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Two dimorphs of 5-methylsulfanyl-1*H*-tetrazole

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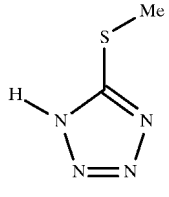
5-Methylsulfanyl-1*H*-tetrazole, $C_2H_4N_4S$, crystallizes in dimorphic forms; the α-form crystallizes at room temperature in the monoclinic crystal system, space group $P2_1/m$, and the β-form crystallizes by sublimation at 423 K in the orthorhombic crystal system, space group *Pbcm*. In both forms, the molecules occupy crystallographic mirror planes and are connected to one another *via* N—H···N hydrogen bonds, the amino H atoms being disordered. The two forms differ from one another in their packing; there are polar layers in the α-form and non-polar layers in the β-form.

Comment

Tetrazoles are acidic heterocycles that are deprotonated under physiological conditions and serve routinely as bioisosteric replacements for carboxylic acids in modern drug design (Kraft *et al.*, 2002). The title compound, (I), decomposes upon heating, at or slightly above its melting point, as do other 5-substituted mercaptotetrazoles. There are two known routes for the decomposition of (I). Lieber & Enkoji (1961) reported that 5-substituted mercaptotetrazoles undergo decomposition, at or near their melting points, to hydrazoic acid and the corresponding thiocyanate. Kroto & Suffolk (1972) and Solouki *et al.* (1976) reported that (I) decomposes mainly through the elimination of thioformaldehyde and the formation of tetrazale, which is split into an N atom, a cyanamide molecule and a carbodiimide molecule.



(I)

Compound (I) has been examined because of its ability to undergo methyl rearrangement in the solid or liquid state (Kaftory & Handelsman-Benory, 1994; Handelsman-Benory *et al.*, 2000; Greenberg *et al.*, 2001; Kaftory *et al.*, 2001; Kaftory, 2002).

Compound (I) crystallizes in dimorphic forms, *viz*. the α-form, (Iα), in space group $P2_1/m$, and the β-form, (Iβ), in space group *Pbcm*. The thermal behavior of (Iα) is indicated by the DSC (differential scanning calorimetry) thermograph shown in Fig. 1. The first small endothermic peak (at 382 K), with a measured enthalpy of 1.81 kJ mol^{-1}, is assigned to a

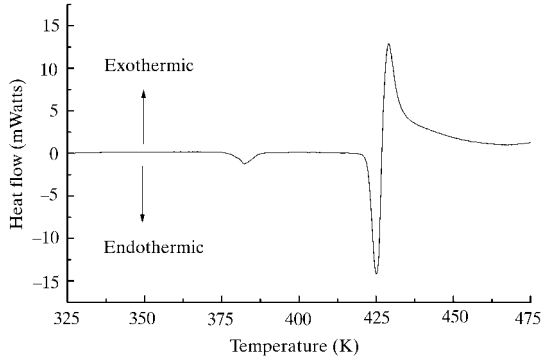


Figure 1
A DSC thermogram for (Iα) (heating rate 5 K min^{-1}, weight of sample 7.8 mg).

phase transition to the β-form. The second endothermic peak (at 425 K, ΔH = 13.10 kJ mol^{-1}) is assigned to the melting point, and the last exothermic peak (at 429 K, ΔH = −33.65 kJ mol^{-1}) is assigned to the decomposition of the compound. The thermal behavior of (Iβ) is indicated by the DSC thermograph shown in Fig. 2. The endothermic peak at 424 K (ΔH = 13.65 kJ mol^{-1}) is assigned to the melting point, and the exothermic peak at 430 K (ΔH = −33.65 kJ mol^{-1}) to the decomposition of the compound. The phase transition from the α-form to the β-form is reversible, although the reverse transition from the β- to the α-form could not be observed in the DSC thermograph because it takes about an hour. However, when the high-temperature phase was left to

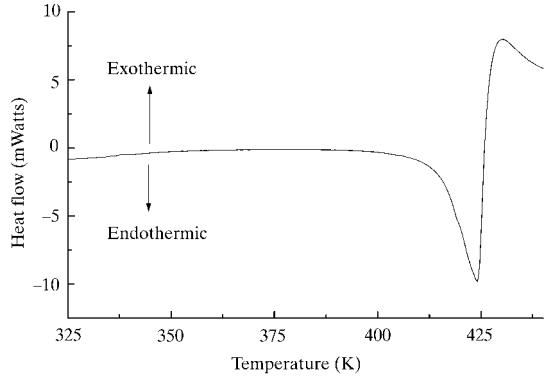


Figure 2
A DSC thermogram for (Iβ) (heating rate 5 K min^{-1}, weight of sample 6.8 mg).

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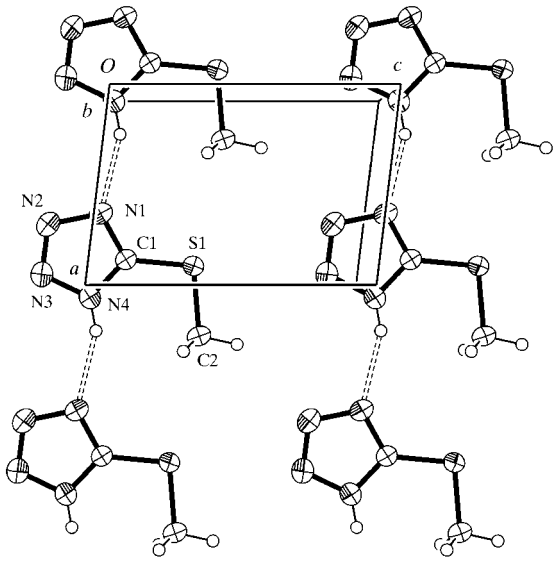

Figure 3
A layer of molecules in the structure of (Iα). Only one of the disordered H atoms is shown. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

stand for an hour, the endotherm at 382 K was observed, thus indicating α-form formation.

Both dimorphs have layer structures, in which the molecules occupy crystallographic mirror sites. The molecules within the layers are connected to one another *via* N—H···N hydrogen bonds (Table 1, and Figs. 3 and 4). The dimorphs differ in the way that the molecules are arranged within the layers. In (Iα), a crystallographic center of inversion lies between the layers and the molecules within the layer are arranged in parallel rows, so that the layer is polar. In (Iβ), alternate rows are reversed, and therefore the layer is non-polar. In both forms, the amino H atoms are disordered. They are disordered equally between two sites in (Iα), which is reflected in the equivalence of the N1—C1 [1.333 (3) Å] and N4—C1 [1.336 (3) Å] bond lengths (Table 1). In (Iβ), the amino H atoms are distributed unevenly, with occupancy factors of 0.79 (3) and 0.21 (3), and the N1—C1 [1.346 (3) Å] and N4—C1 [1.325 (3) Å] bond lengths are significantly different from one another.

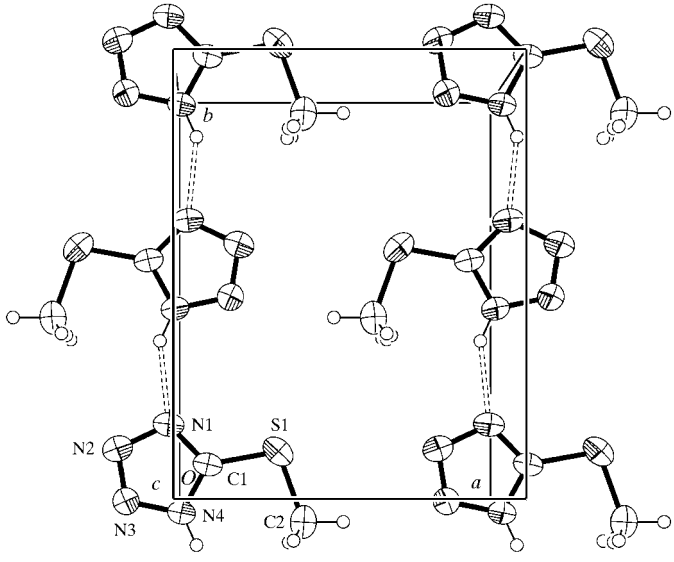

Figure 4
A layer of molecules in the structure of (Iβ). Only one of the disordered H atoms is shown. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

Experimental

Compound (I) was obtained from a commercial source (Aldrich) and was used without further purification. Crystals of (Iα) were grown from an ethanol solution. Crystals of (Iβ) were prepared by sublimation of the α-form at 423 K for 0.5 h. The sublimate was recrystallized immediately from an ethanol solution, giving colorless prismatic crystals of (Iβ).

Dimorph (Iα)

Crystal data

$C_2H_4N_4S$
M_r = 116.15
Monoclinic, $P2_1/m$
a = 5.041 (1) Å
b = 6.547 (1) Å
c = 7.247 (1) Å
β = 96.98 (2)°
V = 237.40 (7) Å^3
Z = 2
D_x = 1.625 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 828 reflections
θ = 2.8–25.5°
μ = 0.54 mm^{-1}
T = 293 (2) K
Prism, colorless
0.51 × 0.30 × 0.24 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
828 measured reflections
479 independent reflections
419 reflections with $I > 2\sigma(I)$
R_{int} = 0.015
θ_{max} = 25.5°
$h = -6 \rightarrow 6$
$k = -6 \rightarrow 7$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.069
S = 1.10
479 reflections
51 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 2.18 (12)

Dimorph (Iβ)

Crystal data

$C_2H_4N_4S$
M_r = 116.15
Orthorhombic, *Pbcm*
a = 7.714 (2) Å
b = 9.833 (2) Å
c = 6.679 (1) Å
V = 506.61 (18) Å^3
Z = 4
D_x = 1.523 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 827 reflections
θ = 2.6–25.0°
μ = 0.50 mm^{-1}
T = 293 (2) K
Prism, colorless
0.36 × 0.21 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.024$
φ scans	$\theta_{max} = 25.0^\circ$
827 measured reflections	$h = -9 \rightarrow 9$
484 independent reflections	$k = -11 \rightarrow 11$
336 reflections with $I > 2\sigma(I)$	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.031$	$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.067$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.95$	$\Delta\rho_{max} = 0.13$ e Å^{-3}
484 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}
45 parameters	

Table 1
Hydrogen-bonding geometry (Å, °) in the dimorphs of (I).

D—H···A	D—H	H···A	D···A	D—H···A
Dimorph (Iα)				
N1—H1N···N4^{i}	0.86	2.08	2.885 (3)	154
N4—H4N···N1^{ii}	0.86	2.08	2.885 (3)	156
Dimorph (Iβ)				
N1—H1N···N4^{iii}	0.86	1.95	2.797 (3)	170
N4—H4N···N1^{iv}	0.86	2.02	2.797 (3)	149

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y, z$; (iii) $-x, y+\frac{1}{2}, z$; (iv) $-x, y-\frac{1}{2}, z$.

The amino H atoms in both forms are disordered, and these atoms were allowed for as riding on the relevant N atoms. The occupancy factors of the amino H atoms in (Iα) were refined at the initial stages. When the occupancies were found to be equal, they were fixed at 0.5. For (Iβ), the occupancy factors of the amino H atoms were refined to 0.8 and 0.2. The methyl H atoms in (Iβ) were found to be disordered between two equally distributed conformations.

For both forms, data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1152). Services for accessing these data are described at the back of the journal.

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