

## 2,4,6-Tris(methylthio)-1,3,5-triazine, 3-methyl-4,6-bis(methylthio)-1,3,5- triazine-2(3*H*)-thione, 1,3-dimethyl-4- methylthio-1,3,5-triazine-2,6(1*H*,3*H*)- dithione and 1,3,5-trimethyl-1,3,5- triazine-2,4,6(1*H*,3*H*,5*H*)-trithione

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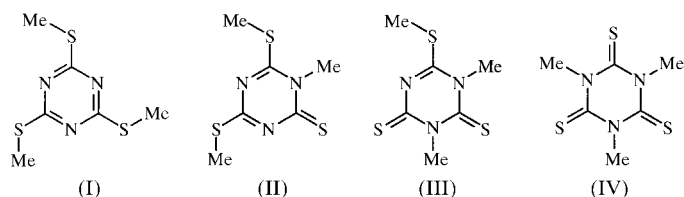
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The crystal structures of four isomers of  $C_6H_9N_3S_3$  were determined. Their molecules tend to be planar, but the tendency is weakened when the number of formal  $N=C$  double bonds in the ring decreases. The structures of the triazine rings in the four compounds were found to be similar to their oxy analogues. All of the compounds form planar layer structures with similar interlayer spacing ranging from 3.41 to 3.60 Å. The molecular packing of each isomer is controlled by weak van der Waals interactions.

### Comment

The crystal structures and thermal stability of trimethyl-substituted derivatives of mono-, di-, and trithiocyanuric acids have been studied in relation to the tendency of some of these compounds to undergo methyl rearrangements in the solid or liquid state (Paoloni *et al.*, 1968; Tosato, 1982, 1984; Kaftory & Handelsman-Benory, 1994; Handelsman-Benory *et al.*, 1995). The order of the methyl rearrangements in the oxygen analogues of the title compounds is (I<sub>o</sub>)→(II<sub>o</sub>)→(III<sub>o</sub>)→(IV<sub>o</sub>), and the reactions take place in the liquid or in the solid state. The corresponding sulfur compounds display an opposite tendency to methyl rearrangements:



(IV)→(III)→(II)→(I) and none of the reactions take place in the solid state (see Figs. 1–4).

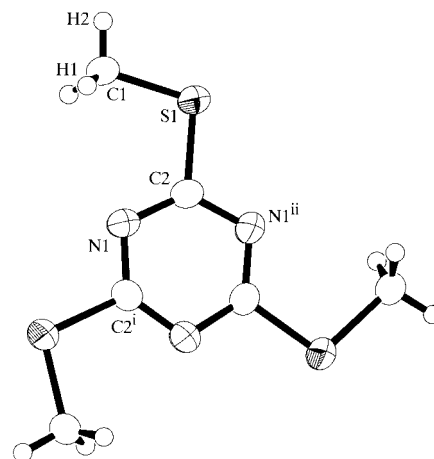


Figure 1

ORTEP (Johnson, 1976) drawing of (I) showing atomic numbering [symmetry codes: (i)  $-x + y, -x, z$ ; (ii)  $-y, x - y, z$ ]. Ellipsoids of atomic displacement for non-H atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radius.

There are three molecules of (III) and two of (IV) in the asymmetric unit. No statistically significant differences in the values of bond lengths and angles were found.

Molecules of (I) and (II) lie in crystallographic mirror planes and molecules of (I) have threefold symmetry. Their planarity can be explained by an effective conjugation of  $N=C$  double bonds resulting from six and five pure  $sp^2$  hybridized atoms in the rings, respectively. On the other hand, r.m.s. deviations of the ring mean planes are 0.0075, 0.0142 and 0.0198 Å for the crystallographically independent molecules of (III) and 0.0391 and 0.0400 Å for (IV) (see Table 1). It should be noted that the molecules of trimethyl-substituted derivatives of cyanuric acid, the oxy analogues of compounds (I), (II) and (III) (Glowka & Iwanicka, 1989; Handelsman-Benory *et al.*, 1995), are planar with r.m.s. deviations of the ring mean plane less than 0.01 Å. In molecules of the oxy analogue of (IV), the deviations are 0.0084 and 0.0145 Å for two crystallographically independent molecules (Thalladi *et*

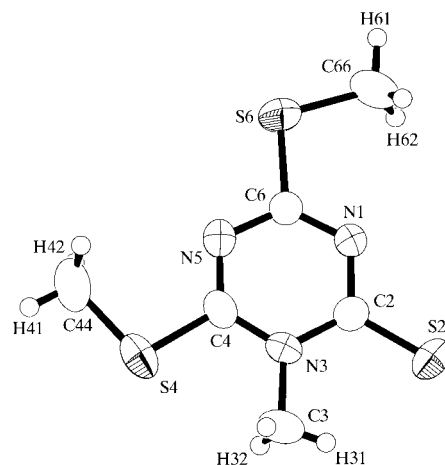


Figure 2

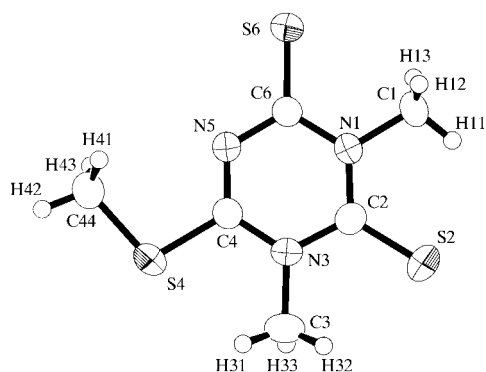
ORTEP (Johnson, 1976) drawing of (II) showing atomic numbering. Ellipsoids of atomic displacement for non-H atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radius.

*al.*, 1998). In general, the planarity of the triazine ring decreases with an increase in the number of S atoms adjacent to methyl groups [such as in (III) and (IV)]. This tendency is a result of steric repulsion between the methyl group and the S atom, which is more pronounced than that in the oxy analogues.

From their work on *s*-triazine derivatives, Glowka & Iwanicka (1989) concluded that the endocyclic bond angles at all N atoms are less than  $120^\circ$  while those at the C atoms are larger than  $120^\circ$ , irrespective of their hybridization. However, from the crystal structures of the title compounds it was found that whenever there is no formally endocyclic double bond at the particular atoms, the above conclusion does not hold. Bond angles at the  $Nsp^3$  atoms range from  $119.5(2)$  to  $126.1(4)^\circ$  and at the  $Csp^2$  atom (as thiocarbonyl) from  $113.6(4)$  to  $118.2(2)^\circ$ .

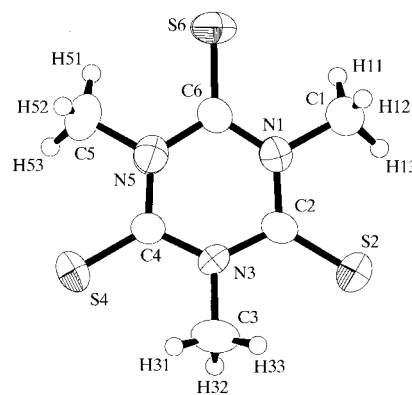
HF/6-31G\*(*d,p*) *ab initio* calculations (Greenberg & Kaftory, 2000) with full optimization of the molecular geometry of (I) and its mono-, di- and trioxo analogues reveals that the alternation of the C–N bond lengths observed in the oxy compound (I<sub>O</sub>) (Krygowski, Howard *et al.*, 1997) also holds in the thio analogues. The C–N bonds that are *cis* to a methoxy or to a methylthio group are *ca*  $0.015 \text{ \AA}$  shorter than the bonds that are *trans* to these groups. Krygowski, Wisiorowski *et al.* (1997) explain this phenomenon as a result of the ‘angular substituent effect’ that enhances double-bond character of the adjacent C–N bond *cis* to these groups. This effect was found to be additive and supports the experimental results whereby all the methoxy (or methylthio) groups bend in the same sense (all clockwise or all anticlockwise).

The effect of replacing the O atoms by S atoms on the geometries within the rings is minimal (see Table 1). However, the bond-length alternation in (II) reveals that conjugation between the two C=N bonds is preferable to conjugation of C=N with C=S. Therefore, the C<sub>6</sub>–N<sub>5</sub> bond is shorter [ $1.341(5) \text{ \AA}$ ] than C<sub>2</sub>–N<sub>1</sub> [ $1.359(5) \text{ \AA}$ ]. The ring structure of (III) shows that since the C<sub>6</sub>=S<sub>6</sub> bond is strongly conjugated with C<sub>4</sub>=N<sub>5</sub>, the lone pair at N<sub>1</sub> prefers conjugation with C<sub>2</sub>=S<sub>2</sub> to that with C<sub>6</sub>=S<sub>6</sub>. As a result, the C<sub>2</sub>–N<sub>1</sub> bond [ $1.375(3) \text{ \AA}$ ] is shorter than C<sub>6</sub>–N<sub>1</sub> [ $1.394(3) \text{ \AA}$ ].



**Figure 3**  
ORTEPII (Johnson, 1976) drawing of one independent molecule (A) of (III) showing atomic numbering. Ellipsoids of atomic displacement for non-H atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radius.

In spite of the fact that the isomers crystallize in different crystallographic systems, all of them form planar layer structures with similar interlayer spacing in the range of  $3.41$  to  $3.60 \text{ \AA}$ , approximately twice the van der Waals radius of sulfur. For all four compounds the interlayer distances are  $0.12$ – $0.22 \text{ \AA}$  longer than those of the corresponding oxy analogues (see Table 1). The molecular volume in all four compounds lies in a relatively narrow range of  $238$ – $252 \text{ \AA}^3$ . The crystal packings all show no abnormally short intermolecular contacts, either within or between the layers. It can be concluded that the crystal arrangements of all the isomers are controlled by weak van der Waals bonds.



**Figure 4**  
ORTEPII (Johnson, 1976) drawing of one independent molecule (A) of (IV) showing atomic numbering. Ellipsoids of atomic displacement for non-H atoms are drawn at the 50% probability level. H atoms are drawn as small circles of arbitrary radius.

## Experimental

The title compounds were synthesized by methylation of trithiocyanuric acid with diazomethane according to the method of Tosato & Paoloni (1966). Crystals of (I) were obtained from a chloroform solution, crystals of (II) and (III) from ethyl acetate solutions and crystals of (IV) from ethanol by slow evaporation of the solvent at room temperature.

### Compound (I)

#### Crystal data

$C_6H_9N_3S_3$   
 $M_r = 219.34$   
Hexagonal,  $P6_3/m$   
 $a = 8.898(2) \text{ \AA}$   
 $V = 476.3(2) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.529 \text{ Mg m}^{-3}$   
Mo  $K\alpha$  radiation

Cell parameters from 25 reflections  
 $\theta = 2.6$ – $12.0^\circ$   
 $\mu = 0.726 \text{ mm}^{-1}$   
 $T = 293(2) \text{ K}$   
Hexagonal prism, colourless  
 $0.20 \times 0.14 \times 0.12 \text{ mm}$

#### Data collection

Philips PW1100 four-circle diffractometer  
 $\omega/2\theta$  scans  
1053 measured reflections  
313 independent reflections  
226 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.084$

$\theta_{max} = 25.01^\circ$   
 $h = 0 \rightarrow 10$   
 $k = -10 \rightarrow 9$   
 $l = -8 \rightarrow 0$   
3 standard reflections  
frequency: 120 min  
intensity decay: none

**Table 1**Comparison of geometrical parameters ( $\text{\AA}$ ,  $^\circ$ ) of the title compounds and their oxy analogues.Oxy analogues are indicated by a subscript *O*. The s.u. of the mean for all bonds and angles does not exceed 0.01  $\text{\AA}$  and 1 $^\circ$ , respectively.

	(I)	(I <sub>O</sub> ) <sup>b,c</sup>	(II)	(II <sub>O</sub> ) <sup>e</sup>	(III)	(III <sub>O</sub> ) <sup>e</sup>	(IV)	(IV <sub>O</sub> ) <sup>f,c</sup>
N1—C2	1.335 (5)	1.312 (4)	1.359 (5)	1.378 (5)	1.375 (3)	1.370 (4)	1.390 (7)	1.374 (4)
N1—C6 <sup>a</sup>	1.344 (5)	1.339 (4)	1.309 (5)	1.299 (4)	1.394 (3)	1.392 (5)	( <i>d</i> )	( <i>d</i> )
N3—C2	—	( <i>d</i> )	1.386 (5)	1.412 (5)	1.390 (3)	1.382 (4)	( <i>d</i> )	( <i>d</i> )
N3—C4	—	( <i>d</i> )	1.356 (6)	1.349 (4)	1.371 (3)	1.364 (5)	( <i>d</i> )	( <i>d</i> )
N5—C4	—	( <i>d</i> )	1.315 (5)	1.310 (4)	1.297 (3)	1.284 (4)	( <i>d</i> )	( <i>d</i> )
N5—C6	—	( <i>d</i> )	1.341 (5)	1.352 (4)	1.364 (3)	1.365 (5)	( <i>d</i> )	( <i>d</i> )
C6—N1—C2 <sup>a</sup>	112.8 (5)	113.3 (3)	116.9 (3)	117.3 (3)	123.4 (2)	123.4 (3)	124.6 (4)	124.2 (3)
C2—N3—C4	—	( <i>d</i> )	120.0 (3)	118.4 (3)	120.0 (2)	118.6 (3)	( <i>d</i> )	( <i>d</i> )
C4—N5—C6	—	( <i>d</i> )	114.7 (3)	113.5 (3)	119.4 (2)	118.2 (3)	( <i>d</i> )	( <i>d</i> )
N1—C2—N3 <sup>a</sup>	127.2 (5)	126.6 (3)	118.0 (3)	117.4 (3)	115.1 (2)	115.6 (3)	115.0 (4)	115.7 (3)
N3—C4—N5	( <i>d</i> )	( <i>d</i> )	122.4 (4)	124.9 (3)	123.9 (2)	126.1 (3)	( <i>d</i> )	( <i>d</i> )
N5—C6—N1	( <i>d</i> )	( <i>d</i> )	128.1 (4)	128.5 (3)	118.0 (2)	118.0 (3)	( <i>d</i> )	( <i>d</i> )
R.m.s. of out-of-plane displacements	0	0	0	0.0039 0.0083	0.0075 0.0142 0.0198	0.0088	0.0391 0.0400	0.0084 0.0145
Interlayer spacing	3.474	3.260	3.407	3.241	3.571	3.347	3.601	3.486

Notes: (*a*) for (I), C6 is C2<sup>i</sup> and N3 is N1<sup>ii</sup> [symmetry codes: (i)  $-x + y, -x, z$ ; (ii)  $-y, x - y, z$ ]; (*b*) from Krygowski, Howard *et al.* (1997); (*c*) the s.u. values were estimated on the basis of data from the Cambridge Structural Database; (*d*) chemically equivalent bonds and angles were averaged; (*e*) from Kafory & Handelsman-Benory (1994); (*f*) from Thalladi *et al.* (1998).

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.088$   
 $S = 1.029$   
 313 reflections  
 31 parameters  
 Only coordinates of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.0347P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.20 \text{ e \AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient: 0.033 (6)

**Compound (II)****Crystal data**

C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>S<sub>3</sub>  
 $M_r = 219.34$   
 Orthorhombic, *Pnma*  
 $a = 16.566 (6) \text{ \AA}$   
 $b = 6.813 (2) \text{ \AA}$   
 $c = 8.926 (3) \text{ \AA}$   
 $V = 1007.4 (6) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.446 \text{ Mg m}^{-3}$

**Data collection**

Philips PW1100 four-circle diffractometer  
 $\omega/2\theta$  scans  
 2410 measured reflections  
 970 independent reflections  
 732 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.060$

Mo  $K\alpha$  radiation  
 Cell parameters from 25 reflections  
 $\theta = 2.5\text{--}18.2^\circ$   
 $\mu = 0.687 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Plate, light yellow  
 $0.32 \times 0.29 \times 0.05 \text{ mm}$   
 $\theta_{\max} = 25.01^\circ$   
 $h = -19 \rightarrow 19$   
 $k = -8 \rightarrow 0$   
 $l = -10 \rightarrow 10$   
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.117$   
 $S = 1.051$   
 970 reflections  
 83 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 0.3375P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.22 \text{ e \AA}^{-3}$

**Compound (III)****Crystal data**

C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>S<sub>3</sub>  
 $M_r = 219.34$   
 Triclinic, *P1*  
 $a = 9.618 (5) \text{ \AA}$   
 $b = 11.435 (6) \text{ \AA}$   
 $c = 13.910 (7) \text{ \AA}$   
 $\alpha = 107.30 (5)^\circ$   
 $\beta = 100.65 (5)^\circ$   
 $\gamma = 93.05 (5)^\circ$   
 $V = 1425.9 (2) \text{ \AA}^3$

$Z = 6$   
 $D_x = 1.533 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 5974 reflections  
 $\theta = 2.17\text{--}27.48^\circ$   
 $\mu = 0.728 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Trigonal prism, yellow  
 $0.30 \times 0.15 \times 0.10 \text{ mm}$

**Data collection**

Nonius KappaCCD diffractometer  
 $\varphi$  scans  
 21286 measured reflections  
 5970 independent reflections  
 4595 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.019$   
 $\theta_{\max} = 27.48^\circ$   
 $h = 0 \rightarrow 12$   
 $k = -14 \rightarrow 14$   
 $l = -16 \rightarrow 16$

**Refinement**

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.044$   
 $wR(F^2) = 0.129$   
 $S = 1.065$   
 5970 reflections  
 334 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 0.5239P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 0.38 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

**Compound (IV)****Crystal data**

C<sub>6</sub>H<sub>9</sub>N<sub>3</sub>S<sub>3</sub>  
 $M_r = 219.34$   
 Monoclinic, *C2*  
 $a = 15.247 (1) \text{ \AA}$   
 $b = 8.792 (1) \text{ \AA}$   
 $c = 16.165 (1) \text{ \AA}$   
 $\beta = 116.60 (1)^\circ$   
 $V = 1937.5 (1) \text{ \AA}^3$   
 $Z = 8$

$D_x = 1.504 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 3563 reflections  
 $\theta = 1.41\text{--}25.38^\circ$   
 $\mu = 0.714 \text{ mm}^{-1}$   
 $T = 293 (2) \text{ K}$   
 Trigonal prism, yellow  
 $0.25 \times 0.25 \times 0.15 \text{ mm}$

## Data collection

Nonius KappaCCD diffractometer	$R_{\text{int}} = 0.083$
$\varphi$ scans	$\theta_{\text{max}} = 25.38^\circ$
15863 measured reflections	$h = 0 \rightarrow 18$
3563 independent reflections	$k = -10 \rightarrow 10$
3323 reflections with $I > 2\sigma(I)$	$l = -19 \rightarrow 17$

## Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = 0.008$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$\Delta\rho_{\text{max}} = 0.38 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.149$	$\Delta\rho_{\text{min}} = -0.32 \text{ e } \text{\AA}^{-3}$
$S = 1.140$	Extinction correction: <i>SHELXL97</i>
3563 reflections	(Sheldrick, 1997)
224 parameters	Extinction coefficient: 0.0089 (12)
H-atom parameters constrained	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 4.3506P]$	Flack parameter = -0.006 (14)
where $P = (F_o^2 + 2F_c^2)/3$	

The coordinates of H atoms in molecules of (I) and in the methyl groups C2 and C4 of (II) were refined; the positions of all other H atoms in (II), (III) and (IV) were calculated. The calculated transmission factors for (II) are 0.807–0.966, but no absorption correction was applied. The data for (III) are 91.4% complete to  $2\theta$  55.0°. The absolute structure of (IV) was determined using 1644 Friedel pairs.

For compounds (I) and (II), data collection: Philips PW1100/20 software (Philips, 1973); for compound (III), data collection: *COLLECT* (Nonius, 1998); for compound (IV), data collection: KappaCCD software. For compounds (I) and (II), cell refinement: Philips PW1100/20 software; for compounds (III) and (IV), cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). For compounds (I) and (II), data reduction: *PROCN* (Hornstra & Stubbe, 1973; Goldberg, 1990); for compounds (III) and (IV), data reduction: *DENZO-SMN*. For all compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976) and *TEXSAN* (Molecular Structure Corporation, 1995); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1377). Services for accessing these data are described at the back of the journal.

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