Crystal structure of (*E*)-3-(iodomethylene)-2,3-dihydro-[1,4]oxazino-[2,3,4-*ij*]quinolin-4-ium triodide — iodine (2:1), $[C_{12}H_9INO]I_3$ $0.5I_2$, $C_{12}H_9I_5NO$

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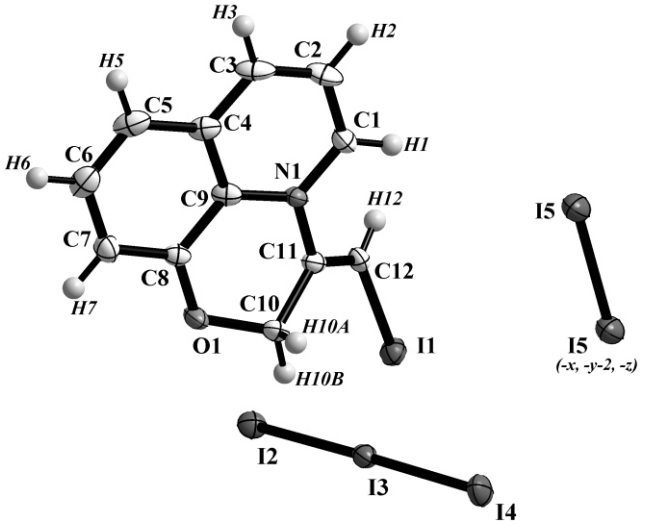

Abstract

$C_{12}H_9I_5NO$, triclinic, $P\bar{1}$ (no. 2), a = 8.6099(5) Å, b = 9.7325(3) Å, c = 12.2098(6) Å, α = 108.972(4)°, β = 101.112(4)°, γ = 104.315(4)°, V = 894.9 Å^3, Z = 2, $R_{gt}(F)$ = 0.0373, $wR_{ref}(F^2)$ = 0.0581, T = 119 K.

Table 1. Data collection and handling.

Crystal:	dark purple rhombohedrals, size 0.0197 0.0669 0.0713 mm
Wavelength:	Mo K radiation (0.71073 Å)
μ:	86.82 cm^{-1}
Diffractometer, scan mode:	Xcalibur, Ruby, Gemini, ω
$2\theta_{max}$:	62.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	15223, 5377
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4365
$N(param)_{refined}$:	172
Programs:	CrysAlis PRO [11], SIR92 [12], SHELX [13], DIAMOND[14], WinGX [15], enCIFer [16]

Source of material

8-(propargyloxy)quinoline was obtained by the reaction of 8-quinolinol with propargyl bromide in acetone/K_2CO_3 with reflux. A solution of 8-(propargyloxy)quinoline (0.145 g, 1 mmol) in 5 mL of dichloromethane was mixed with 0.762 g of iodine (3 mmol) in 15 mL of dichloromethane. Dark purple single crystals for the X-ray diffraction study were obtained after keeping the 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 = 0.97 Å, 0.93 Å and 0.85 Å for methylene, aromatic and methine atoms, respectively) than have been placed in their calculated position and refined isotropically using a rider model with $U_{iso}(H) = 1.2U_{eq}(C)$.

Discussion

Tricyclic quinoline based systems with fused N-1 and C-8 centers are known as important broad-spectrum antibiotics [1]. The title compound was synthesized in the context of obtaining new heteroaromatic systems by heterocyclization with an excess of iodine [2]. The presented crystal structure can be an interesting object with I I non-covalent interactions involving terminal triiodide atoms as donors of electrons and iodine in I_2 molecule as electrophilic species. This type of interactions refers to halogen bonding [3-10]. The asymetric unit of the title compound consists of quinolinium derivative cation, triiodide anion and half of molecular iodine. The atoms N1 and C1-C9, defining the quinolinium part of rings, are essentially planar. The C–C bonds lengths range from 1.366(6) to 1.416(6) Å; the C–N bond distances range from 1.353(5) to 1.390(5) Å. For the exocyclic adduct, formed as a result of cyclization reaction, C–O bond distances range from 1.362(5) to 1.435(5) Å, C11–N1 bond length is 1.451(5) Å and C10–C11 bond length is 1.488(6) Å, that have single bond character. The resulting six-membered ring is partially planar, where the C10 atom of the methylene group is slightly out of plane. The crystal structure confirms the closure of the ring between O1 and N1 atoms, where formed C11–N1 bond is covalent (1.451(5) Å). The C11–C12 bond, that is associated with six-member ring, has double bond character with a bond distance of 1.324(6) Å. The C12–I1 bond (2.082(4) Å) significantly deviated from mean plane of quinolinium moiety, the C11–C12–I1 angle is 123.6(3)°. Crystal packing is formed by multiple interactions of $[C_{12}H_9INO]^+$ cations, triiodide and iodine molecules. The organic cations pack could be represented as the dimeric association established by a π–π interaction. The fused rings are situated in opposite directions and lie nearly parallel to one another; the closest centroid-centroid distance is 3.51(6) Å. The dimers are surrounded by triiodide anions and iodine molecules. The geometry of triiodide is almost linear, I2–I3 and I3–I4 distances are

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2.8752(5) and 2.9572(5) Å, respectively, and I2-I3-I4 angle is 179.028(12)°. Inversion center in I_2 molecule is situated in the middle of the I5–I5 bond (2.7467(6) Å). Each of I5 atoms interacts via halogen bonding with the terminal I4 atom of the triiodide anion (I5 I4 distance is 3.444(1) Å)., to give formally a $[I_8]^{2-}$ unit [9].

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.0079	0.2562	0.3738	0.025
H(2)	2*i*	0.1447	0.1011	0.4083	0.031
H(3)	2*i*	0.2784	0.0018	0.2723	0.031
H(5)	2*i*	0.3536	0.0196	0.0796	0.027
H(6)	2*i*	0.3287	0.0403	0.0888	0.026
H(7)	2*i*	0.1840	0.2054	0.1141	0.025
H(10A)	2*i*	0.0765	0.4799	0.1023	0.023
H(10B)	2*i*	0.1067	0.5053	0.1752	0.023
H(12)	2*i*	0.2358	0.2660	0.2665	0.021

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)	2*i*	0.0459(6)	0.2161(5)	0.3184(4)	0.020(3)	0.027(2)	0.019(2)	0.009(2)	0.007(2)	0.013(2)
C(2)	2*i*	0.1381(6)	0.1236(5)	0.3394(5)	0.030(3)	0.032(3)	0.028(3)	0.013(2)	0.011(2)	0.022(2)
C(3)	2*i*	0.2190(6)	0.0656(5)	0.2588(5)	0.022(3)	0.021(2)	0.036(3)	0.009(2)	0.003(2)	0.015(2)
C(4)	2*i*	0.2135(6)	0.1014(5)	0.1557(4)	0.018(2)	0.015(2)	0.027(3)	0.007(2)	0.009(2)	0.011(2)
C(5)	2*i*	0.2920(6)	0.0438(5)	0.0692(4)	0.018(3)	0.021(2)	0.033(3)	0.009(2)	0.011(2)	0.013(2)
C(6)	2*i*	0.2783(6)	0.0810(5)	0.0310(4)	0.022(3)	0.014(2)	0.029(3)	0.005(2)	0.014(2)	0.005(2)
C(7)	2*i*	0.1893(6)	0.1793(5)	0.0470(4)	0.023(3)	0.019(2)	0.017(2)	0.003(2)	0.008(2)	0.007(2)
C(8)	2*i*	0.1105(6)	0.2370(5)	0.0351(4)	0.014(2)	0.013(2)	0.018(2)	0.002(2)	0.004(2)	0.005(2)
C(9)	2*i*	0.1201(5)	0.1969(5)	0.1367(4)	0.013(2)	0.012(2)	0.017(2)	0.002(2)	0.006(2)	0.005(2)
C(10)	2*i*	0.0006(6)	0.4276(5)	0.1239(4)	0.026(3)	0.018(2)	0.019(2)	0.011(2)	0.011(2)	0.008(2)
C(11)	2*i*	0.0696(6)	0.3379(5)	0.1921(4)	0.021(2)	0.011(2)	0.013(2)	0.007(2)	0.005(2)	0.005(2)
C(12)	2*i*	0.2053(6)	0.3329(5)	0.2286(4)	0.024(3)	0.013(2)	0.019(2)	0.010(2)	0.007(2)	0.007(2)
I(1)	2*i*	0.35420(4)	0.46650(3)	0.20579(3)	0.0209(2)	0.0198(2)	0.0182(2)	0.0101(1)	0.0074(1)	0.0059(1)
I(2)	2*i*	0.41583(4)	0.70685(3)	0.15375(3)	0.0186(2)	0.0183(1)	0.0184(2)	0.0054(1)	0.0041(1)	0.0067(1)
I(3)	2*i*	0.64511(4)	0.96417(3)	0.36655(3)	0.0210(2)	0.0183(1)	0.0162(2)	0.0081(1)	0.0069(1)	0.0075(1)
I(4)	2*i*	0.88032(4)	1.23235(3)	0.58326(3)	0.0320(2)	0.0204(2)	0.0149(2)	0.0054(1)	0.0056(1)	0.0032(1)
I(5)	2*i*	0.39552(4)	0.57862(3)	0.47375(3)	0.0346(2)	0.0206(2)	0.0191(2)	0.0094(1)	0.0072(1)	0.0079(1)
N(1)	2*i*	0.0338(5)	0.2485(4)	0.2179(3)	0.016(2)	0.012(2)	0.016(2)	0.003(2)	0.004(2)	0.004(1)
O(1)	2*i*	0.0211(4)	0.3289(3)	0.0158(3)	0.026(2)	0.023(2)	0.016(2)	0.013(2)	0.010(1)	0.011(1)

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