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Supramolecular Stabilization of $N_2H_7^+$

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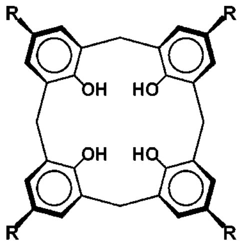
A major goal of supramolecular chemistry is the development of relatively small model systems that mimic processes of biological significance. Since such systems are generally easier to characterize than their biomolecular counterparts, they may afford valuable insight into the complex mechanisms that govern life-sustaining processes. Proton transfer is one of the most common and important chemical reactions in biology, particularly with regard to enzymatic function. In this context, our group has long been interested in the supramolecular stabilization of the oxonium ion. It has been found, for example, that certain crown ethers are effective in the stabilization of $H_5O_2^+$.[1] The $H_5O_2^+$ cation may be regarded as a transition state in the transfer of a proton from H_3O^+ to H_2O. Less studied, though of great importance, is the $N_2H_7^+$ cation, which may be analogously viewed as a transition state in the transfer of a proton from NH_4^+ to NH_3. This proton-bound ammonia dimer has, however, received considerable recent attention from theoreticians who have been interested in its overall structure, energetics, and charge distribution.[2] To our knowledge, the only previous X-ray structural studies of the $N_2H_7^+$ cation involved relatively simple ionic systems such as $[N_2H_7^+][CH_3COO^-]$ and $[N_2H_7^+][I^-]$. In the former study,[3] the structure is dominated by an extensive array of hydrogen bonds and hydrogen atom positions are inferred. In the latter study,[4] owing to high symmetry and disorder at room temperature, and uncertain phase transitions at low temperature, the hydrogen atoms could not be located unambiguously. As an extension of our ongoing studies of small-molecule cluster systems,[5] we report herein the stabilization of a discrete $N_2H_7^+$ cation in a supramolecular environment. In our structural investigation, where we exploit the rich inclusion chemistry of the calixarenes,[6] the important parameters involving the hydrogen atoms are all well resolved.



1: R = H
2: R = Bu^t

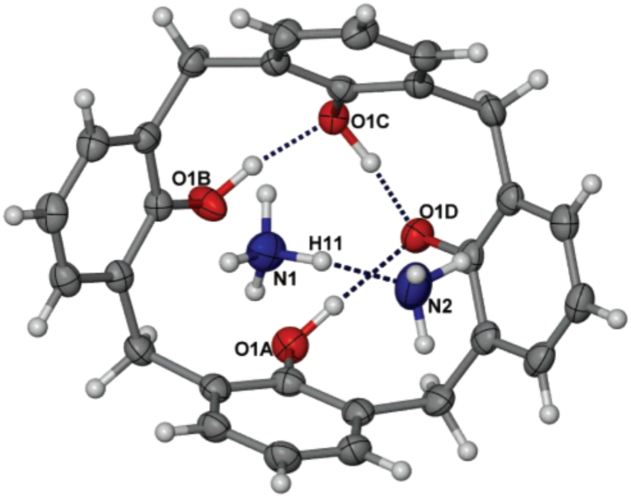


Figure 1. Thermal ellipsoid plot (50% probability) of the asymmetric unit showing the deprotonated calixarene with $N_2H_7^+$ inserted into its cavity. Hydrogen bonds are shown as fragmented cylinders.

A saturated solution of **1** in 5 mL of toluene was cooled on solid CO_2. To this solution was added 0.5 mL of NH_3 (condensed over solid CO_2) and two drops of 2-propanol. The resulting mixture was transferred to a thick-walled glass tube, sealed, and heated to 110 °C. Upon cooling to room temperature over a period of about 45 min, pale yellow, needlelike crystals were formed. A large crystal was selected and cut to a size suitable for structural analysis by single-crystal X-ray diffraction.[7] The asymmetric unit, shown in Figure 1, comprises one calix[4]arene$^-$ anion, one NH_4^+ cation, and one molecule of NH_3. The intensity data were of sufficient quality to reveal all of the hydrogen atoms, thus allowing complete resolution of the structure. One of the phenolic protons of the calixarene has been abstracted and the resulting negative charge on the molecule is counterbalanced by the NH_4^+ cation deeply embedded within its cavity. The cone conformation of the calixarene is maintained by the three O−H···O hydrogen bonds as shown. It is worthy of note that the O(1C)···O(1D) interaction is particularly strong (O···O = 2.486 Å).

A hydrogen bond is formed between the NH_4^+ cation and the NH_3 molecule situated at the rim of the calixarene cavity. The initial positions of the hydrogen atoms attached to both oxygen and nitrogen atoms were obtained from difference electron density maps. Their positional parameters were then refined with the application of soft X−H (X = O, N) bond length restraints. Although the lengths of the X−H vectors are almost certainly slightly underestimated, their directional components can be considered to be quite reliable. It is therefore more appropriate to describe the N−H···N hydrogen bond in terms of the H−N···N angle (3.83°) and the N···N separation (2.765 Å). These parameters indicate that the N−H···N hydrogen bond is both strong and relatively linear.

The extended structure is not dominated by an intricate array of hydrogen bonds as might be expected, considering the number of potential donor and acceptor atoms. The only other hydrogen bond not as yet mentioned is one formed between the ammonium nitrogen atom N(1), situated in the calixarene cavity, and the deprotonated oxygen atom O(1D) of an adjacent calixarene (N···O = 2.786 Å, ∠H−N···O = 1.82°). This type of "second sphere" interaction, shown in Figure 2, results in the formation of a ribbonlike structure

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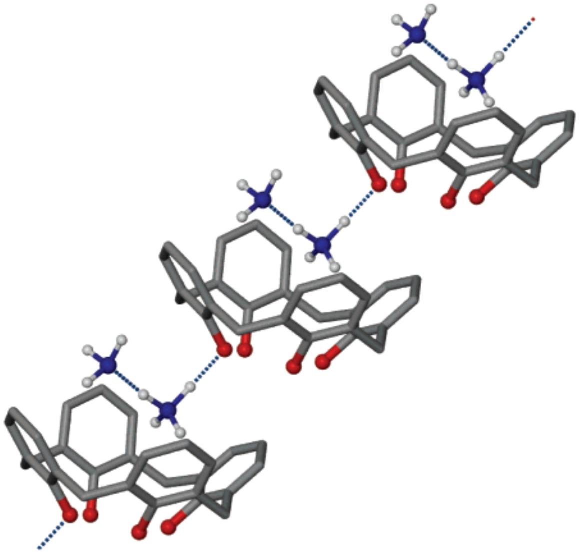

Figure 2. Perspective view showing part of the one-dimensional strand composed of the $\mathbf{1}^-$ and guest $N_2H_7^+$ ions. The NH_4^+ moiety of the latter hydrogen bonds to the deprotonated phenolic oxygen atom of the neighboring calixarene within the strand. Calixarene hydrogen atoms are omitted for clarity.

that propagates by translation of the asymmetric unit along the crystallographic *b* axis.

A detailed analysis of the structure reveals that the ammonium cation does not interact strongly with its host calixarene, i.e., there is no structural evidence for cation−π or N−H···π interactions. It therefore appears that the ammonium ion nestles snugly into the calixarene cavity by making only van der Waals contact with the latter. That the ammonium ion is well-ordered is easily attributed to the two intermolecular hydrogen bonds that are described above, and shown in Figure 2. These interactions lock the orientation of the NH_4^+ in the structure and, together with van der Waals interactions, also its position. However, it is not clear why the three ammonia hydrogen atoms should be similarly ordered since they do not participate in either hydrogen bonding or N−H···π interactions.

More importantly, it is also not clear why protonation occurs, seemingly exclusively, at the nitrogen atom situated deepest within the calixarene cavity. Clearly the abstracted proton could reside at two alternative positions without altering the overall packing motif of the structure. The proton in question could feasibly reside on the ammonia molecule, or at its original source, the now deprotonated phenolic oxygen atom. Indeed, even a disordered model with the proton shared between all three potential parent atoms would be tenable. Owing to the absence of interactions other than those already discussed, two possible scenarios present themselves to account for the observed location of the proton: (a) that its situation deep within the calixarene cavity somehow stabilizes the NH_4^+ moiety and (b) that an electrostatic interaction between the deprotonated phenolic oxygen atom and NH_4^+ dictates the most stable destination of the abstracted proton.

In an attempt to address this question, we employed the same preparative method described above, substituting **2** for **1**. Our reasoning was that, given an analogous complex, steric factors would preclude direct interaction of an ammonium cation situated deep within the calixarene cavity with the deprotonated oxygen atom of a neighboring macrocycle. The resulting structure (to be described in more detail elsewhere) contains a $N_4H_{13}^+$ cluster that is partially inserted into the calixarene cavity with an ammonia molecule most deeply embedded. Notwithstanding the bulky **R** group and the addition of two extra ammonia molecules, the packing motif of $[N_4H_{13}^+][\mathbf{2}^-]$ is quite similar to that of $[N_2H_7^+][\mathbf{1}^-]$. Once again we note that, in the former, a phenolic oxygen atom has relinquished its proton to a single ammonia molecule to which it is then hydrogen bonded. Furthermore, the resulting ammonium ion is situated above the calixarene cavity and donates its remaining three hydrogen atoms to hydrogen bonds formed with the three ammonia molecules. None of these ammonia molecules engage in further hydrogen bonding and there is no evidence for cation−π or N−H···π interactions in the structure. Both of these model systems are therefore consistent with hypothesis (b).

We have described a simple model system that exemplifies proton transfer in a largely hydrophobic environment. We show that the overriding preference for the ammonium cation is to associate directly with the deprotonated phenolic oxygen atom. This suggests that electrostatic interactions may play a key role in the stabilization of intermediate species in the initial stages of complex multistep proton-transfer processes such as those found in biological systems.[8]

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Supporting Information Available: Crystallographic information file (CIF) and thermal ellipsoid plots (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Crystal data for $[N_2H_7^+][\mathbf{1}^-]$: $C_{28}H_{30}N_2O_4$, $M = 458.54$, pale yellow needlelike crystal, $0.35 \times 0.25 \times 0.20$ mm^3, monoclinic, $P2_1/c$ (No. 14), $a = 7.4788(10)$ Å, $b = 18.612(3)$ Å,, $c = 16.626(2)$ Å, $\beta = 98.998(3)°$, $V = 2285.8(5)$ Å^3, $Z = 4$, $D_{calcd} = 1.332$ g cm^{-3}, $F(000) = 976$, λ(Mo Kα) = 0.71073 Å, $T = 173$ K, reflections collected/unique 14193/5034 (R(int) = 0.0401). Final GooF = 1.024, $R1 = 0.0476$, $wR2 = 0.1035$, R indices based on 3409 reflections with $I > 2\sigma(I)$ (refinement on F^2), 347 parameters, 10 restraints, Lp and absorption corrections applied, $\mu = 0.089$ mm^{-1}.
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