

**(E)-5-[Hydroxyimino(phenyl)methyl]-  
1-methyl-3,4-dihydro-2H-pyrrolium  
trifluoromethanesulfonate**Jean-Marie Coustard,<sup>a\*</sup> Ronan Le Toquin,<sup>b</sup> Roland Leo,<sup>b</sup>  
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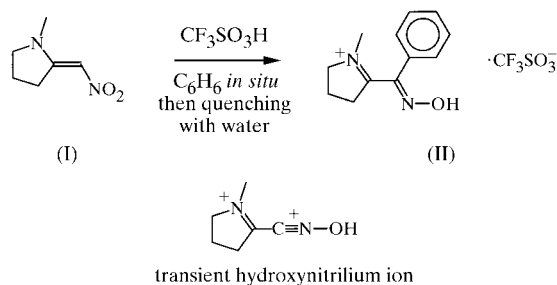
The cation of the title compound,  $C_{12}H_{15}N_2O^+ \cdot CF_3SO_3^-$ , exists as an *E*-configured hydroxyimino derivative conjugated with a nearly planar iminium system. The twist angle between the phenyl ring and the oxime group is  $72.2(2)^\circ$ . An  $O-H \cdots O$  hydrogen bond links the oxime group of the cation to the anion.

**Comment**

1-Heterosubstituted 2-nitroethylene derivatives undergo polyprotonation in trifluoromethanesulfonic acid that leads to loss of water and formation of hydroxynitrilium ions, or *O*-protonated nitrile oxides, which are fairly electrophilic (Coustard, 1995, 1996, 1999). In this medium, 1-methyl-2-nitromethylenepyrrolidine, (I), also undergoes this transformation, leading to the corresponding hydroxynitrilium ion (see Scheme below), which reacts with benzene to afford a stable dication observable either by  $^1H$  or  $^{13}C$  NMR spectroscopy. Quenching with water affords the title compound, (II), which is stable in acidic or neutral aqueous solution. In basic solution, deprotonation of the OH oxime group leads to formation of a conjugated nitroso derivative which dimerizes readily to give a mixture of isomers. In compound (II), the presence of a trifluoromethanesulfonate anion, a phenyl ring and an oxime (or hydroxyimino) group were expected from  $^1H$  and  $^{13}NMR$  data (Coustard, 1999). However, the configuration of the oxime is important from a mechanistic point of view and needed to be confirmed. The unusual behavior of this salt also prompted us to undertake the present X-ray crystallographic analysis.

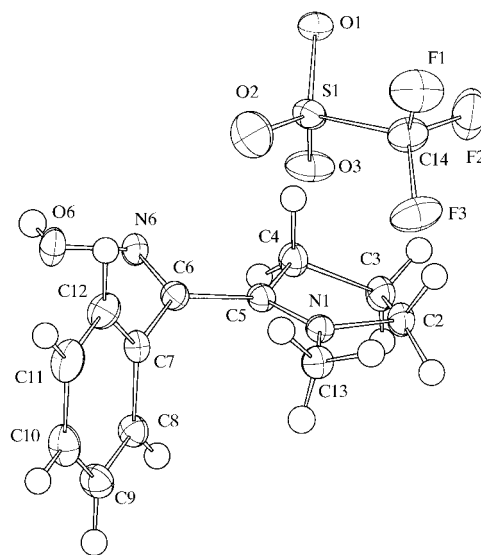
Most of the cation of (II) is nearly planar (Fig. 1), but the aromatic ring lies out of the plane, with a  $C12-C7-C6-N6$  torsion angle of  $72.2(2)^\circ$ . The maximum deviations of the atoms defining the least-squares mean plane through O6, N6, C6, C5, N1 and C13 are observed for C6 and N6, with

respective values of  $-0.116$  and  $0.098$  Å. The atoms of the C5/N1/C2/C3/C4 ring are also approximately coplanar, with maximum deviations from the least-squares mean plane of  $-0.114$  Å for C4 and  $0.135$  Å for C3.



The  $O6-N6-C6-C7$  torsion angle of  $-5.0(2)^\circ$  indicates a *E*-configured oxime group; the adjacent  $C6-C5$  bond adopts an *s-trans* conformation [ $N1-C5-C6-N6-170.2(3)^\circ$ ]. Such an oxime configuration has also been reported for products resulting from hydroxynitrilium ion trapping (Cousson & Coustard, 1998, 1999).

Conjugation of the  $N6=C6-C5=N1$  double-bond system allows delocalization of the positive charge and accounts for the lengthening of both the  $C6-C5$  single bond [ $1.469(2)$  Å, compared with the expected value for a single bond in a dienic conjugated system of  $1.455(11)$  Å; Allen *et al.*, 1987] and the  $C6=N6$  double bond [ $1.290(2)$  Å, compared with the expected value in an unconjugated oxime of  $1.280(13)$  Å; Allen *et al.*, 1987].

**Figure 1**

A view of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

The relatively short distance of  $2.651(2)$  Å between the O1 atom of the trifluoromethanesulfonate anion and the oxime O6 atom implies a hydrogen bond involving H6 [ $H6 \cdots O1$   $1.69$  Å,  $O6 \cdots O1$   $2.651(2)$  Å, and  $O6-H6 \cdots O1$   $177^\circ$ ].

The O3<sup>i</sup>··N2 and O3<sup>i</sup>··C5 distances [symmetry code: (i) 1 - x, ½ + y, ½ - z] of 2.855 (2) and 2.873 (2) Å, respectively, are shorter than expected, the sum of the relevant van der Waals sums (Bondi, 1964) being 3.07 and 3.22 Å. A search of the Cambridge Structural Database (Allen & Kennard, 1993; October 2000 Version) for the fragment F<sub>3</sub>C—SO<sub>3</sub>··N=C indicates that about half the 25 or so occurrences have generally similar distances to those above. In the present case, the short distances may result from the formation of some kind of π-adduct between the π-electrons of the C=N double bond and the O3 atom of the trifluoromethanesulfonate anion. In agreement with this hypothesis is the fact that the O3<sup>i</sup> atom is almost equidistant from N2 and C5, and the dihedral angle between the N2/O3<sup>i</sup>/C5 and N1/C2/C3/C4/C5 planes is 97.54°, indicating that they are almost perpendicular.

In conclusion, compound (II) may be considered as resulting from O-protonation of the nitroso group of α-(N-methyl-1-azacyclopent-1-en-2-yl)-α-nitrosotoluene by trifluoromethanesulfonic acid. The oxime group thus formed is E-configured, in agreement with an electrophilic aromatic substitution mechanism involving the C=N group of the transient hydroxynitrium ion (Hegarty *et al.*, 1980; Nguyen *et al.*, 1991).

## Experimental

The title compound was prepared as described by Coustard (1999).

### Crystal data

C <sub>12</sub> H <sub>15</sub> N <sub>2</sub> O <sup>+</sup> ·CF <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	<i>D</i> <sub>x</sub> = 1.511 Mg m <sup>-3</sup>
<i>M</i> <sub>r</sub> = 352.33	Mo Kα radiation
Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	Cell parameters from 11 326 reflections
<i>a</i> = 11.7643 (5) Å	<i>θ</i> = 1–28°
<i>b</i> = 8.2154 (4) Å	<i>μ</i> = 0.26 mm <sup>-1</sup>
<i>c</i> = 16.5207 (6) Å	<i>T</i> = 120 (2) K
<i>β</i> = 104.10 (2)°	Plate, colourless
<i>V</i> = 1548.6 Å <sup>3</sup>	0.25 × 0.20 × 0.10 mm
<i>Z</i> = 4	

### Data collection

Nonius KappaCCD area-detector diffractometer	<i>R</i> <sub>int</sub> = 0.036
φ rotation scans with 2° steps	<i>θ</i> <sub>max</sub> = 28°
11 326 measured reflections	<i>h</i> = -15 → 15
3595 independent reflections	<i>k</i> = -9 → 10
2749 reflections with <i>I</i> > 3σ( <i>I</i> )	<i>l</i> = -21 → 19

### Refinement

Refinement on <i>F</i>	Weighting scheme: Chebyshev polynomial with 3 parameters, 0.683, 0.650 and 0.343 (Carruthers & Watkin, 1979)
<i>R</i> = 0.044	(Δ/σ) <sub>max</sub> = 0.001
<i>wR</i> = 0.054	Δρ <sub>max</sub> = 0.67 e Å <sup>-3</sup>
<i>S</i> = 1.03	Δρ <sub>min</sub> = -0.49 e Å <sup>-3</sup>
2749 reflections	
209 parameters	
H-atom parameters constrained	

**Table 1**

Selected geometric parameters (Å, °).

O6—N6	1.3757 (18)	N1—C5	1.290 (2)
N6—C6	1.291 (2)		
O6—N6—C6	112.70 (14)	N6—C6—C5	110.41 (15)
N1—C5—C4	111.17 (15)	N6—C6—C7	124.66 (15)
N1—C5—C6	126.52 (16)	C5—C6—C7	124.65 (15)
C4—C5—C6	122.29 (15)		
N1—C5—C6—N6	170.0 (2)	C12—C7—C6—N6	72.0 (2)
O6—N6—C6—C7	-4.9 (2)		

H atoms on C atoms were placed geometrically and the oxime H atom (H6) was located in a difference Fourier synthesis. C—H distances were fixed at 1.00 Å and the O—H distance was fixed at 0.96 Å. The oxime H6 atom had *U*<sub>iso</sub>(H) = 1.55*U*<sub>eq</sub>(O6) and the H atoms of the C13 methyl group had *U*<sub>iso</sub>(H) = 1.3*U*<sub>eq</sub>(C). A common *U*<sub>iso</sub> parameter for all other H atoms converged at 0.046 (2) Å<sup>2</sup>.

Data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Nonius, 1998); cell refinement: DENZO; data reduction: DENZO; program(s) used to solve structure: SHELXS86 (Sheldrick, 1985); program(s) used to refine structure: CRYSTALS (Watkin *et al.*, 1996); molecular graphics: CAMERON (Watkin *et al.*, 1996); software used to prepare material for publication: CRYSTALS.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1441). Services for accessing these data are described at the back of the journal.

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