Refinement

Refinement on F
$R = 0.0371$
$wR = 0.0573$
$S = 1.34$
1781 reflections
181 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F) + 0.0010F^2]$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.30$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1990)

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

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

	x	y	z	U_{eq}
S	0.7175 (1)	0.0365 (1)	0.5606 (1)	0.065 (1)
N	0.5365 (1)	0.1280 (2)	0.5925 (1)	0.047 (1)
O	0.6428 (1)	−0.2793 (2)	0.8496 (1)	0.068 (1)
C(1)	0.6231 (1)	−0.0346 (2)	0.6756 (1)	0.048 (1)
C(2)	0.5358 (1)	−0.0729 (3)	0.7097 (1)	0.050 (1)
C(3)	0.5404 (1)	−0.1513 (3)	0.7679 (1)	0.051 (1)
C(4)	0.6332 (1)	−0.1971 (3)	0.7936 (1)	0.052 (1)
C(5)	0.7212 (1)	−0.1577 (4)	0.7606 (1)	0.071 (1)
C(6)	0.7155 (1)	−0.0781 (3)	0.7025 (1)	0.068 (1)
C(7)	0.6161 (1)	0.0479 (2)	0.6136 (1)	0.048 (1)
C(8)	0.6469 (2)	0.1509 (3)	0.5058 (1)	0.055 (1)
C(9)	0.6736 (2)	0.2054 (3)	0.4455 (1)	0.072 (1)
C(10)	0.6032 (2)	0.2957 (3)	0.4113 (1)	0.070 (1)
C(11)	0.5073 (2)	0.3296 (3)	0.4352 (1)	0.066 (1)
C(12)	0.4805 (2)	0.2756 (3)	0.4949 (1)	0.058 (1)
C(13)	0.5510 (1)	0.1868 (2)	0.5307 (1)	0.048 (1)

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

S—C(7)	1.747 (2)	S—C(8)	1.732 (2)
N—C(7)	1.297 (2)	N—C(13)	1.397 (2)
O—C(4)	1.350 (2)	C(1)—C(2)	1.391 (2)
C(1)—C(6)	1.386 (3)	C(1)—C(7)	1.464 (2)
C(2)—C(3)	1.375 (3)	C(3)—C(4)	1.385 (2)
C(4)—C(5)	1.389 (3)	C(5)—C(6)	1.377 (3)
C(8)—C(9)	1.389 (3)	C(8)—C(13)	1.399 (3)
C(9)—C(10)	1.369 (3)	C(10)—C(11)	1.387 (4)
C(11)—C(12)	1.379 (3)	C(12)—C(13)	1.382 (3)
C(7)—S—C(8)	89.6 (1)	C(7)—N—C(13)	111.5 (1)
C(2)—C(1)—C(6)	117.6 (2)	C(2)—C(1)—C(7)	120.4 (2)
C(6)—C(1)—C(7)	122.0 (2)	C(1)—C(2)—C(3)	121.5 (2)
C(2)—C(3)—C(4)	120.3 (2)	O—C(4)—C(3)	123.3 (2)
O—C(4)—C(5)	117.7 (2)	C(3)—C(4)—C(5)	119.0 (2)
C(4)—C(5)—C(6)	120.1 (2)	C(1)—C(6)—C(5)	121.6 (2)
S—C(7)—N	115.0 (1)	S—C(7)—C(1)	120.3 (1)
N—C(7)—C(1)	124.6 (2)	S—C(8)—C(9)	129.4 (2)
S—C(8)—C(13)	109.5 (1)	C(9)—C(8)—C(13)	121.1 (2)
C(8)—C(9)—C(10)	118.0 (2)	C(9)—C(10)—C(11)	121.4 (2)
C(10)—C(11)—C(12)	120.8 (2)	C(11)—C(12)—C(13)	118.8 (2)
N—C(13)—C(8)	114.4 (2)	N—C(13)—C(12)	125.7 (2)
C(8)—C(13)—C(12)	119.9 (2)		

The structure was solved by direct methods and refined by the full-matrix least-squares method. All H atoms were located from the difference Fourier map. The *SHELXTL/PC* (Sheldrick, 1990) program package was used for all calculations.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: LI1128). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(*Z*)-Ethyl 2-Cyano-3-methylsulfinyl-3-methylthiopropenoate

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Abstract

The title compound, $C_8H_{11}NO_3S_2$, is shown to be formed in the oxidation of ethyl 2-cyano-3,3-bis(methylthio)propenoate with 3-chloroperoxybenzoic acid. The compound contains an $(S_2)C{=}C(C_2)$ unit which is not exactly planar, as indicated by atomic deviations of ±0.130 (1) Å from the least-squares plane through these six atoms. The C—S bond lengths are unexceptional but the bond between the $CH_3(O)S$— group and the alkene C atom is slightly longer than expected [1.837 (3) Å].

Comment

Ketene dithioacetal derivatives (Söderbäck, 1963) are well known reagents for the preparation of different types of heterocyclic compounds. For example, the synthesis of different lactones, pyrazoles and isoxazole derivatives has been reported (Tominaga, Ushirogochi, Matsuda & Kobayashi, 1984; Ram, Haque, Singh, Hussaini & Shoeb, 1993; Ram, Hussaini, Singh &

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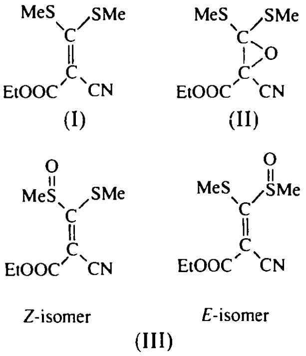
Shoeb, 1993) using ethyl 2-cyano-3,3-bis(methylthio)-propenoate, (I), as the ketene dithioacetal derivative. The epoxidation of (I) was attempted in order to obtain analogues of these compounds and thus to extend their synthetic use.



The oxidation of (I) with 3-chloroperoxybenzoic acid gave a fine crystalline product; the mass spectrum of this product confirmed the insertion of one O atom. The structure of the starting material suggested two possible modes of insertion: as an epoxide link across the double bond, (II), or by attachment to one of the two different S atoms of the *gem* methylthio groups to give the *Z* or *E* form of (III). The ^{1}H NMR and ^{13}C NMR spectra eliminated the epoxide structure (II) but were consistent with structure (III).

The X-ray investigation was undertaken in order to determine unambiguously the isomeric form of the product; the molecular structure obtained, illustrated in Fig. 1, confirms the formation of the *Z* isomer.

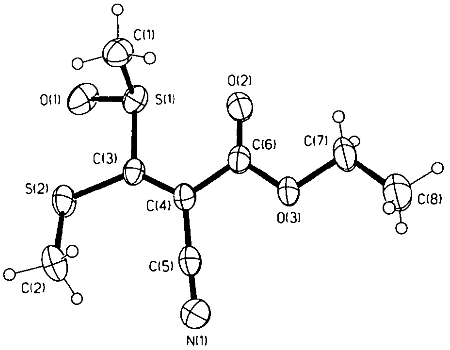


Fig. 1. Molecular structure showing the non-H-atom labelling. Displacement ellipsoids are shown at the 50% probability level.

A search of the Cambridge Structural Database (Allen *et al.*, 1991) indicated that very few structures containing the (—S)$_2$C=C(C—)$_2$ unit and not involving the S atoms as part of a ring system have been reported. Of the eleven references obtained in this search, eight are salts (mainly dithiolates) and therefore not strictly comparable with the title compound. The remaining compounds, 2,2-bis(methylthio)-1,1-ethylenedicarbonitrile (Hummel & Procher, 1986), 1,1-bis(methylthio)-2-*p*-bromobenzoyl-2-cyanoethylene (Abrahamsson, Rehnberg, Liljefors & Sandström, 1974) and 3-[bis(methylthio)methylene]pentane-2,4-dione (Jarvis & Taylor, 1979), have C—S bond lengths in the range 1.716–1.819 Å; a similar range is observed in the title compound but the S(1)—C(3) distance of 1.837 (3) Å is slightly longer than expected and may be due to a steric effect. The C(3)—C(4) bond of 1.354 (4) Å corresponds well to a C=C double bond.

The (S)$_2$C=C(C)$_2$ unit is not exactly planar, as shown by the S(1)—C(3)—C(4)—C(6) and S(2)—C(3)—C(4)—C(5) torsion angles of 12.0 (4) and 9.3 (4)°, respectively; this is comparable with the reported twist angle of 15.2° in 1,1-bis(methylthio)-2-*p*-bromobenzoyl-2-cyanoethylene (Abrahamsson *et al.*, 1974). An alternative statement of the situation in the title compound is that the maximum deviations of atoms from the least-squares plane through S(2), S(1), C(3), C(4), C(5) and C(6) are ±0.130 (1) Å.

Experimental

The title compound was prepared by adding 3-chloroperoxybenzoic acid (0.173 g, 0.001 mol) with continuous stirring at 303 K over a period of 10 min to a solution of ethyl 2-cyano-3,3-bis(methylthio)propenoate, (I) (0.217 g, 0.001 mol), in dry chloroform (15 ml). The contents were stirred and the reaction monitored by TLC; after 30 min the solvent was removed under vacuum to give a solid product. This was recrystallized from petrol (60–80)–chloroform (9:1) to yield colourless needles (0.182 g, 78%), m.p. 360 K.

Crystal data

$C_8H_{11}NO_3S_2$
$M_r = 233.30$
Monoclinic
$P2_1/c$
$a = 5.502 (5)$ Å
$b = 7.036 (7)$ Å
$c = 27.688 (24)$ Å
$\beta = 93.57 (7)°$
$V = 1069.8 (17)$ Å^3
$Z = 4$
$D_x = 1.449$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 9$–$11°$
$\mu = 0.479$ mm^{-1}
$T = 220 (2)$ K
Block
0.53 × 0.18 × 0.10 mm
Colourless

Data collection

Siemens *P*3*R*3 diffractometer
ω–2θ scans
Absorption correction: none
2460 measured reflections
1900 independent reflections
1486 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0381$
$\theta_{\rm max} = 25.05°$
$h = 0 \rightarrow 6$
$k = -1 \rightarrow 8$
$l = -32 \rightarrow 32$
3 standard reflections monitored every 200 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0398$
$wR(F^2) = 0.0937$
$S = 1.057$
1897 reflections
127 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.7312P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.393$ e Å^{-3}
$\Delta\rho_{\min} = -0.241$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	y	z	U_{eq}
S(1)	0.00409 (12)	0.18199 (11)	0.36020 (2)	0.0374 (2)
S(2)	0.16891 (13)	0.46726 (11)	0.29436 (3)	0.0417 (2)
O(1)	−0.1942 (3)	0.2219 (3)	0.32289 (8)	0.0517 (6)
O(2)	0.3436 (4)	0.1360 (3)	0.43134 (7)	0.0544 (6)
O(3)	0.6294 (4)	0.3431 (3)	0.45711 (7)	0.0452 (5)
N(1)	0.6811 (5)	0.7037 (4)	0.38181 (10)	0.0564 (7)
C(1)	0.1667 (5)	−0.0146 (4)	0.33650 (11)	0.0434 (7)
C(2)	0.4489 (5)	0.5728 (5)	0.27759 (10)	0.0459 (7)
C(3)	0.2348 (4)	0.3636 (4)	0.34973 (9)	0.0307 (6)
C(4)	0.4138 (4)	0.4052 (4)	0.38386 (9)	0.0313 (6)
C(5)	0.5666 (5)	0.5693 (4)	0.38189 (9)	0.0383 (7)
C(6)	0.4553 (5)	0.2796 (4)	0.42614 (9)	0.0364 (6)
C(7)	0.6812 (6)	0.2176 (5)	0.49853 (11)	0.0604 (10)
C(8)	0.9026 (6)	0.2827 (6)	0.52545 (13)	0.0671 (11)

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

S(1)—O(1)	1.482 (2)	O(3)—C(7)	1.461 (4)
S(1)—C(1)	1.794 (3)	N(1)—C(5)	1.137 (4)
S(1)—C(3)	1.837 (3)	C(3)—C(4)	1.354 (4)
S(2)—C(3)	1.716 (3)	C(4)—C(5)	1.431 (4)
S(2)—C(2)	1.797 (3)	C(4)—C(6)	1.473 (4)
O(2)—C(6)	1.196 (3)	C(7)—C(8)	1.462 (4)
O(3)—C(6)	1.323 (3)		
C(4)—C(3)—S(2)	129.5 (2)	C(3)—C(4)—C(5)	123.5 (2)
C(4)—C(3)—S(1)	121.3 (2)	C(3)—C(4)—C(6)	119.7 (2)
S(2)—C(3)—S(1)	109.10 (14)	C(5)—C(4)—C(6)	116.9 (2)

H atoms were added at calculated positions and refined using a riding model. The H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which the H atom is attached.

Data collection: Siemens *P3R3* system. Cell refinement: Siemens *P3R3* system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1239). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diphenylarsenic(III) Iodide

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Abstract

$AsPh_2I$ (iododiphenylarsine) contains arsenic in trigonal pyramidal coordination with iodine and two phenyl groups, with effectively equal As—C distances [1.953 (6) and 1.942 (6) Å]. Bond angles at arsenic are 101.7 (2)° between the phenyl groups and a mean of 97.5° between iodine and phenyl. There are no intermolecular As···I interactions shorter than 4.4 Å.

Comment

Although there has been recent interest in the structures of a range of arylantimony(III) halides, including $SbPhX_2$, where X = Cl, Br or I (Mundt, Becker, Stadelmann & Thurn, 1992), $SbArX_2$, where Ar = 4-tolyl and X = Cl or Br, and $SbPh_2Br$ (Millington & Sowerby, 1994), structural information for related As compounds is limited to results from film data for the isostructural diphenylarsenic chloride (Trotter, 1962*a*), bromide (Trotter, 1962*b*) and iodide (Trotter, 1963). For the iodide, only the As—I distance (2.53 Å) was reported.

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