

## ORGANIC COMPOUNDS

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## Diallyl Sulfide and Diallyl Disulfide

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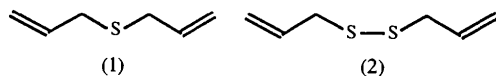
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## Abstract

Single crystals of diallyl sulfide,  $C_6H_{10}S$ , and diallyl disulfide,  $C_6H_{10}S_2$ , were grown in capillaries at low temperature using zone-melting techniques. The molecular and crystal structures of these compounds were determined at 143 and 168 K, respectively.

## Comment

Because of the tightness and regularity in the arrangement of molecules in a crystal lattice, reaction in the solid state often occurs more efficiently and selectively than reaction in solution (Toda, 1995). Our interest is the structural investigation of small unsaturated molecules that pack in a way allowing topochemical reactions in which all elementary steps proceed under crystal lattice control (Schmidt, 1976). In this paper, we present the results of X-ray structural analyses of the sulfur-containing compounds diallyl sulfide, (1), and diallyl disulfide, (2), both of which seem to be good candidates for photochemical reactions under topochemical conditions.



In the molecule of diallyl sulfide (Fig. 1), the central S atom is located at a center of symmetry. The C—S—C angle is  $100.61(2)^\circ$ . The  $C_{sp^2}$ — $C_{sp^2}$  distance of  $1.312(2) \text{ \AA}$  is in the range of typical double-bond lengths [ $1.289(3) \text{ \AA}$ ; Cambridge Structural Database, Version 2.15 of October 1996 (Allen & Kennard, 1993)]. Planes passing through atoms C1—C2—C3 and C1\*—C2\*—C3\* are oriented nearly parallel to one another [dihedral angle  $13.3(2)^\circ$ ] and both are almost perpendicular to the C—S—C plane [dihedral angle  $81.0(1)^\circ$ ]. The packing of diallyl sulfide seems to satisfy the topochemical postulates. There are two sets of parallel-lying double bonds with intermolecular distances of  $4.029$  and  $4.099 \text{ \AA}$ . It should, however, be pointed out that there are even shorter intermolecular distances of  $3.500$  and  $3.604 \text{ \AA}$  observed. These short distances,

however, are between non-parallel-lying double bonds and thus exclude the possibility of photochemical reactions of these bonds under topochemical conditions. Furthermore, short intramolecular distances between almost parallel terminal double bonds ( $3.984$  and  $3.989 \text{ \AA}$ ) suggest that a competing intramolecular photochemical reaction cannot be ruled out (see Fig. 2).

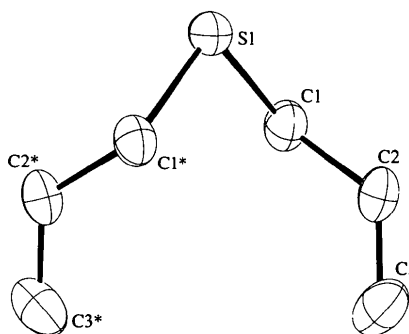


Fig. 1. View of the molecule of diallyl sulfide showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

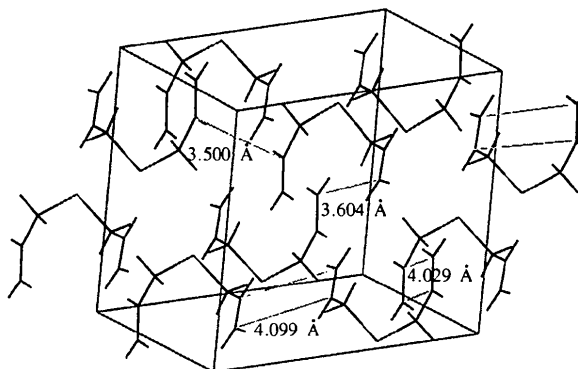


Fig. 2. Packing of diallyl sulfide.

Diallyl disulfide (Fig. 3) is not located at a crystallographic symmetry element. The C—S bonds of  $1.830(2)$  and  $1.837(2) \text{ \AA}$  are significantly longer than the C—S bonds in (1) [ $1.815(1) \text{ \AA}$ ] and the S—C—C angle is wider [ $113.0(1)^\circ$ ] than that observed in diallyl sulfide [ $112.1(1)^\circ$ ]. The S—S distance of  $2.032(1) \text{ \AA}$  and the average  $C_{sp^2}$ — $C_{sp^2}$  distance of  $1.304 \text{ \AA}$  lie in the range of typical sulfur—sulfur and terminal double-bond lengths ( $2.032$  and  $1.289 \text{ \AA}$ ; Allen *et al.*, 1987). If we define plane1 as passing through C11—S1—S2 and plane2 as passing through S1—S2—C21 then these planes are oriented nearly perpendicular to one another [dihedral angle  $89.0(1)^\circ$ ] and perpendicular to the plane composed of atoms C11—C13, C21—C23 [the dihedral angles are  $85.9(2)$  and  $81.2(3)^\circ$ , respectively]. Similar to di-

allyl sulfide, diallyl disulfide packs in a way that satisfies topochemical postulates. In the unit cell, sets of parallel-lying double bonds are observed. The shortest observed distances between them are 3.853 and 4.062 Å. At this point, it should be noted that similar to diallyl sulfide, there are even shorter intermolecular distances of 3.828 Å. These bonds, however, are oriented in a way which does not allow photochemical reaction under topochemical conditions.

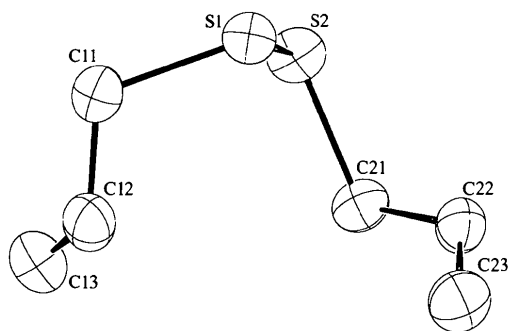


Fig. 3. View of the molecule of diallyl disulfide showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 50% probability level.

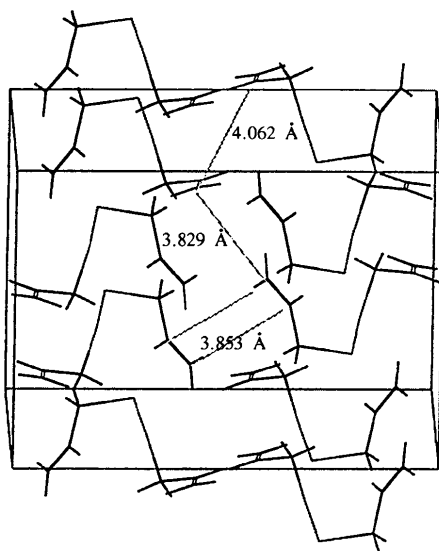


Fig. 4. Packing of diallyl disulfide.

## Experimental

Diallyl sulfide and diallyl disulfide were grown by a zone-melting technique in a capillary of outer diameter 0.3 mm using a CO<sub>2</sub>-laser beam as heat source (Boese & Nussbaumer, 1994).

### Compound (1)

#### Crystal data

C<sub>6</sub>H<sub>10</sub>S  
M<sub>r</sub> = 114.20

Mo Kα radiation  
λ = 0.71069 Å

Monoclinic

C2/c

a = 11.1118 (13) Å

b = 10.3425 (11) Å

c = 6.219 (2) Å

β = 103.75 (2)°

V = 694.2 (3) Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.093 Mg m<sup>-3</sup>

D<sub>m</sub> not measured

Cell parameters from 25 reflections

θ = 10.42–26.69°

μ = 0.350 mm<sup>-1</sup>

T = 143 K

Cylinder

0.6 × 0.2 × 0.2 mm

Colorless

#### Data collection

Enraf–Nonius CAD-4 diffractometer

ω–2θ scans

Absorption correction: none

789 measured reflections

789 independent reflections

751 reflections with

I > 2σ(I)

θ<sub>max</sub> = 27.35°

h = -7 → 8

k = -9 → 9

l = 0 → 9

3 standard reflections

frequency: 30 min

intensity decay: 10%

#### Refinement

Refinement on F<sup>2</sup>

R(F) = 0.0395

wR(F<sup>2</sup>) = 0.0998

S = 1.248

789 reflections

53 parameters

All H atoms refined

w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.056P)<sup>2</sup>

+ 0.1509P]

where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.242 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.661 e Å<sup>-3</sup>

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) for (1)

$$U_{eq} = (1/3) \sum_i \sum_j U^{ij} a_i^* a_j^*$$

	x	y	z	U <sub>eq</sub>
C1	0.06100 (12)	0.28454 (12)	0.0779 (2)	0.0319 (3)
C2	0.17179 (11)	0.21366 (13)	0.2058 (2)	0.0340 (3)
C3	0.1777 (2)	0.0882 (2)	0.2376 (3)	0.0466 (4)
S1	0	0.39658 (4)	1/4	0.0366 (2)

Table 2. Selected geometric parameters (Å, °) for (1)

C1—C2	1.490 (2)	C2—C3	1.312 (2)
C1—S1	1.8144 (13)		
C2—C1—S1	112.13 (9)	C3—C2—C1	124.93 (13)

### Compound (2)

#### Crystal data

C<sub>6</sub>H<sub>10</sub>S<sub>2</sub>

M<sub>r</sub> = 146.26

Monoclinic

P2<sub>1</sub>/n

a = 5.3456 (12) Å

b = 13.940 (3) Å

c = 10.8447 (10) Å

β = 96.152 (13)°

V = 803.5 (3) Å<sup>3</sup>

Z = 4

D<sub>x</sub> = 1.209 Mg m<sup>-3</sup>

D<sub>m</sub> not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 25 reflections

θ = 12.99–24.82°

μ = 0.567 mm<sup>-1</sup>

T = 168 K

Cylinder

0.6 × 0.2 × 0.2 mm

Colorless

## Data collection

Enraf–Nonius CAD-4 diffractometer  
 $\theta_{\max} = 27.39^\circ$   
 $h = -6 \rightarrow 6$   
 $k = 0 \rightarrow 18$   
 $l = 0 \rightarrow 13$   
 Absorption correction: none  
 1812 measured reflections  
 1812 independent reflections  
 1634 reflections with  $I > 2\sigma(I)$   
 3 standard reflections  
 frequency: 30 min  
 intensity decay: 10%

## Refinement

Refinement on  $F^2$   
 $R(F) = 0.0498$   
 $wR(F^2) = 0.1355$   
 $S = 1.101$   
 1812 reflections  
 113 parameters  
 All H atoms refined  
 $w = 1/[\sigma^2(F_o^2) + (0.1049P)^2 + 0.1396P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.766 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.733 \text{ e } \text{Å}^{-3}$   
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ ) for (2)

$$U_{eq} = (1/3)\sum_i\sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
C11	0.5820 (4)	0.83649 (14)	0.9424 (2)	0.0377 (4)
C12	0.5490 (5)	0.8573 (2)	1.0738 (2)	0.0440 (5)
C13	0.3679 (7)	0.9086 (2)	1.1091 (3)	0.0602 (7)
C21	0.1651 (4)	0.6497 (2)	1.0875 (2)	0.0377 (4)
C22	0.3244 (4)	0.56510 (14)	1.1197 (2)	0.0412 (5)
C23	0.5286 (5)	0.5670 (2)	1.1986 (2)	0.0486 (5)
S1	0.53204 (8)	0.71000 (3)	0.90186 (4)	0.0336 (2)
S2	0.16519 (8)	0.68598 (4)	0.92458 (4)	0.0367 (2)

Table 4. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ ) for (2)

C11—C12	1.483 (3)	C21—S2	1.837 (2)
C11—S1	1.830 (2)	C22—C23	1.313 (3)
C12—C13	1.295 (4)	S1—S2	2.0303 (8)
C21—C22	1.475 (3)		
C12—C11—S1	112.97 (14)	C23—C22—C21	123.8 (2)
C13—C12—C11	124.2 (2)	C11—S1—S2	104.33 (7)
C22—C21—S2	112.84 (14)	C21—S2—S1	105.17 (7)

An absorption correction was not applied because  $\mu$  was small for both compounds. A correction was applied to both compounds for 10% decay. The structures were solved by direct methods (*SHELXS86*; Sheldrick, 1990) and refined by full-matrix least squares where the quantity minimized was  $[\sum(F_o - F_c)^2]$  (*SHELXL93*; Sheldrick, 1993). The H atoms were refined using a riding model.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *DATAP* (Coppens, Leiserowitz & Rabinovich, 1965); molecular graphics: *ORTEPII* (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1003). Services for accessing these data are described at the back of the journal.

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## Tetravinylsilane

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## Abstract

A single crystal of tetravinylsilane, C<sub>8</sub>H<sub>12</sub>Si, was grown in a capillary at low temperature using zone-melting techniques. Intensity data were collected at 95 K. The title compound crystallizes in space group *Pbca* with one molecule in the asymmetric unit.

## Comment

The structure of the title compound is of interest for the synthesis of new silicon-containing materials, for example, dendrimers and polymers (Seyferth, Son, Rheingold & Ostrander, 1994). We have investigated the structure of tetravinylsilane, (I), in order to determine whether it is a suitable candidate for solid-state photochemistry (Schmidt, 1976).

