C4—C3—C7	109.8 (4)	N11—C15—C16	107.4 (5)
N1—C4—N2	107.4 (5)	N12—C16—C15	107.6 (6)
N1—C4—C3	124.9 (5)	N13—C17—N14	112.0 (5)
N2—C4—C3	127.7 (5)	N13—C17—C13	126.0 (5)
N1—C5—C6	107.5 (6)	N14—C17—C13	121.9 (5)
N2—C6—C5	107.1 (6)	N13—C18—C19	110.8 (6)
N3—C7—N4	111.6 (5)	N14—C19—C18	105.8 (5)

Table 3. *Dihedral angles (°) in the HBIP zwitterions in HBIP-2 and HBIP-1*

The planes of the imidazole rings are denoted (1) and (3) whether they contain atoms N1 (or N11) or N3 (or N13); the planes of the carboxylate groups are denoted (2).

Dihedral angle	HBIP-2 Molecule (I)	HBIP-2 Molecule (II)	HBIP-1
(1)–(2)	79.2 (3)	166.3 (3)	102.8
(1)–(3)	108.3 (3)	76.0 (3)	66.7
(2)–(3)	37.3 (3)	88.2 (3)	10.5

Table 4. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
N1—H1···O3	1.654 (7)	2.691 (7)	168.3 (6)
O3—H31···O2^{i}	1.96 (5)	2.822 (6)	162 (4)
O3—H32···O12^{ii}	1.82 (5)	2.664 (6)	160 (5)
N2—H2···N3^{iii}	1.825 (5)	2.796 (6)	152.2 (5)
N4—H4···O12^{ii}	1.892 (6)	2.887 (6)	156.8 (5)
N11—H11···O11^{ii}	1.591 (6)	2.613 (6)	163.4 (6)
N12—H12···O1^{iv}	1.584 (6)	2.608 (6)	163.5 (6)
N14—H14···O2^{iv}	1.819 (6)	2.814 (6)	156.8 (6)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$; (iii) $1 - x, -y, 1 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

As a result of the small number of observed reflections available, only N and O atoms were refined anisotropically; C atoms were assigned isotropic displacement parameters. All H atoms were clearly located on difference Fourier maps and were assigned an arbitrary isotropic displacement parameter, $U = 0.07$ Å^2; the positions of the H atoms of the water molecule were refined using constrained geometry (O—H = 0.9 Å, H—O—H = 100°); the contributions of the other H atoms were computed assuming idealized geometry (C—H, N—H = 1.05 Å).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1988). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CRYSTALS*. Software used to prepare material for publication: *CRYSTALS*.

Financial support from DGICYT(PB93-0688) is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1214). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Creighton, T. E. (1984). In *Proteins, Structures and Molecular Properties*. New York: W. H. Freeman.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Gimeno, B., Soto, L., Sancho, A., Dahan, F. & Legros, J.-P. (1992). *Acta Cryst.* C**48**, 1671–1673.

Joseph, M., Leigh, T. & Swain, M. L. (1977). *Synthesis*, pp. 459–461.

Martinez, M. A., Legros, J.-P., Soto, L. & Sancho, A. (1991). *Polyhedron*, **10**, 1031–1036.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* S1–S19.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Watkin, J. D., Carruthers, J. R. & Betteridge, P. W. (1988). *CRYSTALS User's Guide*. University of Oxford, England.

Acta Cryst. (1996). C**52**, 1228–1230

4-Methoxyphenyl 2-Nitrophenyl Sulfide

R. A. Howie and J. L. Wardell

Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland

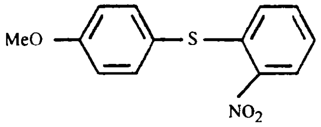
(*Received 24 February 1995; accepted 17 November 1995*)

Abstract

An intramolecular S···O interaction is present in the title compound, $(2\text{-}O_2NC_6H_4)S(C_6H_4OMe\text{-}4)$, with S···O = 2.641 (2) Å and C—S···O = 177.69 (8)°.

Comment

The literature contains various examples of compounds having non-bonded S···O contacts shorter than the sum of the van der Waals radii (3.25 Å) (Kucsman & Kapovits, 1985). A typical group of such compounds is those containing the 2-nitroarylthio unit, $2\text{-}O_2N\text{-}R\text{-}C_6H_3S$, as illustrated by the title compound, (I). The intramolecular S···O1 distance in (I) is 2.641 (2) Å, with a C7—S···O1 angle of 177.69 (8)°; the value of C1—S···O1 is 75.16 (8)°. The nitro group is almost coplanar with the benzene ring (C1–C6) to which it is attached, the angle between the planes of the nitro and aryl units being 5.5 (5)°. In effect, the nitro group is rotated about the N—C2 bond such that O1 and O2 lie on either side of the C1–C6 plane, at a distance of *ca* 0.1 Å in each case. There are no intermolecular contacts involving the S atom, other than the S···O separations, which are at distances less than the sum of the appropriate van der Waals radii.



(I)

The intramolecular S···O separations in solid 2-nitroaryl sulfides are generally between 2.62 and 2.72 Å (Kucsman & Kapovits, 1985). A shorter separation of 2.590 Å was reported for the polycyclic derivative 9-

nitro-1-azaphenoxathiin (in which the ring system may force together the S and O atoms) (Hossain *et al.*, 1982); a longer distance [2.781 (6) Å] was determined for $Ph_3SiCH(SC_6H_3Me\text{-}4\text{-}NO_2\text{-}2)CH_2Cl$ (Howie, Spencer, Wardell & Low, 1992). In the latter case, the steric bulk of the Ph_3Si substituent is considered to prevent a closer contact.

The aromatic rings defined by C1–C6 and C7–C12 in (I) are almost completely planar, with $\Sigma\Delta^2 = 4.6$ and 1.6×10^{-5} Å^2, respectively; the angle between these planes is 88.7 (5)°.

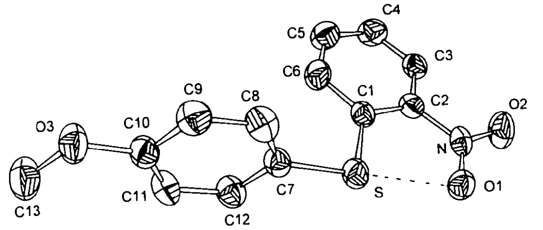


Fig. 1. The molecule of (I) showing the atom-numbering scheme. Displacement ellipsoids are shown at the 40% probability level and H atoms have been omitted for clarity.

Experimental

The title compound was obtained from $Bu_3SnC_6H_4OMe\text{-}4$ and $2\text{-}O_2NC_6H_4SCl$, according to a published procedure, and was recrystallized from EtOH; m.p. 382 K (Wardell & Clarke, 1971).

Crystal data

$C_{13}H_{11}NO_3S$
$M_r = 261.30$
Triclinic
$P\bar{1}$
$a = 9.160 (6)$ Å
$b = 7.819 (5)$ Å
$c = 9.570 (4)$ Å
$\alpha = 80.49 (5)°$
$\beta = 113.72 (4)°$
$\gamma = 98.97 (5)°$
$V = 615.9 (6)$ Å^3
$Z = 2$
$D_x = 1.409$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 10.5–12.0°$
$\mu = 0.25$ mm^{-1}
$T = 298$ K
Needle
0.7 × 0.3 × 0.14 mm
Yellow

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction: none
2175 measured reflections
2045 independent reflections
1674 observed reflections [$I > 3\sigma(I)$]
$R_{int} = 0.005$

$\theta_{max} = 25°$
$h = 0 \rightarrow 10$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$
2 standard reflections monitored every 50 reflections
intensity decay: 2.2 and 2.1%

Refinement

Refinement on *F*
$R = 0.032$
$wR = 0.037$
$S = 1.24$
1674 reflections
168 parameters
H atoms: see below
$w = 1/[\sigma^2(F) + 0.00046F^2]$

$(\Delta/\sigma)_{max} = 0.08$
$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = -0.15$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
S	0.6921 (1)	0.3357 (1)	0.0080 (1)	0.050 (1)
N	0.9350 (2)	0.6647 (2)	0.1069 (2)	0.048 (1)
O1	0.9094 (2)	0.5453 (2)	0.1965 (2)	0.060 (1)
O2	1.0224 (2)	0.7971 (2)	0.1497 (2)	0.074 (1)
O3	0.1912 (2)	−0.1315 (2)	−0.4048 (2)	0.066 (1)
C1	0.7456 (2)	0.5073 (2)	−0.1134 (2)	0.042 (1)
C2	0.8572 (2)	0.6497 (2)	−0.0575 (2)	0.042 (1)
C3	0.9010 (3)	0.7818 (3)	−0.1533 (3)	0.052 (1)
C4	0.8346 (3)	0.7774 (3)	0.3088 (3)	0.061 (1)
C5	0.7231 (3)	0.6400 (3)	−0.3682 (3)	0.061 (1)
C6	0.6792 (2)	0.5082 (3)	0.2737 (2)	0.051 (1)
C7	0.5453 (2)	0.2010 (3)	−0.1254 (2)	0.046 (1)
C8	0.3843 (3)	0.2239 (3)	−0.1768 (3)	0.052 (1)
C9	0.2693 (3)	0.1108 (3)	−0.2702 (3)	0.055 (1)
C10	0.3146 (3)	−0.0275 (3)	−0.3130 (2)	0.050 (1)
C11	0.4743 (3)	−0.0509 (3)	−0.2631 (3)	0.057 (1)
C12	0.5892 (3)	0.0637 (3)	−0.1687 (3)	0.055 (1)
C13	0.2296 (4)	−0.2775 (3)	−0.4501 (3)	0.084 (1)

Table 2. *Selected geometric parameters (Å, °)*

C1—S	1.769 (2)	C7—S	1.780 (2)
O1—N	1.221 (2)	O2—N	1.224 (2)
C2—N	1.460 (3)	C10—O3	1.364 (2)
C13—O3	1.424 (3)	O1···S	2.641 (2)
C7—S—C1	102.6 (1)	O2—N—O1	122.5 (2)
C2—N—O1	118.7 (2)	C2—N—O2	118.8 (2)
C6—C1—S	121.5 (1)	C2—C1—S	122.9 (1)
C3—C2—N	116.4 (2)	C1—C2—N	121.1 (2)
C12—C7—S	120.3 (2)	C8—C7—S	120.2 (2)
C9—C10—O3	115.1 (2)	C11—C10—O3	124.9 (2)
C7—S···O1	177.69 (8)	C1—S···O1	75.16 (8)

Data collection used ω-scan rates of 1.0 ($I_p < 150$) to 29.3° min^{-1} ($I_p > 2500$), where I_p is the pre-scan intensity. The scan width was 0.6° in ω. Refinement was by full-matrix least-squares techniques. All non-H atoms were refined anisotropically. H atoms were placed in calculated positions with C—H = 0.98 Å and refined riding upon the C atom to which they are attached, with separate group U_{iso} values for methyl and aryl H atoms. The methyl group was refined as a rigid body. All computations were performed on the Sun SPARC-server (UNIX operating system) of the Computing Centre of the University of Aberdeen.

Data collection and cell refinement: Nicolet P3 diffractometer software (Nicolet XRD Corporation, 1980). Data reduction: *RDNIC* (Howie, 1980). Structure solution and refinement software: *SHELXS*86 (Sheldrick, 1985) and *SHELX*76 (Sheldrick 1976). Molecular graphics: *ORTEX* (McArdle, 1994). Software used to prepare data for publication: *XPUB* (Low, 1980).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1031). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Hossain, M. B., Dwiggins, C. A., van der Helm, D., Sen Gupta, P. K., Turley, J. C. & Martin, G. E. (1982). *Acta Cryst.* B**38**, 881–888.

Howie, R. A. (1980). *RDNIC. Data Reduction Program for Nicolet P3 Diffractometer.* University of Aberdeen, Scotland.

Howie, R. A., Spencer, G. M., Wardell, J. L. & Low, J. N. (1992). *J. Organomet. Chem.* **437**, 111–125.

Kucsman, A. & Kapovits, I. (1985). *Nonbonded Sulfur-Oxygen Interaction in Organic Sulfur Compounds. Organic Sulfur Chemistry: Theoretical and Experimental Advances*, edited by F. Bernardi, I. G. Csizmadia & A. Mangini, pp. 191–245, and references therein. Amsterdam: Elsevier.

Low, J. N. (1980). *XPUB. Program for the Preparation of Tabular Crystallographic Data.* University of Dundee, Scotland.

McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.

Nicolet XRD Corporation (1980). *Nicolet P3/R3 Data Collection Operators Manual.* Nicolet XRD Corporation, 10061 Bubb Road, Cupertino, California 95014, USA.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Wardell, J. L. & Clarke, P. L. (1971). *J. Organomet. Chem.* **26**, 345–352.

Acta Cryst. (1996). C**52**, 1230–1232

3-Mésityl-6-méthyl-7-méthylthio-4-phényl-6*H*-isoxazolo[5,4-*e*][1,2,4]triazépine

PAUL TOLEDANO,[a] MOULAY Y. AIT ITTO[b] ET AÏSSA HASNAOUI[b]

[a]*Laboratoire de Chimie de la Matière Condensée, Université Pierre et Marie Curie, 4 Place Jussieu, Tour 54, 75252 Paris CEDEX 05, France, et* [b]*Laboratoire des Substances Naturelles et des Hétérocycles, Faculté des Sciences Semlalia, Département de Chimie, B.P. S15 Marrakech, Maroc*

(*Reçu le 26 juin 1995, accepté le 12 septembre 1995*)

Abstract

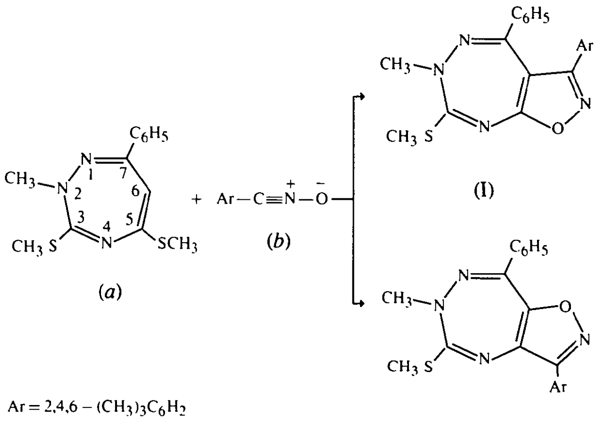
The condensation reaction of mesitonitrile oxide with 2-methyl-3,5-bis(methylthio)-7-phenyl-1,2,4-triazepine is *peri* and regioselective. The 1,3-dipolar cycloaddition occurs in a unique way on the C═C double bond of the 1,2,4-triazepine and leads to the title compound, $C_{22}H_{22}N_4OS$. The isoxazole ring is planar while the triazepine ring adopts a boat conformation.

Commentaire

Récemment, des travaux entrepris dans notre laboratoire ont pu montrer la régio et la périsélectivité de cycloaddition (4+2) π électron et dipolaire-1,3 sur des 1,2,4-triazépines et 1,4-diazépines (Hasnaoui, Lavergne & El Messaoudi, 1985; El Mouhtadi, Hasnaoui, Goupil, El Messaoudi & Lavergne, 1988; Hasnaoui, Baouid & Lavergne, 1991; El Messaoudi, Hasnaoui, El Mouhtadi & Lavergne, 1992; Baouid, Benharref, Hasnaoui & Lavergne, 1994). Afin de développer ce travail de recherche qui vise la préparation de systèmes bihétérocycliques susceptibles de présenter des activités biologiques, nous avons réalisé la condensation de la 2-méthyl-3,5-diméthylthio-7-phényl-1,2,4-triazépine avec l'oxyde de mésitonitrile.

Les oxydes de nitriles sont des dipôles-1,3 très réactifs vis à vis des doubles liaisons. Ils sont, par ce fait, de bons précurseurs des isoxazolines, produits réputés pour leur activité pharmaceutique (Nordmann, Graff, Maurer & Gähwiler, 1985; Taylor & Ray, 1991; Scobie & Threadgill, 1992).

L'analyse des données spectrales montre que l'attaque du dipôle (*b*) se fait sur la double liaison C═C de la triazépine (*a*). Toutefois, selon le sens de cette attaque, deux régioisomères (I) et (II) peuvent être obtenus.



Ar = 2,4,6 – $(CH_3)_3C_6H_2$

(II)

L'analyse cristallographique permet d'attribuer au composé formé la structure (I). Elle montre que l'oxygène du dipôle (*b*) est lié au carbone C5 de la triazépine (*a*). Ce résultat corrobore les travaux de Martin & Dupré (1983) et prouve que la réaction de cycloaddition de l'oxyde de mésitonitrile avec la triazépine (*a*) est totalement régiosélective.

La maille comporte deux unités asymétriques formées chacune d'une molécule (I).

Le cycle triazépine adopte une configuration en bateau. N2, N1, C4 et C3 sont situés dans un même plan *P*1 (déviation maximum 0,04 Å). N2, C1, N3 et C2 forment un autre plan *P*2 (déviation maximum 0,01 Å). La distance de C3 à *P*2 est de 0,55 Å. Les angles dièdres entre *P*1, *P*2 et le plan intermédiare *P*3 des atomes N2, C2 et C3 sont de 140,8 et 155,1°. Le cycle isoxazole, pentagonal, C2, O, N4, C7, C3 forme un plan *P*4 (déviation maximum 0,01 Å). L'angle dièdre entre *P*1 et *P*4 est de 139,2°, entre *P*2 et *P*4, il est de 34,4°, entre *P*3 et *P*4, il est de 148,7°. L'angle entre le plan

Acta Crystallographica Section C
ISSN 0108-2701 ©1996