An Adaptable and Dynamically Porous Organic Salt Traps Unique Tetrahalide Dianions**

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Figure S5. (a): Simulated powder XRD pattern from single crystal XRD of 3a. (b): Experimental powder XRD pattern obtained after slow heating 2a up to 170 °C, cooling to rt, and gentle grinding. The good agreement between the two powder XRD patterns evidences that the release of one I₂ molecule from 2a affords quantitatively 3a.
Figure S6. Top: Experimental powder XRD pattern of 3a obtained from 1a and I₂ via solution crystallization. Bottom: Powder XRD pattern of 2a formed by exposing 3a (sample at the top) to I₂ for one day at rt. Release and adsorption of I₂ is a reversible process.


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Figure S8. TG plot showing the release of I₂ molecules upon heating 2b. We note that the first molecule is released between ca. 80-160 ºC corresponding to the temperatures also observed in the powder XRD analysis. The release of one I₂ molecule corresponds to 29.1 % and the experimental value is 29.2 %.

Figure S9. (a) Crystal structure of 3b viewed along the c-axis showing the encapsulation of the dianion I₂Br₂⁻ by the hexamethonium cations. (b) The same structure viewed along the b-axis showing the cation-anion intercalation. Halogen bonding is indicated by dashed lines. Colour code: sky blue, hydrogen; grey, carbon; blue, nitrogen; brown, bromine; violet, iodine.

Figure S10. Cation and anion units in 3b and some geometric information. Colour code: light grey, hydrogen; dark grey, carbon; blue, nitrogen; brown, bromine; violet, iodine.

Figure S11. Top: Experimental powder XRD pattern of 3b formed on slow heating of 2b. Bottom: Experimental powder XRD pattern of 2b formed on exposing 3b to vapors of I₂ for one day at rt. Release and adsorption of I₂ is a reversible process.


Variable temperature in situ powder XRD of 2c.

Figure S12. Powder XRD of 2c at different temperatures: (a) 25 ºC; (b) 100 ºC; (c) 120 ºC and (d) 160 ºC. Heating rate 0.6 ºC/min. Red dots indicate the new phase of 3c. The formation of the new phase occurs cleanly.

Figure S13. TG plot of 2c showing the release of I₂ molecules upon heating. We note that the first molecule is released between ca. 100-170 ºC corresponding to the temperature range observed in the powder XRD analysis. The calculated percentage mass loss for the release of one I₂ molecule is 32.5 % and the experimental value is 29.97 %.

Figure S14. DSC plot of 2c measured at slow heating rate (1 ºC/min). The DSC curve shows two endothermic peaks. Gas flow: Nitrogen 100.0 mL/min.

Structure determination of 3c from powder XRD data.

Figure S15. Le Bail (top) and Rietveld (bottom) refinements for 3c. Experimental (red + marks line), calculated (green solid line) and difference (lower pink line) powder XRD profiles. Reflection positions are indicated by tick marks.
**Figure S16.** (a) Crystal structure of 3c viewed along the c-axis showing the encapsulation of the dianion I$_2$Cl$_2$ by the hexamethonium cation. (b) The same structure viewed along the b-axis showing the cation-anion intercalation. Halogen bonding is indicated by dashed lines. Colour code: sky blue, hydrogen; grey, carbon; blue, nitrogen; green, chlorine; violet, iodine.

**Figure S17.** The cation and anion units in 3c and some geometric information. Colour code: light grey, hydrogen; dark grey, carbon; blue, nitrogen; green, chlorine; violet, iodine.

**Figure S18.** Top: Experimental powder XRD pattern of 3c formed on slow heating of 2c. Bottom: Experimental powder XRD pattern of 2c formed on exposing 3c to vapors of I$_2$ for one day at rt. Release and adsorption of I$_2$ is a reversible process.

**Figure S19.** (a): On annealing 3c for 72 h at high temperature, complete loss of I$_2$ occurs and hexamethonium chloride dihydrate (1c$\cdot$2H$_2$O) is formed. (b): The powder XRD pattern of thus formed 1c$\cdot$2H$_2$O.

**Figure S20.** Photographs showing the colour change observed on interconversion of hexamethonium bis-chlorode (1c, white, left), bis-diiodo-chloride (2c, brown, mid), and diiododi-chloride (3c, orange, right).

6. **Synthesis, crystal structure determination, and thermal analysis of tetramethonium bis-triiodide (([CH$_3$]$_3$N$^+$)(CH$_2$)$_4$N$^+$)(CH$_3$)$_3$$\cdot$2I$_3^-$) (4).**

**Solution synthesis.**

**Figure S21.** View of the crystal packing of the bis-triiodide of tetramethonium. Color code: Blue, nitrogen; grey, carbon; light grey, hydrogen; violet, iodine.

**Figure S22.** TG plot of the bis-triiodide of tetramethonium. The calculated percentage mass loss for the release of one I$_2$ molecule is 27% and the experimental value for a possible stepwise weight loss is 57%.

7. **Synthesis and thermal analysis of octamethonium bis-triiodide (([CH$_3$]$_3$N$^+$)(CH$_2$)$_8$N$^+$)(CH$_3$)$_3$$\cdot$2I$_3^-$).**

**Solution synthesis:**

**Figure S23.** TG plot of the bis-triiodide of octamethonium. The calculated percentage mass loss for the release of one I$_2$ molecule is 25.6% but no stepwise weight loss is observed.

8. **Crystallographic data and figures of 1b anhydrous and 4.**

**Table 3.** Crystallographic data of 1b anhydrous and 4.

**Figure S24.** (Left) Ball and stick representation of 1b anhydrous view along a-axes. (Right) Space fill representation of 1b anhydrous view along c-axes (y+90°). Color code: Light grey, hydrogen; dark grey, carbon; blue, nitrogen; brown, bromine.
Figure S25. (Left) Ball and stick representation of 4 view along a-axes (z+90°). (Right) Asymmetric unit of 4. Color code: Light grey, hydrogen; dark grey, carbon; blue, nitrogen; violet, iodine.

9. Check cif files

- 2b check cif
- 1b anhydrous check cif
- 4 check cif

10. Cif files

- 3b and 3c cif files
1. Experimental Details.

Commercial HPLC-grade solvents were used without further purification. All the compounds were commercially available and used without further purification.

TG/DSC analysis was carried out on a TA Instruments Q600 Simultaneous TGA/DSC instrument.

Variable temperature and in situ powder XRD experiments were carried out on a Bruker D8 Advance diffractometer operating in reflection mode with Ge-monochromated Cu Kα1 radiation (λ = 1.5406 Å) and a linear position-sensitive detector; with a 2θ range 5–40°, a step size 0.016° and exposure time 1.5 s per step.

Powder XRD data for ab initio structure determination was recorded at ambient temperature on a Bruker D8 diffractometer (transmission mode; Ge-monochromated CuKα1; λ = 1.5406 Å; Vantec detector covering 12° in 2θ; 2θ range, 4° – 70°; step size, 0.017°). Data collection time 14 h. The high background observed in the powder XRD pattern is due to the fact that the data collection was carried out using a foil-type sample holder, with the powder sample held between two pieces of tape.
2. Synthesis and crystal structure determination of 2a-c.

**Solution synthesis, gas-solid synthesis, and single crystal X-ray analysis of 2a:** See ref. 1a.

**Solution synthesis of 2b:** A solution of I$_2$ (0.130 mmol) in methanol (2 mL) is added dropwise and at room temperature to a solution of hexamethonium bromide dihydrate (1b·2H$_2$O) (0.065 mmol) in methanol (2 mL). Dark brown single crystals of 2b precipitate immediately and the solution is further stirred for 2h. The crystals are filtered, rapidly dried using a funnel and a pump, then used for X-ray single crystal diffraction or synthesis of 3b. Powder XRD analysis of ca. 50 mg of a thus obtained sample of 2b show a diffraction pattern matching well with the simulated pattern from single crystal data (Figure S2) thus proving the homogeneity and purity of the sample.

**Gas-solid synthesis of 2b:** In a sealed jar, finely powdered 1b·2H$_2$O (0.260 mmol) is exposed to vapors of I$_2$ (excess) at room temperature for 2 days. The white staring powder changes gradually to a dark brown solid. After 1 day, the white-brown solid is manually mixed in order to avoid that only crystallites at the surface are massively exposed to I$_2$ and react with it.

![Figure S1](image)

Figure S1. Synthesis of 2b via gas-solid reaction.

**Single Crystal X-ray analysis of 2b:** A single crystal of 2b is mounted in the diffractometer for X-ray analysis. Structure refinement indicates the presence of the mixed trihalide [Br···I–I]$.^{-}$ This anion is isostructural to [I···I–I]$^{-}$ and [Cl···I–I]$^{-}$ anions in their hexamethonium salts. The overall packing of 2b consists of couples of nearly linear and slightly asymmetric [Br···I–I]$^{-}$ anions which pile up into columnar domains embraced by four cationic columns. Structure refinement has shown some orientational disorder associated with [Br···I–I]$^{-}$ anions couples which occupy the space embraced by four cationic columns. They adopt two arrangements, namely [Br···I–I]$^{-}$···[I–I···Br]$^{-}$ and [Br···I–I]$^{-}$···[Br···I–I]$^{-}$, with a site occupancy factor of 0.89 and 0.11, respectively. The two outermost positions in the anions couples are preferentially occupied by bromine, the lighter halogen, in order to locate the lighter halogen atom closer to the trimethylammonium moieties and maximize electrostatic interactions and hydrogen bondings (see manuscript). A similar orientational disorder has already been observed in 2c.$^{1b}$

It is interesting to observe that the short XB$s$ between halide anions and diiodine molecules in 2a, 2b and 2c [298.26(8), 284.88(5) and 272.65(4) pm, respectively, which correspond to ~0.73 times the sum of the van der Waals radius of iodine and the Pauling ionic radius of the halide anion] result in I–I bond elongation in the trihalide anion with respect to I$_2$ (2.72 Å).
Figure S2. Top: Simulated powder XRD patterns of 2b; mid: Experimental powder XRD pattern of 2b obtained from 1b and I₂ in solution; bottom: Experimental powder XRD pattern of 2b obtained from gas-solid reaction from 1b and I₂ (bottom). The good agreement of the three patterns confirms that the single crystal structure is representative of the bulk powders and suggests that the solution and gas-solid synthesis afford homogeneous samples.
Figure S3. View of the dimers formed by two [Br···I-I]− anions via type-I halogen-halogen interactions in 2b. The type-I interaction is shown as dashed line. The major orientational isomer (site occupancy factor of 0.89) is reported. Color code: Sky blue, carbon; light grey, hydrogen; brown, bromine; violet, iodine.

Solution synthesis, gas-solid synthesis, and single crystal X-ray analysis of 2c: See ref. 1b.

Table 1. Crystallographic data for 2a\textsuperscript{1a}, 2b and 2c\textsuperscript{1c}.

<table>
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<th>Crystal</th>
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<th>2b</th>
<th>2c\textsuperscript{1c}</th>
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<td>C\textsubscript{12}H\textsubscript{30}N\textsubscript{2}\textsuperscript{2+}, 2(I\textsubscript{2}Br−)</td>
<td>C\textsubscript{12}H\textsubscript{30}N\textsubscript{2}\textsuperscript{2+}, 2(I\textsubscript{2}Cl−)</td>
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<td>$\Delta F$ min [eÅ$^3$]</td>
<td>-0.773</td>
<td>-0.661</td>
<td>-0.652</td>
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Note: *Single Crystal X-ray Diffraction.* Data were collected on a Bruker KAPPA APEX II diffractometer with Mo-Kα radiation (λ= 0.71073) and CCD detector at room temperature (excluding structures 2b which were collected at 220 K using Bruker KRYOFLEX device). The structures were solved by SIR2002³ and refined by SHELXL-97⁴ programs, respectively. The refinement was carried out by full-matrix least-squares on F². Hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms. CIF files containing crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 2.** Geometrical parameters (distance, Å and angle, °) of selected hydrogen bonds⁵ involving the outermost positions in the trihalide moieties and the ammonium head in the cation moiety in 2a, 2b and 2c.

<table>
<thead>
<tr>
<th>HBs</th>
<th>X····H (distance, Å)</th>
<th>X····H–C (angle, °)</th>
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<td>2a</td>
<td></td>
<td></td>
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<tr>
<td>I1····H5A-C5</td>
<td>3.0768(7)</td>
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<td>3.1793(5)</td>
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<td>2b</td>
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<td>2c</td>
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<td>155.3(2)</td>
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<td>153.4(3)</td>
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<td>Cl1····H5C-C5</td>
<td>2.789(1)</td>
<td>159.3(3)</td>
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⁵: sum of vdW radii +0.1

**Variable temperature in situ powder XRD of 2a.** 50 mg *ca.* of microcrystalline 2a were placed in the sample holder of the diffractometer and were heated, from rt to 170 °C, at 0.01 °C/sec heating rate. Diffraction data were collected every 10 °C. After reaching 170 °C and measuring the diffractogram (measuring time *ca.* 1h) the sample was cooled to rt and powder XRD pattern was recorded once more. All diffraction patterns showed a good crystallinity of the sample. Peak positions were matching but intensities were not matching with the experimental pattern of a sample of 3a from solution crystallization and the simulated pattern from single crystal analysis of 3a.\textsuperscript{1a} However, after gently grinding the product a perfect match was observed.

**Figure S4.** Powder XRD of a sample of 2a at different temperatures: (a) 25 °C; (b) 120 °C; (c) 140 °C and (d) 160 °C. Heating rate 0.01 °C/sec. Red dots indicate the new phase corresponding to the formation of 3a.
Figure S5. (a): Simulated powder XRD pattern from single crystal XRD of 3a. (b): Experimental powder XRD pattern obtained after slow heating 2a up to 170 °C, cooling to rt, and gentle grinding. The good agreement between the two powder XRD patterns evidences that the release of one I₂ molecule from 2a affords quantitatively 3a.
Figure S6. Top: Experimental powder XRD pattern of 3a obtained from 1a and I₂ via solution crystallization. Bottom: Experimental powder XRD pattern of 2a formed by exposing 3a (sample at the top) to I₂ for one day at rt. Release and adsorption of I₂ is a reversible process.

Variable temperature in situ powder XRD of 2b. The experiments of in situ powder XRD at variable temperature (from rt to 160 °C) were performed as described above for 2a (0.01 °C/sec heating rate). After reaching 160 °C and measuring the diffractogram the sample was cooled to rt and powder XRD pattern was recorded once more. The diffraction patterns after heating showed good crystallinity of the sample and were completely different from the starting 2b consistent with formation of 3b. C,H,N analysis (%) for 3b: C_{12}H_{30}Br_{2}I_{2}N_{2}: calcd: C 23.40, H 4.91, N 4.55; found: C 23.72, H 4.94, N 4.65.

Structure determination of 3b from powder XRD data: The powder XRD pattern of a sample obtained after reaching 160 °C was indexed using the program LZON\(^5\) to give a unit cell with monoclinic metric symmetry (a = 25.84 Å, b = 7.27 Å, c = 5.59 Å; β = 93.6°; V = 1047.8 Å\(^3\)) with good figures of merit (FOM = 50.48). The space group was assigned from systematic absences as C2/m. Unit cell and profile refinement, carried out using the Le Bail method,\(^6\) gave an excellent fit (R\(_{wp}\) = 3.25 %, R\(_{p}\) = 2.45 %) for these lattice parameters and space group. Structure solution was carried out using the direct-space genetic algorithm (GA) technique\(^7\) implemented in the program EAGER,\(^8\) followed by Rietveld refinement using the GSAS program package. In the Rietveld refinement, standard restraints were applied to bond lengths and angles to maintain molecular geometry and isotropic displacement parameters were refined. Final Rietveld refinement: a = 25.8309(10) Å, b = 7.26762(30) Å, c = 5.58438(27) Å; β = 93.602(4)°; V = 1046.28(11) Å\(^3\); R\(_{wp}\) = 3.39 %, R\(_{p}\) = 2.55 %; 3878 profile points; 98 refined variables. CCDC number: 952028.

**Figure S7.** Le Bail (top) and Rietveld (bottom) refinements for 3b. Experimental (red + marks line), calculated (green solid line) and difference (lower pink line) powder XRD profiles. Reflection positions are indicated by tick marks.
Figure S8. TG/DSC plots for 2b. The two peaks in the DSC plot reveal two separate endothermic phenomena associated with I\textsubscript{2} loss. The TG plot confirms the stepwise release of I\textsubscript{2} molecules upon heating 2b. As observed from powder XRD analysis, the first I\textsubscript{2} molecule is released between ca. 80-160 °C, corresponding to a 29.2 % mass loss (calculated 29.1%).
Figure S9 (a) Crystal structure of 3b viewed along the $c$-axis showing the encapsulation of the dianion $I_2Br_2^{-2}$ by the hexamethonium cations. (b) The same structure viewed along the $b$-axis showing the cation-anion intercalation. Halogen bonding is indicated by dashed lines. Colour code: sky blue, hydrogen; grey, carbon; blue, nitrogen; brown, bromine; violet, iodine.

Figure S10. Cation and anion units in 3b and some geometric information. Colour code: light grey, hydrogen; dark grey, carbon; blue, nitrogen; brown, bromine; violet, iodine.
Release and adsorption of I$_2$ is a reversible process.

**Figure S11.** Top: Experimental powder XRD pattern of 3b formed on slow heating of 2b. Bottom: Experimental powder XRD pattern of 2b formed on exposing 3b to vapors of I$_2$ for one day at rt. Release and adsorption of I$_2$ is a reversible process.

Variable temperature in situ powder XRD of 2c. The experiments of in situ powder XRD at variable temperature were performed by heating ca. 50 mg of microcrystalline powders of 2c in the sample holder of the diffractometer at 0.01 °C/sec heating rate. Following the same protocol described in 2b, the sample was measured every 10 °C from rt to 170 °C. After reaching 170 °C and measuring the diffractogram (measuring time ca. 1h) the sample was cooled to rt and its powder XRD was recorded once more. The diffraction patterns showed good crystallinity and a new crystal phase was substituting for 2c at temperatures higher than 100 °C consistent with formation of 3c. C,H,N analysis (%) for 3c: C_{12}H_{30}Cl_{2}I_{2}N_{2}: calcd: C 27.34, H 5.74, N 5.31; found: C 28.62, H 5.94, N 5.49.

Figure S12. Powder XRD of a sample of 2c at different temperatures: (a) 25 °C; (b) 100 °C; (c) 120 °C and (d) 160 °C. Heating rate 0.6 °C/min. Red dots indicate the formation of the new crystal phase of 3c.
Figure S13. TG plot of 2c showing the release of I₂ molecules upon heating. We note that the first molecule is released between *ca.* 100-170 °C corresponding to the temperature range observed in the powder XRD analysis. The calculated percentage mass loss for the release of one I₂ molecule is 32.5 % and the experimental value is 29.97 %.
Figure S14. DSC plot of 2c measured at slow heating rate (1 °C/min). The DSC curve shows two endothermic peaks. Gas flow: Nitrogen 100.0 mL/min.
Structure determination of 3c from powder XRD data: The powder XRD pattern of 3c was indexed using the program ITO\textsuperscript{9} to give a unit cell with monoclinic metric symmetry \((a = 26.08 \text{ Å}, b = 6.88 \text{ Å}, c = 5.65 \text{ Å}, \beta = 95.5^\circ; V = 1010.3 \text{ Å}^3)\) with good figures of merit (FOM = 143.8). The space group was assigned from systematic absences as \(C2/m\). Unit cell and profile refinement, carried out using the Le Bail method, gave an excellent fit \((R_{wp} = 3.07 \%, R_p = 2.34 \%)\) for these lattice parameters and space group. As the unit cell is very similar to that of 3b and as the space group is identical, the structure of 3b was used as the starting point for Rietveld refinement of 3c (but with the Br atom in 3b replaced by a Cl atom in 3c). Rietveld refinement was carried out using the GSAS program package. In the Rietveld refinement, standard restraints were applied to bond lengths and angles to maintain the molecular geometry and isotropic displacement parameters were refined. Final Rietveld refinement: \(a = 26.0883(4) \text{ Å}, b = 6.88603(10) \text{ Å}, c = 5.65418(10) \text{ Å}, \beta = 95.5164(15); V = 1011.04(4) \text{ Å}^3; R_{wp} = 3.27 \%, R_p = 2.46 \%; 3878\) profile points; 98 refined variables. CCDC number: 952029.

Figure S15. Le Bail (top) and Rietveld (bottom) refinements for 3c. Experimental (red + marks line), calculated (green solid line) and difference (lower pink line) powder XRD profiles. Reflection positions are indicated by tick marks.
Figure S16. (a) Crystal structure of 3c viewed along the c-axis showing the encapsulation of the dianion I$_2$Cl$_2$ by the hexamethonium cation. (b) The same structure viewed along the b-axis showing the cation-anion intercalation. Halogen bonding is indicated by dashed lines. Colour code: sky blue, hydrogen; grey, carbon; blue, nitrogen; green, chlorine; violet, iodine.

Figure S17. The cation and anion units in 3c and some geometric information. Colour code: sky blue, hydrogen; dark grey, carbon; blue, nitrogen; green, chlorine; violet, iodine.
Figure S18. Top: Experimental powder XRD pattern of 3c formed on slow heating of 2c. Bottom: Experimental powder XRD pattern of 2c formed on exposing 3c to vapors of I₂ for one day at rt. Release and adsorption of I₂ is a reversible process.
Figure S19. (a): On annealing 3c for 72 h at high temperature, complete loss of I₂ occurs and hexamethonium chloride dihydrate (1c·2H₂O) is formed. (b): The powder XRD pattern of thus formed 1c·2H₂O.
Figure S20. Photographs showing the colour change observed on interconversion of hexamethonium bis-chloride (1c, white, left), bis-diiodochloride (2c, brown, mid), and diiododichloride (3c, orange, right).
6. Synthesis, crystal structure determination, and thermal analysis of tetramethonium bis-triiodide \(((\text{CH}_3)_3\text{N}^+(\text{CH}_2)_4\text{N}^+(\text{CH}_3)_3\cdot2\text{I}^-)\) (4).

**Solution synthesis:** A solution of I\(_2\) (0.13 mmol) in methanol (2 mL) is added dropwise and at room temperature to a solution of tetramethonium iodide dihydrate (0.065 mmol) in methanol (2 mL). Slow evaporation of the solvent at rt afforded brownish crystals, m.p. 205-201 °C. Single crystal XRD revealed the bis-triiodide of tetramethonium was formed. The compound adopts the P\(_{bca}\) space group and the crystal packing is completely different from 2a-c. The simulated and experimental powder XRD patterns are nicely similar, indicating that the tetramethonium bis-triiodide was formed exclusively.

![Figure S21](image_url)

**Figure S21.** View of the crystal packing of the bis-triiodide of tetramethonium. Color code: Blue, nitrogen; grey, carbon; light grey, hydrogen; violet, iodine.
**Figure S22.** TG plot of the bis-triiodide of tetramethonium. The calculated percentage mass loss for the release of one I₂ molecule is 27% and the experimental value for a possible stepwise weight loss is 57%.
7. Synthesis and thermal analysis of octamethonium bis-triiodide ((CH$_3$)$_3$N$^+$(CH$_2$)$_8$N$^+$(CH$_3$)$_3$2I$_3^-$).

**Solution synthesis:** The same procedure as for the preparation of octamethonium bis-triiodide was used. A poorly crystalline compound was obtained, mp 101-106 °C. The formation of octamethonium bis-triiodide was confirmed by microanalysis: C$_{14}$H$_{34}$N$_2$I$_6$ calcd.: C, 16.95; H, 3.45; N, 2.82; I, 76.77. Exp.: C, 17.22; H, 3.77; N, 2.69.

![Figure S23](image.png)

**Figure S23.** TG plot of the bis-triiodide of octamethonium. The calculated percentage mass loss for the release of one I$_2$ molecule is 25.6% but no stepwise weight loss is observed.
8. Crystallographic data and figures of anhydrous 1b and 4.

Table 3. Crystallographic data of anhydrous 1b and 4.

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<td>Pbca</td>
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Note: *Single Crystal X-ray Diffraction*. Data were collected on a Bruker KAPPA APEX II diffractometer with Mo-K$\alpha$ radiation ($\lambda= 0.71073$) and CCD detector at low temperature using Bruker KRYOFLEX device. The structures were solved by SIR2002 and refined by SHELXL-97 programs, respectively. The refinement was carried out by full-matrix least-squares on $F^2$. Hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms. CIF files containing crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).
Figure S24. (Left) Ball and stick representation of anhydrous 1b view along $a$-axes. (Right) Space fill representation of anhydrous 1b view along $c$-axes ($y+90^\circ$). Color code: Light grey, hydrogen; dark grey, carbon; blue, nitrogen; brown, bromine.

Figure S25. (Left) Ball and stick representation of 4 view along $a$-axes ($z+90^\circ$). (Right) Asymmetric unit of 4. Color code: Light grey, hydrogen; dark grey, carbon; blue, nitrogen; violet, iodine.
9. Check cifs

- CheckCIF/PLATON report 2b

No syntax errors found. Please wait while processing ....

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<td>Hall group</td>
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Correction method= MULTI-SCAN

Data completeness= 0.998 Theta(max)= 27.480
R(reflections)= 0.0292( 1054) wr2(reflections)= 0.0678( 1509)
S = 1.033 Npar= 64

The following ALERTS were generated. Each ALERT has the format

test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

**Alert level C**

PLAT342_ALERT_3_C Low Bond Precision on C-C Bonds ............... 0.0087 Ang

**Alert level G**

PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite 3
PLAT164_ALERT_4_G Nr. of Refined C-H Atoms in Heavy-Atom Struct. 2
PLAT301_ALERT_3_G Note: Main Residue Disorder ....................... 12 Perc.
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ... !
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints ....... 3

0 ALERT level A = Most likely a serious problem - resolve or explain
0 ALERT level B = A potentially serious problem, consider carefully
1 ALERT level C = Check. Ensure it is not caused by an omission or oversight
5 ALERT level G = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
3 ALERT type 3 Indicator that the structure quality may be low
1 ALERT type 4 Improvement, methodology, query or suggestion
Datablock 2b - ellipsoid plot

CheckCIF/PLATON report anhydrous 1b

No syntax errors found. Please wait while processing ....

Datablock: 1b anhydrous
Bond precision: C-C = 0.0020 Å

Wavelength=0.71073 Å

Cell:

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\begin{align*}
a &= 5.4796(4) \\
b &= 13.1109(11) \\
c &= 11.5815(9) \\
\alpha &= 90 \\
\beta &= 93.580(4) \\
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\]

Temperature: 93 K

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<tr>
<td>Sum formula</td>
<td>C12 H30 Br2 N2</td>
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<tr>
<td>Mr</td>
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Correction method = MULTI-SCAN

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wr2(reflections) = 0.0481 (2897)

S = 1.005

Npar = 118

The following ALERTS were generated. Each ALERT has the format test-name_ALERT_alert-type_alert-level.

Click on the hyperlinks for more details of the test.

**Alert level A**

**Alert level B**

**Alert level C**

**Alert level G**"
CheckCIF/PLATON report 4

No syntax errors found.  Please wait while processing ....
Interpreting this report
Datablock: 4

Bond precision:  C-C = 0.0167 Å  Wavelength=0.71073 Å
Cell:  a=13.6234(15)  b=20.837(3)  c=32.520(4)
      alpha=90  beta=90  gamma=90
Temperature: 103 K

  Calculated  Reported
Volume  9232(2)  9231(2)
Space group  P b c a  P b c a
Hall group  -P 2ac 2ab  -P 2ac 2ab
Moiety formula  C10 H26 N2, 2(I3)  C10 H26 N2 2+, 2(I3 1-)
Sum formula  C10 H26 I6 N2  C10 H26 I6 N2
Mr  935.73  935.73
Dx, g cm\(^{-3}\)  2.693  2.693
Z  16  16
Mu (mm\(^{-1}\))  8.068  8.068
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</table>

**Alert level A** = Most likely a serious problem - resolve or explain

**Alert level B** = A potentially serious problem, consider carefully

**Alert level C** = Check. Ensure it is not caused by an omission or oversight

**Alert level G** = General information/check it is not something unexpected

**Alert level A** = CIF construction/syntax error, inconsistent or missing data

**Alert level B** = Indicator that the structure model may be wrong or deficient

**Alert level C** = Indicator that the structure quality may be low

**Alert level G** = Improvement, methodology, query or suggestion

**Alert level C** = Informative message, check

---

PLATON version of 19/04/2012; check.def file version of 14/04/2012

**Datablock 4 - ellipsoid plot**
10. cif file from X-ray powder data

3b

# 6. SAMPLE PREPARATION DATA

# (In the unusual case where multiple samples are used in a single Rietveld study, this information should be moved into the phase blocks)

# The following three fields describe the preparation of the material. The cooling rate is in K/min. The pressure at which the sample was prepared is in kPa. The temperature of preparation is in K.

_pd_prep_cool_rate          ?
_pd_prep_pressure            ?
_pd_prep_temperature         ?

_pd_char_colour               # use ICDD colour descriptions
data_I2BR_overall
# pointers to the phase blocks
loop_  _pd_phase_block_id
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# pointers to the diffraction patterns
loop_  _pd_block_diffractogram_id
?

# Information for phase 1
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_pd_block_id
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# 8. Phase information from GSAS

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_cell_angle_gamma 90.0
_cell_volume 1046.28(11)
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_symmetry_space_group_name_H-M C2/m
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    2 -x,+y,-z
    -1 -x,-y,-z
    -2 +x,-y,+z
    101 +x+1/2,+y+1/2,+z
    102 -x+1/2,+y+1/2,-z
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# ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS

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<td>0.0</td>
<td>-0.04077</td>
<td>1.0</td>
<td>Uiso</td>
</tr>
<tr>
<td>H</td>
<td>0.28319</td>
<td>0.10999</td>
<td>-0.23528</td>
<td>1.0</td>
<td>Uiso</td>
</tr>
<tr>
<td>H</td>
<td>0.47541</td>
<td>0.10998</td>
<td>-0.18611</td>
<td>1.0</td>
<td>Uiso</td>
</tr>
</tbody>
</table>

# MOLECULAR GEOMETRY
# 6. SAMPLE PREPARATION DATA

# (In the unusual case where multiple samples are used in a single Rietveld study, this information should be moved into the phase blocks)

# The following three fields describe the preparation of the material. The cooling rate is in K/min. The pressure at which the sample was prepared is in kPa. The temperature of preparation is in K.

_pd_prep_cool_rate ?
_pd_prep_pressure ?
_pd_prep_temperature ?

_pd_char_colour ? # use ICDD colour descriptions
data_I2CL_overall

_refine_ls_shift/su_max 1.46
_refine_ls_shift/su_mean 0.15
_computing_structure_refinement GSAS
_refine_ls_number_parameters 97
_refine_ls_goodness_of_fit_all 1.23
_refine_ls_number_restraints 88
_refine_ls_matrix_type full

# pointers to the phase blocks
loop__pd_phase_block_id
2013-07-19T09:20|I2CL_phase1|||
# pointers to the diffraction patterns
loop  _pd_block_diffractogram_id

# Information for phase 1
data_I2CL_phase_1

_pd_block_id
2013-07-19T09:20|I2CL_phase1|||

# 8. Phase information from GSAS
_pd_phase_name
"from C:/Documents and Settings/keat/My Documents/work_station/Javi"
_cell_length_a 26.0883(4)
_cell_length_b 6.88603(10)
_cell_length_c 5.65418(10)
_cell_angle_alpha 90.0
_cell_angle_beta 95.5164(15)
_cell_angle_gamma 90.0
_cell_volume 1011.04(4)
_symmetry_cell_setting monoclinic
_symmetry_space_group_name_H-M "C 1 2/m 1"
loop  _symmetry_equiv_pos_site_id _symmetry_equiv_pos_as_xyz
\1 +x,+y,+z
2 -x,+y,-z
-1 -x,-y,-z
-2 +x,-y,+z
101 +x+1/2,+y+1/2,+z
102 -x+1/2,+y+1/2,-z
-101 -x+1/2,-y+1/2,-z
-102 +x+1/2,-y+1/2,+z

# ATOMIC COORDINATES AND DISPLACEMENT PARAMETERS

loop  
_atom_site_type_symbol
_atom_site_label
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_thermal_displace_type
_atom_site_U_iso_or_equiv
_atom_site_symmetry_multiplicity

I
I1 0.44690(15) 0.5 0.4582(9) 1.0 Uiso 0.0759(15) 4
Cl
Cl2 0.32619(33) 1.5 0.3214(16) 1.0 Uiso 0.043(4) 4
N
N3 0.33165(7) 0.0 -0.0589(14) 1.0 Uiso 0.057(4) 4
C
C4  0.38302(8)  0.0  0.0902(10)  1.0  Uiso  0.057(4)  4
C7  0.32731(16) -0.1793(4) -0.2142(14)  1.0  Uiso  0.057(4)  8
C5  0.42658(5)  0.0  -0.0711(7)  1.0  Uiso  0.057(4)  4
C6  0.47816(5)  0.0  0.08033(29)  1.0  Uiso  0.057(4)  4
C8  0.28865(12)  0.0  0.1026(18)  1.0  Uiso  0.057(4)  4
H4  0.38567(12)  0.11591(12)  0.1912(10)  1.0  Uiso  0.068(5)  8
H71 0.3606(26) -0.206(24) -0.27(4)  1.0  Uiso  0.070(6)  8
H72 0.317(10) -0.290(8) -0.121(14)  1.0  Uiso  0.070(6)  8
H73 0.301(8) -0.158(15) -0.348(27)  1.0  Uiso  0.070(6)  8
H81 0.25535(8)  0.00002  0.0064(22)  1.0  Uiso  0.070(6)  4
H82 0.29139(18)  0.11608(9)  0.2034(18)  1.0  Uiso  0.070(6)  8
H51 0.42399(8)  0.11615(12) -0.1717(7)  1.0  Uiso  0.068(5)  8
H61 0.48072(10)  0.11605(11)  0.18110(27)  1.0  Uiso  0.068(5)  8

_loop__atom_type_symbol
  _atom_type_number_in_cell
    I  4.0
    Cl  4.0
    N  4.0
    C  24.0
    H  60.0

# If you change Z, be sure to change all 3 of the following
  _chemical_formula_sum "C6 H15 Cl I N"
  _chemical_formula_weight 263.55
  _cell_formula_units_Z 4

# MOLECULAR GEOMETRY

_loop__geom_bond_atom_site_label_1
  _geom_bond_atom_site_label_2
  _geom_bond_distance
  _geom_bond_site_symmetry_1
  _geom_bond_site_symmetry_2
  _geom_bond_publ_flag

_loop__geom_angle_atom_site_label_1
  _geom_angle_atom_site_label_2


