

Thioacetanilide at 120 K

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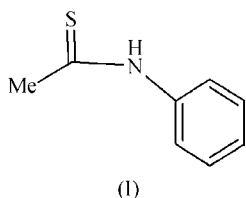
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The title compound, C₈H₉NS, has four symmetry-independent molecules in the asymmetric unit. These molecules link into two independent infinite N—H...S hydrogen-bonded chains in the *a*-axis direction with graph-set notation C₂²(8). The NH—CS group adopts a *trans* conformation and forms a dihedral angle of about 50° with the phenyl ring. The intermolecular hydrogen-bond energy calculated by the density functional theory (DFT) method is −14.95 kJ mol^{−1}. The correlation between the IR spectrum of this compound and the hydrogen-bond energy is also discussed. This molecular system is of interest because of its biological function.

Comment

The title compound, (I), belongs to the thioamides, which have a thiocarbonyl and an amino group capable of forming hydrogen bonds. The objects of our research are the IR spectra of thioamide crystals in the frequency range of the proton and deuteron stretching vibrations in hydrogen bonds.



Characteristic isotopic and spectroscopic effects, called self-organization effects, are observed in this vibration frequency range (Flakus, 1989, 2003; Flakus & Bańczyk, 1999). As a result of structural and polarized IR spectroscopic investigations of hydrogen-bonded molecular systems, an even richer set of data concerning the complexity of ν_{X-H} band-generation mechanisms could be obtained. Measurements of the polarized IR spectra of diverse spatially oriented hydrogen-bond systems present in the lattices of molecular crystals allow us to estimate the polarization properties of the transitions,

found in the excited states of proton vibrations in the crystal structures, which contribute to the ν_{X-H} band-generation mechanisms in the crystalline spectra. Thus, for a reliable interpretation of the reasons for the self-organization mechanism, the crystal structure of the hydrogen-bonded system must be known. In the case of (I), a crystallographic study has not been reported until now.

In this article, the result of our structural studies of the hydrogen bonds of (I) is presented. This molecular system is of special interest for researchers, as (I) is one of the smaller molecules with a thiopeptide group, which is capable of associating with other thiopeptide groups to form hydrogen bonds. The biological function of (I) has attracted interest in recent years. Thus, the metabolism and acute toxicity of (I) have been studied in rats (Trennery & Warning, 1983). The proton magnetic resonance and IR spectra of solutions of (I) have been reported (Birchall & Gillespie, 1963; Galabov *et al.*, 2003). The conformational stability of the thioamide group in (I) has been discussed using density functional theory (DFT) (Galabov *et al.*, 2003).

Compound (I) crystallizes with four molecules in the asymmetric unit (Fig. 1). All four molecules adopt the *trans* conformation of the —NH—CS— group with comparable bond lengths and angles. The N—C(=S) and C=S bond lengths are in the region of 1.329 and 1.675 Å, respectively, and compare well with those of related compounds, such as thioacetamide (Jeffrey *et al.*, 1984) and *N*-methylthiobenzamide (Śmiszek-Lindert *et al.*, 2007). These lengths are also in good agreement with those calculated at the B3LYP/6-31G** level of theory (Galabov *et al.*, 2003). The —CS—NH— group is almost planar in each molecule and the dihedral angles with the phenyl ring are in the range 45–53°. The calculated dihedral angle between the aromatic ring and the —NH—CS— group is in the region of 0 (180)°. This is a very surprising fact, because in the literature the *trans* isomer is reported to be almost planar, with deviations from planarity smaller than 3° (Galabov *et al.*,

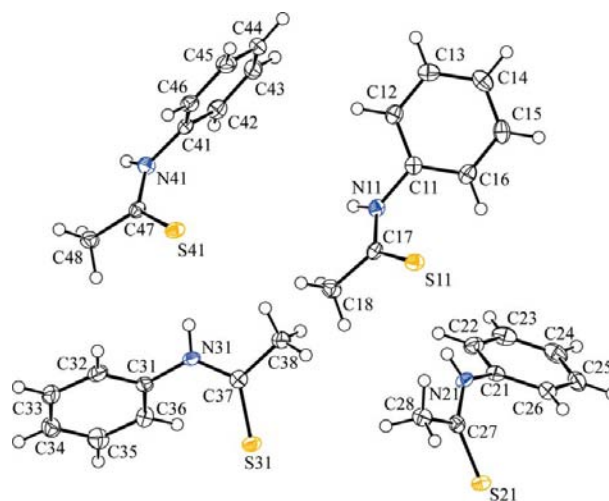


Figure 1

The four symmetry-independent molecules of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

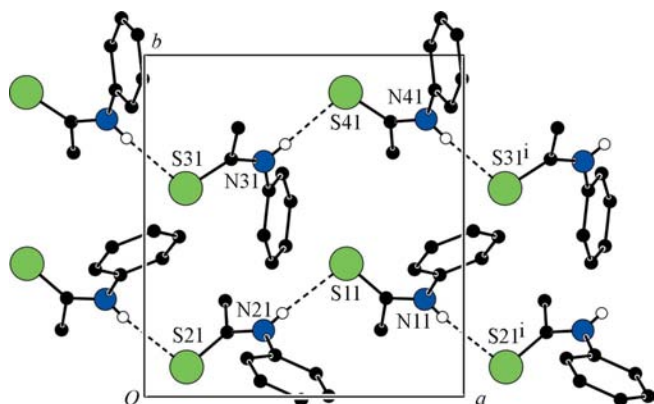


Figure 2
A view along the c axis of the hydrogen-bonded chains of (I). [Symmetry code: (i) $x+1, y, z$.]

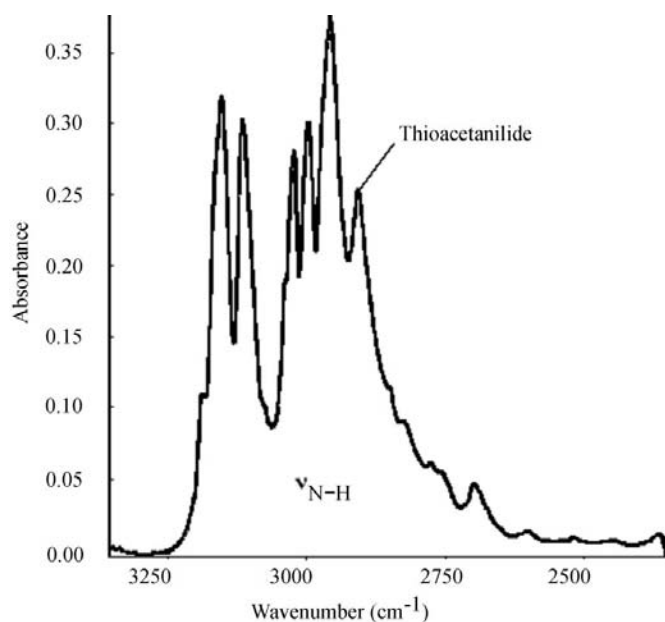


Figure 3
The IR spectrum of (I) measured by the KBr pellet technique at room temperature presented in the $\nu_{\text{N-H}}$ frequency range.

2003). A search of the Cambridge Structural Database (CSD, Version 5.28; *Conquest*, Version 1.9; Allen, 2002) was carried out to check the reported angle. This angle varies in related compounds, such as formanilide (Omondi *et al.*, 2008), acetanilide (Brown, 1966) and larger molecules with a thioacetamide group, such as (*Z*)-*N*-(2-*tert*-butylphenyl)propanethioamide (Dantale *et al.*, 2002), in which this dihedral angle could adopt a larger value (9.1, 20.0 and 70.9°, respectively).

For a comparison of the bond lengths and angles with other thioacetanilide derivatives, a search of the CSD yielded only one structure, namely thioacetanilide *S*-oxide [CSD refcodes SACANO (Jarchow, 1969) and SACANO01 (Kraeft, 1967)]. In that compound, the thioacetanilide is found in the *cis* form of the $-\text{NH}-\text{CS}-$ group. A comparison of the bond lengths and angles indicates that the $\text{N1}-\text{C1}$ and $\text{C1}-\text{S1}$ bond

lengths and $\text{N1}-\text{C7}-\text{S1}$ and $\text{N1}-\text{C7}-\text{C8}$ angles are mostly affected by the atom type bound to the S atom: an H atom in (I) by hydrogen bonding and an O atom in thioacetanilide *S*-oxide.

In the crystal structure of (I), the molecules interact *via* $\text{N}-\text{H}\cdots\text{S}$ hydrogen bonds to form two different infinite zigzag chains parallel to the a axis with graph-set notation $D_1^1(2)$ and $C_2^2(8)$ (Fig. 2) (Bernstein *et al.*, 1990; Grell *et al.*, 1999). The values of the hydrogen-bond distances are in the range 3.0–4.0 Å and therefore they can be treated as weak hydrogen bonds (Desiraju & Steiner, 1999). The strength of the hydrogen bonds in this compound was also investigated by IR spectroscopy. The band of the isolated $\text{N}-\text{H}$ stretching vibration, $\nu_{\text{N-H}}$, is located at a frequency of 3400 cm^{-1} . In the case of (I), we observed this band in the frequency range $3200\text{--}2800\text{ cm}^{-1}$, with a shift of about 400 cm^{-1} (Fig. 3). This relative shift is larger than 5% and is characteristic of a strong hydrogen bond (Desiraju & Steiner, 1999). Thus, the energy of the intermolecular hydrogen bonds was also calculated.

The initial geometry of (I) was optimized using the *MM*+ molecular modelling method implemented in *HYPERCHEM* (Hypercube, 1998). In the next step, DFT calculations were performed using the *GAUSSIAN03* software package (Frisch *et al.*, 2003) with the B3LYP hybrid function. The theoretical investigation of the hydrogen bonds was performed using *GAUSSIAN03* at the B3LYP/6-31G** level of theory. A cluster (57 atoms) consisted of three neighbouring molecules of (I) with two intermolecular hydrogen bonds, *viz.* $\text{N1}-\text{H}\cdots\text{S2}$ and $\text{N2}-\text{H}\cdots\text{S3}$. The energy of the intermolecular hydrogen bonds was calculated and corrected to basis set superposition error (BSSE) using a standard procedure (Boys & Bernardi, 1970). The total energy of the two hydrogen bonds was estimated at -29.9 kJ mol^{-1} . This value indicates that the hydrogen bonds are strong (Desiraju & Steiner, 1999). Calculated hydrogen-bond distances for these two intermolecular hydrogen bonds ($\text{N1}-\text{H}\cdots\text{S2}$ and $\text{N2}-\text{H}\cdots\text{S3}$) were $\text{N}-\text{H} = 1.019$ and 1.018 Å , $\text{H}\cdots\text{S} = 2.692$ and 2.746 Å , and $\text{N}\cdots\text{S} = 3.677$ and 3.764 Å , respectively. The calculated $\text{N}-\text{H}\cdots\text{S}$ angles for these hydrogen bonds were 162 and 177° , respectively. The obtained values of the hydrogen-bond geometry correspond well with the experimental data.

Our knowledge of the hydrogen-bond geometry enables us to recognize the type of self-organization mechanism. Therefore, we plan to carry out further studies on the polarized IR spectra of this compound and its isotopic derivatives.

Experimental

Thioacetanilide was purchased from Sigma–Aldrich and used without further purification. It was dissolved in a water–acetone mixture (1:1 *v/v*). After several days, yellow single crystals of (I) suitable for single-crystal X-ray diffraction analysis had formed. The crystals were mounted on a quartz glass capillary and cooled to 120 K with a cold dry nitrogen gas stream (Oxford Cryosystems equipment); the temperature stability was $\pm 0.1\text{ K}$. The IR spectrum of a polycrystalline sample of (I) was measured in transmission at room temperature using the KBr pellet technique on a Nicolet Magna 560 FT-IR spectrometer with 4 cm^{-1} resolution.

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N11—H11N...S21 ⁱ	0.84 (2)	2.53 (2)	3.3504 (18)	166 (2)
N21—H21N...S11	0.85 (2)	2.51 (2)	3.3375 (18)	164.0 (19)
N31—H31N...S41	0.86 (2)	2.47 (2)	3.3251 (18)	174.8 (19)
N41—H41N...S31 ⁱ	0.87 (2)	2.45 (2)	3.3224 (18)	176 (2)

Symmetry code: (i) $x + 1, y, z$.**Crystal data**

C₈H₉NS
M_r = 151.22
 Monoclinic, *P*₂₁/*n*
a = 9.8858 (4) Å
b = 10.5330 (4) Å
c = 30.3073 (13) Å
 β = 94.050 (4)°

Data collection

Oxford Diffraction KM-4-CCD
 diffractometer with a Sapphire3
 detector
 19399 measured reflections

V = 3147.9 (2) Å³
Z = 16
 Mo *K*α radiation
 μ = 0.33 mm⁻¹
T = 120 (2) K
 0.3 × 0.12 × 0.06 mm

5572 independent reflections
 3903 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.025

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.093$
S = 1.00
 5572 reflections
 381 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
 $\Delta\rho_{\max} = 0.23 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.39 \text{ e } \text{Å}^{-3}$

The aromatic and methyl H atoms were treated as riding on their parent atoms, with C—H = 0.95 and 0.98 Å, respectively, and with *U*_{iso}(H) = 1.2 and 1.5 times *U*_{eq}(C), respectively. H atoms involved in hydrogen bonding were located in a difference Fourier map (ΔF) and refined freely with isotropic displacement parameters.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97*

(Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *publCIF* (Westrip, 2008).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3238). Services for accessing these data are described at the back of the journal.

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