 49.08, 55.80, 100.86, 119.93, 124.61, 126.36, 126.97, 139.04, 145.69, 146.48, 149.63, 150.77, 153.13. Found (%): C, 46.46; H, 4.16; I, 38.89; N, 4.20. Calc. for C$_{100}$H$_{112}$I$_8$N$_8$O$_8$ (%): C, 46.75; H, 4.39; I, 39.51; N, 4.36.

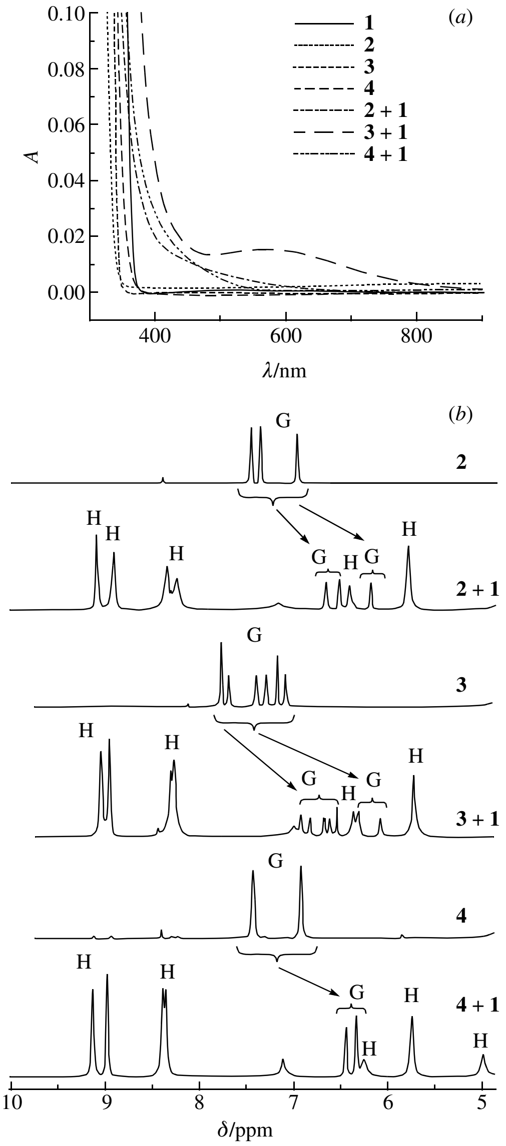


Figure 1 (*a*) Absorption spectra in H_2O (0.1 mM) (1 cm cell) and (*b*) fragments of ^1H NMR spectra in D_2O (1 mM) of free **1**–**4** and **2** + **1**; **3** + **1**, **4** + **1**; H: proton signals of host **1**; G: proton signals of guests **2**–**4**.

tinuous variation (Job) methods. In the molar ratio method, the experiment was carried out with a fixed concentration of guests **2**–**4** (1 mM), while the concentration of **1** was varied. In Job's method, the total concentration of **1** and guests ($C_1 + C_{\text{guest}}$) was kept 1 mM and the concentrations of the host and guests were varied. For guest **2**, the molar ratio plots showed the similar curves for all three protons H1–H3 [Figure 2(*a*)]. The curves slowly rise at $C_1/C_2 = 0\sim1$ and steeply increase in the region 2–10 without reaching a clear plateau. In the Job's experiment [Figure 2(*b*)], the proton curves reach a maximum at $C_2/(C_1 + C_2) = 0.66$ on the abscissa axis but do not have symmetric surface at this point. The analysis of curves obtained from the mole ratio and Job's methods assumes two complex formations with 1:1 and 1:2 stoichiometries.

In contrast to **2** for guests **3** and **4** the careful analysis of titration data shows difference in the curve slope for all protons. For example, for guest **3**, the curves for H5–H7 protons are steeper than those for H1, H2 protons in the mole ratio method.

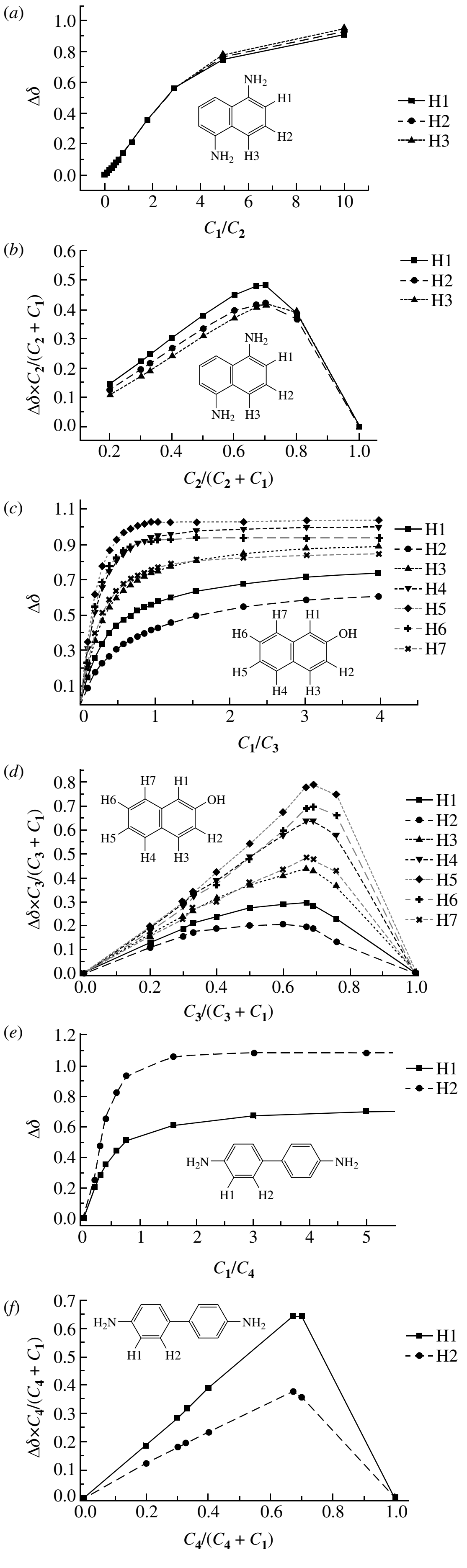


Figure 2 (*a*), (*c*), (*e*) Plots of complexation-induced shifts for the protons of **2**, **3** and **4**, respectively (1 mM) as functions of C_1/C_G; (*b*), (*d*), (*f*) Job's plot for protons of **2**, **3** and **4**, respectively; $\Delta\delta = \delta_G - \delta_{obs}$; G: guests **2**–**4**.

---

‡ All NMR experiments were performed in D_2O solutions at 30 °C on a Bruker AVANCE-600 spectrometer with a 5 mm diameter inverse probe head with Z-active shielded gradients working at 600.000 MHz in ^1H, 150.864 MHz in ^{13}C.

The curves of H4–H7 protons reach a plateau at the C_1/C_3 molar ratio 1:1, while the curves of H1, H2 protons do only at 3:1 [Figure 2(*c*)].

The Job's experiment [Figure 2(*d*)] shows that the plots obtained for H1–H7 protons are inconsistent with each other: if the curves of H5–H7 protons reach a maximum at 0.68 on the abscissa axis, then the curves of other protons do not achieve a maximum at this point. Similar to **2**, the analysis of data for **3** assumes the formation of 1:1 and 1:2 complexes. Probably, the shielding effect for H5–H7 protons is stronger in a 1:2 adduct than that in a 1:1 adduct, and for this reason the curves get to a plateau at a ratio of 1:1 in the molar ratio method [Figure 2(*c*)] and accomplishes a maximum at 0.68 point in the continuous variation method [Figure 2(*d*)]. For H1, H2 protons, the shielding effect in the 1:1 adduct is higher than that in the 1:2 adducts. Therefore, the curves do not reach a plateau at a ratio of 1:1 in the molar ratio method. In the Job's method, the curves for H1, H2 protons have a maximum at 0.5–0.67 on the abscissa axis proposing the formation of 1:1 and 1:2 adducts. Note that **1** is a charged host molecule, while guests **2**–**4** are neutral in D_2O. For this reason, the ionic strengths of solution at the terminal points are different to cause an error in stoichiometry determination.[10] The Job's experiment in a saline solution with a constant ionic strength (0.1 M NaCl) does not qualitatively affect the Job plot picture and assumes 1:1 and 1:2 complex formation, similar to the experiment performed in an aqueous solution.

Analogously to **3**, the titration curves of **4** in the molar ratio and Job's experiments are different for H1 and H2 protons. Similarly to **2**, **3**, the analysis of them supposes two complex formations between host **1** and guest **4** with 1:1 and 1:2 stoichiometries [Figures 2(*e*),(*f*)].

Compound **1** consists of hydrophobic C_5H_{11} chains on the down-rim of a calixarene platform and hydrophilic viologen units on the upper-rim; therefore, **1** can form supramolecular assemblies that compete with host–guest complexation in aqueous solution. Here, we do not report the investigation of the influence of self-organization of **1** on its host–guest properties. The competition of host–guest complexation with the self-assembling of **1** in aqueous media will be considered elsewhere.

Stability constants K_1 and K_2 were determined by direct analysis of the molar ratio titration curves using the DynaFit software.[11] The fitting of theoretical curves to the sets of experimental data was performed for all protons of **2**–**4**. As guest protons have different curvature of titration isotherm, we have tried to fit the values of K_1, K_2, $\Delta\delta_{1:1}$, $\Delta\delta_{1:2}$ in such a way as K_1 and K_2 would be in compliance for each proton. For the curves of protons of guest **3**, the values of K_1 and K_2 are slightly different for each proton, but in all causes the second stability constant K_2 is higher than the first stability constant K_1 by two orders of magnitude, conforming to the preferable formation of a 1:2 complex, as compared to the 1:1 complex for guest **3**. The stability constants were determined with the following lg K values: lg K_1(**1**:**2**) = 2.6±0.1, lg K_2(**1**:**2**) = 2.1±0.1; lg K_1(**1**:**3**) = = 2.7±0.4, lg K_2(**1**:**3**) = 4.7±0.3; lg K_1(**1**:**4**) = 3.8±0.1, lg K_2(**1**:**4**) = = 3.5±0.4. As evident from the results obtained, host **1** binds guests **3** and **4** stronger than **2**. The second association constant K_2 is higher than K_1 for **3** assumed that **1** prefers to bind two guest species **3**. For guests **2** and **4**, the first and second binding constants are similar.

In summary, water-soluble calix[4]resorcinarene **1** can form stable CT complexes with electron-rich aromatic compounds in aqueous media.

This work was supported by the Russian Foundation for Basic Research (grant nos. 05-03-32558-a and 06-03-32199-a).

References

1 P. M. S. Monk, in *The Viologens: Physicochemical Properties, Synthesis, and Applications of the Salts of 4,4'-Bipyridine*, Wiley-VCH, Chichester, 1998.

2 H.-J. Kim, J. Heo, W. S. Jeon, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi and K. Kim, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 1526.

3 (*a*) A. Neison, J. M. Belitsky, S. Vidal, C. S. Joiner, L. G. Baum and J. F. Stoddart, *J. Am. Chem. Soc.*, 2004, **126**, 11914; (*b*) A. Yasuda and J. Seto, *J. Appl. Electrochem.*, 1998, **18**, 333; (*c*) C. Lee, C. W. Kim and J. W. Park, *J. Electroanal. Chem.*, 1994, **374**, 115; (*d*) J. W. Park, N. H. Choi and J. H. Kim, *J. Phys. Chem.*, 1996, **100**, 769; (*e*) A. Mirzoian and A. E. Kaifer, *Chem. Eur. J.*, 1997, **3**, 1052; (*f*) T. Matsue, T. Kato, U. Akiba and T. Osa, *Chem. Lett.*, 1985, 1825; (*g*) T. Ujiie, T. Morozumi, T. Kimura, T. Ito and H. J. Nakamura, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 2002, **42**, 301; (*h*) H. Yonemura, S. Kusano, T. Matsuo and S. Yamada, *Tetrahedron Lett.*, 1998, **39**, 6915.

4 (*a*) H.-J. Kim, W. S. Jeon, Y. H. Ko and K. Kim, *PNAS*, 2002, **99**, 5007; (*b*) W. S. Jeon, A. Y. Ziganshina, J. W. Lee, Y. H. Ko, J.-K. Kang, C. Lee and K. Kim, *Angew. Chem., Int. Ed. Engl.*, 2003, **42**, 4097; (*c*) W. C. Jeon, H.-J. Kim, C. Lee and K. Kim, *Chem. Commun.*, 2002, 1828.

5 (*a*) A. Arduini, F. Ciesa, M. Fragassi, A. Pochini and A. Sechi, *Angew. Chem., Int. Ed. Engl.*, 2005, **44**, 278; (*b*) A. R. Bernardo, T. Lu, E. Cordova, L. Zhang, G. W. Gokel and A. E. Kaifer, *J. Chem. Soc., Chem. Commun.*, 1994, 529.

6 J. W. Park, S. Y. Lee, H. J. Song and K. K. Park, *J. Org. Chem.*, 2005, **70**, 9505.

7 (*a*) C. Peinador, E. Roman, Kh. Abboud and A. E. Kaifer, *Chem. Commun.*, 1999, 1887; (*b*) R. Toba, J. M. Quintela, C. Peinador, E. Roman and A. E. Kaifer, *Chem. Commun.*, 2002, 1768; (*c*) E. Roman, M. Chas, J. M. Quintela, C. Peinador and A. E. Kaifer, *Tetrahedron*, 2002, **58**, 699.

8 H. Boerrigter, W. Verboom and D. N. Reinhoudt, *J. Org. Chem.*, 1997, **62**, 7148.

9 S. K. Lee, S. Y. Shin, S. Lee, C. Lee and J. W. Park, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1983.

10 M. Beck and I. Nagypal, *Chemistry of Complex Equilibria*, Akademiai Kiado, Budapest, 1989.

11 P. Kuzmic, *Anal. Biochem.*, 1996, **237**, 260.

Received: 25th October 2006; Com. 06/2804