

Host size effect in the complexation of two bis(*m*-phenylene)-32-crown-10-based cryptands with a diazapyrenium salt

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Dedicated to Professor Xian-Tu He on the occasion of his 70th birthday

Abstract—*N,N'*-Dimethyl-2,7-diazapyrenium bis(hexafluorophosphate) binds a *C*₃-symmetric bis(*m*-phenylene)-32-crown-10-based cryptand more strongly than *N,N'*-dimethyl-4,4'-bipyridinium bis(hexafluorophosphate) partly because of its better fit in size with the cryptand host cavity, while it binds a relatively smaller pyridyl cryptand less strongly due to its worse fit in size with the cryptand host cavity and the lack of hydrogen bonding to the pyridyl nitrogen atom of the host.

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The design and preparation of inclusion complexes are hot topics in supramolecular chemistry not only due to their topological importance, but also because of their potential applications in nanotechnology.¹ Following the observation that bis(*m*-phenylene)-32-crown-10 (BMP32C10, **1a**) diol derivative **1b** and paraquat (**2**) formed a taco complex in the solid state,² for the preparation of large supramolecular systems, Gibson, Huang, and co-workers designed and prepared a series of crown ether-based cryptands, which complex paraquat derivatives,^{2,3} diquat,⁴ and monopyridinium salts⁵ much more strongly than the corresponding simple crown ethers. It seems that the cavity of cryptand **3a** is too big for paraquat **2** since a water hydrogen-bonding bridge was found between two β-pyridinium hydrogen atoms of **2** and the third ethyleneoxy chain of **3a** in the crystal structure of **3a·2** (Fig. 1).² Furthermore, Stoddart and co-workers found that diazapyrenium salts bound 34- and 36-membered crown ethers more strongly than relatively smaller paraquat derivatives.⁶ Therefore, we reasoned that diazapyrenium salt **4**

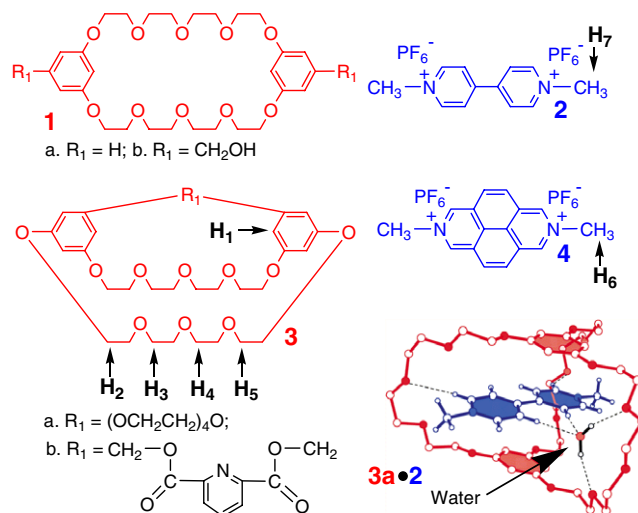


Figure 1. Compounds used in this study and the X-ray structure² of **3a·2**.

should bind cryptand **3a** more strongly than paraquat **2** partly because of its better fit in size with **3a**. Another driving force for the study presented here is the wide use of diazapyrenium salts in the fabrication of inclusion complexes.^{6,7} Herein, we report our study of

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complexation between two cryptands (**3a**² and **3b**^{3c}) and diazapyrenium **4**.⁶

Partial proton NMR spectra of **4**, a mixture of **3a** and **4**, **3a**, a mixture of **3a** and **2**, and **2** are shown in Figure 2; only one set of peaks was found for the solution of **3a** and **4** (Fig. 2b), indicating fast-exchange complexation. A significant upfield shift of aromatic protons H₁ of the host was observed (Fig. 2b and c). This chemical shift change is much larger than that for the complexation between **3a** and **2** (Fig. 2c and d). Furthermore, the singlet (Fig. 2c) corresponding to H₁ of **3a** split into two close broad peaks (Fig. 2d) after complexation between **3a** and **2**, but remained a singlet (Fig. 2b) after complexation between **3a** and **4**. Bipyridinium salt **2** is not so symmetric as diazapyrenium salt **4** and, furthermore, **2** has only two conjugated aromatic rings while **4** has four conjugated aromatic rings. Therefore, aromatic protons H₁ of **3a** are in different chemical environments in **2**:**3a** and **4**:**3a**. As can be seen from Figure 1, formation of **2**:**3a** desymmetrizes the cryptand from its original C₃ character; two of the H₁ protons lie in equivalent positions along the long axis of the guest, while the third one lies approximately orthogonal to it, thus making them non-equivalent and yielding two broad peaks. The larger aromatic moiety of diazapyrenium guest **4**, however, does not place the three H₁ protons of the host in substantially different environments and the singlet, though broadened, is retained. It was also found that α- and γ-ethyleneoxy protons H₂ and H₃ on host **3a** moved upfield while its β- and δ-ethyleneoxy protons H₅ and H₄ moved downfield. Aromatic protons of diazapyrenium guest **4** shifted upfield, while its N-methyl protons H₆ shifted downfield. These chemical shift changes are similar to those of bipyridinium salt **2** upon its complexation with **3a** (Fig. 2d and e).² The stoichiometries of the complexes between cryptand hosts **3** and diazapyrenium guest **4** were both determined to be 1:1 in solution by Job plots⁸ (the one for **3a**:**4** is shown in Fig. 3) using UV–vis absorption data.

The association constant (*K*_a) of **3a**:**4**, 1.97 (±0.17) × 10⁶ M⁻¹,⁹ is 31 times higher than that of **3a**:**2** in acetone,

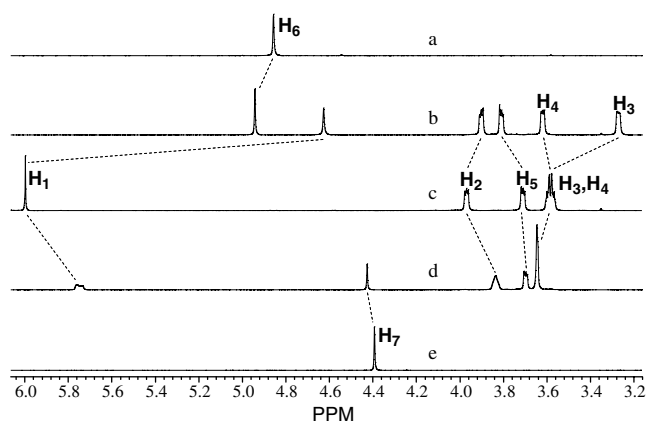


Figure 2. Partial proton NMR spectra (500 MHz, acetonitrile-*d*₃, 22 °C) of diazapyrenium salt **4** (a), 4.00 mM cryptand **3a** and **4** (b), **3a** (c), 4.00 mM **3a** and paraquat salt **2** (d), and **2** (e).

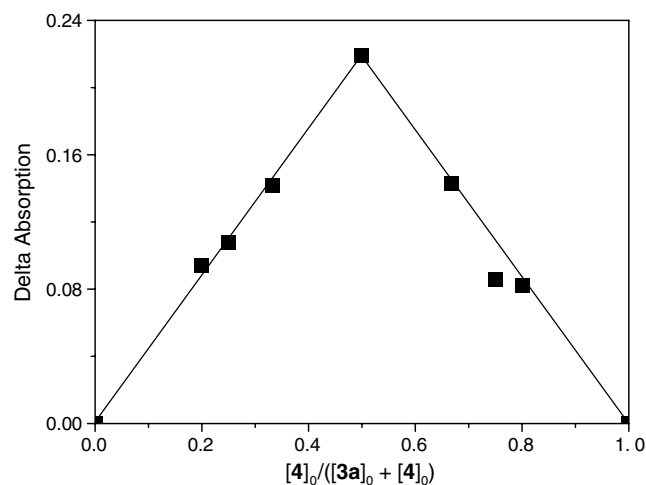


Figure 3. Job plot showing the 1:1 stoichiometry of the complex between cryptand **3a** and diazapyrenium salt **4** by plotting the absorption difference at 420 nm (characteristic of **4**) against the mole fraction of **4**. [**3a**]₀ + [**4**]₀ = 5.0 × 10⁻⁵ M in acetone.

6.1 × 10⁴ M⁻¹.² Furthermore, *K*_a of **3b**:**4**, 1.41 (±0.16) × 10⁶ M⁻¹,⁹ is lower than that, 5.0 × 10⁶ M⁻¹, of **3b**:**2** in acetone.^{3c} The association constant increase from **3a**:**2** to **3a**:**4** results from stronger face-to-face π-stacking interactions and better size fit between the host and guest. The association constant decrease from **3b**:**2** to **3b**:**4** is caused by worse size fit and the lack of hydrogen bonding with the pyridyl nitrogen of host **3b** as shown by the following X-ray analysis; in the case of **3b**:**2** a β-pyridinium hydrogen of **2** forms a hydrogen bond to the pyridyl nitrogen, providing additional binding strength.^{3c}

The 1:1 stoichiometry of complexation between cryptand **3** and diazapyrenium salt **4** was confirmed by electrospray ionization mass spectrometric characterization of solutions of **3** and **4** in acetonitrile. Three relevant peaks were found for **3a**:**4**: *m/z* 1105.1 (53%) [**3a**:**4**-PF₆]⁺, 991.1 (19%) [**3a**:**4**-PF₆-CH₂=CH-O-CH₂-CH₂-O-CH=CH₂]⁺,¹¹ and 480.3 (100%) [**3a**:**4**-2PF₆]²⁺. For **3b**:**4** four relevant peaks were found: *m/z* 1106.1 (100%) [**3b**:**4**-PF₆]⁺, 960.1 (68%) [**3b**:**4**-PF₆-HPF₆]⁺, 954.2 (69%) [**3b**:**4**-2PF₆-2CH₃+Na]⁺, and 480.6 (11%) [**3b**:**4**-2PF₆]²⁺. No peaks were found for complexes with other stoichiometries.

The formation of inclusion [2]complexes **3a**:**4** and **3b**:**4** was confirmed by X-ray analyses (Figs. 4 and 5).¹² X-ray quality, yellow, single crystals of **3a**:**4** were grown by vapor diffusion of isopropyl ether into an acetonitrile/acetone solution of **4** with excess **3a**. The 1:1 complex **3a**:**4** is stabilized by hydrogen bonding and face-to-face π-stacking interactions in the solid state. One N-methyl hydrogen (A and B in Fig. 3a) and one α-pyridinium hydrogen (C and D in Fig. 4) are directly hydrogen bonded to ethyleneoxy oxygen atoms of cryptand host **3a**. The biggest difference between the crystal structure of **3a**:**4** and that² of **3a**:**2** is that there is no hydrogen-bonding water bridge in the cavity of

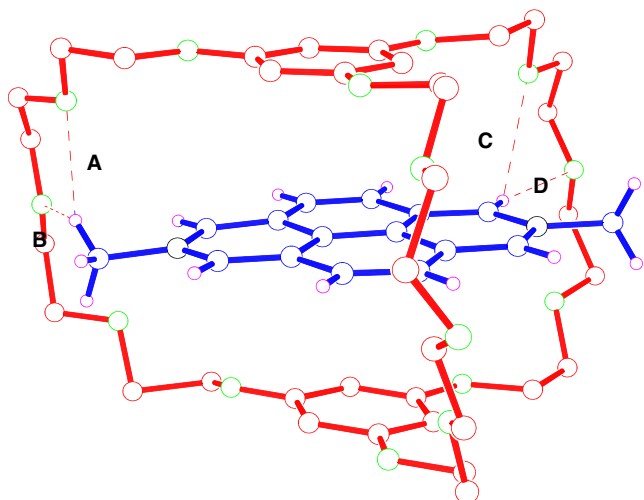


Figure 4. A ball-stick view of X-ray structure of **3a·4**. Compound **3a** is red, **4** is blue, hydrogens are magenta, oxygens are green, and nitrogens are black. PF_6 counterions, solvent molecules, and hydrogens except the ones on **4** were omitted for clarity. Hydrogen-bond parameters: H \cdots O distances (Å), C–H \cdots O angles (°), C \cdots O distances (Å) **A**, 2.43, 152, 3.31; **B**, 2.60, 132, 3.32; **C**, 2.67, 107, 3.07; **D**, 2.46, 160, 3.35. The centroid–centroid distance (Å) and dihedral angle (°) between the phenylene rings of **3a**: 7.14 and 3.9.

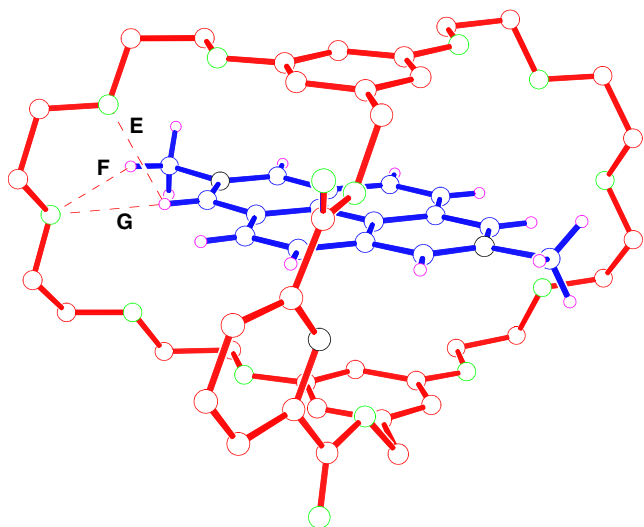


Figure 5. A ball-stick view of X-ray structure of **3b·4**. Compound **3b** is red, **4** is blue, hydrogens are magenta, oxygens are green, and nitrogens are black. PF_6 counterions, solvent molecules, and hydrogens except the ones on **4** were omitted for clarity. Hydrogen-bond parameters: H \cdots O distances (Å), C–H \cdots O angles (°), C \cdots O distances (Å) **E**, 2.54, 118, 3.08; **F**, 2.67, 151, 3.54; **G**, 2.38, 161, 3.28. The centroid–centroid distance (Å) and dihedral angle (°) between the phenylene rings of **3b**: 7.14 and 4.6.

3a for the former but there is one for the latter, indicating that diazapyrenium **4** has a better fit in size with the cavity of **3a** than paraquat **2**. This better size fit is one reason for the 31-fold increase in association constant from **3a·2** to **3a·4**. Another contribution comes from stronger face-to-face π -stacking interactions between the electron-rich aromatic rings of host **3** and

the electron-poor aromatic moiety of guest **4** due to the bigger π -electron-conjugated system of the latter relative to paraquat **2**. The two aromatic rings of cryptand host **3a** in **3a·4** are almost parallel with a dihedral angle of 3.9°, smaller than the corresponding value, 9.8°, in **3a·2**.² This is presumably in order to maximize face-to-face π -stacking and charge transfer interactions between host **3a** and guest **4**. The two aromatic rings of **3a** have a centroid–centroid distance of 7.14 Å, a value bigger than the corresponding values, 6.94 Å in **3a·2**,² 6.79 Å in a complex of **3a** with diquat,⁴ and 6.88 Å in a complex of **3a** with a monopyridinium salt.^{5a} This distance increase takes place presumably due to the bigger size of diazapyrenium guest **4** compared with these other guests.

The 1:1 complex **3b·4** is also stabilized by hydrogen bonding and face-to-face π -stacking interactions in the solid state. One *N*-methyl hydrogen (**F** in Fig. 5) and one α -pyridinium hydrogen (**E** and **G** in Fig. 5) are directly hydrogen bonded to ethyleneoxy oxygen atoms of cryptand host **3b**. As expected for face-to-face π -stacking interactions between the host and guest, the two phenylene rings of cryptand host **3b** in **3b·4** are almost parallel with a dihedral angle of 4.6°, smaller than the corresponding value, 7.4°,^{3e} in **3b·2** but a little bigger than the corresponding value, 3.9°, for the two phenylene rings of cryptand host **3a** in **3a·4**. What is interesting here is that the centroid–centroid distances between the phenylene rings of cryptand host in **3a·4** and **3b·4** have the same value, 7.14 Å (Figs. 4 and 5), very close to the corresponding value, 7.19 Å, for **3b·2**.^{3e} However, there is an obvious difference between the crystal structures of **3a·4** and **3b·4**. The diazapyrenium guest **4** is threaded unsymmetrically into the cavity of the 32-crown-10 part of the cryptand host in **3b·4** (Fig. 5), but it is nearly symmetrically located in **3a·4** and also the paraquat unit is nearly symmetrically located in **3b·2**.^{3e} This is presumably due to the smaller cavity of **3b** compared with **3a** and the bigger size of **4** compared with **2**. Furthermore, no hydrogens of diazapyrenium guest **4** are hydrogen bonded to the pyridyl nitrogen of host **3b** in **3b·4** (Fig. 5), while one β -pyridinium hydrogen of bipyridinium guest **2** is hydrogen bonded to the pyridyl nitrogen of host **3b** in **3b·2**.^{3e} Both the worse size fit and the lack of hydrogen bonding with the pyridyl nitrogen of host **3b** account for the above mentioned association constant decrease from **3b·2** to **3b·4**.

In summary, we demonstrated that bis(*m*-phenylene)-32-crown-10-based cryptands **3** complex dimethyl diazapyrenium salt **4** strongly. These cryptand/diazapyrenium complexes have 1:1 stoichiometries in solution, gaseous phase, and solid state. Diazapyrenium **4** binds *C*₃-symmetric bis(*m*-phenylene)-32-crown-10-based cryptand **3a** more strongly than paraquat **2** partly because of its better fit in size with the cryptand host cavity, while it binds relatively smaller cryptand **3b** more weakly than paraquat **2** because of its worse fit in size with the cryptand host and its lack of hydrogen bonding to the pyridyl nitrogen of the host. Currently we are using this new and efficient cryptand/diazapyrenium rec-

ognition motif in preparation of other supramolecular systems.

Acknowledgments

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Supplementary data

Job plots for **3-4**, determination of association constants, mass spectra of complexes, and full proton NMR spectra. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.08.038.

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- Fluorimetric titrations of diazapyrenium guest **4** (5.56×10^{-6} M, $\lambda_{\text{excitation}} = 400$ nm) with hosts **3** were carried out in acetone at 25 °C. The data at high [3]₀ were analyzed using the modified Benesi–Hildebrand equation $I_0/(I - I_0) = \{a/(b - a)\} \{(1/K_a)[3]_0^{-1} + 1\}$,¹⁰ where a and b are constants and I and I_0 are the fluorescence emission intensities at $\lambda_{\text{emission}} = 420$ nm for various initial concentrations of **3** and in its absence, respectively. The association constant K_a was obtained from the ratio of the y -intercept to the slope of the plot and its error was based on the errors of the y -intercept and the slope. More details are provided in the **Electronic Supplementary data**.
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- Crystal data of **3a-4**: prism, yellow, 0.127 × 0.088 × 0.056 mm³, C₆₀H₈₀F₁₂N₆O₁₅P₂, FW 1415.24, monoclinic, space group $P2_1/c$, $a = 25.52(2)$, $b = 11.020(9)$, $c = 24.85(2)$ Å; $\beta = 84.501(19)^\circ$; $V = 6955(10)$ Å³, $Z = 4$, $D_c = 1.352$ g cm⁻³, $T = 293(2)$ K, $\mu = 1.60$ cm⁻¹, 35,712 measured reflections, 12,908 independent reflections, 835 parameters, 14 restraints, $F(000) = 2960$, $R_1 = 0.1022$, $wR_2 = 0.2195$ [$I > 2\sigma(I)$], maximum residual density

0.482 e Å⁻³, and GOF (F^2) = 0.871. Crystal data of **3b·4**: prism, yellow, 0.478 × 0.425 × 0.097 mm³, C₅₅H₆₄F₁₂N₄O₁₅P₂, FW 1311.04, triclinic, space group $P\bar{1}$, $a = 11.5990(12)$, $b = 12.2724(12)$, $c = 21.607(2)$ Å; $\alpha = 104.641(2)^\circ$, $\beta = 93.065(2)^\circ$, $\gamma = 92.351(2)^\circ$; $V = 2966.8(5)$ Å³, $Z = 2$, $D_c = 1.468$ g cm⁻³, $T = 293(2)$ K, $\mu = 1.80$ cm⁻¹, 15,745 measured reflections, 10,882 independent reflections, 849 parameters, 1 restraint, $F(000) = 1360$, $R_1 = 0.0685$, $wR_2 = 0.1741$ [$I > 2\sigma(I)$], maximum

residual density 0.496 e Å⁻³, and GOF (F^2) = 0.821. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 645804 and 645803. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 144-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].