Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Anion Receptor with Two Imidazolium Rings on the Glycoluril

Hyungil Kim[a]; Sungjae In[a]; Jongmin Kang[a]
[a] Department of Applied Chemistry, Sejong University, Seoul, South Korea

To cite this Article Kim, Hyungil , In, Sungjae and Kang, Jongmin(2006) 'Anion Receptor with Two Imidazolium Rings on the Glycoluril', Supramolecular Chemistry, 18: 2, 141 — 145
To link to this Article: DOI: 10.1080/10610270600564702
URL: http://dx.doi.org/10.1080/10610270600564702

Supramolecular Chemistry, April 2006 Vol. 18 (2), pp. 141–145

Taylor & Francis
Taylor & Francis Group

Anion Receptor with Two Imidazolium Rings on the Glycoluril

HYUNGIL KIM, SUNGJAE IN and JONGMIN KANG*

Department of Applied Chemistry, Sejong University, Seoul 143-747, South Korea

Received (in Southampton, UK) 1 November 2005; Accepted 9 January 2006

We have synthesized an anion receptor with two imidazolium groups on the glycoluril. This receptor showed high affinity for Y-shaped anions such as acetate and benzoate. Although the association constants of these anions for the receptor 4 are too large to be estimated from ^{1}H NMR titration, the receptor 4 has at least 560-fold selectivity for acetate or benzoate over iodide and 360-fold selectivity over nitrate.

Keywords: Carboxylate selective; Anion receptor; Imidazolium ring; Glycoluril

INTRODUCTION

A host–guest complementarity is required for the design of anion receptor due to wide geometries of anions. For the design of artificial anion receptor, hydrogen bonds have been employed as anion recognition elements due to their directionality. Hydrogen bonds are arranged through a space in a rigid and convergent manner. This has been achieved by utilizing molecular scaffold to arrange hydrogen bonding groups [1–4]. While most of hydrogen bonding anion receptors utilize N–H—anion or O–H—anion hydrogen bonds, 1,3-disubstituted imidazolium groups are recently introduced as new anion binding hydrogen bonding moiety by forming $(C–H)^+$—anion hydrogen bonds between C(2)–H in imidazolium rings and the guest anion [5–9]. Recently, we introduced glycoluril as a new molecular scaffold to arrange two or four amide groups at the corner of glycoluril [10,11]. When four amide groups are arranged at the four corners of glycoluril, the receptor **1** showed a high affinity for fluoride ion. However, when only two amide groups are arranged at the one side of glycoluril, the receptor **2** showed good affinities for Y shaped anions such as acetate and benzoate. We also introduced 1,3-disubstituted imidazolium groups at the four corners of glycoluril [12]. This receptor **3** showed only 1:2 stoichiometry irrespective of shapes of anions (Fig. 1a). Although the receptor **3** showed relatively high affinities for chloride and acetate among the anions we investigated, the association constants for the 1:1 binding could not be calculated. Therefore, we synthesized the receptor **4**. In this receptor, two 1,3-disubstituted imidazolium groups are arranged only at the one side of glycoluril and the receptor **4** would bind various anions in 1:1 stoichiometry (Fig. 1b; Scheme 1).

EXPERIMENTAL

Synthesis and Characterization

Compound 5

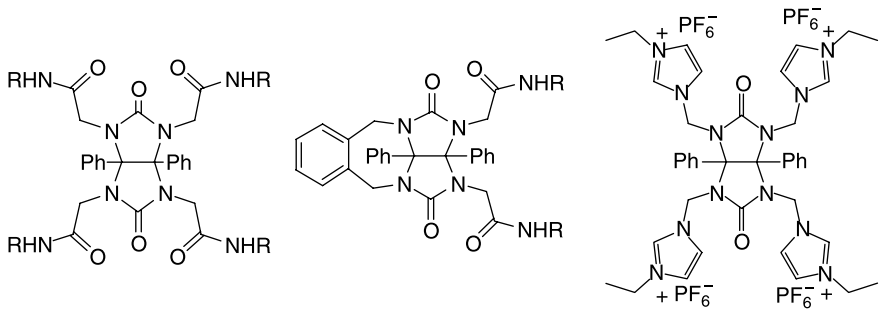
To a solution of 1.9 ml 4-methoxybenzylamine in 40 ml distilled water was added 1.8 g potassium cyanate and refluxed for an hour [13]. After the reaction mixture was cooled to 0°C 8 ml, HCl was added. Filtration of white precipitate gave 0.74 g (28%) of product. ^{1}H NMR ($CDCl_3$) 7.20 (d, 2H, $J = 8.0$), 6.84 (d, 2H, $J = 8.0$), 4.75 (s, 1H), 4.30 (s, 2H), 4.27 (d, 2H); ^{13}C NMR (DMSO-d_6) δ 158.93, 133.65, 129.20, 114.48, 55.90, 43.16. HRMS(FAB) calculated for $C_9H_{12}N_2O_4H^+$: 181.0977; found: 181.0976.

Compound 6

To a solution of 1.3 g of compound **5** and 0.74 g benzil in 30 ml benzene was added 1 ml trifluoro acetic acid.

*Corresponding author. E-mail: kangjm@sejong.ac.kr

ISSN 1061-0278 print/ISSN 1029-0478 online © 2006 Taylor & Francis
DOI: 10.1080/10610270600564702



1 **2** **3**

The reaction mixture was refluxed under Dean–stark apparatus for 24 h. The precipitated solid was filtered and washed with ethanol. 1.29 g (67%) of product was obtained. ^{1}H NMR ($CDCl_3$) 6.96 (m, 18H), 5.54 (s, 2H), 4.37 (d, 2H, $J = 16.0$), 3.89 (d, 2H, $J = 16.0$), 3.74 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 159.79, 138.79, 133.82, 131.81, 129.86, 129.18, 129.05, 128.89, 128.76, 128.25, 127.99, 114.19, 91.21, 81.33, 55.84, 45.11. HRMS(FAB) calculated for $C_{32}H_{30}N_4O_4H^+$: 535.2345; found: 535.2394.

Compound 7

To a solution of 0.5 g compound **6** and 0.28 g paraformaldehyde in 5 ml DMSO was added 1.5 ml 1 M NaOH solution. The reaction mixture was stirred for 24 h. Then, 1 ml 1 M HCl and 20 ml distilled water was added. The white precipitate was treated with 10 ml pyridine and 10 ml acetic anhydride for 12 h. Evaporation of solvent in vacuo and silicagel chromatography with 1% methanol in dichloromethane gave 0.4 g (63%) of product **7**. ^{1}H NMR ($CDCl_3$) 6.85 (m, 18H), 5.74 (d, 2H, $J = 12.0$), 5.27 (d, 2H, $J = 12.0$), 4.41 (d, 2H, $J = 16.0$), 3.93 (d, 2H, $J = 16.0$), 3.74 (s, 6H), 2.03 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 159.22, 158.80, 131.90, 131.52, 129.95 129.92, 129.67, 129.23, 128.72, 128.57, 128.17, 114.34, 90.18, 86.86, 67.82, 55.62, 46.27, 21.33. HRMS(FAB) calculated for $C_{38}H_{38}N_4O_8H^+$: 679.2768; found: 679.2749.

Compound 8

To a solution of 0.4 g compound **7** in 3 ml dichloromethane was added 2 ml thionyl chloride and stirred for 5 h. Evaporation of solvent gave 0.37 g (99%) of product **8**. ^{1}H NMR ($CDCl_3$) 6.88 (m, 18H), 5.47 (d, 2H, $J = 12.0$), 5.36 (d, 2H, $J = 12.0$), 4.42 (d, 2H, $J = 16.0$), 3.86 (d, 2H, $J = 16.0$), 3.75 (s, 6H); ^{13}C NMR ($CDCl_3$) 159.27, 157.61, 130.98, 130.68, 130.38, 130.17 129.39, 129.13, 129.01, 128.87, 128.60, 114.29, 89.90, 87.20, 55.63, 54.24, 46.23. HRMS(FAB) calculated for $C_{34}H_{32}Cl_2N_4O_4H^+$: 631.1879; found: 631.1830.

Compound 9

To a solution of 0.1 g imidazole and 0.1 g sodium hydride in 10 ml DMF at 70°C was added 0.37 g of compound **8**. After stirring 4 h, 30 ml distilled water was added. Filtration of solid gave 0.38 g (93%) of compound **9**. ^{1}H NMR ($CDCl_3$) 7.51 (s, 2H), 6.99 (m, 18H), 6.51 (d, 2H, $J = 8.0$), 6.37 (d, 2H, $J = 8.0$), 5.35 (d, 2H, $J = 14.0$), 5.12 (d, 2H, $J = 14.0$), 4.44 (d, 2H, $J = 16.0$), 3.94 (d, 2H, $J = 16.0$), 3.77 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 159.87, 159.55, 137.64, 131.01, 130.77, 130.62, 130.40, 129.62, 129.58, 129.15, 128.96, 128.83, 128.72, 119.45, 114.62, 90.23, 88.83, 55.85, 53.71, 46.74. HRMS(FAB) calculated for $C_{40}H_{38}N_8O_4H^+$: 695.3094; found: 695.3040.

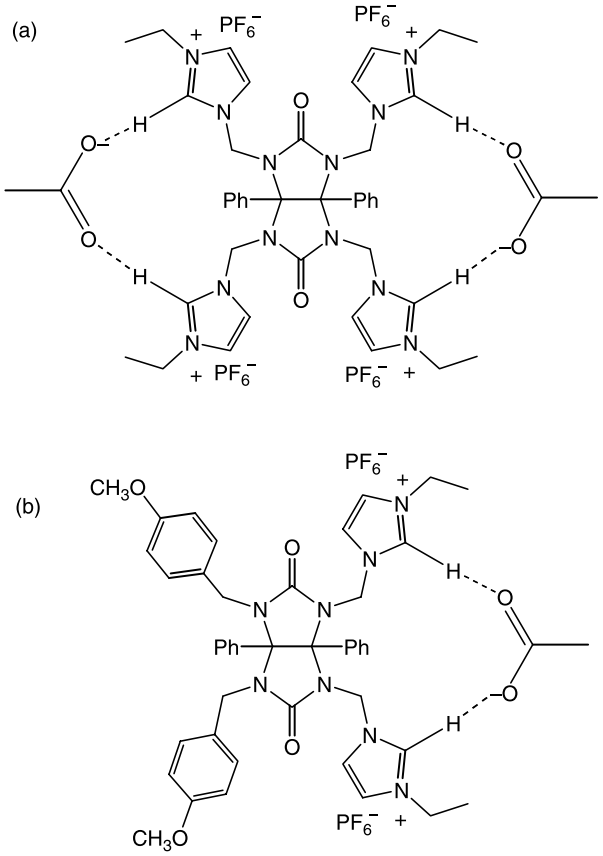
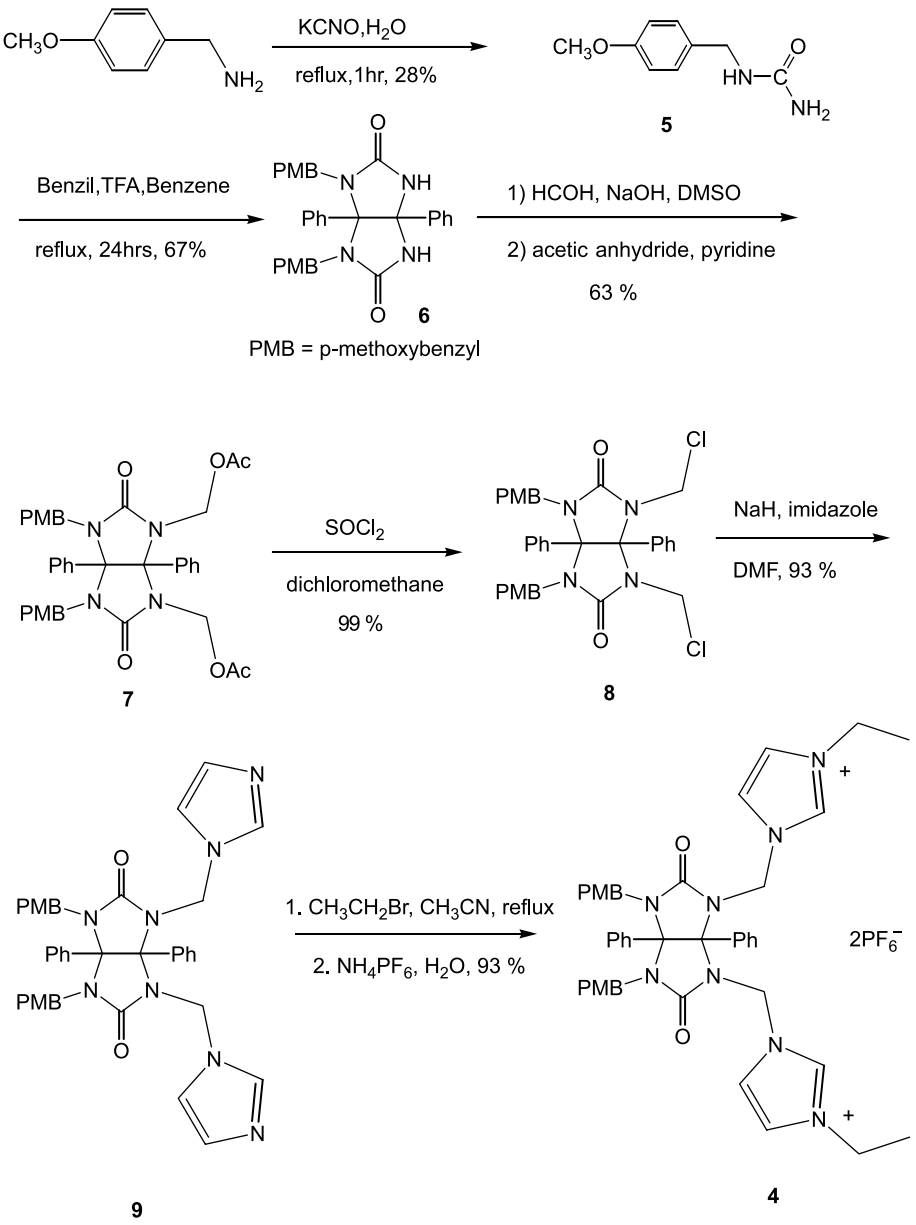


FIGURE 1 The Possible 1:2 binding between the receptor 3 and acetate.



SCHEME 1 The Synthetic procedure for the anion receptors **4**.

Compound 4

To a solution of 0.12 g compound 9 in 10 ml acetonitrile was added 1.24 ml ethyl bromide and refluxed for 12 h. After evaporation of solvent, the reaction mixture was dissolved in 15 ml distilled water and 0.14 g ammonium hexafluorophosphate was added and stirred. Filtration of solid gave 0.15 g (93%) of product. ^{1}H NMR (DMSO-d_6) 9.00 (s, 2H), 8.00 (s, 2H), 7.53 (s, 2H), 7.19 (m, 14H), 6.59 (d, 2H, $J = 8.0$), 6.37 (d, 2H, $J = 8.0$), 6.09 (d, 2H, $J = 16.0$), 5.80 (d, 2H, $J = 16.0$), 4.53 (d, 2H, $J = 16.0$), 4.29 (q, 4H, $J = 7.0$), 4.01 (d, 2H, $J = 16.0$), 3.73 (s,6H), 1.41 (t, 6H, $J = 7.0$); ^{13}C NMR ($CDCN_3$) δ 159.44, 159.27, 135.49, 130.79, 130.33, 130.23, 130.08, 129.51, 129.41, 128.72, 128.63, 128.40, 128.32, 123.31, 122.31, 114.11, 89.95, 88.53, 55.91, 55.17, 45.84, 45.70, 14.67. HRMS(FAB) M−PF_6 calculated for $C_{44}H_{48}N_8O_4PF_6$: 897.3441; found: 897.3471.

RESULTS AND DISCUSSION

The complexation ability of the receptor **4** was measured by standard ^{1}H NMR titration experiments in 10% DMSO-d_6 in CD_3CN using a constant host concentration (4 mM) and increasing concentrations of anions. The chemical shift data were analyzed by EQNMR [14]. The addition of tetrabutylammonium halide salts to the solution of receptor **4** in 10% DMSO-d_6 in CD_3CN resulted in downfield shifts in C(2) proton of imdazolium moieties. In case of chloride ion, C(2) protons

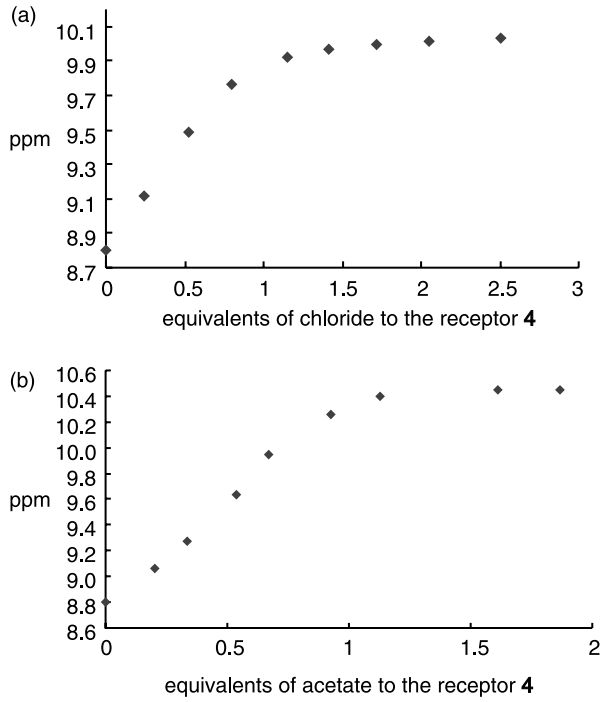


FIGURE 2 Changes in the C(2) proton of imdazolium moieties in 4 with (a) increasing chloride ion concentrations (b) increasing acetate ion concentrations.

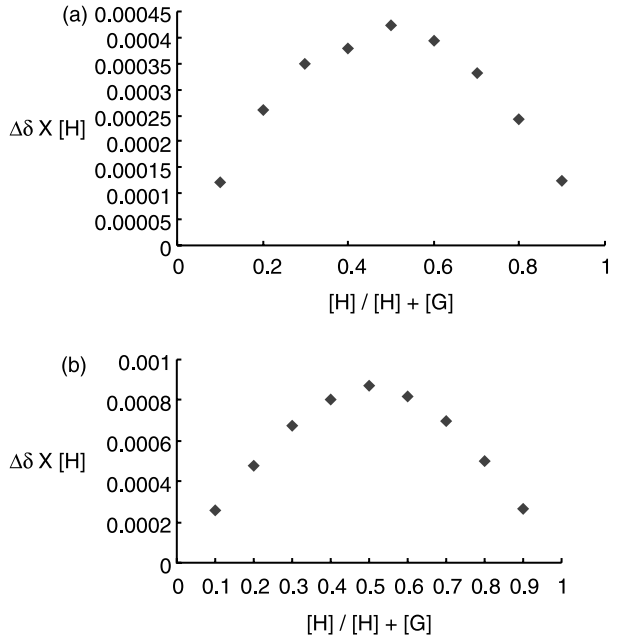


FIGURE 3 The Job plot of **4** and (a) tetrabutylammonium nitrate (b) tetrabutylammonium hydgrogen sulfate.

originally resonating at = 8.80 was shifted to = 10.00 upon addition of about 1 equivalent of chloride ion, which indicates 1:1 binding, as shown in Fig. 2a. The association constant was calculated as $3.7 \times 10^4 \pm 6.6 \times 10^3$. Assuming that the 1:1 binding stoichiometry applies to the association between spherically shaped halide ions and receptor **4**, the association constants between other halides and receptor **4** were calculated $1.6 \times 10^3 \pm 1.5 \times 10^2$ for bromide, and $1.8 \times 10^2 \pm 9.6$ for iodide. For the receptor **4**, about 200-fold selectivity for chloride over iodide was observed. In addition, the receptor **4** showed high affinity for Y-shaped anions such as acetate and benzoate. The addition of tetrabutylammonium acetate or tetrabutylammonium benzoate salts to the solution of receptor **4** in 10% DMSO-d_6 in CD_3CN also resulted in downfield shifts in C(2) proton of imdazolium moieties. The C(2) proton moved 1.65 ppm for 1 equivalent acetate ion and 1.63 ppm for 1 equivalent benzoate ion. No further shift was observed, which also indicates 1:1 binding (Fig. 2b). The association constants calculated for both acetate and benzoate exceeded 10^5, which is too large to accept as reliable association constant from ^{1}H NMR titration experiments [15]. The association constants of acetate and benzoate could be only assessed that they are bigger than 10^5. The possible binding mode of the receptor 4 and acetate is shown in Fig. 1b. The binding of receptor **4** to the Y-shaped carboxylate reminds us of the binding of the receptor **2** to the Y-shaped carboylates [11]. Hydrogen bonding moieties arranged at the one side of glycoluril are preorganized for the Y-shaped carboylate anions.

We also investigated the binding of other anions with the receptor **4**. Job plot experiments showed 1:1 binding for nitrate and hydrogen sulfate (Fig. 3). The association constants calculated from ^{1}H NMR titrations are $2.7 \times 10^2 \pm 17$ for nitrate and $1.5 \times 10^3 \pm 1.06 \times 10^2$ for hydrogen sulfate respectively. In case of cyanide, the Job plot was not symmetric. The maximum appeared when the mole fraction was 0.38, which indicates mixed stoichiometry.

In conclusion, we have synthesized an anion receptor with two imidazolium groups on the glycoluril. This receptor showed high affinity for Y-shaped anion such as acetate and benzoate. The association constants of these anions are too large to be estimated from ^{1}H NMR titration. The receptor **4** has at least 560-fold selectivity for acetate or benzoate over iodide and 360-fold selectivity over nitrate.

Acknowledgements

This study was supported by a grant from the Korea Association of Small Businesses Innovation Research 2005.

References

[1] Llinares, J. M.; Powell, D.; Bowman-James, K. *Coord. Chem. Rev.* **2003**, 57.
[2] Bondy, C. R.; Loeb, S. J. *Coord. Chem. Rev.* **2003**, 77.

[3] Choi, K.; Hamilton, A. D. *Coord. Chem. Rev.* **2003**, 101.
[4] Ilioudis, C. A.; Steed, J. W. J. *Supramol. Chem.* **2001**, 165.
[5] Ihm, H.; Yun, S.; Kim, H. G.; Kim, J. K.; Kim, K. S. *Org. Lett.* **2002**, 2897.
[6] Yun, S.; Ihm, H.; Kim, H. G.; Lee, C-I.; Indrajit, B.; Oh, K. S.; Gong, Y. J.; Lee, J. W.; Yoon, J.; Lee, H. C.; Kim, K. S. *J. Org. Chem.* **2003**, 2467.
[7] Kim, S. K.; Singh, N. J.; Kim, S. J.; Kim, H. G.; Kim, J. K.; Lee, J. W.; Kim, K. S.; Yoon, *J. Org. Lett.* **2003**, 2083.
[8] Yoon, J.; Kim, S. K.; Singh, N. J.; Lee, J. W.; Yang, Y. J.; Chellappan, K.; Kim, K. S. *J. Org. Chem.* **2004**, 581.
[9] Kim, S. K.; Kang, B-G.; Koh, H. S.; Yoon, Y. J.; Jung, S. J.; Jeong, B.; Lee, K-D.; Yoon *J. Org. Lett.* **2004**, 4655.
[10] Kang, J.; Ju, H. -K.; Jo, J. -H. *Supramol. Chem.* **2004**, 175.
[11] Kang, J.; Jo, J. -H.; In, S. *Tetrahedron Lett.* **2004**, 5225.
[12] In, S.; Kang, J. *Tetrahedron Lett.* **2005**, 7165.
[13] Chegaev, K. Y.; Kravchenko, A. N.; Lebedev, O. V.; Strelenko, Y. A. *Mendeleev Commun.* **2001**, 32.
[14] Hynes, M. J. *J. Chem. Soc. Dalton. Trans.* **1993**, 311.
[15] *Frontiers in Supramolecular Chemistry*; Wilcox, C. S., Schneider, H., Dürr, H., Eds.; VCH: Weinheim, 1991; p 123.