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1-(2,4-Dichlorophenyl)-3-pivaloylthiourea

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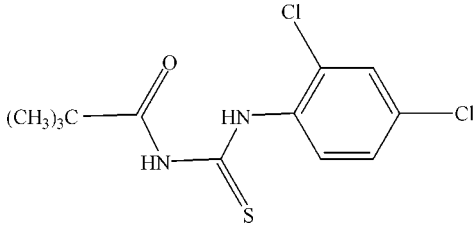
Key indicators: single-crystal X-ray study; T = 153 K; mean σ(C–C) = 0.002 Å; R factor = 0.031; wR factor = 0.089; data-to-parameter ratio = 20.5.

In the structure of the title compound, $C_{12}H_{14}Cl_2N_2OS$, the plane of the thioamide and amide groups forms a dihedral angle of 59.4 (1)° with the aromatic plane. The crystal packing shows intermolecular N—H···S and C—H···O hydrogen bonds, resulting in chains along [001].

Related literature

For related literature, see: Saeed & Flörke (2006, 2007).



Experimental

Crystal data

$C_{12}H_{14}Cl_2N_2OS$
M_r = 305.21
Triclinic, $P\overline{1}$
a = 5.7613 (13) Å
b = 10.672 (2) Å
c = 11.687 (3) Å
α = 89.971 (4)°
β = 87.442 (4)°
γ = 79.142 (4)°
V = 705.0 (3) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.60 mm^{-1}
T = 153 (2) K
0.50 × 0.35 × 0.20 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.754, T_{max} = 0.890
6176 measured reflections
3335 independent reflections
3067 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.089
S = 1.11
3335 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1	0.88	1.88	2.5990 (17)	137
N1—H1A···S1^{i}	0.88	2.73	3.5814 (14)	163
C9—H9A···O1^{ii}	0.95	2.51	3.1203 (19)	122

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2002); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FJ2064).

References

Bruker (2002). *SMART* (Version 5.62), *SAINT* (Version 6.02), *SHELXTL* (Version 6.10) and *SADABS* (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Saeed, A. & Flörke, U. (2006). *Acta Cryst.* E**62**, o2924–o2925.
Saeed, A. & Flörke, U. (2007). *Acta Cryst.* E**63**, o1390–o1392.

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supplementary materials

Acta Cryst. (2007). E**63**, o4614 [**doi:10.1107/S1600536807055808**]

1-(2,4-Dichlorophenyl)-3-pivaloylthiourea

A. Saeed and U. Flörke

Experimental

A freshly distilled solution of pivaloyl chloride (1.20 g, 10 mmol) in acetone (50 ml) was added dropwise to a suspension of potassium thiocyanate (0.97 g, 10 mmol) in acetone (30 ml) and the reaction mixture was refluxed for 30 min. After cooling to room temperature, a solution of 2,4-dichloroaniline (10 mmol) in acetone (10 ml) was added and the resulting mixture refluxed for 2.0 h. The reaction mixture was poured into cold water when the thiourea was precipitated as a solid. Recrystallized from aqueous ethanol as colourless crystals (2.47 g, 81.0 mmol, 81%). IR (KBr) cm^{-1}: 3351 (free NH), 3200 (assoc. NH), 1667 (CO), 1610, 1529, 1325 II, 1160 III, 744, 762; ^{1}H NMR ($CDCl_3$) 1,27 (9*H*, s, pivaloyl), 7.31–7.75 (aromatic), 9.19 (1*H*, s, broad, NH); 12.76 (1*H*, s, broad, NH); EIMS m/e: 281, 283, 149, 119, 91, 64.9; Analysis calculated for $C_{12}H_{14}Cl_2N_2OS$ C, 47.22; H, 4.62; N, 9.18; S, 10.51 found C, 47.03; H, 4.21; N, 9.03; S, 10.59

Refinement

Hydrogen atoms were located in difference syntheses, refined at idealized positions riding on the C/N (C/N—H = 0.88–0.98 Å) atoms with isotropic displacement parameters U_{iso}(H) = 1.2U(C/N_{eq}) and 1.5(methyl-C). Methyl H atoms were refined on the basis of rigid groups allowed to rotate but not tip.

Figures

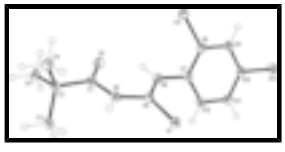

Fig. 1. Molecular structure of I. Displacement ellipsoids are drawn at the 50% probability level.

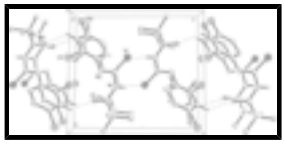

Fig. 2. Crystal packing of I viewed along [100] with hydrogen bond indicated as dashed lines. H-atoms not involved are omitted.

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Crystal data

$C_{12}H_{14}Cl_2N_2OS$	$Z = 2$
$M_r = 305.21$	$F_{000} = 316$
Triclinic, $P\overline{1}$	$D_x = 1.438$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 5.7613$ (13) Å	Cell parameters from 831 reflections

b = 10.672 (2) Å	θ = 2.6–28.3º
c = 11.687 (3) Å	μ = 0.60 mm^{-1}
α = 89.971 (4)º	T = 153 (2) K
β = 87.442 (4)º	Prism, colourless
γ = 79.142 (4)º	0.50 × 0.35 × 0.20 mm
V = 705.0 (3) Å^3	

Data collection

Bruker SMART APEX diffractometer	3335 independent reflections
Radiation source: sealed tube	3067 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.018
T = 153(2) K	θ_{max} = 27.9º
φ and ω scans	θ_{min} = 1.7º
Absorption correction: multi-scan (SADABS; Bruker, 2002)	$h = -7 \rightarrow 7$
T_{min} = 0.754, T_{max} = 0.890	$k = -14 \rightarrow 13$
6176 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.031	H-atom parameters constrained
$wR(F^2)$ = 0.089	$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 0.2299P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.11	$(\Delta/\sigma)_{max} < 0.001$
3335 reflections	$\Delta\rho_{max}$ = 0.43 e Å^{-3}
163 parameters	$\Delta\rho_{min}$ = −0.22 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	0.30159 (7)	0.38856 (4)	0.00947 (3)	0.02712 (11)
Cl2	−0.31541 (7)	0.07079 (4)	0.07202 (3)	0.02971 (11)
S1	0.26725 (6)	0.38832 (3)	0.43598 (3)	0.02211 (10)
O1	0.1561 (2)	0.72933 (11)	0.19875 (10)	0.0315 (3)
N1	0.2906 (2)	0.61858 (11)	0.35704 (10)	0.0207 (2)
H1A	0.3711	0.6227	0.4187	0.025*
N2	0.1156 (2)	0.49459 (12)	0.23844 (10)	0.0230 (3)
H2A	0.1067	0.5600	0.1919	0.028*
C1	0.2497 (2)	0.72796 (14)	0.29081 (12)	0.0206 (3)
C2	0.3301 (3)	0.84537 (13)	0.33826 (12)	0.0205 (3)
C3	0.2641 (3)	0.86311 (15)	0.46723 (13)	0.0257 (3)
H3A	0.0919	0.8757	0.4794	0.039*
H3B	0.3204	0.9378	0.4959	0.039*
H3C	0.3382	0.7870	0.5084	0.039*
C4	0.2103 (3)	0.96304 (15)	0.27303 (14)	0.0288 (3)
H4A	0.0386	0.9756	0.2873	0.043*
H4B	0.2484	0.9502	0.1908	0.043*
H4C	0.2675	1.0385	0.2994	0.043*
C5	0.6003 (3)	0.82520 (16)	0.31594 (14)	0.0285 (3)
H5A	0.6382	0.8139	0.2336	0.043*
H5B	0.6761	0.7491	0.3565	0.043*
H5C	0.6584	0.8998	0.3435	0.043*
C6	0.2191 (2)	0.50284 (13)	0.33738 (12)	0.0192 (3)
C7	0.0187 (3)	0.38919 (14)	0.20202 (12)	0.0203 (3)
C8	0.0899 (2)	0.33226 (13)	0.09547 (12)	0.0194 (3)
C9	−0.0097 (3)	0.23329 (13)	0.05465 (12)	0.0206 (3)
H9A	0.0411	0.1941	−0.0174	0.025*
C10	−0.1855 (3)	0.19333 (13)	0.12204 (12)	0.0211 (3)
C11	−0.2635 (3)	0.24941 (15)	0.22733 (13)	0.0239 (3)
H11A	−0.3855	0.2210	0.2717	0.029*
C12	−0.1605 (3)	0.34757 (15)	0.26677 (13)	0.0241 (3)
H12A	−0.2127	0.3868	0.3387	0.029*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.02866 (19)	0.0297 (2)	0.02442 (19)	−0.00995 (15)	0.00276 (14)	0.00234 (14)
Cl2	0.0356 (2)	0.0256 (2)	0.0317 (2)	−0.01407 (16)	−0.00617 (15)	−0.00329 (15)
S1	0.02430 (18)	0.01953 (18)	0.02304 (18)	−0.00448 (13)	−0.00539 (13)	0.00337 (13)
O1	0.0466 (7)	0.0285 (6)	0.0238 (5)	−0.0152 (5)	−0.0138 (5)	0.0067 (4)
N1	0.0249 (6)	0.0192 (6)	0.0192 (5)	−0.0062 (5)	−0.0066 (4)	0.0005 (4)
N2	0.0314 (7)	0.0212 (6)	0.0187 (6)	−0.0096 (5)	−0.0056 (5)	0.0013 (5)
C1	0.0208 (6)	0.0214 (7)	0.0205 (6)	−0.0061 (5)	−0.0012 (5)	0.0005 (5)
C2	0.0213 (6)	0.0190 (7)	0.0220 (7)	−0.0058 (5)	−0.0032 (5)	0.0002 (5)

C3	0.0317 (8)	0.0206 (7)	0.0236 (7)	−0.0016 (6)	−0.0016 (6)	−0.0032 (5)
C4	0.0343 (8)	0.0213 (7)	0.0316 (8)	−0.0064 (6)	−0.0074 (6)	0.0057 (6)
C5	0.0232 (7)	0.0315 (8)	0.0323 (8)	−0.0090 (6)	−0.0003 (6)	0.0008 (6)
C6	0.0189 (6)	0.0191 (6)	0.0194 (6)	−0.0035 (5)	0.0000 (5)	−0.0023 (5)
C7	0.0232 (7)	0.0193 (6)	0.0191 (6)	−0.0050 (5)	−0.0055 (5)	0.0006 (5)
C8	0.0207 (6)	0.0195 (6)	0.0181 (6)	−0.0035 (5)	−0.0025 (5)	0.0035 (5)
C9	0.0253 (7)	0.0185 (7)	0.0175 (6)	−0.0020 (5)	−0.0039 (5)	−0.0006 (5)
C10	0.0241 (7)	0.0174 (6)	0.0230 (7)	−0.0059 (5)	−0.0074 (5)	0.0001 (5)
C11	0.0248 (7)	0.0268 (7)	0.0216 (7)	−0.0084 (6)	−0.0015 (5)	0.0013 (6)
C12	0.0262 (7)	0.0276 (7)	0.0193 (7)	−0.0069 (6)	−0.0005 (5)	−0.0026 (6)

Geometric parameters (Å, °)

Cl1—C8	1.7390 (14)	C3—H3C	0.9800
Cl2—C10	1.7382 (15)	C4—H4A	0.9800
S1—C6	1.6728 (15)	C4—H4B	0.9800
O1—C1	1.2237 (18)	C4—H4C	0.9800
N1—C1	1.3890 (18)	C5—H5A	0.9800
N1—C6	1.3959 (18)	C5—H5B	0.9800
N1—H1A	0.8800	C5—H5C	0.9800
N2—C6	1.3348 (19)	C7—C12	1.392 (2)
N2—C7	1.4202 (19)	C7—C8	1.396 (2)
N2—H2A	0.8800	C8—C9	1.388 (2)
C1—C2	1.528 (2)	C9—C10	1.385 (2)
C2—C4	1.534 (2)	C9—H9A	0.9500
C2—C3	1.541 (2)	C10—C11	1.387 (2)
C2—C5	1.541 (2)	C11—C12	1.386 (2)
C3—H3A	0.9800	C11—H11A	0.9500
C3—H3B	0.9800	C12—H12A	0.9500
C1—N1—C6	127.71 (12)	C2—C5—H5A	109.5
C1—N1—H1A	116.1	C2—C5—H5B	109.5
C6—N1—H1A	116.1	H5A—C5—H5B	109.5
C6—N2—C7	125.49 (12)	C2—C5—H5C	109.5
C6—N2—H2A	117.3	H5A—C5—H5C	109.5
C7—N2—H2A	117.3	H5B—C5—H5C	109.5
O1—C1—N1	121.45 (13)	N2—C6—N1	115.21 (12)
O1—C1—C2	121.99 (13)	N2—C6—S1	125.67 (11)
N1—C1—C2	116.55 (12)	N1—C6—S1	119.12 (11)
C1—C2—C4	108.52 (12)	C12—C7—C8	118.96 (13)
C1—C2—C3	111.07 (12)	C12—C7—N2	121.05 (13)
C4—C2—C3	109.68 (12)	C8—C7—N2	119.79 (13)
C1—C2—C5	106.99 (12)	C9—C8—C7	121.34 (13)
C4—C2—C5	109.64 (12)	C9—C8—Cl1	118.80 (11)
C3—C2—C5	110.87 (13)	C7—C8—Cl1	119.83 (11)
C2—C3—H3A	109.5	C10—C9—C8	118.08 (13)
C2—C3—H3B	109.5	C10—C9—H9A	121.0
H3A—C3—H3B	109.5	C8—C9—H9A	121.0
C2—C3—H3C	109.5	C9—C10—C11	122.05 (13)
H3A—C3—H3C	109.5	C9—C10—Cl2	118.93 (11)

H3B—C3—H3C	109.5	C11—C10—Cl2	119.02 (11)
C2—C4—H4A	109.5	C12—C11—C10	118.92 (13)
C2—C4—H4B	109.5	C12—C11—H11A	120.5
H4A—C4—H4B	109.5	C10—C11—H11A	120.5
C2—C4—H4C	109.5	C11—C12—C7	120.63 (14)
H4A—C4—H4C	109.5	C11—C12—H12A	119.7
H4B—C4—H4C	109.5	C7—C12—H12A	119.7
C6—N1—C1—O1	−5.8 (2)	C12—C7—C8—C9	−1.7 (2)
C6—N1—C1—C2	174.84 (13)	N2—C7—C8—C9	−176.72 (13)
O1—C1—C2—C4	16.44 (19)	C12—C7—C8—Cl1	176.39 (11)
N1—C1—C2—C4	−164.22 (13)	N2—C7—C8—Cl1	1.40 (19)
O1—C1—C2—C3	137.09 (15)	C7—C8—C9—C10	0.9 (2)
N1—C1—C2—C3	−43.57 (17)	Cl1—C8—C9—C10	−177.21 (11)
O1—C1—C2—C5	−101.78 (16)	C8—C9—C10—C11	0.3 (2)
N1—C1—C2—C5	77.55 (15)	C8—C9—C10—Cl2	179.26 (11)
C7—N2—C6—N1	−176.92 (13)	C9—C10—C11—C12	−0.7 (2)
C7—N2—C6—S1	3.0 (2)	Cl2—C10—C11—C12	−179.65 (12)
C1—N1—C6—N2	5.6 (2)	C10—C11—C12—C7	−0.1 (2)
C1—N1—C6—S1	−174.33 (11)	C8—C7—C12—C11	1.3 (2)
C6—N2—C7—C12	58.5 (2)	N2—C7—C12—C11	176.24 (14)
C6—N2—C7—C8	−126.57 (16)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O1	0.88	1.88	2.5990 (17)	137
N1—H1A···S1^{i}	0.88	2.73	3.5814 (14)	163
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Fig. 1

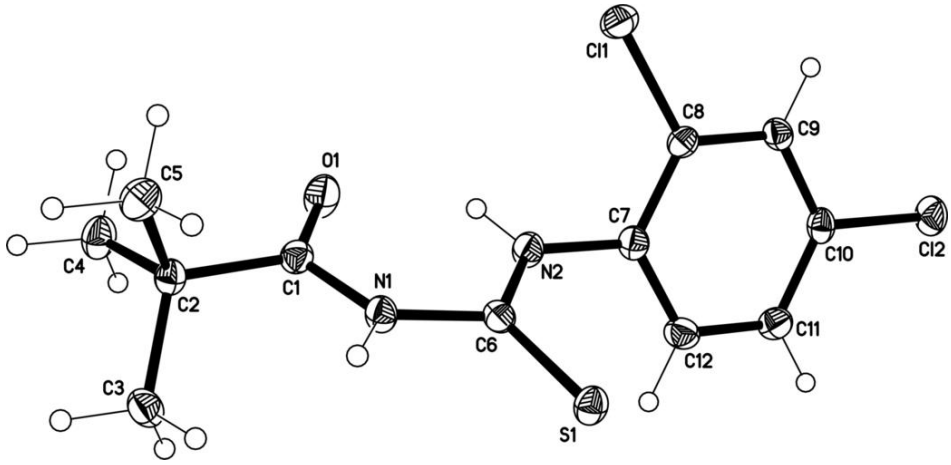

Fig. 2