Acta Cryst. (1985). C**41**, 1090–1092

1,4-Dithianium-1-bis(methoxycarbonyl)methylide,* $C_9H_{14}O_4S_2$

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(*Received* 5 *December* 1984; *accepted* 15 *March* 1985)

Abstract. $M_r = 250{\cdot}34$, $P2_1/n$, $a = 12{\cdot}942\ (4)$, $b = 10{\cdot}344\ (6)$, $c = 8{\cdot}974\ (5)$ Å, $\beta = 108{\cdot}87\ (4)°$, $V = 1137\ (1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}462$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 40{\cdot}6$ cm^{-1}, $F(000) = 528$, room temperature, $R = 0{\cdot}036$ for 1306 unique reflections. The $S^+—C^-$ distance is 1·722 (3) Å which is statistically equivalent to the average $S^+—C^-$ distance observed for a series of sulfonium ylides. The four $S^+—C(sp^3)$ distances are statistically equivalent and average 1·802 (4) Å. The 1,4-dithiane ring adopts a chair conformation and is almost perpendicular to the carbanion moiety.

Introduction. When S possesses a formal positive charge, its 3*d* orbitals are contracted, thus increasing the possibility for overlap with adjacent *s* and *p* orbitals of second- and third-row elements. Sulfoxides, sulfonium ylides and sulfilimines possess a positively charged S and an adjacent second-row element. Each of these systems offers certain advantages and disadvantages for the investigation of bonding in organosulfur compounds. Sulfoxides have a large positive charge on the S atom and are amenable to investigations of bond angles, distances, and force constants about the S. By way of contrast, sulfonium ylides (and sulfilimines) may possess more complex groups bonded to S (*e.g.* R' in $R_2S^+—C^-R'_2$). and the effects of S upon these groups can be investigated. Moreover, one may now be able to assess the rotational barriers in bonds about S (*e.g.*, $S^+—C^-$). Sulfonium ylides also are of interest since they represent particularly stable carbanions and should offer an excellent opportunity to evaluate any back-bonding into S orbitals.

As part of our continuing study of bonding in organosulfur compounds (Vicković, Watson & Ternay, 1984; Galloy, Watson, Craig, Guidry, Morgan, Ternay & Martin, 1983; Abbady, Askari, Morgan, Ternay, Galloy & Watson, 1982; Abbady, Craig, Ternay, Martin, Galloy & Watson, 1981) we have examined a number of heterocyclic sulfoxides and related sulfonium ylides. In general, we find that the O of a sulfoxide has the same conformational preference as does the methylide C of the ylides in S-containing heterocyclic analogs of 9,10-dihydroanthracene (Ternay, 1981).

In this report we describe the solid-state structure of 1,4-dithianium-1-bis(methoxycarbonyl)methylide. This mono-ylide is of interest since there are relatively few detailed studies of the stereochemistry/geometry of such systems. Moreover, sulfoxides of such heterocycles often exhibit an unusual conformational preference, one in which the sulfinyl O exists preferentially in the axial, rather than the equatorial, conformation.

Experimental. A large crystal ground into an ellipsoid of dimensions 0·2 × 0·2 × 0·3 mm was mounted on a Syntex $P2_1$ diffractometer; data collected using a θ:2θ scan; $\Delta\theta_{\max} = 119°$; graphite-monochromated radiation; lattice parameters from least-squares refinement of 15 reflections ($10{\cdot}59° \le 2\theta \le 27{\cdot}14°$); angles measured by a centering routine associated with the diffractometer; systematic absences ($0k0$ $k = 2n + 1$, $h0l$ $h + l = 2n + 1$) consistent with space group $P2_1/n$ (non-standard space group selected for convenience); a monitored reflection (220) showed no change in intensity greater than $2\sigma(I)$; 1418 independent reflections measured ($0 \le h \le 11$, $0 \le k \le 11$, $-9 \le l \le 9$) with 1306 intensities greater than $3\sigma(I)$; Lorentz and polarization corrections applied; absorption corrections applied (spherical shape assumed and equivalent distances and angles analyzed for effectiveness of correction); direct methods (*MULTAN*78: Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) revealed all nonhydrogen atoms; H-atom positions obtained from a subsequent difference Fourier synthesis and included in the full-matrix least-squares refinement; $\sum w(|F_o| - |F_c|)^2$ minimized; $w = 1/\sigma^2(F_o)$ from counting statistics; 192 parameters refined using 1306 reflections; final $R = 0{\cdot}036$, $wR = 0{\cdot}041$, $S = 3{\cdot}2$, $(\Delta/\sigma)_{\mathrm{avg}} = 0{\cdot}13$, $(\Delta/\sigma)_{\max} = 0{\cdot}68$ (thermal parameter); highest peak in final difference map 0·55 e Å^{-3} located near S atom; all calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976); atomic scattering factors for C, S and O those of Cromer & Mann (1968), those for H from Stewart,

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[*] IUPAC name: 1,4-dithianylium-1-[bis(methoxycarbonyl)]-methanide.

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0108-2701/85/071090-03$01.50

Davidson & Simpson (1965); scattering factors were corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). No correction for secondary extinction.

Discussion. Table 1 lists atomic positional parameters and U_{eq} values; Table 2 gives interatomic distances, valence angles and torsion angles.*

Table 1. *Atomic positional coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^2$)

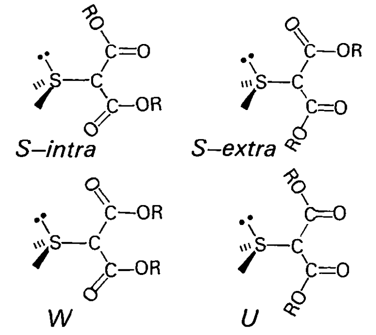
$$U_{eq} = \tfrac{1}{3}[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha].$$

	x	*y*	*z*	U_{eq}
S(1)	726 (1)	2179 (1)	5074 (1)	31 (1)
C(2)	−108 (3)	2427 (4)	3054 (4)	39 (1)
C(3)	−400 (3)	1122 (4)	2220 (4)	43 (2)
S(4)	757 (1)	337 (1)	1920 (1)	46 (1)
C(5)	1620 (4)	157 (4)	3933 (5)	47 (2)
C(6)	1920 (3)	1429 (4)	4824 (5)	44 (2)
C(7)	1117 (3)	3661 (3)	5948 (4)	33 (2)
C(8)	771 (3)	3963 (3)	7274 (4)	34 (2)
O(9)	1079 (2)	4843 (3)	8191 (3)	47 (1)
O(10)	18 (2)	3098 (2)	7438 (3)	44 (1)
C(11)	1698 (3)	4515 (3)	5242 (4)	36 (2)
O(12)	1944 (2)	4289 (3)	4072 (3)	47 (2)
O(13)	1976 (2)	5653 (2)	6033 (3)	44 (1)
C(14)	−346 (4)	3317 (4)	8775 (5)	59 (3)
C(15)	2525 (4)	6570 (4)	5342 (5)	52 (2)

Table 2. *Interatomic distances* (Å), *valence angles* (°) *and selected torsion angles* (°)

S(1)—C(2)	1·803 (3)	C(8)—O(9)	1·205 (4)
S(1)—C(6)	1·807 (5)	C(8)—O(10)	1·366 (5)
S(1)—C(7)	1·722 (3)	O(10)—C(14)	1·442 (6)
C(2)—C(3)	1·530 (6)	C(7)—C(11)	1·434 (6)
C(3)—S(4)	1·799 (4)	C(11)—O(12)	1·214 (5)
S(4)—C(5)	1·800 (4)	C(11)—O(13)	1·362 (4)
C(5)—C(6)	1·523 (6)	O(13)—C(15)	1·440 (6)
C(7)—C(8)	1·435 (6)		
C(2)S(1)C(6)	101·2 (2)	C(8)C(7)C(11)	125·5 (3)
C(2)S(1)C(7)	108·9 (2)	C(7)C(8)O(9)	127·4 (4)
C(6)S(1)C(7)	107·6 (2)	C(7)C(8)O(10)	111·8 (3)
S(1)C(2)C(3)	109·8 (3)	O(9)C(8)O(10)	120·7 (4)
C(2)C(3)S(4)	112·7 (3)	C(8)O(10)C(14)	115·1 (3)
C(3)S(4)C(5)	100·0 (2)	C(7)C(11)O(12)	125·8 (3)
S(4)C(5)C(6)	114·0 (3)	C(7)C(11)O(13)	113·0 (3)
C(5)C(6)S(1)	110·7 (3)	O(12)C(11)O(13)	121·2 (4)
S(1)C(7)C(8)	116·6 (3)	C(11)O(13)C(15)	115·4 (3)
S(1)C(7)C(11)	117·8 (3)		
S(1)C(2)C(3)S(4)	−69·7 (3)	S(1)C(7)C(8)O(9)	168·2 (3)
C(2)C(3)S(4)C(5)	61·0 (3)	S(1)C(7)C(8)O(10)	−10·9 (4)
C(3)S(4)C(5)C(6)	−59·6 (3)	S(1)C(7)C(11)O(12)	0·0 (4)
S(4)C(5)C(6)S(1)	66·4 (3)	S(1)C(7)C(11)O(13)	−179·4 (2)
C(5)C(6)S(1)C(2)	−61·3 (3)	C(7)C(8)O(10)C(14)	178·3 (3)
C(6)S(1)C(2)C(3)	63·0 (3)	C(7)C(11)O(13)C(15)	−177·7 (3)
C(3)C(2)S(1)C(7)	176·1 (3)	O(9)C(8)C(7)C(11)	−15·8 (6)
C(5)C(6)S(1)C(7)	−175·4 (3)	C(8)C(7)C(11)O(12)	−176·0 (3)
C(2)S(1)C(7)C(8)	119·1 (3)	C(8)C(7)C(11)O(13)	4·6 (5)
C(6)S(1)C(7)C(11)	51·7 (3)	C(11)C(7)C(8)O(10)	165·1 (3)

Fig. 1 is an *ORTEP* (Johnson, 1971) drawing of the title compound. The malonylide fragment of ylides of this type may adopt several conformations. Using the carbonyl O atoms as reference, these may be described as *W, S* and *U*.



As can be seen, there are two possible *S* arrays. In one, (*'intra'*) one carbonyl O resides *trans* to the nonbinding S electron pair. In the other (*'extra'*) an alkoxy group's O is *trans* to that nonbonding electron pair. The title compound, like many other ylides which we have studied, adopts the *S-intra* conformation. The S adopts a flattened tetrahedral geometry which can be described as a distorted trigonal bipyramid if the nonbonding O is included in the coordination sphere. This approximates the environment of many hypervalent S compounds and permits one nonbonding electron pair of the O to be directed *trans* to the S lone-pair electrons, *i.e.* toward the positive end of the dipole.

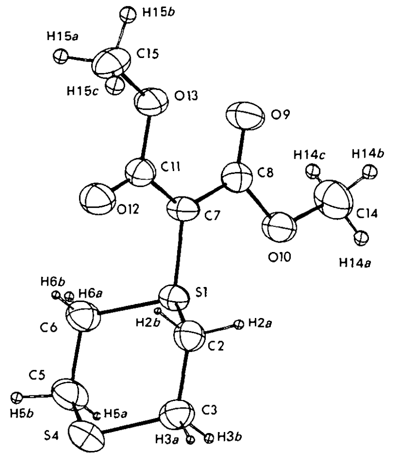


Fig. 1. *ORTEP* drawing of 1,4-dithianium-1-bis(methoxycarbonyl)-methylide. The thermal ellipsoids are drawn at the 35% probability level. H atoms are shown as spheres of arbitrary radius.

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* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42126 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The S^+—C^- distance of 1·722 (3) Å is statistically equivalent to the 1·718 (8) Å average value observed for a series of sulfonium ylides. The ylide S is 0·688 (3) Å out of the plane of the three attached C atoms. The malonylide moiety shows significant deviations from planarity with O(9) being out of the least-squares plane by 0·23 (1) Å, and torsion angles within the group deviating by more than 15° from the planar values of 0 and 180°. This may be associated with the two closest intermolecular contacts of $O(9)\cdots H(2a)(-x, 1-y, 1-z) = 2{\cdot}64\ (4)$ and $O(9)\cdots H(6a)(0{\cdot}5-x, 0{\cdot}5+y, 0{\cdot}75-z) = 2{\cdot}32\ (4)$ Å. The carbanion exhibits the usual orientation with the π system being essentially perpendicular to the S lone pair. This leads to $O(9)\cdots O(13)$, $O(10)\cdots S^+$, and $O(12)\cdots S^+$ intramolecular distances of 2·693 (4), 2·739 (3), and 2·996 (4) Å, respectively.

The dithiane fragment adopts a chair conformation, and the smaller C—S—C angles lead to torsion angles larger than those observed in cyclohexane. The two S^+—$C(sp^3)$ distances of 1·805 (3) Å are statistically equivalent to the two S—$C(sp^3)$ distances of 1·800 (3) Å indicating little net effect of the positive charge. Literature values for $C(sp^3)$—S distances in 1,3- and 1,4-dithianes range from 1·785 to 1·836 Å (Kalff & Romers, 1965, 1966; McPhail, Onan & Koshimies, 1976; Carey, Smith, Mahen & Bryen, 1977; Kobayashi & Iitaka, 1977; Bukowska-Strzyżewska & Pniewska, 1979; Dobrowolska & Bukowska-Strzyżewska, 1980). The variation is partially associated with the location of the S atoms in the chair and boat conformations. It is interesting to compare these results to those for the corresponding mono-ylide of thianthrene, which also adopts the *S-intra* conformation in the solid state (Ternay, Baack, Chu, Napoleone, Martin & Alfaro, 1982). In this mono-ylide the six-membered ring is in a boat conformation and possesses two types of S—$C(sp^2)$ bonds. The bond distances are marginally not equivalent. The bonds to the positively charged S are longer [1·790 (5) and 1·785 (5) Å] than those to the neutral (*i.e.,* sulfide) S [1·767 (5) and 1·778 (5) Å].

The preferred conformation of the sulfinyl O in 1,4-oxathiane *S*-oxide (Frieze & Evans, 1975), thiane *S*-oxide (Lambert & Kreske, 1966) and *trans*-1,4-dithiane 1,4-dioxide (Shearer, 1959; Chen & LeFevre, 1963) is axial. It has been suggested that this is due to specific attractive interactions in axial sulfoxides (Allinger, Hirsch, Miller & Tyminski, 1969). Zefirov (1975), on the other hand, has discussed this phenomenon in terms of 'long-range' (orbital) interactions. In contrast the present X-ray analysis indicates that the methylide C prefers the equatorial conformation. Thus, either the attractive interactions discussed by Allinger are absent or they are overwhelmed by repulsive interactions in the axial conformer. If Zefirov's analysis of the factors controlling conformation is correct, the steric repulsions in the axial geometry outweigh orbital stabilization.

Whatever the reason(s), this system (unlike phenothiazines, thioxanthenes, and similar heterocycles) is one where the sulfoxides and malonylide-based sulfonium ylides do not have the same conformational preference.

We thank the Robert A. Welch Foundation (Y484) and the TCU Research Foundation for their financial support.

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