Synthesis, Structure and Spectroscopy of a New Polyiodide in the α,ω-Diazaniumalkane Iodide/Iodine System

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The reaction of 1,4-diaminobutane with hydroiodic acid in the presence of iodine yields the title compound 1,4-diazaniumbutane tetraiodide, $C_4H_{14}N_2I_4$ (**1**). The title compound has been structurally characterized by crystallographic and spectroscopic methods (Raman and IR). **1** is built up by centrosymmetric 1,4-diazaniumbutane cations in *all-trans* conformation and linear I_4^{2-} anions. Both, cations and anions are located on centers of inversion $(2/m)$ in the monoclinic space group $C2/m$. The hydrogen bonds between the azanium groups and the terminal iodine atoms of the I_4^{2-} anions lead to a three-dimensional framework. The structural parameters of the tetraiodide anion, derived from X-ray crystallographic data are in excellent agreement with the results from Raman spectroscopy. The Raman and IR data for the analogous α,ω-diazaniumalkane tetraiodide salts $(H_3N\text{-}(CH_2)_6\text{-}NH_3)I_4$ (**2**) and $(H_3N\text{-}(CH_2)_7\text{-}NH_3)I_4$ (**3**) are reported, and the structures of **1**, **2** and **3** are compared.

Key words: Polyiodide, α,ω-Diazaniumalkane, Tetraiodide, Crystal Structure, Raman Spectroscopy

Introduction

Hundreds of polyiodides have been characterized by spectroscopic and crystallographic methods in the last decades. Polyiodides are defined as extended parts of salt structures that fulfill the general formula $I_{2m+n}{}^{n-}$ ($n = 1-4$, $m =$ integer) [1]. They are built from I^-, $I_3{}^-$ and I_2 units and are known for their strong tendency to concatenate to extended motifs by halogen bonding [2]. There is also a general interest in the azaniumalkane iodide/triiodide systems as they are known to modify the redox chemistry in dye-sensitized solar cells (DSSC) [3]. Furthermore, polyiodide chains conduct the electric current in the solid state by a Grotthuss-like mechanism [4]. Higher polyiodides can therefore be considered as a snapshot of this phenomenon. The concept of *crystal engineering* gave the chase for new, tailored polyiodides a significant boost in the last years [5]. Several groups have synthesized new polyiodide-containing compounds using stick-shaped cationic tectons [6]. For some classes of tectons it has been shown that the majority of structures of the polyiodides constructed fit with the lengths and shapes of the templates used [7]. This selective and robust synthetic protocol for solid polyiodides is now termed *dimensional caging* [7a]. Also the caging of new polyiodides in organo-macrocycles [8] and of iodine in metal organic frameworks [9] have recently been reported. Especially the semi-flexible cationic α,ω-diazaniumalkane tectons have successfully been used for the *dimensional caging* of polyiodides $(H_3N(CH_2)_nNH_3)I_2 \cdot I_2$; $n = 3$ [10a], 5 [10b], 6 [10c], 7 [10d], 9 [10e], 10 [10f]). In particular, the caging of the tetraiodide dianion has intensively been studied in the recent past [7b,7d,11]. We now report on the new polyiodide salt $(H_3N(CH_2)_4NH_3)I_4$ (**1**) and compare its structure with that of the two analogous compounds $(H_3N(CH_2)_6NH_3)I_4$ (**2**) [10c] and $(H_3N(CH_2)_7NH_3)I_4$ (**3**) [10d].

Results and Discussion

The reaction of 1,4-diaminobutane with hydroiodic acid in the presence of a slight excess of iodine yielded dark-red, block-shaped crystals. These crys-

tals were found to be 1,4-diazaniumbutane tetraiodide, $C_4H_{14}N_2I_4$ (**1**).

*1,4-Diazaniumbutane tetraiodide (**1**)*

In the title structure the 1,4-diazaniumbutane cations and the tetraiodide anions are both located on centers of inversion ($2/m$ sites) in the centrosymmetric, monoclinic space group $C2/m$. The bond lengths of the organic dication are in the expected range (Table 1). The fully ordered 1,4-diazaniumbutane dication is in the *all-trans* conformation and fits exactly with the restrictions of the $2/m$ site symmetry. The $2/m$-symmetric I_4^{2-} anion shows the typical short I-I distance of the two central iodine atoms (Fig. 1), only slightly longer than in solid iodine [12]. The bond length between the central and the terminal iodine atoms of 3.4175(4) Å is clearly within the typical range of secondary I-I halogen bonding (Table 1) [1, 2]. The terminal iodine atoms are involved in three non-forkated medium-strong hydrogen bonds [13]. These hydrogen bonding connections form a three-dimensional framework. For a better understanding it is worth cutting the three-dimensional hydrogen-bonded framework into

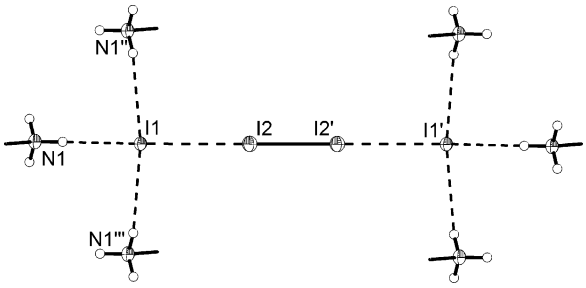

Fig. 1. The six hydrogen-bonded azanium groups connected to the I_4^{2-} anion in **1** with view parallel to the mirror plane through N1, I1, I2, I2′, I1′ ($' = -x, y, -1-z$, $'' = 0.5-x, 0.5+y, 1-z$, $''' = 0.5-x, -0.5+y, 1-z$; hydrogen atoms are drawn with arbitrary radii, non-hydrogen atoms are shown as 70% probability ellipsoids).

Table 1. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses[a].

I1–I2	3.4175(4)	I2–I2′	2.7491(6)
N1–C1	1.493(6)	C1–C2	1.506(6)
C2–C2″	1.512(9)	I1–I2–I2′	179.61(2)
N1–C1–C2	110.1(4)	C1–C2–C2″	112.3(5)

[a] Symmetry operations: $' = -x, +y, -1-z$, $'' = 1+x, -y, 2+z$.

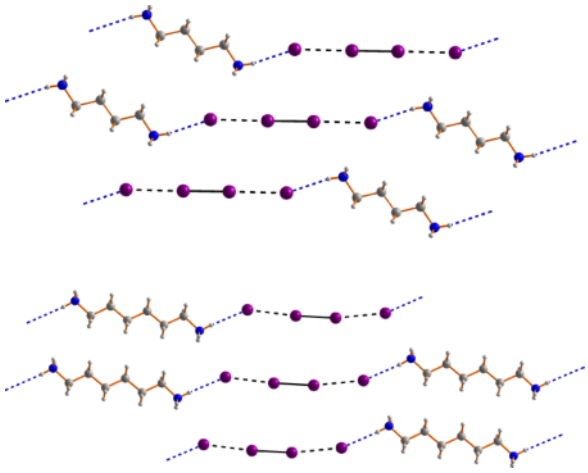

Fig. 2 (color online). Similarity of the primary hydrogen bonding motif in 1,4-diazaniumbutane tetraiodide (**1**) (upper part) and 1,6-diazaniumhexane tetraiodide (**2**) (lower part).

slices, even though the lengths of the different hydrogen bonds are comparable. The hydrogen bonds in *trans* position to the I1···I2 secondary halogen bond (Fig. 1) construct infinite zig-zag chains along [103] (Fig. 2 upper part; H···I1: 2.61(6) Å; N1···I1: 3.523(4) Å).

These chains are packed side by side within the crystallographic mirror plane affecting each other only by van der Waals interactions. A very similar arrangement is found in the structure of 1,6-diazaniumhexane tetraiodide (**2**) (Fig. 2, lower part) [10c]. The shortest H···I distances in **2** are also those connecting cations and anions to polymeric chains (H···I: 2.71/2.71 Å; N···I: 3.595(2)/3.593(2) Å). Even though the angles between the rod-shaped cations and the almost linear anions are different, the cations and the anions are arranged parallel to the neighboring building blocks in each case.

Additional hydrogen bonds are present perpendicular to the chain direction in compounds **1** and **2**. These hydrogen bonds (H···I1: 2.84(4) Å; N1···I1: 3.5911(9) Å) are just as strong as those present in the crystallographic mirror plane. The set of all hydrogen bonds leads to similar three-dimensional frameworks in both cases. Typical for both structures is the hydrogen bonding ring motif [graph set: $R_4^2(8)$] [14], which is common for this class of compounds [15]. In Fig. 3 (upper and middle part) the isostructural relation of **1** and **2** is apparent. The differences are related to the needs of cationic tectons of different size. As

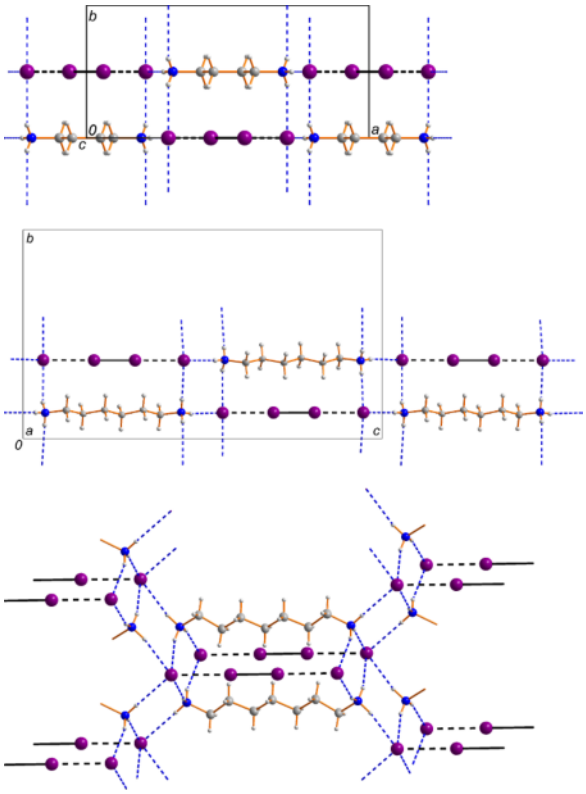

Fig. 3 (color online). Structural comparison of 1,4-diazaniumbutane tetraiodide (**1**) (upper part), 1,6-diazaniumhexane tetraiodide (**2**) (middle) and 1,7-diazaniumheptane tetraiodide (**3**) (lower part).

a consequence, compound **2** crystallizes in the monoclinic space group $P2_1/n$ with the cations and the tetraiodide anions both in general positions. Where **1** features exactly a crystallographic mirror symmetry, this symmetry element is only marginally realized for the tetraiodide anion and the azanium groups of **2** (Fig. 3, middle part). This structural pseudo-symmetry produces serious problems and correlations during the refinement process. In the structure of 1,7-diazaniumheptane tetraiodide (**3**) (Fig. 3, lower part) some structural features are also similar to those of **1** and **2**. The 1,7-diazaniumheptane cation is positioned side by side to the tetraiodide anion. The characteristic $R_4^2(8)$ hydrogen bonding motif is also present in this structure, but obviously the resulting hydrogen bonded three-dimensional framework is completely different. Two cations and two anions form square prismatic subunits (Fig. 3, lower part) which are further connected to extended units. Preliminary results for the 1,8-diazaniumoctane hexaiodide suggest that for compounds with longer chains the structure type of **1** and **2** is also possible. A reason for the exceptional position of **3** most likely is the fact that the length of the tetraiodide anion of 9.71 Å is very similar to the dimension of the 1,7-diazaniumheptane (N–N distance = 10.03 Å). The cations in **1** and **2** are significantly shorter (1,4-diazaniumbutane: N–N distance = 6.24 Å; 1,6-diazaniumhexane: N–N distance = 8.79 Å) and unable to form a structure like that. The construction of two cations and two anions forming an undistorted building block is a nice new example for the masterly achievement of dimensional caging [7a].

The Raman spectroscopic results for **1** are in excellent agreement with those of the crystal structure analysis. The structure of the tetraiodide anion can be understood as an iodine molecule coordinated by two iodide donors. These iodide anions are electron-poorer than those present in I_4^{2-} anions trapped in van der Waals gaps [7b]. Two stretching modes are observed for the I_2 molecule in the solid phase of elemental iodine, at 180 and 189 cm^{-1} with symmetries A_g and B_{3g}, respectively [16]. Any shift of the I–I vibration to lower values is caused by a weakening of the I–I bond. The appearance of a strong band at 171 cm^{-1} (I_2 vibration) and a weak band at 110 cm^{-1} for **1**, as well as similar strong bands in **2** (176 cm^{-1}) and **3** (177 cm^{-1}), are in excellent accordance to the results of related studies on tetraiodide dianions and iodine molecules coordinated to donors [17].

Conclusion

The structure of the title compound 1,4-diazaniumbutane tetraiodide fits very well into the general structural chemistry of α,ω-diazaniumalkane tetraiodides. In all three compounds **1**–**3** the rod-shaped α,ω-diazaniumalkane tectons form three-dimensional, hydrogen-bonded frameworks. In each structure the azanium groups of the dications are only connected to the terminal iodine centers of the almost linear tetraiodide anions. The title compound is isostructural but not isotypic to **2**. The structure of 1,7-diazaniumheptane tetraiodide (**3**) is different in its details. Even though **3** has the hydrogen bonding motif $R_4^2(8)$, the equivalence of the length of the I_4^{2-} anion and the 1,7-diazaniumheptane dication leads to an individual structure type.

Experimental Section

General considerations: All chemicals were obtained from commercial sources and used as purchased. Mid-IR spectra were measured at room temperature on an Excalibur FTS 3500 spectrometer (Digilab, Germany) with an apodized resolution of 2 cm^{-1} using an MIRacle ATR unit (Attenuated Total Refection, Pike Technologies, Madison, USA) in the region of 4000 – 530 cm^{-1}. Raman spectra were recorded on a MultiRam spectrometer (Bruker Optics, Germany) with an apodized resolution of 8 cm^{-1} equipped with an Nd-YAG laser (1064 nm) and an RT-InGaAs-detector (4000 – 70 cm^{-1}, 128 scans, 10 mW). Elemental analyses (C, H, N) were performed with a Euro EA3000 instrument (HEKA-Tech, Germany). Elemental analysis of iodine: In a typical experiment 100 mg of the title compound was dissolved in 15 mL of a water/acetone (10 : 1) mixture. After adding some drops of acetic acid and heating up to approximately 100 °C, zinc powder was added until the solution turned colorless. Filtering off the excess of zinc yielded a clear solution which was analyzed by a classical precipitation titration ($AgNO_3$ solution (0.1 mol L^{-1}); potentiometric endpoint; Ag/AgCl//Ag electrodes) [18]. The melting points were determined using the Mettler–Toledo melting point system MP90 (range: r. t.–220 °C, 2 °C min^{-1}). The measurements were repeated three times to verify the observations.

*1,4-Diazaniumbutane tetraiodide (**1**)*

In a typical reaction, 0.14 g (1.6 mmol) of 1,4-diaminobutane and 0.81 g (3.2 mmol) of iodine were stirred in 15 mL of 57 % aqueous hydroiodic acid and heated at 100 °C yielding a dark colored solution. Upon slow cooling to room temperature, dark-red, block-shaped, shiny crystals were formed at the bottom of the reaction vessel within one to two days. The yield exceeded in all cases 80 %. – M. p. = 122 °C. – Mid-IR (single crystal, ATR; cm^{-1}): $\nu = 3388$ (s, br), 3068 (vs), 3021 (vs), 2997 (vs), 2899 (s, sh), 2639 (m), 2568 (m), 2533 (m), 2492 (m), 2454 (m), 2419 (m), 1848 (m, br), 1614 (m, br), 1579 (m), 1556 (s), 1471 (s), 1444 (m, sh), 1394 (w), 1326 (m), 1278 (m), 1100 (m), 1082 (w, sh), 1022 (m), 911 (w), 868 (m), 734 (w). – Raman (powder sample; cm^{-1}): $\nu = 3050$ (w, br), 2950 (vw), 2923 (w), 2840 (vw), 2800 (vw), 1596 (vw), 1547 (w), 1470 (m), 1173 (m, br), 986 (vw), 951 (w), 171 (vs), 112 (m). – Elemental analysis for $C_4H_{14}N_2I_4$ (598.8): calcd. C 8.0, H 2.4, N 4.7, I 84.9; found C 7.5, H 2.3, N 4.5, I 82.8 (I_2 vapor pressure).

*1,6-Diazaniumhexane tetraiodide (**2**)*

Mid-IR (single crystal, ATR; cm^{-1}): $\nu = 446$ (s, br), 3122 (vs, br), 2932 (s), 2859 (m), 1567 (s), 1468 (s), 1395 (vw), 1300 (vw), 1219 (w), 1098 (m), 1060 (w), 1030 (w), 975 (w), 916 (m), 814 (w), 780 (w), 723 (w). – Raman (powder sample; cm^{-1}): $\nu = 2960$ (m), 2913 (m), 2850 (m, sh), 2830 (w, sh), 1579 (w), 1450 (m, br), 1393 (w), 1320 (w, br), 1160 (w), 1033 (w), 923, 849 (w), 727 (vw), 310 (w), 176 (vs).

*1,7-Diazaniumheptane tetraiodide (**3**)*

Mid-IR (single crystal, ATR; cm^{-1}): $\nu = 3169$ (s, sh), 3061 (vs, br), 3019 (vs, sh), 2980 (vs, sh), 2953 (s, sh), 2933 (vs), 2856 (s), 2573 (m), 1923 (m, br), 1578 (m), 1463 (s), 1440 (s), 1385 (m), 1324 (w), 1275 (w), 1230 (w), 1180 (w), 1158 (m), 1122 (m), 1030 (w), 984 (m), 922 (m), 909 (m, sh), 872 (m), 808 (w), 761 (m), 722 (m). – Raman (powder sample; cm^{-1}): $\nu = 3056$ (vw, br), 2907 (w), 2855 (vw), 1600 (vw), 1438 (w), 1390 (vw), 1306 (vw), 1161 (vw), 1062 (vw), 1034 (w), 991 (vw), 913 (w) , 309 (vw), 258 (vw), 177 (vs), 110 (w).

*Crystal structure determination of **1***

A dark-red, block-shaped single crystal of **1** suitable for X-ray diffraction was harvested from the bulk sample. The crystal was mounted on an Oxford Xcalibur four-circle diffractometer [19] equipped with an EOS detector and a cooling device. Data collection and reduction followed the standard routine yielding a completeness of more than 99 % of reflections necessary for the Laue class. An absorption correction was applied using indexed faces. Structure solution by Direct Methods [20] yielded all iodine atom positions. Secondary structure solution and simultaneous successive refinement of the primary structure gave the complete model. In the latest stages of the refinement of **1** the positional parameters of all atoms were refined freely. For all hydrogen atoms isotropic displacement parameters and for the non-hydrogen atoms anisotropic displacement parameters were refined.

Crystal structure data: $C_4H_{14}I_4N_2$, $M_r = 597.77$, crystal size = 0.35 × 0.25 × 0.13 mm^3, monoclinic, $C2/m$, $a = 15.3941(5)$, $b = 6.9949(2)$, $c = 6.5524(2)$ Å, $\beta = 103.958(4)°$, $V = 684.73(4)$ $Å^3$, $T = 117$ K, $Z = 2$, $D_{calcd} = 2.90$ g cm^{-1}, $\mu(MoK_\alpha) = 9.1$ mm^{-1}, refl. measured/unique/R_{int}: 1401/729/0.015, hkl range: $-18 \le h \le 14$, $-5 \le k \le 8$, $-4 \le l \le 8$, $2\vartheta_{max} = 52°$ (completeness > 99 %), refl. with $F^2 > 2\sigma(F^2)$: 687, param. refined: 47, $R1$ $[F^2 > 2\sigma(F^2)] = 0.0157$, $wR2$ $[F^2 > 2\sigma(F^2)] = 0.0352$, $R1$ (all data) = 0.0166, $R2$ (all data) = 0.0356, GoF = $S = 1.054$, $\Delta\rho_{fin}$ (max/min) = 0.91/ – 0.55 e $Å^{-3}$.

CCDC 868709 contains 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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