N-(p-Tolyl)thioacetamide

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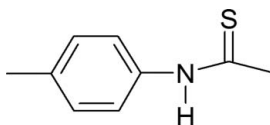Correspondence e-mail: wiola.lindert@wp.pl

The reaction of N-(p-tolyl)acetamide with phosphorus penta-sulfide in toluene gives the title compound, $C_9H_{11}NS$. The amide group forms N—H···S hydrogen bonds with adjacent molecules, linking them into chains.

Related literature

For related literature, see: Flakus & Jabłońska (2004); Flakus et al. (2002, 2003, 2007); Tabakovic et al. (1979). For discussion of hydrogen bonding, see: Desiraju & Steiner (1999).

Experimental

Crystal data

$C_9H_{11}NS$	$V = 1801.11\ (18)$ Å^3
$M_r = 165.25$	$Z = 8$
Orthorhombic, $Pbca$	Mo $K\alpha$ radiation
$a = 13.6695\ (9)$ Å	$\mu = 0.29$ mm^{-1}
$b = 8.7917\ (5)$ Å	$T = 298\ (2)$ K
$c = 14.9870\ (8)$ Å	$0.4 \times 0.3 \times 0.2$ mm

Data collection

Oxford Diffraction KM-4 CCD Sapphire3 diffractometer	3039 independent reflections
Absorption correction: none	1913 reflections with $I > 2\sigma(I)$
16454 measured reflections	$R_{int} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.113$	
$S = 1.06$	
3039 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
105 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1^i	0.875 (14)	2.555 (15)	3.3926 (10)	160.6 (12)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis CCD*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3*, (Farrugia, 1997); software used to prepare material for publication: *publCIF* (Westrip, 2007).

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supplementary materials

N-(*p*-Tolyl)thioacetamide

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Comment

The title compound, (I), was prepared from *N-p*-tolyl-acetamide and phosphorus pentasulfide in toluene as a solvent (see *Experimental*).

Determination of crystal structure (I) was necessary for our spectral studies. The *N-p*-tolyl-thioacetamide is the subject of our study of a generation mechanism of the IR-spectra of hydrogen bonded molecular crystals (Flakus *et al.*, 2003; Flakus & Jabłońska, 2004). IR-spectroscopy is still considered as a basic and most powerful tool used in hydrogen bond research, providing experimental data which helps us fine understand dynamical mechanisms of interactions occurring within single hydrogen bonds. These interactions are responsible for the unique IR-spectral properties of the hydrogen bond. A particular value of the IR-spectroscopy in hydrogen bond research results from very spectacular effects accompanying hydrogen bond formation in molecular systems. The most important effects are observed in the frequency ranges of the proton stretching vibration bands ν_{N-H}, corresponding to the stretching motions N–H bonds in the N–H···S hydrogen bridges (Flakus *et al.*, 2002, 2007).

The molecular structure of (I) is shown in Fig.1 and stabilized by weak intermolecular N–H···S hydrogen bonds formed by N1, H1 and S1 (Fig.2). In the crystal structure of (I) the molecules interact *via* N–H···S hydrogen bonds forming infinite zigzag chains parallel to the *b* axis. The values of the H···S and N···S distances and N–H···S angle characterize this bond as a weak hydrogen bond (Desiraju & Steiner, 1999). The band of the isolated N–H stretching vibration, ν_{N-H}, is located in the 3200–2850 cm^{-1} frequency range. The study of the IR-spectra of (I) showed that the hydrogen bond is intermediate between medium-strength and weak hydrogen bonds.

Experimental

Phosphorus pentasulfide (0.745 g, 0.1 mol) was added small portions of *N-p*-tolyl-acetamide (2.5 g, 0.5 mol) in toluene (6.71 ml) at 351 K with stirring. The reaction mixture was then brought to reflux for 3 h. After heating the hot reaction mixture was decanted and the solution was concentrated to give a yellow precipitate. The precipitate was dissolved in diethyl ether and the solution was left for crystallization at room temperature. After a few hours, the deposited yellow crystals were collected and recrystallized from diethyl ether, giving crystals of (I) suitable for X-ray diffraction. The yield 1.858 g, 67%; m.p. 405–408 K; literature m.p. 406–408 K (Tabakovic *et al.*, 1979).

The IR-spectra of *N-p*-tolyl-thioacetamide crystals were measured by a transmission method, with the help of the FT—IR Nicolet Magna spectrometer, for two different, mutually perpendicular polarizations of IR-beam. Spectra were measured for the ν_{N-H} and ν_{N-D} band frequency ranges at temperatures of 298 and 77 K. The IR-spectra were measured at 2 cm^{-1} resolution. The IR-spectrum of polycrystalline sample of (I) was measured at room temperature using the KBr pellet technique.

supplementary materials

Refinement

All H atoms on C atoms were generated geometrically and refined as riding atoms with C–H = 0.93 − 0.96 Å. Their isotropic displacement parameters were constrained with U_{iso}(H) values of $1.5U_{eq}$(C). The H atom attached on N atom located from diffrerence Fourier map and refined with U_{iso}(H) values of $1.2U_{eq}$(N).
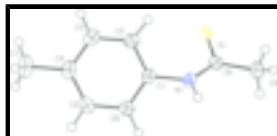
Figures

Fig. 1. The conformation of *N-p*-tolyl-thioacetamide molecule with the atom numbering scheme. Atomic displacement ellipsoids represent 50% probability level. H atoms are depicted as small circles of arbitrary radii.
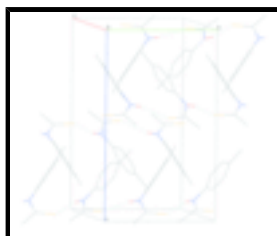

Fig. 2. The crystal packing of (I), viewed approxyimately down the *a* axis. Hydrogen bonds are shown as dashed lines. C-bonds H atoms have been omitted for clarity.

N-(*p*-Tolyl)thioacetamide

Crystal data

$C_9H_{11}NS$	$D_x = 1.219$ Mg m^{-3}
$M_r = 165.25$	Melting point: 407 K
Orthorhombic, *Pbca*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2ab	Cell parameters from 1536 reflections
$a = 13.6695$ (9) Å	θ = 3.0–32.9º
$b = 8.7917$ (5) Å	μ = 0.29 mm^{-1}
$c = 14.9870$ (8) Å	$T = 298$ (2) K
$V = 1801.11$ (18) Å^3	Needle, yellow
$Z = 8$	$0.4 \times 0.3 \times 0.2$ mm
$F_{000} = 704$	

Data collection

Oxford Diffraction KM-4 CCD Sapphire3 diffractometer	1913 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.025$
Monochromator: graphite	$\theta_{max} = 32.9º$
$T = 298(2)$ K	$\theta_{min} = 3.0º$
ω scans	$h = -20 \rightarrow 20$
Absorption correction: none	$k = -13 \rightarrow 5$
16454 measured reflections	$l = -21 \rightarrow 22$

3039 independent reflections

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.113$	$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3039 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
105 parameters	$\Delta\rho_{min} = -0.37$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
S1	0.11536 (2)	0.75352 (3)	0.49664 (2)	0.02683 (11)
N1	0.23686 (7)	0.54385 (11)	0.56042 (7)	0.0241 (2)
H1	0.2650 (10)	0.4555 (16)	0.5524 (9)	0.029*
C1	0.27830 (8)	0.64005 (12)	0.62737 (7)	0.0216 (2)
C2	0.22042 (9)	0.69940 (13)	0.69516 (8)	0.0270 (3)
H2	0.1536	0.6797	0.6961	0.032*
C3	0.26225 (11)	0.78768 (14)	0.76113 (9)	0.0312 (3)
H3	0.2230	0.8271	0.8062	0.037*
C4	0.36230 (10)	0.81878 (15)	0.76139 (8)	0.0295 (3)
C5	0.41883 (10)	0.75891 (14)	0.69322 (9)	0.0314 (3)
H5	0.4856	0.7789	0.6921	0.038*
C6	0.37780 (9)	0.66954 (14)	0.62649 (9)	0.0276 (3)
H6	0.4170	0.6297	0.5815	0.033*
C7	0.40770 (13)	0.91366 (16)	0.83449 (10)	0.0434 (4)
H7A	0.4252	0.8492	0.8837	0.065*
H7B	0.3616	0.9888	0.8542	0.065*

H7C	0.4652	0.9632	0.8121	0.065*
C8	0.16556 (9)	0.58052 (13)	0.50401 (7)	0.0220 (2)
C9	0.13179 (9)	0.45255 (14)	0.44517 (9)	0.0303 (3)
H9A	0.1837	0.3799	0.4384	0.045*
H9B	0.1139	0.4921	0.3877	0.045*
H9C	0.0761	0.4038	0.4718	0.045*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02523 (17)	0.02055 (16)	0.03471 (19)	0.00065 (11)	−0.00623 (12)	0.00032 (11)
N1	0.0275 (5)	0.0173 (4)	0.0274 (5)	0.0023 (4)	−0.0020 (4)	−0.0026 (4)
C1	0.0255 (6)	0.0175 (5)	0.0219 (5)	0.0004 (4)	−0.0016 (4)	0.0012 (4)
C2	0.0268 (6)	0.0276 (6)	0.0267 (6)	−0.0010 (5)	0.0030 (5)	0.0010 (5)
C3	0.0399 (8)	0.0299 (6)	0.0237 (6)	0.0022 (6)	0.0030 (5)	−0.0025 (5)
C4	0.0414 (8)	0.0202 (6)	0.0269 (6)	−0.0015 (5)	−0.0087 (5)	0.0018 (5)
C5	0.0268 (6)	0.0315 (6)	0.0360 (7)	−0.0032 (5)	−0.0064 (6)	0.0016 (5)
C6	0.0246 (6)	0.0288 (6)	0.0294 (6)	0.0018 (5)	−0.0007 (5)	−0.0019 (5)
C7	0.0605 (10)	0.0322 (7)	0.0375 (8)	−0.0049 (7)	−0.0179 (7)	−0.0031 (6)
C8	0.0218 (5)	0.0202 (5)	0.0240 (6)	−0.0035 (4)	0.0028 (4)	0.0010 (4)
C9	0.0332 (7)	0.0259 (6)	0.0318 (7)	−0.0058 (5)	−0.0039 (5)	−0.0046 (5)

Geometric parameters (Å, °)

S1—C8	1.6723 (12)	C4—C7	1.5104 (18)
N1—C8	1.3299 (15)	C5—C6	1.3900 (18)
N1—C1	1.4293 (14)	C5—H5	0.9300
N1—H1	0.875 (14)	C6—H6	0.9300
C1—C6	1.3847 (16)	C7—H7A	0.9600
C1—C2	1.3893 (17)	C7—H7B	0.9600
C2—C3	1.3809 (18)	C7—H7C	0.9600
C2—H2	0.9300	C8—C9	1.5021 (17)
C3—C4	1.3947 (19)	C9—H9A	0.9600
C3—H3	0.9300	C9—H9B	0.9600
C4—C5	1.385 (2)	C9—H9C	0.9600
C8—N1—C1	126.39 (9)	C1—C6—C5	119.69 (12)
C8—N1—H1	116.7 (9)	C1—C6—H6	120.2
C1—N1—H1	116.6 (9)	C5—C6—H6	120.2
C6—C1—C2	119.74 (11)	C4—C7—H7A	109.5
C6—C1—N1	119.56 (10)	C4—C7—H7B	109.5
C2—C1—N1	120.66 (11)	H7A—C7—H7B	109.5
C3—C2—C1	119.92 (12)	C4—C7—H7C	109.5
C3—C2—H2	120.0	H7A—C7—H7C	109.5
C1—C2—H2	120.0	H7B—C7—H7C	109.5
C2—C3—C4	121.21 (13)	N1—C8—C9	114.64 (10)
C2—C3—H3	119.4	N1—C8—S1	124.28 (9)
C4—C3—H3	119.4	C9—C8—S1	121.08 (9)
C5—C4—C3	118.07 (12)	C8—C9—H9A	109.5

C5—C4—C7	121.05 (13)	C8—C9—H9B		109.5
C3—C4—C7	120.88 (13)	H9A—C9—H9B		109.5
C4—C5—C6	121.36 (12)	C8—C9—H9C		109.5
C4—C5—H5	119.3	H9A—C9—H9C		109.5
C6—C5—H5	119.3	H9B—C9—H9C		109.5

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···S1[i]	0.875 (14)	2.555 (15)	3.3926 (10)	160.6 (12)

Symmetry codes: (i) −*x*+1/2, *y*−1/2, *z*.

Fig. 1

Fig. 2