Marole M. Maluleka, Malose J. Mphahlele* and Eugene E. Onwu

Crystal structure of 8-bromo-6-oxo-2-phenyl-6*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carbaldehyde, $C_{18}H_{11}BrNO_2$

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.33 × 0.23 × 0.21 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.86 mm ⁻¹
Diffractometer, scan mode:	Bruker D8, ω -scans
$\theta_{\max}$, completeness:	25.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	38588, 2679, 0.050
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2294
$N(\text{param})_{\text{refined}}$:	199
Programs:	Bruker programs [1], WinGX [2], SHELX [3], PLATON [4]

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Abstract

$C_{18}H_{11}BrNO_2$, orthorhombic, *Pbcn* (no. 60), $a = 20.745(2)$ Å, $b = 6.7956(8)$ Å, $c = 20.470(3)$ Å, $V = 2885.8(6)$ Å³, $Z = 8$, $R_{\text{gt}}(F) = 0.034$, $wR_{\text{ref}}(F^2) = 0.0846$, $T = 173(2)$ K.

CCDC no.: 1905612

The crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

To a three necked round-bottom flask equipped with a stirrer bar, condenser and rubber septa was added in sequence 6-bromo-8-iodo-4-oxo-1,4-dihydroquinoline-3-carbaldehyde (0.50 g, 1.32 mmol), $PdCl_2(PPh_3)_2$ (0.04 g, 0.66 mmol), CuI

(0.02 g, 0.13 mmol), Cs_2CO_3 (0.51 g, 1.58 mmol) and dioxane (20 mL). The mixture was purged with nitrogen gas for 20 minutes and a balloon filled with nitrogen gas was connected to the top of the condenser. Phenylacetylene (0.20 g, 1.98 mmol) was added via syringe and the mixture was heated at 80 °C under inert atmosphere for 6 h. The mixture was quenched with an ice-cold water and the product was extracted with chloroform. The combined organic solutions were washed with brine and dried over anhydrous $MgSO_4$. The salt was filtered off and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as an eluent and then recrystallized from chloroform to afford 8-bromo-6-oxo-2-phenyl-6*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carbaldehyde as a solid (0.25 g, 58%); m.p. 224–225 °C; IR: $\nu_{\max}$ (ATR) 545, 769, 876, 933, 1067, 1170, 1295, 1353, 1488, 1590, 1638, 1683 cm⁻¹; ¹H-NMR: δ_H (500 MHz, $CDCl_3$) 7.20 (1H, s, =CH), 7.62 (1H, t, $J = 8.5$ Hz), 7.66 (2H, d, $J = 9.0$ Hz), 7.76 (2H, d, $J = 8.5$ Hz, Ar), 8.07 (1H, $J = 1.5$ Hz, H-5), 8.29 (1H, d, $J = 1.5$ Hz, H-7), 8.57 (1H, s, CHO) 10.1 (1H, s, NH); ¹³C-NMR: δ_C (125 MHz, $CDCl_3$) 111.0, 114.3, 119.8, 121.2, 124.1, 124.9, 127.8, 128.0, 129.8, 130.6, 132.1, 134.7, 139.9, 142.8, 176.9, 189.3; HRMS (ES): found 352.9874. $C_{18}H_{11}NO_2$ ⁷⁹Br requires 352.9874.

Experimental details

Intensity data was determined on a Bruker Venture D8 Photon CMOS diffractometer with graphite-monochromated $MoK\alpha_1$ (λ 0.71073 Å) radiation at 173 K using an Oxford Cryostream

*Corresponding author: Malose J. Mphahlele, Department of Chemistry, College of Science Engineering and Technology, University of South Africa, Private Bag x06, Florida park 1710, South Africa, e-mail: mphahmj@unisa.ac.za

Marole M. Maluleka and Eugene E. Onwu: Department of Chemistry, College of Science Engineering and Technology, University of South Africa, Private Bag x06, Florida park 1710, South Africa

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

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
Br1	0.12347(2)	0.55390(5)	0.18357(2)	0.03413(12)
N1	0.32690(10)	0.4160(3)	0.38247(10)	0.0156(5)
O1	0.14270(10)	0.3816(3)	0.45174(10)	0.0307(5)
O2	0.29123(11)	0.3186(4)	0.57954(10)	0.0362(5)
C1	0.19774(13)	0.3937(4)	0.43012(13)	0.0180(6)
C2	0.25529(13)	0.3730(4)	0.47096(13)	0.0182(6)
C3	0.31659(13)	0.3838(4)	0.44683(13)	0.0172(6)
H3	0.352267	0.368652	0.475484	0.021*
C4	0.27517(12)	0.4434(4)	0.34148(13)	0.0159(5)
C5	0.21142(12)	0.4332(4)	0.36048(13)	0.0166(5)
C6	0.16561(14)	0.4660(4)	0.31142(14)	0.0213(6)
H6	0.120848	0.460544	0.321027	0.026*
C7	0.18660(14)	0.5064(4)	0.24899(14)	0.0223(6)
C8	0.25136(14)	0.5195(4)	0.23043(13)	0.0219(6)
H8	0.263328	0.54906	0.186716	0.026*
C9	0.29749(13)	0.4877(4)	0.27853(13)	0.0190(6)
C10	0.36696(13)	0.4883(4)	0.28292(14)	0.0217(6)
H10	0.39575	0.515482	0.247969	0.026*
C11	0.38449(12)	0.4438(4)	0.34528(14)	0.0195(6)
C12	0.44807(13)	0.4253(4)	0.37594(13)	0.0210(6)
C13	0.49394(14)	0.5716(4)	0.36522(15)	0.0284(7)
H13	0.483744	0.68156	0.338496	0.034*
C14	0.55435(14)	0.5567(5)	0.39352(16)	0.0327(7)
H14	0.585726	0.656048	0.386145	0.039*
C15	0.56885(14)	0.3966(5)	0.43255(15)	0.0290(7)
H15	0.610192	0.387388	0.452268	0.035*
C16	0.52415(14)	0.2508(5)	0.44317(15)	0.0284(7)
H16	0.534823	0.14091	0.46975	0.034*
C17	0.46345(13)	0.2640(4)	0.41506(14)	0.0236(6)
H17	0.432457	0.163536	0.42245	0.028*
C18	0.24742(15)	0.3436(4)	0.54193(13)	0.0249(6)
H18	0.204869	0.344439	0.559091	0.03*

600 cooler. Data reduction was carried out using the program SAINT+, version 6.02 [1] and face-indexed [1] absorption corrections were made using the program XPREP [1]. Space group assignments was made using XPREP [1]. The structure was solved in the WinGX [2] Suite of programs, using direct methods through using SHELXS [3] and refined using full-matrix least-squares/difference Fourier techniques on F² using SHELXL [3]. All hydrogen atoms were placed at idealized positions and refined as riding atoms with isotropic parameters 1.2 times those of their parent atoms. Diagrams and publication material were generated using ORTEP-3 [2], and PLATON [4].

Discussion

Multisubstituted pyrrolo[3,2,1-*ij*]quinolines exhibit wide range of biological properties including analgesic, antipyretic, anti-inflammatory, antiviral, anticonvulsant and antimitotic properties and some derivatives have also found application in agriculture as antibacterial and

antifungal agents against the diseases of rice plants [5–10]. Non-conventional approach towards these compounds involve the use of transition metal catalysed tandem Sonogashira cross-coupling of 8-halogenated quinolin-4-one or quinoline scaffold with terminal acetylene and subsequent cycloisomerization of the intermediate 8-alkynylated derivative to append a five membered ring [11–16]. Chloromethyleneiminium salt commonly known as the Vilsmeier-Haack (V–H) reagent has been employed extensively in the formylation, cyclization and ring annulation reactions [16]. The Vilsmeier reaction of 2-aminoacetophenone has previously been shown to afford 4-chloroquinoline-3-carbaldehyde, which upon acid-mediated hydrolysis afforded the 4-oxoquinoline-3-carbaldehyde derivatives [17]. This reagent has also been used before to convert 8-methyl-2-phenyl-4*H*-pyrrolo[3,2,1-*ij*]quinolin-6(5*H*)-one into 6-chloro-8-methyl-2-phenyl-4*H*-pyrrolo[3,2,1-*ij*]quinoline-1,5-dicarbaldehyde [13]. In this investigation, 2-amino-5-bromo-3-iodoacetophenone was subjected to the Vilsmeier-Haack reaction followed by acid-mediated hydrolysis of the intermediate 6-bromo-4-chloro-8-iodoquinoline-3-carbaldehyde to afford 5-bromo-4-chloro-8-iodo-4-oxoquinoline-3-carbaldehyde. This mixed dihalogenated quinolinone derivative was found to undergo Sonogashira cross-coupling via Csp²–I substitution to afford 8-bromo-6-oxo-2-phenyl-6*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carbaldehyde.

Single crystals of the title compound suitable for X-ray analysis were obtained by slow evaporation of chloroform and the structure of the compound was distinctly confirmed by single crystal X-ray diffraction (XRD) analysis. 8-Bromo-6-oxo-2-phenyl-6*H*-pyrrolo[3,2,1-*ij*]quinoline-5-carbaldehyde crystallizes in the *Pbcn* space group, and the asymmetric unit contains one molecule of the compound. The crystal structure reveals that the pyrroloquinolinone moiety is planar with the 2-aryl group twisted out of plane [torsion angles: N(1)–C(11)–C(12)–C(17) = 48.7(4)° or C(10)–C(11)–C(12)–C(13) = 47.3(5)°]. Oxygen atom of the 5-carbaldehyde group is in anti-orientation relative to the 6-oxo atom presumably to avoid electronic repulsion. The molecules are aligned in parallel planes and are held together by several intermolecular C–H···O and C–H···Br bond interactions and further stabilized by π···π stacking.

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