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ORIGINAL PAPER

The Synthesis and Crystal Structure of 5-Methyl-1-(1-naphthyl)-1,2,3-triazol-4-carboxyl Acid

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Abstract 5-Methyl-1-(1-naphthyl)-1,2,3-triazol-4-carboxyl acid **3** was synthesized from 1-aminonaphthalene. The yielded product **3** was investigated with X-ray crystallographic, NMR, MS and IR techniques. Compound **3,** $C_{14}H_{11}N_3O_2$, Mr = 253.26, crystallizes in the orthorhombic space group Pbca with unit cell parameters a = 10.068(2), b = 12.353(2), c = 20.102(4) Å, V = 2500.1(8) Å^3, Z = 8, Dx = 1.346 Mgm^{-3}. The final R was 0.0474. The molecular packing is stabilized by intermolecular O–H···N interactions.

Keywords Crystal structure · 1,2,3-Triazol-4-carboxyl acid · 5-Methyl-1-(1-naphthyl)-1,2,3-triazol-4-carboxyl acid · H-bond · Synthesis

Introduction

Certain compounds having 1,2,3-triazole nucleus have been reported as antibacterial [1], antifungal, antiviral, anti-inflammatory, immunity [2], analgesic [3], inhibitors to tumor proliferation, invasion, metastasis [4], anti-HIV [5, 6] and useful in treating CRF-related disorders. For this reason, 5-methyl-1-(1-naphthyl)-1,2,3-triazol-4-carboxylic acid was synthesized.

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In this paper, we report the crystal structure of 5-methyl-1-(1-naphthyl)-1,2,3-triazol-4-carboxylic acid **3.**

The route of synthesis is in Scheme 1.

Experimental Section

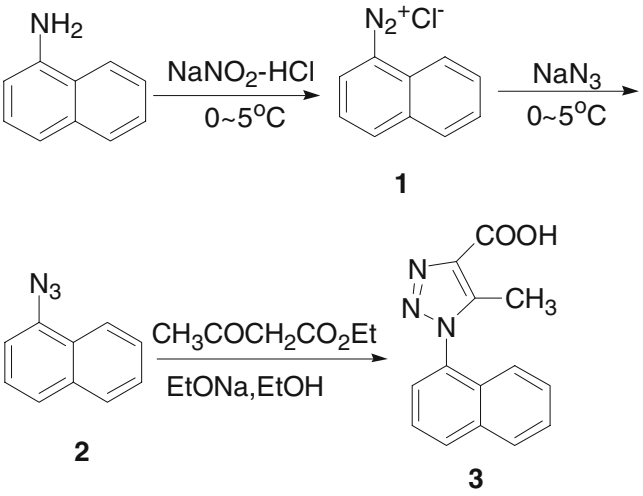
Melting points were uncorrected and determined on an XT_4-100× microscopic melting point apparatus. IR spectra were obtained in KBr discs on a Nicolet 170SX FT-IR spectrometer. MS were performed on an HP-5988A spectrometer (EI at 70 eV). ^{1}H NMR spectra ($CDCl_3$) were recorded on a Varian Mercury plus-200 MHz instrument with TMS as an internal standard.

The Preparation of 5-Methyl-1-(1-naphthyl)-1,2,3-triazol-4-carboxylic Acid 3

5-Methyl-1-(1-naphthyl)-1,2,3-triazol-4-carboxylic acid **3** was prepared following methods in the literature [3]. The yield of **3** is a yellow crystalline solid, m.p. 185–186 C, (25%). IRυ_{max}: 3,429(O–H); 3,060, 2,987(C–H); 1,725(C=O); 1,598, 1,558, 1,511, 1,452(Ar-ring); 1,274(C–O); 1,185(C–N); 964.5 (N=N–N) cm^{-1}. ^{1}H NMR(200 MHz, $CDCl_3$)δ_H: 2.479(s, 3H, CH_3–), 7.175–7.211(d, 1H, J = 8 Hz, Ar–H), 7.553–7.726(m, 4H, Ar–H); 8.022–8.059(d, 1H, J = 8 Hz, Ar–H), 8.131–8.171(d, 1H, J = 8 Hz, Ar–H), 12.80–13.25(b, 1H, –COOH) ppm. MS M/z(%): 253 (M^+, 9%), 236(1, M-17), 225(1, M-28 or –N_2), 224 (2, 225-1), 209(4, M-44 or –CO_2), 196(1, M-44-13), 181(45), 180(100, M-28-45), 178(20), 169(3, $C_{10}H_7N_3$), 153(18, $C_{10}H_7$–NC), 140(9, $C_{10}H_6N$), 127(80, $C_{10}H_7$), 115(6), 101(16), 83(36), 77(38), 75(22), 63(17).

The purified product was dissolved in a mixture of water and ethanol. The crystals were obtained by slow evaporation of this solvent mixture after 10 days.

Scheme 1 The synthesis route of title compound



Crystal Structure Determinations and Refinement

Suitable single crystals were selected and mounted on the tip of a glass fiber. Preliminary examination and data collection were performed with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer operating in the $\omega/2\theta$ scanning mode. The structure was determined by direct methods (SHELXS-97) [7] and refined by full covariance matrix methods (SHELXL-97) [8]. The crystal data, data collection and refinement parameters for the structure are given in Table 1.

The structure of the title compound is shown in Fig. 1. Figure 1 is the ORTEP drawing of the title compound **3** showing the atom numbering scheme (Ellipsoids: 50% probability). Bond lengths and angles are given in Tables 2 and 3. The geometric calculations were performed using the program SHELX-97.

Results and Discussion

In recent years, the synthesis and characteristics of 5-amino-1-(4-chlorophenyl)-1,2,3-triazol-4-yl and 5-methyl-1-(4-methylphenyl)-1,2,3-triazol-4-yl related derivatives have been investigated [9–12]. These heterocyclic compounds also contain the 1,2,3-triazole ring. IR peaks at 3,429 and 1,724 cm^{-1} for compound **3** are assigned to $\nu_{C=O}$ for COOH. The N–N=N vibration at 964.5 cm^{-1} is in agreement with values reported for 1*H*-1,2,3-triazole [12] and differs from 2*H*-1,2,3-triazole [13]. In the ^{1}H NMR spectrum for compound **3**, the chemical shift for the methyl group in the triazole ring, (δ2.711 ppm), is agreement with values reported [14] (δ2.61–2.74 ppm).

The 1,2,3-triazole ring system is nearly planar [15]. The bond lengths N1–N2 1.356(3) Å, N2–N3 1.303(3) Å are agreement with the values reported for triazole, N–N

Table 1 Crystal data and summary of data collection and structure refinement

Compound	$C_{14}H_{11}N_3O_2$
CCDC deposit No.	288148
Color	Yellow/block
Formula weight	253.26
Temperature, °C	20 (293 K)
Crystal system	Orthorhombic
Space group	Pbca
Unit-cell dimensions	$a = 10.068(2)$ Å
	$b = 12.353(2)$ Å
	$c = 20.102(4)$ Å
Volume (Å^3)	2500.1(8)
Z	8
D_{calc}, g cm^{-3}	1.346
$F(000)$	1,056
Index ranges	$0 \le h \le 11$;
	$0 \le k \le 14$;
	$0 \le l \le 23$
Absorption coefficient, mm^{-1}	0.093
Diffractometer/scan	Enraf-Nonius CAD4,
	$\omega/2\theta$
Radiation/λ	Mo$k\alpha$/0.71073 Å
θ_{min}, θ_{max} (°)	2.03–24.94
Reflections measured	2,182
Independent/observed reflections	1,240
Data/restraints/parameters	2,182/0/172
Refinement method	Full-matrix
	Least-squares on F^2
Goodness-of-fit on F^2	1.06
shift/su_max	0.0495
Final R indices	$R_1 = 0.0474$, $wR_2 = 0.1197$
R indices [$I > 2\sigma(I)$]	$R_1 = 0.1120$, $wR_2 = 0.1604$
Largest diff. peak and hole	0.244 and −0.215e Å^{-3}

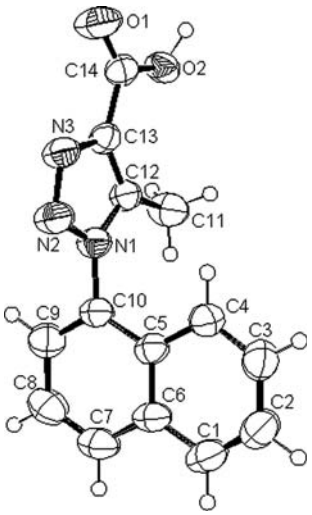


Fig. 1 ORTEP drawing of the title compound **3** showing the atom numbering scheme (Ellipsoids: 50% probability)

Table 2 Bond lengths (Å)

Atoms length	Atoms length
O1–C14	1.201(4)
O2–C14	1.311(4)
N1–C12	1.350(4)
N1–N2	1.356(3)
N1–C10	1.440(4)
N2–N3	1.303(3)
N3–C13	1.355(4)
C1–C2	1.343(5)
C1–C6	1.410(5)
C2–C3	1.392(5)
C3–C4	1.369(5)
C4–C5	1.416(4)
C5–C10	1.415(4)
C5–C6	1.419(4)
C6–C7	1.411(5)
C7–C8	1.359(5)
C8–C9	1.401(5)
C9–C10	1.351(4)
C11–C12	1.480(4)
C12–C13	1.372(4)
C13–C14	1.470(4)

1.351(11), 1.287(11) Å [16]. The C12–N1 1.350(4) Å and C13–N3 1.355(4) Å are between the bond lengths of C=N and C–N.

In the crystal structure, there is an intermolecular O2–H(2)···N3′ hydrogen bond involving the carboxylic acid O–H atom and the triazole 3 position N atom. The molecular packing is stabilized by intermolecular O2–H(2)···N3′ interactions. It is differ from molecules of general carboxylic acid for instance 2,4-dimethylbenzoic

Table 3 All non-hydrogen bond angles (°)

Atoms	Angle
C12–N1–N2	111.8(2)
C12–N1–C10	129.0(3)
N2–N1–C10	119.2(2)
N3–N2–N1	105.9(2)
N2–N3–C13	110.1(2)
C2–C1–C6	121.2(3)
C1–C2–C3	120.8(3)
C4–C3–C2	120.8(3)
C3–C4–C5	119.6(3)
C10–C5–C4	123.4(3)
C10–C5–C6	117.3(3)
C4–C5–C6	119.3(3)
C1–C6–C7	122.6(3)
C1–C6–C5	118.3(3)
C7–C6–C5	119.1(3)
C8–C7–C6	121.5(3)
C7–C8–C9	119.8(3)
C10–C9–C8	120.1(3)
C9–C10–C5	122.4(3)
C9–C10–N1	118.9(3)
C5–C10–N1	118.7(3)
N1–C12–C13	103.7(3)
N1–C12–C11	122.6(3)
C13–C12–C11	133.7(3)
N3–C13–C12	108.6(3)
N3–C13–C14	120.3(3)
C12–C13–C14	131.2(3)
O1–C14–O2	124.8(3)
O1–C14–C13	123.0(3)
O2–C14–C13	112.1(3)

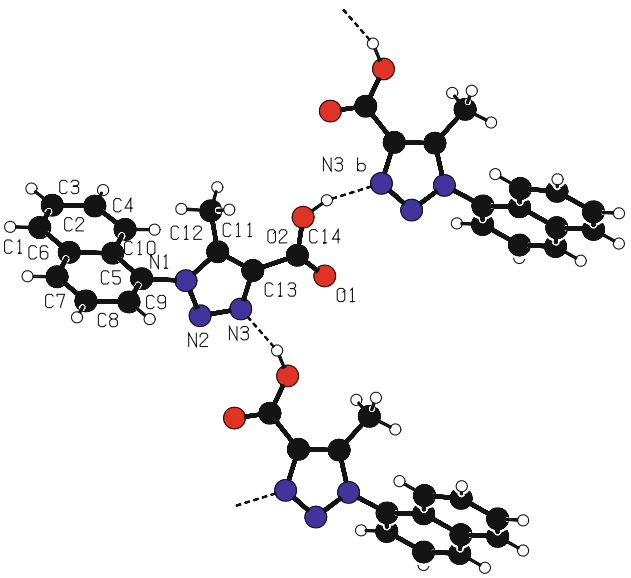


Fig. 2 The H-bond structure of the compound **3** (PWT drawing for the Platon)

acid, form typical centrosymmetric hydrogen-bonded dimers [17]. The bond length of Donor-H···Acceptor is 2.72 Å(O–H 0.94; H···N3 1.82 Å), the bond angle is 162. The H-bond structure of the compound **3** is shown in Fig. 2.

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15. C12–N1–N2–N3 0.7(9); N1–N2–N3–C13 −2.1(10); N2–N3–C13–C12 2.7(10); N1–C12–C13–N3 −2.0(9); N2–N1–C12–C13 0.8(9); the dihedral angel of geom. torsion is 0.7 ∼ 2.7 degrees
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