

## 2-(4-Bromophenyl)-5,7-dimethyl[1,3]oxazolo[3,2-a]pyrimidin-4-ium perchlorate

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## Key indicators

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$   
 R factor = 0.045  
 wR factor = 0.115  
 Data-to-parameter ratio = 14.7

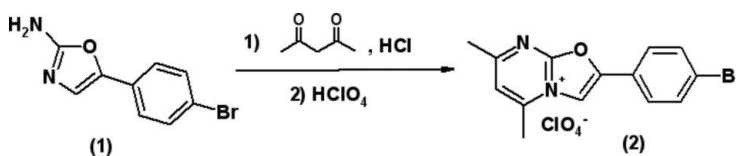
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\text{C}_{14}\text{H}_{12}\text{BrN}_2\text{O}^+\cdot\text{ClO}_4^-$ , was synthesized from the parent 2-aminoxazole and acetylacetone and characterized by  $^1\text{H}$  NMR and single-crystal X-ray diffraction. The bromophenyl fragment and the essentially planar nine-membered bicyclic system form a dihedral angle of  $10.50 (11)^\circ$ .

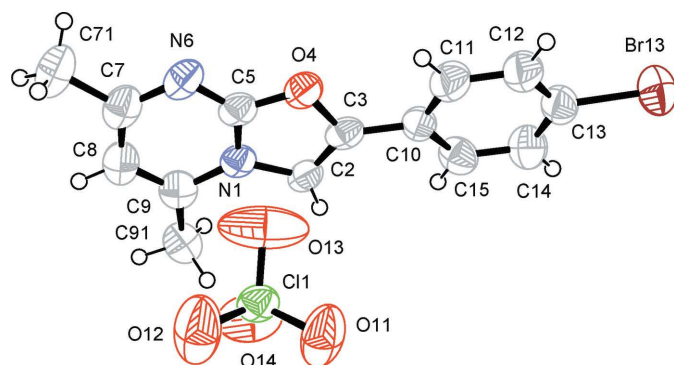
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## Comment

In a previous communication (Rybakov *et al.*, 2006b), we reported the crystal structure of 5-(4-bromophenyl)-1,3-oxazol-2-amine, (1), prepared by a novel method. Here we report the synthesis and crystal structure of its derivative, 2-(4-bromophenyl)-5,7-dimethyl[1,3]oxazolo[3,2-a]pyrimidin-4-ium perchlorate, (2), obtained by condensation of (1) with acetylacetone. Condensation of 2-aminoxazoles (azines) with 1,3-dicarbonyl compounds (and their synthetic equivalents) is a well known strategy towards the formation of cationic bicyclic systems with a bridgehead N atom. Examples of reactions of this type are known for 2-aminopyridines and 2-amino-(benzo)thiazoles (Nesmeyanov & Rybinskaya, 1958; Shulga & Chuiguk, 1971, 1972). There is only one report on the condensation of acetylacetone and 4,5-disubstituted 2-aminoxazole derivatives (Chuiguk & Leshenko, 1974). We found that the reaction between acetylacetone and (1) led to the oxazolo[3,2-a]pyrimidinium salt, (2), with good yield. Compound (2) was characterized by  $^1\text{H}$  NMR.



The bond lengths in the oxazolopyrimidinium ring system of (2) (Fig. 1 and Table 1) confirm its aromatic nature. The dihedral angle between the essentially planar nine-membered bicyclic system and the benzene ring is  $10.50 (11)^\circ$ , 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 oxazolopyrimidinium salts (Albov *et al.*, 2004a,b) and in an oxazolopyrimidine salt [ $1.79 (7)^\circ$ ; Rybakov *et al.*, 2006a]. 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) [ $\text{O13}\cdots\text{C5} = 2.841 (6) \text{ \AA}$ ,  $\text{O13}\cdots\text{N1} = 2.930 (5) \text{ \AA}$  and  $\text{O11}\cdots\text{C9}^{\text{iii}} = 2.966 (5) \text{ \AA}$ ; symmetry code: (iii)  $x, y, z + 1$ ]. There is a weak  $\text{C11}-\text{H11}\cdots\text{O4}$  intramolecular hydrogen



**Figure 1**

The molecular structure of (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level with H atoms shown as spheres of arbitrary radius.

bond (Table 2). 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) and the oxazolopyrimidine salt (Rybakov *et al.*, 2006*a*). From a search of the Cambridge Structural Database (Version 5.27; Allen, 2002), we found N—H···N hydrogen bonding for two analogs of the salt (2), *viz.* 6-nitro-2-phenylimidazo[1,2-*a*]pyridine (Aslanov *et al.*, 1983) and 2-phenylimidazo[1,2-*a*]pyridine (Tafeenko *et al.*, 1996), with N···H distances of 2.53 and 2.50 Å, respectively. Weak C—H···O interactions (Table 2) are observed in the crystal structure of (2).

## Experimental

The synthesis of the starting compound, (1), was described by Rybakov *et al.* (2006*a*). Concentrated hydrochloric acid (36 ml) and then acetylacetone (22.7 g, 0.228 mol) were added to (1) (18 g, 0.076 mol). The reaction mixture was refluxed for 4 h, keeping the temperature in the range 393–413 K. To the cooled reaction mixture concentrated perchloric acid (20 ml) and diethyl ether (200 ml) were added. The precipitate was filtered off, washed with diethyl ether and ethanol, and recrystallized from acetonitrile (yield 66%, m.p. 588–590 K).

### Crystal data

$C_{14}H_{12}BrN_2O^+ \cdot ClO_4^-$	$Z = 4$
$M_r = 403.62$	$D_x = 1.660 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 15.742 (4) \text{ \AA}$	$\mu = 5.25 \text{ mm}^{-1}$
$b = 13.292 (4) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 7.718 (3) \text{ \AA}$	Block, colourless
$\beta = 91.14 (2)^\circ$	$0.15 \times 0.15 \times 0.15 \text{ mm}$
$V = 1614.6 (9) \text{ \AA}^3$	

### Data collection

Enraf–Nonius CAD-4	1986 reflections with $I > 2\sigma(I)$
diffractionmeter	$R_{\text{int}} = 0.025$
$\omega$ scans	$\theta_{\text{max}} = 75.0^\circ$
Absorption correction: none	1 standard reflection
3354 measured reflections	frequency: 60 min
3090 independent reflections	intensity decay: 7%

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.045$   
 $wR(F^2) = 0.115$   
 $S = 0.96$   
 3090 reflections  
 210 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.056P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$

**Table 1**

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

N1—C5	1.339 (5)	C5—N6	1.296 (5)
N1—C9	1.376 (4)	N6—C7	1.341 (5)
N1—C2	1.406 (4)	C7—C8	1.403 (6)
C2—C3	1.341 (5)	C7—C71	1.502 (6)
C3—O4	1.390 (5)	C8—C9	1.348 (6)
C3—C10	1.458 (5)	C9—C91	1.478 (6)
O4—C5	1.331 (4)		
C5—N1—C9	119.9 (3)	O4—C5—N1	109.8 (3)
C5—N1—C2	108.2 (3)	C5—N6—C7	114.4 (4)
C9—N1—C2	131.8 (3)	N6—C7—C8	121.8 (4)
C3—C2—N1	105.6 (3)	N6—C7—C71	116.3 (4)
C2—C3—O4	109.5 (3)	C8—C7—C71	121.9 (4)
C2—C3—C10	132.9 (4)	C9—C8—C7	121.6 (4)
O4—C3—C10	117.6 (3)	C8—C9—N1	115.0 (4)
C5—O4—C3	106.8 (3)	C8—C9—C91	127.2 (4)
N6—C5—O4	122.9 (3)	N1—C9—C91	117.8 (4)
N6—C5—N1	127.3 (4)		

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C2—H2···O11 <sup>i</sup>	0.93	2.39	3.290 (6)	164
C11—H11···O4	0.93	2.48	2.812 (5)	101
C15—H15···O11 <sup>i</sup>	0.93	2.52	3.411 (6)	160
C91—H91A···O14	0.96	2.49	3.241 (6)	135
C91—H91C···O12 <sup>ii</sup>	0.96	2.50	3.402 (6)	156

Symmetry codes: (i)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (ii)  $-x + 2, -y, -z$ .

All H atoms were refined using a riding model, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aromatic H atoms, and C—H = 0.96 Å and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for CH<sub>3</sub> H atoms.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; 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: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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