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The crystal structure of 3-ammonio-4-aminobenzoate, $C_7H_8N_2O_2$ – a second polymorph

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Abstract

$C_7H_8N_2O_2$, monoclinic, $P2_1/n$ (no. 14), $a = 8.9884(6)$ Å, $b = 6.0490(4)$ Å, $c = 12.1290(8)$ Å, $\beta = 95.400(2)^\circ$, $V = 656.54(8)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0340$, $wR_{ref}(F^2) = 0.0978$, $T = 200$ K.

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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 obtained upon recrystallization of the compound from methanol.

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Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	$0.53 \times 0.35 \times 0.11$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.12 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.1° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5578, 1571, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1295
$N(\text{param})_{\text{refined}}$:	120
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

All nitrogen-bound H atoms were located on a difference Fourier map and refined freely.

Comment

Chelate ligands have found widespread use in coordination chemistry due to the increased stability of coordination compounds they can form in comparison to monodentate ligands. The stability of these compounds is enhanced further if the denticity of the ligand is increased upon incorporation of more and more potential donor sites [7]. Especially derivatives of benzoic acids offering the possibility to act as a chelate ligand are interesting in this aspect as chemical factors such as pH values could influence the protonation/deprotonation of acidic functional groups and fine-tune the denticity of the resulting ligand species. Examples would be benzoic acid derivatives bearing multiple hydroxy or amino groups. In continuation of our interest in the structures of polyfunctional carboxylic acids [8–14] the title compound seemed intriguing. Although the molecular and crystal structure of the latter have been reported earlier in a C centred space group [15],

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.85407 (10)	0.41707 (15)	−0.11063 (7)	0.0237 (2)
O2	0.77074 (10)	0.08228 (15)	−0.07068 (8)	0.0261 (2)
N1	0.37216 (11)	0.25979 (18)	0.18943 (9)	0.0199 (2)
H711	0.3488 (18)	0.140 (3)	0.1459 (14)	0.032 (4)*
H712	0.291 (2)	0.361 (3)	0.1745 (14)	0.039 (5)*
H713	0.374 (2)	0.210 (3)	0.2691 (16)	0.047 (5)*
N2	0.47055 (12)	0.66069 (19)	0.29016 (9)	0.0236 (3)
H721	0.4261 (19)	0.567 (3)	0.3337 (14)	0.035 (5)*
H722	0.5114 (19)	0.781 (3)	0.3234 (14)	0.035 (4)*
C1	0.78346 (13)	0.2857 (2)	−0.05217 (10)	0.0189 (3)
C2	0.70840 (13)	0.38375 (19)	0.04149 (9)	0.0172 (3)
C3	0.58797 (12)	0.27305 (19)	0.08042 (9)	0.0173 (3)
H3	0.560296	0.131288	0.051671	0.021*
C4	0.50862 (12)	0.36681 (19)	0.16011 (9)	0.0169 (3)
C5	0.55061 (13)	0.56941 (19)	0.20983 (10)	0.0173 (3)
C6	0.67177 (13)	0.6802 (2)	0.16978 (10)	0.0191 (3)
H6	0.702408	0.819034	0.200751	0.023*
C7	0.74743 (13)	0.5910 (2)	0.08603 (10)	0.0189 (3)
H7	0.826778	0.671634	0.058525	0.023*

an initial unit cell determination of the compound available to us after recrystallization from methanol unambiguously showed the presence of a compound presenting itself in a primitive space group. To clarify the situation the structure was determined.

The analysis of the data proves the presence of the 3,4-diaminobenzoic acid. The molecule is present in a zwitterionic tautomer with protonation observed on the amino group in *meta* position to the carboxylate substituent. Very similar C–O bond lengths of 1.2543(15) Å and 1.2734(14)° confirm the deprotonation of the carboxyl group; moreover, these values are in good agreement with values found for other benzoate salts whose metrical parameters have been deposited with the Cambridge Structural Database [16]. Intracyclic C–C–C angles span a range of 117.05(10)–121.74(10)° with the smallest angle on the carbon atom bearing the amino group and the largest angle on the carbon atom bearing the ammonio group. The molecule is approaching planarity with an O–C–C–C dihedral angle of −22.16(17)° for the carboxylate group.

In the crystal, classical hydrogen bonds of the N–H⋯O type are observed that employ every pnictogen-bound hydrogen atom as donor as well as both carboxylate oxygen atoms as acceptor. In terms of graph-set analysis [17, 18], the descriptor for these hydrogen bonds is C₁¹(7)C₁¹(8)C₁¹(8)R₂²(14)R₂²(14) at the unary level with both cyclic patterns being supported by hydrogen atoms of the ammonio group. In addition, C–H⋯π contact stems from

the CH group in *meta* position to the carboxylate substituent. In total, the molecules are connected to undulated double sheets along [1 0 1]. π-Stacking is observed with the shortest distance measured between two centers of gravity at just 3.6442(7) Å.

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