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Methyl *N*-(4-chlorophenyl)-*N*′-cyanocarbamimidothioate

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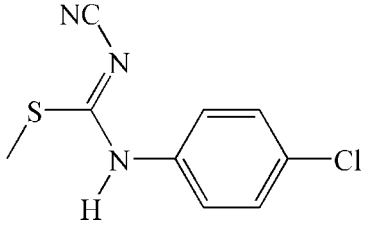
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.058; wR factor = 0.132; data-to-parameter ratio = 14.2.

Short halogen–halogen and sulfur–sulfur interactions have been exploited in the design of supramolecular assemblies. The intermolecular Cl···Cl (3.581 Å) and S···S (3.282 Å) distances in the crystal structure of the title compound, $C_9H_8ClN_3S$, are shorter than the sum of the van der Waals radii. Classical N—H···N and C—H···N hydrogen bonds also contribute to the stabilization of the crystal structure.

Related literature

For related literature, see: Dai *et al.* (2004); Karan & Arunan (2004); Lan *et al.* (2005, 2006); Tilley & Ramuz (1980); Wu (1977); Zou *et al.* (2005).



Experimental

Crystal data

$C_9H_8ClN_3S$
M_r = 225.69
Orthorhombic, *Pbcn*
a = 38.708 (17) Å
b = 7.160 (3) Å
c = 7.407 (3) Å
V = 2052.8 (16) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.54 mm^{-1}
T = 293 (2) K
0.15 × 0.12 × 0.08 mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997*b*)
T_{min} = 0.924, T_{max} = 0.958
7728 measured reflections
1809 independent reflections
1498 reflections with $I > 2\sigma(I)$
R_{int} = 0.046

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.058
$wR(F^2)$ = 0.132
S = 1.25
1809 reflections
127 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5A···N2^{i}	0.93	2.66	3.467 (5)	146
N3—H3A···N1^{ii}	0.86	2.18	2.974 (5)	154

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

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Sheldrick, 1997*b*).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2024).

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supplementary materials

Acta Cryst. (2007). E**63**, o3018 [**doi:10.1107/S1600536807024130**]

Methyl *N*-(4-chlorophenyl)-*N*'-cyanocarbamimidothioate

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Comment

N-(4-chlorophenyl)-*N*'-cyano-carbamimidothioic acid, methyl ester (I) has been used as an intermediate in the synthesis of potassium channel openers, which show considerable biomolecular current-voltage rectification characteristics. (Lan *et al.*, 2005, 2006)It is also an important reagent for heterocyclic drugs, such as triazoles and oxadiazoles(Wu, 1977; Tilley & Ramuz, 1980).

The molecular structure and atom-labeling scheme are shown in Fig. 1. The bonds N2—C3, N2—C2 and N3—C3 [1.320 (5), 1.322 (5) and 1.331 (5) Å, respectively] have partial double-bond character. The triple-bond character of C2—N1 [1.157 (5) Å] and the N1—C2—N2 angle of 173.8 (4) ° defining the linearity of the cyano moiety, are typical of this group of *N*-cyano compounds.

The distances of Cl1···Cl1^{i} [symmetry code: (i) 1/2 − *x*, *y* − 1/2, *z*] (3.581 Å) and S1···S1^{ii} [symmetry code: (ii) −*x*, *y*, 3/2 − *z*] (3.282 Å) in the lattice, lower than the sum of the van der Waals for the corresponding atoms, demonstrate the existence of short contacts (Dai *et al.*, 2004; Karan & Arunan, 2004; Zou *et al.*, 2005). The Cl1···Cl1 interactions are responsible for the formation of one-dimensional chains, and the S1···S1 interactions bridge them, as shown in Fig. 2.

There also exists classical hydrogen bonds in the structure, C5—H5a···N2^{iii} [symmetry code: (iii) *x*,-*y* + 1,*z* − 1/2] and N3—H3a···N1 [symmetry code: (iv) *x*,*y*,*z* − 1].

Experimental

The title compound was synthesized by the reaction of 4-chloroaniline and dimethyl cyanoimidodithiocarbonate according to the method of Lan *et al.* (2005) in a yield of 80%. Single crystals of (I) were grown by slow evaporation, in air, of an ethanol/tetrahydrofuran (1/1, *v*/*v*) solution. Selected analytical data: m.p. 464–466 K; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.57 (s, 3H), 2.49 (s, 1H), 7.27–7.91 (m, 4H).

Refinement

H atoms were included using a riding model with C—H = 0.96 or 0.97 Å and $U_{iso} = 1.2U_{eq}$ of the parent C atom.

Figures

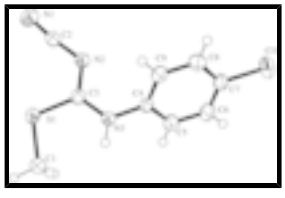

Fig. 1. Molecular structure of the title compound. Displacement ellipsoids are drawn at 50% probability level and H atoms are shown as small spheres of arbitrary radii.

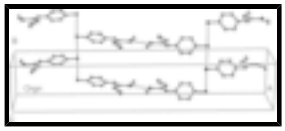

Fig. 2. The crystal structure of (I), viewed along the *c* axis. Dashed lines indicate S···S and Cl···Cl short contacts, H atoms are omitted for clarity.

Methyl *N*-(4-chlorophenyl)-*N*'-cyanocarbamimidothioate

Crystal data

$C_9H_8ClN_3S$	F_{000} = 928
M_r = 225.69	D_x = 1.461 Mg m^{-3}
Orthorhombic, *Pbcn*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2n 2ab	Cell parameters from 797 reflections
a = 38.708 (17) Å	θ = 2.9–26.9º
b = 7.160 (3) Å	μ = 0.54 mm^{-1}
c = 7.407 (3) Å	*T* = 293 (2) K
V = 2052.8 (16) Å^3	Prism, colourless
Z = 8	0.15 × 0.12 × 0.08 mm

Data collection

Bruker APEX CCD area-detector diffractometer	1809 independent reflections
Radiation source: fine-focus sealed tube	1498 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.046
T = 293(2) K	θ_{max} = 25.0º
φ and ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Sheldrick, 1997b)	*h* = −46→31
T_{min} = 0.924, T_{max} = 0.958	*k* = −7→8
7728 measured reflections	*l* = −8→8

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.058	H-atom parameters constrained
$wR(F^2)$ = 0.132	$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 3.8026P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.25	$(\Delta/\sigma)_{max}$ = 0.002
1809 reflections	$\Delta\rho_{max}$ = 0.33 e Å^{-3}
127 parameters	$\Delta\rho_{min}$ = −0.24 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 $F^2 > 2\text{sigma}(F^2)$ 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	0.25094 (2)	0.21867 (15)	0.35499 (15)	0.0468 (3)
S1	0.03929 (2)	0.24739 (17)	0.66683 (12)	0.0438 (3)
N1	0.07780 (9)	0.2476 (6)	1.1032 (5)	0.0581 (11)
N2	0.10311 (7)	0.2383 (5)	0.7964 (4)	0.0392 (8)
N3	0.09994 (7)	0.2402 (4)	0.4876 (4)	0.0342 (7)
H3A	0.0871	0.2430	0.3929	0.041*
C1	0.02332 (10)	0.2496 (7)	0.4414 (5)	0.0572 (13)
H1A	−0.0015	0.2530	0.4433	0.086*
H1B	0.0309	0.1391	0.3796	0.086*
H1C	0.0319	0.3580	0.3797	0.086*
C2	0.08802 (9)	0.2437 (6)	0.9566 (5)	0.0379 (9)
C3	0.08436 (9)	0.2411 (5)	0.6478 (5)	0.0320 (8)
C4	0.13666 (8)	0.2348 (5)	0.4620 (4)	0.0299 (8)
C5	0.15109 (9)	0.3549 (5)	0.3371 (5)	0.0379 (9)
H5A	0.1372	0.4398	0.2758	0.045*
C6	0.18627 (10)	0.3491 (6)	0.3029 (5)	0.0406 (10)
H6A	0.1960	0.4288	0.2178	0.049*
C7	0.20661 (9)	0.2253 (5)	0.3951 (5)	0.0331 (8)
C8	0.19262 (10)	0.1033 (5)	0.5193 (5)	0.0392 (9)
H8A	0.2067	0.0194	0.5806	0.047*
C9	0.15734 (9)	0.1071 (6)	0.5517 (5)	0.0391 (9)
H9A	0.1476	0.0240	0.6337	0.047*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0281 (5)	0.0518 (6)	0.0605 (6)	−0.0003 (4)	0.0086 (5)	−0.0044 (5)
S1	0.0271 (5)	0.0766 (8)	0.0277 (5)	−0.0002 (5)	0.0040 (4)	−0.0015 (5)
N1	0.048 (2)	0.098 (3)	0.0285 (18)	−0.003 (2)	0.0025 (16)	−0.0017 (19)
N2	0.0275 (15)	0.066 (2)	0.0236 (15)	−0.0017 (15)	−0.0002 (12)	−0.0048 (15)
N3	0.0263 (15)	0.054 (2)	0.0229 (14)	0.0006 (14)	0.0002 (12)	−0.0020 (14)
C1	0.029 (2)	0.108 (4)	0.034 (2)	0.003 (2)	−0.0016 (17)	0.000 (3)

C2	0.0252 (18)	0.060 (3)	0.029 (2)	−0.0022 (17)	−0.0018 (15)	−0.0022 (19)
C3	0.0298 (18)	0.038 (2)	0.0285 (18)	−0.0021 (15)	0.0024 (15)	−0.0050 (17)
C4	0.0242 (17)	0.041 (2)	0.0246 (17)	0.0002 (15)	0.0027 (14)	−0.0056 (16)
C5	0.0329 (19)	0.045 (2)	0.036 (2)	0.0035 (17)	0.0017 (17)	0.0049 (18)
C6	0.037 (2)	0.046 (2)	0.039 (2)	−0.0054 (17)	0.0092 (17)	0.0082 (18)
C7	0.0273 (18)	0.038 (2)	0.0340 (19)	−0.0029 (15)	0.0023 (15)	−0.0049 (16)
C8	0.038 (2)	0.043 (2)	0.037 (2)	0.0065 (17)	−0.0011 (17)	0.0090 (18)
C9	0.035 (2)	0.050 (2)	0.032 (2)	−0.0015 (18)	0.0059 (17)	0.0108 (19)

Geometric parameters (Å, °)

Cl1—C7	1.742 (4)	C1—H1C	0.9600
S1—C3	1.751 (4)	C4—C5	1.381 (5)
S1—C1	1.781 (4)	C4—C9	1.385 (5)
N1—C2	1.156 (5)	C5—C6	1.386 (5)
N2—C3	1.318 (5)	C5—H5A	0.9300
N2—C2	1.323 (5)	C6—C7	1.368 (5)
N3—C3	1.331 (4)	C6—H6A	0.9300
N3—C4	1.435 (4)	C7—C8	1.379 (5)
N3—H3A	0.8600	C8—C9	1.387 (5)
C1—H1A	0.9600	C8—H8A	0.9300
C1—H1B	0.9600	C9—H9A	0.9300
C3—S1—C1	105.72 (18)	C9—C4—N3	121.8 (3)
C3—N2—C2	120.3 (3)	C4—C5—C6	120.0 (4)
C3—N3—C4	124.5 (3)	C4—C5—H5A	120.0
C3—N3—H3A	117.7	C6—C5—H5A	120.0
C4—N3—H3A	117.7	C7—C6—C5	119.6 (4)
S1—C1—H1A	109.5	C7—C6—H6A	120.2
S1—C1—H1B	109.5	C5—C6—H6A	120.2
H1A—C1—H1B	109.5	C6—C7—C8	121.1 (3)
S1—C1—H1C	109.5	C6—C7—Cl1	120.0 (3)
H1A—C1—H1C	109.5	C8—C7—Cl1	118.9 (3)
H1B—C1—H1C	109.5	C7—C8—C9	119.3 (3)
N1—C2—N2	173.8 (4)	C7—C8—H8A	120.3
N2—C3—N3	119.7 (3)	C9—C8—H8A	120.3
N2—C3—S1	118.8 (3)	C4—C9—C8	119.9 (3)
N3—C3—S1	121.5 (3)	C4—C9—H9A	120.0
C5—C4—C9	119.9 (3)	C8—C9—H9A	120.0
C5—C4—N3	118.2 (3)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5A···N2^{i}	0.93	2.66	3.467 (5)	146
N3—H3A···N1^{ii}	0.86	2.18	2.974 (5)	154

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

Fig. 1

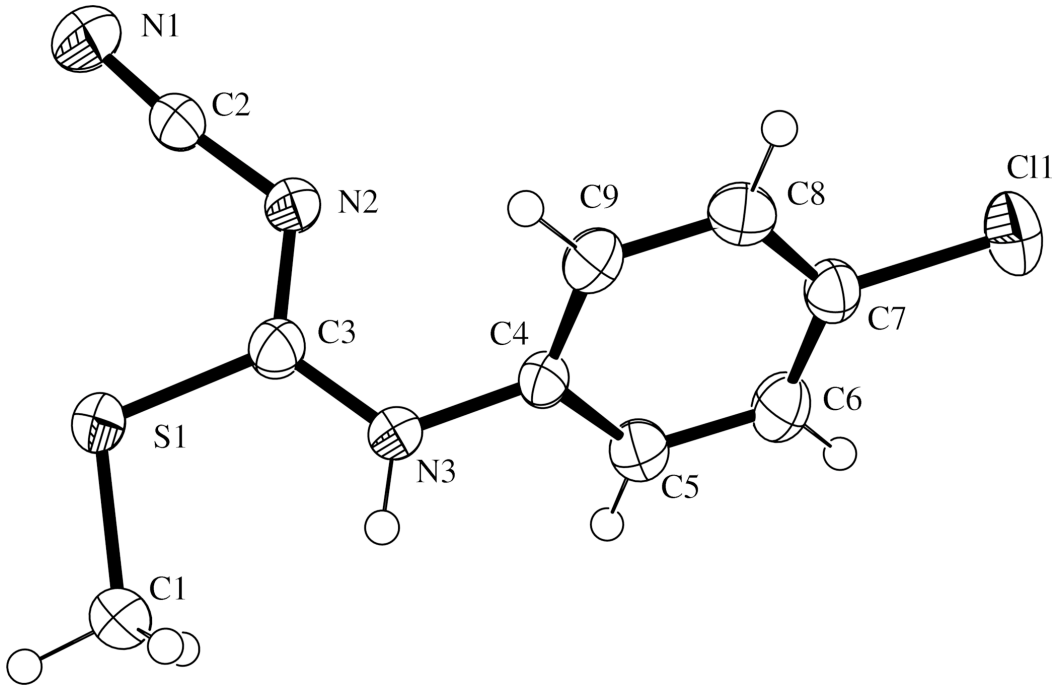

Fig. 2