3′-Methylacetanilide and N-benzyl-thioacetamide at low temperature

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Molecules of the title compounds, 3′-methylacetanilide [or N-(m-tolyl)acetamide], $C_9H_{11}NO$, (I), and N-benzylthioacetamide, $C_9H_{11}NS$, (II), are connected by a framework of intermolecular N—H···O and N—H···S hydrogen bonds, respectively, forming chains with the graph-set description C(4), which run along the b axis. Analyses of the crystal structures of (I) and (II) are helpful in the elucidation of a generation mechanism of the IR spectra of hydrogen-bonded molecular crystals. The correlation between the IR spectra of studied compounds and structural data is also discussed.

Comment

3′-Methylacetanilide, (I), and the sulfur analogue N-(m-tolyl)thioacetamide, as well as N-benzylthioacetamide, (II), and the oxygen analogue N-benzylacetamide, have been the subject of our studies for a generation mechanism of the IR spectra of hydrogen-bonded molecular crystals. The theoretical analyses of (I) and (II) and of their analogues N-(m-tolyl)thioacetamide and N-benzylacetamide, respectively, preceded by measurement of the IR spectra of polycrystalline
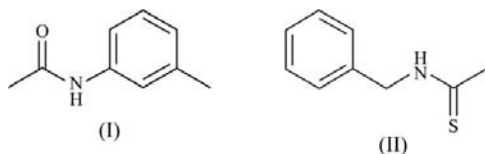
and monocrystalline samples, concerned characteristic isotopic and spectroscopic effects, e.g. linear dichroic effects, self-organization and temperature effects. These effects were observed in the solid-state IR spectra of hydrogen and deuterium bonds at the frequency ranges of the v_{N-H} and v_{N-D} bands, respectively. Some spectacular effects are especially visible for those systems where the proton acceptor is sulfur or oxygen (Flakus et al., 2003, 2004, 2005, 2006, 2007). Accordingly, for a reliable interpretation of the isotopic and spec-

troscopic effects, determination of the crystal structures of (I) and (II) is indispensable. In the case of both N-(m-tolyl)thioacetamide (Śmiszek-Lindert et al., 2007a) and N-benzylacetamide (Śmiszek-Lindert & Kusz, 2007), crystallographic studies have been reported previously.

Compound (I) crystallizes with one molecule in the asymmetric unit cell (Fig. 1). In each molecule, the six-membered ring (C1–C6) forms a planar skeleton, with r.m.s. deviations from the mean plane of 0.0023 Å; atoms O1, C8, C9 are significantly out of the benzene ring plane by 0.5411 (13), 0.2385 (13) and 0.1325 (16) Å, respectively. The benzene ring is not coplanar with the –CO—NH– plane [torsion angles: C8—N1—C1—C2 = −165.66 (9)° and C8—N1—C1—C6 = 15.95 (16)°]; the dihedral angle between the plane of the benzene ring and the plane of the –CO—NH– group is 14.89 (10)°. Moreover, in the molecule of (I), the –CO—NH– group adopts a trans conformation. By comparison, in N-(m-tolyl)thioacetamide, the –CS—NH– group also adopts a trans conformation; however, different from (I), the –CS—NH– group is twisted out of the benzene ring plane [torsion angles: C8—N1—C1—C2 = 135.02 (15)° and C8—N1—C1—C6 = −47.40 (2)°]. The dihedral angle between the plane of the benzene ring and the plane of the –CS—NH– group is 48.35 (12)° (Śmiszek-Lindert et al., 2007a). This is very surprising because, in the literature, trans acetanilides and thioacetanilides have planar main skeletons with the amide and thioamide groups lying in the plane of the aromatic ring. The deviations from planarity are smaller than 3° (Galabov et al., 2003). The length of the C8=O1 bond [1.2312 (13) Å] is very similar to that of the corresponding bond [1.230 (9) Å] in the analogous compound 4′-methylacetanilide (Haisa et al., 1977) and these values are both different from bonds of this type [average value 1.224 (1) Å; Allen et al., 1997]. The elongation of the C=O bond lengths is connected with electron shift accompanying formation of an intermolecular N—H···O hydrogen bond. The length of the C8—N1 single bond [1.3568 (13) Å] is typical for bonds of this type [average value 1.351 (1) Å; Allen et al., 1997]. The C—N bond length differs slightly from the values found in similar structures, for example, p-aminoacetanilide [1.344 (4) Å; Haisa et al., 1977], 4′-methylacetanilide [1.349 (3) Å; Haisa et al., 1977] and p-hydroxyacetanilide [1.341 (6) Å; Haisa et al., 1974], and other amide derivatives, such as acetanilide (1.330 Å; Brown & Corbridge, 1954) or trans-N-phenylformamide [1.3359 (18) Å;
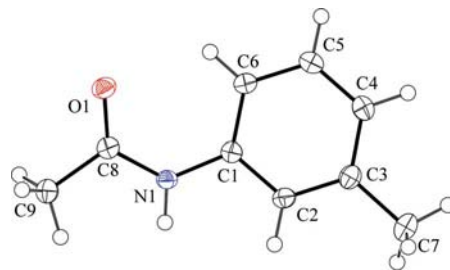

Figure 1
The molecule of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
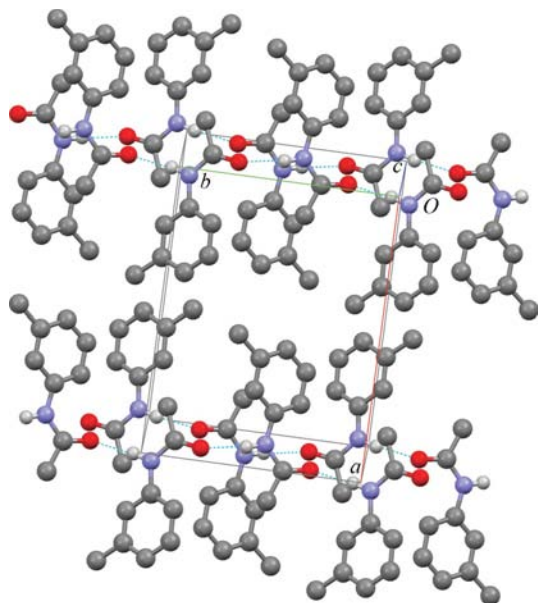
organic compounds

Figure 2
The arrangement of molecules of (I) in the unit cell. Intermolecular N—H···O interactions are represented by dashed lines.

Figure 3
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded $C(4)$ chain along the b axis. Molecules labelled with an asterisk (*) or a hash (#) are at the symmetry positions $(-x, y + \frac{1}{2}, \frac{1}{2} - z)$ and $(-x, y - \frac{1}{2}, \frac{1}{2} - z)$, respectively.

Figure 4
The IR spectrum of a polycrystalline sample of (I) measured at 293 K by the KBr pellet technique in the ν_{N-H} band frequency range.

Omondi *et al.*, 2008]. The C1—N1 single bond is shortened [Table 1; average value 1.4260 Å; Allen *et al.* (1987)], but this shortening always occurs when an N atom is attached to a benzene ring; a summary of corresponding bond lengths in other compounds has already been reported (Brown, 1949). The sum of the angles around the amide N atom is 360°, which indicates that the geometry around this atom is trigonal planar (sp^2-hybridization). An almost identical angle sum (359.87°) around the thioamide N atom is observed in the case of N-(m-tolyl)thioacetamide (Śmiszek-Lindert *et al.*, 2007a).

The crystal structure of (I) is stabilized by intermolecular N—H···O hydrogen bonds (Fig. 2). Atom N1 of the NH group in the molecule at (x, y, z) acts as a hydrogen-bond donor *via* atom H1 to carbonyl atom O1 of the molecule at $(-x, y + \frac{1}{2}, \frac{1}{2} - z)$ (Fig. 3). These interactions form a zigzag chain running parallel to the [010] direction with graph-set motif $C(4)$ (Bernstein *et al.*, 1995; Etter *et al.*, 1990). The same graph-set motif is found in N-(m-tolyl)thioacetamide (Śmiszek-Lindert *et al.*, 2007a).

The IR spectrum of a polycrystalline sample of (I) is shown in Fig. 4. The values of the H···O and N···O distances, as well the N—H···O angle (Table 2), characterize this as a medium-strength hydrogen bond (Desiraju & Steiner, 1999; Steiner, 2002). The strength of the hydrogen bond is supported by spectroscopic measurements. Analysis of the IR spectrum shows that the band of the isolated N—H stretching vibration, ν_{N-H}, is located in the frequency range 3380–2900 cm^{-1}, with the centre of gravity at *ca* 3198 cm^{-1}. The ν_{N-H} band in (I) is shifted towards the lower frequencies by about *ca* 202 cm^{-1}, or 6%, in relation to the unperturbed value at 3400 cm^{-1}. This relative shift is larger than 5% and is characteristic of a medium-strength hydrogen bond (Desiraju & Steiner, 1999). The N—H···O hydrogen bond has an N···O distance of 2.8882 (12) Å, shorter than the values of 2.935 (3), 3.088 (4)
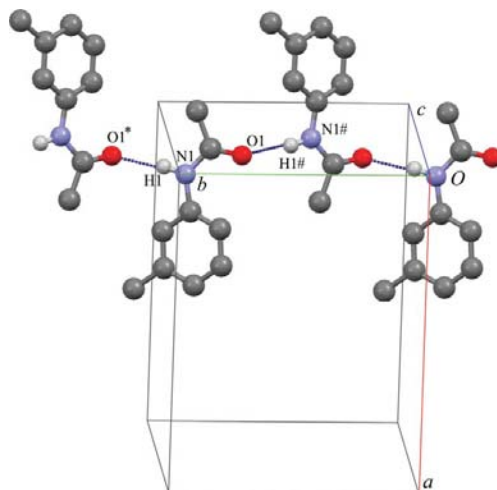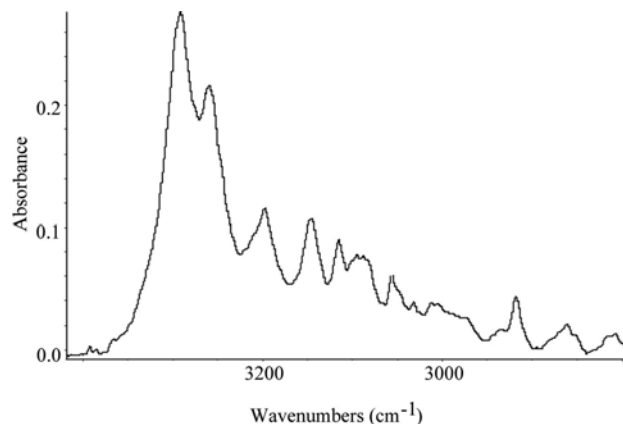
and 2.904 (8) Å found in acetanilide (Johnson *et al.*, 1995), *p*-aminoacetanilide (Haisa *et al.*, 1977) and 4′-methylacetanilide (Haisa *et al.*, 1977), respectively. The N—H···O angle of (I) is almost linear, as is also the case in acetanilide [172.3 (4)°; Johnson *et al.*, 1995].

The molecule of (II) with the atom-labelling scheme is shown in Fig. 5. As revealed by X-ray structure analysis, the molecule of (II) is not planar. The –CS—NH– group is twisted out of the benzene ring plane [torsion angles: C2—C1—C7—N1 = −143.30 (12)° and C6—C1—C7—N1 = 39.01 (17)°]. The dihedral angle between the plane of the benzene ring and the plane of the –CS—NH– group is 86.30 (7)°. Nevertheless, the –CH$_2$– group directly attached to the benzene ring is almost coplanar with it, as shown by the relevant torsion angles [C7—C1—C2—C3 = −177.31 (12)° and C7—C1—C6—C5 = 177.66 (12)°]. The C8═S1 bond (Table 3) is approximately 0.04 Å longer than the average C═S double-bond length of 1.654 (2) Å (Allen *et al.*, 1997) and also longer than in thioamide compounds studied previously by us, for example N-(m-tolyl)thioacetamide [1.6565 (15) Å; Śmiszek-Lindert *et al.*,
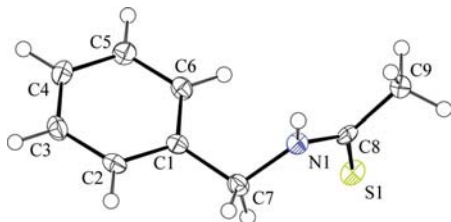
Figure 5
The molecule of compound (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
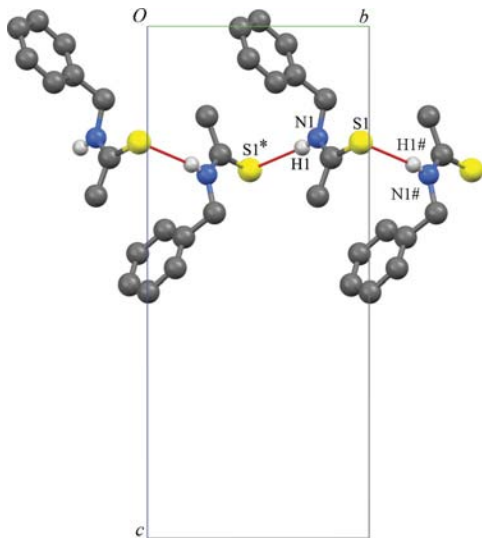

Figure 6
Part of the crystal structure of (II), viewed along the *a* axis. Hydrogen bonds are shown as dashed lines. Molecules labelled with an asterisk (*) or a hash (#) are at the symmetry positions $(2 - x, y - \frac{1}{2}, \frac{1}{2} - z)$ and $(2 - x, y + \frac{1}{2}, \frac{1}{2} - z)$, respectively.

Figure 7
The IR spectrum of a polycrystalline sample of (II) measured at 293 K by the KBr pellet technique in the ν_{N-H} band frequency range.

2007*a*], *N*-(*p*-tolyl)thioacetamide [1.6723 (12) Å; Śmiszek-Lindert *et al.*, 2007*b*], *N*-benzylthioformamide [1.6652 (11) Å; Śmiszek-Lindert *et al.*, 2007*c*] and *N*-methylthiobenzamide [1.6630 (2) Å; Śmiszek-Lindert *et al.*, 2007*d*]. The lengthening of the C=S double bond is probably connected with an electron shift accompanying the formation of the N—H···S hydrogen bond. The C8—N1 single-bond length in *N*-benzylthioacetamide is consistent with the average value found in the fragment X_2C=S (X = C, N, O or S) of 1.322 (2) Å (Allen *et al.*, 1997). The average value is very close to the values found in similar structures, *i.e.* thioacetanilide (Michta *et al.*, 2008), *N*-methylthioacetamide (Flakus *et al.*, 2007), *N*-(2-hydroxyethyl)-2-thiofuramide (Galešić *et al.*, 1987) or *N*-(*m*-tolyl)thioacetamide (Śmiszek-Lindert*et al.*, 2007*a*). The value of the C=S bond length of 1.61 Å is cited in the literature as representing 100% double-bond character, *e.g.* thioformaldehyde, in the gas phase (Johnson *et al.*, 1971). Moreover, C=S bond lengths of *ca* 1.74 Å are cited as representing *ca* 50% double-bond character, as in the case of dithiolate anions (Johnson *et al.*, 1971; Fausto *et al.*, 1989).

In the crystal structure, molecules of (II) are linked by a single N—H···S hydrogen bond into infinite zigzag chains which run parallel to the [010] direction. An intermolecular
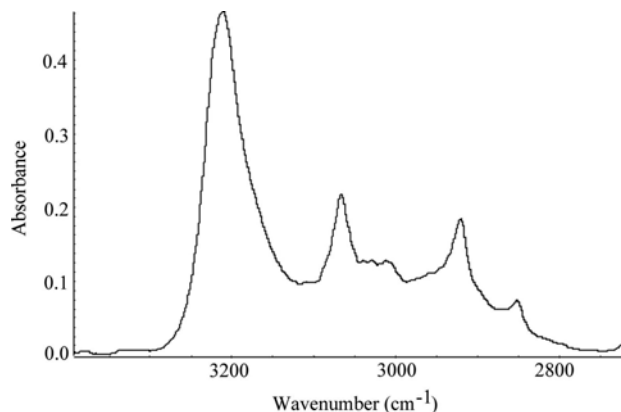
N—H···S hydrogen bond between donor atom N1 and acceptor atom S1 can be described by the graph-set motif *C*(4) (Bernstein *et al.*, 1995; Etter *et al.*, 1990) (Fig. 6). Atom N1 in the molecule at (x, y, z) acts as an intermolecular hydrogen-bond donor *via* atom H1 to atom S1 at $(2 - x, y - \frac{1}{2}, \frac{1}{2} - z)$. The values of the H···S and N···S distances and the N—H···S angle (Table 4) characterize this as a weak hydrogen bond (Desiraju & Steiner, 1999; Steiner, 2002). The strength of the hydrogen bond in this compound was also investigated by IR spectroscopy. The ν_{N-H} proton-stretching band covers the range 3300–2990 cm^{-1} (Fig. 7), with the centre of gravity at *ca* 3140 cm^{-1}. This band is shifted towards the lower frequencies by *ca* 260 cm^{-1}, or 8%. This relative shift is larger than 5% and is characteristic of a medium-strength hydrogen bond (Desiraju & Steiner, 1999).

Knowledge of the hydrogen-bond geometry in the molecular crystals of amides and thioamides enables us to interpret and understand isotopic and spectroscopic effects in IR spectra. Further studies on the polarized IR spectra of the title compounds and their isotopic derivatives will be carried out in the future.

Experimental

3′-Methylacetanilide, (I), was purchased from Sigma–Aldrich (98% pure). White plate-shaped crystals suitable for diffraction analysis were obtained by slow evaporation of an ethanol–acetone (3:1 *v*/*v*) solution at 281 K. *N*-Benzylthioacetamide, (II), was obtained by the reaction of *N*-benzylacetamide with phosphorus pentasulfide. Phosphorus pentasulfide (0.61 g, 0.1 mol) was added in small portions to a solution of *N*-benzylacetamide (2.06 g, 0.5 mol) in toluene (5.50 ml) at 343–353 K with stirring. The reaction mixture was then brought to reflux for 2 h. The hot reaction mixture was decanted and the solution concentrated to give a yellow precipitate. The precipitate was dissolved in petroleum ether and the solution left for crystallization at room temperature. Single crystals of (II) suitable for X-ray diffraction analysis were obtained by slow evaporation of a diethyl ether–acetone (3:1 *v*/*v*) solution [yield: 1.55 g, 67.83%; m.p. 338–339 K, literature m.p. 338 K (Schlatter, 1942)]. The IR spectra of polycrystalline samples of (I) and (II) dispersed in KBr were measured by the transmission method at room temperature using an FT–IR Nicolet Magna 560 spectrometer with a resolution of 2 cm^{-1}.

organic compounds

Compound (I)

Crystal data

$C_9H_{11}NO$
$M_r = 149.19$
Monoclinic, $P2_1/c$
$a = 12.280 (3)$ Å
$b = 9.4471 (19)$ Å
$c = 7.3028 (15)$ Å
$\beta = 99.97 (3)°$

$V = 834.4 (3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 100 (2)$ K
$0.4 \times 0.4 \times 0.07$ mm

Data collection

Oxford Diffraction KM-4-CCD
 Sapphire3 diffractometer
7872 measured reflections

2807 independent reflections
1965 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.135$
$S = 1.00$
2807 reflections
105 parameters

H atoms treated by a mixture of
 independent and constrained
 refinement
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

O1—C8	1.2312 (13)	C2—C3	1.3912 (15)
N1—C8	1.3568 (13)	C3—C4	1.3960 (15)
N1—C1	1.4109 (14)	C4—C5	1.3870 (16)
N1—H1	0.882 (13)	C5—C6	1.3904 (15)
C1—C2	1.3995 (14)	C8—C9	1.5046 (15)
C1—C6	1.3999 (14)		
C8—N1—C1—C2	−165.66 (9)	C8—N1—C1—C6	15.95 (16)

Table 2
Hydrogen-bond geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O1^i	0.882 (13)	2.011 (14)	2.8882 (12)	172.3 (12)

Symmetry code: (i) $-x, y + \frac{1}{2}, -z + \frac{1}{2}$.

Compound (II)

Crystal data

$C_9H_{11}NS$
$M_r = 165.25$
Orthorhombic, $P2_12_12_1$
$a = 5.5957 (11)$ Å
$b = 8.2201 (16)$ Å
$c = 19.278 (4)$ Å

$V = 886.7 (3)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.30$ mm^{-1}
$T = 95 (2)$ K
$0.6 \times 0.15 \times 0.14$ mm

Data collection

Oxford Diffraction KM-4-CCD
 Sapphire3 diffractometer
Absorption correction: analytical
 [CrysAlis RED (Oxford Diffrac-
 tion, 2006); analytical numeric
 absorption correction using a
 multifaceted crystal model based
 on expressions derived by Clark
 & Reid (1995)]
$T_{min} = 0.974, T_{max} = 0.990$

5596 measured reflections
1557 independent reflections
1496 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.066$
$S = 1.00$
1557 reflections
104 parameters
H atoms treated by a mixture of
 independent and constrained
 refinement

$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}
Absolute structure: Flack (1983),
 618 Friedel pairs
Flack parameter: −0.01 (6)

Table 3
Selected geometric parameters (Å, °) for (II).

S1—C8	1.6917 (14)	C2—C3	1.397 (2)
N1—C8	1.3230 (17)	C3—C4	1.3883 (19)
N1—C7	1.4669 (17)	C4—C5	1.390 (2)
C1—C6	1.3938 (19)	C5—C6	1.3974 (19)
C1—C2	1.3994 (19)	C8—C9	1.507 (2)
C1—C7	1.5197 (19)		
C6—C1—C7—N1	39.01 (17)	C2—C1—C7—N1	−143.30 (12)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$S1^i	0.858 (16)	2.554 (17)	3.4056 (13)	171.8 (15)

Symmetry code: (i) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$.

The amide and thioamide H atoms were located in a difference Fourier map and were refined freely; all other H atoms were introduced in geometrically idealized positions and refined with an appropriate riding model, with C—H = 0.95 (aromatic), 0.99 (methylene) or 0.98 Å (methyl). The isotropic displacement parameters were constrained with U_{iso}(H) values of $1.2U_{eq}$(C,N) for H atoms in CH or NH groups and $1.5U_{eq}$(C) for methyl H atoms.

For both compounds, 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: ORTEP-3 (Farrugia, 1997) and Mercury (Macrae et al., 2006); software used to prepare material for publication: publCIF (Westrip, 2008).

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