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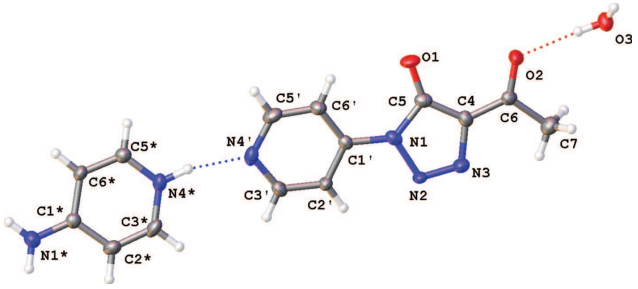
Crystal structure of 4-aminopyridinium 4-acetyl-(pyridin-4-yl)-1H-1,2,3-triazol-5-olate monohydrate, $C_{14}H_{16}N_6O_3$



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Abstract

$C_{14}H_{16}N_6O_3$, triclinic, space group $P\bar{1}$ (no. 2), $a = 7.7890(5)$ Å, $b = 8.6069(6)$ Å, $c = 12.4753(8)$ Å, $\alpha = 77.064(4)°$, $\beta = 72.754(3)°$, $\gamma = 67.148(3)°$, $V = 730.40(9)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0594$, $wR_{ref}(F^2) = 0.1542$, $T = 297(2)$ K.

CCDC no.: 1832047

Table 1: Data collection and handling.

Crystal:	Plate, colourless
Size:	0.30 × 0.23 × 0.08 mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ:	0.881 mm^{-1}
Diffractometer, scan mode:	Bruker AXS D8-Venture, φ and ω-scans
θ_{max}, completeness:	59.02°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10456, 2104, 0.059
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1774
$N(param)_{refined}$:	217
Programs:	Bruker programs [1], SHELX [2, 3], OLEX2 [4], PLATON [5]

Source of material

The title compound was obtained according to similar syntheses described earlier [6, 7], in two steps: i) 583 µL of acetylacetoacetate (1 eq.; 4.61 mmol) and 433 mg (1 eq.; 4.61 mmol) of 4-aminopyridine (4-AP) was dissolved in dry toluene. Then, 1 g of 4 Å MS was added and the resulting mixture was refluxed per 6 hours. Finally the solvent was remove under reduced pressure and the crude product was cooled at 0 °C to precipitate the 4-AP what did not react and gave 791 mg of a yellow oily compound. ii) When the oily compound was isolated, this was dissolved in 10 mL of MeCN and 2 eq. of triethylamine (1.41 mL; 9.22 mmol) was added to the solution. The resulting mixture was put in an ice bath and, 710 µL (1 eq., 4.61 mmol) of tosyl azide was added slowly to the mixture and a white precipitate was formed immediately. The resulting slurry was stirred 2 hours, isolating the white precipitate. This was washed with cold diethyl ether (3 times) affording 152 mg (11.1%) of a white solid. Recrystallization by slow evaporation into saturated hot methanol of the title compound, yielded crystals suitable for X-ray structure determination. **FTMS-ESI(+)** (based on $C_5H_7N_2{}^+C_9H_7N_4O_2{}^-$) $[M]^+$ m/z calcd.: 95.060; found: 95.061 (1 ppm), $[M]^-$ m/z calcd.: 203.060; found: 203.060 (0 ppm). **FT-IR** (KBr pellet, cm^{-1}): 3454 (s), 3405 (vs), 3398 (vs) νasym/sym (–NH_2), ν (OH), 3374 (s), ν (N—H) 3226 (m), 3158 (m), 3145 (m), 3122 (m), 3110 (m) ν(C—H aryl), 3047 (w), 3016 (w), 2927 (w), ν (C—H alkyl), 2510 (w; broad), ν(N^+—H) 1668 (vs), 1650 (vs), 1598 (vs) ν(C=O), ν(C=N) and/or ν (C = C), 1525 (s), δ (NH_2), 1205 (s), ν (C—O). 754(s) δ (C—H). **^{1}H NMR** (300 MHz, DMSO-d_6, 298 K): δ 8.54 (d, $^3J = 6.3$ Hz, 2H; H3/H5′), 8.11(d, $^4J = 1.6$ Hz, 2H; H3*/H5*), 8.09 (d, $^4J = 1.5$ Hz, 2H; H2′/H6′), 8.0 (s, 2H; –NH_2), 6.78 (d, $^3J = 7.3$ Hz, 2H; H2*/H6*), 2.29 (t, 3H; H7), 4-aminopyridinium proton not observed. **^{13}C{^{1}H} NMR** (75 MHz, DMSO-d_6, 298 K): 159.9 (C6/C1*), 150.7 (C3′ /C5′/C5), 144.25 (C1′), 140.4 (C3*/C5*), 128.0 (C4), 111.6 (C2′/C6′), 109.0 (C2*/C6*), 26.58 (C7).

Experimental Details

Solid-state FT-IR spectra were recorded on a Thermo Scientific Model nicolet avatar 330 spectrophotometer with KBr disks in

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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	0.4414(3)	0.4239(3)	0.80310(19)	0.0521(7)
O2	0.6740(3)	0.0847(3)	0.92808(19)	0.0559(7)
O3	0.7607(3)	−0.1905(3)	1.0977(2)	0.0522(7)
H3A	0.724998	−0.109041	1.047075	0.078
H3B	0.681670	−0.243470	1.119743	0.078
N1	0.6620(4)	0.4527(3)	0.6343(2)	0.0410(7)
N1*	0.1549(4)	1.5748(4)	0.0301(2)	0.0526(8)
H1*A	0.236364	1.570643	−0.034107	0.063
H1*B	0.047503	1.657889	0.039373	0.063
N2	0.8567(3)	0.3579(3)	0.5855(2)	0.0378(7)
N3	0.9126(4)	0.2295(3)	0.6554(2)	0.0470(7)
N4′	0.3959(4)	0.9059(3)	0.4421(2)	0.0465(7)
N4*	0.2776(4)	1.1949(3)	0.2892(2)	0.0433(7)
H4*	0.295(6)	1.107(5)	0.346(4)	0.075(13)
C1′	0.5677(4)	0.6072(4)	0.5727(2)	0.0329(7)
C1*	0.1950(4)	1.4531(4)	0.1150(2)	0.0364(7)
C2′	0.6718(4)	0.6656(4)	0.4725(2)	0.0370(8)
H2′	0.801636	0.606302	0.447216	0.044
C2*	0.3687(5)	1.3161(4)	0.1027(3)	0.0473(9)
H2*	0.460142	1.311345	0.034628	0.057
C3′	0.5814(5)	0.8118(4)	0.4111(3)	0.0441(8)
H3′	0.653373	0.848381	0.343293	0.053
C3*	0.4041(5)	1.1913(4)	0.1887(3)	0.0501(9)
H3*	0.519104	1.100169	0.178311	0.060
C4	0.7655(5)	0.2294(4)	0.7526(3)	0.0402(8)
C5	0.6041(5)	0.3697(4)	0.7414(3)	0.0414(8)
C5′	0.3007(5)	0.8453(5)	0.5420(3)	0.0511(9)
H5′	0.171883	0.907698	0.567490	0.061
C5*	0.1118(5)	1.3264(4)	0.3049(3)	0.0424(8)
H5*	0.025963	1.329908	0.375200	0.051
C6	0.8000(4)	0.0985(4)	0.8425(3)	0.0388(8)
C6′	0.3788(5)	0.7008(4)	0.6076(3)	0.0446(8)
H6′	0.304791	0.666184	0.675187	0.054
C6*	0.0666(4)	1.4541(4)	0.2210(3)	0.0386(8)
H6*	−0.050204	1.542804	0.233765	0.046
C7	0.9982(5)	−0.0334(5)	0.8360(3)	0.0568(10)
H7A	1.042271	−0.036593	0.900893	0.085
H7B	1.084367	−0.004585	0.768474	0.085
H7C	0.993941	−0.142827	0.834411	0.085

the 4000 to 400 cm^{-1} range. NMR spectra were recorded with a Bruker Avance III 400 spectrometer. All NMR spectra are reported in parts per million (ppm, d) relative to tetramethylsilane (Me_4Si) for ^{1}H and ^{13}C NMR spectra, with the residual solvent proton and carbon resonances used as internal standards. Coupling constants (J) are reported in Hertz (Hz), and integrations are reported as number of protons. The following abbreviations are used to describe peak patterns: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. ^{1}H and ^{13}C NMR chemical shift assignments are supported by data obtained from ^{1}H–^{1}H COSY, ^{1}H–^{13}C HMQC, and ^{1}H–^{13}C HMBC NMR experiments, and are given according to the numbering scheme of the molecular structure of the title compound.

All H atoms bonded to C atoms were refined as riding, with C—H distances of 0.93 Å (for aromatic rings), 0.96 Å (for CH_3) and U_{iso}(H) values of 1.2U_{eq}(C) (for CH in aromatic rings), and 1.5U_{eq}(C) (for CH_3). The N—H distances of 0.86 Å and U_{iso}(H) value of 1.2U_{eq}(N) (for NH_2 group) and 0.91(4) Å (for NH^+) which was isotropically refined.

Discussion

The title compound, was formed by accident, instead of the expected triazole derivate, attempting to obtain the analogue isomer previously reported [8]. A search in the latest version of the Cambridge structural database [9], for related compounds yielded only 2 structures namely 3-phenyl-4-(triisopropylsiloxy)-5-(2,2-dimethylpropanoyl)-1,2,3-triazole (REFCODE REWFOO) [10] and, 4-acetyl-3-(2-oxo-2-phenylethyl)-1-phenyl-1H-1,2,3-triazol-3-ium-5-olate (REFCODE IJOWUB) [11]. Additionally, there are two other related structures with 4-carboxylate moiety, namely 2-thienylammonium 5-hydroxy-4-methoxycarbonyl-1-(2-thienyl)-1,2,3-triazole (REFCODE CETTIE) [12] and, the other included as a fragment in the compound bis(h^5-cyclopentadienyl)-((2-bis (di-isopropylamino)phosphino(imino)methyl) phenyl-C,N)-(1-naphthyl-4-ethoxcarbonyl-5-oxy-1,2,3-triazoline)-zirconium benzene solvate (REFCODE QEMHIZ) [13]. To the best of our knowledge, this is the first example of this type of compound with 4-aminopyridinium (4-AP$^+$) as a counterion.

The molecular structure of the title compound, has dihedral angles with 3.9(5)°, 3.7(4)°, 4.7(4)°, between the acetyl moiety and the triazole ring, the carbonyl and the enolato moiety and, the 4-pyridil with the triazole ring, respectively. These acute angles and the O—C, C—C and C—N bond lengths ranging between measured values for single and double bonds [14], are indicative of a high co-planarity and a substantial delocalization of the electron density through a π-conjugated system.

On the other hand, the hydrogen bonding interactions generated with the counter ion has slight high angle. However, this situation was reported earlier in homoconjugated dimers with aminopyridine – aminopyridinium compounds, generating interpenetrated networks [15]. In the case of the title compound, this generates a 2D network along to [111] plane. Actually, a plausible reaction mechanism of the title compound is under study.

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