Acta Crystallographica Section C
**Crystal Structure
Communications**

ISSN 0108-2701

2,5-Dichloro-2,5-dihydrothiophene 1-oxide: determinaton of the complete stereochemistry

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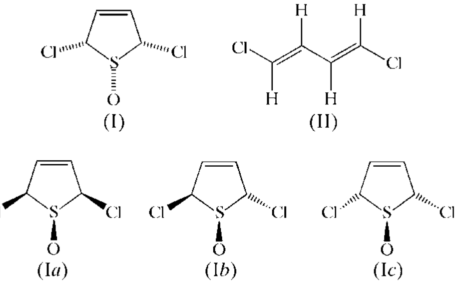
Received 3 August 2004
Accepted 7 February 2005
Online 11 March 2005

The title five-membered heterocycle, $C_4H_4Cl_2OS$, adopts an envelope conformation with the S atom at the tip of the flap. All three ring substituents, *viz*. the sulfoxide O atom and the two Cl atoms, are *cis* to each other. The two C atoms α to the sulfoxide group are also bonded to chlorine. The electron-withdrawing chlorine substituents give rise to weak C—H···O hydrogen bonds with the sulfoxide O atom of a symmetry-related molecule [H···O = 2.44 (2) and 2.61 (2) Å, C···O = 3.143 (3) and 3.302 (2) Å and C—H···O = 129.9 (19) and 135.1 (19)°]. There is also a possible weak C—H···Cl interaction. Chains of molecules held together by these weak interactions run parallel to the *a* axis.

Comment

Several decades ago, Kergomard & Vincent (1967) reported the synthesis of 2,5-dichloro-2,5-dihydrothiophene 1-oxide, (I) (stereochemistry not shown), from the reaction of thiophene and sodium hypochlorite. Also isolated were monochlorothiophenes and dichlorothiophenes. The preparation of sulfoxide (I) was also described in a patent (Kergomard & Thiolliere, 1965) and its use as an inhibitor of spore formation in mushrooms was claimed. In addition, the authors stated that the double bond is only slightly reactive towards peracetic acid and displays no reaction with chlorine or bromine. The narrow melting point range, reported by Kergomard & Vincent (1967) simply as 385 K, indicated that a single isomer was formed of the three possible shown in the scheme. Additional evidence that sulfoxide (I) is a single isomer was provided by a ^{13}C NMR spectrum (obtained by us) that had just two signals, one at 130.96 p.p.m. (the sp^2 hybridized C atoms) and the other at 69.92 p.p.m. (the sp^3 hybridized C atoms). From the ^{1}H NMR spectrum of (I), Kergomard & Vincent (1967) concluded that the two Cl substituents were *cis* to one another, which meant that the stereochemistry could be that of either (I*a*) or (I*c*).

Haynes & Placek (1981), who extended the experimental efforts of Zawaski (1978), attempted to oxidize the sulfoxide to the sulfone using hydrogen peroxide in the presence of zirconium tetrachloride with diglyme as the solvent. The only product isolated was (*E*,*E*)-1,4-dichloro-1,3-butadiene, (II). Assuming that the sulfoxide was converted to the sulfone, a retro-Diels–Alder reaction following the Woodward–Hoffman rules would produce the single diene if the Cl substituents were *cis* to one another. Thus, formation of (*E*,*E*)-1,4-dichloro-1,3-butadiene is further indirect evidence that the two Cl substituents are indeed *cis* to one another.



The unanswered question was the stereo-relationship of the O atom to the two Cl substituents. To confirm the stereochemistry indicated by the above observations and to establish with certainty all aspects of the stereochemistry of sulfoxide (I), a sample was crystallized from chloroform, the solvent used by Kergomard & Vincent (1967).

The crystal structure of (I) reveals that the stereochemistry is that of (I*a*), with the two Cl atoms and the O atom all *cis* to each other, as shown in the displacement ellipsoid plot in Fig. 1. The five-membered ring itself adopts an envelope conformation; the four C atoms are almost coplanar [torsion angle = −0.3 (3)°], with the S atom at the tip of the flap.

One interesting aspect of the packing in the crystal structure of (I), as shown in Fig. 2, is the weak C—H··· O hydrogen bonding involving atoms C2, C5 and the sulfoxide O atom. Apparently, the electron-withdrawing atoms Cl2 and Cl5 bonded to C2 and C5 promote a positive charge on H2 and H5. Although the H···O distances shown in Table 2 are longer than those in O—H···O hydrogen bonds, they are typical of distances observed for similar weak hydrogen bonds (Desiraju & Steiner, 1999). As has been observed for other weak hydrogen bonds (Glusker, 1998), the C—H···O bond angle deviates significantly from 180°. The packing diagram in Fig. 2 shows the possibility that there may actually be a bifurcated or three-center C2—H2···(O,Cl2) hydrogen bond (H2···Cl2 = 2.90 Å, C2···Cl2 = 3.67 Å and C2—H2···Cl = 144°). The H2 atom is only 0.23 Å from the plane formed by atoms C2, O and

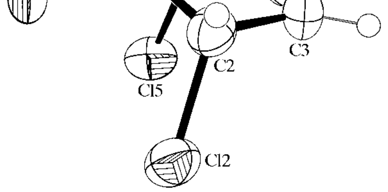


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

DOI: 10.1107/S0108270105004257

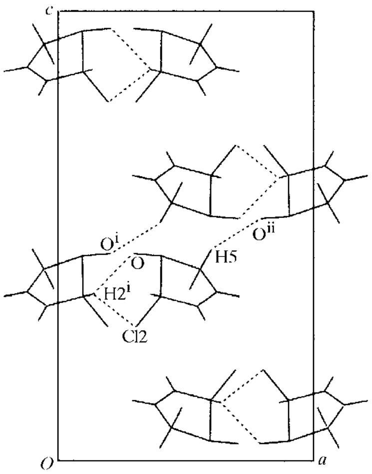


Figure 2
A packing diagram for (I), with the weak C—H···O bonds to the sulfoxide O atom indicated by dotted lines. A very weak interaction between atoms H2 and Cl2 is also indicated by a dotted line. [Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.]

Cl2; this tendency toward planarity is characteristic of atoms that participate in a three-center interaction (Desiraju & Steiner, 1999). The molecules held together by these weak interactions form chains parallel to the *a* axis.

Experimental

The title compound was prepared following the procedure described by Kergomard & Vincent (1967). Crystallization from chloroform produced colorless hexagonal plates of (I) suitable for X-ray diffraction.

Crystal data

$C_4H_4Cl_2OS$
$M_r = 171.03$
Orthorhombic, *Pbca*
$a = 10.1041\ (4)$ Å
$b = 7.2210\ (3)$ Å
$c = 17.8026\ (7)$ Å
$V = 1298.91\ (9)$ Å^3
$Z = 8$
$D_x = 1.749$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 9966 reflections
$\theta = 2.3$–28.3°
$\mu = 1.21$ mm^{-1}
$T = 294\ (2)$ K
Plate, colorless
0.70 × 0.46 × 0.18 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.632$, $T_{max} = 0.804$
9966 measured reflections

1606 independent reflections
1429 reflections with $I > 2\sigma(I)$
$R_{int} = 0.023$
$\theta_{max} = 28.3°$
$h = -13 \rightarrow 13$
$k = -9 \rightarrow 9$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.089$
$S = 1.04$
1606 reflections
79 parameters
H atom: see below

$w = 1/[\sigma^2(F_o^2) + (0.0444P)^2 + 0.801P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.57$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Two low-angle reflections (106 and 204) were omitted from the refinement. Idealized positions for atoms H3 and H4 were calculated at 0.93 Å from atoms C3 and C4, respectively, with U_{iso}(H) = 1.2U_{eq}(C). Because they participate in a weak hydrogen bond, the positions of atoms H2 and H5 were refined, with U_{iso}(H) = 1.2U_{eq}(C).

Table 1
Selected geometric parameters (Å, °).

S—O	1.4781 (14)	C2—Cl2	1.781 (2)
S—C2	1.844 (2)	C3—C4	1.315 (4)
S—C5	1.846 (2)	C4—C5	1.477 (3)
C2—C3	1.492 (3)	C5—Cl5	1.785 (2)
O—S—C2	110.92 (9)	C4—C3—C2	115.76 (19)
O—S—C5	110.40 (9)	C3—C4—C5	116.38 (19)
C2—S—C5	90.46 (9)	C4—C5—Cl5	112.54 (14)
C3—C2—Cl2	112.81 (15)	C4—C5—S	102.99 (16)
C3—C2—S	102.85 (15)	Cl5—C5—S	110.78 (10)
Cl2—C2—S	111.84 (11)		
C5—S—C2—C3	29.27 (15)	C3—C4—C5—S	22.8 (2)
S—C2—C3—C4	−22.4 (2)	C2—S—C5—C4	−29.48 (14)
C2—C3—C4—C5	−0.3 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O^i	0.91 (3)	2.44 (2)	3.143 (3)	135 (2)
C5—H5···O^{ii}	0.96 (2)	2.61 (2)	3.302 (2)	130 (2)

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

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1997*b*); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *ORTEP-3* (Farrugia, 1997), *MERCURY* (Bruno *et al.*, 2002) and *SHELXTL*.

Diffraction data were obtained by VBP during sabbatical leave in the laboratory of Jerome Karle (Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC), with the expert assistance of Clifford F. George and Richard Gilardi.

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