C5—C6	1.387 (3)	C19—C25	1.419 (3)
C6—C7	1.524 (3)	C20—O21	1.367 (3)
C7—C8	1.535 (3)	C20—C22	1.407 (3)
C8—C9	1.562 (3)	C22—C23	1.373 (3)
C10—C9	1.535 (3)	C23—C24	1.419 (3)
C10—C11	1.540 (3)	C24—C25	1.426 (3)
C11—C7	1.573 (3)	C24—C29	1.432 (3)
C11—C12	1.530 (3)	C25—C26	1.421 (3)
C12—C13	1.555 (3)	C26—C27	1.369 (4)
C13—N14	1.478 (3)	C27—C28	1.396 (4)
C15—N14	1.478 (3)	C28—C29	1.354 (4)
C16—C7	1.566 (3)		
C2—C1—C6	120.3 (5)	C7—C16—N14	107.2 (4)
C13—C1—C6	113.4 (4)	C7—C16—O21	107.6 (4)
C1—C2—C3	119.6 (5)	C17—C16—C7	114.6 (4)
C2—C3—C4	120.3 (5)	C17—C16—N14	112.2 (4)
C3—C4—C5	120.7 (6)	C17—C16—O21	106.2 (4)
C4—C5—C6	118.9 (5)	N14—C16—O21	108.9 (4)
C5—C6—C7	127.6 (5)	C16—C17—N18	125.9 (5)
C1—C6—C5	120.1 (5)	C17—N18—C19	115.3 (4)
C1—C6—C7	112.2 (4)	C20—C19—N18	120.9 (5)
C6—C7—C8	115.4 (4)	C20—C19—C25	119.8 (5)
C11—C7—C6	108.6 (4)	C25—C19—N18	119.2 (4)
C11—C7—C8	101.9 (4)	C19—C20—O21	121.2 (5)
C11—C7—C16	106.3 (4)	C19—C20—C22	122.6 (5)
C16—C7—C6	105.0 (4)	C22—C20—O21	116.1 (4)
C16—C7—C8	118.9 (4)	C16—O21—C20	114.3 (4)
C7—C8—C9	103.8 (4)	C20—C22—C23	117.9 (5)
C10—C9—C8	106.4 (5)	C22—C23—C24	122.2 (5)
C11—C10—C9	106.3 (4)	C23—C24—C25	118.6 (5)
C10—C11—C7	102.2 (4)	C23—C24—C29	122.2 (5)
C10—C11—C12	117.6 (4)	C25—C24—C29	119.3 (5)
C12—C11—C7	111.4 (4)	C19—C25—C24	118.8 (5)
C11—C12—C13	106.9 (4)	C19—C25—C26	122.8 (5)
C12—C13—N14	105.1 (4)	C24—C25—C26	118.5 (5)
C1—C13—C12	106.7 (4)	C25—C26—C27	119.8 (5)
C1—C13—N14	111.1 (4)	C26—C27—C28	121.9 (7)
C13—N14—C15	116.2 (4)	C27—C28—C29	120.3 (7)
C13—N14—C16	115.2 (4)	C24—C29—C28	120.3 (5)
C15—N14—C16	115.2 (4)		

Data collection: CAD-4 diffractometer software (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer software. Data reduction: local program. Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances involving H atoms have been deposited with the IUCr (Reference: PA1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Thiodicarb

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Abstract

Dimethyl *N*,*N*′-[thiobis(methyliminocarbonyloxy)]bis(ethanimidothiolate), $C_{10}H_{18}N_4O_4S_3$, is an example of a sulfenylated biscarbamate insecticide. The molecule has an approximate twofold axis through the central S atom which joins the two methyliminocarbonyloxyethanimidothiolate units. One of the two arms is planar in the crystal. Semi-empirical geometry optimization for an isolated molecule favors a model with both arms planar and, thus, crystal packing may be responsible for the observed non-planarity in one arm. Bond lengths and angles have similar values to those of the 'monomeric' carbamate insecticide methomyl.

Comment

The title compound, (I), is an example of a sulfenylated biscarbamate insecticide (D'Silva, 1985). Thiodicarb acts as a toxocant by cholinesterase inhibition and is used on many crops to control lepidopterous and other pests. It is related to the carbamate insecticide methomyl, (II), with an S atom linking two methomyl units *via* the carbamate N atoms. Both geometric isomers [(*E*) and (*Z*)] of (II) are known. Methomyl consists of the (*Z*) isomer shown (D'Silva, 1971; Waite & Sim, 1971; Takusagawa & Jacobson, 1977), but the technical grade may contain traces of the (*E*) isomer

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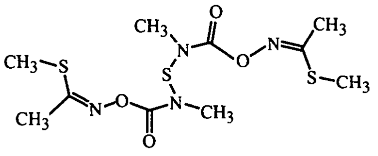
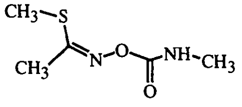
as an impurity. This study was undertaken to determine the stereochemistry of the imide bond in (I), which has been established as (*Z*).



(I)



(II)

An *ORTEP*II (Johnson, 1976) drawing of (I) is shown in Fig. 1. There are no significant differences between the bond lengths and angles in the two halves of the molecule, despite torsion angle differences of 28° about O1—N1 (O4—N4) and 8° about O1—C4 (O4—C7). Additionally, these values are similar to those reported for the (*E*) and (*Z*) isomers of (II) (Aranda, Gauvrit, Cesario, Guilhem, Pascard & Tran Huu Dau, 1983; Takusagawa & Jacobson, 1977). The average deviations from the least-squares planes of the ten atoms in each of the arms are 0.039 and 0.271 Å for the S3 and S2 units, respectively.

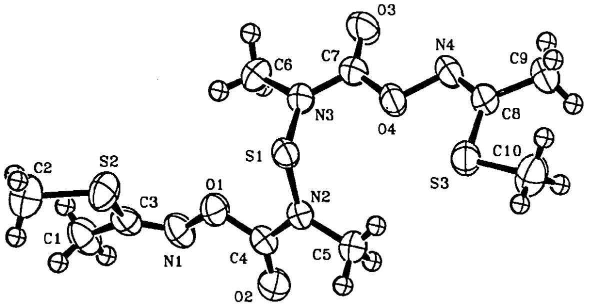


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I). The C, N, O and S atoms are shown as 50% probability ellipsoids, and H atoms as 0.1 Å spheres.

Geometry optimizations of the observed structure of (I) and of a model with two planar arms were performed by the AM1 semi-empirical procedure (Dewar, Zoebisch, Healy & Stewart, 1985), using the *MOPAC* suite of programs (Stewart, 1990), to determine if the observed lack of planarity in (I) was a consequence of crystal-packing forces. Surprisingly, the two model starting points (observed and planar) did not converge to the same structure. The torsion angles around the N—O and O—C bonds in the arms of the AM1-optimized observed structure are 168.0 and 170.9°, and 147.3 and 166.9°, respectively, while those of the optimized planar structure are 177.7 and 177.6°, and 168.5 and 171.4°, respectively. Additionally, the calculated heat of formation for the optimized planar model is 0.4 kcal mol^{-1} (1 cal = 4.184 J) smaller than that of the optimized X-ray model. These results suggest that the conformations of the two arms are closely related and that crystal-packing forces are the most likely reason for the torsion-angle differences found in (I). In the X-ray structure, the cross-arm distances are O1···C6 = 3.231 (5) and O4···C5 = 3.509 (5) Å, whereas these distances are 3.24 and 3.28 Å, respectively, in the optimized planar model. There are no unusual intermolecular distances.

Experimental

The title compound (Rhone-Poulenc AG) was prepared as described by D'Silva (1985).

Crystal data

$C_{10}H_{18}N_4O_4S_3$
$M_r = 354.5$
Triclinic
$P\bar{1}$
$a = 5.9355$ (6) Å
$b = 11.258$ (1) Å
$c = 13.7293$ (7) Å
$\alpha = 113.667$ (6)°
$\beta = 98.617$ (7)°
$\gamma = 91.947$ (8)°
$V = 826.3$ (3) Å^3
$Z = 2$
$D_x = 1.42$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 19.99$–$24.86°$
$\mu = 4.13$ mm^{-1}
$T = 293$ K
Flat, knife blade
0.25 × 0.11 × 0.04 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
θ–2θ scans
Absorption correction: ψ scan
$T_{\min} = 0.79$, $T_{\max} = 1.00$
4873 measured reflections
3164 independent reflections
2354 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.035$
$\theta_{\max} = 70°$
$h = 0 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 15$
8 standard reflections
frequency: 60 min
intensity decay: 7.1 (3)%

Refinement

Refinement on F
$R = 0.037$
$wR = 0.050$
$S = 1.23$
2354 reflections
263 parameters
All H atom parameters refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.09$

$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: Zachariasen (1968)
Extinction coefficient: $1.4 (9) \times 10^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S1	0.4412 (1)	−0.06653 (6)	0.14388 (5)	3.64 (2)
S2	0.7715 (1)	−0.3453 (1)	−0.11434 (7)	5.17 (3)
S3	0.0855 (1)	0.13087 (8)	0.41409 (6)	4.71 (3)

O1	0.7987 (4)	−0.2248 (2)	0.1005 (2)	4.43 (7)
O2	0.8192 (4)	−0.2765 (2)	0.2439 (2)	5.31 (9)
O3	0.6980 (4)	0.2884 (2)	0.2828 (2)	5.38 (8)
O4	0.4245 (3)	0.1730 (2)	0.3175 (1)	4.15 (7)
N1	1.0082 (4)	−0.2872 (2)	0.0815 (2)	4.39 (9)
N2	0.5621 (4)	−0.1433 (2)	0.2183 (2)	3.71 (8)
N3	0.6136 (4)	0.0711 (2)	0.1810 (2)	3.76 (8)
N4	0.4042 (5)	0.2958 (2)	0.4052 (2)	4.62 (9)
C1	1.2150 (6)	−0.4038 (4)	−0.0530 (4)	5.1 (1)
C2	0.844 (1)	−0.4522 (5)	−0.2425 (3)	6.4 (2)
C3	1.0033 (5)	−0.3426 (2)	−0.0203 (2)	3.73 (9)
C4	0.7377 (5)	−0.2203 (2)	0.1925 (2)	3.71 (9)
C5	0.4579 (7)	−0.1412 (4)	0.3097 (3)	4.8 (1)
C6	0.8039 (7)	0.0723 (4)	0.1233 (3)	4.9 (1)
C7	0.5893 (5)	0.1879 (3)	0.2627 (2)	3.9 (1)
C8	0.2457 (5)	0.2793 (3)	0.4534 (2)	4.0 (1)
C9	0.2054 (9)	0.3984 (3)	0.5481 (3)	5.7 (1)
C10	−0.1158 (8)	0.1677 (5)	0.5058 (3)	5.9 (2)

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

S1—N2	1.684 (2)	S1—N3	1.677 (2)
S2—C2	1.813 (4)	S3—C10	1.803 (4)
S2—C3	1.730 (3)	S3—C8	1.732 (3)
O1—N1	1.455 (3)	O4—N4	1.447 (3)
O1—C4	1.347 (3)	O4—C7	1.364 (3)
O2—C4	1.188 (3)	O3—C7	1.190 (3)
N1—C3	1.277 (4)	N4—C8	1.278 (4)
N2—C4	1.374 (3)	N3—C7	1.374 (3)
N2—C5	1.472 (4)	N3—C6	1.476 (4)
C1—C3	1.495 (4)	C8—C9	1.503 (4)
N2—S1—N3	105.7 (1)	S1—N3—C7	124.2 (2)
S1—N2—C4	124.1 (2)	S1—N3—C6	120.1 (2)
S1—N2—C5	118.5 (2)	S3—C8—N4	123.2 (2)
S2—C3—N1	122.9 (2)	S3—C8—C9	121.4 (2)
S2—C3—C1	122.0 (3)	N4—O4—C7	110.5 (2)
N1—O1—C4	111.4 (2)	O4—N4—C8	109.0 (2)
O1—N1—C3	108.6 (2)	O3—C7—O4	124.8 (3)
O1—C4—O2	125.5 (3)	O4—C7—N3	110.8 (2)
O1—C4—N2	110.6 (2)	O3—C7—N3	124.3 (3)
O2—C4—N2	123.9 (3)	N4—C8—C9	115.4 (3)
N1—C3—C1	115.1 (3)	C8—S3—C10	103.4 (2)
C2—S2—C3	103.6 (2)	C6—N3—C7	115.7 (2)
C4—N2—C5	117.0 (2)		
S1—N2—C4—O1	0.3 (3)	O3—C7—N3—C6	6.1 (5)
S1—N2—C4—O2	−178.3 (2)	N1—O1—C4—N2	170.4 (2)
S2—C3—N1—O1	−3.1 (3)	N1—C3—S2—C2	−173.1 (3)
O1—N1—C3—C1	176.0 (2)	N2—S1—N3—C6	90.3 (3)
O1—C4—N2—C5	173.0 (3)	N2—S1—N3—C7	−90.9 (2)
O2—C4—O1—N1	−11.0 (4)	C1—C3—S2—C2	7.8 (3)
O2—C4—N2—C5	−5.7 (4)	C3—N1—O1—C4	150.4 (2)
S1—N3—C7—O3	−172.8 (3)	N3—C7—O4—N4	178.5 (2)
S1—N3—C7—O4	7.2 (4)	N4—C8—S3—C10	−177.5 (3)
S3—C8—N4—O4	−0.8 (4)	N3—S1—N2—C5	104.9 (2)
O4—N4—C8—C9	179.2 (3)	N3—S1—N2—C4	−82.5 (2)
O4—C7—N3—C6	−173.8 (3)	C9—C8—S3—C10	2.5 (4)
O3—C7—O4—N4	−1.4 (4)	C7—O4—N4—C8	178.7 (2)

The θ scan width was 1.5(0.83 + 0.14tanθ)°. The scan was recorded as 96 steps with the two outermost 16-step blocks for background determination. The θ scan speed was 5.49–2.06° min^{-1}. Correction for dispersion was made using *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.3.1).

The structure was solved using *MITHRIL* (Gilmore, 1983). Crystallographic calculations were performed with the *TEXSAN* system (Molecular Structure Corporation, 1987) on Digital Equipment Corporation MicroVAX II and VAXStation II computers. Molecular graphics were prepared using *ORTEP*II (Johnson, 1976) and *ChemDraw* (Cambridge Scientific Computing, 1989). Other material for publication was produced using *PLOTMD* (Luo, Ammon & Gilliland, 1989).

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: CR1160). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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4-Substituted 1-Methyl-1*H*-2,3-benzodiazepine Compounds

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Abstract

The structures of a series of six 1-methyl-1*H*-2,3-benzodiazepine compounds, 1(*R*)-methyl-4-[1(*R*)-phenylethyl]-1*H*-2,3-benzodiazepine ($C_{18}H_{18}N_2$), (1), 1(*R*)-methyl-4-[1(*R*),2,2-trimethylpropyl]-1*H*-2,3-benzo-