

# Synthesis, Structure and Thermal Decomposition of a New Iodine Inclusion Compound in the 2,2-Dimethylpropane-1,3-diamine/HI/I<sub>2</sub> System

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The reaction of 2,2-dimethylpropane-1,3-diamine with hydroiodic acid in the presence of iodine gave a new polyiodide best described as bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1), (C<sub>5</sub>H<sub>16</sub>N<sub>2</sub>)<sub>2</sub>I<sub>4</sub>·I<sub>2</sub> (**1**). The title compound can be transformed into the known 2,2-dimethylpropane-1,3-diazanium diiodide, (C<sub>5</sub>H<sub>16</sub>N<sub>2</sub>)I<sub>2</sub> (**2**), upon iodine release at 433 K and  $2 \times 10^{-3}$  mbar. Both compounds have been characterised by spectroscopic methods (Raman and IR) and powder diffraction. For **1** the single-crystal structure determination has been successful. The asymmetric unit of **1** consists of one half 2,2-dimethylpropane-1,3-diazanium cation and two half iodide anions, all lying in a mirror plane. In addition, there is one quarter of an iodine molecule located near to a centre of inversion ( $2/m$  site) which is disordered over two positions with occupancy factors of 0.22 and 0.78. The structure of the title compound contains cube-shaped structural units in which the -NH<sub>3</sub><sup>+</sup> groups of four 2,2-dimethylpropane-1,3-diazanium cations occupy the corners. The iodide anions lie near the midpoints of eight of the twelve edges, and the disordered iodine molecule fills the void in the centre. Weak I⋯I interactions between the disordered iodine molecules and adjacent iodide anions may also allow a description as conceivable I<sub>4</sub><sup>2-</sup> dianions. The cube-type building units are further connected to adjacent ones by weak to medium strong N–H⋯I hydrogen bonds resulting in a two-dimensional layered structure parallel to the *ab* plane.

**Key words:** Polyiodides, 2,2-Dimethylpropane-1,3-diamine, Crystal Structure, Raman Spectroscopy, Powder Diffraction

## Introduction

Numerous polyiodide-containing compounds have been characterised by spectroscopic and crystallographic methods in the last decades. Polyiodides in the solid state are defined as extended parts of salt structures that fulfil the general formula I<sub>2m+n</sub><sup>n-</sup> ( $n = 1 - 4$ ,  $m = \text{integer}$ ). Formally, all polyiodides are built from I<sup>-</sup>, I<sub>3</sub><sup>-</sup> and I<sub>2</sub> units and show a strong tendency to concatenate to extended motifs by halogen-halogen interactions [1–5]. There is a general interest in diazaniumalkane diiodides, and especially in polyiodides as they have a significant influence on the redox chemistry in dye-sensitised solar cells [6–11]. Furthermore, it is well known that polyiodide chains conduct the electric current by a Grotthuss-like mechanism in the

solid state [12]. Therefore, the structures of higher polyiodides can be considered as a snapshot and model systems of this phenomenon. In the recent past, several groups focused their activities towards the synthesis of new, tailored polyiodides using stick-shaped cations whose lengths and shapes fit with the structures of the polyiodide anions [13–18]. This selective and robust synthetic protocol for solid polyiodides is now connected with the term *dimensional caging* [14]. In particular, the semi-flexible  $\alpha,\omega$ -diazaniumalkane cations have successfully been used for the synthesis of a series of new polyiodide salts [19–26]. Recently, great efforts have been made to synthesise new compounds which can resorb iodine reversibly [27–32]. Elemental iodine has received increasing attention in life sciences [33], in studies of the marine biosphere [34, 35]

and in nuclear industries [36]. Here we report on the new polyiodide salt bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1) (**1**) and its thermal decomposition.

## Results and Discussion

From the reaction of 2,2-dimethylpropane-1,3-diamine with hydroiodic acid in the presence of excess iodine, dark-red platelet crystals were obtained. They were found to be bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1),  $(C_5H_{16}N_2)_2I_4 \cdot I_2$  (**1**). A powder sample of compound **1** was heated at 433 K and  $2 \times 10^{-3}$  mbar to give 2,2-dimethylpropane-1,3-diazanium diiodide,  $(C_5H_{16}N_2)I_2$  (**2**) with release of iodine.

### Structure of bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1) (**1**)

The asymmetric unit of bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1),  $(C_5H_{16}N_2)_2I_4 \cdot I_2$ , consists of one half 2,2-dimethylpropane-1,3-diazanium cation and two half iodide anions, all lying on a mirror plane (Fig. 1). In addition, there is one quarter of an iodine molecule located near a centre of inversion ( $2/m$  site), disordered over two positions with occupancy factors of 0.22 and 0.78. In the dication the N1–C1–C2–C3–N2 chain exhibits an

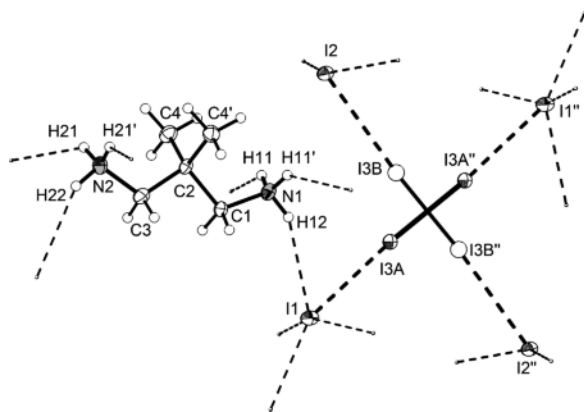


Fig. 1. The asymmetric unit of the title compound plus the symmetry-related atoms completing the 2,2-dimethylpropane-1,3-diazanium cation and the two conceivable  $I_4^{2-}$  dianions (displacement ellipsoids are drawn at the 45% probability level; hydrogen atoms and the lower occupied iodine molecule are drawn as spheres with arbitrary radii; symmetry codes: ' =  $x, 1 - y, z$ ; '' =  $2 - x, y, 1 - z$ ).

Table 1. Selected bond lengths (Å), angles (deg), dihedral angles (deg), and hydrogen bonding (Å, deg) for **1** with estimated standard deviations in parentheses.

I3A–I3A''	2.7514(8)	I3B–I3B''	2.752(2)
I1–I3A	3.124(2)	I2–I3B	3.3641(4)
N1–C1	1.488(6)	N2–C3	1.472(6)
C1–C2	1.534(6)	C2–C3	1.535(6)
C2–C4	1.528(4)	I1–I3A–I3A''	176.12(6)
I2–I3B–I3B''	176.37(2)	N1–C1–C2	114.3(4)
N2–C3–C2	115.7(4)	C1–C2–C3	101.6(3)
C1–C2–C4	111.4(2)	C4–C2–C4'	110.5(4)
N1–C1–C2–C3	180.0(3)	N2–C3–C2–C1	180.0(3)
N1–C1–C2–C4	62.0(4)	N2–C3–C2–C4'	61.5(4)
Symmetry codes: ' = $x, 1 - y, z$ ; '' = $2 - x, y, 1 - z$ .			
	D–H	H...A	D...A
N1–H11...I1'	0.898(10)	2.83(2)	3.5812(7)
N1–H12...I1	0.899(10)	2.74(3)	3.559(4)
N2–H21...I2''	0.897(10)	2.88(3)	3.6227(9)
N2–H22...I1'''	0.900(10)	2.69(3)	3.513(4)
C1–H1B...I3A'	0.970(3)	2.9069(5)	3.847(2)
C3–H3A...I3B''	0.970(3)	2.9480(2)	3.894(2)
Symmetry codes: ' = $1.5 - x, -0.5 + y, 1 - z$ ; '' = $-0.5 + x, -0.5 + y, z$ ; ''' = $1 - x, y, 1 - z$ .			
	Angle		
			142(3)
			151(4)
			141(3)
			153(5)
			163(3)
			166(3)

*all-transoid* conformation. The N1–C1–C2 and N2–C3–C2 angles are widened, and the C1–C2–C3 angle is compressed (Table 1) due to steric requirements of the two methyl groups. These findings are in good agreement with those of other 2,2-dimethylpropane-1,3-diazanium salts [37–39].

The title structure contains cube-shaped building units in which the  $-NH_3^+$  groups of four 2,2-dimethylpropane-1,3-diazanium cations occupy the corners. Iodide anions are located near the midpoints of eight of the twelve edges, and the disordered iodine molecule fills the void in the centre (Fig. 2). Each 2,2-dimethylpropane-1,3-diazanium cation is connected with six iodide anions *via* three non-bifurcated, weak to medium strong N–H...I hydrogen bonds per azanium group (Table 1; Fig. 3). The resulting characteristic hydrogen bonding motifs are two different rings, composed of azanium groups and iodide anions, which can be classified as second- and third-level graph-sets  $R_4^2(8)$  and  $R_6^3(12)$ , respectively [40–43]. These hydrogen-bonded rings form ribbons running along [010] (Fig. 3). Additionally, there are hydrogen bonds connecting neighbouring ribbons in the [100] direction ( $R_4^2(16)$ ) to form two-dimensional frameworks which are packed layerwise parallel to the crystallographic *ab* plane (Fig. 4). The voids present in this

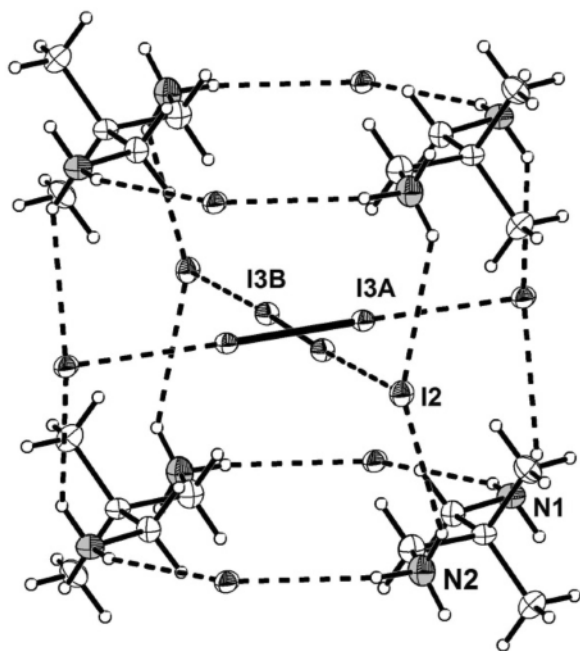


Fig. 2. The cube-shaped building units present in the title structure. The  $\text{-NH}_3^+$  groups of four 2,2-dimethylpropane-1,3-diazanium cations occupy the corners of the 'cube' while on eight of the twelve edges iodide anions are located near the midpoints. The disordered iodine molecule fills the central void. Displacement ellipsoids are drawn at the 45 % probability level.

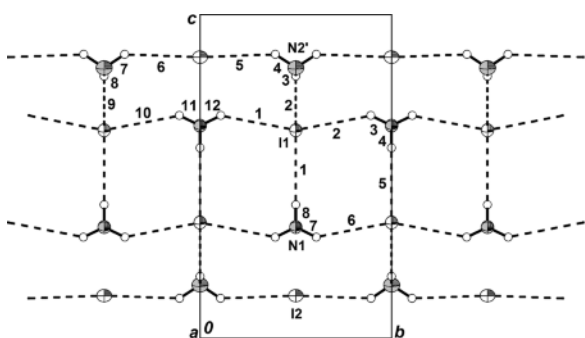


Fig. 3. View on the hydrogen-bonded ribbons running along [010] formed by azanium groups and iodide anions (graph-set descriptors  $R_4^2(8)$  and  $R_6^3(12)$  are indicated with numbers; symmetry code: ' =  $1 - x, y, 1 - z$ ). Displacement ellipsoids are drawn at the 45 % probability level.

hydrogen-bonded framework are occupied by iodine molecules. Due to a disorder of the iodine molecules over two positions, there are obviously two energetically similar possibilities for their fitting. In both orientations the iodine molecules which are located around

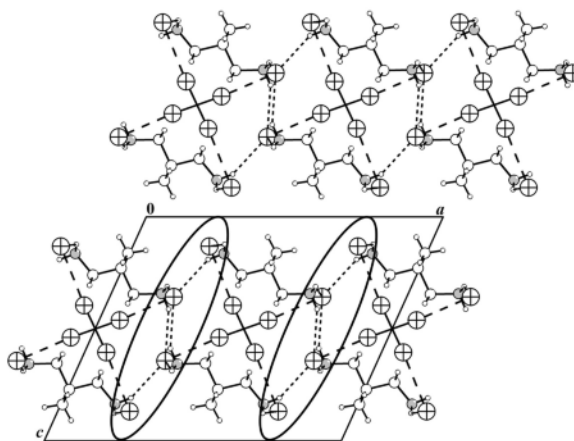


Fig. 4. View along [010] on the title structure, showing the layered packing of the hydrogen-bonded frameworks composed of 2,2-dimethylpropane-1,3-diazanium cations, iodine molecules and iodide anions (ribbons shown in Fig. 3 are encircled and lie parallel to the crystallographic  $bc$  plane at  $a = 1/4$  and  $3/4$ ).

a  $2/m$ -symmetric site show the typical short I–I distances ( $2.75 \text{ \AA}$ ), only slightly longer than in solid iodine [44]. The secondary I...I distances between the disordered iodine molecules and the adjacent iodide anions of the hydrogen-bonded framework amount to  $3.1240(16)$  and  $3.3641(4) \text{ \AA}$ , respectively. Both values are clearly within the typical range of secondary halogen bonds [4] and comparable to those found for other polyiodide structures [21, 23, 45]. Hence, the structural motif of a linear  $\text{I}_4^{2-}$  dianion is present here (Fig. 1). An analysis of the binding pocket of the caged iodine molecule seems to be worthwhile. Very weak non-classical C–H...I interactions between the  $\text{CH}_2$  groups of the organic dication and the iodine molecule can be discussed on the basis of any H...I distances shorter than  $3 \text{ \AA}$ . It appears that the aliphatic parts as well as the ionic parts of the hydrogen-bonded framework create a pocket which can accommodate both orientations of a caged iodine molecule (Fig. 5).

#### Vibrational spectroscopy of **1**

The Raman spectroscopic results are in excellent agreement with those of the crystal structure analysis. Since the linear  $\text{I}_4^{2-}$  dianion can be understood as an iodine molecule interacting with two iodide donors, a shift of the I–I vibration to lower wavenumbers compared to elemental iodine would be expected

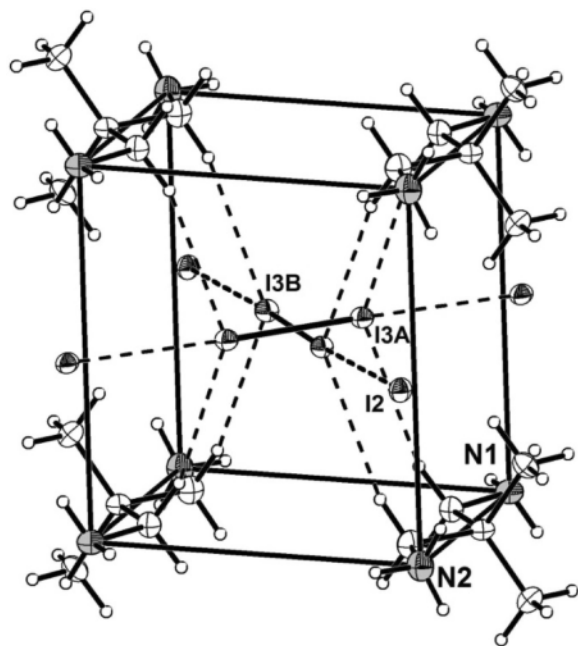


Fig. 5. The pocket containing the caged iodine molecule. Very weak non-classical C–H...I interactions between the CH<sub>2</sub> groups of the 2,2-dimethylpropane-1,3-diazanium cations and the disordered iodine molecule are shown as dashed lines.

due to a weakening of the I–I bond. For the solid phase of elemental iodine, two stretching modes are observed at 180 and 189 cm<sup>−1</sup> with symmetries A<sub>g</sub> and B<sub>3g</sub>, respectively [46–48]. The Raman spectrum of the title compound shows one very strong band at 173 cm<sup>−1</sup> which is in good accordance to the results of related studies on tetraiodide dianions [49–51]. The typical Raman bands of the 2,2-dimethylpropane-1,3-diazanium cation can be found as much weaker bands. On the basis of calculated vibrational frequencies [52], the IR bands of the title compound can be assigned to the NH ( $\nu$  = 3078, 3014 and 2967 cm<sup>−1</sup>;  $\delta$  = 1382 and 1364 cm<sup>−1</sup>), CH ( $\nu$  = 2949 and 2912 cm<sup>−1</sup>;  $\delta$  = 1574, 1467 and 1451 cm<sup>−1</sup>), CC ( $\nu$  = 1364 and 1078 cm<sup>−1</sup>;  $\delta$  = 951 cm<sup>−1</sup>), and NC ( $\nu$  = 988 cm<sup>−1</sup>) vibrations of the 2,2-dimethylpropane-1,3-diazanium cation.

#### *Thermal decomposition of 1 to 2,2-dimethylpropane-1,3-diazanium diiodide (2)*

Bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1) (**1**) decomposes at 433 K and

$2 \times 10^{-3}$  mbar under release of iodine. Subsequent powder diffraction experiments (Fig. 6) have shown that the resulting colourless powder is 2,2-dimethylpropane-1,3-diazanium diiodide (**2**) which has already been crystallographically characterised by Dou *et al.* [37]. Similarly to the structure of **1**, the structure of 2,2-dimethylpropane-1,3-diazanium diiodide (**2**) contains hydrogen-bonded R<sub>4</sub><sup>2</sup>(8) rings, composed of azanium groups and iodide ions, which form ribbons running along [010]. These ribbons are linked approximately along [001] by the 2,2-dimethylpropane-1,3-diazanium cations resulting in two-dimensional hydrogen-bonded networks which are packed layerwise along [100].

### Conclusion

We have shown that the reaction of 2,2-dimethylpropane-1,3-diamine with hydroiodic acid in the presence of iodine gives the new iodine inclusion compound bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1) (**1**). The structure of **1** contains cube-like building units which are further connected by weak to medium strong N–H...I hydrogen bonds to form a two-dimensional framework. The title compound was found to be thermally decomposed to the known 2,2-dimethylpropane-1,3-diazanium diiodide (**2**) [37] under release of iodine. The structures of both compounds have been verified by Raman and IR spectroscopy as well as powder diffraction experiments. This contribution provides a further example demonstrating the capability of  $\alpha,\omega$ -diazaniumalkanes to assist in the building of porous architectures.

### Experimental Section

#### *General considerations*

All chemicals were obtained from commercial sources and used as purchased. The Raman spectra were measured using a Bruker MULTIRAM spectrometer (Nd: YAG laser at 1064 nm; InGaAs detector) with an apodized resolution of 8 cm<sup>−1</sup> in the region of 4000–70 cm<sup>−1</sup>. IR spectroscopic data were collected on a Digilab FT3500 spectrometer with an apodized resolution of 2 cm<sup>−1</sup> using a MIRacle ATR unit (Pike Technologies) between 4000 and 560 cm<sup>−1</sup>. Elemental analyses (C, H, N) were performed with a HEKA-Tech Euro EA3000 instrument. Powder X-ray diffraction patterns were measured on a Stoe Stadi-P diffractometer working in transmission mode with Debye-Scherrer geometry. The

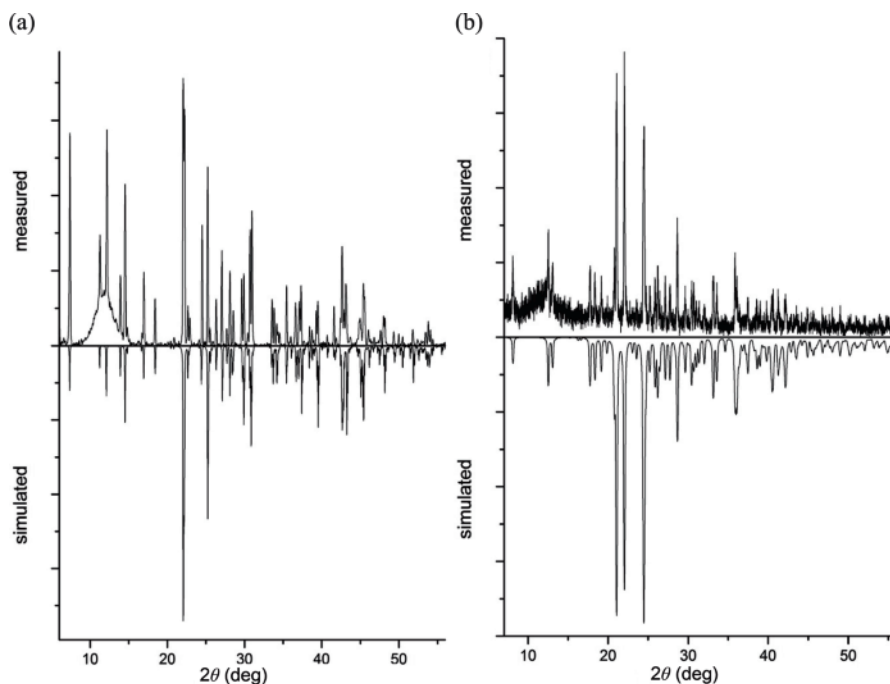


Fig. 6. (a) Comparison of the measured and the simulated powder diffraction patterns of bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodide (**1**). (b) Comparison of the measured and the simulated powder patterns of 2,2-dimethylpropane-1,3-diazanium diiodide (**2**). The uplift of the underground at round about  $2\theta = 12^\circ$  can be assigned to a foil used for sample preparation.

used  $\text{CuK}\alpha_1$  radiation was monochromatised by a Ge(111) monochromator. Comparative powder patterns were simulated from the single-crystal data with the programme POWDERCELL 2.3.

*Bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodide (1 : 1) (1)*

Bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodide (**1**) was synthesised by dissolving 0.16 g (1.6 mmol) 2,2-dimethylpropane-1,3-diamine and 0.81 g (3.2 mmol) iodine in 15 mL of 57% aqueous hydroiodic acid. Heating to 373 K yielded a dark solution. Upon slow cooling to room temperature dark-red platelets crystallised at the bottom of the reaction vessel within one to two days. – Raman (powder sample):  $\nu$  ( $\text{cm}^{-1}$ ) = 2953(w), 2889(w), 1543(w), 1495(vw), 1474(w), 1077(vw), 1029(w), 990(vw), 953(vw), 720(w), 173(vs). – IR (single crystal, ATR):  $\nu$  ( $\text{cm}^{-1}$ ) = 3379(vs, br), 3078(vs, br), 3014(vs, br), 2967(s), 2949(s), 2912(s), 2551(w), 2318(w), 1619(w, br), 1574(m), 1467(m), 1451(m), 1364(w), 1078(w), 1019(w), 988(w), 951(vw), 841(w). – Elemental analysis:  $\text{C}_{10}\text{H}_{32}\text{N}_4\text{I}_6$  (969.79): calcd. C 12.4, H 3.3, N 5.8; found C 11.9, H 3.3, N 5.9.

*2,2-Dimethylpropane-1,3-diazanium diiodide (2)*

2,2-Dimethylpropane-1,3-diazanium diiodide (**2**) was prepared by heating a powder sample of **1** (0.5 g) at 433 K under reduced pressure ( $2 \times 10^{-3}$  mbar). After three days all of the powder had turned colourless, and elemental iodine was deposited in a cryo trap. – Raman (powder sample):  $\nu$  ( $\text{cm}^{-1}$ ) = 2957(s), 2916(m), 1542(m), 1492(m), 1481(m), 1073(w), 1029(m), 993(vw), 959(w), 716(m). – IR (single crystal, ATR):  $\nu$  ( $\text{cm}^{-1}$ ) = 3092(vs, br), 3022 (vs, br), 2985(s), 2971(s), 2909(s), 2693(w), 2638(w), 2580(w), 2531(w), 1818(w, br), 1583(s), 1491(s), 1467(s), 1449(m), 1381(w), 1333(m), 1207(w), 1101(vw), 1054(m), 1000(w), 935(w), 886(w), 849(w), 823(vw). – Elemental analysis:  $\text{C}_5\text{H}_{16}\text{N}_2\text{I}_2$  (358.00): calcd. C 16.8, H 4.5, N 7.8; found C 16.9, H 4.2, N 7.7.

*X-Ray structure determination*

A single crystal of the title compound was selected directly from the mother liquor and rapidly transferred into the cold gas stream of the Xcalibur diffractometer equipped with an EOS detector [53]. The data collection generally followed the routine procedure with an increase of the exposure time,



Table 2. Crystal structure data for **1**.

Bis(2,2-dimethylpropane-1,3-diazanium) tetraiodide-diiodine (1 : 1) ( <b>1</b> )	
Empirical formula	C <sub>10</sub> H <sub>32</sub> N <sub>4</sub> I <sub>6</sub>
<i>M<sub>r</sub></i>	969.79
Crystal size, mm <sup>3</sup>	0.32 × 0.26 × 0.09
Crystal system	monoclinic
Space group	<i>C2/m</i>
<i>a</i> , Å	15.7727(4)
<i>b</i> , Å	7.0363(1)
<i>c</i> , Å	13.0376(3)
β, deg	114.513(3)
<i>V</i> , Å <sup>3</sup>	1316.52(6)
<i>Z</i>	4
<i>D</i> <sub>calcd.</sub> , g cm <sup>−3</sup>	2.45
μ (MoKα), mm <sup>−1</sup>	7.1
Absorption corr.	analytical
<i>T</i> <sub>min</sub> / <i>T</i> <sub>max</sub>	0.152/0.525
<i>F</i> (000), e	876
<i>T</i> , K	102
λ, Å	0.71073
2θ <sub>max</sub> , deg	51.00
Completeness, %	99.8
Measured/indep. reflexions/ <i>R</i> <sub>int</sub>	10 311/1315/0.022
Ref. parameters/restraints	78/6
<i>R</i> [ <i>F</i> > 4 σ( <i>F</i> )]	0.0156
<i>wR</i> ( <i>F</i> <sup>2</sup> , all data)	0.0392
<i>S</i> (GoF)	1.21
Δρ <sub>min</sub> /max, e Å <sup>−3</sup>	−0.84/0.96

which is often needed for this class of compounds [24–26]. An analytical absorption correction was applied [53]. The structure solution and the refinement succeeded using the SHELX programme system [54]. For more information on crystallographic details see Table 2.

CCDC 996392 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](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Computational methods

The optimised geometry and vibrational frequencies of the 2,2-dimethylpropane-1,3-diazanium cation were calculated at the density functional theory level by use of the B3LYP method, as implemented in the programme GAUSSIAN 09 [52]. The 6-311G basis set was used. Calculations were performed on the HILBERT Cluster at the Heinrich-Heine-Universität Düsseldorf. The geometry of the 2,2-dimethylpropane-1,3-diazanium cation has been confirmed by frequency analysis to be a minimum of the corresponding potential energy surface. Geometry optimisation resulted in an *all-transoid* conformation of the N1–C1–C2–C3–N2 chain with an eclipsed arrangement of the two –NH<sub>3</sub><sup>+</sup> groups. The C<sub>2v</sub> symmetry of the organic dication was verified. The calculated vibrational frequencies were assigned to the measured IR and Raman bands with the aid of GAUSSVIEW 3.0 [55]. All over, the calculated frequencies are in good agreement with the experimental values, except the NH stretching modes of the –NH<sub>3</sub><sup>+</sup> groups. The calculated frequencies of the dication in the vapour phase are shifted to higher energies owing to the absence of hydrogen bonds, which are present in the solid state.

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