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Tetrahedron
Tetrahedron 63 (2007) 171–176

Anion recognition by bisimidazolium and bisbenzimidazolium cholapods

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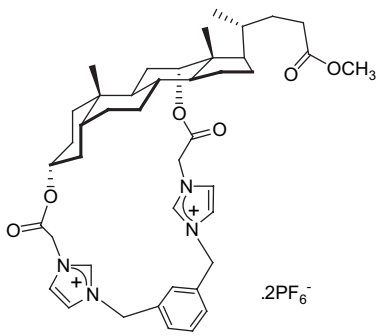
Received 9 June 2006; revised 11 September 2006; accepted 12 October 2006
Available online 3 November 2006

Abstract—Bile acid-based acyclic receptors bearing two imidazole and benzimidazole moieties have been synthesized. Anion binding studies using ^{1}H NMR revealed that imidazolium receptor exhibits high selectivity for chloride ion while benzimidazolium receptor showed selectivity for Y-shaped acetate ion through hydrogen bond interactions involving imidazolium C-2 and acetyl methylene hydrogens.

1. Introduction

The design and synthesis of receptors capable of binding anionic guest is of prime importance in supramolecular chemistry, due to its biological, medical, and environmental relevances.[1] The selective binding of anions by host molecules depends upon the size and geometry of anions as well as the host molecule. Receptors having amide, urea, pyrrole, ammonium, or guanidinium groups as binding sites have been designed for anion recognition.[2] Sato et al. have reported receptors with 1,3-disubsituted imidazolium groups, which bind anions by forming $(C–H)^+\cdots X^-$ ionic hydrogen bonds between the imidazolium rings and the guest anion.[3]

Recently, bile acids, because of their rigid framework, facial amphiphilicity, and suitably oriented hydroxyl groups, have attracted considerable interest for the design of receptors for anion recognition.[4,5] Davis et al. have designed steroid-derived cholapods with urea/thiourea groups for anion recognition.[5] Certain cholapods have been found to be able to transport chloride ions across vesicles and cell membranes.[6] Hence, the design of steroid-based receptors capable of selective recognition of anions is of particular interest. We have recently reported bile acid-based cyclic imidazolium receptors **1** and **2**. Receptor **1** has a moderate selectivity for the fluoride ion while receptor **2** shows high selectivity and affinity for the chloride ion.[7] Interestingly, the single crystal X-ray analysis of the complexes of these receptors with bromide ion revealed the participation of the methylenic hydrogens of both the acetyl groups in the hydrogen bond interaction with the bromide ion. To further examine the importance of $CH\cdots X^-$ hydrogen bond interactions in anion recognition and to see the effect of flexibility on the selectivity of anion binding, we synthesized various cholapods having $–COCH_2–$ and imidazolium/benzimidazolium groups and their anion recognition properties have been studied.



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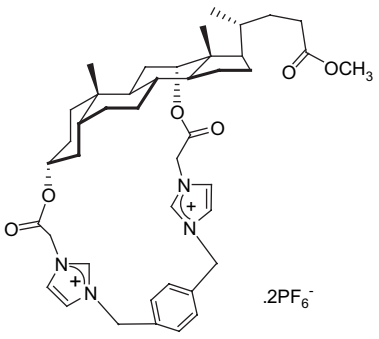

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Keywords: Anion recognition; Bile acid; Cholapod; Hydrogen bond; Imidazolium receptor.
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0040–4020/$ - see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.tet.2006.10.037

2. Results and discussion

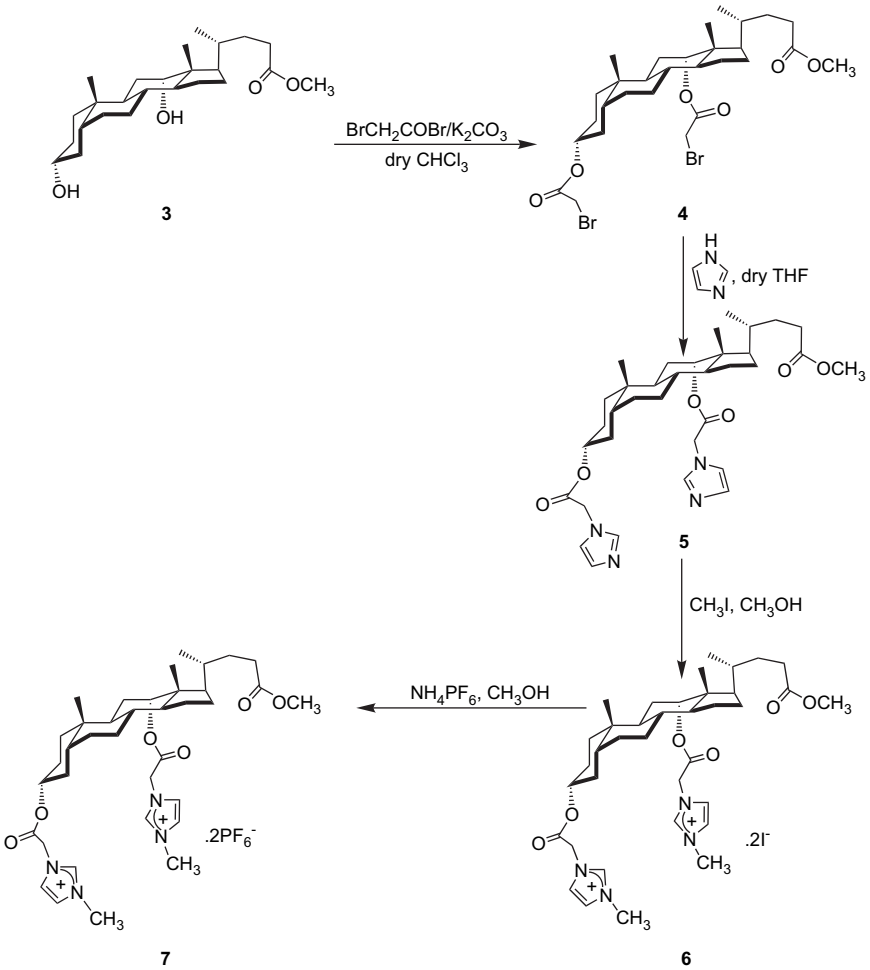
2.1. Synthesis and binding studies

The deoxycholic acid-based receptors **7** and **10** have been synthesized as shown in Schemes 1 and 2. First, methyl 3α,12α-bis{*O*-(N_1-imidazole)acetyl}deoxycholate[7] **5** and methyl 3α,12α-bis{*O*-(N_1-benzimidazole)acetyl}deoxycholate **8** were synthesized from methyl deoxycholate. Then, N-alkylation of the imidazole and benzimidazole groups in compounds **5** and **8** was carried out in methanol and chloroform, respectively, with methyl iodide to give diiodide salts **6** and **9**. Subsequently, these compounds **6** and **9** were anion exchanged with a saturated methanolic solution of NH_4PF_6 to give bis(hexafluorophosphate) salts **7** and **10**.

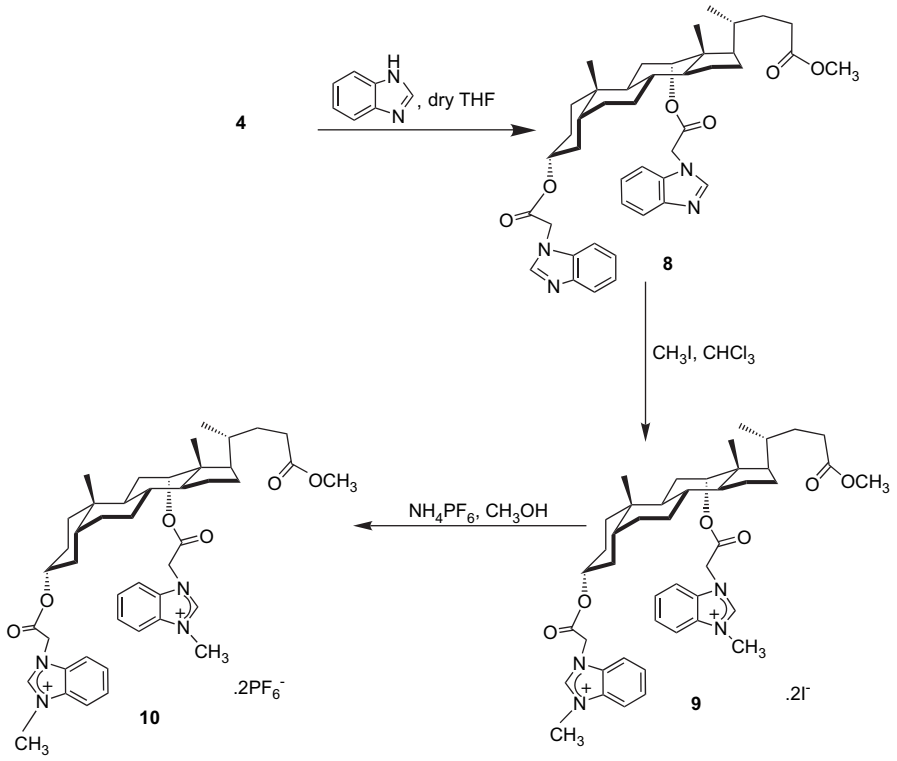
The binding properties of bile acid-based receptors **7** and **10** toward various anions were examined on the basis of ^{1}H NMR titration experiments. The addition of tetrabutylammoniun salts to receptors **7** and **10** in $CDCl_3$ solution, resulted in large downfield chemical shifts of the C-2 protons of the imidazolium/benzimidazolium moieties, which suggested complexation of the anion through $(C–H)^+\cdots X^-$ ionic hydrogen bonds. In addition to the downfield shifts of the C-2 protons of the imidazolium groups, significant changes and downfield shifts in the methylene protons were also observed. The involvement of the $–CH_2–$ hydrogens as an important motif was established on the basis of the comparison of ^{1}H NMR of compounds **5** and **6**. In compound **5**, the $–CH_2–$ proton appears as a broad singlet at δ 4.74 ppm whereas in compound **6**, the $–CH_2–$ protons split into two sets of doublets and appeared in the range δ 5.39–5.49 ppm and 5.70–5.86 ppm (Fig. 1).

In the case of the bisbenzimidazolium system, the $–CH_2–$ protons in compound **8** appear as two separate multiplets at δ 4.75 ppm and 5.07 ppm, which on binding with iodide ion shifts downfield and appears at δ 5.65 ppm and 5.91 ppm (Fig. 2). These results clearly indicate that in both cases, $–CH_2–$ hydrogens participate significantly in the anion recognition.

The addition of tetrabutylammoniun salts like chloride, bromide, fluoride, iodide, acetate, and hydrogen sulfate to the host solutions in $CDCl_3$, resulted in downfield shifts of the C(2)–H protons of imidazolium/benzimidazolium units and methylene protons. The association constants were calculated on the basis of the chemical shift changes of the C(2)–H protons of imidazolium/benzimidazolium units using WinEQNMR program,[8] which revealed the evidence for 1:1 stoichiometry. ^{1}H NMR titration results indicate that receptor **7** exhibits high selectivity and binding for



Scheme 1.



Scheme 2.

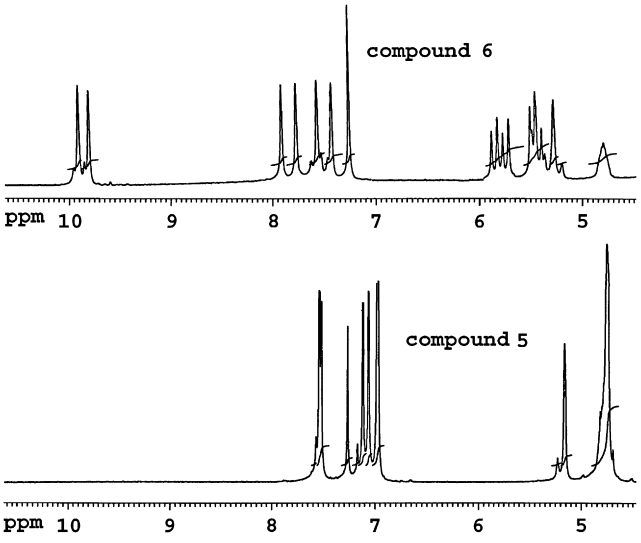


Figure 1. Selected regions of the ^{1}H NMR spectra of compounds **5** and **6**.

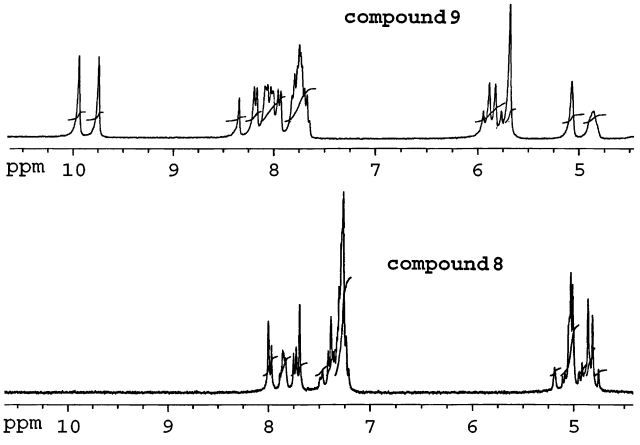


Figure 2. Selected regions of the ^{1}H NMR spectra of compounds **8** and **9**.

chloride ion with an association constant 2500 M^{-1}, while receptor **10** shows a moderate selectivity for the acetate anion 285 M^{-1}. It has been observed that the values of binding constants for bisbenzimidazolium receptor are, in general, relatively lower than the corresponding bisimidazolium receptor (Table 1). This can be explained on the basis of the involvement of the hydrogen-donor groups in the receptors in the anion binding. In the bisbenzimidazolium receptor, only one of the imidazole moieties is involved in the anion binding, which is evident from the single crystal X-ray structure of compound **9** (Fig. 3).

Table 1. Association constants (K_a)[a] for 1:1 complexes of hosts with anions in $CDCl_3$ at 298 K

Host	Anions[b]	K_a (M^{-1})	Host	Anions[b]	K_a (M^{-1})
7	Cl^-	2500	**10**	Cl^-	230
	Br^-	550		Br^-	210
	F^-	650		F^-	150
	I^-	150		I^-	115
	CH_3COO^-	250		CH_3COO^-	285
	HSO_4^-	400		HSO_4^-	130

[a] Estimated error <10%.
[b] Anions existed in their tetrabutylammonium salts.

2.2. X-ray crystallographic studies

The involvement of $-CH_2-$ hydrogens in the anion recognition has also been confirmed by the single crystal X-ray of

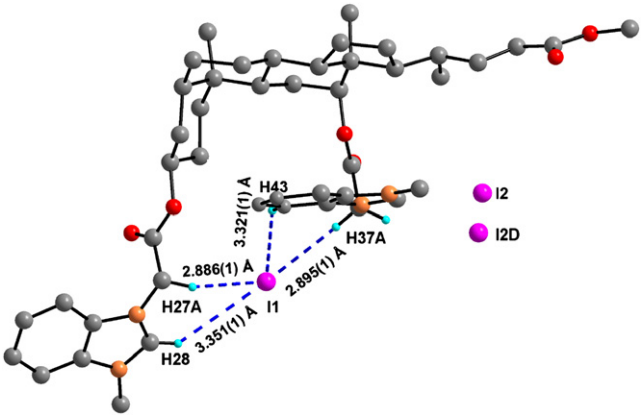


Figure 3. Ball-and-Stick model of $C_{45}H_{60}I_2N_4O_6$ showing C–H···I interactions. Hydrogen atoms are omitted for clarity.

compound **9** as shown in Figure 3. Its unit cell packing diagram is given in Figure 4.

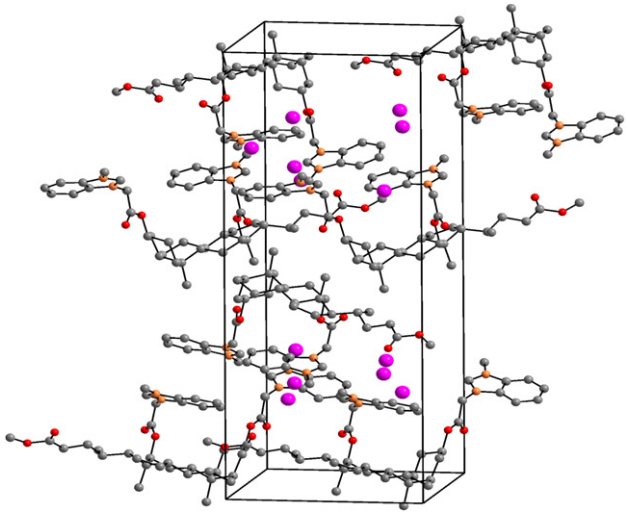


Figure 4. Unit cell packing diagram of $C_{45}H_{60}I_2N_4O_6$.

Colorless crystals of **9-(I)$_2$** were grown by slow evaporation of methanol/hexane solution. The crystal system of **9-(I)$_2$** is orthorhombic and reveals that one iodide is centered in the cavity, which forms strong hydrogen bonds with methylene protons of both the acetyl units. The H27A···I1 and H37A···I1 distances are 2.886 Å and 2.895 Å, respectively, and C27–H27A–I1 and C37–H37A–I1 bond angles are 145.58° and 175.53°, respectively. It also forms hydrogen bonds with a proton (H28) of benzimidazole ring and with a proton (H43) of the benzene ring[9] having distances 3.351 Å and 3.321 Å, and bond angles 138.45° and 145.15°, respectively. Due to the presence of imidazole ring of the benzimidazole moiety at 12α-position in the opposite direction, the C-2 proton of benzimidazole unit at 12α-position does not participate in the intramolecular anion binding with the iodide ion. Another iodide is observed to be in distorted form with 50% occupancy factor.

3. Conclusion

In conclusion, acyclic bisimidazolium and bisbenzimidazolium receptors (cholapods) **7** and **10** were synthesized. The cholapod **7** shows high selectivity and affinity for chloride ion. The cholapod **10**, however, shows a moderate selectivity for the acetate ion. ^{1}H NMR and X-ray data of these cholapods show that in addition to C-2 hydrogens of imidazolium moieties, there is strong involvement of the methylene hydrogens in the anion binding.

4. Experimental

4.1. General

All the reagents used in the study were purchased from Sigma-Aldrich or Merck and were chemically pure. Reactions were carried out under a nitrogen atmosphere and the solvents used were dried and distilled. Methanol was dried over magnesium and iodine, THF was dried over sodium and benzophenone, and distilled before use. Column chromatography was performed on silica gel (60–120 mesh) obtained from Merck. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-P300 MHz spectrometer and chemical shifts are reported in parts per million with TMS as the internal standard. Standard IR spectra were recorded on a Nicolet Protégé 460 spectrometer, using KBr pellets while X-ray data was recorded using a Bruker SMART CCD single crystal diffractometer. Elemental analyses were taken on a Perkin–Elmer 240C Elemental analyzer. The mass spectra were measured on a JEOL SX102/DA-6000 Mass spectrometer instrument.

4.1.1. 3α,12α-Bis(bromoacetyl)deoxycholate 4 and 3α,12α-bis{*O*-(N_1-imidazole)acetyl}deoxycholate 5. Compounds **4** and **5** were prepared using the experimental procedure given in Ref. 7 (Supplementary data).

4.1.2. 3α,12α-Bis{*O*-(N_1-methylimidazolium)acetyl}-deoxycholate diiodide salt 6. To a solution of compound **5** (0.20 g, 0.32 mmol) in 10 mL of methanol was added an excess of methyl iodide (0.41 mL, 6.61 mmol). The reaction mixture was stirred at room temperature overnight. After the evaporation of solvent, the residue was dried in vacuum and recrystallized from chloroform/hexane to give **6** as a yellow powder (0.23 g, 84%). Mp: 110–112 °C. IR (KBr) 3085, 2945, 1742, 1621 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.74 (s, 3H, 18-Me), 0.83 (d, J=5.5 Hz, 3H, 21-Me), 0.88 (s, 3H, 19-Me), 0.91–2.34 (26H, steroidal H), 3.66 (s, 3H, OCH_3), 4.06 (s, 3H, Im N-CH_3), 4.12 (s, 3H, Im N-CH_3), 4.80 (br s, 1H, 3β-H), 5.27 (s, 1H, 12β-H), 5.39–5.49 (d, J=17.3 Hz, 1H; d, J=17.6 Hz, 1H, 2X OCOCHa**Hb**–), 5.70–5.86 (d, J=17.4 Hz, 1H; d, J=17.7 Hz, 1H, 2X OCO-C**Ha**Hb–), 7.46 (s, 1H, ImH), 7.59 (s, 1H, ImH), 7.77 (s, 1H, ImH), 7.91 (s, 1H, ImH), 9.78 (s, 1H, ImH-2), 9.89 (s, 1H, ImH-2); ^{13}C NMR ($CDCl_3$) δ 174.7, 165.4, 137.4, 137.1, 124.0, 123.2, 122.8, 51.3, 50.7, 50.3, 49.0, 46.8, 37.0, 35.1, 34.5, 34.2, 33.9, 33.6, 30.9, 30.2, 27.1, 26.6, 26.3, 25.5, 22.4, 17.7, 12.0; FAB-MS: 779 [M−I]$^+$, 651 [M−2I−1]$^+$; Anal. Calcd for $C_{37}H_{56}I_2N_4O_6\cdot 2H_2O$: C, 47.14; H, 6.42; N, 5.94. Found: C, 46.94; H, 6.01; N, 5.84.

4.1.3. 3α,12α-Bis{*O*-(N_1-methylimidazolium)acetyl}-deoxycholate bis(hexafluorophosphate) salt 7. Compound **6** (0.10 g, 0.11 mmol) was dissolved in an excess of saturated methanolic solution of NH_4PF_6 (6 mL). The reaction

mixture was stirred at room temperature for 2 h. Then the precipitate was collected and purified by recrystallization from methanol to give **7** as colorless crystals (0.08 g, 78%). Mp: 151–153 °C. IR (KBr) 3169, 2948, 1751, 1578 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.73 (s, 3H, 18-Me), 0.79 (s, 3H, 21-Me), 0.90 (s, 3H, 19-Me), 1.12–2.33 (26H, steroidal H), 3.65 (s, 3H, OCH_3), 3.84 (s, 3H, Im N-CH_3), 3.94 (s, 3H, Im N-CH_3), 4.76 (br s, 1H, 3β-H), 4.87–5.15 (m, 4H, $OCOCH_2$), 5.26 (s, 1H, 12β-H), 7.24 (s, 1H, ImH), 7.26 (s, 1H, ImH), 7.34 (s, 1H, ImH), 7.44 (s, 1H, ImH), 8.45 (s, 1H, ImH-2), 8.60 (s, 1H, ImH-2); ^{13}C NMR ($CDCl_3$) δ 174.9, 165.6, 165.2, 137.3, 137.0, 123.6, 123.3, 51.4, 49.7, 49.1, 47.2, 45.1, 41.6, 36.0, 35.4, 34.7, 34.2, 33.8, 31.4, 34.2, 33.8, 31.4, 31.4, 31.0, 30.4, 27.3, 26.6, 25.8, 22.7, 22.75, 17.4, 12.26; FAB-MS; 797 $[M-PF_6]^+$, 651 $[M-2PF_6-1]^+$; Anal. Calcd for $C_{37}H_{56}N_4F_{12}O_6P_2\cdot 2H_2O$: C, 45.40; H, 6.18; N, 5.72. Found: C, 45.70; H, 6.40; N, 5.80.

4.1.4. 3α,12α-Bis{*O*-(N_1-benzimidazole)acetyl}deoxycholate 8. A mixture of compound **4** (1.50 g, 2.26 mmol) and benzimidazole (1.06 g, 9.05 mmol) in dry THF (8 mL) was stirred at room temperature for 8 h. Then the reaction was worked up and the compound was purified as described above for compound **5** to give **8** as a white solid (1.22 g, 75%). Mp: 94–96 °C. IR (KBr) 2945, 2866, 1737, 1616, 1498 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.55 (s, 3H, 18-Me), 0.67 (d, J=6.2 Hz, 3H, 21-Me), 0.83 (s, 3H, 19-Me), 0.98–2.20 (26H, steroidal H), 3.68 (s, 3H, OCH_3), 4.75–4.94 (m, 3H, 3β-H, $OCOCH_2$), 5.00–5.08 (m, 3H, 12β-H, $OCOCH_2$), 7.20–7.99 (m, 10H, BIH); ^{13}C NMR ($CDCl_3$) δ 174.5, 166.7, 166.2, 143.6, 143.3, 134.1, 123.4, 122.4, 120.5, 120.4, 109.3, 51.5, 48.3, 46.9, 44.7, 41.4, 35.1, 34.5, 33.8, 31.6, 31.1, 30.5, 26.9, 26.4, 25.5, 25.1, 23.0, 22.6, 17.5, 11.9; ESI-MS (*m*/*z*): 723.4 $(M+H)^+$; Anal. Calcd for $C_{43}H_{54}N_4O_6\cdot 1.5H_2O$: C, 68.86; H, 7.66; N, 7.47. Found: C, 68.98; H, 7.50; N, 7.57.

4.1.5. 3α,12α-Bis{*O*-(N_1-methylbenzimidazolium)acetyl}deoxycholate diiodide salt 9. To a solution of compound **8** (0.20 g, 0.27 mmol) in 10 mL of chloroform was added an excess of methyl iodide (0.38 mL, 5.96 mmol). Then the reaction mixture was stirred at room temperature overnight. After the completion of reaction, the insoluble precipitate was filtered off and dried in vacuum. The product was purified by recrystallization from chloroform/hexane to give **9** as colorless crystals (0.26 g, 80%). Mp 180–182 °C; IR (KBr) 3036, 2944, 1742, 1615 cm^{-1}; ^1H NMR (DMSO) δ 0.61 (s, 3H, 18-Me), 0.73 (br s, 3H, 21-Me), 0.86 (s, 3H, 19-Me), 1.01–2.25 (26H, steroidal H), 3.61 (s, 3H, OCH_3), 4.11 (s, 3H, BIH N-CH_3), 4.21 (s, 3H, BIH N-CH_3), 4.83 (br s, 1H, 3β-H), 5.04 (s, 1H, 12β-H), 5.65–5.91 (m, 4H, $OCOCH_2$), 7.65–8.31 (m, 8H, BIH), 9.71 (s, 1H, BIH-2), 9.91 (s, 1H, BIH-2); ^{13}C NMR (DMSO) δ 173.6, 165.9, 143.4, 131.5, 131.3, 126.8, 126.6, 113.897, 113.6, 113.2, 51.2, 48.1, 47.7, 40.9, 40.3, 40.0, 34.7, 34.1, 22.6, 17.5, 11.9; FAB-MS; 879 $[M-I]^+$, 751 $[M-2I-1]^+$; Anal. Calcd for $C_{45}H_{60}N_4O_6I_2\cdot 2H_2O\cdot 2CHCl_3$: C, 44.05; H, 5.19; N, 4.37. Found: C, 44.19; H, 5.69; N, 4.29.

4.1.6. 3α,12α-Bis{*O*-(N_1-methylbenzimidazolium)acetyl}deoxycholate bis(hexafluorophosphate) salt 10. Compound **9** (0.10 mg, 0.09 mmol) was dissolved in an excess of saturated methanolic solution of NH_4PF_6 (6 mL). After stirring the reaction mixture at room temperature for 2 h, the reaction was worked up and the compound was purified as described above for compound **7** to yield **10** as colorless crystals (0.087 g, 85%). Mp 180–182 °C; IR (KBr) 3171, 3115, 2952, 1754, 1619 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.74 (s, 3H, 18-Me), 0.80 (d, J=5.1 Hz, 3H, 21-Me), 0.90 (s, 3H, 19-Me), 1.06–2.25 (26H, Steroidal H), 3.70 (s, 3H, OCH_3), 4.12 (s, 3H, BIH N-CH_3), 4.19 (s, 3H, BIH N-CH_3), 4.87 (br s, 1H, 3β-H), 5.20–5.48 (m, 5H, $OCOCH_2$, 12β-H), 7.66–7.76 (br s, 8H, BIH), 9.22 (s, 1H, BIH-2), 9.30 (s, 1H, BIH-2); ^{13}C NMR ($CDCl_3$) δ 174.6, 165.3, 164.7, 142.4, 131.4, 127.5, 127.1, 113.3, 113.1, 112.7, 51.5, 48.9, 47.6, 41.5, 35.3, 34.7, 22.7, 17.7, 12.1; ESI-MS (*m*/*z*): 1065.2 $[M+Na]^+$, Anal. Calcd for $C_{45}H_{60}N_4F_{12}O_6P_2\cdot 2H_2O\cdot CH_3OH$: C, 49.73; H, 6.17; N, 5.04. Found: C, 49.77; H, 5.79; N, 5.26.

4.2. Crystal data for 9-$(I)_2$

A colorless crystal with dimensions of 0.23×0.17×0.09 mm was obtained by slow evaporation of compound **9** in methanol/hexane solution having molecular formula $C_{45}H_{60}N_4O_6$ $0.5(I_2)I$, MW=1006.77, orthorhombic, space group $P2_12_12_1$, a=11.8167(16) Å, b=13.4409(18) Å, c=30.412(4) Å, α=90°, β=90°, γ=90°, V=4830.3(11) $Å^3$, T=298 K, D_{calcd}=1.384 g/cm^3, μ=1.349 mm^{-1}, Z=4, λ=0.71073 Å, ω and ϕ scans, 48,515 reflections collected, 5021 independent, 530 refined parameters, $R1/wR2$ ($I\geq 2\sigma(I)$)=0.0793/0.2073 and $R1/wR2$ (all data)=0.1151/0.2331, maximum (minimum) residual electron density 1.166 (−0.732) $eÅ^{-3}$. Crystallographic data for the structure have been deposited with Cambridge Crystallographic Database Centre as supplementary publication number CCDC 600830.

^1H NMR titration method: all NMR titration experiments were performed on a 300 MHz spectrometer at 298 K. A solution (10 mM) of receptors in $CDCl_3$ was titrated with an aliquot of a stock solution (60 mM or 70 mM) of tetrabutylammonium salts in the same solvent. The changes in the chemical shift of the C-2 proton of imidazole/benzimidazole moieties were monitored. The ^1H NMR saturation data were analyzed using WinEQNMR program. Every titration was repeated at least once.

Acknowledgements

We thank the Council of Scientific and Industrial Research, New Delhi for fellowship to M.C. We also thank Department of Science and Technology, New Delhi for funding a single crystal diffractometer under FIST to the Department of Chemistry, IIT Delhi, India.

Supplementary data

X-ray data file (CIF), NMR and Mass spectra, Binding isotherms are available in supplementary data. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2006.10.037.

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