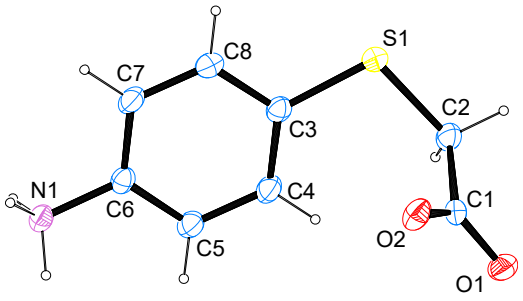
Marius Maritz, Eric C. Hosten and Richard Betz*

Crystal structure of 2-((4-Aminophenyl)thio)acetic acid, $C_8H_9NO_2S$



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Abstract

$C_8H_9NO_2S$, triclinic, $P\bar{1}$ (no. 2), a = 6.6909(5) Å, b = 7.9787(6) Å, c = 8.5551(6) Å, α = 80.065(3)°, β = 68.175(3)°, γ = 77.676(4)°, V = 412.01(5) Å^3, Z = 2, $R_{gt}(F)$ = 0.0263, $wR_{ref}(F^2)$ = 0.0784, T = 200(2) K.

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Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	0.55 × 0.40 × 0.26 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.35 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.4°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7367, 2043, 0.016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1962
$N(param)_{refined}$:	121
Programs:	Bruker [1], SHELX [2], WinGX/ORTEP [3], Mercury [4], PLATON [5]

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
S1	0.86314 (4)	0.45337 (3)	0.23719 (3)	0.02281 (10)
O1	0.44385 (14)	0.26733 (11)	0.11461 (12)	0.0280 (2)
O2	0.77454 (13)	0.14798 (10)	0.11801 (10)	0.02400 (18)
N1	0.81173 (15)	−0.03503 (12)	0.86435 (11)	0.01898 (19)
H71	0.777 (3)	0.025 (2)	0.955 (2)	0.038 (4)*
H72	0.949 (3)	−0.098 (2)	0.853 (2)	0.031 (4)*
H73	0.715 (3)	−0.110 (2)	0.882 (2)	0.032 (4)*
C1	0.61727 (17)	0.27145 (13)	0.13599 (12)	0.0181 (2)
C2	0.63110 (18)	0.44303 (13)	0.18412 (14)	0.0215 (2)
H2A	0.4982	0.4750	0.2820	0.026*
H2B	0.6277	0.5319	0.0885	0.026*
C3	0.82922 (17)	0.31455 (13)	0.42685 (13)	0.0184 (2)
C4	0.64742 (17)	0.23321 (14)	0.51432 (14)	0.0214 (2)
H4	0.5279	0.2553	0.4751	0.026*
C5	0.64105 (17)	0.11987 (14)	0.65878 (13)	0.0212 (2)
H5	0.5176	0.0644	0.7179	0.025*
C6	0.81505 (17)	0.08827 (13)	0.71595 (13)	0.0178 (2)
C7	0.99396 (18)	0.17179 (14)	0.63364 (14)	0.0221 (2)
H7	1.1106	0.1524	0.6759	0.027*
C8	1.00095 (18)	0.28393 (14)	0.48911 (14)	0.0225 (2)
H8	1.1238	0.3405	0.4318	0.027*

The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Aldrich). Crystals suitable for the diffraction study were taken straight from the commercially-provided compound.

Experimental details

The C-bound H atoms were geometrically placed and refined as riding with U_{iso}(H) = 1.2–1.5 U_{eq} (C) using the appropriate SHELXL commands. The N-bound H atoms were freely refined.

***Corresponding author: Richard Betz**, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa, e-mail: Richard.Betz@mandela.ac.za. https://orcid.org/0000-0002-5730-2152
Marius Maritz and Eric C. Hosten, Department of Chemistry, Nelson Mandela University, Summerstrand Campus (South), University Way, Summerstrand, PO Box 77000, Port Elizabeth 6031, South Africa. https://orcid.org/0000-0003-4173-2550 (E.C. Hosten)

Comment

Benzoic acid and its derivatives have found widespread use as ligands in coordination chemistry for a variety of transition metals, rare earth metals and actinides as well as elements from the s- and p-block of the periodic table. These aromatic acids can act as neutral or – upon deprotonation – as anionic ligands and serve as mono- or bidentate ligands. By varying the substituents on the phenyl moiety, the acidity of the carboxylic acid group can be fine-tuned. Furthermore, polyfunctional carboxylic acids are intriguing due to their ability to give rise to coordination polymers that can be at the heart of synthesizing metal–organic framework (MOF) structures [6]. The rules of how the interplay of acidity constants, denticity as well as the spatial pretense of the substitution backbone on those carboxylic acids influences on the coordination patterns realized in solution and in the solid state are still a field of lively research and debate that goes beyond the mere enhanced stability of coordination compounds featuring chelating ligands [7]. At the onset of a broader study aimed at elucidating further aspects in the field of coordination chemistry of multidentate ligands, (4-aminothiophenoxy)acetic acid was chosen as an interesting ligand as it combines two protic donor groups (the amino group and the carboxyl group) as well as divalent sulphur as a neutral donor atom. To allow for comparisons of metrical parameters in the free ligand and envisioned target molecules, the molecular and crystal structure of the title compound were determined. Structural information about the closely-related nitro compound [8] as well as the nitro compound featuring a sulfinyl group as linker [9] is available. Furthermore, we have determined the structures of a series of other polyfunctional carboxylic acids [10–15].

The title compound is the 2-((4-aminophenyl)thio) acetic acid derivative. The structure solution shows the title compound to be present in its zwitterionic tautomer in the solid state. The two C–O bond lengths differ slightly with values of 1.2478(13) and 1.2613(13) Å for C1–O1 and C1–O2, respectively. The C–S bond lengths to the aromatic system on the one hand and the methylene group on the other hand are in good agreement with other values reported for similar compounds whose metrical parameters have been deposited with the Cambridge Structural Database [16]. The least-squares plane as defined by the carbon atoms of the aromatic moiety on the one hand and the non-hydrogen atoms of the acetic acid moiety on the other hand intersect at an angle of 68.29(4)°.

In the crystal, classical hydrogen bonds of the N–H···O type as well as C–H···O contacts whose range falls by more than 0.1 Å below the sum of van der Waals radii of the atoms participating in them are observed. While the former involve all hydrogen atoms of the protonated amino group as donors and both oxygen atoms of the carboxylate group as acceptors – O_2 acts as two-fold acceptor –, the C–H···O contacts are supported by one of the hydrogen atoms of the methylene group as donor as well as O1 the oxygen atom – as acceptor. In terms of graph-set analysis [17, 18], the classical hydrogen bonds require a $C_1^1(10)R_2^2(20)R_2^2(20)$ descriptor at the unitary level while the C–H···O contacts necessitate a $R_2^2(8)$ descriptor at the same level. The crystal structure of the title compound is further characterized by π-stacking interactions with the shortest distance between two centers of gravity measured at 3.6804(7) Å. Overall, the molecules are connected to a three-dimensional network.

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