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Acta Cryst. (1991). **C47**, 1515–1517

Structure of *N*-Methanesulfonyl-*N*-phenylhydroxylamine from Fenton's Reagent on Nitrosobenzene in DMSO

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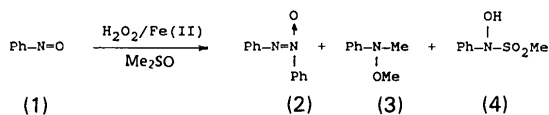
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(Received 13 March 1990; accepted 10 December 1990)

Abstract. $C_7H_9NO_3S$, $M_r = 187.2$, monoclinic, $P2_1/c$, $a = 9.047$ (3), $b = 8.774$ (3), $c = 10.943$ (3) Å, $\beta = 97.4$ (1)°, $V = 861.4$ (5) Å³, $Z = 4$, $D_x = 1.44$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 30.5$ cm⁻¹, $F(000) = 392$, $T = 293$ K, final $R = 0.058$ for 1421 symmetry-independent observed reflections. The SO₂ group in the methanesulfonylhydroxylamine moiety adopts an orientation such that the N lone-pair bisects the O—S—O angle. Significant deviation from coplanarity is observed in the benzene ring.

Introduction. In our investigation of the reactivity of nitrosobenzenes with Fenton's reagent in dimethylsulfoxide (Me₂SO), we have isolated compounds (2), (3) and (4) (Cardellini, Greci, Stipa, Rizzoli, Sgarabotto & Ugozzoli, 1990).



The expected product from this reaction was (3), which was identified by elemental analysis and from spectroscopic data. Azoxybenzene (2) was most likely formed from nitrosobenzene (1) and phenylhydroxylamine which originated from (1) after re-

duction with methanesulfinic acid (Rudqvist & Torsell, 1971). (2) was identified by a comparison with an authentic sample (Vogel, 1984).

Though it has already been reported in the literature that methanesulfonic acid reacts with nitroso compounds leading to sulfonylated hydroxylamines of type (4) (Wayer, Geluk, Enbrts & Boer, 1970; Balyaev, Gornostaev & Suboch, 1975), it was difficult to foresee in the reaction of (1) with Fenton's reagent the formation of the *N*-methanesulfonyl-*N*-phenylhydroxylamine; in the present work the X-ray structural analysis of this product is reported.

Experimental. Dark, almost black prismatic crystals obtained by slow crystallization from benzene/ligroin. Siemens AED diffractometer on line to an IBM PS/2 M30 computer, Ni-filtered Cu $K\alpha$ radiation, θ - 2θ scan, scan width from $(\theta-0.60)^\circ$ to $[\theta + 0.60 + (\Delta\lambda/\lambda)\tan\theta]^\circ$; scan speed $3.0^\circ \text{ min}^{-1}$. Crystal dimensions $0.67 \times 0.33 \times 0.71$ mm. Cell dimensions based on 30 $(\theta, \chi, \varphi)_{hkl}$ ($20 \leq \theta \leq 30^\circ$) measured intensities; 1640 ($-13 \leq h \leq 13$, $0 \leq k \leq 10$, $0 \leq l \leq 11$) symmetry-independent reflections ($3 \leq \theta \leq 70^\circ$) collected at $T = 293$ K with a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) procedure. One standard reflection every 50, no significant variation. Corrections for Lorentz and polarization effects, but not for absorption. Structure solved by direct methods

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Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^4 \text{ \AA}^2$) for non-H atoms with e.s.d.'s in parentheses

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	U_{eq}
S(4)	3956 (1)	2150 (1)	9552 (1)	452 (3)
O(4)	3706 (2)	4787 (2)	8684 (2)	600 (7)
O(41)	3131 (2)	1064 (2)	10154 (2)	602 (7)
O(42)	5393 (2)	2595 (3)	10141 (2)	676 (8)
N(4)	2931 (2)	3765 (2)	9394 (2)	457 (6)
C(1)	-1593 (4)	3364 (4)	7987 (5)	825 (16)
C(2)	-624 (4)	4038 (5)	7272 (4)	773 (13)
C(3)	873 (4)	4150 (4)	7702 (3)	602 (9)
C(4)	1385 (3)	3618 (3)	8882 (2)	443 (7)
C(5)	404 (4)	3023 (4)	9635 (4)	634 (10)
C(6)	-1096 (4)	2882 (4)	9163 (6)	820 (17)
C(41)	4142 (4)	1533 (4)	8065 (3)	608 (11)

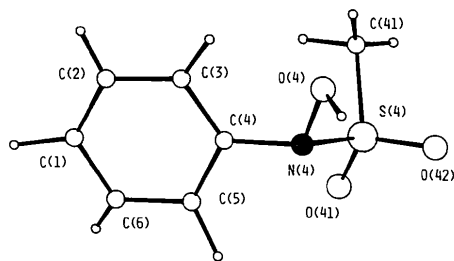


Fig. 1. Perspective view of the molecule.

(SHELXS86; Sheldrick, 1986). 1421 symmetry-independent observed reflections [$I > 2\sigma(I)$], 145 parameters in full-matrix least-squares refinement; all H atoms located in the difference-Fourier map refined isotropically. $\sum w(F_o - F_c)^2$ minimized with $w = [\sigma^2(F_o) + 0.0052F_o^2]^{-1}$. SHELX76 system (Sheldrick, 1976), final $R = 0.058$, $wR = 0.068$; maximum shift of parameters 0.8σ , $\Delta\rho_{max} 0.61$, $\Delta\rho_{min} -0.49 \text{ e \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

All calculations were carried out on the GOULD 6040 POWERNODE computer of the Centro di Studio per la Strutturistica Diffattometrica del CNR of Parma. Bibliographic searches were carried out using the Cambridge Structural Database Files through the Servizio Italiano di Diffusione Dati Cristallografici, Parma.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are given in Table 1.* The arbitrary numbering scheme used in the crystal analysis is shown in Fig. 1, which represents a perspective view of the molecule.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53811 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (\AA), angles ($^\circ$) and selected torsion angles ($^\circ$) with e.s.d.'s in parentheses

S(4)—O(41)	1.423 (2)	C(1)—C(2)	1.381 (6)
S(4)—O(42)	1.429 (2)	C(1)—C(6)	1.374 (8)
S(4)—N(4)	1.690 (2)	C(2)—C(3)	1.379 (5)
S(4)—C(41)	1.744 (4)	C(3)—C(4)	1.395 (4)
O(4)—N(4)	1.428 (3)	C(4)—C(5)	1.388 (5)
N(4)—C(4)	1.444 (3)	C(5)—C(6)	1.394 (5)
O(41)—S(4)—O(42)	118.4 (2)	C(2)—C(1)—C(6)	120.5 (4)
O(41)—S(4)—N(4)	107.2 (2)	C(1)—C(2)—C(3)	120.3 (4)
O(41)—S(4)—C(41)	110.1 (2)	C(2)—C(3)—C(4)	119.1 (3)
O(42)—S(4)—N(4)	105.8 (2)	N(4)—C(4)—C(3)	121.3 (3)
O(42)—S(4)—C(41)	108.3 (2)	N(4)—C(4)—C(5)	117.7 (3)
N(4)—S(4)—C(41)	106.4 (2)	C(3)—C(4)—C(5)	120.9 (3)
S(4)—N(4)—O(4)	106.3 (2)	C(4)—C(5)—C(6)	118.7 (4)
S(4)—N(4)—C(4)	117.1 (2)	C(1)—C(6)—C(5)	120.4 (5)
O(4)—N(4)—C(4)	111.3 (2)		
O(41)—S(4)—N(4)—O(4)	-174.5 (2)	C(41)—S(4)—N(4)—C(4)	68.5 (2)
O(41)—S(4)—N(4)—C(4)	-49.3 (2)	S(4)—N(4)—C(4)—C(3)	-109.3 (3)
O(42)—S(4)—N(4)—O(4)	58.4 (2)	S(4)—N(4)—C(4)—C(5)	75.0 (3)
O(42)—S(4)—N(4)—C(4)	-176.5 (2)	O(4)—N(4)—C(4)—C(3)	13.3 (4)
C(41)—S(4)—N(4)—O(4)	-56.7 (2)	O(4)—N(4)—C(4)—C(5)	-162.4 (3)

Table 3. Analysis of the planarity

(a) Distances ($\text{\AA} \times 10^3$) of relevant atoms from the mean plane with standard deviations in parentheses; starred atoms were not used to define the plane

Plane A: C(1)—C(6)
C(1) 22 (4), C(2) -23 (4), C(3) -6 (4), C(4) 14 (3), C(5) -23 (4)
C(6) 0(4), N(4)* -23 (2)

Plane B: S(4), O(4), C(4)
N(4)* -447 (2)

Plane C: S(4), O(41), O(42)
Plane D: S(4), N(4), C(41)

(b) Angles ($^\circ$) between planes

A-B	46.2 (1)	A-C	160.9 (1)	A-D	108.4 (1)
B-C	138.5 (2)	B-D	98.2 (2)	C-D	89.9 (1)

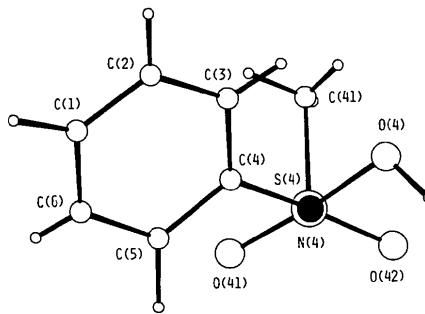


Fig. 2. Projection of the molecule along the S(4)—N(4) bond.

The intramolecular bond lengths and angles, in line with the hybridization expected for the atoms involved, and torsion angles reported in Table 2, show a conformational geometry of the methanesulfonylhydroxylamine moiety which is similar to that found in analogous derivatives studied previously (Rizzoli, Sgarabotto, Ugozzoli, Cardellini, Greci & Stipa, 1990). The position adopted by the SO_2 group with respect to the N(4) atom is comparable with the N lone-pair that bisects the

Table 4. *Puckering and asymmetry parameters of the phenyl moiety*

Puckering parameters*			
q_2 (Å)	0.041 (4)	Q_T (Å)	0.041 (4)
q_3 (Å)	-0.001 (4)	θ_2 (°)	90.9 (6.0)
Asymmetry parameters*			
$\Delta C_1(C1)$	0.015 (2)	$\Delta C_2(C1)$	0.015 (1)
$\Delta C_1(C2)$	0.015 (2)	$\Delta C_2(C2)$	0.015 (1)
$\Delta C_1(C3)$	0.029 (2)	$\Delta C_2(C3)$	0.000 (2)
$\Delta C_1(C1-C2)$	0.024 (2)	$\Delta C_2(C1-C2)$	0.000 (2)
$\Delta C_1(C1-C6)$	0.012 (2)	$\Delta C_2(C1-C6)$	0.021 (2)
$\Delta C_1(C2-C3)$	0.012 (2)	$\Delta C_2(C2-C3)$	0.021 (2)

* Puckering and asymmetry parameters were calculated by use of the general program *PARST* (Nardelli, 1983).

O=S=O angle (see Fig. 2) and the analysis of the planarity reported in Table 3.

The phenyl C atoms deviate significantly from coplanarity: the conformational analysis reported in Table 4 indicates that the benzene ring adopts a deformation very close to the twist-boat conformation (Cremer & Pople, 1975). A quantitative evaluation of how the phenyl ring deviates from ideal symmetry can be derived from the asymmetry parameters (Duax, Weeks & Rohrer, 1976) reported in Table 4. They show that a high degree of symmetry is due to the presence of two twofold rotational axes, one through the C(3) atom and the other intersecting the C(1)—C(2) bond.

Molecular packing is determined by hydrogen bonds of the type O—H...O involving the hydroxylic O(4) atom and the sulfonic O(42) atom in the

equivalent position $1-x, 1-y, 2-z$ [O(4)...O(42) 2.706(3), H(40)...O(42) 1.74 (8) Å, O(4)—H(40)...O(42) 165 (8)°]. Other contacts are consistent with van der Waals interactions.

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Acta Cryst. (1991). **C47**, 1517–1520

Structure of the Antiviral Drug Ethyl 4-{2-[1-(6-Methyl-3-pyridazinyl)-4-piperidinyl]ethoxy}benzoate*

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(Received 16 July 1990; accepted 27 November 1990)

Abstract. $C_{21}H_{27}N_3O_3$, $M_r = 369.5$, triclinic, $P\bar{1}$, $a = 6.801$ (7), $b = 11.08$ (1), $c = 26.82$ (4) Å, $\alpha = 79.2$ (1), $\beta = 86.5$ (1), $\gamma = 82.52$ (9)°, $V = 1967$ (4) Å³, $Z = 4$, $D_m = 1.25$, $D_x = 1.247$ Mg m⁻³, graphite-monochromated Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, $\mu =$

0.079 mm⁻¹, $F(000) = 792$, $T = 293$ K, final $R = 0.079$ for 3724 unique reflections with $|F_o| \geq 4|\sigma F_o|$. The asymmetric unit contains two molecules, *A* and *B*. They show pseudo-symmetry at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$, which is only broken by a 180° rotation of the ethyl-ethoxy moiety connected to the benzoate ring. The crystal structure is stabilized by hydrogen bonds between an N atom of the pyridazinyl ring of molecule *A* and an

* Internal code of Janssen Pharmaceutica: R77975.

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