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Contorted Conformations of 1,4-Butylidenedipyridinium and 1,10-Decylidenedipyridinium Cationic Guests in a Cucurbit[8]uril Host

Xin Xiao,^[a] Qian Wang,^[a] Yi-Hua Yu,^[b] Zhi-You Xiao,^[a] Zhu Tao,^{*[a]} Sai-Feng Xue,^[a] Qian-Jiang Zhu,^[a] Jing-Xin Liu,^{*[c]} and Xin-Hua Liu^[c]

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1,4-Butylidenedipyridinium (C₄DP²⁺) and 1,10-decylidenedipyridinium (C₁₀DP²⁺) cationic guests form highly stable 1:1 inclusion complexes in aqueous solution with a cucurbit[8]uril (Q[8]) host. Single-crystal structure analysis of the inclusion complexes revealed that the alkyl chain of the C_nDP²⁺ (n = 4, 10) cationic guest adopts an unconventional contorted conformation, which is attributed to favorable

Introduction

Alkyl chains are well known to adopt fully extended conformations in the free space of solutions, which minimizes steric interactions and energies.^[1] Helical or folding conformations occur frequently in natural biochemical structures, such as in proteins and nucleic acids.^[2] However, several synthetic hydrophobic host systems in which the alkyl chains adopt contorted conformations have been observed in the past decade.^[3–6] In particular, Rebek Jr. and coworkers synthesized and studied a series of cylindrical capsules in which multifarious alkanes are encapsulated.^[6] Their results clearly show that alkyl chains can be compressed to fit within the synthetic cylindrical capsules when their internal strains are compensated.

Cucurbit[*n*]urils^[7,8] (n = 5–8, 10, hereafter abbreviated Q[*n*]; Figure 1), a class of organic macrocyclic cavitands that are barrel shaped with two identical portals fringed by carbonyl groups, have received increased interest. For example, the Kim group discovered a U-shaped conformation of the alkyl chains embedded in Q[8].^[9] We recently discovered that the long alkyl chain of *N*,*N*'-bis(4-dimethyl-aminobenzyl)dodecane-1,12-diamine adopts different chiral

[a] Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University and Institute of Applied Chemistry, Guizhou University, Guiyang 550025, P. R. China Fax: +86-851-3620906
E-mail: gzutao@263.net
[b] Key Laboratory of Optical and Magnetic Resonance

Spectroscopy of the East China Normal University, Ministry of Education of China, Shanghai 200062, P. R. China

[c] College of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, P. R. China E-mail: jxliu411@ahut.edu.cn host-guest interactions (including charge-dipole and hydrophobic interactions) when bound within the cavity of the Q[8] host. Moreover, their crystal structures suggest that the alkyl chain and the aromatic group can be encapsulated into the Q[8] host simultaneously, and the alkyl chain is more favorably encapsulated into the Q[8] host than the aromatic group.

helical conformations when bound within the cavities of two Q[8] hosts.^[10] We noticed that the alkyl chain section of each guest is situated within the cavity of the Q[8] host, whereas the aromatic groups are located outside the portals of the Q[8] host.



Figure 1. Molecular structure of cucurbit[*n*]urils (n = 5-8, 10).

It is well known that aromatic groups participate in many kinds of chemical reactions, and the cavity of Q[8] is large enough to accommodate two aromatic molecules.^[11] Is it possible to have one alkyl chain and one aromatic group residing in the cavity of Q[8]? With this idea in mind, we synthesized 1,4-butylidenedipyridinium (C₄DP²⁺) dibromide^[12] and 1,10-decylidenedipyridinium ($C_{10}DP^{2+}$) dibromide (Experimental Section). Each of the two organic dicationic guests contains an alkylene group and two aromatic (pyridinium) groups. In the present work, we investigated the formation of a 1:1 host-guest inclusion complex between a Q[8] host and a $C_n DP^{2+}$ guest (n = 4, 10) by ¹H NMR and UV spectroscopy. We also obtained the X-ray crystal structures of the complexes formed between C₄DP²⁺ or $C_{10}DP^{2+}$ and Q[8], in which the alkyl chains of the guests adopt an unconventional contorted conformation inside the Q[8] cavity. More importantly, we found that the Q[8] cavity can accommodate the alkyl chain and the aromatic group simultaneously, and if the alkyl chain is long enough, the aromatic group will be squeezed out of the Q[8] cavity.



Results and Discussion

Description of ¹H NMR and UV Spectroscopy of the Two Inclusion Complexes

As confirmed by ¹H NMR spectroscopy, the Q[8] host forms a 1:1 host-guest inclusion complex with the $C_n DP^{2+}$ cationic guest. The ¹H NMR spectra of $C_4 DP^{2+}$ in the absence and presence of Q[8] (1.0 equiv.) in neutral D₂O solution are shown in Figure 2, in which separate signals for each methylene and methylidyne group of the guest are clearly seen. In the presence of the Q[8] host (1.0 equiv.), all carbon atoms of the guest showed distinct upfield-shifted proton signals ($\Delta \delta \approx 0.36$ –0.60 ppm, Figure 2b), which indicates that the whole guest is deeply buried inside the cavity of the Q[8] host. Closer inspection revealed that the 8.8×9.1 Å (equatorial width \times depth) cavity of Q[8] can accommodate no more than six linearly arranged atoms in a fully extended conformation. We conclude that folding must occur during encapsulation of the C₄DP²⁺ guest. However, no correlation through space between the host and the guest in the NOESY spectrum of the Q[8] \cdot C₄DP²⁺ complex indicates that the encapsulated $C_4 DP^{2+}$ undergoes chemical exchange with the free C_4DP^{2+} (Figure 3).



Figure 2. ¹H NMR spectra (400 MHz, D_2O) of C_4DP^{2+} in the (a) absence and (b) presence of Q[8] (1.0 equiv).

Theoretically, the cavity of Q[8] is not large enough to accommodate the whole $C_{10}DP^{2+}$ guest even in a contorted conformation. To our surprise, however, in the presence of the Q[8] host, all the $C_{10}DP^{2+}$ protons experience considerable upfield shifts (Figure 4), of which the alkane protons (C5–C8) exhibit a large upfield shift ($\Delta \delta \approx 0.44$ –1.10 ppm), whereas the pyridinium protons (C1-C3) and the methylene protons (C4) attached to the pyridinium group show a smaller upfield shift ($\Delta \delta \approx 0.25 - 0.34$ ppm), indicating the formation of an inclusion complex. This observation can be explained as follows: The chemical exchange of the folding $C_{10}DP^{2+}$ in and out of the cavity of Q[8] is slow but near the intermediate rate on the NMR timescale, which leads to broadening of the signals for the included methylene and methylidyne moieties of the guest. No correlation through space between Q[8] and $C_{10}DA^{2+}$ in the corresponding NOESY spectrum could further confirm this explanation



Figure 3. NOESY spectrum of the Q[8] $\cdot C_4 DP^{2+}$ complex in D_2O at 20 °C.

(Figure 5). Although ¹H NMR spectroscopy suggests that the alkyl chains of C_4DP^{2+} and $C_{10}DP^{2+}$ adopt a folding conformation when bound within the cavity of Q[8], the precise dimensional conformations of these two inclusion complexes are still unknown.



Figure 4. ¹H NMR spectra (400 MHz, D_2O) of $C_{10}DP^{2+}$ in the (a) absence and (b) presence of Q[8] (1.0 equiv.).



Figure 5. NOESY spectrum of the Q[8]·C $_{10}$ DP²⁺ complex in D₂O at 20 °C.

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To better understand the interaction between Q[8] and $C_n DP^{2+}$, we carried out UV titration experiments. As shown in Figure 6, the UV spectrum of $C_4 DP^{2+}$ has a peak with $\lambda_{\text{max}} = 259 \text{ nm}$. As the concentration of Q[8] is increased in a solution containing a fixed concentration of C₄DP²⁺, a slow decrease in absorbance is observed. According to the mol ratio method, the experimental data of the absorbance (A) vs. the ratio of the number of moles of Q[8] host to C₄DP²⁺ guest ($N_{O[8]}/N_{g1}$) can be fitted to a 1:1 host-guest inclusion model. For this 1:1 inclusion complex, the UV spectra data yield an equilibrium association constant of $1.87 \times 10^4 \text{ m}^{-1}$, which indicates that the inclusion complex is quite stable. In addition, continuous variation Job's plot was constructed (Figure 7), which shows that the UV spectrum data fit well to the same 1:1 stoichiometry of the host-guest inclusion complex.



Figure 6. (a) UV titration of $C_4 DP^{2+}$ dibromide with increasing concentration of Q[8] and (b) absorbance (A) vs. the ratio of the number of mol of host and guest $N_{Q[8]}/N_{g1}$.



Figure 7. Continuous variation Job's plot for Q[8] and the guest on the basis of UV spectra.

As depicted in Figure 8a, the interaction between Q[8] and $C_{10}DP^{2+}$ showed a similar UV spectrum. According to the experimental data and the mol ratio method mentioned above, we obtained the curve of absorbance (*A*) vs. the ratio of the number of mol of host and guest ($N_{Q[8]}/N_{g2}$; Figure 8b), which suggests the formation of a 1:1 host–guest inclusion complex between the Q[8] host and the $C_{10}DP^{2+}$ guest in aqueous solution. Again, the corresponding UV spectrum data were used to determine the equilibrium association constant value, which was found to be $1.46 \times 10^5 \text{ m}^{-1}$. Clearly, the UV behavior of these two inclusion complexes is consistent with the results obtained by ¹H NMR spectroscopy.



Figure 8. (a) UV titration of $C_{10}DP^{2+}$ dibromide with increasing concentrations of Q[8] and (b) absorbance (A) vs. the ratio of the number of mol of host and guest $N_{\text{Q[8]}}/N_{\text{g2}}$.

Description of Crystal Structures of the Two Inclusion Complexes

To confirm the exact dimensional conformation of the two Q[8]·C₄DP²⁺ and Q[8]·C₁₀DP²⁺ inclusion complexes, we determined their X-ray crystal structures. Slow evaporation of a hydrochloric acid aqueous solution containing a 1:1 mixture of C₄DP²⁺ dibromide and Q[8] at room temperature resulted in the formation of crystals of the type Q[8]·C₄DP²⁺, which crystallized in the space group $R\bar{3}$.^[13] The X-ray crystal structure of Q[8]·C₄DP²⁺ (Figure 9) clearly shows that the whole C₄DP²⁺ guest is buried deep inside the cavity of the Q[8] host to form an inclusion complex, as suggested by ¹H NMR and UV spectroscopy. Two included terminal pyridinium rings of the C₄DP²⁺ guest are neither aspectant nor parallel to each other, which may be



attributed to unfavorable electrostatic repulsions between them. It is noticeable that the butylidene chain of the C_4DP^{2+} guest adopts a folded conformation when bound within the Q[8] cavity. The shortest distance between the hydrogen atoms of the butylidene chain and the hydrogen atoms of the methylene of the Q[8] host is 3.46 Å. Most interestingly, the folding of the C₄DP²⁺ guest inside the cavity of Q[8], just as a contorted leaf sprig is confined to a small space, leads to severe ellipsoidal deformation of the Q[8] host. Thus, in order to accommodate the leaf-sprigshaped $C_4 DP^{2+}$ guest and to provide a better complementary shape, the Q[8] host undergoes severe ellipsoidal deformation spontaneously during the encapsulation process. In the crystal structure of $Q[8] \cdot C_4 DP^{2+}$, the opened molecular capsule is surrounded by water molecules and chloride and bromide anions, and they interact to form a complicated hydrogen-bonding network.



Figure 9. X-ray crystal structure of the inclusion complex Q[8]- C_4DP^{2+} . Solvate water molecules and anions are omitted for clarity.

At first glance, the inclusion complex $Q[8]\cdot C_4 DP^{2+}$ is structurally very similar to its counterpart $Q[8]\cdot C_{12}DA^{2+}$, a previously reported host–guest complex of a U-shaped bolaamphiphile embedded in $Q[8].^{[9c]}$ However, at least two significant differences exist between the inclusion complex $Q[8]\cdot C_4 DP^{2+}$ and its counterpart $Q[8]\cdot C_{12}DA^{2+}$. Firstly, in the inclusion complex $Q[8]\cdot C_4 DP^{2+}$, the leaf-sprig-shaped guest is entirely encapsulated into the cavity of Q[8]. The inclusion complex somewhat resembles an opened molecular capsule. In the host–guest complex $Q[8]\cdot C_{12}DA^{2+}$, two nitrogen atoms of the U-shaped guest lie above the mean oxygen plane of the portal of the Q[8] host. Secondly, the leaf-sprig-shaped guest of the inclusion complex $Q[8]\cdot C_4 DP^{2+}$ is accumbent, whereas the U-shaped guest of the host–guest complex $Q[8]\cdot C_{12}DA^{2+}$ is upstanding.

The crystal of the inclusion complex $Q[8] \cdot C_{10}DP^{2+}$ was obtained by the same method as that illustrated for the inclusion complex $Q[8] \cdot C_4DP^{2+}$. The structure of $Q[8] \cdot C_{10}DP^{2+}$ (Figure 10) clearly reveals that one pyridinium group and the whole alkyl chain of the $C_{10}DP^{2+}$ cationic guest were encapsulated into the hydrophobic cavity of the Q[8] host, whereas another pyridinium group resides outside the portal and is almost parallel with the mean oxygen plane of the portal. It should be noted that the decylidene chain of the $C_{10}DP^{2+}$ guest adopts a severely contorted conformation when bound within the Q[8] cavity. At the same time, the Q[8] host also experience an ellipsoidal deformation, which can be attributed to the internal pressure of the alkane. It is interesting that the decylidene chain in the $C_{10}DP^{2+}$ cation is so long, much longer than the butylidene chain in the C_4DP^{2+} cation, that the cavity of Q[8] is not large enough to accommodate the whole $C_{10}DP^{2+}$ cation is so long as though encapsulation of the alkyl chain favored over that of the aromatic group. It must be noted that there are many tetrahedral $[ZnCl_4]^{2-}$ counterions between these inclusion complexes, and they form a complicated hydrogen-bonding network.



Figure 10. X-ray crystal structure of the inclusion complex Q[8]· $C_{10}DP^{2+}$. Solvate water molecules and anions are omitted for clarity.

To better understand the formation of the Q[8]·C₄DP²⁺ and Q[8]·C₁₀DP²⁺ complexes, we carried out ITC experiments. The result is shown in Figure 11, indicating that the complexation of C₄DP²⁺ with Q[8] is driven by both enthalpy and entropy ($\Delta H^{\circ} = -26.222 \text{ kJ mol}^{-1}$, $T\Delta S^{\circ} =$ 11.742 kJ mol⁻¹), whereas the formation of the Q[8]· C₁₀DP²⁺ complex is almost exclusively enthalpy ($\Delta H^{\circ} =$ -39.753 kJ mol⁻¹, $T\Delta S^{\circ} = -0.339 \text{ kJ mol}^{-1}$) driven. Obvi-



Figure 11. (a) ITC profile of Q[8] with C₄DP²⁺ at 298.15 K: Δ*H*° = -26.222 kJ mol⁻¹, *T*Δ*S*° = 11.742 kJ mol⁻¹; (b) ITC profile of Q[8] with C₁₀DP²⁺ at 298.15 K: Δ*H*° = -39.753 kJ mol⁻¹, *T*Δ*S*° = -0.339 kJ mol⁻¹.

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ously, the contorted conformation of the alkyl chains in these inclusion complexes creates sterically unfavorable gauche interactions.^[13] However, their equilibrium association constant values, determined by UV titration experiments, suggest that the two inclusion complexes are highly stable. What causes the assemblies of the two inclusion complexes and what causes the high enthalpy? At least two driving forces can be identified. Strong charge-dipole interactions between the guest and the carbonyl oxygen atom at the portals of the Q[8] host appear to be the major driving force. In addition, the reciprocal conformational changes in the host-guest partners maximize hydrophobic interactions between the surfaces of the folded guest and the inner wall of the Q[8] host. Because the flexible alkyl chain can be compressed to fit within the Q[8] cavity and conform to its shape, it is not surprising that the aromatic group is preferentially squeezed out of the Q[8] cavity.

Conclusions

In summary, through ¹H NMR and UV spectroscopy, we have demonstrated that a Q[8] host can accommodate C_4DP^{2+} and $C_{10}DP^{2+}$ cationic guests to form highly stable 1:1 inclusion complexes. The X-ray crystal structures of these two inclusion complexes, $Q[8] \cdot C_4 DP^{2+}$ and $Q[8] \cdot C_4 DP^{2+}$ $C_{10}DP^{2+}$, clearly show that the alkyl chains of the cationic guests adopt contorted conformations, and internal strains are compensated by favorable host-guest interactions (including charge-dipole and hydrophobic interactions), when bound within the cavity of Q[8]. More importantly, we found that the Q[8] cavity can accommodate the alkyl chain and the aromatic group simultaneously. In comparison with the aromatic group, the alkyl chain is more favorably encapsulated into the Q[8] cavity. The main reason is that the alkyl chain is flexible and can be compressed to fit inside the Q[8] cavity.

Experimental Section

Materials and Methods: 1,4-Dibromobutane, 1,10-dibromodecane, pyridine, and solvents employed were used as supplied without further purification. Q[8] was synthesized according to literature methods.^[7] The NMR spectra were recorded at 20 °C with a Varian INOVA-400 spectrometer. UV absorption spectra of the host–guest complex were recorded with an Agilent 8453 spectrophotometer at room temperature.

Isothermal Titration Calorimetry: Microcalorimetric experiments were performed by using an isothermal titration calorimeter Nano ITC 2G (TA, USA). Each experiment consisted of 25 consecutive injections (10 μ L) of a guest solution (C₄DP²⁺ or C₁₀DP²⁺ dibromide: 1×10^{-3} M) into the microcalorimetric reaction cell (1 mL) charged with a solution of Q[8] (1×10^{-4} M). The heat of reaction was corrected for the heat of dilution of the guest solution determined in the separate experiments. All solutions were degassed prior to titration experiment by sonication. Computer simulations (curve fitting) were performed using the Nano ITC analysis software.

C₄DP²⁺ Dibromide: The guest was prepared by heating a mixture of 1,4-dibromobutane (1.0 equiv.), pyridine (3.0 equiv.), and polyethylene glycol (0.01 equiv.) at reflux for 4 h. The resulting precipitate was filtered, and the residue was collected, washed with diethyl ether, and air dried. The end product was obtained in 81.8% yield based on 1,4-dibromobutane. ¹H NMR (400 MHz,D₂O): $\delta = 8.74$ (d, J = 6 Hz, 4 H), 8.44 (t, J = 8 Hz, 2 H), 7.96 (t, J = 7 Hz, 4 H), 4.57 (s, 4 H), 2.01 (s, 4 H) ppm. MS: m/z (%) = 52 (58) [CH₃CH₂ + Na⁺], 79 (100) [C₅H₅N]⁺.

C₁₀**DP**²⁺ **Dibromide:** The guest was prepared by heating a mixture of 1,10-dibromodecane (1.0 equiv.), pyridine (3.0 equiv.), and polyethylene glycol (0.01 equiv.) at reflux for 4 h. The resulting precipitate was filtered, and the residue was collected, washed with diethyl ether, and air dried. The end product was obtained in 68.2% yield based on 1,10-dibromodecane. ¹H NMR (400 MHz, D₂O): $\delta = 8.68$ (d, J = 6 Hz, 4 H), 8.39 (t, J = 8 Hz, 2 H), 7.91 (t, J = 7 Hz, 4 H), 4.45 (t, J = 7 Hz, 4 H), 1.85 (t, J = 7 Hz, 4 H), 1.161 (s, 8 H), 1.099 (s, 4 H) ppm. MS: m/z (%) = 149.1 (100) [M/2⁺], 379.1 (10) [M + Br]⁻.

Q[8]·C₄DP²⁺: To a solution of C₄DP²⁺ dibromide (0.075 g, 0.20 mmol) dissolved in H₂O (35 mL) and HCl (6 M, 5 mL) was added Q[8] (0.27 g, 0.20 mmol). The mixture was stirred and heated at 50 °C for 10 min and then filtered. Slow evaporation of the filtrate over a period of five weeks provided rod-shaped colorless crystals.

Q[8]·C₁₀DP²⁺: To a solution of $C_{10}DP^{2+}$ dibromide (0.092 g, 0.20 mmol) and ZnCl₂ (0.014 g, 0.20 mmol) dissolved in H₂O (40 mL) and HCl (6 M, 5 mL) was added Q[8] (0.27 g, 0.20 mmol). The mixture was stirred and heated at 50 °C for 10 min and then filtered. Slow evaporation of the filtrate over a period of four weeks provided rod-shaped colorless crystals.

Single-Crystal X-ray Crystallography: Diffraction data for the complexes Q[8]·C₄DP²⁺ and Q[8]·C₁₀DP²⁺ were collected at 173 K with a Bruker SMART Apex-II CCD diffractometer using graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å). Absorption corrections were applied by using the multiscan program SADABS. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package,^[14] respectively. All non-hydrogen atoms were refined with anisotropic displacement parameters. The carbon-bound hydrogen atoms were introduced at calculated positions. All hydrogen atoms were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. For the complexes Q[8]·C₄DP²⁺ and Q[8]·C₁₀DP²⁺, no hydrogen atoms are given for all isolated water molecules, as it is difficult and unnecessary.

Crystal Data for Complex Q[8]·C₄DP²⁺: $(C_{48}H_{48}N_{32}O_{16})_6$ · $(C_{14}H_{18}N_2Cl_2)_6$ · $(H_2O)_{91}$ · $(KBr)_2$, $M_r = 11563.80$, hexagonal, space group $R\bar{3}$, a = 29.4138(12) Å, c = 52.9469(16) Å, V = 39671(3) Å³, Z = 3, $D_{calcd.} = 1.452$ g cm⁻³, F(000) = 18138, GoF = 1.187, $R_1 = 0.1090$ [$I > 2\sigma(I)$], $wR_2 = 0.3079$ (all data).

Crystal Data for Complex Q[8]·C₁₀**DP**²⁺: $(C_{48}H_{48}N_{32}O_{16})$ · $(C_{20}H_{30}N_2Cl_2)$ · $(H_2O)_5$ ·ZnCl₂, $M_r = 1924.89$, orthorhombic, space group *Pna2*₁, a = 21.793(6) Å, b = 18.812(5) Å, c = 20.983(6) Å, V = 8602(4) Å³, Z = 4, $D_{calcd.} = 1.486$ g cm⁻³, F(000) = 4000, GoF = 1.089, $R_1 = 0.0872$ [$I > 2\sigma(I)$], $wR_2 = 0.2407$ (all data).

CCDC-787351 (for Q[8]·C₄DP²⁺) and -798915 (for Q[8]·C₁₀DP²⁺) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



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