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2-Chloroethyl ethyl sulfide: a mustard gas analogue

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2-Chloroethyl ethyl sulfide (Cl–CH$_2$–CH$_2$–S–CH$_2$–CH$_3$ or C$_4$H$_9$ClS) is used as an analogue for mustard gas in biomedical studies. The Cl—C—C—S and the two C—C—S—C torsion angles are −177.38 (9), 83.17 (14) and 73.81 (16)°, respectively, and are similar to values that have been predicted, by *ab initio* quantum calculations, for the corresponding parameters in mustard gas. There are no strong intermolecular interactions, and the packing in the crystal structure bears some resemblance to hexagonal close packing.

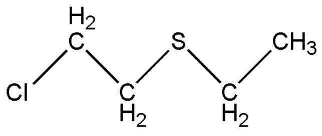
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.003 Å
R factor = 0.024
wR factor = 0.064
Data-to-parameter ratio = 25.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Mustard gas, or bis(2-chloroethyl)sulfide, is a notorious chemical warfare agent. 2-Chloroethyl ethyl sulfide, (I), is also a highly toxic blistering agent and has been used as an analogue for mustard gas in biomedical studies (see, for example, Das *et al.*, 2003). It is a liquid under ambient conditions and was crystallized at 200 K in a capillary using Boese's laser-assisted zone-refinement method (Boese & Nussbaumer, 1994). Diffraction data were then collected at 150 K.



(I)

Several computational studies have been carried out on the structure of mustard gas. While high-level [MP2/6-31G(*d*)] *ab initio* methods predict that it should adopt a C_2 structure, molecular mechanics have been reported to favour an 'all-*anti*' C_{2v} structure (Glukhovtsev *et al.*, 1998). The energetic differences between conformers are all less than 10 kJ mol^{-1}. The

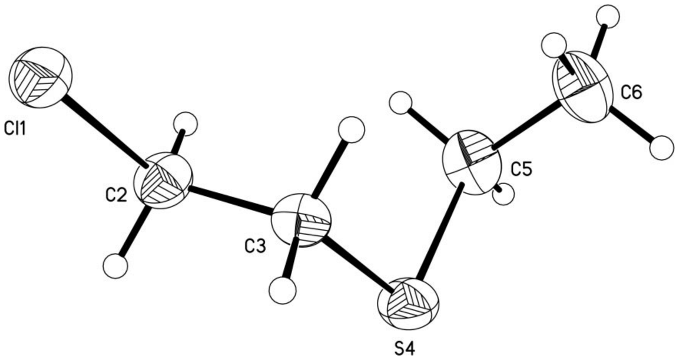


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as circles of arbitrary radii.

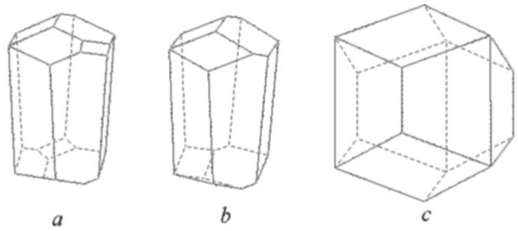


Figure 2
(*a*) Smoothed molecular Voronoi–Dirichlet polyhedron (VDP), showing the local topology in the crystal structure of (I). (*b*) As (*a*) but with two small faces omitted. (*c*) VDP corresponding to perfect hexagonal close packing.

molecular structure of (I) in the solid state (Fig. 1) more closely resembles the predicted C_2 conformation of mustard gas, with torsion angles Cl1—C2—C3—S4 −177.38 (9), C2—C3—S4—C5 83.17 (14) and C3—S4—C5—C6 73.81 (16)°. The corresponding Cl—C—C—S and C—C—S—C torsion angles in mustard gas were predicted to be 179.9 and 82.2°, respectively. The bond distances and angles in (I) are unremarkable (Table 1) and agree well with the corresponding values predicted for mustard gas.

Commonly accepted values for the van der Waals radii of C, H, Cl and S are 1.70, 1.20, 1.75 and 1.80 Å, respectively (Bondi, 1964). When X-ray-derived H-atom positions are used, there appear to be no intermolecular contacts in (I) which fall within the sums of these values. If the C—H distances are normalized to the typical value observed by neutron diffraction (1.08 Å), there is only one weak Cl1$\cdots$H61($\frac{1}{2}+x, \frac{1}{2}-y, z$) contact measuring 2.92 Å; the sum of the van der Waals radii of Cl and H is 2.95 Å. There are also a few H$\cdots$H contacts of around 2.38 Å; these, too, are weak by comparison with the van der Waals threshold (2.40 Å) for such contacts. The weakness of the intermolecular bonding in (I) explains the relatively low melting point of this material.

Topological analysis of the packing in the crystal structure of (I) was carried out using the program *TOPOS*3.1 (Blatov *et al.*, 1999). Distances between nearest-neighbour centroids are in the range 4.94–9.34 Å. Analysis of these, following the method of Peresypkina & Blatov (2000*a*,*b*), shows that although the coordination sequence in (I) is formally 14–54–126, two faces of the smoothed molecular Voronoi–Dirichlet polyhedron (VDP) are rather smaller than the other 12 (area 1.04% of the full solid angle of 4π steradian, compared with 4.02–13.05%; Fig. 2*a*). These two faces correspond to centroid–centroid distances of 9.34 Å, whereas the other distances are in the range 4.94–8.59 Å. Either neglecting these two interactions, or analysing the lattice molecular VDP, yields a coordination sequence of 12–44–96. This is the same as that observed in a hexagonally close-packed hard-sphere structure (Fig. 2*b* and *c*).

The most notable difference between the VDPs shown in Fig. 2 is that those calculated for (I) are less isometric than that calculated for perfect hexagonal close-packing, reflecting the long thin shape of (I). Blatov has shown that this deviation from sphericity can be measured using the dimensionless normalized second moment of inertia, $\tilde{G}_3$(mol) (Peresypkina & Blatov, 2003). This parameter adopts a value of 1 for a sphere and 0.9774 for ideal close-packed structures; for (I), $\tilde{G}_3$(mol) is 0.7924.

Experimental

A single crystal of (I) was grown in a Pyrex capillary mounted on a Bruker *SMART APEX* diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986) and a laser-assisted optical heating and crystallization device (OHCD; Boese & Nussbaumer, 1994). The sample, which had a tendency to super-cool, was frozen at 200 K and a crystal grown using Boese's laser-assisted zone-refinement method. This caused the sample to crystallize into one continuous crystalline column of length 1 mm and o.d. 0.3 mm. The crystal was therefore larger than the diameter of the X-ray beam (0.5 mm). This is frequently an issue in *in situ* crystallization experiments on low-melting-point compounds, where there is little experimental control over the length of a crystal. Görbitz (1999) has shown that multi-scan absorption correction procedures are quite efficient for large organic crystals. The refinement statistics presented here suggest that, in this case, an effective correction for absorption and other effects has been achieved.

Crystal data

C_4H_9ClS
M_r = 124.63
Orthorhombic, $Pna2_1$
a = 15.343 (3) Å
b = 8.5760 (14) Å
c = 4.8863 (8) Å
V = 642.96 (18) Å^3
Z = 4
D_x = 1.287 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3540 reflections
θ = 3–29°
μ = 0.78 mm^{-1}
T = 150 K
Cylinder, colourless
1.00 × 0.30 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)
$T_{\min}$ = 0.352, $T_{\max}$ = 0.790
4048 measured reflections

1441 independent reflections
1313 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.030
$\theta_{\max}$ = 28.3°
$h = -19 \rightarrow 19$
$k = -9 \rightarrow 11$
$l = -6 \rightarrow 6$

Refinement

Refinement on F^2
$R(F)$ = 0.024
$wR(F^2)$ = 0.064
S = 1.01
1438 reflections
56 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0194P)^2 + 0.136P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.36 e Å^{-3}
$\Delta\rho_{\min}$ = −0.25 e Å^{-3}
Absolute structure: Flack (1983); 598 Friedel pairs
Flack parameter = 0.23 (12)

Table 1
Selected geometric parameters (Å, °).

Cl1—C2	1.810 (2)	S4—C5	1.820 (2)
C2—C3	1.513 (3)	C5—C6	1.512 (3)
C3—S4	1.818 (2)		
C3—C2—Cl1	109.43 (12)	C5—S4—C3	100.67 (10)
S4—C3—C2	110.83 (12)	C6—C5—S4	114.06 (14)
C5—S4—C3—C2	83.17 (14)	Cl1—C2—C3—S4	−177.38 (9)
C3—S4—C5—C6	73.81 (16)		

H atoms were placed geometrically (C—H = 1.0 Å) after each refinement cycle, with U_{iso}(H) = 1.2U_{eq}(C). Three outlying reflections (120, 12,0,4 and the 12,0,$\overline{4}$) were omitted from the refinement.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *CRYSTALS* (Watkin *et al.*, 2003); molecular graphics: *XP* (Sheldrick, 1997); software used to prepare material for publication: *CRYSTALS*, *enCIFer* (CCDC, 2002), *PLATON* (Spek, 2003) and *WinGX* (Farrugia, 1999).

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