Crystal structure of 3,4-dihydroxy-1,5-dimethyl-2-phenylpyrazolium chloride, [C\textsubscript{11}H\textsubscript{13}N\textsubscript{2}O\textsubscript{2}]Cl

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Abstract

C\textsubscript{11}H\textsubscript{13}ClN\textsubscript{2}O\textsubscript{2}, triclinic, \textit{P\textsubscript{T}} (no. 2), \textit{a} = 7.150(5) Å, 
\textit{b} = 8.380(2) Å, \textit{c} = 10.586(2) Å, \textit{\alpha} = 71.80(2)°, 
\textit{\beta} = 84.05(5)°, \textit{\gamma} = 87.47(5)°, \textit{V} = 599.3 Å\textsuperscript{3}, \textit{Z} = 2,
\textit{R}\textsubscript{wp}(\textit{F}) = 0.049, \textit{wR}\textsubscript{wp}(\textit{F}^2) = 0.176, \textit{T} = 293 K.

Source of material

The title compound was obtained by dissolving 4-hydroxyantipyrine (0.408 g, 0.002 mole) in acetonitrile (10 ml) and then adding carefully of titanium tetrachloride (0.39 g, 0.002 mole) under nitrogen. A week later white crystals appear from the acetonitrile solution. TiCl\textsubscript{4} catalyzes the reaction. A suitable crystal was taken for X-ray diffraction studies.

Experimental details

The two H atoms involved in hydrogen bonding (H1 and H2) were first located from a difference Fourier map and then refined isotropically. Other H atoms were positioned geometrically and treated as riding on their parent atoms with d(C—H) = 0.96 Å (CH\textsubscript{3}) and 
\textit{U} \textit{wp}(\textit{C}) = 1.5 \textit{U} \textit{wp}(\textit{C}) or d(C—H) = 0.93 Å (aromatic) and 
\textit{U} \textit{wp}(\textit{H}) = 1.2 \textit{U} \textit{eq}(\textit{C}). The attempts at recrystallization of the compound did not improve crystals quality, which explains the relatively large residual values.

Discussion

4-Hydroxyantipyrine is one of the main metabolites of antipyrine in man and rat [1]. Together with 3-hydroxyantipyrine and 4,4'-dihydroxyantipyrine, they are excreted in free form or as glycoconjugates [2]. Beside our works on metal complexes based on the antipyrine skeleton [3,4], we had prepared a new derivate of 4-hydroxyantipyrine, starting from the reaction of titanium tetrachloride and an acetonitrile solution of 4-hydroxyantipyrine. The molecule consists of a Cl anion and a cation formed by a pyrazol ring P1 [C7-C9/N1-N2] and a phenyl ring P2 [C1-C6] which are planar within 0.005 and 0.008 Å, respectively, with an interplanar angle of 77.7(1)°. Bond lengths within the molecule correspond with the average C—C distance for a phenyl ring [1.371(4) Å] and the angles are normal. The comparison between this cation and the 4-hydroxyantipyrine [5] shows that the presence of a second hydroxyl group on pyrazol ring (via C7) instead of 4-hydroxyantipyrine, starting from the reaction of titanium catalyzes the reaction. As suitable crystal was taken for X-ray diffraction studies.

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The two H atoms involved in hydrogen bonding (H1 and H2) were first located from a difference Fourier map and then refined isotropically. Other H atoms were positioned geometrically and treated as riding on their parent atoms with d(C—H) = 0.96 Å (CH\textsubscript{3}) and 
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\textit{R}\textsubscript{wp}(\textit{F}) = 0.049, \textit{wR}\textsubscript{wp}(\textit{F}^2) = 0.176, \textit{T} = 293 K.

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Discussion

4-Hydroxyantipyrine is one of the main metabolites of antipyrine in man and rat [1]. Together with 3-hydroxyantipyrine and 4,4'-dihydroxyantipyrine, they are excreted in free form or as glycoconjugates [2]. Beside our works on metal complexes based on the antipyrine skeleton [3,4], we had prepared a new derivate of 4-hydroxyantipyrine, starting from the reaction of titanium tetrachloride and an acetonitrile solution of 4-hydroxyantipyrine. The molecule consists of a Cl anion and a cation formed by a pyrazol ring P1 [C7-C9/N1-N2] and a phenyl ring P2 [C1-C6] which are planar within 0.005 and 0.008 Å, respectively, with an interplanar angle of 77.7(1)°. Bond lengths within the molecule correspond with the average C—C distance for a phenyl ring [1.371(4) Å] and the angles are normal. The comparison between this cation and the 4-hydroxyantipyrine [5] shows that the presence of a second hydroxyl group on pyrazol ring (via C7) instead of a carbonyl group induces some differences within 3 e.s.d. in bond lengths and angles in P1; the most significative variations are around N2: N2—N1 [1.364(2) Å], N2—C9 [1.338(3) Å], N1—N2—C9 [108.7(2)°] compared with homologous values [1.406(2) Å, 1.387(2) Å, 105.6(1)°, respectively] observed in the 4-hydroxyantipyrine. The crystal packing is governed by two O—H···Cl hydrogen bonds [O1—H1···Cl: 2.920(2) Å, 166(3)°; O2—H2···Cl: 2.980(2) Å, 172(3)°]. Moreover, the packing is ensured by \textit{\pi}—\textit{\pi} stacking interactions which occur between P1 pyrazol rings through inversion centre at (1/2,1/2,1/2) with a centroid-to-centroid distance of 3.769(3) Å, an average spacing of 3.58 Å with an offset of 18.2°. In addition there are two C—C—O interactions [C2—H2···O2: 3.451(4) Å, 161° and C6—H6···O2: 3.450(4) Å, 153°] and one C—H···Cg (\textit{\pi}-ring) interactions [H10A···Cg: 2.94 Å; C10—H10A···Cg: 144°; i: x,y,1−z] with Cg centroid of P1 phenyl ring. The crystalline cohesion is ensured by van der Waals contacts, the shortest being 3.451(4) Å.
Table 1. Data collection and handling.

Crystal: colorless parallelepipdedic, size 0.18 x 0.20 x 0.25 mm
Wavelength: Mo Kα radiation (0.71073 Å)
μ: 3.06 cm⁻¹
Diffractometer, scan mode: Enraf-nonus CAD4, ω/2θ
2θ_max: 59.98°
N(hkl)_measured, N(hkl)_unique: 3691, 3471
Criterion for exclusion: I/σ(I) > 2 (I) 0.00, 1004
N(param/struct): 153
Programs: SIR92 [6], SHELXL-97 [7], CAMERON [8], WinGX [9], ORTEP-III [10]

Table 2. Atomic coordinates and displacement parameters (in Å²).

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References

3. Bekaert, A.; Lemoine, P.; Brion, J. D.; Viossat, B.: Crystal structure of bis[acetoxy-κ¹O₂O₂][bis(acetoxy-κ¹O₂O₂)-κN phenazone] dioxoaruran, [U₃O₅(CH₃COO)₃(C₂H₅N₂C₂(CH₃)₂O)]₂. Z. Kristallogr. NCS 221 (2006) 45-46.