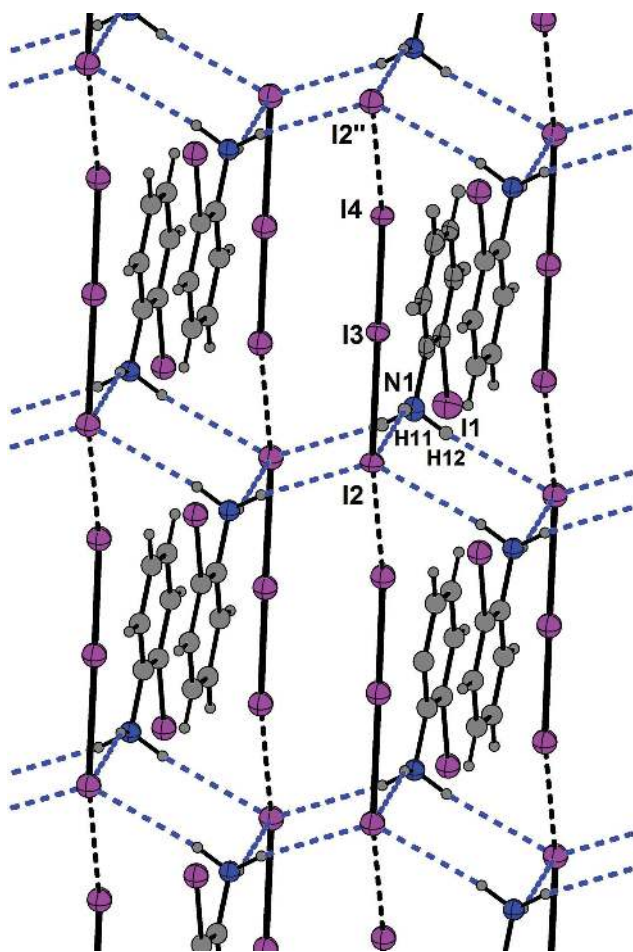


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Halogen and hydrogen bonding in the layered crystal structure of 2-iodoanilinium triiodide, $C_6H_7I_4N$



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
θ_{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 $0.63 \text{ e } \text{Å}^{-3}$ is found 1.03 Å from I1 and the deepest hole of $-0.84 \text{ e } \text{Å}^{-3}$ is found 1.01 Å 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 ($\text{N1-H11} \cdots \text{I2}$: $3.643(4) \text{ Å}$, $\text{N1-H12} \cdots \text{I2}'$: $3.677(2) \text{ Å}$; $' = 2 - x, -y, 1 - z$). 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: $3.1069(4) \text{ Å}$ and I3–I4 $2.7895(4) \text{ Å}$. These measures indicate a serious asymmetry, which is comparable to the situation in the structure of 1,8-diammoniooctane hexaiodide [21] (I–I distances: $2.7739(4) \text{ Å}$, $3.1778(4) \text{ Å}$). 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'': $3.5752(4) \text{ Å}$, $'' = -1 + x, y, z$). 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 ($>4.1 \text{ Å}$) 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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References

- Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.5.2. Crystal Impact, Bonn, Germany (2018).
- Oxford Diffraction: CrysAlis^{PRO}, (version 1.171.33.42). Oxford Diffraction Ltd., Oxford, UK (2009).
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
- Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **71** (2015) 3–8.
- Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B.: ShelXle: a Qt graphical user interface for SHELXL. *J. Appl. Crystallogr.* **44** (2011) 1281–1284.
- Tilden, W. A.: On the periodides of some of the organic bases. *J. Chem. Soc.* **18** (1865) 99–105.
- Bartashevich, E.; Yushina, I.; Kropotina, K.; Muhitdinova, S.; Tsirelson, V.: Testing the tools for revealing and characterizing the iodine-iodine halogen bond in crystals. *Acta Crystallogr. B* **73** (2017) 217–226.
- Blake, A. J.; Devillanova, F. A.; Gould, R. O.; Li, W. S.; Lippolis, V.; Parsons, S.; Radek, C.; Schröder, M.: Template self-assembly of polyiodide networks. *Chem. Soc. Rev.* **27** (1998) 195–205.
- Svensson, P. H.; Kloo, L.: Synthesis, structure, and bonding in polyiodide and metal iodide-iodine systems. *Chem. Rev.* **103** (2003) 1649–1684.
- Bof de Oliveira, A.; Beck, J.; Daniels, J.: Synthesis, crystal structure and Hirshfeld analysis of a new crystalline modification of the radical ion salt octamethylenetetrafulvalenium triiodide (OMTTF)₃. *Acta Crystallogr. E* **74** (2018) 1547–1552.
- Denker, M.; Breunig, H. J.; Ebert, K. H.; Behrens, U.: Iodketten in (Me₄Sb)₃I₈ und isolierte Triiodid-Ionen in Me₄AsI₃. *Angew. Chem.* **106** (1994) 1023–1024.
- Reiss, G. J.; van Megen, M.: Two new polyiodides in the 4,4'-bipyridinium diiodide/iodine system. *Z. Naturforsch. B* **67** (2012) 5–10 and references cited.
- Thirman, J.; Engelage, E.; Huber, S. M.; Head-Gordon, M.: Characterizing the interplay of Pauli repulsion, electrostatics, dispersion and charge transfer in halogen bonding with energy decomposition analysis. *Phys. Chem. Chem. Phys.* **20** (2018) 905–915.
- O'Regan, B.; Grätzel, M.: A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. *Nature* **353** (1991) 737–739.
- Correa-Baena, J.-P.; Abate, A.; Saliba, M.; Tress, W.; Jesper Jacobsson, T.; Grätzel, M.; Hagfeldt, A.: The rapid evolution of highly efficient perovskite solar cells. *Energy Environ. Sci.* **10** (2017) 710–727.
- Li, B.; Nie, Z.; Vijayakumar, M.; Li, G.; Liu, J.; Sprenkle, V.; Wang, W.: Ambipolar zinc-polyiodide electrolyte for a high-energy density aqueous redox flow battery. *Nature Commun.* **6** (2015) article no. 6303, 8 pages.
- Zhao, Y.; Hong, M.; Bonnet Mercier, N.; Yu, G.; Choi, H. C.; Byon, H. R.: A 3.5 V lithium-iodine hybrid redox battery with vertically aligned carbon nanotube current collector. *Nano Lett.* **14** (2014) 1085–1092.
- Walbaum, C.; Pantenburg, I.; Meyer, G.: Penta-, Hepta- und Oktaiodid-Anionen in Salzen mit Erdalkalimetall-Kronenether-Kationen. *Z. Naturforsch. B* **65** (2010) 1077–1083.
- Walbaum, C.; Pantenburg, I.; Junk, P.; Deacon, G.; Meyer, G.: Bulky cations and four different polyiodide anions in [Lu(Db18c6)(H₂O)₃(thf)₆]₄(I₃)₂(I₅)₆(I₈)(I₁₂). *Z. Anorg. Allgem. Chem.* **636** (2010) 1444–1446.
- Peuronen, A.; Rinta, H.; Lahtinen, M.: N···I halogen bonding supported stabilization of a discrete pseudo-linear [I₁₂]²⁻ polyiodide. *CrystEngComm* **17** (2015) 1736–1740 and references cited therein.
- van Megen, M.; Reiss, G. J.: I₆²⁻ Anion composed of two asymmetric triiodide moieties: a competition between halogen and hydrogen bond. *Inorganics* **1** (2013) 3–13.
- Reiss, G. J.; Leske, P. B.: The twinned crystal structure of bis(4-aminopyridin-1-ium) iodide triiodide, C₂₀H₂₈I₈N₈. *Z. Kristallogr. NCS* **229** (2014) 452–454 and references cited.
- Reiss, G. J.; Leske, P. B.: 2-Aminopyridin-1-ium triiodide. *Acta Crystallogr. E* **69** (2013) o1060–o1061.
- Merkelbach, J.; Majewski, M. A.; Reiss, G. J.: Crystal structure of caffenium triiodide – caffeine (1/1), C₁₆H₂₁I₃N₈O₄. *Z. Kristallogr. NCS* **233** (2018) 941–944.
- Attrell, R. J.; Widdifield, C. M.; Korobkov, I.; Bryce, D. L.: Weak halogen bonding in solid haloanilinium halides probed directly via chlorine-35, bromine-81, and iodine-127 NMR spectroscopy. *Cryst. Growth Des.* **12** (2012) 1641–1653.
- Gray, L.; Jones, P., G.: Secondary bonding interactions in some haloanilinium halides. *Z. Naturforsch. B* **57** (2002) 61–72.
- Reiss, G. J.: I₅⁻ polymers with a layered arrangement: synthesis, spectroscopy, and structure of a new polyiodide salt in the nicotine/HI/I₂ system. *Z. Naturforsch. B* **70** (2015) 735–739.
- Reiss, G. J.: Two iodine-rich (dimethylphosphoryl)methanaminium iodides. *Z. Kristallogr. CM* **232** (2017) 789–795.
- Reiss, G. J.: A cyclic I₁₀²⁻ anion in the layered crystal structure of theophyllinium pentaiodide, C₇H₉I₅N₄O₂. *Z. Kristallogr. NCS (NCRS_2019_0082)* accepted.
- Hu, S.-Z.; Zhou, Z.-H.; Xie, Z.-X.; Robertson, B. E.: A comparative study of crystallographic van der Waals radii. *Z. Kristallogr. CM* **229** (2014) 517–523.
- Grell, J.; Bernstein, J.; Tinhofer, G.: Investigation of hydrogen bond patterns: a review of mathematical tools for the graph set approach. *Crystallogr. Rev.* **8** (2002) 1–56.

32. Reiss, G. J.; van Megen, M.: Synthesis, structure and spectroscopy of a new polyiodide in the α,ω -diazaniumalkane iodide/iodine system. *Z. Naturforsch.* **67B** (2012) 447–451.
33. Marks, T. J.; Kalina, D. W.: Highly conductive halogenated low-dimensional materials. In: *Extended linear chain compounds, Volume 1* (Ed. Miller, J. S.), p. 197–331. Plenum Press, New York, NY, USA (1982).
34. Deplano, P.; Ferraro, J. R.; Mercuri, M. L.; Trogu, E. F.: Structural and Raman spectroscopic studies as complementary tools in elucidating the nature of the bonding in polyiodides and in donor I₂ adduct. *Coord. Chem. Rev.* **188** (1999) 71–95.
35. Yushina, I. D.; Batalov, V. I.; Bartashevich, E. V.; Davydov, A. O.; Zelenovskiy, P. S.; Masunov, A. E.: Raman spectroscopy and theoretic study of hyperpolarizability effect in diiodobutenyl-bis-thioquinolinium triiodide at low temperature. *J. Raman Spectrosc.* **48** (2017) 1411–1413.
36. Abe, H.; Tokita, T.; Iwata, K.; Ozawa, S.: Lithium-triggered spontaneous formation of polyiodides in room-temperature ionic liquid-alcohol solutions. *Spectrochim. Acta A* **212** (2019) 255–261.
37. Shestimerova, T. A.; Yelavik, N. A.; Mironov, A. V.; Kuznetsov, A. N.; Bykov, M. A.; Grigorieva, A. V.; Utochnikova, V. V.; Lepnev, L. S.; Shevelkov, A. V.: From isolated anions to polymer structures through linking with I₂: synthesis, structure, and properties of two complex bismuth(III) iodine iodides. *Inorg. Chem.* **57** (2018) 4077–4087.
38. Kassel, C. J.; Swenson, D. C.; Pigge, F. C.: Charge-assisted halogen bonding in bromo- and iodophenylpyridinium chlorides. *Cryst. Growth Des.* **15** (2015) 4571–4580.
39. Raatikainen, K.; Cametti, M.; Rissanen, K.: The subtle balance of weak supramolecular interactions: the hierarchy of halogen and hydrogen bonds in haloanilinium and halopyridinium salts *Beilstein J. Org. Chem.* **4** (2010) 6 (13 pages).