Malose J. Mphahlele*

Crystal structure of (*E*)-*N*-(4-bromo-2-(1-(hydroxyimino)ethyl)phenyl)benzamide, $C_{15}H_{13}BrN_2O_2$

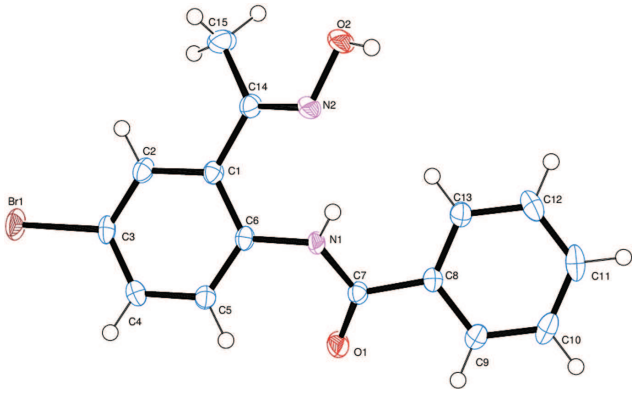

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.31 × 0.13 × 0.08 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	2.94 mm^{-1}
Diffractometer, scan mode:	Bruker D8 Venture, ω
θ_{max}, completeness:	28.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	28562, 3377, 0.043
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2855
$N(param)_{refined}$:	190
Programs:	Bruker [1], WinGX [2], SHELX [3]

https://doi.org/10.1515/ncrs-2018-0115
Received March 22, 2018; accepted June 29, 2018; available online July 17, 2018

Abstract

$C_{15}H_{13}BrN_2O_2$, monoclinic, $P2_1/c$, $a = 7.4754(3)$ Å, $b = 17.6666(7)$ Å, $c = 10.9145(4)$ Å, $\beta = 103.520(1)°$, $V = 1401.48(9)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0290$, $wR_{ref}(F^2) = 0.0713$, $T = 173(2)$ K.

CCDC no.: 1831413

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 *N*-(2-acetyl-5-bromophenyl)benzamide (1.62 g, 5.15 mmol) and hydroxylamine hydrochloride (0.43 g, 6.18 mmol) in pyridine (50 mL) was boiled under reflux for 1 h. The solvent was evaporated under reduced pressure and the crude mixture was quenched with ice-cold water. The resulting precipitate was filtered and then dissolved in chloroform, dried over anhydrous $MgSO_4$ and the salt was evaporated to afford the title compound as a solid (1.25 g, 73%), mp. 158–160 °C (EtOH); ν_{max} (ATR) 510, 581, 659, 790, 814, 876, 963, 1018, 1071, 1253, 1323, 1366, 1389, 1533, 1572, 1634, 3208, 3361 cm^{-1}; **^{1}H NMR** (300 MHz, DMSO-d_6) 2.14 (3H, s, CH_3), 2.18 (3H, s, CH_3), 7.50 (1H, dd, $J = 2.1$ and 8.7 Hz, H-4), 7.58 (1H, d, $J = 2.1$ Hz, H-6), 8.03 (1H, d, $J = 8.7$ Hz, H-3), 10.67 (1H, s, NH), 11.60 (1H, s, OH); **^{13}C NMR** (75 MHz, DMSO-d_6) 13.8, 24.8, 110.0, 115.9, 124.5, 128.9, 131.5, 136.1, 154.5, 168.8; m/z 433 (M + H), HRMS (ES): found 333.1164. $C_{15}H_{14}BrN_2O_2^+$ requires: 333.0168.

Experimental details

The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program *SAINT+* [1] and absorption corrections were made using the program *SADABS* [2]. Hydrogen atoms were located from the difference Fourier map then allowed to ride on their respective parent atoms. Hydrogen atoms involved in hydrogen bonding were located from the difference map and refined freely.

Comment

Ketoximes derived from 2-aminoacetophenone and its *N*-substituted derivatives represent important intermediates in the synthesis of 5- and 6-membered biologically relevant heterocyclic compounds. The 2-aminoacetophenone oxime derivatives, for example, have been found to undergo methanesulfonyl chloride-mediated cyclization in the presence of triethylamine in dichloromethane at room temperature to afford the corresponding 1*H*-indazoles [4]. Under the same reaction conditions, the *N*-aryl *o*-aminoacetophenone oximes afforded a variety of *N*-aryl-1*H*-indazoles and the analogous benzimidazoles when 2-aminopyridine and trimethylamine were used as bases, respectively [5]. The analogous (*o*-amidoalkenyl)aryloximes

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5804(2)	0.36186(10)	0.78821(16)	0.0183(3)
C2	0.4889(3)	0.39465(11)	0.67400(17)	0.0217(4)
H2A	0.4809	0.4482	0.6667	0.026*
C3	0.4102(2)	0.34989(11)	0.57179(16)	0.0212(4)
C4	0.4133(2)	0.27199(11)	0.57966(17)	0.0213(4)
H4	0.3536	0.242	0.5098	0.026*
C5	0.5048(2)	0.23832(11)	0.69114(17)	0.0205(4)
H5	0.5074	0.1847	0.6977	0.025*
C6	0.5929(2)	0.28173(10)	0.79371(16)	0.0179(3)
C7	0.7813(2)	0.17931(10)	0.91591(16)	0.0191(4)
C8	0.8876(2)	0.16133(10)	1.04650(16)	0.0185(3)
C9	0.9250(3)	0.08520(11)	1.07573(19)	0.0251(4)
H9	0.8825	0.0474	1.0138	0.03*
C10	1.0238(3)	0.06464(12)	1.1945(2)	0.0325(5)
H10	1.0481	0.0127	1.214	0.039*
C11	1.0875(3)	0.11928(14)	1.2851(2)	0.0332(5)
H11	1.1556	0.1049	1.3665	0.04*
C12	1.0518(3)	0.19478(13)	1.25688(19)	0.0304(4)
H12	1.0954	0.2323	1.319	0.036*
C13	0.9520(3)	0.21604(11)	1.13762(17)	0.0239(4)
H13	0.928	0.268	1.1185	0.029*
C14	0.6571(3)	0.41287(10)	0.89646(17)	0.0212(4)
C15	0.6947(4)	0.49452(11)	0.8759(2)	0.0353(5)
H15A	0.5872	0.5249	0.8814	0.053*
H15B	0.7198	0.5008	0.7923	0.053*
H15C	0.8017	0.5113	0.9404	0.053*
N1	0.6941(2)	0.24693(9)	0.90371(15)	0.0188(3)
N2	0.6850(2)	0.38320(9)	1.00698(15)	0.0245(3)
O1	0.7766(2)	0.13473(8)	0.82880(12)	0.0301(3)
O2	0.7539(2)	0.43511(9)	1.10317(14)	0.0336(4)
Br1	0.30023(3)	0.39619(2)	0.41576(2)	0.03197(8)
H1	0.701(3)	0.2703(14)	0.962(2)	0.028(6)*
H2	0.758(4)	0.4137(16)	1.158(3)	0.040(8)*

($R = -CH = CHCH_3$/Ph; 1 equiv.) were previously reacted with hydroxylamine hydrochloride (1.1 equiv.) in the presence of pyridine (1.1 equiv.) in ethanol to afford the corresponding quinazoline-3-oxides and pyridinium hydrochloride by way of acid-promoted intramolecular cyclocondensation between the oxime and the amide functionality [6]. The use of an excess of hydroxylamine hydrochloride on the oxime derived from *N*-acetylaminoacetophenone in ethanol under reflux, on the other hand, afforded *N*-oxide of 2,4-dimethylquinazoline [7]. We envisioned that the ketoximes derived from the *N*-(2-acetylphenyl)acetamides and *N*-(2-acetylphenyl)benzamides would undergo the Beckmann rearrangement into the corresponding unsymmetrically substituted *N*,*N*′-diacyl-1,2-phenylenediamines. The latter have been found to undergo cyclodehydration to afford novel 2,4-dicarbo–substituted benz[*d*][1,3,6]oxadiazepines [8–10]. We prepared *N*-(2-acetyl-5-bromophenyl)benzamide as described in the literature [11]. The title crystal structure is depicted in the figure. Bond lengths and angels are all in expected ranges.

Acknowledgements: The author is grateful to the University of South Africa and the National Research Foundation for financial assistance and to Ms A.A. Soqaka for technical assistance. A. Lemmerer of the University of the Witwatersrand is also thanked for the X-ray data collected using a diffractometer acquired through the NRF National Equipment Programme (UID: 78572).

References

1. Bruker. SAINT+, version 6.02 (Includes XPREP and SADABS). Bruker AXS Inc., Madison, Wisconsin, USA (2004).
2. Farrugia, L. J.: WinGX suite for small-molecule single-crystal crystallography. J. Appl. Crystallogr. **3** (2012) 837–838.
3. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
4. Counceller, C. M.; Eichman, C. C.; Wray, B. C.; Stambuli, J. P.: A practical metal-free synthesis of *N*-indazoles. Org. Lett. **10** (2008) 1021–1023.
5. Wray, B. C.; Stambuli, J. P.: Synthesis of *N*-arylindazoles and benzimidazoles from a common intermediate. Org. Lett. **12** (2010) 4576–4579.
6. Heaney, F.; Lawless, E.: 2–Vinyl quinazoline 3–oxides; preparation from acid induced cyclocondensation of 2-acylaminoaryloximes. J. Heterocycl. Chem. **44** (2007) 569–574.
7. Alzogaray, R. A.; Fontán, A.; Camps, F.; Masuh, H.; Orihuela, P. S.; Fernández, D.; Cork, A.; Zerba, E.: Behavioural response of *Triatoma infestans* (Klug) (Hemiptera: Reduviidae) to quinazolines. Molecules **10** (2005) 1190–1196.
8. Mazurkiewicz, R.: Novel synthesis and rearrangement of 3,1,5-benzoxadiazepines. Monatsh. Chem. **119** (1988) 1279–1287.
9. Tandon, V. K.; Kumar, M.: $BF_3{\cdot}Et_2O$ promoted one-pot expeditious and convenient synthesis of 2-substituted benzimidazoles and 3,1,5-benzoxadiazepines. Tetrahedron Lett. **45** (2004) 4185–4187.
10. Heravi, M. M.; Sadjadi, S.; Oskooie, H. A.; Shoar, R. H.; Bamoharram, F. F.: Heteropolyacids as green and reusable catalysts for the synthesis of 3,1,5-benzoxadiazepines. Molecules **12** (2007) 255–262.
11. Dolzhenko-Podchezertseva, A. V.; Korkodinova, L. M.; Vasilyuk, M. V.; Kotegov, V. P.: Synthesis and antiinflammatory activity of *N*-acyl-5-bromoanthanilic acid amides. Pharm. Chem. J. **38** (2002) 647–648.