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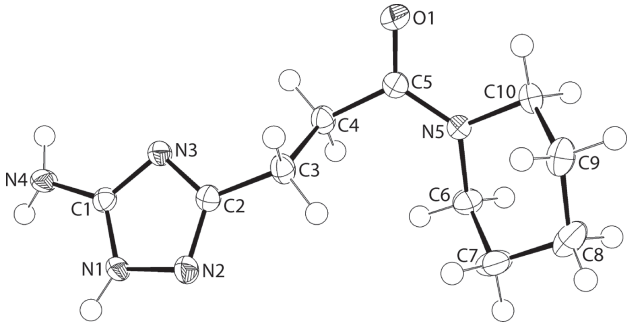
Crystal structure of 3-(5-amino-1*H*-1,2,4-triazol-3-yl)-1-(piperidin-1-yl)propan-1-one, $C_{10}H_{17}N_5O$



https://doi.org/10.1515/ncrs-2019-0094
Received January 29, 2019; accepted February 15, 2019; available online March 15, 2019

Abstract

[$C_{10}H_{17}N_5O$], monoclinic, $P2_1/c$ (no. 14), $a = 8.12150(10)$ Å, $b = 13.2833(2)$ Å, $c = 11.0258(2)$ Å, $\beta = 110.083(2)°$, $V = 1117.14(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0311$, $wR_{ref}(F^2) = 0.0790$, $T = 100(2)$ K.

CCDC no.: 1897358

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

The compound was prepared using a microwave-assisted nucleophilic ring opening of *N*-guanidinosuccinimide with piperidine followed by an *in situ* intramolecular cyclization of the triazole ring as described in the literature [5]. The crystals were obtained from the slow evaporation of an acetonitrile solution of the compound, *M*. pt: 438–440 K.

Table 1: Data collection and handling.

Crystal:	Prism, colourless
Size:	0.13 × 0.10 × 0.04 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	0.74 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω-scans
θ_{max}, completeness:	67°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13479, 1993, 0.030
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1851
$N(param)_{refined}$:	154
Programs:	CrysAlis^{PRO} [1], SHELX [2, 3], WinGX and ORTEP [4]

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.99 Å) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. The N-bound H-atoms were located in difference Fourier maps but were refined with a distance restraint of N—H = 0.88 ± 0.01 Å, and with $U_{iso}(H)$ set to $1.2U_{equiv}(N)$.

Discussion

Interest in molecules related to the title compound stem from the significant biological activity exhibited by 1,2,4-triazoles [6, 7]. This interest prompts investigations into efficient synthesis of these derivatives and in this context, recently two new complementary pathways for the synthesis of N-substituted 3-(5-amino-1*H*-1,2,4-triazol-3-yl) propanamides based on microwave technology were described [5]. The title compound was one of the species prepared in that study and herein its crystal and molecular structures are described.

The molecular structure of the title structure is shown in the Figure (70% displacement ellipsoids) and comprises a 5-amino-1*H*-1,2,4-triazol-3-yl residue connected to a piperidinyl ring *via* a propan-1-one linker. Tautomerism is possible in the 5-amino-1*H*-1,2,4-triazol-3-yl ring and crystallography proves the location of ring-bound hydrogen to be on the N1 atom. The confirmation for this assignment, besides the pattern of intermolecular hydrogen bonding (see below), is seen in the magnitude of the key bond lengths in the ring, *i.e.* the shortening of the C1—N3 [1.3353(14) Å] and C2—N2 [1.3153(15) Å] bond lengths compared to N1—C1 [1.3435(15) Å], C1—N4 [1.3580(14) Å] and C2—N3 [1.3656(14) Å]. The five-membered ring is strictly planar [r.m.s. deviation = 0.004 Å] with the N4

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.21014(10)	0.60094(6)	0.45554(7)	0.0179(2)
N1	0.62336(12)	0.27045(7)	0.91082(9)	0.0147(2)
H1N	0.6756(16)	0.2165(8)	0.9524(12)	0.018*
N2	0.57262(12)	0.27705(7)	0.77780(9)	0.0157(2)
N3	0.49787(12)	0.41829(7)	0.86125(8)	0.0135(2)
N4	0.61209(13)	0.37411(7)	1.08519(9)	0.0164(2)
H2N	0.6160(18)	0.3227(8)	1.1365(12)	0.020*
H3N	0.5707(17)	0.4315(8)	1.1007(13)	0.020*
N5	0.11049(12)	0.45317(7)	0.35760(9)	0.0142(2)
C1	0.57659(13)	0.35488(8)	0.95776(10)	0.0128(2)
C2	0.49991(14)	0.36675(8)	0.75461(10)	0.0135(2)
C3	0.42559(14)	0.40929(9)	0.62122(10)	0.0157(2)
H3A	0.413456	0.354662	0.557645	0.019*
H3B	0.508076	0.459791	0.608852	0.019*
C4	0.24561(14)	0.45915(9)	0.59558(10)	0.0152(2)
H4A	0.159212	0.407622	0.598950	0.018*
H4B	0.254443	0.509921	0.663260	0.018*
C5	0.18422(13)	0.50948(8)	0.46381(10)	0.0132(2)
C6	0.05744(15)	0.34728(9)	0.35458(11)	0.0179(3)
H6A	−0.071125	0.341904	0.311597	0.021*
H6B	0.087296	0.321989	0.444031	0.021*
C7	0.14889(16)	0.28295(9)	0.28251(12)	0.0231(3)
H7A	0.103873	0.213138	0.275512	0.028*
H7B	0.276328	0.281231	0.331630	0.028*
C8	0.11793(16)	0.32484(10)	0.14781(12)	0.0245(3)
H8A	0.188701	0.286451	0.106324	0.029*
H8B	−0.007211	0.317015	0.094293	0.029*
C9	0.16810(16)	0.43552(10)	0.15500(11)	0.0217(3)
H9A	0.138114	0.462672	0.066412	0.026*
H9B	0.296363	0.442173	0.198611	0.026*
C10	0.07395(15)	0.49690(9)	0.22836(10)	0.0182(3)
H10A	0.114983	0.567582	0.236307	0.022*
H10B	−0.053895	0.496396	0.180548	0.022*

[0.046(1) Å] and C3 [0.016(1) Å] atoms lying out of but to the same side of the plane. Overall, the molecule has the shape of the letter U as the aliphatic residues lie to the same side of the bridging region as seen in the values of the C3—C4—C5—O1 [−96.38(12)°] and C5—N5—C6—C7 [−122.45(11)°] torsion angles. The piperidinyl ring adopts a chair conformation.

The observed tautomer is as expected based on literature precedents [8]. However, a compound was recently identified crystallizing with a hydrogen located at the nitrogen atom furthest away from the amino group, that is, existing in the form of the 3-amino-1*H*-tautomer [9]. It is also noted that an example of a crystal comprising both 5-amino-1*H*- and 3-amino-1*H*-tautomers, co-existing in equal proportions, has also been reported [10].

In the molecular packing, the ring-N1—H1n atom forms a hydrogen bond to the O1(carbonyl) atom to form a helical supramolecular chain along the *b*-axis [N1—H1n···O1^{i}: H1n···O1^{i} = 1.898(11) Å, N1···O1^{i} = 2.7751(12) Å with angle at H1n = 179.2(14)° for symmetry operation i: $1-x$, $-1/2+y$, $3/2-z$]. Each of the secondary amine-N4—H atoms forms a hydrogen bond to a triazolyl-nitrogen atom [N4—H2n···N2^{ii}: H2n···N2^{ii} = 2.164(12) Å, N4···N2^{ii} 3.0186(13) Å with angle at H1n = 163.5(13)°; N4—H3n···N3^{iii}: H3n···N3^{iii} = 2.151(11) Å, N4···N3^{iii} = 3.0188(13) Å with angle at H1n = 172.1(13)° for symmetry operations ii: x, $1/2-y$, $1/2+z$ and iii: $1-x$, $1-y$, $2-z$]. These hydrogen bonds link the chains into a supramolecular layer parallel to [1 0 0]. Layers stack along the *a* axis without directional interactions between them.

The most closely related structure in the literature is that of the derivative with an aniline residue connected to the carbonyl-C5 atom [5]. This molecule adopts the same tautomeric form as reported herein.

Acknowledgements: This work is supported by the Ministry of Higher Education, Malaysia under Fundamental Research Grant Scheme (Grant No. FRGS/1/2015/SG01/MUSM/03/1).

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