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Key indicators

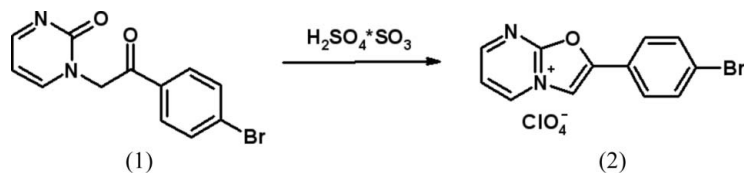
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.041
 wR factor = 0.111
Data-to-parameter ratio = 14.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.2-(4-Bromophenyl)oxazolo[3,2-*a*]pyrimidinium
perchlorate

The title compound, $\text{C}_{12}\text{H}_8\text{BrN}_2\text{O}^+\cdot\text{ClO}_4^-$, was synthesized and characterized by ^1H NMR and single-crystal X-ray diffraction. The essentially planar *p*-bromophenyl fragment and plane of the heterocyclic system form a dihedral angle of $1.79(7)^\circ$. Short intermolecular contacts (*ca* 3.0 \AA) involving O atoms of a perchlorate anion may indicate the positive charge concentration on the bridgehead N atom of the cation.

Received 15 August 2006
Accepted 13 September 2006

Comment

In a previous communication (Rybakov *et al.*, 2006), we reported the synthesis and crystal structure of 1-(4-chlorobenzoylmethyl)pyrimidin-2(1*H*)-one. Here we report the synthesis of the *p*-bromophenyl analog (1) and the cyclization reaction to form the title aromatic oxazolo[3,2-*a*]pyrimidinium cation, (2). This class of oxazolo[3,2-*a*]pyrimidinium cationic bicyclic system can be prepared by two synthetic routes, either from oxazole or from pyrimidine. The first route is by condensation of a 4,5-disubstituted 2-aminooxazole with acetylacetone (Chuiguk & Leshenko, 1974), leading to a 5,7-dimethyloxazolo[3,2-*a*]pyrimidinium salt. Alternatively, 7-diaxyloxazolo[3,2-*a*]pyrimidinium salts have been obtained from *N*-phenacyl-4-arylpurimidine-2-thiones by two different methods (Reimer *et al.*, 1993; Liebscher & Hassoun, 1988). One method involves the cyclization of *N*-phenacyl-4-aryl-pyrimid-2-ones by a somewhat unsafe combination of a dehydrating agent (acetic anhydride) with perchloric acid (Liebscher & Hassoun, 1988). Applying this method to phenacylpyrimidone (1), we obtained only the perchlorate of the starting material [(1)·HClO₄]. Nevertheless, fuming sulfuric acid (20 mass% of SO₃) turned out to be the reagent of choice, and its use resulted in formation of the desired salt (2) from (1) in excellent yield. Compound (2) was characterized by ^1H NMR. The singlet of the CH₂ group [initially observed in parent (1)] disappeared in (2), and a new down-field singlet of the formed oxazole ring appeared at 9.31 p.p.m. Signals of aromatic protons appeared as a characteristic multiplet (*AA'*/*BB'* system), so *ortho*-protons are equivalent (at least in solution).



The bond lengths in the oxazolopyrimidinium ring system of (2) (Fig. 1) confirm its aromatic nature. The dihedral angle between the essentially planar nine-membered bicyclic system

and the benzene ring is $1.79 (7)^\circ$, indicating the presence of conjugation between these aromatic fragments. Similar values for this dihedral angle [$3.77 (7)$ and $5.33 (15)^\circ$] were found in previously reported oxazolopyridinium salts (Albov *et al.*, 2004*a,b*). It is arguable that the positive charge of the cation is concentrated on atom N1, as fairly short intermolecular contacts exist between the cation and the O atoms of the perchlorate anion (having a low-density negative charge) [$\text{O13} \cdots \text{N1} = 2.998 (4)$, $\text{O14} \cdots \text{C2} = 3.157 (4)$, $\text{O13} \cdots \text{C5} = 2.973 (4)$, $\text{O12} \cdots \text{C9} = 2.996 (4)$ and $\text{O14} \cdots \text{C9} = 2.991 (4) \text{ \AA}$]. There is a weak intramolecular hydrogen bond [$\text{H11} \cdots \text{O4} = 2.47 \text{ \AA}$, $\text{C11} \cdots \text{O4} = 2.798 (3) \text{ \AA}$ and $\text{C11}-\text{H11} \cdots \text{O4} = 101^\circ$]. This same weak interaction is observed in the structures of related oxazolopyridine salts (Albov *et al.*, 2004*a,b*; Babaev *et al.*, 1997; Babaev, Bush *et al.*, 1999; Babaev, Rybakov *et al.*, 1999). From a search of the Cambridge Structural Database (Version 5.27; Allen, 2002), we found N \cdots H hydrogen bonding for two analogs of the salt (2), *viz.* 6-nitro-2-phenylimidazo[1,2-*a*]pyrimidine (Aslanov *et al.*, 1983) and 2-phenylimidazo[1,2-*a*]pyrimidine (Tafeenko *et al.*, 1996), with N \cdots H distances of 2.53 and 2.50 \AA , respectively.

Experimental

Dried *N*-phenacylpyrimid-2-one, (1) (0.02 mol), was carefully added to a stirred mixture of 17 ml fuming sulfuric acid (60 mass% of SO_3) and 25 ml of concentrated sulfuric acid. The temperature was kept in the range 273–276 K. The mixture was stirred below 273 K until compound (1) had completely dissolved and was kept for 4 h at room temperature. After this period, the reaction mixture was carefully poured into 500 g of crushed ice, and 10 ml of concentrated perchloric acid was added. The product was isolated by suction and washed with ethanol and diethyl ether, and recrystallized from CH_2Cl_2 – CF_3COOH (20:1) (yield 95%, m.p. 552–554 K).

Crystal data

$\text{C}_{12}\text{H}_8\text{BrN}_2\text{O}^+\cdot\text{ClO}_4^-$	$Z = 4$
$M_r = 375.56$	$D_x = 1.879 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation
$a = 6.291 (2) \text{ \AA}$	$\mu = 6.33 \text{ mm}^{-1}$
$b = 12.052 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 17.688 (4) \text{ \AA}$	Prism, colorless
$\beta = 98.19 (2)^\circ$	$0.15 \times 0.15 \times 0.15 \text{ mm}$
$V = 1327.4 (6) \text{ \AA}^3$	

Data collection

Enraf–Nonius CAD-4 diffractometer	2375 reflections with $I > 2\sigma(I)$
ω scans	$R_{\text{int}} = 0.084$
Absorption correction: none	$\theta_{\text{max}} = 74.9^\circ$
2811 measured reflections	1 standard reflection
2714 independent reflections	frequency: 60 min
	intensity decay: 3%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0909P)^2 + 0.38P]$
$R[F^2 > 2\sigma(F^2)] = 0.041$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.111$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.92$	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
2714 reflections	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
190 parameters	
H-atom parameters constrained	

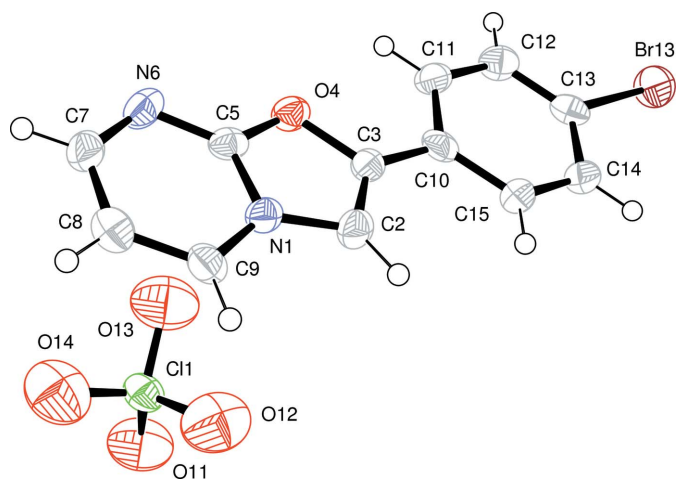


Figure 1

The molecular structure of the title compound, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level with H atoms shown as spheres of arbitrary radius.

Table 1

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

N1–C5	1.352 (3)	O4–C5	1.322 (3)
N1–C9	1.359 (3)	C5–N6	1.317 (3)
N1–C2	1.384 (3)	N6–C7	1.330 (3)
C2–C3	1.342 (3)	C7–C8	1.392 (4)
C3–O4	1.383 (3)	C8–C9	1.360 (4)
C3–C10	1.447 (3)		
C5–N1–C9	119.7 (2)	N6–C5–O4	124.2 (2)
C5–N1–C2	107.63 (19)	N6–C5–N1	125.9 (2)
C9–N1–C2	132.6 (2)	O4–C5–N1	109.9 (2)
C3–C2–N1	106.4 (2)	C5–N6–C7	114.1 (2)
C2–C3–O4	109.3 (2)	N6–C7–C8	124.0 (2)
C2–C3–C10	133.6 (2)	C9–C8–C7	119.2 (2)
O4–C3–C10	117.12 (19)	N1–C9–C8	117.0 (2)
C5–O4–C3	106.82 (17)		

All H atoms were refined using a riding model, with C–H = 0.93 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wokadlo, (1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 1999).

The authors are indebted to the Russian Foundation for Basic Research for covering the licence fee for use of the Cambridge Structural Database.

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