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2-(Nitromethylene)-1,3-dithietane

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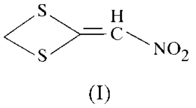
In the crystal structure of the title compound, $C_3H_3NO_2S_2$, the four-membered C_2S_2 ring is planar, as is the whole molecule. The short intramolecular S···O distance of 2.687 (2) Å shows the five-atom system to be conjugated. The molecules pack as a two-dimensional network in the (010) plane through short intermolecular S···O [2.900 (2) and 3.077 (2) Å] interactions.

Comment

In the chemistry of sulfur compounds, ketene dithioacetals occupy an important position as synthetic intermediates for use in the generation of polyfunctional target molecules (Metzner & Thullier, 1994). The ketene dithioacetals are stable and readily amenable to synthetic manipulation. The presence of electron-withdrawing groups such as cyano, nitro, oxo and ester on the olefin make them especially stable for isolation and structure evaluation. Among ketene dithioacetals, nitroketene dithioacetals show impressive and varied reactivity, and are good Michael acceptors. They undergo addition with a variety of nucleophiles to afford functionalized alkenes in a facile manner (Kolb, 1990). In connection with our studies on the synthesis and characterization of various alkyl-substituted nitroketene dithioacetals, we report here the structure of 2-(nitromethylene)-1,3-dithietane, (I).



(I)

The four-membered ring contains two S, one sp^2-hybridized trigonal C and an sp^3-hybridized C atom, and thus the molecule is expected to show unusual bond lengths and angles to accommodate strain in the trigonal carbon (Fig. 1). In addition, the presence of the nitro group induces hydrogen-bond interactions with neighboring molecules. The C_2S_2 moiety is essentially planar and the complete molecule has a maximum deviation of 0.039 (2) Å for the O2 atom. The C2—S distances are shorter than the C1—S distances, and agree with the values reported for Csp^2—S and Csp^3—S distances of 1.741 and 1.817 Å, respectively (Allen *et al.*, 1987). The Csp^2—S and Csp^2—Csp^2 (C2—C3) distances are somewhat longer than the corresponding bonds due to conjugation effects in the molecule (Neidlein *et al.*, 1994). An unusual C—S bond distance of 1.911 (6) Å has been reported for a 1,3-dithiocyclobutane derivative ($C_9H_{12}O_2S_2$; Kapecki *et al.*, 1968). Associated with the described planarity is the intramolecular S···O distance of 2.687 (2) Å, which is considerably shorter than the sum of the van der Waals radii for S and O (3.25 Å). This is in accordance with molecules containing a five-atom conjugated system linking S and O.

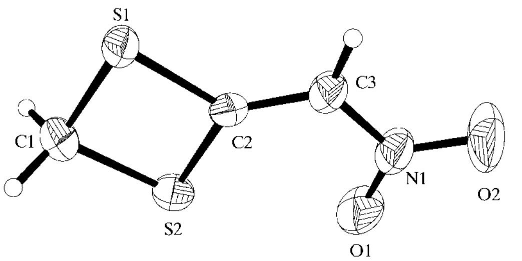


Figure 1
The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

In the solid state, compound (I) shows a hydrogen-bonding interaction between the nitro group and the olefinic H atom of an adjacent molecule to generate a dimeric structure. This structure has a close resemblance to the dimeric structure commonly encountered in aliphatic and aromatic carboxylic acids. However, in the dimeric structure of carboxylic acids, the hydrogen-bonding interactions are classical in nature, in that the interaction is of the O—H···O type, whereas in the present case, the hydrogen-bonding interactions are of the C—H···O type. The increase in the exocyclic angles and the decrease in the endocyclic angles at C2 may be due to the linearity of the molecule. The molecules are stacked along the *a* axis with a repeat distance of 3.920 (1) Å between the centroids of the four-membered rings (Fig. 2). An infinite chain is formed along the *c* axis through intermolecular S···O interactions [S1···O2(x, y, $z-1$) = 2.900 (2) Å and S2···O1($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$) = 3.077 (2) Å]. Also, an intermolecular S1···S2($x+1$, y, z) interaction of 3.639 (1) Å is observed. A similar kind of packing is observed for 2-acetonylidene-4-(dicyanomethyl)-1,3-dithietane [$C_8H_4N_2OS_2$; S···S = 3.684 (1), S···O = 3.392 (2) and S···N = 3.123 (2) Å;

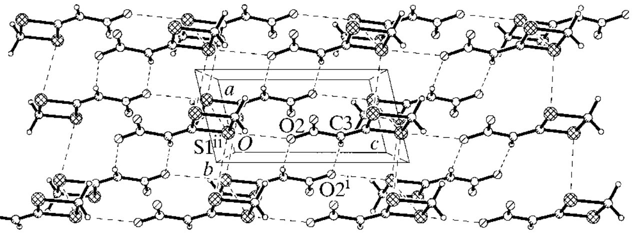


Figure 2
The packing of the title molecules showing the two-dimensional network. [Symmetry codes: (i) $1-x$, $-y$, $2-z$; (ii) x, y, $z+1$.]

Komarova *et al.*, 1990]. C—H···O interactions between the molecules of a chain result in a two-dimensional network in the (010) plane.

Experimental

To a vigorously stirred solution of the dipotassium salt of nitroketene dithioacetate (1 g, 4.7 mol) in 50% aqueous methanol (50 ml), dibromoethane (9.4 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 12 h to completion (thin-layer chromatography). It was then diluted with ice-cold water (50 ml) and the product was extracted with dichloromethane (3 × 25 ml). The organic layer was washed with brine (2 × 10 ml) and dried over anhydrous Na_2SO_4. A pinch of activated charcoal (20 mg) was added to the dichloromethane solution and subsequently filtered through a Whatmann-1 filter paper to remove the coloring impurities. The solvent was removed under reduced pressure to furnish the crude product, which was purified by column chromatography using silica gel (100–200 mesh) and eluting with hexane–ethyl acetate (99:1 to 90:10) [yield 0.2 g (20%), m.p. 382 K]. Spectral data, UV (methanol): λ_{max} 353 nm; IR (nujol): ν 3104, 2925, 2853, 1518, 1464, 1304, 1261, 929 cm^{-1}; ^1H NMR (300 MHz, 1:1 $CDCl_3$–CCl_4): δ (p.p.m.) 3.52 (*m*, 2H), 3.52 (*m*, 2H), 7.53 (*s*, 1H); ^{13}C NMR (300 MHz, 1:1, $CDCl_3$–CCl_4): δ (p.p.m.) 36.76 (C1″), 38.73 (C1′), 125.48 (C2), 165.87 (C1′).

Crystal data

$C_3H_3NO_2S_2$
$M_r = 149.18$
Monoclinic, $P2_1/n$
$a = 3.9198$ (1) Å
$b = 18.3222$ (5) Å
$c = 7.9352$ (2) Å
$\beta = 103.221$ (2)°
$V = 554.80$ (3) $Å^3$
$Z = 4$

$D_x = 1.786$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2751 reflections
$\theta = 2.22$–$28.29°$
$\mu = 0.854$ mm^{-1}
$T = 293$ (2) K
Slab, light green
0.32 × 0.20 × 0.12 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.772$, $T_{max} = 0.904$
3834 measured reflections

1359 independent reflections
1108 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 28.25°$
$h = -5 \rightarrow 3$
$k = -23 \rightarrow 24$
$l = -10 \rightarrow 10$

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.735 (2)	O1—N1	1.244 (3)
S1—C1	1.817 (2)	O2—N1	1.244 (2)
S2—C2	1.728 (2)	N1—C3	1.406 (3)
S2—C1	1.821 (2)		
C2—S1—C1	82.8 (1)	O2—N1—C3	118.5 (2)
C2—S2—C1	82.9 (1)	O1—N1—C3	119.2 (2)
O2—N1—O1	122.3 (2)	S1—C1—S2	94.00 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*A*···O2^i	0.93	2.49	3.387 (3)	163

Symmetry code: (i) $1 - x, -y, 2 - z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0384$
$wR(F^2) = 0.0994$
$S = 0.989$
1359 reflections
73 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0538P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.37$ e $Å^{-3}$
$\Delta\rho_{min} = -0.55$ e $Å^{-3}$

The H atoms were fixed at calculated distances (Csp^2—H = 0.93 Å and Csp^3—H = 0.97 Å) and were allowed to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C)$].

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1398). Services for accessing these data are described at the back of the journal.

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