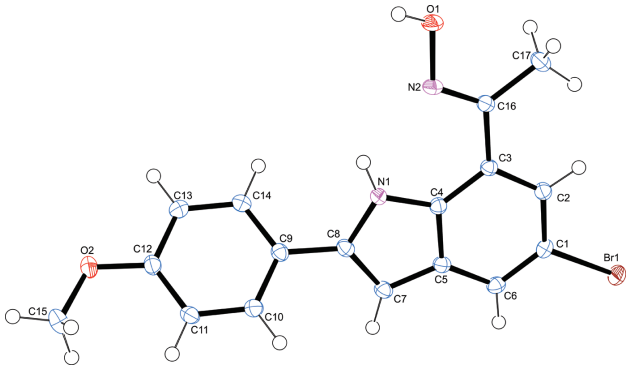
Malose J. Mphahlele*

Crystal structure of 1-(5-bromo-2-(4-methoxyphenyl)-1*H*-indol-7-yl)ethanone oxime, $C_{17}H_{15}BrN_2O_2$



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Abstract

$C_{17}H_{15}BrN_2O_2$, monoclinic, $P2_1/c$, $a = 14.4197(9)$ Å, $b = 7.5423(5)$ Å, $c = 14.9602(9)$ Å, $\beta = 114.665(2)°$, $V = 1478.59(16)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0196$, $wR_{ref}(F^2) = 0.0526$, $T = 173(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A stirred mixture of 1-[5-bromo-2-(4-methoxyphenyl)-1*H*-indol-7-yl]ethanone (0.30 g, 0.87 mmol), hydroxylamine hydrochloride (0.09 g, 1.31 mmol) and pyridine (0.10 g, 1.31 mmol) in ethanol (20 mL) was heated at 80° C for 5 h. The mixture was cooled to room temperature and quenched with an ice-cold water. The product was extracted into chloroform and the combined organic phases were washed with water and dried over anhydrous $MgSO_4$. The salt was filtered

***Corresponding author: Malose J. Mphahlele,** Department of Chemistry, College of Science Engineering and Technology, University of South Africa, P.O. Box 392, Pretoria 0003, South Africa, e-mail: mphahmj@unisa.ac.za

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.53 × 0.23 × 0.20 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	2.79 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture, ω (0.3°)
θ_{max}, completeness:	28.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	63347, 3547, 0.026
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3375
$N(param)_{refined}$:	201
Programs:	Bruker [1], WinGX [2], SHELX [3]

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

Atom	x	y	z	U_{iso}*/U_{eq}
Br1	0.63095(2)	0.33782(2)	0.04747(2)	0.02122(5)
O1	0.43536(7)	0.67988(15)	0.41273(7)	0.0259(2)
H1	0.453902	0.718149	0.470352	0.039*
O2	1.03667(7)	0.39664(15)	0.92571(7)	0.0244(2)
N1	0.71264(8)	0.46782(14)	0.46882(7)	0.0157(2)
H1A	0.676786	0.510402	0.499261	0.019*
N2	0.52037(8)	0.61063(16)	0.40112(8)	0.0199(2)
C1	0.65295(10)	0.38653(17)	0.17989(9)	0.0168(2)
C2	0.57369(9)	0.46502(16)	0.19660(9)	0.0163(2)
H2	0.511898	0.495549	0.142315	0.02*
C3	0.58440(9)	0.49900(16)	0.29225(9)	0.0146(2)
C4	0.67880(9)	0.45241(16)	0.36876(9)	0.0149(2)
C5	0.75886(9)	0.37437(16)	0.35071(9)	0.0160(2)
C6	0.74481(10)	0.33807(16)	0.25409(10)	0.0172(2)
H6	0.796511	0.282346	0.240357	0.021*
C7	0.84197(10)	0.34631(16)	0.44407(9)	0.0176(2)
H7	0.90623	0.295647	0.45537	0.021*
C8	0.81195(9)	0.40599(17)	0.51449(9)	0.0164(2)
C9	0.86974(9)	0.41048(16)	0.62170(9)	0.0161(2)
C10	0.97385(9)	0.44912(18)	0.66198(9)	0.0187(2)
H10	1.005761	0.476387	0.619479	0.022*
C11	1.03174(9)	0.44848(18)	0.76307(9)	0.0191(2)
H11	1.102378	0.476524	0.789342	0.023*
C12	0.98582(10)	0.40667(17)	0.82537(9)	0.0182(2)
C13	0.88175(10)	0.3686(2)	0.78648(10)	0.0236(3)
H13	0.850207	0.34054	0.829191	0.028*
C14	0.82429(10)	0.37175(19)	0.68566(10)	0.0216(3)
H14	0.753234	0.347294	0.659716	0.026*
C15	1.13840(10)	0.4667(2)	0.96883(10)	0.0248(3)

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
H15A	1.182127	0.397577	0.946295	0.037*
H15B	1.165116	0.459658	1.040654	0.037*
H15C	1.137466	0.590764	0.948986	0.037*
C16	0.49967(9)	0.57594(16)	0.31074(9)	0.0155(2)
C17	0.39748(10)	0.6101(2)	0.22759(10)	0.0247(3)
H17A[a]	0.399186	0.57355	0.165425	0.037*
H17B[a]	0.345006	0.542113	0.238182	0.037*
H17C[a]	0.381554	0.736808	0.224892	0.037*
H17D[a]	0.351311	0.66143	0.253574	0.037*
H17E[a]	0.405492	0.692868	0.180817	0.037*
H17F[a]	0.368943	0.498173	0.194107	0.037*

[a]Occupancy: 0.5.

off and the solvent was evaporated under reduced pressure. The residue recrystallized from ethanol to the title compound as a white solid (0.25 g, 80%), m.p. 202–204° C; **IR**: ν_{max} (ATR) 521, 585, 612, 653, 671, 755, 796, 826, 984, 1017, 1172, 1185, 1246, 1323, 1372, 1439, 1460, 1497, 3372, 3518 cm^{-1}; **^{1}H-NMR** (DMSO-d_6) 2.30 (3*H*, s, CH_3), 3.80 (3*H*, s, OCH_3), 6.80 (1*H*, s, 3-H), 7.04 (2*H*, d, $J = 8.7$ Hz, 3′,5′-H), 7.42 (1*H*, d, $J = 1.2$ Hz, 6-H), 7.70 (3*H*, m, 4-H and 2′,6′-H), 10.84 (1*H*, s, NH), 11.57 (1*H*, s, OH); **^{13}C-NMR** (DMSO-d_6) 11.3, 55.7, 98.0, 112.3, 115.0, 121.4, 122.9, 123.4, 124.2, 126.9, 131.6, 132.2, 139.4, 154.2, 159.8; *m*/*z* 359 (100, $M + H$); **HRMS** (ES): found 359.0293. $C_{17}H_{16}N_2O_2$ $^{79}Br^+$ requires 359.0395.

Experimental details

Data reduction was carried out using *SAINT+* and *SADABS* [1]. The crystal structure was solved by Direct Methods using *SHELXTL*. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Hydrogen atoms involved in hydrogen bonding were refined freely [2–4]. Diagrams and publication material were generated using *SHELXTL* and *PLATON* [4].

Comment

The indole nucleus is an important scaffold in numerous natural and synthetic alkaloids and indole have a wide range of application in medicine and materials [5]. Oximes represent important building blocks in the synthesis of amides *via* the Beckmann rearrangement. The oximes derived from the 1-(2,5-diaryl-1*H*-indol-7-yl)ethanones, for example, were previously found to undergo trifluoroacetic acid-mediated Beckmann rearrangement to afford the *N*-(2,5-diaryl-1*H*-indol-7-yl)-acetamides [6]. The *O*-mesyl or tosyl-oximes derived from indole derivatives, on the other hand, have been found to react with liquid ammonia at low temperature to afford diaziridines [7]. Recourse to the literature revealed that a bromine atom on the fused benzo ring of an indole framework imparts significant antitumour activity in both the synthetic [8] and the naturally occurring indole derivatives [9]. This knowledge encouraged us to incorporate an acetamide group on 2-aryl-7-acetyl-5-bromoindoles *via* initial oximation and subsequent Beckmann rearrangement. During this transformation, we were able to obtain crystals of the title compound.

The title crystal structure shows intermolecular {N(1)—H(1)···N(2)} and intermolecular {O(2)—H(2)···O(1)} hydrogen bonding with no π-stacking of the indole. There is co-planarity between the aromatic rings of the indole. The oxime group is also co-planar with the indole with torsion angle C(4)—C(3)—C(16)—N(2) value of 5°. The hydroxyl group is *trans* to the indole framework to avoid steric interaction. The methyl group of the 4-methoxy of the molecule, on the other hand, is rotated towards the C11 with the C(15)—O(1) bond length of 1.44 Å, which is typical for a methoxy group attached to an aromatic ring. The geometry of the oxime moiety reveal that the C3 atom is significantly asymmetrically positioned off the six membered ring.

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