Open Access

Aka Joseph N'gouan*, Frédérica Mansilla-Koblavi, Adeyole Timotou, Ané Adjou and Jules Abodou Tenon

Crystal structure of 5-nitro-2-(pyrrolidin-1-yl)benzaldehyde, $C_{11}H_{12}N_2O_3$

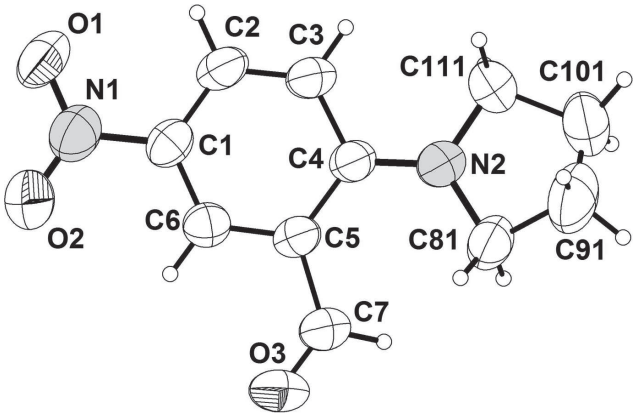

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.25 × 0.20 × 0.10 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.0 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, $\omega/2\theta$-scans
$2\theta_{max}$, completeness:	50°, >92%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	1729, 1729, 0.045
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1475
$N(param)_{refined}$:	149
Programs:	SIR2004 [1], PLATON [2], SHELX [3]

DOI 10.1515/ncrs-2016-0318
Received November 3, 2016; accepted March 5, 2017; available online April 1, 2017

Abstract

$C_{11}H_{12}N_2O_3$, monoclinic, $P2_1/n$ (no. 14), $a = 8.1726(2)$ Å, $b = 7.1419(2)$ Å, $c = 18.4875(6)$ Å, $\beta = 100.376(1)$, $V = 1061.43(4)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0533$, $wR_{ref}(F^2) = 0.1212$, $T = 298$ K.

CCDC no.: 1536055

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

Pyrrolidine (5.46 g, 66 mmol) and sodium hydrogenocarbonate (5.54 g, 66 mmol) were added to 2-chloro-5-nitrobenzaldehyde (8 g, 42 mmol) dissolved in ethanol. The mixture was heated to reflux during 24 h under inert conditions. After cooling to ambient temperature, the mixture was poured into 150 ml of dichloromethane, then washed twice with 50 ml of water. The organic layer was dried on magnesium sulfate, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel using DCM/hexane (80/2). Yellow crystals (7 g) of the title compound were obtained with 72.31% yield.

Experimental details

H atoms were placed at chemically acceptable positions using instructions AFIX 43 for the aromatic group and AFIX 23 for methylene groups. The hydrogen atom attached to C7 was located from difference fourier map and refined isotropically. All C atoms involved in the pyrrolidine ring are disordered over two positions with different occupancy factors (0.58 and 0.42), their temperature factors were restrained using the DELU instruction of SHELX-2014/7 [3].

Discussion

A variety of tricyclic indolinic derivatives have been discovered and approved to be useful in the treatment of many deseases [4–6]. But the biological activity shown by a set of analogue compounds depends on position and nature of substituents on a common scaffold [7]. In intending to synthesize new tricyclic indolinic derivatives, especially those with a nitro-aryl function, the title compound has been synthesized

***Corresponding author: Aka Joseph N'gouan,** Laboratoire de Cristallographie et Physique Moléculaire, UFR-SSMT, Université Félix Houphouët Boigny Cocody-Abidjan, 22 BP 582 Abidjan 22, Côte d'Ivoire, e-mail: josephngouan@yahoo.fr
Frédérica Mansilla-Koblavi and Jules Abodou Tenon: Laboratoire de Cristallographie et Physique Moléculaire, UFR-SSMT, Université Félix Houphouët Boigny Cocody-Abidjan, 22 BP 582 Abidjan 22, Côte d'Ivoire
Adeyole Timotou and Ané Adjou: Laboratoire de Chimie Organique Structurale, UFR-SSMT, Université Félix, Houphouët Boigny Cocody-Abidjan, 22 BP 582 Abidjan 22, Côte d'Ivoire

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.11867(19)	0.6525(2)	0.44714(9)	0.059
C6	0.18913(19)	0.4822(2)	0.43860(9)	0.057
H6	0.1669	0.4239	0.3929	0.069*
C5	0.29255(18)	0.3941(2)	0.49601(9)	0.055
C4	0.32592(19)	0.4832(2)	0.56631(9)	0.059
C3	0.2534(2)	0.6625(3)	0.57158(10)	0.072
H3	0.2765	0.7261	0.6161	0.087*
C2	0.1520(2)	0.7442(2)	0.51437(10)	0.066
H2	0.1051	0.8607	0.5200	0.079*
C7	0.3595(3)	0.2144(3)	0.47637(13)	0.1019(8)
H7	0.470(3)	0.178(4)	0.5064(15)	0.122*
N2	0.41897(18)	0.4084(2)	0.62709(8)	0.0682(4)
O1	−0.06345(18)	0.8828(2)	0.39664(8)	0.0916(4)
N1	0.0071(2)	0.7370(2)	0.38666(9)	0.0749(4)
O2	−0.0159(3)	0.6579(3)	0.32697(9)	0.1171(6)
O3	0.3292(2)	0.1401(2)	0.41944(9)	0.1130(6)
C91[a]	0.4946(10)	0.1911(8)	0.7157(3)	0.111(2)
H91A[a]	0.3880	0.1698	0.7304	0.133*
H91B[a]	0.5688	0.0882	0.7331	0.133*
C92[b]	0.6168(10)	0.2426(10)	0.7129(3)	0.084(2)
H92A[b]	0.7173	0.3107	0.7086	0.101*
H92B[b]	0.6467	0.1200	0.7337	0.101*
C102[b]	0.5127(19)	0.350(2)	0.7586(8)	0.096(3)
H10A[b]	0.4351	0.2673	0.7770	0.115*
H10B[b]	0.5823	0.4109	0.7999	0.115*
C101[a]	0.5666(16)	0.372(2)	0.7434(6)	0.120(3)
H10C[a]	0.6839	0.3779	0.7407	0.144*
H10D[a]	0.5536	0.3919	0.7940	0.144*
C112[b]	0.424(2)	0.489(2)	0.7066(9)	0.077(3)
H11A[b]	0.4817	0.6077	0.7121	0.092*
H11B[b]	0.3118	0.5073	0.7157	0.092*
C111[a]	0.4670(15)	0.5185(19)	0.6922(6)	0.087(2)
H11C[a]	0.3711	0.5631	0.7113	0.105*
H11D[a]	0.5357	0.6241	0.6837	0.105*
C82[b]	0.503(3)	0.228(3)	0.6404(11)	0.066(3)
H82A[b]	0.5652	0.1999	0.6018	0.079*
H82B[b]	0.4220	0.1286	0.6417	0.079*
C81[a]	0.475(3)	0.215(3)	0.6322(8)	0.076(3)
H81A[a]	0.5797	0.1993	0.6152	0.091*
H81B[a]	0.3924	0.1306	0.6057	0.091*

[a]Occupancy: 0.584(9); [b]Occupancy: 0.416(9).

as a precursor. The crystal structure of the title compound should establish its conformation.

A nitrobenzaldehyde moiety is linked to a pyrrolidine ring to form the title molecule (*cf.* the figure). The bond lengths and angles in the structure are within normal ranges [8]. As usually encountered, the pyrrolidine moiety is disordered [9, 10]. Atoms in this ring, except nitrogen one, are disordered over two positions. According to puckering analysis [11] the disordered pyrrolidine ring adopts envelope conformations in both conformers with respect to the carbon atoms C91 and C92 being out of the plane formed by the four remaining atoms. The puckering parameters are: $q2 = 0.424(14)°$ and $\varphi = 254.1(19)°$ for N2/C81–C111 ring, and $q2 = 0.407(16)°$ and $\varphi = 71(2)$ for N2/C82–C112. The crystal packing is supported by weak C—H···O hydrogen bonds and π−π interactions.

Acknowledgements: We thank the Spectropole service of the Faculty of Sciences and Techniques of Saint Jérome University (France) for using their diffractometer.

References

1. Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagna, R.: SIR2004: an improved tool for crystal structure determination and refinement. J. Appl. Cryst. **38** (2005) 381–388.
2. Spek, A.: Single-crystal structure validation with the program PLATON. J. Appl. Cryst. **36** (2003) 7–13.
3. Sheldrick, G. M.: *SHELXT*-Integrated space-group and crystal-structure determination. Acta Cryst. **C71** (2015) 3–8.
4. Račková, L.; Májeková, M.; Košt'álová, D.; Štefek, M.: Antiradical and antioxidant activities of alkaloids isolated from *Mahonia aquifolium*. Structural aspects. Bioorg. Med. Chem. **12** (2004) 4709–4715.
5. Mokrosz, M. J.; Duszynska, B.; Bojarski, A. J.; Mockrosz, J. L.: Structure-activity relationship studies of CNS agents-XVII. Spiro[piperidine-4′,1-(1,2,3,4-tetrahydro-β-carboline)] as a probe defining the extended topographic model of 5-HT1A receptors. Bioorg. Med. Chem. **3** (1995) 533–538.
6. Ennis, M. D.; Hoffman, R. L.; Ghazal, N. B.; Olson, R. M.; Knauer, C. S.; Chio, C. L.; Hyslop, D. K.; Campbell, J. E.; Fitzgerald, L. W.; Nichols, N. F.: 2,3,4,5-Tetrahydro- and 2,3,4,5,11,11a-hexahydro-1*H*-[1,4]diazepino[1,7-*a*]indoles: new templates for 5-HT2C agonists. Bioorg. Med. Chem. Lett. **13** (2003) 2369–2372.
7. Vaz, R.: Computer assisted molecular design: overview of modern technique in quantitative structure activity relationship (QSAR). Weed Science **44** (1996) 718–733.
8. Allen, F. H.; Walson, D. G.; Orpen, A. G.; Taylor, R.: Tables of bonds lengths by x-ray and neutron diffraction. Part 1. bonds lenths in organic compounds. Perkin Trans. **2** (1987) S1–S19.
9. Fathimunnisa, M.; Manikandan, H.; Selvanayagam, S.; Sridharc, B.: 2′-[2′,4′-difluorobiphenyl-4-yl)carbonyl]-1′-phenyl-1′,2′,5′,6′,7′,7a′-hexahydro-spiro[indole-3,3′-pyrrolizin]-2(1*H*)-one. Acta Crystallogr. **E71** (2015) 915–918.
10. Abdulrahman, I. A.; Raju, S. K.; Natarajan, A.; Ramachandran, A. N.; Janakiraman, S.: Crystal structure of 8-(2-methylphenyl)-11-[(*E*)-(2-methylphenyl)-methylidene]-14-hydroxy-3,13-diazaheptacyclo-[13.7.1.^{9,13}.0^{2,9}.0^{2,14}.0^{3,7}.0^{19,23}]tetracosa-1(22),15,17,19(23),20-pentaen-10- one methanol monosolvate, $C_{37}H_{34}N_2O_2$-CH_3OH, $C_{38}H_{38}N_2O_3$. Z. Kristallogr. – NCS **229** (2014) 175–177.
11. Cremer, D.; Pople, J. A.: General definition of ring puckering coordinates. J. Am. Chem. Soc. **97** (1975) 1354–1358.