Crystal structure of bis(1,3-phenylenedimethanaminium) bis(triiodide) tetraiodide – water (1/2) , $C_8H_{16}I_5N_2O$

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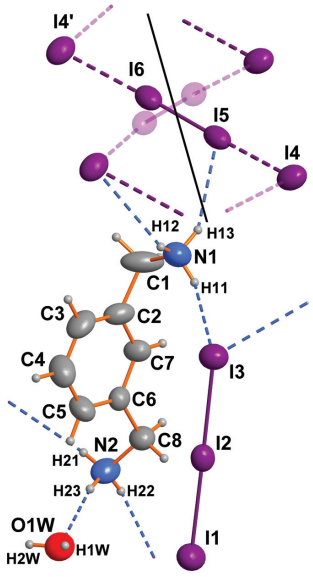

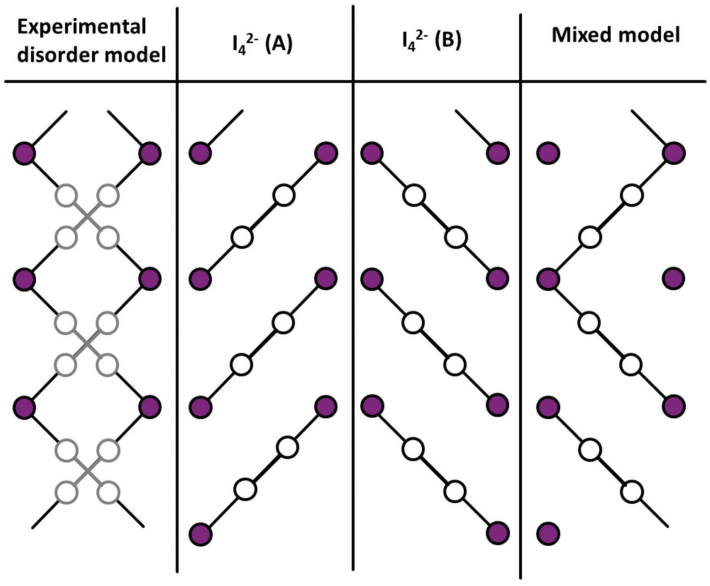

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Abstract

$C_8H_{16}I_5N_2O$, monoclinic, $C2/c$ (no. 15), $a = 34.180(5)$ Å, $b = 7.6817(3)$ Å, $c = 21.421(3)$ Å, $\beta = 137.93(3)°$, $Z = 8$, $V = 3768.7(16)$ Å^3, $R_{gt}(F) = 0.0364$, $wR_{ref} = 0.0737$, $T = 290(2)$ K.

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Tables 1 and 2 contain details on the crystal structure as well as measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

The title compound was synthesized by the reaction of 57% aqueous hydroiodic acid and 1,3-phenylenedimethanamine at ambient conditions.

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Table 1: Data collection and handling.

Crystal:	Black needle
Size:	0.74 × 0.12 × 0.05 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	8.24 mm^{-1}
Diffractometer, scan mode:	Xcalibur, ω
θ_{max}, completeness:	27.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	28854, 4097, 0.049
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3041
$N(param)_{refined}$:	163
Programs:	Diamond [1], CrysAlis^{PRO} [2], SHELX [3-5]

Experimental details

A single crystal of the title compound was directly selected from the mother liquor and mounted on a Xcalibur four-circle diffractometer equipped with an EOS detector [2]. An absorption correction (Numerical absorption correction based on Gaussian integration) was applied [2]. The structure solution and the refinement succeeded using the SHELX program system [3–5].

Atomic coordinates of hydrogen atoms at the water molecule were refined using distance restraints. All other

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
I1	0.21921(2)	1.13733(6)	0.06168(3)	0.07461(15)
I2	0.29324(2)	1.12572(5)	0.25844(3)	0.05662(13)
I3	0.37046(2)	1.11908(6)	0.46076(3)	0.07017(15)
I4	0.40481(2)	0.73934(5)	0.71186(3)	0.06867(15)
I5[a]	0.46031(3)	0.37809(11)	0.72498(5)	0.0647(2)
I6[a]	0.51914(3)	0.08474(11)	0.75254(5)	0.0660(2)
O1W	0.31628(19)	0.8923(6)	0.0587(3)	0.0695(12)
H1W	0.326(3)	0.997(4)	0.085(5)	0.120*
H2W	0.338(3)	0.833(9)	0.057(5)	0.120*
N1	0.4382(2)	0.7048(8)	0.5775(4)	0.0798(16)
H11	0.406345	0.766800	0.531205	0.120*
H12	0.469112	0.774759	0.615110	0.120*
H13	0.433971	0.653327	0.609479	0.120*
C1	0.4464(3)	0.5735(8)	0.5395(4)	0.088(2)
H1A	0.421676	0.474157	0.519286	0.105*
H1B	0.486655	0.534320	0.587797	0.105*
N2	0.3013(2)	0.5969(6)	0.1279(3)	0.0649(14)
H21	0.326015	0.509714	0.150098	0.120*
H22	0.311959	0.689272	0.118241	0.120*
H23	0.265401	0.564663	0.074434	0.120*
C2	0.4317(3)	0.6433(7)	0.4570(4)	0.0573(15)
C3	0.4708(2)	0.7451(8)	0.4712(4)	0.0694(18)
H3	0.507401	0.767834	0.531497	0.083*
C4	0.4561(3)	0.8127(9)	0.3973(5)	0.0748(19)
H4	0.482925	0.879483	0.407048	0.090*
C5	0.4013(3)	0.7825(8)	0.3078(4)	0.0612(16)
H5	0.390919	0.834131	0.257751	0.073*
C6	0.3620(2)	0.6767(7)	0.2916(4)	0.0462(13)
C7	0.3782(2)	0.6082(6)	0.3677(4)	0.0516(14)
H7	0.352212	0.536531	0.358283	0.062*
C8	0.3021(2)	0.6415(8)	0.1957(4)	0.0588(15)
H8A	0.284931	0.546303	0.198820	0.071*
H8B	0.278008	0.743665	0.173783	0.071*

[a]Occupancy: 0.5.

hydrogen atoms were added using a riding model with fixed U_{iso} parameters. The maximum residual peak of 1.53 e Å^{-3} is found 0.87 Å from I4 and the deepest hole of −1.20 e Å^{-3} is found 0.75 Å from I4.

Comment

Nowadays, polyiodides (known in the 19th and the beginning of the 20th century as periodides [6]) are defined as the anionic components of salts that fulfill the general formula $I^{n-}{}_{2m-n}$ ($n = 2$–5, $m =$ integer). Even the most complex polyiodides are composed of some basic ions (I^-, I_3^-) and I_2 molecules, respectively. The aforementioned anions and the diiodine molecule tend to form olygomeric ions and extended aggregates by means of weak to medium strong halogen bonds [7–9]. It is well known that short chain polyiodides are key ions in the charge transfer processes of the classical dye-sensitised solar cells [10, 11]. It should not remain unmentioned that polyiodide species may be used as ambipolar zinc electrolytes [12] and further promoted some developments in the field of lithium–iodine redox batteries [13]. There are new considerations that suggest they might have anti-microbial properties [14]. A well established field of research is the synthesis of new polyiodide-containing salts based on organic cations [15]. We have already shown that the lengths and shapes of cations influence or even determine the topology of the embedded polyiodide anions [16–19] and the inclusion of neutral iodine molecules [20, 21]. Besides the quitous triiodide anion, in recent years the presence of formal I_4^{2-} anions have been reported more often [22, 23]. The formal I_4^{2-} anion is of particular interest as, depending on the interpretation of the iodide–iodine bonds, an alternative description as two iodide anions weakly attached to one I_2 molecule is possible [20, 21]. Another distortion of the formal I_4^{2-} may lead to the adduct of two anions [$I^- \cdot I_3^-$] [24, 25]. This contribution is part of a long term project, which focuses on polyiodides designed and trapped in hydrogen-bonded surroundings [16–21, 26, 27].

The asymmetric unit of the title structure contains one 1,3-phenylenedimethanaminium dication, one discrete triiodide anion, one half of a I_4^{2-} anion as well as a water molecule (left part of the figure). In order to avoid any confusion with true pentaiode salts [15] the more structured compound name bis(1,3-phenylenedimethanaminium) bis(triiodide) tetraiodide – water (1/2) is used. Bond lengths and angles in the cation are in the range of expectation [28–30]. Even though nitrogen-based cations containing an aryl and an alky moiety are well known to stabilize polyiodes [31], it was surprising that not even the crystal structure of the 1,3-phenylenedimethanaminium hydroiodide is reported. The 1,3-phenylenedimethanaminium has a conformational flexibility by a rotation about the C1–C2 and C6–C8 single bonds, respectively (left part of the figure). A dihedral angle of −177.5(4)° for the atoms N1, C2, C8, N2 in this structure leads to double hook shape of the dication. The aminium group N1 forms weak hydrogen bonds with iodine atoms only, whereas the aminium group N2 forms normal to weak hydrogen bonds with two water molecules and one iodine (see the left part of the figure). The donor$\cdots$acceptor distances for N$\cdots$O are 2.879(6) Å and 2.956(7) Å, respectively. The N$\cdots$I distances shown in the left part of the figure range from 3.602(5) Å to 3.811(5) Å. The anionic substructure consists of a triiodide anion and a formal I_4^{2-} anion aranged around a twofold axis. The twofold axis is shown as black line in the left part of the figure. The disrecte triiodode ion (I1-I2-I3) shows the typical asymmetry: I1–I2 = 2.8882(15) Å; I2–I3 = 2.9613(15) Å. In accordance with the literature [16, 27, 32,

33] the asymmetry is dependent on the intermolecular interactions in the solid state, which are mainly hydrogen bonds in this case. The formal I_4^{2-} anion is characterised by a I5–I6 single bond 2.7762(13) Å for the I_2 molecule [34] and two different medium strong halogen bonds [I4–I5 = 3.2538(10) Å, I6–I4′ = 3.3816(10) Å, ′ = 1−x, −1 + y, 1.5 − z]. The 1/1 disorder model of the I_2 moiety in the formal I_4^{2-} anion opens the way for different interpretations (see the right part of the figure). Within the crystal there may be some domains which realise a strictly ordered stacking (columns A and B in the right part of the figure). It nonetheless remains conceivable that iodine moieties change their orientations to create smaller or even extended chain snippets (Mixed model column in the right part of the figure). The shortest iodine iodine distance between the triodide anion and the I_4^{2-} anion is almost 4.0 Å, which rules out any significant bonding interactions as it simply represents the iodine – iodine van der Waals distance in various scales [35].

The formal I_4^{2-} anion in the title structure looks like a snapshot of an intermediate between the well known centrosymmetric arrangement [20] and two discrete anions $[I^- \cdot I_3^-]$ [24, 25] and may lead to a better understanding of the bonding schemes of short-chain polyiodides.

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