

Fluorescence Spectral Studies on the Coordination of Calix[4]-arenes Bearing Boronic Acid Moieties with Monosaccharides

LU, Kui^a (卢奎) WU, Yang-Jie^{*,b} (吴养洁) LI, Yong-Hong^b (李永红)
SHI, Ya-Lin^b (石雅琳) ZHOU, Zhi-Xian^b (周稚仙)

^aDepartment of Chemistry and Chemical Engineering, Zhengzhou Institute of Technology, Zhengzhou, Henan 450052, China

^bDepartment of Chemistry, Zhengzhou University, Zhengzhou, Henan 450052, China

Coordination of ten calix[4]arenes bearing boronic acid moieties with five monosaccharides was studied by fluorescence spectrometry. The stability constants (K_s) of the complexes and Gibbs free energy change ($-\Delta G^\circ$) of the coordination reactions were calculated according to the modified Hilderbrand-Benesi equation. The results obtained indicated that the coordination ability of *D*-($-$)-fructose with calix[4]arenes bearing boronic acid moieties was stronger than that of the other monosaccharides. And these calix[4]arene derivatives might be used for identification of *L*-($-$)-sorbose.

Keywords Calix[4]arene, boronic acid, monosaccharides, coordination, fluorescence spectrometry

Introduction

The calixarenes, as molecular receptors have attracted much attention from chemists due to its excellent ability to recognize ions and neutral molecules.¹⁻⁵ The conformation of calixarene is usually changeable in solution.⁶ An expected conformation can be achieved by modifying the calixarene molecule with appropriate groups that are capable of increasing the steric hindrance or breaking the intramolecular hydrogen bonds.^{7,8} This method would facilitate chemists' study of the host properties of calixarenes and their derivatives. Earlier reports have shown that boronic acid acts as a versatile functional group for saccharide-binding in aqueous systems.⁹

Therefore, when boronic acid is cooperated in calixarenes, the boronic acid moiety would stabilize the conformations of calixarenes as well as expand the properties of calixarenes.

Fluorescence spectrometry is a useful method for studying the relationship between structures and properties of organic compounds. Shinkai, *et al.* reported the coordination reactions of a calix[4]arene bearing boronic acid moieties **I** with *D*-glucose and *D*-fructose and the stability constants of the complexes by using fluorescence spectrometry.¹⁰ Liu, *et al.* reported the supramolecular coordination reactions of β -cyclodextrins bearing aromatic group with adamantanol and the stability constants of the complexes and Gibbs free energy changes of the coordination reaction on the basis of the changes of fluorescence intensities.¹¹

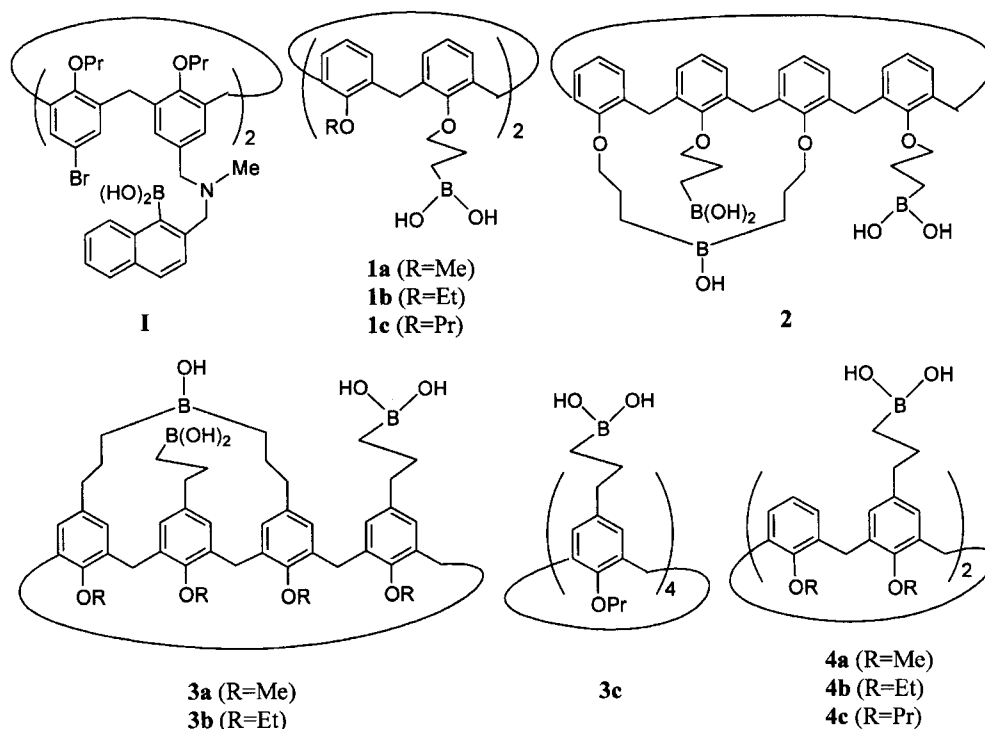
We have reported the syntheses of ten kinds of calix[4]arenes bearing boronic acid moieties (**1**, **2**, **3** and **4**, Scheme 1) and qualitative results of the coordination of these host compounds with *D*-($+$)-glucose, *D*-($-$)-fructose and *D*-($+$)-galactose by using UV spectroscopy.^{12,13} Here we report in details the coordination of these calix[4]arene derivatives with some monosaccharides by using fluorescence spectrometry. The stability constants (K_s) of the complexes as well as Gibbs free energy changes ($-\Delta G^\circ$) of the coordination reactions are given.

* E-mail: wyj@mail.zzu.edu.cn; luckyluke@263.net

Received December 25, 2000; revised May 16, 2001; accepted July 2, 2001.

Project supported by the National Natural Science Foundation of China (No. 29872034) and the Natural Science Foundation of Henan, China (No. 004030100).

Scheme 1



Experimental

Calix[4]arene derivatives **1**, **2**, **3** and **4** were prepared according to published methods.^{12,13} *D*-(+)-glucose, *D*-(-)-fructose, *D*-(+)-galactose, *L*-(-)-sorbitose and *L*-(+)-arabinose were analytical reagent grade. Methanol was guaranteed reagent grade and was distilled before use. Water was redistilled. Fluorescence spectra were determined in methanol-water (33%, *V/V*) at 25 ± 1°C with a HITACHI F-3010 fluorescence spectrophotometer. Both the beams of excitation and emission monochromator were 5 nm and the scanning speed was 250 nm/min. Fluorescence intensities (*F*) associated to the maximum excitation wavelength (λ_{ex}) and the emission wavelength (λ_{em}) were given according to the peaks' height. The concentration of each calix-[4]arene bearing boronic acid moieties was about 10⁻⁷ mol/L.

Results and discussion

In fluorescence spectrometry, the fluorescence intensities of a compound at λ_{ex} and λ_{em} are related to its structure, concentration, and other factors. In the coordination

process of a host compound with a guest compound, the configuration or conformation of the host compound will take place some change.¹¹ The change of configuration or conformation shows as that the value of λ_{ex} and λ_{em} are removed, and fluorescence intensities also are changed in fluorescence spectrometry. Therefore, the coordination of host compound with guest compound could be detected by fluorescence spectral analysis.

The concentration of host compound, *i. e.* calix-[4]arene bearing boronic acid moieties, remained constant in case of fluorescence determination. The fluorescence intensity titration curves of host compounds with guest compounds, *i. e.* monosaccharides, were obtained by monitoring the changes of the fluorescence intensities when the concentrations of guest compounds were changed. The fluorescence intensity titration curves of the typical host compounds, **1a**, **2**, **3a** and **4a** were shown in Figs. 1–4, respectively, which indicated that there were regular changes for the relative fluorescence intensities of the host compounds when the concentrations of the guest compounds were changed. These results revealed that the configurations or conformations of the host compounds were changed in the process of complexation with guest compounds. Thus, the stability constants of complexes could be determined by changes of

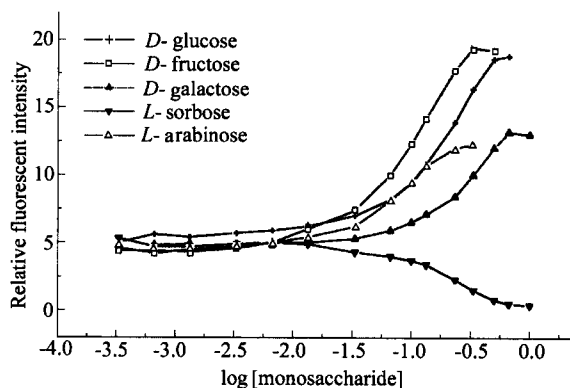


Fig. 1 Fluorescence intensity titration curves of 1a.

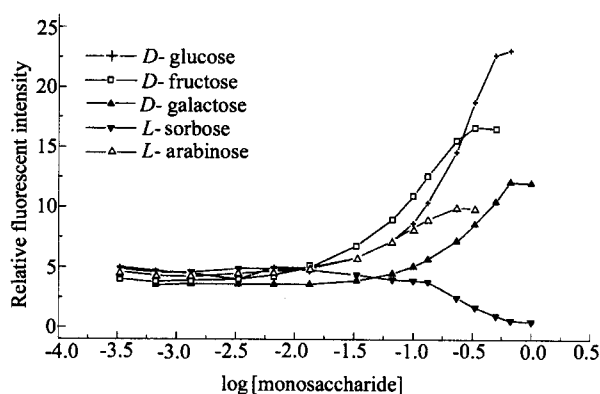


Fig. 4 Fluorescence intensity titration curves of 4a.

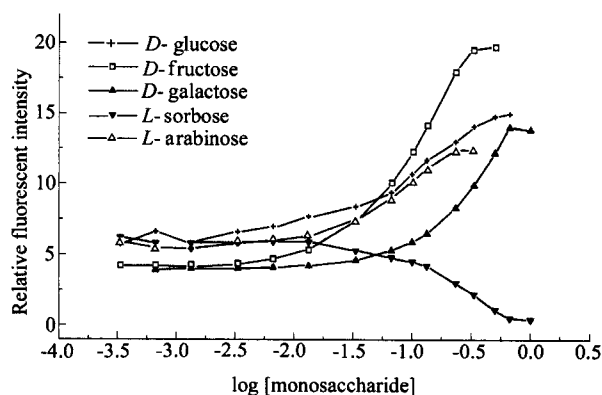


Fig. 2 Fluorescence intensity titration curves of 2.

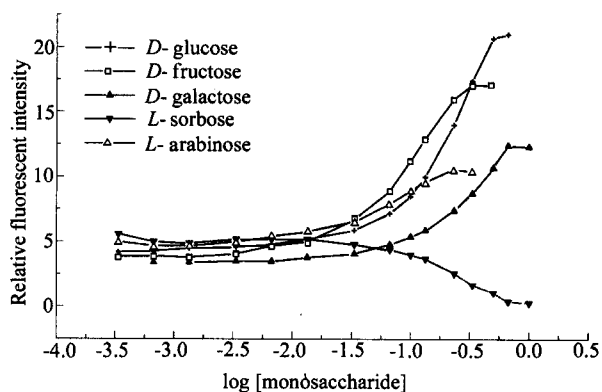


Fig. 3 Fluorescence intensity titration curves of 3a.

$$\frac{C_i[H]}{\Delta F_i} = \frac{C_i}{\alpha} + \frac{1}{\alpha K_s} \quad (1)$$

In Eq. (1), ΔF_i is the difference between the fluorescence intensity F_i of the guest compound with concentration C_i and the fluorescence intensity F_0 of the host compound itself; α is an optical coefficient, and $[H]$ is the concentration of host compound. For all host and guest compounds examined, the plots of $C_i[H]/\Delta F_i$ vs. C_i gave straight lines. The stability constants (K_s) and the Gibbs free energy changes ($-\Delta G^\circ$) could be calculated from the slope ($1/\alpha$) and the intercept ($1/\alpha K_s$) of the lines obtained. The stability constants of the host-guest complexes and the free energy changes of the coordination reactions were listed in Table 1.

The data in Table 1 showed that all of host compounds could be coordinated with five kinds of monosaccharides used. Since the differences among the stability constants of complexes produced were small, the character of the coordination behavior of each host compound with guest compounds should be similar. And the coordination mechanism of 1—4 with monosaccharides should be similar to the mechanism of I with *D*-(+)-glucose and *D*-(-)-fructose. The reason supporting this coordination is based on the fact that two *D*-(+)-glucose complexes, 5 and 6 derived from 2 and 3a, were obtained. The structures of 5 and 6 were identified by elemental analysis, IR, ^1H NMR and mass spectra (atmospheric pressure chemical ionization, APCI-). Both 5 and 6 were 1:1 complexes of calix[4]arenes boronic acid with *D*-(+)-glucose (Scheme 2).^{12,13}

the relative fluorescence intensities caused by changes in the configuration or conformation. In experiments, the concentrations of guest compounds were much higher than those of the host compounds, therefore, the stability constants K_s of the host-guest complexes could be calculated according to the modified Hilderbrand-Benesi Eq. (1).¹⁴

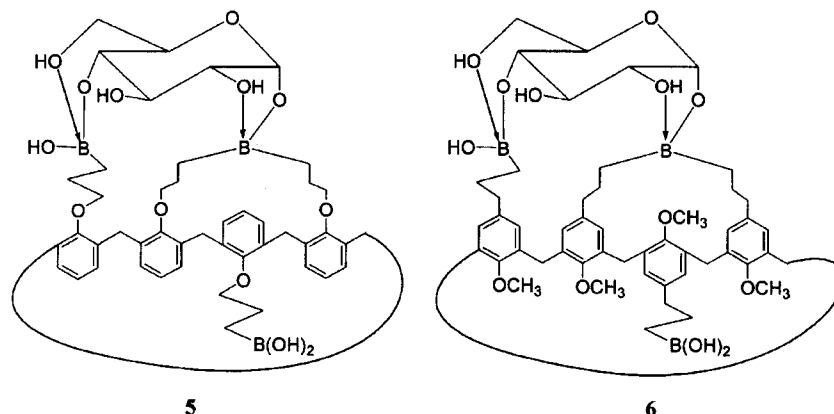
Table 1 Thermodynamic properties of complexes of calix[4]arenes bearing boronic acid moieties with monosaccharides

Compounds	λ_{ex} (nm)	λ_{em} (nm)	Monosaccharide	$\log K_s$	$-\Delta G^\circ$ (kJ/mol)
1a	279	332	<i>D</i> -(+)-glucose	1.85	10.54
			<i>D</i> -(-)-fructose	2.03	11.54
			<i>D</i> -(+)-galactose	1.86	10.60
			<i>L</i> -(-)-sorbitose	1.26	7.18
			<i>L</i> -(+)-arabinose	1.67	9.47
1b	282	342	<i>D</i> -(+)-glucose	1.03	5.85
			<i>D</i> -(-)-fructose	1.12	6.36
			<i>D</i> -(+)-galactose	1.86	10.59
			<i>L</i> -(-)-sorbitose	1.56	8.87
			<i>L</i> -(+)-arabinose	1.60	9.09
1c	283	342	<i>D</i> -(+)-glucose	1.43	8.15
			<i>D</i> -(-)-fructose	2.25	12.81
			<i>D</i> -(+)-galactose	1.01	5.74
			<i>L</i> -(-)-sorbitose	2.08	11.84
			<i>L</i> -(+)-arabinose	1.97	11.21
2	282	341	<i>D</i> -(+)-glucose	1.51	8.60
			<i>D</i> -(-)-fructose	2.07	11.77
			<i>D</i> -(+)-galactose	1.54	8.79
			<i>L</i> -(-)-sorbitose	1.01	5.74
			<i>L</i> -(+)-arabinose	1.60	9.13
3a	281	336	<i>D</i> -(+)-glucose	1.72	9.80
			<i>D</i> -(-)-fructose	1.26	7.16
			<i>D</i> -(+)-galactose	1.80	10.26
			<i>L</i> -(-)-sorbitose	1.73	9.86
			<i>L</i> -(+)-arabinose	2.17	12.33
3b	282	336	<i>D</i> -(+)-glucose	2.18	12.38
			<i>D</i> -(-)-fructose	2.07	11.80
			<i>D</i> -(+)-galactose	2.51	14.27
			<i>L</i> -(-)-sorbitose	1.58	9.00
			<i>L</i> -(+)-arabinose	1.92	10.94
3c	282	337	<i>D</i> -(+)-glucose	1.97	11.21
			<i>D</i> -(-)-fructose	1.58	8.99
			<i>D</i> -(+)-galactose	1.57	8.94
			<i>L</i> -(-)-sorbitose	2.04	11.60
			<i>L</i> -(+)-arabinose	1.86	10.59
4a	280	336	<i>D</i> -(+)-glucose	1.85	10.55
			<i>D</i> -(-)-fructose	1.59	9.03
			<i>D</i> -(+)-galactose	1.43	8.12
			<i>L</i> -(-)-sorbitose	1.22	6.92
			<i>L</i> -(+)-arabinose	1.64	9.32
4b	282	345	<i>D</i> -(+)-glucose	1.79	10.17
			<i>D</i> -(-)-fructose	2.45	13.94
			<i>D</i> -(+)-galactose	1.66	9.45
			<i>L</i> -(-)-sorbitose	1.56	8.88
			<i>L</i> -(+)-arabinose	1.82	10.35
4c	282	345	<i>D</i> -(+)-glucose	1.67	9.48
			<i>D</i> -(-)-fructose	2.37	13.49
			<i>D</i> -(+)-galactose	1.44	8.17
			<i>L</i> -(-)-sorbitose	1.89	10.77
			<i>L</i> -(+)-arabinose	1.85	10.51

For five kinds of monosaccharides determined, both *D*-(+)-glucose and *D*-(+)-galactose showed the stronger coordination ability with host compound **3b**, and

D-(-)-fructose, *L*-(-)-sorbitose and *L*-(+)-arabinose showed the stronger coordination ability with **4b**, **1c** and **3a**, respectively. In all host-guest complexes, the

Scheme 2



stability constants of complexes of almost host compounds with *D*-(-)-fructose were greater. This implicated that *D*-(-)-fructose had a stronger coordination ability with calix[4]arenes bearing boronic acid moieties, which is in agreement with Shinkai's results.¹⁰ Moreover, the coordination selectivity of these calix[4]arenes bearing boronic acid moieties with monosaccharides were insignificant. For ten kinds of host compounds, **1a**, **1c**, **2**, **4b** and **4c** showed stronger coordination ability with *D*-(-)-fructose; **1b** and **3b** showed stronger coordination ability with *D*-(+)-galactose; **3a**, **3c** and **4a** showed stronger coordination ability with *L*-(+)-arabinose, *L*-(-)-sorbose and *D*-(+)-glucose, respectively. These results indicated that the stabilities of host-guest complexes were closely related to the structures of host compounds, and the coordination ability of host compounds with guest compounds. And these results could also be caused by the differences of recognition ability of host compounds to guest compounds.

Furthermore, it can be noticed in Figs. 1—4 that only the curve for *L*-(-)-sorbose reduced and the other four curves ascended when the concentrations of monosaccharides were increased. This phenomena could be related to the configuration of *L*-(-)-sorbose and the configuration matching of *L*-(-)-sorbose with host compounds. A possible explanation for this discrepancy is that the configuration or conformation changes of host compounds were different with respect to *L*-(-)-sorbose and the other monosaccharides when *L*-(-)-sorbose coordinated with host compounds. And these differences could lead to the different changes of fluorescent intensities between *L*-(-)-sorbose and the other monosaccharides. Thus it can be seen that these calix[4]arene derivatives (**1**, **2**, **3** and **4**) may be used for

identifying *L*-(-)-sorbose, and that a monosaccharide sensor for *L*-(-)-sorbose may be designed.

Acknowledgments

We thank Dr. WANG, Hong-Xing and Associate Professor LIN, Lin for valuable discussion of this paper.

References

- Bohmer, V. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 713.
- Zheng, Q. Y.; Chen, C. F.; Huang, Z. T. *Chin. J. Chem.* **2000**, *18*, 104.
- Xing, Y. J.; Zhou, Z. X.; Wu, Y. J. *Chin. J. Chem.* **2001**, *19*, 164.
- Liu, Y.; Zhao, B. T.; Wang, H.; Chen, Q. F.; Zhang, H. Y. *Chin. J. Chem.* **2001**, *19*, 291.
- Liu, F.; Lu, G. Y.; He, W. J.; Wang, Z. S.; Zhu, L. G. *Chin. J. Chem.* **2001**, *19*, 317.
- Gutsche, C. D. *Acc. Chem. Res.* **1983**, *16*, 161.
- Ghidini, E.; Uguzzoli, F.; Ungaro, R.; Harkema, S.; El-Fadl, A. A.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1990**, *112*, 6979.
- Gutsche, C. D.; Bauer, L. J. *Tetrahedron Lett.* **1981**, *22*, 4763.
- James, T. D.; Sandanayake, K. R. A. S.; Shinkai, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1910.
- Linnane, P.; James, T. D.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1997.
- Liu, Y.; Zhang, Y.; Qi, A.; Wang, Q.; Chen, R. *Chin. Sci. Bull.* **1998**, *43*, 166 (in Chinese).
- Lu, K.; Wu, Y. J.; Wang, H. X.; Zhou, Z. X. *Polyhedron* **1999**, *18*, 1153.
- Lu, K.; Wu, Y. J.; Xing, Y. J.; Zou, D. P.; Zhou, Z. X. *Chin. J. Chem.* **1999**, *17*, 674.
- Liu, Y.; Li, B.; Han, B.; Li, Y.; Chen, R. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1275.

(E200012288 SONG, J. P.; LING, J.)