The layered crystal structure of piperazine-1,4-diium diiodide – diiodine (1:1), $C_4H_{12}I_4N_2$

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Abstract

$C_4H_{12}I_4N_2$, triclinic, $P\bar{1}$ (no. 2), $a = 6.4800(6)$ Å, $b = 7.4090(7)$ Å, $c = 8.0824(8)$ Å, $\alpha = 63.939(10)^\circ$, $\beta = 67.290(10)^\circ$, $\gamma = 69.471(9)^\circ$, $V = 313.8$ Å³, $Z = 1$, $R_{gt}(F) = 0.0201$, $wR_{ref}(F^2) = 0.0507$, $T = 100$ K.

Table 1. Data collection and handling.

Crystal:	orange-red blocks, size 0.163×0.305×0.5395 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	98.83 cm ⁻¹
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	50.95°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4047, 1157
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1127
$N(param)_{refined}$:	49
Programs:	CrysAlisPRO, SHELX, DIAMOND [1–3]

Source of material

86.1 mg (1 mmol) piperazine, 253.8 mg (1 mmol) I_2 and 0.15 mL hydroiodic acid (58%; 2 mmol) were sealed in a thick-walled borosilicate glass tubing. Heating up to 130 °C and slow cooling (10 °C/h) to room temperature gave orange-red crystals of the title compound in almost quantitative yield. The **Raman spectrum** (Bruker MULTIRAM spectrometer (Nd:YAG-Laser at 1064 nm; RT-InGaAs-detector; back scattering geometry)) shows only one very strong signal at 169 cm⁻¹ whereas all other signals are weak.

Experimental details

The hydrogen atoms attached to the carbon atoms were included in the latest stages of the refinement using a riding model with their U_{iso} values set to $1.2U_{eq}(C)$. For the positions of the hydrogen atoms of the NH_2^+ group the AFIX 24 option of the SHELX system [2] was used which allows a change of the N–H distance during the refinement. One common U_{iso} value was refined for these two hydrogen atoms. The highest difference electron density peak (1.04 e⁻Å⁻³) is 0.88 Å apart from I1.

Discussion

Polyiodides, built from I^- , I_2 and I_3^- subunits, fulfill the general formula I_{2m+n}^{n-} ($n = 1-4$, $m = \text{integer}$) [4–8] and are connected *via* halogen bonds. The halogen bonding received much attention because of its influence on the functionality of biological systems and its role in the crystal engineering of new materials for various applications [9, 10]. Because of their potential use as Agent Defeat Weapons (ADW) [11] there is a general interest in iodine-rich compounds. Furthermore, it has been proved that diaminium and pyridinium iodides and corresponding polyiodides influence the redox chemistry in dye-sensitized solar cells [12, 13]. Several new polyiodides have been synthesized and structurally characterized in the α,ω -diamonioalkane iodide / diiodine system [14–18]. In these cases the lengths of the stick-shaped cations excellently fit with the topologies of the corresponding polyiodides. This synthetic protocol is known as dimensional caging [19]. This contribution is part of our ongoing interest on the synthesis of new polyiodides using nitrogen containing cyclic cations [20–22].

The asymmetric unit of the title structure contains one half of a piperazine-1,4-diium dication ($pipH_2^{2+}$) and one half of a diiodine molecule, both located around inversion centers. Whereas the iodide anion is placed in a general position. The geometric parameters of the $pipH_2^{2+}$ cation - exhibiting an all-chair conformation - are all in the expected ranges (C–C: 1.505(7) Å; C–N: 1.485(6) and 1.498(6) Å). All moieties are connected by hydrogen and halogen bonds, respectively (Figure, upper part; $' = 1-x, 1-y, 1-z$; $'' = 2-x, -y, -z$) [23]. Each dication is connected to four iodide an-

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ions by N–H...I hydrogen bonds (N...I: 3.531(4) and 3.486(4) Å) forming polymeric strands along *a* (Figure, lower part). In these strands the characteristic hydrogen bonding ring motif can be classified by the $R_4^2(14)$ graph set descriptor [24]. Parallel strands are connected *via* diiodine molecules by halogen bonds in the (011) plane to form a layered structure (Figure, lower part). Consequently, the structure comprises almost linear I₄^{2−} sub-units, which show the typical bond lengths of 2.7530(7) Å for the central I–I bond and 3.3488(6) Å for the secondary interaction between the I₂ molecule and the two hydrogen bonded iodide anions [14, 25–27]. In the solid state two stretching modes are expected

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(12)	2i	0.766(8)	0.249(5)	0.408(2)	0.04(1)
H(11)	2i	0.529(6)	0.273(3)	0.4536(8)	0.04(1)
H(1A)	2i	0.6289	0.5317	0.1775	0.016

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
I(1)	2i	0.23022(5)	0.24153(5)	0.30700(4)	0.0096(2)	0.0128(2)	0.0203(2)	−0.0017(1)	−0.0037(1)	−0.0078(1)
I(2)	2i	0.77669(6)	0.07414(5)	0.08832(4)	0.0186(2)	0.0144(2)	0.0128(2)	−0.0061(1)	−0.0030(1)	−0.0046(1)
N(1)	2i	0.6341(7)	0.3256(6)	0.4445(6)	0.010(2)	0.010(2)	0.018(2)	−0.001(2)	−0.003(2)	−0.007(2)
C(1)	2i	0.6174(8)	0.5366(7)	0.2989(7)	0.015(2)	0.010(2)	0.013(2)	−0.003(2)	−0.003(2)	−0.004(2)
C(2)	2i	0.6073(8)	0.3264(7)	0.6367(7)	0.015(2)	0.011(2)	0.016(2)	−0.002(2)	−0.006(2)	−0.005(2)

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