

and are all within the range of that expected for a σ -bonded carbon framework. There are two types of C—O bonds in this structure. C(1) possesses a trigonal-planar geometry and forms a double bond to O(1) measuring 1.216 (3) Å. As a consequence of the crystallographically imposed symmetry C(1) is perfectly coplanar with the three atoms to which it is attached. Bonds to the hydroxyl groups by C(3) and its symmetry-related equivalent, C(3a), measure 1.446 (3) Å.

This structure constitutes the first example of this type of product to be identified in photochemical studies of the azoxybenzenes. Although it was obtained in fairly good yield as the sole product along with unreacted 4-methoxyazoxybenzene starting material, at this time its origin remains obscure and we are at a loss to propose a reasonable mechanism based on what is currently known regarding the photochemistry of azoxy compounds. It is similar in some respects to diacetone alcohol

which has been isolated following irradiation of neat acetone (Przybytek, Singh & Kagan, 1969).

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Structure of 5-Chloro-2-methylthio-3*H*-indol-3-one 3-Oxime *O*-Methyl Ether

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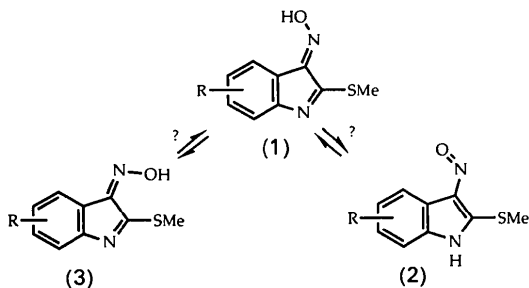
Abstract. C₁₀H₉ClN₂OS, $M_r = 240.71$, monoclinic, $C2/c$, $a = 23.671$ (6), $b = 5.480$ (1), $c = 20.644$ (8) Å, $\beta = 123.82$ (2)°, $V = 2225$ (1) Å³, $Z = 8$, $D_x = 1.437$ g cm⁻³, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å, $\mu = 46.12$ cm⁻¹, $F(000) = 992$, $T = 296$ K, $R = 0.053$ for 974 observed [$I/\sigma(I) \geq 3$] reflexions. All skeletal atoms in the title oxime ether lie in one plane, including both methyl C atoms, with a mean deviation from the plane of only 0.006 Å. The *S*-methyl group is oriented away from the oxime unit which has *E* geometry. The structure of the oxime ether, along with a comparison of its UV/VIS absorption spectrum with that of the corresponding oxime and

with other 2-methylthio-3*H*-indol-3-one 3-oximes, demonstrates that the tautomeric equilibrium between 2-methylthio-3*H*-indol-3-one 3-oxime and 2-methylthio-3-nitrosoindole lies on the side of the former.

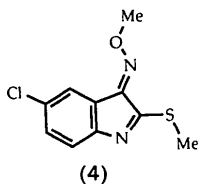
Introduction. We have shown (Kearney, Jackson & Joule, 1992) that treatment of 1-(*N*-arylamino)-1-methylthio-2-nitroethenes with trifluoromethanesulfonic acid effects a cyclization to indole derivatives. The products were shown to have the constitution of 2-methylthio-3*H*-indol-3-one 3-oximes, (1), though for such compounds there is the possibility of their existing in the alternative nitroso form (2), or in an alternative geometrical form, (3)

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(in which the intramolecular hydrogen bonding now possible might be thought to be a stabilizing influence), or, of course, as a mixture of these forms.



Experimental. Reaction of 5-chloro-3-methylthio-3*H*-indol-3-one 3-oxime with iodomethane in the presence of sodium hydride as base, in DMF at room temperature, gave a monomethyl derivative, m.p. 379–380 K, in 64% yield. ^1H NMR measurements on the methylated product suggested that the methyl group was on the O atom (δ_{H} MeO 4.25) and that, therefore, the product possessed a structure corresponding to (1) or (3), but since no close models exist for the chemical shift of a methyl in the alternative situation [an *N*-methylated version of (2)], an X-ray examination was undertaken and showed the product to have the structure and stereochemistry depicted below (4).



A red acicular crystal of (4), of approximate dimensions $0.020 \times 0.040 \times 0.200$ mm, was mounted on a glass fibre and used for data collection on a Rigaku AFC-5R diffractometer with graphite-monochromated $\text{Cu } K\alpha$ radiation and a 12 kW rotating-anode generator. Cell constants and an orientation matrix were determined by least-squares refinement using the setting angles of 14 carefully centred reflexions in the range $71.02 < 2\theta < 77.53^\circ$. Data were collected at 296 (1) K using the $\omega/2\theta$ scanning technique to a maximum 2θ value of 120.1° . ω scans of several intense reflexions, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 6.0° . Scans of $(0.94 + 0.30\tan\theta)^\circ$ were made at a speed of $8.0^\circ \text{ min}^{-1}$ (in ω). The weak reflexions [$I < 10.0\sigma(I)$] were rescanned and the counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflexion. The ratio of peak counting time to background

counting time was 2:1. The diameter of the incident-beam collimator was 0.5 mm and the crystal was 400.0 mm from the detector. Of the 1917 reflexions, 1862 were unique ($R_{\text{int}} = 0.057$). Intensities of three representative reflexions, measured after every 200 reflexions, declined by -1.10% , so a linear correction factor was applied. The linear absorption coefficient for $\text{Cu } K\alpha$ is 46.1 cm^{-1} . An empirical absorption correction, using the program *DIFABS* (Walker & Stuart, 1983), was applied which resulted in transmission factors in the range 0.77–1.21. The range of hkl was h 0–26, k 0–6, l –22–18.

The structure was solved by direct methods (Sheldrick, 1985). Non-H atoms were refined anisotropically. H atoms were located by difference synthesis and their positions given isotropic temperature factors then refined. The final cycle of full-matrix least-squares refinement was based on 974 observed reflexions [$I > 3.00\sigma(I)$] and 172 variable parameters and converged (largest parameter shift was 0.01 times its e.s.d.) with unweighted and weighted factors of $R = 0.053$ and $wR = 0.060$. The standard deviation, S , of an observation of unit weight was 1.76. The weighting scheme was based on counting statistics and included a factor ($p = 0.03$) to downweight the intense reflexions. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflexion order in data collection, $\sin\theta/\lambda$, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.23 and $-0.23 \text{ e } \text{Å}^{-3}$, respectively.

All calculations were performed using the *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1985). Neutral-atom scattering factors were taken from Cromer & Waber (1974), anomalous-dispersion effects were included in F_c (Ibers & Hamilton, 1964), and the values of f' and f'' were those of Cromer (1974).

Discussion. The atomic parameters for 5-chloro-2-methylthio-3*H*-indol-3-one 3-oxime *O*-methyl ether, (4), are listed in Table 1,* Table 2 lists bond lengths and bond angles. Fig. 1 shows a *PLUTO* (Motherwell & Clegg, 1978) drawing of the molecule and the numbering system used in Tables 1 and 2. All atoms in the title oxime ether lie in one plane, with a mean deviation from the plane of only 0.006 Å , including the methyl groups of both the methoxy and the methylthio which is oriented away from the 3-oxime ether substituent; the imine double bond has *E* geometry.

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54992 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HE0045]

Table 1. Positional and thermal parameters of oxime ether (4) with e.s.d.'s in parentheses

H atoms refined with isotropic thermal parameters. Non-H atoms refined anisotropically. $B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

	x	y	z	B_{eq} (Å ²)
Cl(1)	0.68202 (8)	-0.0576 (4)	0.9327 (1)	6.26 (9)
S(1)	0.30473 (8)	0.0294 (4)	0.8272 (1)	4.77 (7)
O(1)	0.4290 (2)	-0.4194 (9)	0.7710 (2)	5.3 (2)
N(1)	0.4315 (2)	0.213 (1)	0.9114 (3)	3.9 (2)
N(2)	0.3884 (3)	-0.286 (1)	0.7870 (3)	4.6 (2)
C(1)	0.3900 (3)	0.050 (1)	0.8629 (3)	3.7 (2)
C(2)	0.4227 (3)	-0.119 (1)	0.8375 (3)	3.7 (3)
C(3)	0.4923 (3)	0.036 (1)	0.8782 (3)	3.7 (2)
C(4)	0.5499 (4)	-0.105 (1)	0.8808 (4)	4.5 (3)
C(5)	0.6091 (3)	0.027 (1)	0.9277 (4)	4.2 (3)
C(6)	0.6110 (4)	0.224 (1)	0.9703 (4)	4.5 (3)
C(7)	0.5543 (3)	0.296 (1)	0.9691 (4)	4.1 (3)
C(8)	0.4954 (3)	0.166 (1)	0.9213 (3)	3.5 (2)
C(9)	0.3881 (6)	-0.604 (2)	0.7139 (6)	6.1 (4)
C(10)	0.2959 (4)	0.289 (2)	0.8724 (5)	5.2 (4)
H(4)	0.547 (3)	-0.23 (1)	0.855 (3)	4 (2)
H(6)	0.649 (2)	0.318 (9)	0.997 (2)	2 (1)
H(7)	0.554 (3)	0.43 (1)	0.998 (3)	5 (1)
H(91)	0.357 (4)	-0.53 (2)	0.669 (5)	8 (3)
H(92)	0.421 (3)	-0.68 (1)	0.709 (4)	7 (2)
H(93)	0.356 (5)	-0.68 (2)	0.726 (6)	15 (4)
H(101)	0.316 (5)	0.43 (2)	0.863 (5)	13 (4)
H(102)	0.325 (3)	0.27 (1)	0.928 (4)	6 (2)
H(103)	0.253 (4)	0.31 (2)	0.851 (4)	9 (3)

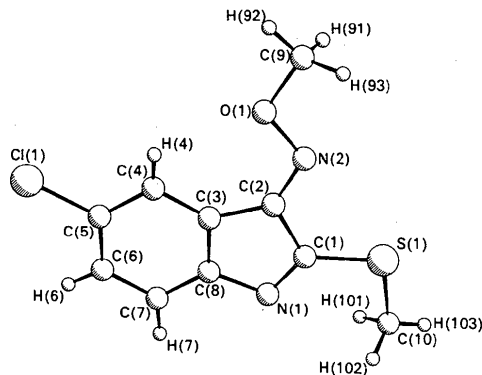
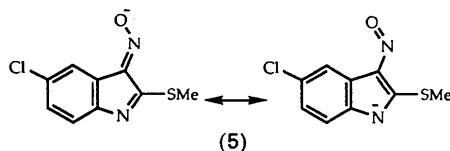


Fig. 1. PLUTO drawing of oxime ether (4), showing numbering scheme used in Tables 1 and 2.

The formation of (4) by methylation in the presence of base does not, in itself, provide conclusive evidence for the tautomeric/geometrical form of the oxime, since this process must involve the common resonance-stabilized anion, (5), which would be formed either from (1) or (3) by deprotonation at the O atom or from (2) by deprotonation at the ring N atom.



Although no model exists for the UV/VIS absorption of tautomeric form (2), the crystalline ether (4) provides an excellent model for (1). Comparison of the absorption of (1) [λ_{max} (log ϵ): 267 (4.64), 320sh

Table 2. Bond lengths (Å) and angles (°) in oxime ether (4) with e.s.d.'s in parentheses

Cl(1)—C(5)	1.735 (6)	C(1)—C(2)	1.477 (8)
S(1)—C(1)	1.724 (6)	C(2)—C(3)	1.444 (8)
S(1)—C(10)	1.777 (8)	C(3)—C(4)	1.387 (8)
O(1)—N(2)	1.385 (6)	C(3)—C(8)	1.393 (8)
O(1)—C(9)	1.440 (9)	C(4)—C(5)	1.382 (9)
N(1)—C(1)	1.293 (7)	C(5)—C(6)	1.375 (9)
N(1)—C(8)	1.434 (7)	C(6)—C(7)	1.387 (9)
N(2)—C(2)	1.283 (7)	C(7)—C(8)	1.376 (8)
C(4)—H(4)	0.84 (6)	C(9)—H(93)	1.0 (1)
C(6)—H(6)	0.91 (4)	C(10)—H(101)	1.01 (9)
C(7)—H(7)	0.97 (6)	C(10)—H(102)	0.96 (6)
C(9)—H(91)	0.89 (8)	C(10)—H(103)	0.86 (7)
C(9)—H(92)	0.96 (6)		
C(1)—S(1)—C(10)	100.0 (4)	C(2)—C(3)—C(8)	105.0 (5)
N(2)—O(1)—C(9)	109.1 (6)	C(4)—C(3)—C(8)	119.3 (6)
C(1)—N(1)—C(8)	105.8 (5)	C(3)—C(4)—C(5)	118.4 (7)
O(1)—N(2)—C(2)	111.3 (5)	Cl(1)—C(5)—C(4)	119.3 (5)
S(1)—C(1)—N(1)	125.5 (5)	Cl(1)—C(5)—C(6)	119.5 (5)
S(1)—C(1)—C(2)	121.8 (5)	C(4)—C(5)—C(6)	121.2 (6)
N(1)—C(1)—C(2)	112.6 (5)	C(5)—C(6)—C(7)	121.6 (6)
N(2)—C(2)—C(1)	121.1 (6)	C(6)—C(7)—C(8)	116.7 (7)
N(2)—C(2)—C(3)	134.3 (6)	N(1)—C(8)—C(3)	112.1 (5)
C(1)—C(2)—C(3)	104.5 (5)	N(1)—C(8)—C(7)	125.1 (6)
C(2)—C(3)—C(4)	135.6 (6)	C(3)—C(8)—C(7)	122.7 (6)
C(3)—C(4)—H(4)	117 (4)	H(91)—C(9)—H(92)	110 (7)
C(5)—C(4)—H(4)	124 (4)	H(91)—C(9)—H(93)	98 (7)
C(5)—C(6)—H(6)	121 (3)	H(92)—C(9)—H(93)	128 (8)
C(7)—C(6)—H(6)	118 (3)	S(1)—C(10)—H(101)	109 (5)
C(6)—C(7)—H(7)	124 (3)	S(1)—C(10)—H(102)	109 (4)
C(8)—C(7)—H(7)	120 (3)	S(1)—C(10)—H(103)	108 (6)
O(1)—C(9)—H(91)	110 (6)	H(101)—C(10)—H(102)	103 (6)
O(1)—C(9)—H(92)	101 (4)	H(101)—C(10)—H(103)	110 (8)
O(1)—C(9)—H(93)	110 (6)	H(102)—C(10)—H(103)	118 (6)

(3.67) and 417 (3.52) nm] with that of (4) [λ_{max} (log ϵ): 267 (4.69), 321sh (3.81) and 426 (3.59) nm], reveals a very good agreement, from which we conclude that (1) [or possibly (3), but not (2)] represents the preferred form of the system. The data for the electronic absorption of a range of 2-methylthio-3H-indol-3-one oximes (Kearney, Jackson & Joule, 1992) suggest strongly that all adopt the oxime tautomeric forms.

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