Crystal structure of (*E*)-3-(1-iodoethylidene)-2,3-dihydro-[1,4]thiazino-[2,3,4-*ij*]quinolin-4-ium triiodide, $C_{13}H_{11}I_4NS$

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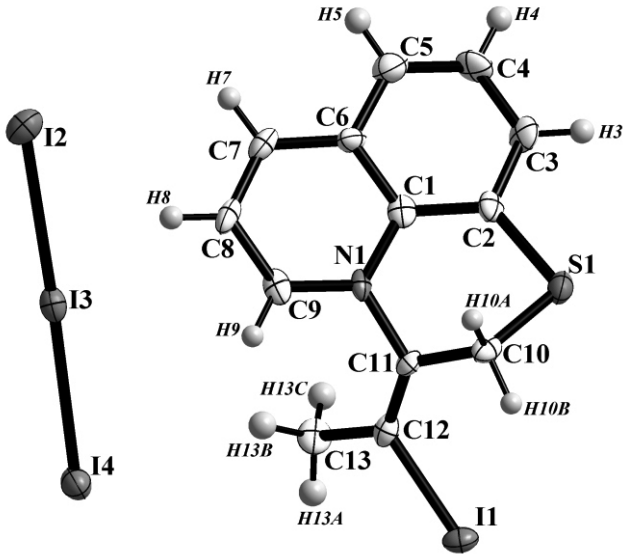

Abstract

$C_{13}H_{11}I_4NS$, monoclinic, *C*2/*c* (no. 15), a = 29.508(1) Å, b = 8.3747(3) Å, c = 14.9533(5) Å, β = 105.945(4)°, V = 3553.1 Å^3, Z = 8, $R_{gt}(F)$ = 0.056, $wR_{ref}(F^2)$ = 0.0705, T = 120 K.

Table 1. Data collection and handling.

Crystal:	red rhombohedrals, size 0.0197×0.0438×0.0470 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	71.21 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Ruby, Gemini, ω
$2\theta_{max}$:	62.8°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11872, 5275
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3619
$N(param)_{refined}$:	173
Programs:	CrysAlis PRO, SIR92, SHELX, DIAMOND, WinGX, enCIFer [10-15]

Source of material

8-(But-2-yn-1-ylthio)quinoline was prepared by method described in [3] from sodium 8-quinolinethiolate with 1-bromobut-2-yne as alkylating agent. The title compound was synthesized by the reaction of 8-(but-2-yn-1-ylthio)quinoline with iodine. The solutions of iodine (0.381 g, 1.5 mmol) and 8-(but-2-yn-1-ylthio)-quinoline (0.107 g, 0.5 mmol) in dichloromethane (10 ml) were mixed. Single crystals for the X-ray diffraction study were obtained after keeping the resulting mixture at room temperature in closed flask for 48 hours, yield: 0.447 g (55 %).

Experimental details

Position of the H atoms were calculated based on geometric criteria (C–H = 0.96 Å and 0.93 Å for methyl and aromatic atoms, respectively) than have been placed in their calculated position and refined isotropically using a riding model with U_{iso}(H) = 1.5 U_{eq}(C) for methyl and U_{iso}(H) = 1.2 U_{eq}(C) for all others.

Discussion

Tricyclic quinoline based systems, including sulfur-containing derivatives, are known as effective antibiotics [1-2]. A number of syntheses for 8-thioquinoline compounds with fused N-1/C-8 centers [3-5] were reported. Represented crystal structure can be a convenient model for studying cation···triiodide anion interactions [6-7] as it illustrates I···I non-covalent interactions involving terminal triiodide atoms as donors of electrons and iodine atom in =C12-I1 group as electron acceptor. This type of interactions can be attributed to halogen bonding [8]. The asymmetric unit of title structure consists of one quinolinium derivative cation $[C_{13}H_{11}INS]^+$ and one triiodide anion. The six-membered ring, formed as the result of cyclization process, deviates from planarity. The C10 atom of methylene group is significantly out of plane (16.4°). Molecular conformation is stabilized by intramolecular contacts C13–H13c···N1' (D···A distance of 2.957(7) Å; ' = *x*,*y*,*z*), C10–H10b···I1' (D···A distance of 3.362(6) Å; ' = *x*,*y*,*z*) and C13–H13A···I1' (D···A distance of 3.036(7) Å; ' = *x*,*y*,*z*). The triiodide anion is symmetric and nearly linear with I2–I3 and I3–I4 distances of 2.9130(7) Å and 2.9114(7) Å; the I2–I3–I4 angle of 177.97(2)°. Terminal atom of triiodide involved in the short contact with iodine of =C12–I1 group: I4···I1' (' = –*x*+2,*y*,–*z*+½; distance is 3.6988(6) Å, angle is close to right angle (82.62°)). This I···I distance is slightly longer than those values reported for triiodide - triiodide interactions [9]. The triiodide anion is situated near the organic cation so that central I6 atom is located over the center of the π-system with centroid···I3 distances of 3.81 Å. The axis of triiodide anions is inclined on 25.7° in respect to the plane of quinolinium ring. This mutual orientation is a result of charge-transfer interactions which favor location of iodide donor orbital toward the nitrogen or adjacent carbon of quinolinium rings. A particularly interesting feature of crystal packing is the formation of dimeric structural motifs represented by $[C_{13}H_{11}INS]^+$ organic cations and triiodide anions linked via C10–H10B···I4' (H···A distance of 3.1161(5) Å; ' = *x*,–*y*+1,*z*+½) and I4···I1' (distance of 3.6988(6) Å; ' = –*x*+2,*y*,–*z*+½) contacts. In each dimer the I3 atoms of triiodide an-

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ions participate in the C10–H10A···I3' (H···A distance of 3.1515(4) Å; ' = *x*,–*y*,*z*+½) interaction which engages the formation of tetrameric association. The tetramers are linked together by C5–H5···I2' (H···A distance of 3.0740(5) Å; ' = –*x*+½+1,–*y*–½,–*z*) contacts and form neutral two-dimensional sheet. Finally, these adjacent sheets are stacked in series along *c*-axis direction forming an overall layered packing.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	8*f*	0.7553	0.0965	–0.188	0.028
H(4)	8*f*	0.7018	–0.1032	–0.187	0.029
H(5)	8*f*	0.7269	–0.3492	–0.1305	0.031
H(7)	8*f*	0.7932	–0.5336	–0.0539	0.025
H(8)	8*f*	0.8725	–0.5745	0.0061	0.025
H(9)	8*f*	0.9240	–0.3623	0.0241	0.022
H(10A)	8*f*	0.9076	–0.0465	–0.1531	0.021
H(10B)	8*f*	0.9330	0.0984	–0.0927	0.021
H(13A)	8*f*	0.9276	–0.0378	0.2037	0.033
H(13B)	8*f*	0.9565	–0.1818	0.1809	0.033
H(13C)	8*f*	0.9014	–0.1806	0.1434	0.033

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

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	8*f*	0.8293(2)	–0.1712(7)	–0.0828(4)	0.023(4)	0.015(3)	0.012(3)	0.003(3)	0.006(3)	–0.003(3)
C(2)	8*f*	0.8135(2)	–0.0222(8)	–0.1246(4)	0.023(4)	0.016(4)	0.012(3)	0.002(3)	0.003(3)	–0.001(3)
C(3)	8*f*	0.7662(2)	–0.0018(8)	–0.1620(4)	0.029(4)	0.012(3)	0.030(4)	0.006(3)	0.011(3)	–0.003(3)
C(4)	8*f*	0.7339(2)	–0.1226(8)	–0.1626(5)	0.013(3)	0.031(4)	0.030(4)	0.005(3)	0.006(3)	–0.003(3)
C(5)	8*f*	0.7488(2)	–0.2682(8)	–0.1279(4)	0.025(4)	0.021(4)	0.032(4)	–0.005(3)	0.008(3)	–0.004(3)
C(6)	8*f*	0.7970(2)	–0.2990(8)	–0.0878(4)	0.015(3)	0.019(4)	0.017(3)	–0.003(3)	0.004(3)	0.000(3)
C(7)	8*f*	0.8141(2)	–0.4497(8)	–0.0517(4)	0.028(4)	0.015(4)	0.020(4)	–0.006(3)	0.010(3)	–0.003(3)
C(8)	8*f*	0.8612(2)	–0.4731(8)	–0.0135(4)	0.034(4)	0.013(4)	0.018(3)	–0.005(3)	0.010(3)	0.002(3)
C(9)	8*f*	0.8920(2)	–0.3464(7)	–0.0039(4)	0.028(4)	0.016(4)	0.011(3)	0.009(3)	0.007(3)	–0.004(3)
C(10)	8*f*	0.9065(2)	0.0255(7)	–0.1029(4)	0.020(4)	0.018(4)	0.013(3)	–0.004(3)	0.005(3)	–0.003(3)
C(11)	8*f*	0.9092(2)	–0.0673(7)	–0.0164(4)	0.021(4)	0.010(3)	0.018(3)	–0.001(3)	0.004(3)	–0.005(3)
C(12)	8*f*	0.9328(2)	–0.0319(7)	0.0709(4)	0.019(4)	0.013(3)	0.021(3)	0.003(3)	0.011(3)	0.002(3)
C(13)	8*f*	0.9292(2)	–0.1156(8)	0.1575(4)	0.031(4)	0.021(4)	0.014(3)	0.001(3)	0.007(3)	–0.003(3)
I(1)	8*f*	0.97762(2)	0.16719(5)	0.09670(3)	0.0200(2)	0.0219(2)	0.0194(2)	–0.0042(2)	0.0037(2)	–0.0060(2)
I(2)	8*f*	0.81707(2)	0.17704(6)	0.11366(3)	0.0290(3)	0.0232(3)	0.0304(3)	–0.0057(2)	0.0114(2)	–0.0017(2)
I(3)	8*f*	0.88885(2)	0.37338(5)	0.23805(3)	0.0231(2)	0.0184(2)	0.0173(2)	0.0051(2)	0.0072(2)	0.0036(2)
I(4)	8*f*	0.96263(2)	0.55954(5)	0.36431(3)	0.0257(3)	0.0222(3)	0.0221(2)	0.0030(2)	0.0022(2)	0.0008(2)
N(1)	8*f*	0.8763(2)	–0.1994(6)	–0.0349(3)	0.023(3)	0.012(3)	0.007(2)	0.003(2)	0.006(2)	0.001(2)
S(1)	8*f*	0.85164(6)	0.1362(2)	–0.1333(1)	0.030(1)	0.0133(9)	0.0200(9)	–0.0004(8)	0.0042(7)	0.0020(7)

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