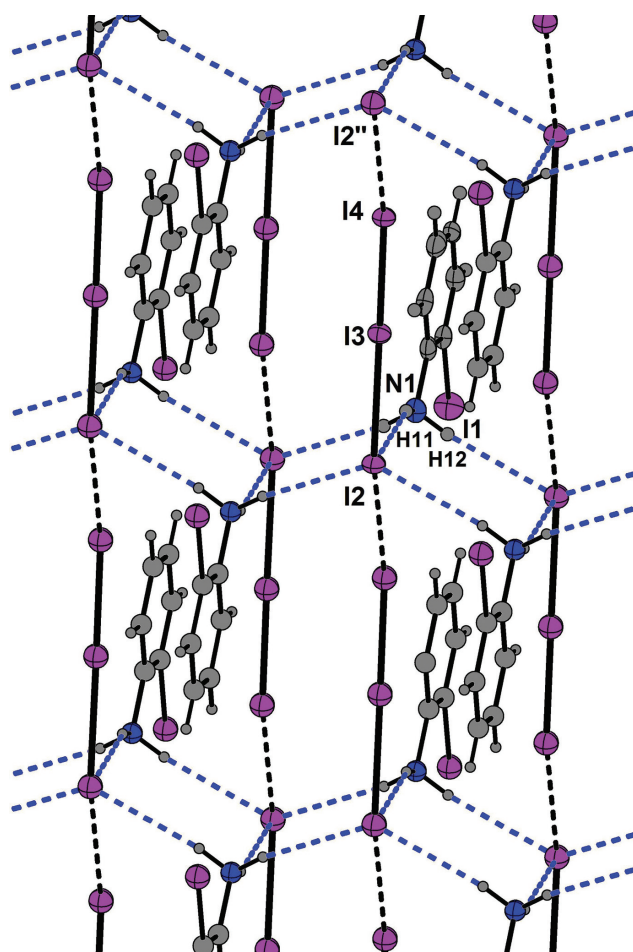


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Halogen and hydrogen bonding in the layered crystal structure of 2-iodoanilinium triiodide, $C_6H_7I_4N$



Abstract

$C_6H_7I_4N$, monoclinic, $P2_1/m$ (no. 11), $a = 9.2818(2)$ Å, $b = 6.55289(16)$ Å, $c = 11.0561(3)$ Å, $\beta = 114.051(3)^\circ$, $V = 614.08(3)$ Å³, $Z = 2$, $R_{gt}(F) = 0.0180$, $wR_{ref}(F^2) = 0.0367$, $T = 109(2)$ K.

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A part of the layered title crystal structure is shown in the figure. 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.

Table 1: Data collection and handling.

Crystal:	Orange plate
Size:	$0.25 \times 0.13 \times 0.01$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	10.1 mm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, φ and ω
$\theta_{\max}$, completeness:	27.0° , $>99\%$
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	6606, 1466, 0.034
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1296
$N(\text{param})_{\text{refined}}$:	76
Programs:	Diamond [1], CrysAlis ^{PRO} [2], SHELX [3, 4]

Source of material

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 4 cm^{-1} in the region of $4000\text{--}70 \text{ cm}^{-1}$. The title compound was synthesized by dissolving 0.22 g (1 mmol) 2-iodoaniline and 0.25 g (1 mmol) diiodine in 1 mL of 57% aqueous hydroiodic acid. Heating to 300 K for a few minutes yielded a dark colored solution. Evaporation at room temperature gave dark orange plate crystals of the title compound (systematic name: 2-iodobenzenaminium triiodide).

Experimental details

A single crystal of the title compound was directly selected from the mother liquor and rapidly transferred into the cold

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
I1	0.88099(4)	0.250000	0.03135(3)	0.02161(10)
N1	0.8563(5)	0.250000	0.3175(4)	0.0163(9)
H11	0.849(4)	0.250000	0.396(3)	0.034(10)*
H12	0.911(4)	0.138(5)	0.315(3)	0.034(10)*
C1	0.6981(6)	0.250000	0.2069(5)	0.0155(11)
C2	0.6836(6)	0.250000	0.0786(5)	0.0138(10)
C3	0.5335(6)	0.250000	−0.0243(5)	0.0165(11)
H3	0.522156	0.250000	−0.111808	0.020*
C4	0.4018(6)	0.250000	0.0040(5)	0.0195(11)
H4	0.301644	0.250000	−0.064539	0.023*
C5	0.4188(6)	0.250000	0.1348(5)	0.0215(12)
H5	0.329780	0.250000	0.153573	0.026*
C6	0.5663(6)	0.250000	0.2365(5)	0.0163(11)
H6	0.577935	0.250000	0.324080	0.020*
I2	0.95898(4)	0.250000	0.67290(3)	0.01430(9)
I3	0.60419(3)	0.250000	0.62212(3)	0.01337(8)
I4	0.28733(4)	0.250000	0.58194(3)	0.01551(9)

gas-stream ($T = 100$ K) of the Xcalibur four-circle diffractometer equipped with an EOS detector [2]. An absorption correction (Gaussian method) was applied [2]. The structure solution and the refinement were carried out using the SHELX program system [3–5]. Atomic coordinates of hydrogen atoms involved in hydrogen bonds were refined using distance restraints. All other hydrogen atoms were added using a riding model with fixed U_{iso} parameters. The maximum residual peak of $0.63 \text{ e } \text{\AA}^{-3}$ is found $1.03 \text{ \AA}$ from I1 and the deepest hole of $-0.84 \text{ e } \text{\AA}^{-3}$ is found $1.01 \text{ \AA}$ from I3.

Comment

Today, polyiodides (in the 19th and the beginning of the 20th century periodides [6]) are defined as the anionic parts of salts that fulfill the general formula I^{n-}_{2m-n} ($n = 2-5$, $m = \text{integer}$). Even polyiodides with a complex topology are constructed of basic units: I^- , I_3^- and I_2 . Thus, the triiodide anion has been considered as the simplest polyiodide species. These ions and the I_2 molecule tend to form extended aggregates by means of halogen bonds [7–9]. Especially for the I_3^- anion many polymeric structures that contain triiodide anions only are reported [9, 10]. Some of them are outstretched [11] and others show more complicated topologies [12]. Extended theoretical studies on the phenomenon of halogen bonding led to a deeper understanding of this type of non-covalent interaction [13]. Polyiodides are of interest not only because of their unique structures, but also because of their applications. Short chain polyiodides are key ions in the charge transfer processes of the classical dye-sensitised solar cells [14, 15]. Moreover, polyiodide species may be used as ambipolar zinc electrolytes [16] and contributed to developments in the

field of lithium–iodine redox batteries [17]. However, there is still an academic interest in new polyiodide-containing salts based on organic cations as the lengths and shapes of cations influence the topology of the polyiodide anions [12, 18–21]. We have already shown that heterocyclic cations like pyridinium derivatives [22, 23] or naturally occurring bases like caffeine [24] are excellent educts for the synthesis of polyiodide containing salts. In particular, there is profound interest in the competition between hydrogen and halogen bonding in haloanilinium halogenides [25, 26]. This contribution is part of a project, which focuses on polyiodides trapped in hydrogen-bonded surroundings [27–29].

All non-hydrogen atoms are located on the mirror plane in the centrosymmetric space group $P2_1/m$. Bond lengths and angles in the cation are within the expected range [26]. Each cation donates three hydrogen bonds to three adjacent triiodide anions ($\text{N1-H11} \cdots \text{I2}$: $3.643(4) \text{ \AA}$, $\text{N1-H12} \cdots \text{I2'}$: $3.677(2) \text{ \AA}$; $' = 2 - x, -y, 1 - z$). These geometric descriptors indicate charge-supported $\text{N-H} \cdots \text{I}$ hydrogen bonds [21].

The I–I distances in the formal triiodide anion of the title structure are: I2-I3 : $3.1069(4) \text{ \AA}$ and I3-I4 : $2.7895(4) \text{ \AA}$. These measures indicate a serious asymmetry, which is comparable to the situation in the structure of 1,8-diammoniooctane hexaiodide [21] (I–I distances: $2.7739(4) \text{ \AA}$, $3.1778(4) \text{ \AA}$). The more covalent part of the title anion (I3-I4) is only halogen bonded to the I2'' atom of a neighboring triiodide anion (I4-I2'' : $3.5752(4) \text{ \AA}$, $'' = -1 + x, y, z$). This secondary $\text{I} \cdots \text{I}$ bonding interaction is weak, but significantly shorter than any van der Waals distances in various scales [30]. Further significant $\text{I} \cdots \text{I}$ interactions can be ruled out as the corresponding iodine to iodine distances ($>4.1 \text{ \AA}$) are longer than the van der Waals sum.

The more ionic atom I2 solely forms the already mentioned hydrogen bonds. Consequently, the halogen bond and the three hydrogen bonds on one side of the triiodide anion, and only one halogen bonding interaction on the other side, can be made responsible for the observed asymmetry (*cf.* the figure).

The hydrogen bonds (blue dashed bonds in the figure) connect cations and triiodide anions resulting in a zig-zag ladder sub structure along the [010] direction. This substructure consists of ring motifs formed by two aminium groups and two triiodide anions (*cf.* the figure). This arrangement, which can be classified using the graph set descriptors $R_4^2(8)$ and $C_2^2(4)$ [31], are typical for this class of compounds [21, 32]. Halogen bonds (black dashed bond in the figure) connect adjacent ladders to form a layered structure.

Within the Raman spectrum of the title compound the lines which are characteristic for an asymmetric triiodide anion [21, 33] are found at $109 \text{ cm}^{-1}(\text{vs})$ and $155 \text{ cm}^{-1}(\text{vs})$. A general overview on the spectroscopy of triiodide species

is given by Deplano *et al.* in 1999 [34], but the topic is still a matter of intense research activity [35–37]. Salts which are based on iodoanilines and structurally related compounds are an interesting system to study halogen bonds in competition with other forces that influence the packing schemes of the corresponding crystal structures [26, 38, 39].

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