Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

4-Chloroanilinium thiocyanate

Siti Fairus M. Yusoff, F. Salem Halima and Bohari M. Yamin*

School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
Correspondence e-mail: bohari@pkrisc.cc.ukm.my

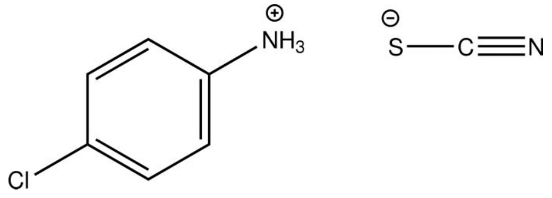
Received 23 May 2012; accepted 24 May 2012

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.039; wR factor = 0.108; data-to-parameter ratio = 16.5.

In the title compound, $C_6H_7ClN^+\cdot NCS^-$, the benzene ring and the protonated amine and chloro substituents are nearly planar, with a maximum deviation of 0.002 (2) Å for the N atom. In the crystal, the molecules are linked by N—H···N and N—H···S hydrogen bonds into a chain along the b axis.

Related literature

For bond-length data see: Allen *et al.* (1987) and for a description of the Cambridge Structural Database, see: Allen (2002). For related thiocyanate structures, see: Salem *et al.* (2012); Selvakumaran *et al.* (2011); Khawar Rauf *et al.* (2008).



Experimental

Crystal data

$C_6H_7ClN^+\cdot NCS^-$
M_r = 186.66
Orthorhombic, *Pbca*
a = 7.743 (2) Å
b = 7.199 (2) Å
c = 31.913 (10) Å

V = 1778.8 (10) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.60 mm^{-1}
T = 298 K
0.50 × 0.43 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min}$ = 0.754, $T_{\max}$ = 0.841

10422 measured reflections
1846 independent reflections
1628 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.108
S = 1.18
1846 reflections
112 parameters
3 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···N2$^{\rm i}$	0.87 (2)	2.03 (1)	2.888 (2)	172 (2)
N1—H1B···N2$^{\rm ii}$	0.86 (1)	2.08 (1)	2.911 (3)	162 (2)
N1—H1C···S1$^{\rm iii}$	0.87 (2)	2.48 (3)	3.285 (2)	155 (2)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

The authors would like to thank the Malaysian Government and Universiti Kebangsaan Malaysia for the research grants UKM-GUP-NBT-68–27–110.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2362).

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supplementary materials

Acta Cryst. (2012). E**68**, o1988 [doi:10.1107/S160053681202377X]

4-Chloroanilinium thiocyanate

Siti Fairus M. Yusoff, F. Salem Halima and Bohari M. Yamin

Comment

The title compound (Fig. 1) is an organic thiocyanate similar to dicylohexylammonium thiocyanate (Khawar Rauf *et al.*, 2008; Selvakumaran *et al.*, 2011) and recently 2-cyclohexan-1-iminium thiocyanate (Salem *et al.*, 2012). The *para*-anilinium cation is planar except the hydrogen atoms of the ammonium moiety. The maximum deviation is 0.002 (2) Å for N1 atom from the least square plane. The thiocyanate ion is linear with N2–C7–S1 bond angle of 179.5 (2)°. The bond lengths and angles are in normal range (Allen *et al.*, 1987; 2002). In the crystal structure, the molecules are linked by the intermolecular hydrogen bonds between the hydrogen atoms of the ammonium moiety with the nitrogen and sulfur atoms of the thiocynato anion (Table 1) to form one-dimensional chain along the *b* axis (Fig. 2).

Experimental

All solvents and chemicals were of analytical grade and were used without purification. The title compound was prepared by mixing ammonium thiocyanate (0.76 g, 0.01 mol) and *para*-chloroaniline (1.27 g, 0.01 mol) in the presence of HCl. The mixture was refluxed for 1 h. Single crystals were obtained from the solution after one day of evaporation. Yield 85%; m.p: 390.5–393.2 K.

Refinement

After their location in the difference map, the H-atoms attached to the C were fixed geometrically at ideal positions and allowed to ride on the parent atoms with C—H = 0.93 Å, with $U_{iso}(H)=1.2U_{eq}(C,)$ However, the protonated amino hydrogen atoms were located from the Fourier map and refined isotropically.

Computing details

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008), *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2009).

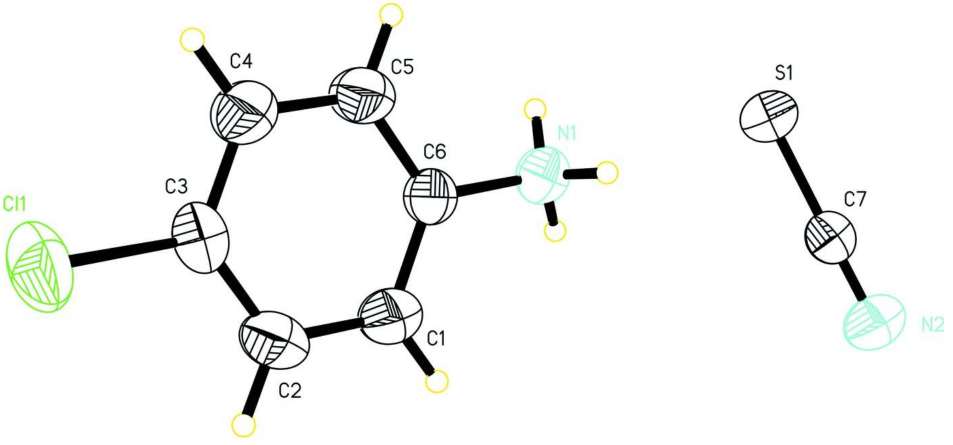

Figure 1

Molecular structure of the title compound, (I), with 50% probability displacement ellipsoids.

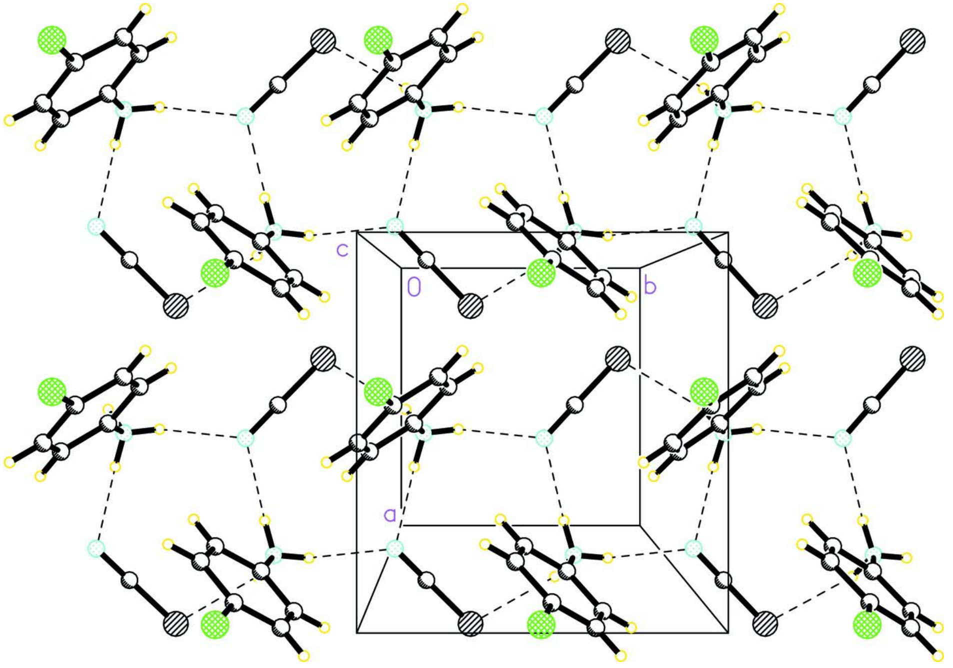

Figure 2

Packing diagram of (I), viewed down *b* axis. The dashed lines denote hydrogen bonds.

4-Chloroanilinium thiocyanate

Crystal data

$C_6H_7ClN^+\cdot NCS^-$
$M_r = 186.66$
Orthorhombic, *Pbca*
Hall symbol: -P 2ac 2ab
$a = 7.743$ (2) Å
$b = 7.199$ (2) Å
$c = 31.913$ (10) Å
$V = 1778.8$ (10) Å^3
$Z = 8$
$F(000) = 768$
$D_x = 1.394$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4443 reflections
$\theta = 1.2$–26.5°
$\mu = 0.60$ mm^{-1}
$T = 298$ K
Slab, colourless
0.50 × 0.43 × 0.30 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 83.66 pixels mm^{-1}
ω scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.754$, $T_{\max} = 0.841$
10422 measured reflections
1846 independent reflections
1628 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.024$
$\theta_{\max} = 26.5°$, $\theta_{\min} = 1.2°$
$h = -5 \rightarrow 9$
$k = -9 \rightarrow 8$
$l = -38 \rightarrow 40$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.108$
$S = 1.18$
1846 reflections
112 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.6879P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.002$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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}
Cl1	0.41886 (10)	0.01916 (11)	0.749321 (18)	0.0681 (2)
S1	0.66687 (7)	0.20120 (7)	0.468838 (17)	0.04316 (18)
N1	0.5614 (2)	0.1442 (3)	0.56935 (6)	0.0404 (4)
H1A	0.6668 (16)	0.111 (4)	0.5642 (7)	0.048 (7)*
H1B	0.550 (3)	0.2589 (17)	0.5623 (8)	0.062 (8)*
H1C	0.490 (3)	0.082 (4)	0.5539 (7)	0.068 (8)*
N2	0.4214 (2)	0.4537 (3)	0.43930 (7)	0.0510 (5)
C1	0.4128 (3)	0.2283 (4)	0.63414 (7)	0.0581 (6)
H1	0.3576	0.3241	0.6199	0.070*
C2	0.3805 (4)	0.1992 (4)	0.67630 (8)	0.0638 (7)
H2	0.3038	0.2757	0.6906	0.077*
C3	0.4620 (3)	0.0576 (3)	0.69664 (6)	0.0446 (5)
C4	0.5754 (3)	−0.0562 (3)	0.67624 (7)	0.0561 (6)
H4	0.6301	−0.1524	0.6904	0.067*
C5	0.6076 (3)	−0.0262 (3)	0.63414 (7)	0.0526 (6)
H5	0.6847	−0.1023	0.6198	0.063*

C6	0.5263 (2)	0.1152 (3)	0.61366 (6)	0.0363 (4)
C7	0.5235 (3)	0.3494 (3)	0.45172 (6)	0.0367 (4)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0875 (5)	0.0781 (5)	0.0387 (3)	−0.0028 (4)	0.0118 (3)	0.0012 (3)
S1	0.0390 (3)	0.0415 (3)	0.0490 (3)	0.0027 (2)	0.0001 (2)	0.0058 (2)
N1	0.0408 (10)	0.0419 (10)	0.0387 (9)	−0.0012 (8)	−0.0013 (8)	0.0028 (7)
N2	0.0441 (10)	0.0450 (10)	0.0639 (12)	0.0019 (9)	−0.0057 (9)	0.0067 (9)
C1	0.0664 (16)	0.0605 (14)	0.0473 (13)	0.0269 (13)	−0.0001 (11)	0.0027 (11)
C2	0.0710 (16)	0.0712 (16)	0.0491 (13)	0.0305 (14)	0.0105 (12)	−0.0039 (12)
C3	0.0497 (12)	0.0505 (12)	0.0338 (9)	−0.0063 (10)	0.0016 (9)	−0.0028 (9)
C4	0.0690 (16)	0.0528 (13)	0.0465 (12)	0.0168 (12)	0.0043 (11)	0.0104 (10)
C5	0.0606 (14)	0.0531 (13)	0.0440 (12)	0.0189 (11)	0.0098 (10)	0.0047 (10)
C6	0.0354 (9)	0.0366 (10)	0.0368 (10)	−0.0023 (8)	−0.0018 (8)	−0.0012 (7)
C7	0.0372 (10)	0.0338 (9)	0.0392 (10)	−0.0066 (8)	0.0024 (8)	−0.0005 (8)

Geometric parameters (Å, º)

Cl1—C3	1.736 (2)	C1—H1	0.9300
S1—C7	1.634 (2)	C2—C3	1.363 (3)
N1—C6	1.455 (3)	C2—H2	0.9300
N1—H1A	0.866 (10)	C3—C4	1.365 (3)
N1—H1B	0.860 (10)	C4—C5	1.384 (3)
N1—H1C	0.868 (10)	C4—H4	0.9300
N2—C7	1.160 (3)	C5—C6	1.364 (3)
C1—C6	1.365 (3)	C5—H5	0.9300
C1—C2	1.385 (4)		
C6—N1—H1A	108.8 (16)	C2—C3—Cl1	119.39 (18)
C6—N1—H1B	111.9 (19)	C4—C3—Cl1	119.33 (18)
H1A—N1—H1B	108 (3)	C3—C4—C5	119.0 (2)
C6—N1—H1C	110.9 (19)	C3—C4—H4	120.5
H1A—N1—H1C	111 (3)	C5—C4—H4	120.5
H1B—N1—H1C	107 (3)	C6—C5—C4	119.9 (2)
C6—C1—C2	119.4 (2)	C6—C5—H5	120.1
C6—C1—H1	120.3	C4—C5—H5	120.1
C2—C1—H1	120.3	C5—C6—C1	120.9 (2)
C3—C2—C1	119.5 (2)	C5—C6—N1	119.10 (18)
C3—C2—H2	120.3	C1—C6—N1	120.02 (19)
C1—C2—H2	120.3	N2—C7—S1	179.5 (2)
C2—C3—C4	121.3 (2)		
C6—C1—C2—C3	−0.3 (4)	C3—C4—C5—C6	−0.1 (4)
C1—C2—C3—C4	0.2 (4)	C4—C5—C6—C1	0.0 (4)
C1—C2—C3—Cl1	−179.0 (2)	C4—C5—C6—N1	−179.8 (2)
C2—C3—C4—C5	0.1 (4)	C2—C1—C6—C5	0.2 (4)
Cl1—C3—C4—C5	179.2 (2)	C2—C1—C6—N1	180.0 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N2^{i}	0.87 (2)	2.03 (1)	2.888 (2)	172 (2)
N1—H1*B*···N2^{ii}	0.86 (1)	2.08 (1)	2.911 (3)	162 (2)
N1—H1*C*···S1^{iii}	0.87 (2)	2.48 (3)	3.285 (2)	155 (2)

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