Topochemically controlled solid-state methyl rearrangement in thiocyanurates

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4,6-Dimethoxy-3-methyl-1,3,5-triazine-2(3H)-thione crystallizes in two polymorphic forms, needles and plates. In the needle-shaped crystals (9a) the molecules occupy the crystallographic mirror plane, thus the layers are stacked along the b axis. The molecules of the other polymorph [plate-shape crystals, (9b)] are packed in a herringbone packing mode. Upon heating, (9b) undergoes a phase transition to form (9a). At 378 K the needles undergo O $\rightarrow$ S topochemically controlled methyl transfer in the solid state to produce 1-methyl-4-methoxy-6-methylthio-1,3,5-triazine-2(1H)-one in 75% yield. The enthalpy of the rearrangement is estimated to be -39.1 kJ mol^{-1}. 1-Methyl-6-methoxy-4-methylthio-1,3,5-triazine-2(1H)-thione crystallizes in space group $P2_1$ with two crystallographically independent molecules in the asymmetric unit. Compound (9b) undergoes O $\rightarrow$ S methyl transfer in the solid state at 373 K. The rearrangement is topochemically assisted and the product, 1-methyl-2,4-bismethylthio-1,3,5-triazine-6(1H)-one, is obtained in quantitative yield. The enthalpy of the rearrangement is estimated to be -58.8 kJ mol^{-1}. The crystal structures of the compounds as well as their DSC thermographs are described and discussed. Energy calculation by *ab initio* methods shows that the driving force for the reactions is the difference between the molecular energies of the pre-rearranged compounds and their products, 54.2 and 59.3 kJ mol^{-1} in the two cases, respectively.

1. Introduction

Generally, the rate of monomolecular chemical reaction in the solid state is expected to be much slower than the rate of the same reaction when it is carried out in solution because of the rigidity imposed by the packing of molecules and the limited space available for molecular changes. In special cases the condition is expected to be reversed for bimolecular or multimolecular reactions. There are special conditions for a reaction to be executed in solution or in the molten state, which is statistically limited or controlled. However, in the solid state in cases where the molecules are packed in a suitable arrangement that enable a reaction to take place, the reaction will proceed faster than in the other states of matter.

Over 120 years ago Hoffmann & Olshausen (1870) and later Klason (1885) gathered evidence that methyl esters of cyanuric acid and their thio derivatives undergo alkyl migration. From the end of the 1960s to the mid-1980s, the methyl rearrangement of methyl esters of cyanurates and thiocyanurates were investigated (Paolini *et al.*, 1968; Tosato, 1979, 1982, 1984). This investigation covers all possible methyl migrations and their products. It was pointed out that the methyl rear-

rangement can take place in the solid state, but firm conclusions were not made. There are several other known examples of solid-state methyl rearrangements, such as the conversion of methyl p-dimethylaminobenzenesulfonate (MSE) into the zwitterionic product p-trimethylammoniobenzenesulfonate (ZWT), first discovered by Kuhn & Ruelius (1950). Later, it was found (Sukenik et al., 1975) that the rate of the rearrangement increases with temperature below the melting temperature. In the melt, there is a sharp decrease of the reaction rate. Based on reaction-rate measurement it appears that the solid-state rearrangement is at least 25 times faster than that in the melt and it was attributed to the crystal structure (Sukenik et al., 1977). The distinction between intra- and intermolecular methyl rearrangement was established by a 'double label scrambling' experiment. The crystal structure was later reinvestigated using X-ray diffraction intensity data taken at different temperatures (Sarma & Dunitz, 1990), showing that some relevant interatomic distances as well as the approaching angle of the methyl group to a N atom of a neighboring molecule vary significantly at elevated temperature.

5-Methoxy-2-aryl-1,3,4-oxadiazoles is another remarkable example of a family of compounds that undergo a Chapman-like rearrangement, which occurs much faster in the crystal than in the melt (Dessolin & Golfier, 1986; Dessolin et al., 1992). The Chapman-like rearrangement is always difficult and requires temperatures higher than 473 K. In contrast, the rearrangement takes place exceptionally easily for 5-methoxy-2-aryl-1,3,4-oxadiazoles. The rearrangement takes place in the melt, at temperatures between 393 and 413 K, and also takes place even more rapidly in the crystalline state.

The mechanism of the solid-state reaction was the subject of two publications. Gavezzotti & Simonetta (1977) proposed a two-step mechanism involving a molecular ion-pair intermediate for the conversion of MSE into ZWT. A model system was used for studying the conversion of 5-methoxy-2-aryl-1,3,4-oxadiazole (Dessolin et al., 1992). The transition-state structure for the methyl exchange was localized with an analytical gradient and the energies were calculated at the restricted Hartree–Fock level with a 3-21G-basis set. These computations suggest that the starting point of the conversion is the formation of an anion and a cation, followed by the transfer of the methyl group between these ions and an adjacent molecule in the same plane. These substitutions are domino-like, propagating in chains.

Some other examples of solid-state methyl migration are known. A thermally induced non-topochemical solid-state methyl rearrangement of methyl-2-(methylthio)benzenesulfonate to the zwitterionic 2-(dimethylsulfonium)benzenesulfonate was observed (Venugopalan et al., 1991). This rearrangement is known to proceed in solution by intermolecular methyl transfer. The crystal structure of the pre-reacted compound shows that the molecular packing is not conducive to intermolecular methyl transfer. By fast-atom-bombardment mass spectroscopy on reaction products of mixed crystals composed of pre-reacted compound and its deuteriomethylated species, and from the results obtained

from the reaction rate study, it was concluded that the reaction proceeds not topochemically but rather at defects.

The conversion of oxocyanurate and thiocyanurates (1)–(4) in the melt was thoroughly investigated (Paolini et al., 1968; Tosato, 1979, 1982, 1984) and a mechanism was proposed (Paolini et al., 1968) to explain the formation of (4) (X1, X2 and X3 are O atoms) via the intermediates (2) (X1, X2 and X3 are O atoms) and (3) (X1, X2 and X3 are O atoms) by O → N methyl migration. By appropriate labeling it was shown without doubt that the rearrangement is intermolecular (Paolini et al., 1968). Kaftory and co-workers have studied the relation between the crystal structures of methoxy triazines (1)–(4) and (5)–(8), and their thermal behavior with respect to methyl rearrangement (Kaftory & Handelsman-Benory, 1994; Handelsman-Benory et al., 2000; Taycher et al., 2001). One can distinguish between three different types of rearrangements: (i) liquid-state, (ii) topochemically controlled solid state and (iii) non-topochemically controlled solid state.

(1)   (2)   (3)   (4)
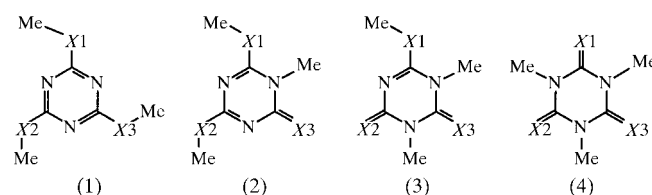
The present work describes the methyl rearrangement of two thiocyanurates, (9) and (11), in relation to their crystal structures.
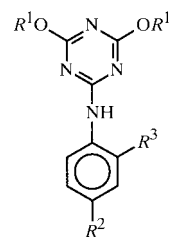
(5) R^1=Me, R^2=R^3=H
(6) R^1=Et, R^2=R^3=H
(7) R^1=Me, R^2=H, R^3=NO$_2$
(8) R^1=Me, R^2=NO$_2$, R^3=H

2. Experimental

4,6-Dimethoxy-3-methyl-1,3,5-triazine-2(3H)-thione (9) and 1-methyl-6-methoxy-4-methylthio-1,3,5-triazine-2(1H)-thione (11) were synthesized from 3-methyl-4,6-bismethylthio-1,3,5-triazine-2(3H)-thione (Tosato, 1982) by methanalysis with CH$_3$ONa (Tosato, 1984). The mixture of products was separated by preparative chromatography. The two polymorphs of (9) were obtained by slow evaporation of ethyl acetate solution of the compound as light yellow crystals having the shape of needles (9a) or plates (9b). 1-Methyl-4-methoxy-6-methylthio-1,3,5-triazine-2(1H)-one (10) was obtained by the solid-state rearrangement of (9). Its structure was elucidated from the following ^{1}NMR (CDCl$_3$) spectra: δ2.57 (3H, SCH$_3$), 3.48 (3H, NCH$_3$), 3.97 (3H, OCH$_3$). Light yellow crystals of (11) were obtained by slow evaporation of ethyl acetate solution. 1-Methyl-2,4-bismethylthio-1,3,5-triazine-6(1H)-one (12) was obtained by heating (11) to 393 K. Colorless prisms of (12) were obtained from a solution of ethyl acetate. Crystallographic data, and details of data collection and refinement

are given in Table 1. The H atoms were calculated and fixed during the refinement. The H atoms of one of the methyl groups in (9a) (at C6) were found to be disordered between two possible orientations. Geometric constraints were introduced during the refinement of the H atoms at C5. The H atoms of the methyl groups in (12) were found to be disordered between two possible orientations. Thermal behavior was studied using a DSC-PL of the Polymer Laboratory. NMR spectra were collected on a Bruker AC200 and AC400 diffractometer. High-temperature X-ray diffraction was carried out using a home-built camera using conventional film detection. Other relevant tables are given as supplementary material.[1] A comparison of bond lengths and bond angles of the two polymorphs (9a) and (9b), of the two crystallographically independent molecules of (11), and for (12), is given in Tables 2–4, respectively. The crystal structures of (9a), (9b), (11) and (12) are shown in Figs. 1, 3, 4 and 6, respectively, and the DSC thermographs of (9a), (9b) and (11) are shown in Figs. 2 and 5. Atomic numbering is given below.

(9)   (11)   (12)
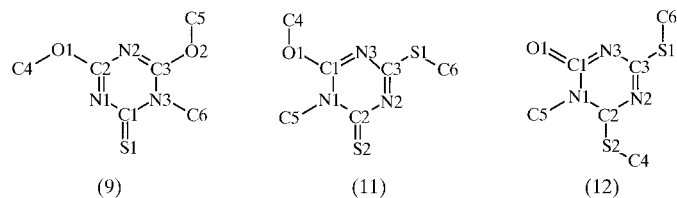
3. Results and discussion

3.1. Crystal structure and thermal behavior of (9)

4,6-Dimethoxy-3-methyl-1,3,5-triazine-2(3H)-thione crystallizes in two polymorphic forms, needle crystals (9a) and plates (9b). The polymorph (9a) crystallizes in layers, where the molecules are lying on a crystallographic mirror plane. Such a layer is shown in Fig. 1. Fractional coordinates have been deposited and a comparison of bond-lengths and bond-angles of the two polymorphs is given in Table 2. The thermal behavior of (9a) is shown by the DSC thermograph given in Fig. 2. The exothermic peak starting at 378 K with an enthalpy of -39.1 kJ mol^{-1} is assigned to the methyl rearrangement that takes place in the solid state. It is possible to envisage three possible routes of methyl transfer in the solid (marked either by dashed bonds or by open bonds in Fig. 1).

(i) O $\rightarrow$ N methyl transfer (marked by dashed bonds) leading to (10b). The relevant geometry includes a O(2)—C(5) bond distance of 1.484 (9) Å, C(5)$\cdots$N(1) intermolecular distance of 3.732 (9) Å and O(2)—C(5)$\cdots$N(1) approaching angle of 131.3 (6)°. Although the geometry is very similar to that found in other systems that undergo methyl rearrangement in the solid state (Handelsman-Benory et al., 2000), there is strong evidence that (10b) is not present in the mixture of products.

(ii) O $\rightarrow$ S methyl transfer (marked by one-line filled bonds), leading to (10a). The relevant geometry includes a
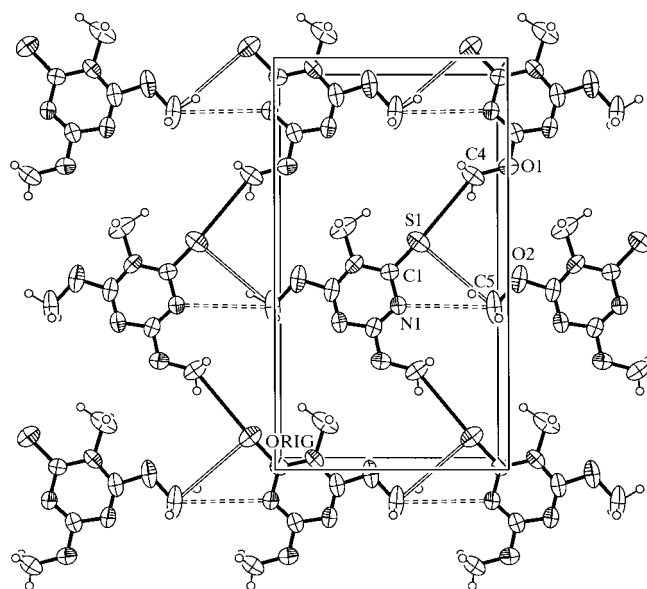
Figure 1
The structure of a layer of (9a) down the b axis (the a axis is upward, only one orientation of the disordered methyl H atoms is shown).
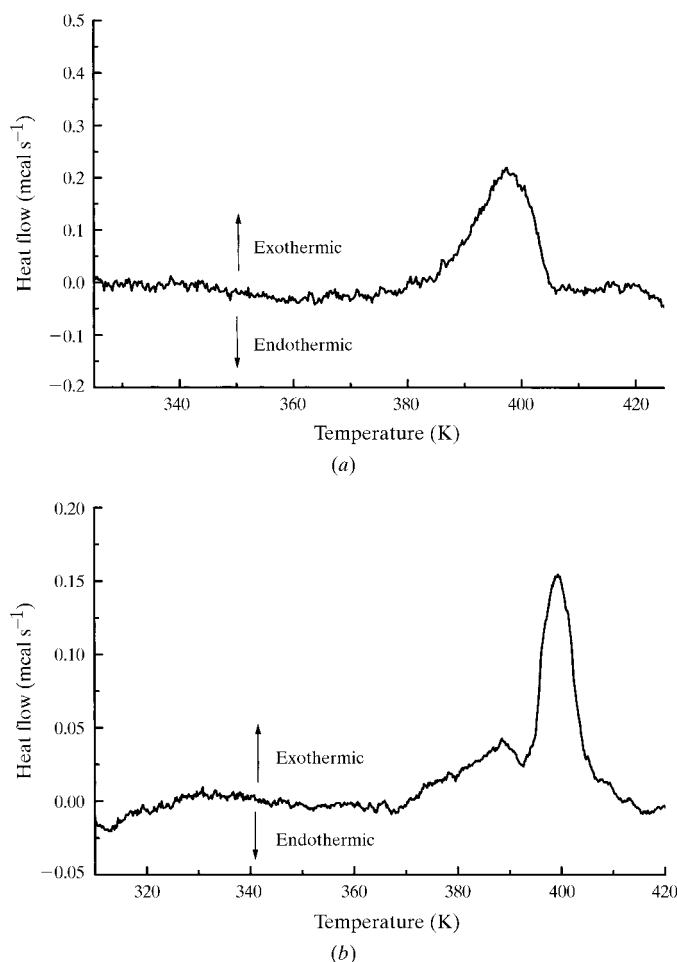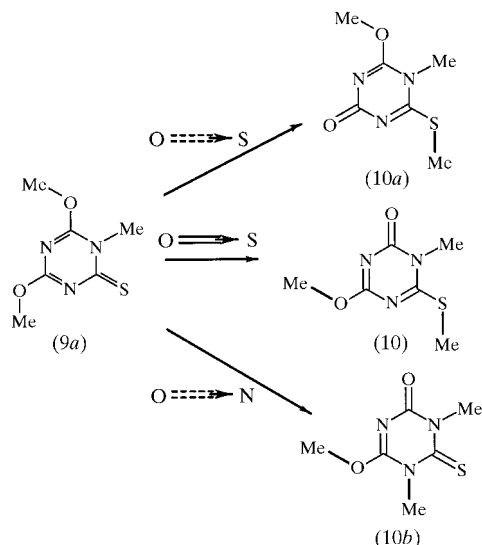

Figure 2
DSC thermographs of (a) (9a) and (b) (9b), taken at a heating rate of 3° min^{-1}.

O(1)—C(4) bond distance of 1.439 (8) Å, C(4)···S(1) intermolecular distance of 3.350 (8) Å and O(1)—C(4)···S(1) approaching angle of 144.6 (6)°. There is no indication that this compound is being produced in significant amounts during the rearrangement.

(iii) O → S methyl transfer (marked by open bonds) leading to (10). The relevant geometry includes a O(2)—C(5) bond distance of 1.484 (9) Å, C(5)···S(1) intermolecular distance of 3.892 (9) Å and O(2)—C(5)···S(1) approaching angle of 91.3 (6)°. The C(5)···S(1)—C(1) angle of 92.7 (6)° is somewhat closer to a trigonal angle (120°), which is expected for the direction of the lone-pair electrons of the sp^2 S atom.

Analysis of the product mixture by ^{1}H NMR spectra clearly shows that the major product (75%) is that of (10), which means that route (iii) is the winning one in the competition.
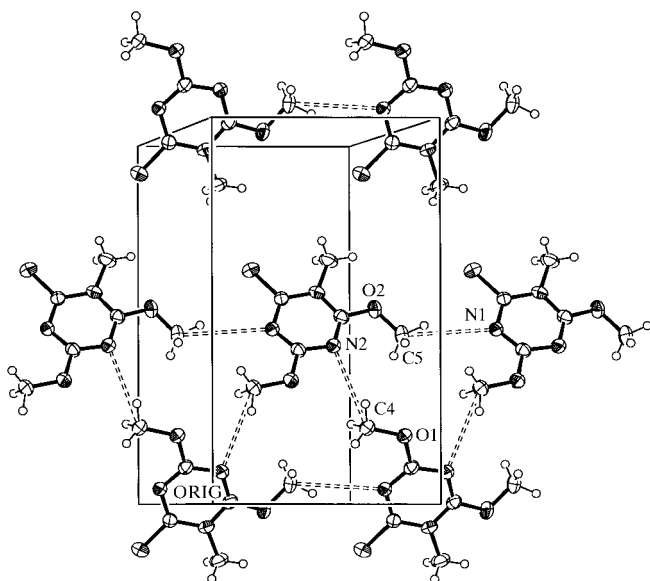
These results are in agreement with the findings of Tosato (1982). Molecules in (9b) are packed in a herringbone arrangement. A top view of a layer is shown in Fig. 3. Fractional coordinates have been deposited.

The crystal structure shows that appropriate geometrical conditions exist for an O → N methyl transfer in the solid state (marked by the dashed bonds in Fig. 3). For example, the intermolecular C(5)···N(1) distance is 3.558 (5) Å and O(2)—C(5)···N(1) approaching angle is 129.2 (3)°. At the other possible reaction site the relevant geometries are C(4)···N(2) 3.434 (5) Å and O(1)—C(4)···N(2) 118.4 (3)°. Nevertheless, the major product of the rearrangement is identical with that obtained as a result of the rearrangement of (9a). Two exothermic peaks can be seen in the DSC thermograph. The first may be assigned to a phase transition to the (9a) polymorph, which then undergoes O → S methyl transfer as discussed above. Supporting evidence for the phase transformation was obtained from the change of the X-ray powder diffraction pattern of (9b) during heating. The transformation is from a single crystal to polycrystals. As a result of the phase transformation, rows of parallel molecules that are inclined to each other in the monoclinic $P2_1/c$ space group move into the mirror plane of the orthorhombic $Pnma$ space group so that the rows are parallel to each other. The same type of phase
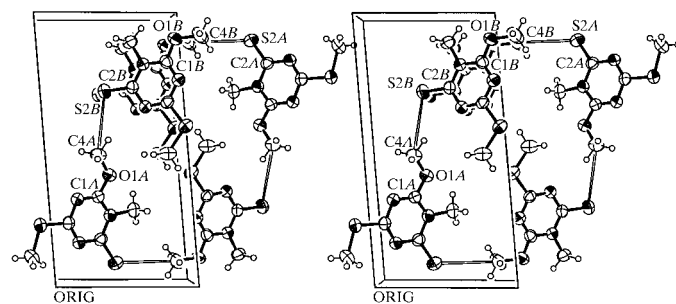

Figure 4
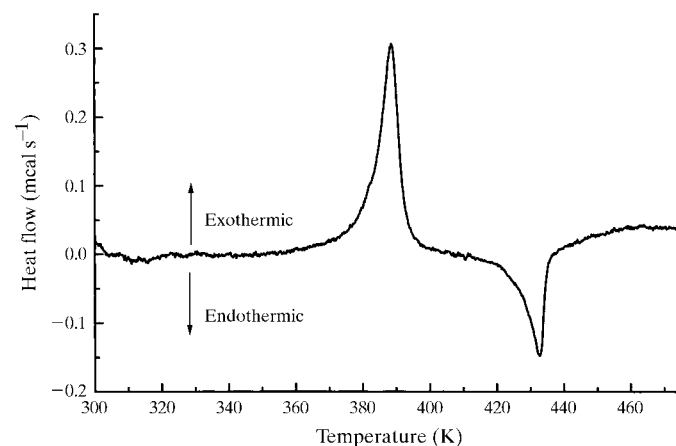Stereoscopic view of the crystal structure of (11) down the b axis (the c axis is upward).

Figure 5
DSC thermograph of (11), taken at a heating rate of 3° min^{-1}.

Figure 3
The crystal structure of (9b).

Table 1
Experimental details.

	(9a)	(9b)	(11)	(12)
Crystal data				
Chemical formula	$C_6H_9N_3O_2S$	$C_6H_9N_3O_2S$	$C_6H_9N_3OS_2$	$C_6H_9N_3OS_2$
Chemical formula weight	187.22	187.22	203.28	203.28
Cell setting, space group	Orthorhombic, $Pnma$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1$	Orthorhombic, $Pnma$
a, b, c (Å)	15.231 (5), 6.778 (3), 8.626 (3)	7.657 (3), 14.361 (7), 8.433 (4)	7.7771 (8), 8.0041 (7), 14.9762 (16)	15.712 (7), 6.730 (3), 8.731 (4)
β (°)	90	110.99 (3)	94.629 (1)	90
V (Å³)	890.5 (6)	865.8 (7)	928.63 (16)	923.2 (6)
Z	4	4	4	4
D_x (Mg m⁻³)	1.396	1.436	1.454	1.463
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	20	25	2592	25
θ range (°)	7.2–19.5	2.9–12.7	3.94–24.36	2.6–18.5
μ (mm⁻¹)	0.328	0.337	0.530	0.533
Temperature (K)	293 (2)	293 (2)	300 (2)	293 (2)
Crystal form, color	Needle, light yellow	Plates, light yellow	Plate, light yellow	Prism, colorless
Crystal size (mm)	0.33 × 0.27 × 0.19	0.45 × 0.38 × 0.24	0.40 × 0.30 × 0.25	0.30 × 0.22 × 0.17
Data collection				
Diffractometer	Philips PW 1100 diffract-ometer	Philips PW 1100	Siemens SMART	Philips PW 1100
Data collection method	$\omega/2\theta$ scans	$\omega/2\theta$ scans	ω scans	$\omega/2\theta$ scans
No. of measured, independent and observed parameters	981, 857, 560	1730, 1520, 902	10 006, 3203, 2629	934, 891, 639
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.0546	0.0906	0.0254	0.0318
θ_{max} (°)	25.00	25.00	28.29	24.99
Range of h, k, l	$-4 \rightarrow h \rightarrow 18$ $0 \rightarrow k \rightarrow 8$ $-4 \rightarrow l \rightarrow 10$	$-9 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 16$ $-10 \rightarrow l \rightarrow 9$	$-10 \rightarrow h \rightarrow 10$ $-5 \rightarrow k \rightarrow 6$ $-19 \rightarrow l \rightarrow 13$	$-4 \rightarrow h \rightarrow 18$ $0 \rightarrow k \rightarrow 8$ $-3 \rightarrow l \rightarrow 10$
Intensity decay (%)	4.2	4	0	3
Refinement				
Refinement on	F^2	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0609, 0.154, 1.104	0.0527, 0.1592, 1.075	0.05, 0.1196, 1.051	0.049, 0.1171, 1.076
No. of reflections and parameters used in refinement	857, 84	1520, 112	3203, 217	891, 76
H-atom treatment	Mixed	Mixed	Mixed	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.2249P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 2.0096P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0803P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0495P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	0.000	0.000	0.001	0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å⁻³)	0.203, −0.362	0.366, −0.359	0.638, −0.231	0.282, −0.238

Computer programs used: *PW* 1100/20 (Philips, 1973), *SHELXL*97 (Sheldrick, 1997b), *SHELXS*97 (Sheldrick, 1997a), *SMART* V.4.209 (Siemens, 1995), *SAINT* V.4.050 (Siemens, 1995), *XSCANS* (Siemens, 1994), *ORTEP*III (Farrugia, 1997).

transition proposed here was also detected when 1,3,5-trimethyl-2,4,6-trioxohexahydro-*S*-triazine [(9) where the S atom is replaced by an O atom] is heated before it undergoes methyl transfer in the solid state (Kaftory, 2001). Calculation of the relative molecular energy of (9) was carried out by *ab initio* methods using a polarized 6-31G** basis set. The results of the geometrical optimization by the Hartree–Fock method were used as the starting point for optimization by B3LYP and B3W91 methods (Foresman & Frisch, 1996) with no symmetry restrictions. These calculations (Greenberg & Kaftory, 2001) show that the molecular energy of (10) is lower by 54.2 kJ mol⁻¹ than that of (9). It is therefore concluded that the difference in the molecular energy is the driving force for the rearrangement.

3.2. Crystal structures and thermal behavior of (11) and (12)

1-Methyl-6-methoxy-4-methylthio-1,3,5-triazine-2(1*H*)-thione (11) crystallizes in a chiral space group, $P2_1$, with two crystallographically independent molecules in the asymmetric
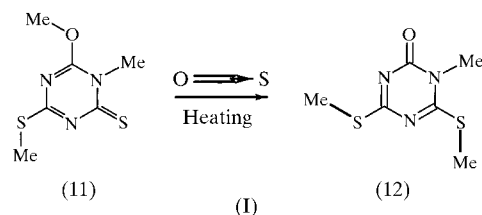
unit. The crystal structure is shown stereoscopically in Fig. 4. Fractional coordinates have been deposited and a comparison

Table 2
Comparison of bond lengths (Å) and angles (°) of (9a) and (9b).

S1—C1	1.630 (5)	1.659 (4)
O1—C2	1.338 (6)	1.338 (5)
O1—C4	1.439 (8)	1.446 (5)
O2—C3	1.376 (6)	1.326 (5)
O2—C5	1.484 (9)	1.469 (5)
N1—C2	1.293 (6)	1.315 (5)
N1—C1	1.349 (6)	1.360 (5)
N2—C3	1.303 (8)	1.305 (5)
N2—C2	1.352 (6)	1.350 (5)
N3—C3	1.339 (7)	1.362 (5)
N3—C1	1.409 (6)	1.398 (5)
N3—C6	1.475 (7)	1.474 (5)
C2—O1—C4	116.9 (5)	117.3 (3)
C3—O2—C5	114.0 (6)	115.7 (3)
C2—N1—C1	117.7 (4)	117.1 (3)
C3—N2—C2	111.9 (5)	113.5 (4)
C3—N3—C1	118.5 (4)	118.9 (3)
C3—N3—C6	122.4 (5)	120.3 (3)
C1—N3—C6	119.1 (5)	120.9 (3)
N1—C1—N3	117.0 (4)	117.8 (4)
N1—C1—S1	122.1 (4)	121.3 (3)
N3—C1—S1	120.9 (4)	120.9 (3)
N1—C2—O1	120.2 (4)	119.7 (3)
N1—C2—N2	129.2 (5)	128.4 (4)
O1—C2—N2	110.7 (5)	112.0 (4)
N2—C3—N3	125.7 (4)	124.3 (4)
N2—C3—O2	121.3 (5)	121.6 (4)
N3—C3—O2	113.0 (5)	114.1 (3)

Table 3
Selected bond lengths (Å) and angles (°) of (11).

	Molecule A	Molecule B
S1A—C3A	1.744 (3)	1.736 (3)
S1A—C6A	1.786 (3)	1.790 (4)
S2A—C2A	1.663 (3)	1.666 (3)
O1A—C1A	1.323 (3)	1.324 (3)
O1A—C4A	1.465 (5)	1.472 (5)
N1A—C1A	1.364 (4)	1.366 (4)
N1A—C2A	1.399 (4)	1.383 (4)
N1A—C5A	1.476 (4)	1.477 (4)
N2A—C3A	1.317 (4)	1.318 (4)
N2A—C2A	1.356 (4)	1.366 (4)
N3A—C1A	1.295 (4)	1.292 (4)
N3A—C3A	1.347 (4)	1.347 (4)
C3A—S1A—C6A	103.24 (18)	103.5 (2)
C1A—O1A—C4A	115.2 (3)	115.2 (3)
C1A—N1A—C2A	118.3 (3)	118.6 (3)
C1A—N1A—C5A	119.7 (3)	120.2 (3)
C2A—N1A—C5A	121.9 (3)	121.2 (3)
C3A—N2A—C2A	117.6 (3)	117.2 (3)
C1A—N3A—C3A	114.4 (3)	114.5 (3)
N3A—C1A—O1A	122.4 (3)	122.6 (3)
N3A—C1A—N1A	124.4 (3)	124.2 (3)
O1A—C1A—N1A	113.1 (3)	113.2 (3)
N2A—C2A—N1A	117.9 (3)	118.2 (3)
N2A—C2A—S2A	121.3 (2)	120.7 (2)
N1A—C2A—S2A	120.8 (2)	121.2 (2)
N2A—C3A—N3A	127.3 (3)	127.2 (3)
N2A—C3A—S1A	121.2 (2)	120.7 (2)
N3A—C3A—S1A	111.5 (2)	112.1 (2)

of bond lengths and bond angles of the two independent molecules is given in Table 3. The thermal behavior of (11) is shown by the DSC thermograph given in Fig. 5. The first exothermic peak, starting at 373 K with an enthalpy of -58.8 kJ mol^{-1}, is assigned to the methyl transfer. A single product is formed, (12), as a result of the rearrangement [see
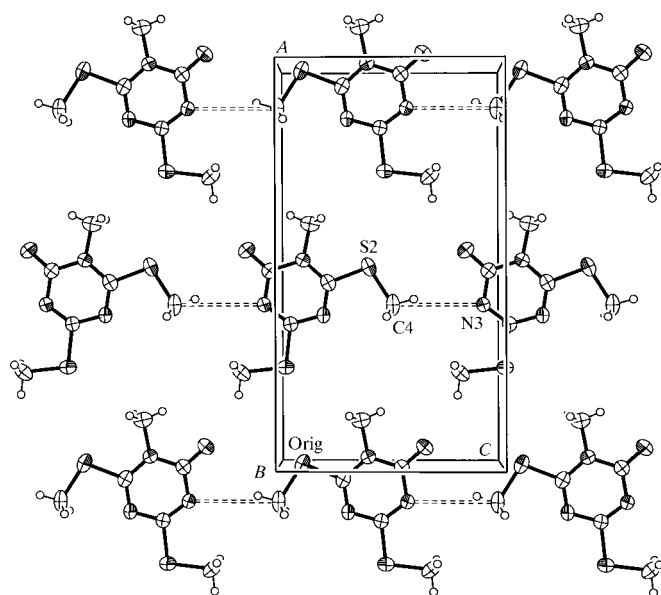

Figure 6
The structure of a layer of (12), down the *b* axis (the *a* axis is upward; only one orientation of the disordered methyl H atoms is shown).

(I)], which then melts at 423 K with an enthalpy of 26.1 kJ mol^{-1}. The low rearrangement temperature indicates that it is topochemically assisted (Taycher *et al.*, 2001). Open bonds in Fig. 4 show a proposed route of methyl transfer. The methyl groups are being transferred from O atoms to S atoms of neighboring molecules in a screw fashion.

The relevant geometries are as follows: O(1A)—C(4B) 1.472 (5), C(4B)···S(2A) 3.847 (5) Å; O(1B)—C(4B)···S(2A) 174.2 (3) and C(4B)···S(2A)—C(2A) 127.5 (3)°. At the other site of the rearrangement the geometry is as follows: O(1A)—C(4A) 1.464 (4), C(4A)···S(2B) 3.886 (3) Å; O(1A)—C(4A)···S(2B) 113.5 (3) and C(4A)···S(2B)—C(2B) 89.9 (3)°.

The crystal structure of the rearrangement product (12) is isomorphic with that of (9a) and is given in Fig. 6. Fractional coordinates have been deposited and bond lengths and angles are given in Table 4, respectively. It was mentioned above that the methyl group prefers to bind to an S atom rather than to an N atom, therefore, upon heating (9a) (10) is formed and not (10b). The impassiveness of the solid (12) when heating, although the geometry shows that a rearrangement may take place by S → N methyl transfer, is another support to the discrimination between S and N atoms during the methyl transfer, as mentioned earlier. The C(4)···N(3) intermolecular distance is 3.585 (5) Å and the approaching angle S(2)—C(4)···N(3) is 122.2 (3)°. The driving force of the rearrangement is the molecular energy. Compound (12) has lesser energy of 59.3 kJ mol^{-1}, as calculated by the same procedure as discussed above.

Table 4
Selected bond lengths (Å) and angles (°) of (12).

S1—C3	1.742 (4)	N1—C1	1.406 (5)
S1—C6	1.789 (5)	N1—C5	1.478 (5)
S2—C2	1.745 (4)	N2—C2	1.315 (5)
S2—C4	1.787 (5)	N2—C3	1.362 (5)
O1—C1	1.222 (5)	N3—C3	1.308 (5)
N1—C2	1.353 (5)	N3—C1	1.377 (5)
C3—S1—C6	102.9 (2)	O1—C1—N1	120.1 (4)
C2—S2—C4	101.3 (2)	N3—C1—N1	116.9 (4)
C2—N1—C1	120.2 (3)	N2—C2—N1	123.4 (4)
C2—N1—C5	121.1 (3)	N2—C2—S2	119.7 (4)
C1—N1—C5	118.7 (3)	N1—C2—S2	117.0 (3)
C2—N2—C3	114.0 (4)	N3—C3—N2	128.1 (4)
C3—N3—C1	117.4 (4)	N3—C3—S1	120.3 (3)
O1—C1—N3	123.1 (4)	N2—C3—S1	111.6 (3)

3.3. Molecular geometry

The discussion of the molecular geometry is based mainly on the crystal structures of (9b), (11) and (12), since the accuracy of the geometrical parameters of (9a) is lower due to the higher atomic displacement parameters. It is possible to distinguish between three different S—C bonds: double bonds which range between 1.659 and 1.666 Å, S—C(sp^2) single bonds in the range 1.736–1.745 Å and S—C(sp^3) single bonds in the range 1.786–1.790 Å. These values are in agreement with the average values obtained from the data available from the Cambridge Crystallographic Data Center (Orpen *et al.*, 1994): 1.671, 1.751 and 1.789 Å, respectively. The chemically equivalent O—C bond lengths are 1.222 Å (O =C), 1.323–1.338 Å (O—Csp^2 bond) and 1.462–1.472 Å (O—Csp^3 bond).

Steric and electronic effects are best observed by the differences in bond angles. For example, although the S—CH$_3$ group is connected to a C atom that is symmetrically bonded to two N atoms, the outer-ring bond angles N—C—S are not identical. The outer-ring bond angle involved with a C=N double bond [see, for example, N(3)=C(3)—S(1) in (12)] is in all cases larger than the other outer-ring bond angle. The former bond angle ranges between 111.5 and 114.1°, the second between 119.5 and 121.3°. The inner-ring bond angle at the same C atom is dependent on its next-neighbor atoms, an Nsp^2 atom on both sides or an Nsp^2 atom on one side and an Nsp^3—CH$_3$ group on the second. The bond angle involved with the former was found to be significantly larger, 127.2–128.4° compared with 123.4–124.4°.

4. Conclusions

The crystal structures of the two compounds (9) and (11) discussed above are an excellent representative of a large group of compounds that undergo a topochemically controlled solid-state reaction. These examples also show that although geometrically more than a single type rearrangement can take place and a methyl group can be transferred from an O atom either to an N or to an S atom of a neighboring molecule, only one possibility is actually taking place. Similar chemical systems are shown to undergo methyl rearrangement either in the solid or in the liquid state at higher temperatures when the

structure does not provide the necessary structural condition for a topochemically controlled reaction (Taycher *et al.*, 2001). As a result of the topochemically assisting conditions available for (9) and (11), the solid-state rearrangement is shown to occur at relatively low temperatures.

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