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N-Alkyl Ammonium Resorcinarene Polyiodides

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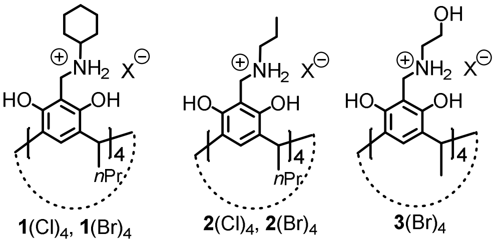
Four *N*-alkyl ammonium resorcinarene halides incorporating polyiodides were obtained and structurally analyzed by single crystal X-ray crystallography. Unexpected formation of triiodides and the pentaiodide anions in these structures were proposed as the result of the heterolytic dissociation of molecular iodine I_2 in the presence of electron donors in the *N*-alkyl ammonium resorcinarene halide system, from which the I^- further binds one or two molecular I_2 molecules resulting to I_3^- or I_5^- species, respectively.

Halogen bonding,[1] as a non-covalent interaction is analogous to hydrogen bonding in both strength and directionality. Halogen bonding is widely used in the design and construction of small and large supramolecular assemblies with novel applications in crystal engineering, material science and biological systems.[2-8]s Within the broad area of halogen bonding, polyhalides assembled by halogen···halogen interactions are particularly interesting. Charge transfers between the halides and the molecular halogen stabilizing the polyhalide species and endowing the final polyhalides have potential electronic and photophysical properties.[9-11]

The chemistry of *N*-alkyl ammonium resorcinarene halides (NARXs) as receptors and supramolecular synthons was recently developed.[12] The bowl-shaped C_{4v} symmetry of the resorcinarene core in the NARXs is maintained by intramolecular hydrogen bonds between adjacent hydroxyl groups. The large organic salt molecules feature hydrogen bonded cyclic geometry with the aromatic groups providing the pre-organized deep electron-rich interior cavities. The halides in the circular hydrogen bond seam $(\cdots NArRH_2^+\cdots X^-\cdots)_4$ with their hydrogen and halogen bond acceptor ability introduces the possibility of extending the cavity size in the presence of suitable donors.[13] This broadens the ability of the NARXs to act as receptors for a larger variety of guest molecules as well as increasing their potential as synthons for larger supramolecular networks and assemblies.[13] Molecular iodine I_2 as a halogen bond donor was successfully used to construct a halogen-bonded dimeric capsule with a NARX, where $[Cl\cdots I\text{-}I\cdots Cl]^{2-}$ species was detected in the solid state as the main factor linking the two capsule halves.[9] To further investigate the nucleophilicity of the halides in NARXs towards I_2, in this contribution, I_2 was introduced to four NARXs: *N*-cyclohexyl ammonium resorcinarene chloride **1**(Cl_4) and bromide **1**(Br_4); *N*-propyl ammonium resorcinarene chloride **2**(Cl_4) and bromide **2**(Br_4), and the water soluble *N*-ethanol ammonium resorcinarene bromide **3**(Br_4). Surprisingly, triiodide anions were observed from the mixture of I_2 with **1**(Cl_4), **1**(Br_4) and **2**(Br_4); while the rare linear penta-iodide anion was detected in the system containing I_2 and **3**(Br_4) in MeOH.



Scheme 1. The *N*-alkyl ammonium resorcinarene halides (NARXs) **1**(X_4)-**3**(X_4).

Crystals of 1,4-dioxane@**1**($Cl_3\bullet I_3$) were obtained by slow evaporation of methanol solution of 1:2 molar mixture of **1**(Cl_4) and I_2 in the presence of 1,4-dioxane. Unlike in the reported capsular assembly between an analogue of **1**(Cl_4) with shorter lower rim in which three ordered 1,4-dioxane molecules were entrapped in the cavity with the species $[Cl\cdots I\text{–}I\cdots Cl]^{2-}$ stabilizing the two capsule halves, in the new assembly,

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Electronic Supplementary Information (ESI) available: [synthesis and details of crystallographic study]. See DOI: 10.1039/x0xx00000x a stable triiodide I_3^- anion was formed, which replaced one of the chlorides from the cation-anion seam. The triiodide does not form part of the cation-anion hydrogen-bonded seam, instead it is located above the resorcinarene skeleton. The bowl-shape of the resorcinarene frame is still preserved with one 1,4-dioxane molecule trapped in the cavity via two N-H···O hydrogen bonds, although only two chlorides are positioned in the cation-anion seam. However, due to the steric hindrance between the large I_3^- and the four *N*-cyclohexyl ammonium arms, one of the arms rotates 180° with the ammonium hydrogens pointing outwards and is hydrogen-bonded to one additional *exo*-1,4-dioxane molecule (Fig. 1A). The *exo*-cavity-1,4-dioxane molecule simultaneously hydrogen bonds to two adjacent resorcinarene molecules forming a dimer [1,4-dioxane@**1**(Cl_3•I_3)]•1,4-dioxane•[1,4-dioxane@**1**(Cl_3•I_3)] (Fig. 1C). In addition to the linkage of 1,4-dioxane, the dimer is also connected by the third Cl^- and a disordered water molecule via multipole hydrogen bonds (Fig. 1C). Along the crystallographic *b*-axis, the resorcinarene framework is arranged in a head-to-tail manner, with the I_3^- squeezing in the space between the upper rim of one resorcinarene and the lower rim of another. This kind of arrangement causes two of the four propyl groups at the lower rim to fold in gauche conformation. Intermolecular O-H···O hydrogen bonds are responsible for the structural extension along the *a*-axis (Fig. S1).

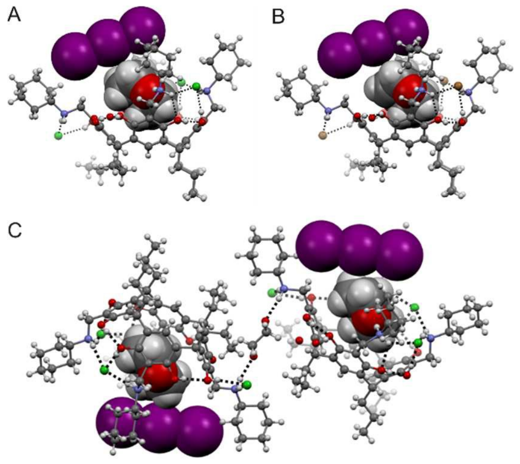
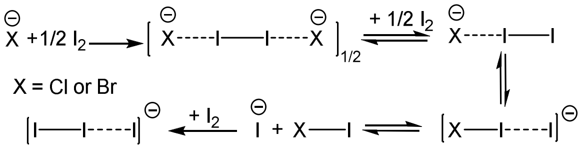


Fig. 1. The structural unit in **1**(Cl_3•I_3) (A) and **1**(Br_3•I_3) (B), as well as the dimer [1,4-dioxane@**1**(Cl_3•I_3)]•1,4-dioxane•[1,4-dioxane@**1**(Cl_3•I_3)] (C).

The formation of the triiodide anion in this structure 1,4-dioxane@**1**(Cl_3•I_3) is unexpected. We propose that it is the result of the heterolytic dissociation of I_2 in the presence of electron donor of either Br^- or the solvent methanol molecule. The produced I^-, further interacts with one I_2 molecule giving rise to the I_3^- anion (Scheme 2). It is noteworthy that the difference between triiodide and chlorodiiodide is evident from the difference Fourier map, therefore the species of I_3^- can undoubtedly be confirmed by single crystal X-ray analysis.

To further investigate this process, we extended the study to **1**(Br_4), an analogue of **1**(Cl_4), and with the more flexible *N*-propyl group **2**(Cl_4) and **2**(Br_4). Single crystal analysis of **1**(Br_4) which is the bromide analogue of **1**(Cl_4), reveal an isomorphic structure 1,4-dioxane@**1**(Br_3•I_3). The single crystal were obtained by slowly evaporating the methanol solvent from the 1:2 mixture of **1**(Br_4) and I_2 under the same conditions as for **1**(Cl_4) (Fig. 1B). Unfortunately, we could not isolate any suitable single crystals from the reaction of **2**(Cl_4) with I_2. However, the bromide analogue **2**(Br_4) resulted in a self-included dimer with six bromides and two triiodides.



Scheme 2. The proposed process of the formation of triiodide in the system.

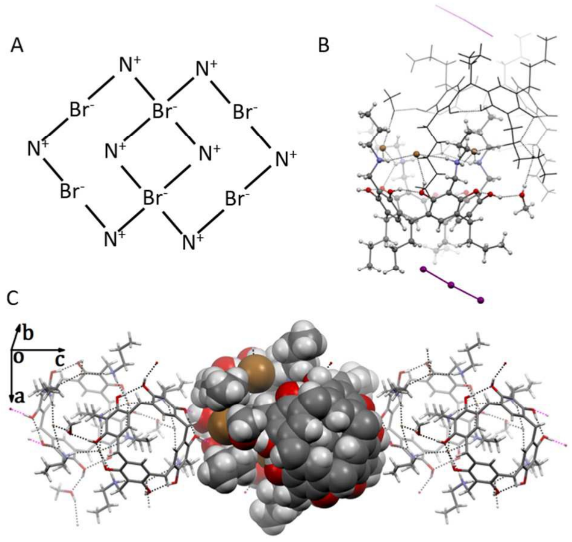


Fig. 2. (A) Schematic representation of the cation-anion hydrogen bond pattern in the self-included dimer. (B) The dimeric structure of [**2**(Br_3•$\mathbf{I_3}$)]$_2$; to make it clear, the second NARX were drawn in black lines. (C) The hydrogen-bonded 1D polymer of dimers along the *c* direction with the dimer in the middle in CPK mode. The inter-dimeric hydrogen bonds were shown in violet dashed lines and other HBs are in black. The lower propyl groups and the triiodides were omitted for clarity.

The formation of the self-included dimer is not unusual. We have previously reported a self-included dimeric assembly of other *N*-propyl ammonium halides.[12a,14] Usually, one of the *N*-propyl ammonium arms from one NARX resides in the cavity of the second molecule with the help of six halide anions, which further bind the two resorcinarene dimer halves via multiple inter- and intramolecular hydrogen bonds. In this structure, for each resorcinarene cation, four Br^- anions are situated between the ammonium arms, among which, two are shared by the two receptors with four NH···Br^- hydrogen bonds for each Br^- as depicted in the schematic of Fig. 2A. The other four Br^- anions are all involved in one OH···Br and two NH···Br interactions. The dimer formally shows two positive charges and as a result, two triiodide anions appear in between the four propyl groups at the lower rim. It is worth noting that although 1,4-dioxane was used in the crystal growth process, it was not found in the $[\mathbf{2}(Br_3{\bullet}I_3)]_2$ assembly. The stability of the self-included dimer overrides the possible host-guest binding process of 1,4-dioxane. The formation of such a dimer involves six of the eight anions thus releasing the two "free" anions to be involved in the triiodide formation.

In the reaction of NARX $\mathbf{3}(Br_4)$ with I_2 in methanol, we surprisingly found a very rare linear I_5^- anion in the crystal structure. The water soluble NARX $\mathbf{3}(Br_4)$ was synthesized according to recently reported procedures.[15] Therein, the chloride analogues were shown to bind a series of alkanes, haloalkanes and arenes in water via hydrophobic interactions. The crystal structure of one chloride analogue showed a dimeric capsule with two 1,4-dioxane molecules trapped within the interior cavity similar to the Rebek's classical hydrogen bonded cylindrical capsule.[16] Here, the dimeric capsule $[\mathbf{3}(Br_{3.5})]_2{\bullet}I_5$ is formed in which the two salt molecules are arranged in a staggered pair. The two capsule halves are held together by eight OH···Br intermolecular hydrogen bonds. Due to the high symmetry of the structure, each Br^- anion has 0.9 occupancy with the whole capsule bearing one positive charge, which is counter-balanced by one I_5^- anion. Highly disordered solvent molecules were observed in the cavity of the capsule. In general the formation of the I_5^- anion can be regarded to be an adduct of the I_3^- with an additional I_2, or I^- and two I_2, molecules. Structures of I_5^- anion have been intensively reported,[10] however, in most cases they display a "V" or "L" shaped geometry. The linear I_5^- species is rarely reported.[17,18] In $[\mathbf{3}(Br_{3.5})]_2{\bullet}I_5$, the formally centrosymmetric I_5^- is considered as a halogen-bonded adduct of I^- and two I_2, with the central I···I···I halogen bond distance of 3.191 Å (x 2, R_{XB}=0.81)[19] and the terminal I-I length of 2.841 Å (x 2). Strong charge transfer interaction occurs from the I_2 and the central I^- anion, elongating the terminal I-I bonds. The linear geometry of the I_5^- here is also due to the molecular packing in the crystal lattice (Fig. 3B).

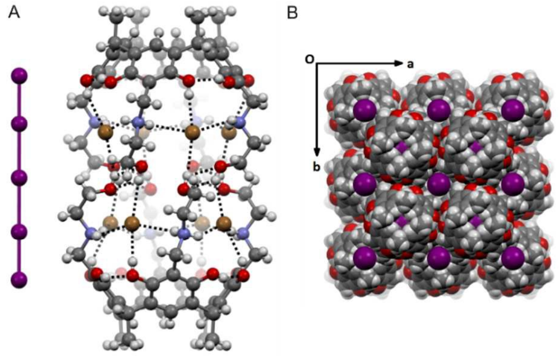


Fig. 3. The hydrogen bonded dimeric capsule in $[\mathbf{3}(Br_{3.5})]_2{\bullet}I_5$ (A) and its solid state packing in CPK mode (B).

Conclusions

In summary, we present four $NARX_3I_n$ (n = 3 or 5 and X = Cl or Br) compounds, three triiodide and one with a linear penta-iodide anion. Single crystal X-ray diffraction study confirms that in two *N*-cyclohexyl and one *N*-propyl NARX compounds triiodide anion is formed which then replaces one of the original halides. The *N*-ethanol NARX $\mathbf{3}(Br_4)$ resulted in a rare linear penta-iodide entrapped within the crystal lattice. Formation of the polyiodides in this system is proposed to be as a result of the heterolytic dissociation of I_2 in the presence of NARX halide anions. The electron donor properties of the NARX halides and/or the solvent methanol molecule is probably responsible for this process. The penta-iodide is described as a halogen bonded adduct of I^- and two I_2. In addition to their anion exchange properties, this study further highlights that the *N*-alkyl ammonium resorcinarene halides are versatile molecular building blocks for the design and construction of larger supramolecular assemblies.

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References

1. G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati and K. Rissanen, *Pure Appl. Chem.,* 2013, **85**, 1711–1713.
2. E. Corradi, S. C. Meille, M. T. Messina, P. Metrangolo and G. Resnati, *Angew. Chem. Int. Ed.*, 2000, **39**, 1782-1786.
3. M. Erdelyi, *Chem. Soc. Rev.*, 2012, **41**, 3547-3557.
4. T. M. Beale, M. G. Chudzinski, M. G. Sawar and M. S. Taylor, *Chem. Soc. Rev.,* 2013, **42**, 1667-1680.
5. M. R. Scholfield, C. M. Vander Zanden, M. Carter and P. S. Ho, *Protein Sci.*, 2013, **22**, 139-152.
6. L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney and P. D. Beer, *Chem. Rev.*, 2015, **115**, 7118-7195.
7. G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati and G. Terraneo, *Chem. Rev.*, 2016, **116**, 2478-2601.
8. A. Bertolani, L. Pirrie, L. Stefan, N. Houbenov, J. S. Haataja, L. Catalano, G. Terraneo, G. Giancane, L. Valli, R. Milani, O. Ikkala, G. Resnati and P. Metrangolo, *Nat. Commun.,* 2015, **6**, 754
9. N. K. Beyeh, F. Pan and K. Rissanen, *Angew. Chem. Int. Ed.*, 2015, **54**, 7303-7307.
10. P. H. Svensson and L. Kloo, *Chem. Rev.*, 2003, **103**, 1649-1684.
11. C. Walbaum, M. Richter, U. Sachs, I. Pantenburg, S. Riedel, A. Mudring and G. Meyer, *Angew. Chem. Int. Ed.*, 2013, **52**, 12732-12735.
12. (a) N. K. Beyeh, M. Cetina, M. Lofman, M. Luostarinen, A. Shivanyuk and K. Rissanen, *Supramol. Chem.*, 2010, **22**, 737-750; (b) N. K. Beyeh, A. Ala-Korpi, F. Pan, H. H. Jo, E. V. Anslyn and K. Rissanen, *Chem. Eur. J.*, 2015, **21**, 9556-9562; (c) F. Pan, N. K. Beyeh and K. Rissanen, *RSC Adv.*, 2015, **5**, 57912-57916; (d) F. Pan, N. K. Beyeh, S. Bertella and K. Rissanen, *Chem. Asian J.*, 2016, **11**, 782-788.

13. (a) F. Pan, N. K. Beyeh and K. Rissanen, *J. Am. Chem. Soc.*, 2015, **137**, 10406-10413; (b) N. K. Beyeh, A. Valkonen, S. Bhowmik, F. Pan and K. Rissanen, *Org. Chem. Front.*, 2015, **2**, 340-345; (c) N. K. Beyeh, F. Pan, S. Bhowmik, T. Makela, R. H. A. Ras and K. Rissanen, *Chem. Eur. J.*, 2016, **22**, 1355-1361.
14. N. K. Beyeh, A. Ala-Korpi, M. Cetina, A. Valkonen and K. Rissanen, *Chem. Eur. J.*, 2014, **20**, 15144-15150.
15. N. K. Beyeh, F. Pan, R. H. A. Ras, *Asian J. Org. Chem.*, 2016, DOI: 10.1002/ajoc.201600187R1.
16. T. Amaya and J. J. Rebek, *J. Am. Chem. Soc.*, 2004, **126**, 14149-14156.
17. T. Akutagawa, Y. Abe, Y. Nezu, T. Nakamura, M. Kataoka, A. Yamanaka, K. Inoue, T. Inabe, C. A. Christensen and J. Becher, *Inorg. Chem.*, 1998, **37**, 2330-2331.
18. T.-Y. Dong, H.-M. Lin, M.-Y. Hwang, T.-Y. Lee, L.-H. Tseng, S.-M. Peng and G. Lee, *J. Organomet. Chem.*, 1991, **414**, 227-244.
19. (a) J. P. M. Lommerse, A. J. Stone, R. Taylor, F. H. J. Allen, *J. Am. Chem. Soc.*, 1996, **118**, 3108-3116; (b) L. Brammer, E. A. Bruton, P. Sherwood, *Cryst. Growth Des.*, 2001, **1**, 277-290. (c) F. Zordan, L. Brammer, L. P. Sherwood, *J. Am. Chem. Soc.*, 2005, **127**, 5979-5989.

N-Alkyl Ammonium Resorcinarene Polyiodides

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Heterolytic dissociation of molecular iodine I_2 led to the unexpected formation of triiodides and linear pentaiodide in the solid state when four *N*-alkyl ammonium resorcinarene halides are reacted with molecular iodine I_2.