5-Bromo-2,3-dihydro-4-methyl-3-nitrothiophene 1,1-dioxide

Laura H. Strauss,[a]* Victoria V. Abzianidze,[b] Valentina M. Berestovitskaya[b] and Irina E. Efremova[b]

[a]Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423, USA, and [b]Department of Organic Chemistry, Herzen State Pedagogical University of Russia, St Petersburg, 191186, Russia

Correspondence e-mail: laura.strauss@uni.edu

The title compound, $C_5H_6BrNO_4S$, crystallizes in the centrosymmetric space group $P2_1/c$. Three weak $C—H\cdots O$ hydrogen bonds dominate the packing of the molecules in the solid. These weak hydrogen bonds and a short intermolecular $O\cdots Br$ contact of 3.003 (2) Å are discussed using a Mulliken population analysis.

Comment

Thiolene 1,1-dioxides are an easily accessible class of heterocyclic compounds and among their derivatives are compounds with useful properties. Nitro-containing thiolene 1,1-dioxides have proved to be useful models for studying theoretical problems such as allyl–vinyl isomerization and oxime–nitronic tautomerism (Perekalin *et al.*, 1994). The introduction of a halogen atom into the ring of nitrothiolene 1,1-dioxide leads to the appearance of specific properties. Bromo derivatives of 3-methyl-4-nitro-thiolene 1,1-dioxide have been shown to undergo halo- and prototropic rearrangements under mild conditions (Efremova *et al.*, 2002). The title compound, 2-bromo-3-methyl-4-nitro-2-thiolene 1,1-dioxide, (I), is the major product formed during these transformations.

(I)
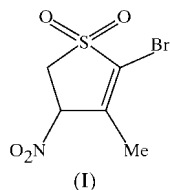
One molecule of (I) is contained in the asymmetric unit, with all atomic positions located on general positions. The structure of (I) is very similar to that of the structural isomer 4-bromo-3-methyl-4-nitro-2-thiolene 1,1-dioxide, (II) (Efremova *et al.*, 2003). The bond lengths and angles for both isomers are comparable; data for (I) are given in Table 1. The five-membered heterocyclic ring in both compounds has an envelope conformation, with atoms S1, C2, C3 and C4 in the

same plane, as expected, due to the sp^2 hybridization of atoms C2 and C3. Atom C5 is out of this plane by 0.218 (6) Å in (I), pointing away from the nitro group on C4 towards the less sterically hindered side of the molecule (Fig. 1). In the isomer, (II), with both the bromine and the nitro group on C4, atom C5 points above the plane towards the nitro group.

The packing of the molecules in (I) is mainly dependent on three weak hydrogen bonds, $C5—H5A\cdots O2$, $C4—H4\cdots O2$ and $C4—H4\cdots O4$ (Table 2), consistent with previous observations (Desiraju & Steiner, 1999). These hydrogen bonds are the result of the electron-withdrawing nature of the sulfonyl and nitro groups. The Mulliken population analysis (Mulliken, 1955) for a molecule of (I) from Hartree–Fock calculations using a 3-21G(*) basis set (*PC Spartan Pro*; Wavefunction, 2000) confirmed that the O atoms of these two groups carry significant negative atomic charges; the average atomic charge on the O atoms in the sulfonyl group is −0.56 (1) e, and that on the O atoms in the nitro group is −0.374 (4) e. Atoms H4 and H5A are in close proximity to the –SO_2 and –NO_2 groups, which makes them the most positively charged H atoms in the compound. The Mulliken population analysis verified this,
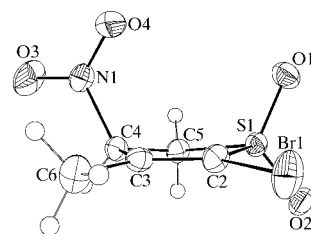

Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
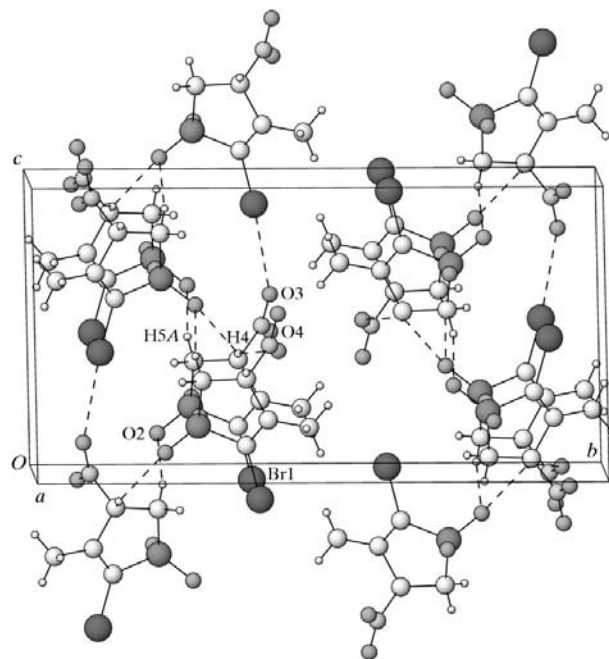

Figure 2
The cell of (I) viewed along *a* (*c* vertical). The dashed lines indicate the short contacts between molecules of (I).

DOI: 10.1107/S0108270103000842
© 2003 International Union of Crystallography

organic compounds

with atomic charges of 0.321 (3) and 0.325 (2) e for atoms H4 and H5*A*, respectively. For comparison, the H atoms in the C6 methyl group have an average atomic charge of 0.255 (11) e, and atom H5*B* has an atomic charge of 0.304 (2) e.

These hydrogen-bonding interactions result in a layered network of molecules of (I) perpendicular to the *b* axis (Fig. 2). Within these sheets, there is also a short intermolecular interaction of 3.002 (3) Å between atom Br1 and atom O3 of the nitro group. The Mulliken population analysis showed that the Br atom has a very small positive atomic charge [0.080 (1) e], consistent with an unexpected weak attractive interaction with O3 located at $(-1 + x, y, -1 + z)$.

Experimental

Bromine (0.83 g, 0.26 ml, 5 mmol) was added dropwise into a stirred suspension of sodium 1,1-dioxo-3-methyl-2-thiolenyl-4-nitronate (0.5 g, 2.5 mmol) in dry ether (15 ml) at room temperature. The sodium salt dissolved and colourless crystals were formed. After 1.5 h, crystals of NaBr were filtered off and the mother liquor was concentrated by evaporation in a Petri dish. A colorless oil (0.63 g) was formed, which was crystallized from methanol to give a colorless deposit, and this was washed with methanol and dried. This preparation produced both the title compound, 2-bromo-3-methyl-4-nitro-2-thiolene 1,1-dioxide, (I), and 2,4-dibromo-3-methyl-4-nitro-2-thiolene 1,1-dioxide. Fractional recrystallization from chloroform yielded 0.25 g (39%) of (I) (m.p. 433–434 K) and 0.24 g (29%) of 2,4-dibromo-3-methyl-4-nitro-2-thiolene 1,1-dioxide (m.p. 372–373 K). Elemental analysis of (I), found: C 23.49 and 23.44, H 2.53 and 2.51, N 5.49 and 5.51%; calculated for $C_5H_6BrNO_4S$: C 23.40, H 2.34, N 5.47%.

Crystal data

$C_5H_6BrNO_4S$	$D_x = 2.00$ Mg m^{-3}
$M_r = 256.08$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3563
$a = 5.0733$ (10) Å	reflections
$b = 18.465$ (4) Å	$\theta = 1.0-27.5°$
$c = 10.029$ (2) Å	$\mu = 5.05$ mm^{-1}
$\beta = 115.12$ (3)°	$T = 185$ (2) K
$V = 850.6$ (3) Å^3	Rod, colorless
$Z = 4$	$0.31 \times 0.24 \times 0.11$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	1933 independent reflections
	1603 reflections with $I > 2\sigma(I)$
φ and ω scans to fill Ewald sphere	$R_{int} = 0.040$
Absorption correction: multi-scan (*HKL*2002; Otwinowski & Minor, 1997)	$\theta_{max} = 27.4°$
	$h = -6 \rightarrow 6$
	$k = -23 \rightarrow 23$
$T_{min} = 0.287$, $T_{max} = 0.574$	$l = -12 \rightarrow 12$
7018 measured reflections	

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.754 (3)	C5—S1	1.784 (3)
C2—C3	1.332 (4)	C6—C3	1.487 (4)
C3—C4	1.520 (4)	C2—Br1	1.868 (3)
C4—C5	1.524 (4)	N1—C4	1.522 (3)
S1—C2—C3	114.65 (19)	C2—C3—C4	112.8 (2)
S1—C2—Br1	117.29 (14)	C2—C3—C6	127.7 (2)
Br1—C2—C3—C6	−0.1 (4)	S1—C2—C3—C4	0.4 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C5—H5*A*$\cdots$O2^i	0.97	2.34	3.286 (3)	163
C4—H4$\cdots$O2^{ii}	0.98	2.50	3.238 (3)	132
C4—H4$\cdots$O4^{iii}	0.98	2.52	3.388 (3)	147

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0290P)^2 + 0.7325P]$
$R(F) = 0.031$	
$wR(F^2) = 0.073$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1933 reflections	$\Delta\rho_{max} = 0.34$ e Å^{-3}
111 parameters	$\Delta\rho_{min} = -0.53$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97 (Sheldrick, 1997)
	Extinction coefficient: 0.0029 (9)

H atoms were treated as riding, with C—H distances in the range 0.96–0.98 Å.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Dowty, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Desiraju, G. R. & Steiner, T. (1999). Editors. *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press Inc.

Dowty, E. (1997). *ATOMS for Windows*. Version 4.0. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Efremova, I. E., Abzianidze, V. V. & Berestovitskaya, V. M. (2002). *J. Chem. Heterocycl. Compd*, **8**, 1153–1155. (In Russian.)

Efremova, I. E., Abzianidze, V. V., Swenson, D., Bartak, D. & Berestovitskaya, V. M. (2003). *J. Gen. Chem.* (*Russia*), **73**, 685–690.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Mulliken, R. S. (1955). *J. Chem. Phys.* **23**, 1833–1840, 1841–1854, 2338–2342, 2343–2346.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Perekalin, V. V., Lipina, E. S., Berestovitskaya, V. M. & Efremov, D. A. (1994). *Nitroalkenes (Conjugated Nitro Compounds)*, edited by V. M. Berestovitskaya, p. 256. New York: John Wiley & Sons.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Wavefunction (2000). *PC Spartan Pro*. Version 1.0.5. Wavefunction Inc., Irvine, California, USA.