Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

(*E*)-3-Methoxy-3-methylsulfanylisothiochroman-4-one oxime

Jean-Marie Coustard,[a]* Ronan Le Toquin,[b] Roland Leo,[b] Werner Paulus[b] and Alain Cousson[c]

[a]Facuté des Sciences, Laboratoire de Chimie 12, UMR CNRS 6514, Avenue du Recteur Pineau, F-86022 Poitiers, France, [b]Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511 CNRS-Université de Rennes 1, Campus de Beaulieu, Avenue du Général Leclerc, F-35042 Rennes, France, and [c]Laboratoire Léon Brillouin, CEA CNRS, CEN Saclay, F-91191 Gif-sur-Yvette CEDEX, France

Correspondence e-mail: jean-marie.coustard@gmx.net

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.002 Å
R factor = 0.036
wR factor = 0.043
Data-to-parameter ratio = 15.9

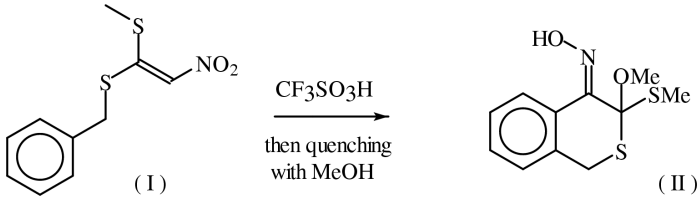
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 11 December 2000
Accepted 8 February 2001
Online 19 February 2001

The title compound, $C_{11}H_{13}NO_2S_2$, (II), is formed from methanol trapping of the cyclic cation derived from 1-methylthio-1-benzylthio-2-nitroethylene (I), in triflic acid. Compound (II) is characterized by its *E*-configured oxime and the boat conformation of its non-aromatic ring.

Comment

In trifluoromethanesulfonic acid, 1,1-bis(methylthio)-2-nitroethene undergoes polyprotonation that leads to loss of water and formation of the hydroxynitrilium ion (O-protonated nitrile oxide). This cation is an electrophile that is able to react with a tethered aromatic ring, either intermolecularly or intramolecularly (Coustard, 1995). In this way, when a solution of 1-methylthio-1-benzylthio-2-nitroethylene, (I), in trifluoromethanesulfonic acid was quenched with methanol, the title compound, (II), was obtained in a good yield (Coustard, 2001). A view of this molecule is presented in Fig. 1.



(I) (II)

The non-aromatic ring adopts a slighly distorted boat conformation with torsion angles C9—C8—S1—C7 and C9—C1—C6—C7 of −3.4 (2) and 2.7 (4)°, respectively. The C8 atom of the ortholactone function is bonded to an axial MeS group [C11—S2—C8—S1 −173.65 (8)° and N1—C9—C8—S2 −114.67 (13)°] and to an equatorial MeO group [O2—C8—C9—C1 −171.08 (12)°].

The C9, N1, and O1 atoms of the oxime function and the aromatic ring are not coplanar, as seen in the torsion angle C2—C1—C9—N1 of 57.3 (4)°. The oxime function is *E* configured [C1—C9—N1—O1 0.1 (3)°] with an unusually short C9—N1 bond of 1.2559 (9) Å as compared with the mean value of 1.280 (13) Å for $Csp^3{=}N{-}OH$ (Allen *et al.*, 1987). The observed oxime configuration (Hegarty, 1980) is in agreement with the postulated mechanism of formation which implied electrophilic addition of the transient hydroxynitrilium ion on the phenyl ring.

Experimental

The title compound was prepared by cyclization of 1-ethylthio-1-benzylthio-2-nitroethylene, (I), in trifluoromethanesulfonic acid and quenching with methanol (Coustard, 2001). Crystallization from ethyl acetate afforded colourless crystals suitable for X-ray analysis.

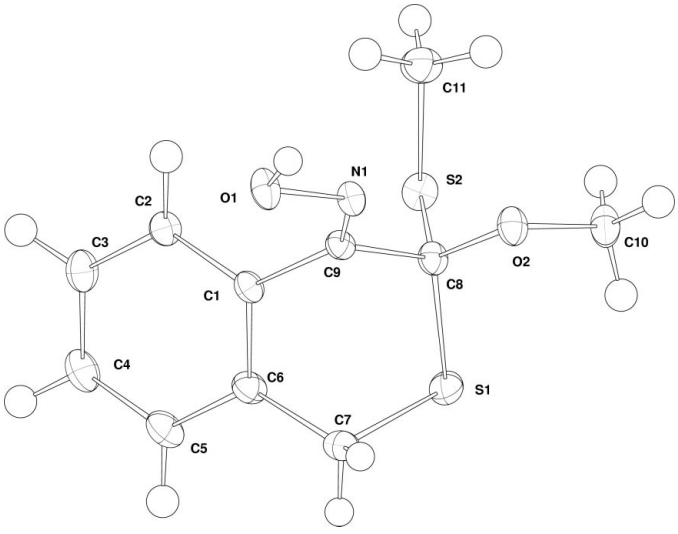


Figure 1
A view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Crystal data

$C_{11}H_{13}NO_2S_2$
M_r = 255.35
Orthorhombic, *Pbca*
a = 9.3725 (2) Å
b = 10.7012 (2) Å
c = 23.0919 (4) Å
V = 2316.0 Å^3
Z = 8
D_x = 1.46 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16060 reflections
θ = 1–28°
μ = 0.44 mm^{-1}
T = 120 K
Plate, colourless
0.30 × 0.20 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
φ rotation scans with 2° step
16 060 measured reflections
2823 independent reflections
2317 reflections with $I > 3\sigma(I)$
R_{int} = 0.044
θ_{max} = 28.0°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 30$
Intensity decay: none

Refinement

Refinement on F
R = 0.036
wR = 0.043
S = 1.055
2317 reflections
146 parameters
Only H-atom U's refined
Weighting: Chebychev polynomial with 3 parameters (Carruthers & Watkin, 1979): 0.668, 0.599, 0.382
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.86 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

H atoms bonded to C atoms were placed geometrically and their positional parameters were not refined. O-bonded H atoms were located from a difference map but their positional parameters were not refined. Displacement parameters were refined for all H atoms.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1998); cell refinement: *DENZO*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *CRYSTALS* (Watkin, Prout, Carruthers & Betteridge, 1996); molecular graphics: *CAMERON* (Watkin, Prout & Pearce, 1996); software used to prepare material for publication: *CRYSTALS*.

Thanks are extended to CNRS for financial support

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.
Carruthers, J. R. & Watkin, D. J. (1979). *Acta Cryst*, A**35**, 698–699.
Coustard, J.-M. (1995). *Tetrahedron*, **51**, 10929–10940.
Coustard, J.-M. (2001). *Eur. J. Org. Chem.* In the press.
Hegarty, A. F. (1980). *Acc. Chem. Res.* **13**, 448–454.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1985). *SHELXS*86. University of Göttingen, Germany.
Watkin, D. J., Prout, C. K., Carruthers, R. J. & Betteridge, P. (1996). *CRYSTALS*. Issue 10. Chemical Crystallography Laboratory, University of Oxford, England.
Watkin, D. J., Prout, C. K. & Pearce, L. J. (1996). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.