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Tris(1-phenacyl-2-pyridone) Hydroxonium Tetrafluoroborate, a Hydrogen-Bonded Complex

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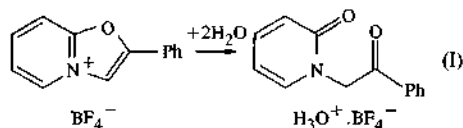
Abstract

The hydrolytic cleavage of 2-phenyloxazolo[3,2-*a*]-pyridinium tetrafluoroborate results in the formation of the title tris(1-phenacyl-2-pyridone) hydroxonium tetrafluoroborate complex, $3C_{13}H_{11}NO_2 \cdot H_3O^+ \cdot BF_4^-$. The structure is built up from hydrogen-bonded cations and disordered BF_4^- anions. The strong hydrogen bonding causes considerable redistribution of electron density in the pyridone moiety.

Comment

Recently, it was found that mesoionic 2-oxo-3-benzoyloxazolo[3,2-*a*]pyridine can be transformed to oxazolo[3,2-*a*]pyridinium tetrafluoroborate by the action of H_2SO_4 and HBf_4 (Babaev & Orlova, 1997). Having attempted to confirm the structure of this compound, we discovered that prolonged standing of the reaction mixture (one week at room temperature) resulted in the unexpected formation of *N*-phenacyl-2-pyridone, (I). Although the ring opening of the former compound is known to occur by the action of alkali (Pauls

& Kroehnke, 1976), no data on the extremely mild hydrolysis by the action of water have been reported. The formation of pyridone is the result of hydrolytic cleavage of the oxazolium fragment by two molecules of water (see scheme below).



The first water molecule causes ring opening and formation of pyridone, while the second serves as the acceptor of a proton. The *N*-phenacyl-2-pyridone molecule forms a strong hydrogen bond *via* the pyridone O atom to the H_3O^+ cation positioned on the 3 axis [$O2 \cdots H1$ 1.50 (2), $O2 \cdots O1$ 2.524 (2) Å and $O2 \cdots H1 - O1$ 171 (2)°]. As a result of hydrogen bonding, the C2—O2 bond in the present structure is 0.02 Å longer than the longest in known structures containing the *N*-alkylated pyridone moiety (Nawata, Matsuura, Ando & Iitaka, 1990; Hsu & Craven, 1974; Schwalbe & Saenger, 1973). The other bond lengths and angles are ordinary for compounds of this type. In the difference Fourier maps, no sign of proton transfer from H_3O^+ to the pyridone O atom was found. The BF_4^- anion is orientationally disordered over two sets of sites and does not form any considerably short contacts with the hydrogen-bonded complex cation; the shortest $F \cdots H$ (pyridone) distances are 2.40 Å, *i.e.* 0.2 Å shorter than the sum of the van der Waals radii. We have not

found any examples of such compounds with the H_3O^+ cation coordinated by three neutral organic molecules in a search of the Cambridge Structural Database (Allen & Kennard, 1993).

Experimental

Single crystals of the title compound were obtained by evaporation of a water solution of 2-phenyloxazo[3,2-*a*]pyridinium tetrafluoroborate. Chemical analysis: found C 62.75, H 4.40%; $C_{39}H_{36}BF_4N_3O_7$ requires C 62.83, H 4.46%.

Crystal data

$3C_{13}H_{11}NO_2 \cdot H_3O^+ \cdot BF_4^-$

$M_r = 745.52$

Trigonal

$R\bar{3}$

$a = 14.020$ (2) Å

$c = 33.005$ (5) Å

$V = 5618.3$ (14) Å³

$Z = 6$

$D_x = 1.322$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.7107$ Å

Cell parameters from 22 reflections

$\theta = 15.4$ – 17.0°

$\mu = 0.104$ mm⁻¹

$T = 293$ (2) K

Irregular

$0.55 \times 0.40 \times 0.33$ mm

Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer

ω scans

Absorption correction: none

2724 measured reflections

2724 independent reflections

1355 reflections with

$I > 2\sigma(I)$

$\theta_{max} = 26.9^\circ$

$h = 0 \rightarrow 15$

$k = 0 \rightarrow 15$

$l = -41 \rightarrow 42$

2 standard reflections

frequency: 150 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.053$

$wR(F^2) = 0.130$

$S = 1.027$

2724 reflections

225 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.051P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.012$

$\Delta\rho_{max} = 0.151$ e Å⁻³

$\Delta\rho_{min} = -0.154$ e Å⁻³

Extinction correction:

SHELXL93

Extinction coefficient:

0.0011 (2)

Scattering factors from

International Tables for Crystallography (Vol. C)

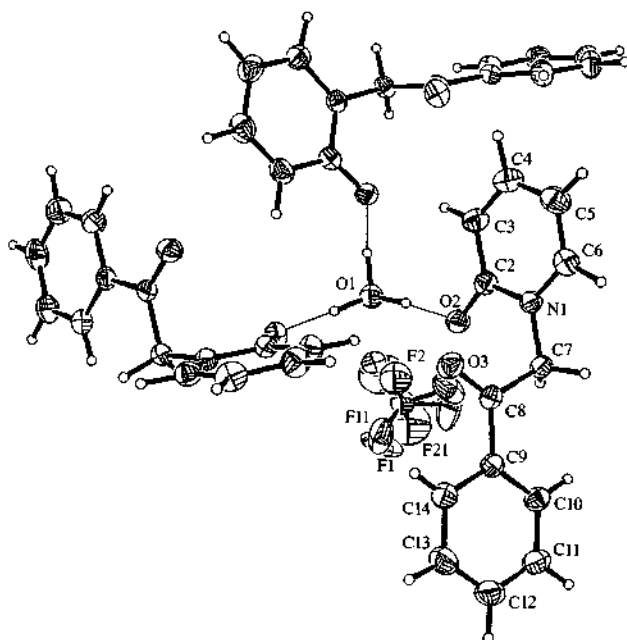


Fig. 1. The formula unit of tris(1-phenacyl-2-pyridone) hydroxonium tetrafluoroborate showing 25% probability displacement ellipsoids.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^* a_i a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1	1/3	2/3	0.02200 (9)	0.0633 (8)
N1	0.55916 (14)	0.55407 (14)	0.08376 (5)	0.0502 (5)
O2	0.44653 (13)	0.57930 (12)	0.04134 (5)	0.0603 (5)
O3	0.36388 (13)	0.39143 (13)	0.10647 (5)	0.0657 (5)
C2	0.5147 (2)	0.6164 (2)	0.07057 (7)	0.0534 (6)
C3	0.5497 (2)	0.7171 (2)	0.09097 (9)	0.0659 (7)
C4	0.6222 (2)	0.7485 (2)	0.12176 (8)	0.0747 (8)
C5	0.6657 (3)	0.6831 (3)	0.13395 (9)	0.0742 (8)
C6	0.6330 (2)	0.5866 (2)	0.11477 (7)	0.0612 (7)
C7	0.5208 (2)	0.4469 (2)	0.06510 (8)	0.0512 (6)
C8	0.4073 (2)	0.3640 (2)	0.08081 (7)	0.0493 (6)
C9	0.3530 (2)	0.2508 (2)	0.06390 (7)	0.0518 (6)

C10	0.4024 (2)	0.2193 (2)	0.03446 (7)	0.0590 (7)
C11	0.3484 (3)	0.1142 (2)	0.01876 (9)	0.0704 (8)
C12	0.2450 (3)	0.0404 (3)	0.03236 (10)	0.0810 (9)
C13	0.1952 (3)	0.0699 (3)	0.06187 (11)	0.0825 (9)
C14	0.2491 (2)	0.1753 (2)	0.07741 (9)	0.0681 (7)
F1†	0.5770 (6)	0.3274 (8)	0.1594 (3)	0.236 (6)
F1††	0.5684 (6)	0.3173 (5)	0.1372 (3)	0.145 (5)
F2†	2/3	1/3	0.1069 (3)	0.145 (4)
F2††	2/3	1/3	0.1905 (4)	0.228 (9)
B1	2/3	1/3	0.1498 (2)	0.083 (2)

† Site occupancy = 0.580 (12). †† Site occupancy = 0.420 (12).

Table 2. Selected geometric parameters (\AA , $^\circ$)

N1—C6	1.362 (3)	C2—C3	1.412 (3)
N1—C2	1.374 (3)	C3—C4	1.345 (4)
N1—C7	1.455 (3)	C4—C5	1.392 (4)
O2—C2	1.272 (2)	C5—C6	1.349 (4)
C6—N1—C2	122.4 (2)	N1—C2—C3	116.3 (2)
C6—N1—C7	119.4 (2)	C4—C3—C2	121.0 (3)
C2—N1—C7	118.1 (2)	C3—C4—C5	120.7 (3)
O2—C2—N1	117.8 (2)	C6—C5—C4	118.9 (3)
O2—C2—C3	125.8 (2)	C5—C6—N1	120.6 (3)
C6—N1—C7—C8	101.1 (2)	N1—C7—C8—C9	177.7 (2)
C2—N1—C7—C8	-75.6 (2)	O3—C8—C9—C14	1.1 (3)
N1—C7—C8—O3	-2.2 (3)	O3—C8—C9—C10	179.8 (2)

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *SHELXS96* (Sheldrick, 1996). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTECH* (McArdle, 1995). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1311). Services for accessing these data are described at the back of the journal. A packing diagram has also been deposited.

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