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1-Oxo-3-phenyl-1,2-dihydropyrido[1,2-*a*]-pyrazin-5-ium hexafluorophosphate

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Key indicators

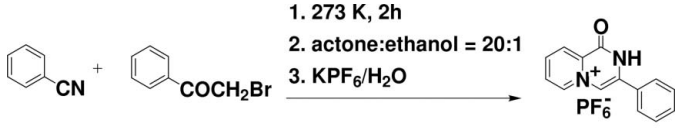
Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
R factor = 0.067
wR factor = 0.231
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the structure of the title compound, $C_{14}H_{11}N_2O^+\cdot PF_6^-$, all the bond lengths and angles have normal values. The pyrido[1,2-*a*]pyrazinium system and the phenyl ring are conjugated. In the crystal structure, the phenylpyrido[1,2-*a*]pyrazinium rings are arranged in parallel layers.

Comment

Quaternary aza-aromatic salts are widely used in organic synthesis. The first representative of a pyrido[1,2-*a*]pyrazine system has been described by Schwab *et al.* (1954). Batori *et al.* (1990) obtained pyrido[1,2-*a*]pyrazinium-1- and -3-olates. Szafran *et al.* (2005) have described the stucture of pyrido[1,2-*a*]pyrazinium bromide. We have confirmed the stucture of the title compound, (3), by ^{1}H NMR, ^{13}C NMR and single-crystal X-ray diffraction analysis.



(1) (2) (3)

All bond lengths and angles in (3) have normal values. The C7—O1 bond length [1.228 (3)Å] and the O1—C7—C8 angle [120.2 (2)°] show that the oxopyrido[1,2-*a*]pyrazinium system is in the keto form and is conjugated. The repulsion of H5 and H10 results in an angle of 18.63 (3)° between the pyrido-[1,2-*a*]pyrazinium system and phenyl ring, and the repulsion of H4 and H5 results in an angle of 3.73 (3)° between the pyridinium and pyrazinium rings. Two cations are linked by an N—H···O hydrogen bond and a weak C—H···O interaction forms a dimer in the same layer. The pyrido[1,2-*a*]pyrazinium cations are arranged in parallel layers in the crystal structure. The layers are linked by π–π stacking [$Cg1\cdots Cg2^{i}$ = 3.838 (13) Å, where *Cg*1 is the centroid of ring C1/C2/C3/C4/N1/C8 and *Cg*2 is the centroid of ring C9–C14; symmetry code: (i) $x+1, y, z$] and N—H···O hydrogen-bond interactions [N2—H2···O1^{ii}: N—H = 0.86 Å, H···O = 2.00 Å, N···O = 2.838(6) Å and N—H···O = 164°; symmetry code: (ii) $1-x, 2-y, -z$], which produce a three-dimensional structure.

Experimental

2-Cyanopyridine (10 mmol), (1), was mixed with 2-bromoacetophone (10 mmol), (2), heated at 363 K for 2 h, then cooled to room temperature. The resulting yellow solid was pulverized, triturated with acetone and ethanol (10 ml, 20:1), then collected by filtration and washed with acetone. A saturated aqueous solution (10 ml) of

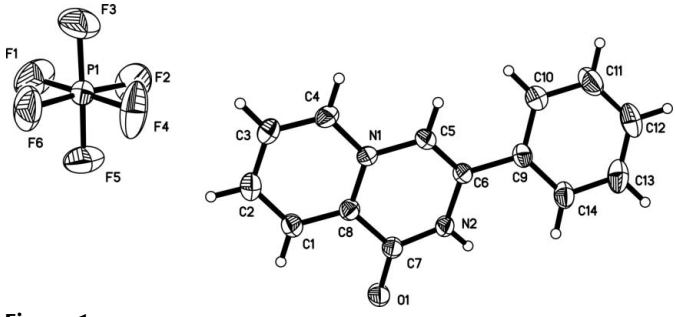


Figure 1
The molecular structure of (3) with 30% probability displacement ellipsoids.

potassium hexafluorophosphate (10 mmol) was added to an aqueous solution (30 ml) of the above solid (10 mmol) and stirred for 5 min. The precipitate was filtered off and washed with water. Single crystals of the product suitable for X-ray cystallographic analysis were obtained by recrystallization from acetonitrile and petroleum ether (1:10). ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.44 (*s*, *br*, H2), 9.39–9.33 (*m*, H5), 8.81–8.76 (*m*, H4), 8.65–8.58 (*m*, H6, H7), 8.46–8.42 (*m*, H8), 7.87–7.62 (*m*, H10, H11, H12, H13, H14).

Crystal data

$C_{14}H_{11}N_2O^+\cdot PF_6^-$
M_r = 368.22
Triclinic, $P\overline{1}$
a = 8.036 (2) Å
b = 8.724 (2) Å
c = 11.881 (2) Å
α = 91.13 (2)°
β = 109.52 (2)°
γ = 106.38 (2)°
V = 747.2 (3) Å^3
Z = 2
D_x = 1.637 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 295 (2) K
Prism, colorless
0.25 × 0.25 × 0.15 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.939, T_{max} = 0.963
3315 measured reflections
2693 independent reflections
1580 reflections with $I > 2\sigma(I)$
R_{int} = 0.016
θ_{max} = 25.2°
3 standard reflections
frequency: 3600 min
intensity decay: 0.001%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.231
S = 1.05
2693 reflections
218 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1102P)^2 + 1.1617P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.68 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.051 (4)

All the H atoms were placed in calculated positions (N—H = 0.86, C—H = 0.93Å) and refined using a riding model, with U_{iso}(H) = 1.2U_{eq}(parent atom).

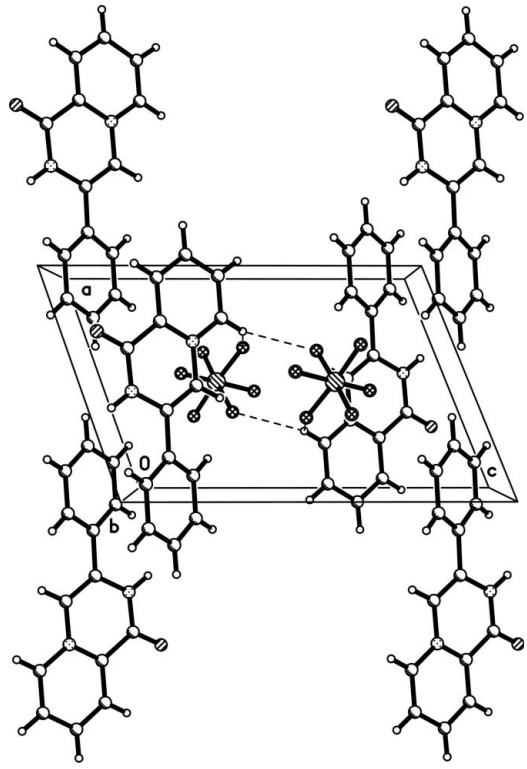


Figure 2
A view of the packing of (3) down the *b* axis. Hydrogen bonds are shown as dashed lines.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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