The twinned crystal structure of bis((4-aminopyridin-1-ium) iodide triiodide, $C_{20}H_{28}I_8N_8$

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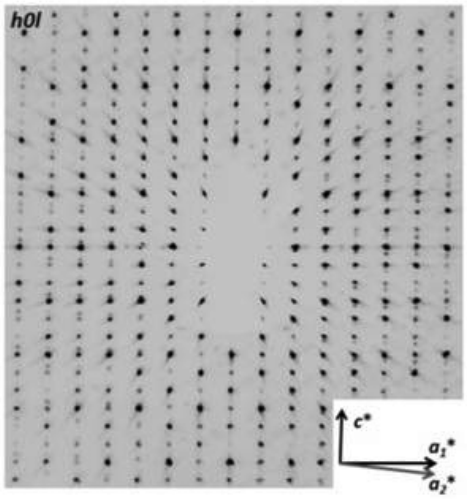
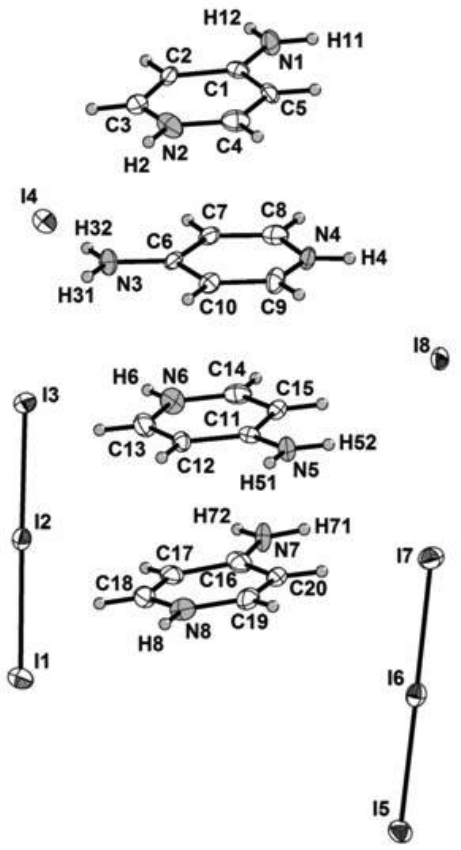
Received June 26, 2014, accepted September 24, 2014, available online October 10, 2014, CCDC no. 1267/4181





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Abstract

$C_{20}H_{28}I_8N_8$, *C*2/*c* (no. 15), a = 17.2334(2) Å, b = 13.95310(10) Å, c = 29.3522(3) Å, β = 91.0960(10)°, V = 7056.7 Å^3, Z = 8, $R_{gt}(F)$ = 0.0458, $wR_{ref}(F^2)$ = 0.1195, T = 290 K.

Table 1. Data collection and handling.

Crystal:	brown blocks, size 0.1871×0.2420×0.4296 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	70.56 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Eos, ω
$2\theta_{max}$:	50.6°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7988, 7988
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 7793
$N(param)_{refined}$:	331
Programs:	CrysalisPRO, SHELX, DIAMOND [1–3]

Source of material

4-Aminopyridine (0.16 g; 1.7 mmol) was dissolved in 10 ml concentrated hydroiodic acid yielding a brown mixture. This mixture was heated to 90 °C and then slowly cooled to room temperature. Within a few days orange needles grew from this solution. **Elemental analysis** ($[C_5H_7N_2]_2I[I_3]$): Calcd., %: C, 17.21; H, 2.02; N, 8.03; I, 72.74. Found, %: C, 16.94; H, 1.92; N, 8.04; I, 73.17. For details on the elemental analytical methods used, see general procedures given in the literature [4, 5]. For the quantitative analysis of iodine alternatively aluminium was used as the reducing agent. The **Raman spectrum** (Bruker MULTIRAM spectrometer (Nd:YAG-Laser at 1064 nm; RT-InGaAs-detector; back scattering geometry)) shows two very strong bands at 154 and 105 cm^{-1} which can be assigned to the triiodide anion [6].

Experimental details

All investigated crystals suffer from the same non-merohedral twinning (180° about (1, 0, –0.03) in the reciprocal space and 180° about [1 0 0] in the direct space). An image of the *h*0*l* layer (constructed from the raw diffraction data [1]) of the reciprocal lattice of the title structure is shown in the upper figure. The increasing offset of the reflections of the second, smaller component (direction a_2*) towards higher diffraction angles can be clearly seen. The data collection for this study was undertaken using a crystal with a relatively large ratio of the twin components (0.93 : 0.07). In addition there is an orientational disorder (ratio 3 : 1) of one of the four crystallographically independent cations (For clarity not shown in the figure; see tables). All hydrogen atoms were included in the final stages of the refinement using riding models. The U_{iso} values of the hydrogen atoms are set to plausible values in respect to the U_{eq} values of the atoms they are attached to. The largest difference electron density peaks (< 2 e/Å^3) are located near iodine atom positions.

Discussion

Polyiodides are defined as extended parts of salt structures that fulfil the general formula I_{2m+n}^{n-} (n = 1–4, m = integer). They are built from I^-, I_3^- and I_2 units and show a strong tendency to concatenate *via* halogen-halogen interactions [7–10]. As polyiodide chains conduct the electric current by a Grotthuss-like mechanism in the solid state [11], the structures of higher polyiodides can be considered as snapshots of this phenomenon. Some studies were focused on the synthesis of new, tailored polyiodides using stick-shaped cations whose lengths and shapes fit with the structures of the polyiodide anions [12–14]. Especially the semi-flexible α,ω-diazaniumalkane cations assisted the synthesis of a series of new polyiodides [5, 15–18]. This contribution is part of our general interest in the hydrogen bonding topologies of aminopyridinium salts [19] and of our attempts to synthesise polyiodides using simple *N*-heterocyclic cations [20–22]. The asymmetric unit of the title structure consists of four crystallographically independent 4-aminopyridin-1-ium cations, two iodide and two triiodide anions. The geometric parameters of all moieties are in the expected ranges. The cations are stacked face to face along the *b* direction (see lower part of the figure; ellipsoids are drawn at the 50% level). These stacks of cations show an almost hexagonal rod packing. To fill the needs of packing and hydrogen bonding all cations are roughly parallel to each other (distances of the ring centres: 3.48–3.68 Å) and their NH_2 groups are primarily oriented towards the iodide counter anions. Each channel between the stacks of cations is alternatively filled with the iodide and the triiodide anions. The iodide anions as the better hydrogen bond acceptors are involved in hydrogen bonds with H···I distances below 3 Å. Several weaker N–H···I hydrogen bonds connect all moieties to a three dimensional framework. The shortest interionic I···I distances between neighbouring anions are found to be > 3.89 Å which rules out any significant influence of halogen bonding on the architecture of the title structure.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(11)	8*f*		0.0637	0.9143	0.0356	0.027
H(12)	8*f*		–0.0145	0.9121	0.0563	0.027
H(2A)	8*f*		–0.0326	0.8762	0.1359	0.023
H(3A)	8*f*		0.0262	0.8351	0.2037	0.031
H(2)	8*f*		0.1557	0.8228	0.2076	0.032
H(4A)	8*f*		0.2334	0.8398	0.1479	0.029
H(5A)	8*f*		0.1805	0.8808	0.0793	0.020
H(31)	8*f*		0.0670	0.5949	0.2182	0.023
H(32)	8*f*		–0.0046	0.6116	0.1901	0.023
H(7A)	8*f*		–0.0003	0.6372	0.1082	0.021
H(8A)	8*f*		0.0759	0.6475	0.0456	0.029
H(4)	8*f*		0.2042	0.6254	0.0539	0.025
H(9A)	8*f*		0.2652	0.6026	0.1203	0.028
H(10A)	8*f*		0.1947	0.5902	0.1849	0.021
H(51)	8*f*		0.2885	0.3603	0.1489	0.023
H(52)	8*f*		0.2860	0.3759	0.0987	0.023
H(12A)	8*f*		0.1727	0.3448	0.1926	0.019
H(13A)	8*f*		0.0407	0.3482	0.1918	0.028
H(6)	8*f*		–0.0239	0.3755	0.1259	0.028
H(14A)	8*f*		0.0335	0.3950	0.0587	0.028
H(15A)	8*f*		0.1660	0.3935	0.0565	0.021
H(71)	8*f*	0.762	0.0581	0.1642	0.0225	0.026
H(72)	8*f*	0.762	–0.0133	0.1499	0.0496	0.026
H(17A)	8*f*	0.762	–0.0116	0.1088	0.1268	0.026
H(18A)	8*f*	0.762	0.0583	0.0905	0.1929	0.027
H(8)	8*f*	0.762	0.1888	0.0959	0.1905	0.027
H(19A)	8*f*	0.762	0.2561	0.1283	0.1276	0.029
H(20A)	8*f*	0.762	0.1893	0.1466	0.0602	0.026
H(73)	8*f*	0.238	–0.0582	0.0951	0.1401	0.026
H(74)	8*f*	0.238	–0.0445	0.1191	0.0915	0.026
H(16B)	8*f*	0.238	0.0529	0.1481	0.0586	0.029
H(18B)	8*f*	0.238	0.0583	0.0905	0.1929	0.027
H(19B)	8*f*	0.238	0.1909	0.0951	0.1925	0.027
H(81)	8*f*	0.238	0.2520	0.1280	0.1275	0.029
H(20B)	8*f*	0.238	0.1893	0.1466	0.0602	0.026

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	8*f*		0.0351(5)	0.9057(6)	0.0589(3)	0.016(4)	0.030(5)	0.022(5)	0.000(4)	0.004(4)	0.006(4)
C(1)	8*f*		0.0671(6)	0.8828(7)	0.0986(4)	0.022(5)	0.012(5)	0.020(5)	–0.004(4)	–0.001(4)	0.000(4)
C(2)	8*f*		0.0210(6)	0.8690(7)	0.1378(4)	0.019(5)	0.014(5)	0.026(6)	0.001(4)	0.011(4)	–0.002(4)
C(3)	8*f*		0.0562(7)	0.8453(7)	0.1781(4)	0.039(7)	0.017(5)	0.022(6)	0.004(5)	0.010(5)	–0.001(4)
N(2)	8*f*		0.1346(6)	0.8363(6)	0.1816(3)	0.042(6)	0.021(5)	0.016(4)	–0.009(4)	–0.007(4)	0.000(4)
C(4)	8*f*		0.1800(6)	0.8481(8)	0.1449(4)	0.022(6)	0.019(5)	0.032(6)	–0.002(4)	–0.004(5)	0.000(5)
C(5)	8*f*		0.1486(6)	0.8717(7)	0.1041(3)	0.017(5)	0.016(5)	0.018(5)	–0.003(4)	0.005(4)	0.004(4)
N(3)	8*f*		0.0450(5)	0.6053(6)	0.1921(3)	0.014(4)	0.029(5)	0.014(4)	–0.005(4)	0.001(3)	0.000(4)
C(6)	8*f*		0.0878(6)	0.6116(7)	0.1547(3)	0.015(5)	0.014(5)	0.018(5)	0.001(4)	0.004(4)	–0.004(4)
C(7)	8*f*		0.0532(6)	0.6295(7)	0.1111(3)	0.019(5)	0.016(5)	0.018(5)	0.007(4)	0.000(4)	–0.003(4)
C(8)	8*f*		0.0985(6)	0.6353(7)	0.0741(4)	0.029(6)	0.017(5)	0.027(6)	0.002(4)	–0.003(5)	–0.001(4)
N(4)	8*f*		0.1766(5)	0.6233(6)	0.0780(3)	0.025(5)	0.020(4)	0.018(5)	–0.002(4)	0.012(4)	–0.004(4)
C(9)	8*f*		0.2115(6)	0.6084(8)	0.1186(4)	0.016(5)	0.028(6)	0.026(6)	–0.004(4)	0.008(5)	–0.003(5)
C(10)	8*f*		0.1698(6)	0.6015(7)	0.1570(4)	0.018(5)	0.016(5)	0.018(5)	–0.002(4)	–0.002(4)	–0.005(4)
N(5)	8*f*		0.2623(5)	0.3680(6)	0.1239(3)	0.015(4)	0.027(5)	0.014(4)	0.000(4)	0.002(3)	0.003(4)
C(11)	8*f*		0.1858(6)	0.3678(7)	0.1243(3)	0.018(5)	0.011(4)	0.015(5)	–0.001(4)	–0.002(4)	0.001(4)
C(12)	8*f*		0.1454(6)	0.3549(7)	0.1654(3)	0.018(5)	0.017(5)	0.013(5)	–0.001(4)	0.001(4)	–0.002(4)
C(13)	8*f*		0.0670(6)	0.3575(8)	0.1648(4)	0.021(6)	0.024(6)	0.025(6)	–0.002(4)	0.003(5)	0.005(5)
N(6)	8*f*		0.0259(5)	0.3733(7)	0.1254(3)	0.006(4)	0.031(5)	0.033(5)	–0.003(4)	0.000(4)	0.004(4)
C(14)	8*f*		0.0624(6)	0.3855(7)	0.0854(4)	0.026(6)	0.018(5)	0.025(6)	0.004(4)	–0.009(5)	0.000(4)
C(15)	8*f*		0.1413(6)	0.3839(7)	0.0840(3)	0.023(5)	0.015(5)	0.016(5)	0.003(4)	0.003(4)	–0.002(4)
N(7)	8*f*	0.762	0.0365(6)	0.1519(8)	0.0481(4)	0.017(6)	0.033(7)	0.015(6)	–0.006(5)	0.007(5)	–0.003(5)
C(16)	8*f*	0.762	0.0805(7)	0.1356(7)	0.0855(4)	0.034(6)	0.015(5)	0.023(6)	–0.006(4)	0.000(5)	–0.002(4)
C(17)	8*f*	0.762	0.0421(6)	0.1142(7)	0.1267(4)	0.021(6)	0.014(5)	0.030(6)	–0.003(4)	0.003(5)	0.001(4)
C(18)	8*f*	0.762	0.0837(6)	0.1017(7)	0.1657(4)	0.030(6)	0.019(5)	0.019(6)	–0.002(4)	0.003(5)	0.001(4)
N(8)	8*f*	0.762	0.1631(5)	0.1056(7)	0.1655(3)	0.030(5)	0.022(5)	0.016(5)	0.003(4)	–0.008(4)	–0.002(4)
C(19)	8*f*	0.762	0.2022(6)	0.1242(7)	0.1268(4)	0.026(6)	0.017(5)	0.030(6)	–0.002(4)	0.008(5)	–0.006(4)
C(20)	8*f*	0.762	0.1623(6)	0.1369(7)	0.0870(4)	0.031(6)	0.015(5)	0.019(5)	0.002(4)	0.006(5)	0.000(4)

Table 3. continued.

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(7A)	8*f*	0.238	–0.027(2)	0.109(2)	0.119(1)	0.017(6)	0.033(7)	0.015(6)	–0.006(5)	0.007(5)	–0.003(5)
C(16A)	8*f*	0.238	0.0805(7)	0.1356(7)	0.0855(4)	0.034(6)	0.015(5)	0.023(6)	–0.006(4)	0.000(5)	–0.002(4)
C(17A)	8*f*	0.238	0.0421(6)	0.1142(7)	0.1267(4)	0.021(6)	0.014(5)	0.030(6)	–0.003(4)	0.003(5)	0.001(4)
C(18A)	8*f*	0.238	0.0837(6)	0.1017(7)	0.1657(4)	0.030(6)	0.019(5)	0.019(6)	–0.002(4)	0.003(5)	0.001(4)
C(19A)	8*f*	0.238	0.1631(5)	0.1056(7)	0.1655(3)	0.030(5)	0.022(5)	0.016(5)	0.003(4)	–0.008(4)	–0.002(4)
N(8A)	8*f*	0.238	0.2022(6)	0.1242(7)	0.1268(4)	0.026(6)	0.017(5)	0.030(6)	–0.002(4)	0.008(5)	–0.006(4)
C(20A)	8*f*	0.238	0.1623(6)	0.1369(7)	0.0870(4)	0.031(6)	0.015(5)	0.019(5)	0.002(4)	0.006(5)	0.000(4)
I(1)	8*f*		0.12980(4)	0.01853(5)	0.28630(2)	0.0259(4)	0.0163(3)	0.0194(3)	–0.0013(3)	–0.0036(3)	0.0016(3)
I(2)	8*f*		0.12998(3)	0.23110(5)	0.29022(2)	0.0143(3)	0.0206(3)	0.0142(3)	0.0017(2)	0.0012(2)	0.0006(2)
I(3)	8*f*		0.13523(4)	0.44019(5)	0.29431(2)	0.0186(3)	0.0167(3)	0.0207(3)	0.0026(3)	0.0013(3)	0.0003(3)
I(4)	8*f*		0.14679(4)	0.71863(5)	0.28900(2)	0.0197(3)	0.0200(3)	0.0163(3)	–0.0038(3)	–0.0041(3)	0.0009(3)
I(5)	8*f*		0.35170(4)	–0.20338(5)	0.05151(2)	0.0177(3)	0.0195(3)	0.0261(4)	–0.0017(3)	0.0022(3)	0.0039(3)
I(6)	8*f*		0.36397(4)	0.00660(5)	0.04785(2)	0.0135(3)	0.0230(3)	0.0161(3)	0.0017(3)	0.0000(3)	–0.0006(3)
I(7)	8*f*		0.36998(4)	0.21513(5)	0.04258(2)	0.0243(4)	0.0182(3)	0.0269(4)	0.0010(3)	0.0013(3)	–0.0025(3)
I(8)	8*f*		0.34645(4)	0.50898(5)	0.03253(2)	0.0150(3)	0.0214(3)	0.0186(3)	0.0018(3)	0.0063(3)	0.0028(3)

Acknowledgments. We acknowledge support for the publication fee by the Deutsche Forschungsgemeinschaft (DFG) and the open access publication fund of the Heinrich-Heine-Universität Düsseldorf.

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