ChemComm
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ESI-FTICR investigation of triethylammonium ion-driven resorcin[4]arene dimer formation and structure

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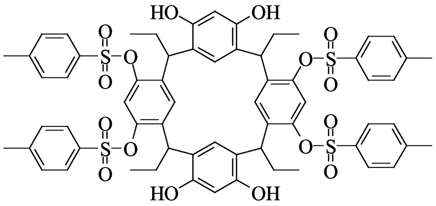
Received (in Cambridge, UK) 11th March 2002, Accepted 11th April 2002
First published as an Advance Article on the web 24th April 2002

In the course of mass spectrometric measurements a self-assembled hydrogen bonded resorcinarene dimer was observed, the formation of which was driven by the binding of triethylammonium ion as a guest and as an ionic label.

As a result of the biological importance of the weak interactions in naturally occurring macromolecules, the self-association and non-covalent bonding in synthetic compounds has been widely investigated in recent years in the field of supramolecular chemistry. Resorcinarenes and their derivatives[1] have turned out to be promising compounds in the study of self-assembling inclusion compounds where interactions are based on weak forces such as hydrogen bonding, π–π interactions and cation–π interactions.[2–5] Most recently, some interesting solid state structures of resorcinarene dimers and inclusion assemblies investigated by X-ray crystallography[6,7] have been reported. With the improvement in soft ionization techniques, mass spectrometry[8–10] has also proved to be a convenient method for application in studies of non-covalently bound assemblies. We have utilized electrospray mass spectrometry in an investigation of the gas phase structure of the resorcinarene tetrasulfonate **1**† dimer formed *via* triethylammonium ion **2** attachment. The formation of a non-covalently bonded dimeric system is often considered to be a guest-driven process and for that reason our choice was to use an ionic guest-carrying positive charge to ionize the dimers. The formation of the dimer with a triethylammonium ion was found to be a specific process which is strongly affected by the size and structure of the used alkylammonium ion, while in the measurements performed with some other alkylammonium ions, metal ions or a proton attachment, the formation of the corresponding dimer was minor in comparison with the dimer formed with the triethylammonium ion. Various different mass spectrometric methods were used to obtain information about the structure of the dimeric ion formed. These included collision-induced dissociation (CID), differentiation in a solvent medium, and gas phase ion molecule reactions.



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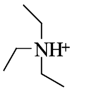

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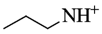

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In an acetonitrile solution the measured ESI-mass spectrum shows the $[\mathbf{1}@\mathbf{2}]^+$ ion as a base peak (Fig. 1). The next abundant ion is the easily formed $[\mathbf{1}\cdot\mathbf{1}@\mathbf{2}]^+$ ion. Resorcinarene **1** also forms monomeric and dimeric sodium and potassium ion adducts, which can be seen before the triethylammonium adducts in a mass spectrum. These ions arise from the impurities in the system.

Given the hypothesis that the dimeric structure formed would have a hydrogen-bonded nature, the evidence supporting this hypothesis was obtained from a measurement in which the solvent medium that was used shifted in a more polar direction (Table 1).

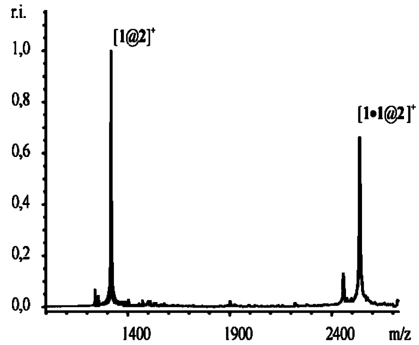

Fig. 1 ESI-Mass spectra of resorcin[4]arene **1** (4.1 μM) and Et_3NHCl (12.3 μM) recorded in an acetonitrile solution containing 0.1% of methanol and 0.5% of chloroform.

After the addition of even a minor amount of water to the acetonitrile solvent medium, the intensity of the dimeric ion peak decreased greatly to less than half its original intensity. At the same time, the intensity of the peak of the monomeric ion $[\mathbf{1}@\mathbf{2}]^+$ remained almost unchanged. This distinction between the peaks of the monomeric and dimeric ions can be considered to have been caused by the hydrogen bonds involved in the formation of the dimeric ion, and when a highly polar solvent like water is added to the measurement solution, the hydrogen bonds essential for the stabilized structure become impossible.

Probably the most remarkable finding concerning the structure of the dimeric ion was obtained from the gas phase ion molecule reactions with a neutral *n*-propylamine. The isolated dimeric ion $[\mathbf{1}\cdot\mathbf{1}@\mathbf{2}]^+$ was able to change its guest triethylammonium ion **2** into a propylammonium ion **3** formed from the neutral propylamine present in the cell, and the peak corresponding to the $[\mathbf{1}\cdot\mathbf{1}@\mathbf{3}]^+$ ion was found in the spectra in significantly short reaction times (Fig. 2).

The finding strongly indicates that it is not possible for the guest ion to be bound in the middle of the dimeric structure, which is rather similar to a closed capsule, existing between the two resorcinarene molecules. If that were the case, it would require a dissociation of the dimeric structure, a triethylammonium ion **2** interaction with the propylamine, a proton transfer from the triethylammonium ion **2** to the propylamine, and

Table 1 Effects of water addition to dimeric ion formation

Addition of water H_2O (%)[b]	$[\mathbf{1}\cdot\mathbf{1}@\mathbf{2}]^+$ intensity[a]	$[\mathbf{1}\cdot\mathbf{1}@\mathbf{2}]^+:[\mathbf{1}@\mathbf{2}]^+$ ratio[a]
0	0.48	0.082
1	0.22	0.047
5	0.07	0.023
10	0.10	0.014

[a] Calculated from the average value from repetition measurements. [b] All the solutions contain 0.1% methanol and 0.5% chloroform.

DOI: 10.1039/b202404g

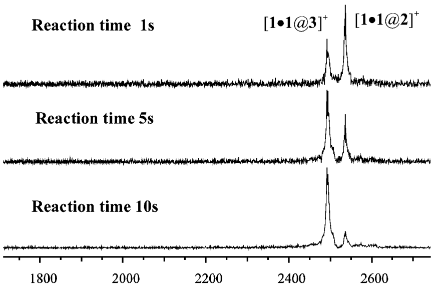

Fig. 2 Gas phase reaction of the $[\mathbf{1}{\cdot}\mathbf{1}@\mathbf{2}]^+$ ion with the neutral propylamine.

finally the inclusion of the propylammonium ion **3** formed and reformation of the dimeric structure and the connecting hydrogen bonds. In energetic and entropic terms, this would obviously not be a very favourable process.

In CID measurements, where the dimeric ion peak corresponding to the $[\mathbf{1}{\cdot}\mathbf{1}@\mathbf{2}]^+$ ion was isolated, its dissociation to the corresponding monomeric ion $[\mathbf{1}@\mathbf{2}]^+$ was clearly observed. The increasing collision energy caused a dissociation of the monomeric ion formed, and the peak corresponding to the free guest ion $[\mathbf{2}]^+$ can be observed in the spectra (Fig. 3). The results gathered from the CID measurements support the results from ion molecule reactions.

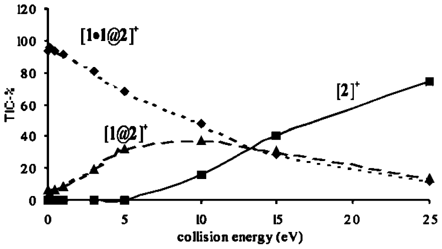

Fig. 3 Collision-induced dissociation of the $[\mathbf{1}{\cdot}\mathbf{1}@\mathbf{2}]^+$ dimer. Percentage of the total ion current (TIC %) as a function of collision energy.

In order to support the experimental results accumulated from the mass spectrometric measurements, we also added a theoretical aspect to the structure of the monomer. Starting from a solid-state structure,[7] an *ab initio* geometry optimization using Gaussian98[11] was completed with the host monomer without the guest ion. The calculation yielded a structure which can be used in building a dimer (Fig. 4). In order to ensure that the conformation obtained was the most favourable in energy terms, optimizations were also done, starting from alternative conformations. Unfortunately, some of the calculations were unsuccessful owing to the large size of the molecule and to the polar effect, which was caused by the sulfurs. It was found from the completed calculations that the conformation obtained commencing from the solid-state structure possessed the lowest energy.

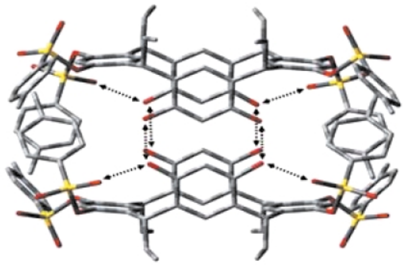

Fig. 4 Dimer structure (C_2) build of geometry-optimized monomers (C_s). Hydrogens not shown. Arrows indicate hydrogen-bonding sites.

The structure has four potential hydrogen-bonding sites between the monomers. The presence of the hydrogen bonds had already been observed in the mass spectrometric measurements. Tosylium substituents of the resorcin[4]arene form possible binding sites for a guest ion. The binding of a guest ion would be a consequence of hydrogen bonding between the S=O group of the host and the NH group of the guest ion. An additional favourable interaction would arise from positive CH–π attractions between aromatic rings of the hosts substituents and alkyl chains of the guest ion. In this position the guest would have a location where it can easily interact with the species present in the gas phase. This accords strongly with the results obtained from the ion molecule reactions with neutral propylamine.

The above mentioned individual measurements give us relevant information of the structure of the dimer formed and the forces involved in the interaction. In conclusion, we are able to state that the features of guest-driven dimerization and the structure of this kind of dimer can be studied by means of mass spectrometric data.

Dr Alexander Shivanyuk is thanked for synthesizing the resorcin[4]arenes used in this study. Funding by the Academy of Finland, Grant 68194, is gratefully acknowledged.

Notes and references

† Experimental: mass spectrometric measurements were performed using a Bruker BioApex 47e mass spectrometer equipped with a 4.7 T bore superconducting magnet and electrospray ionization source (Analytica of Branford). Resorcin[4]arene **1** was dissolved in $CHCl_3$. Guest **2** as a chloride was first dissolved in methanol and then diluted in acetonitrile. The sample was prepared in acetonitrile with a concentration of 4.1 μM and 1 : 3 host : guest ratio. The sample was induced through an on-axis sprayer with a flow rate of 60 $\mu l\ h^{-1}$ and N_2 (225 °C) as a carrier gas. In collision-induced dissociation measurements Ar was used as a collision gas with a CHEF procedure. In ion-molecule reactions propylamine pressure of 5×10^{-8} Torr was used as a reagent in the cell.

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