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4-(4-Chlorophenyl)-2-(trichloromethylsulfanyl)-1,3-thiazole

Jens Hartung,[a]* Philipp Schmidt,[b] Ingrid Svoboda[c] and Hartmut Fuess[c]

[a]Fachbereich Chemie, Organische Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Straße, D-67663 Kaiserslautern, Germany, [b]Institut für Organische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany, and [c]Strukturforschung, FB11 Material- und Geowissenschaften, Technische Universität Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany

Correspondence e-mail: hartung@chemie.uni-kl.de

Key indicators

Single-crystal X-ray study
T = 303 K
Mean σ(C–C) = 0.007 Å
R factor = 0.032
wR factor = 0.085
Data-to-parameter ratio = 9.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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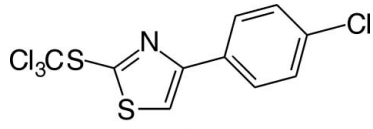
In the title compound, $C_{10}H_5Cl_4NS_2$, the CCl_3 group is displaced by 78.4 (4)° from the thiazole plane. The torsion angle between the heterocyclic core and the 4-chlorophenyl substituent is −7.0 (6)°.

Comment

4-(4-Chlorophenyl)-2-(trichloromethylsulfanyl)-1,3-thiazole, (I), is the major thiazole-derived product obtained in radical chain reactions between *N*-(alkoxy)-4-(4-chlorophenyl)thiazole-2(3*H*)-thiones and $BrCCl_3$ (Hartung *et al.*, 2003). Its formation marks an important cornerstone for a mechanistic interpretation of thiohydroxamate-based radical reactions in general (Crich & Quintero, 1989; Hartung *et al.*, 2002). The identity of (I) was confirmed by X-ray crystallographic analysis in order to supplement results from spectroscopic and spectrometric studies.



(I)

Atoms S1, C2, N3, C4 and C5 of the thiazole entity in (I) form a plane [deviations of 0.02 (1) Å for C4 and C5], which is rotated by N3—C4—C6—C7 = −7.0 (6)° from the plane of the 4-chlorophenyl substituent (Fig. 1). The heterocyclic core has the shape of a distorted pentagon (Table 1), which originates in particular from restraints imposed by the endocyclic S atom (Estes *et al.*, 1978). The difference in bond lengths to S2 is in accord with a change in hybridization from sp^3 at C12 to sp^2 at C2 (Zhang *et al.*, 2003). The trichloromethyl substituent in (I) is displaced from the thiazole plane by N3—C2—S2—C12 = 78.4 (4)°. The absolute configuration about the stereogenic C2—S2 axis was not established, since the Flack (1983) parameter was indeterminate [value = −0.09 (13)]. A view

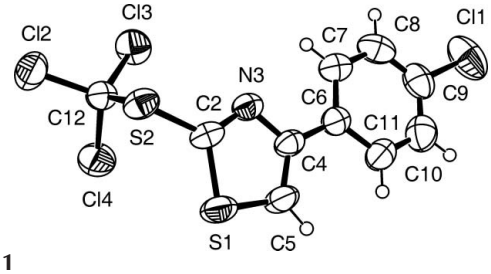


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

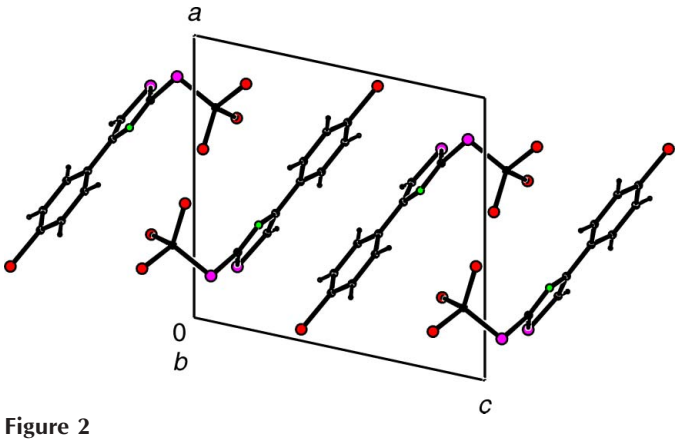


Figure 2
Packing of (I) in the solid state, viewed along [010].

along [010] indicates that (I) is packed in sheets (Fig. 2) that give rise to close S···S (S1···S2*A* = 3.456 Å) and Cl—Cl contacts [Cl1···Cl4*A* = 3.546 (7) Å]. CCl_3 substituents of adjacent molecules point toward one another. The closest distance between CCl_3 groups of neighbouring molecules, *viz.* Cl3···Cl3*A* = 3.705 (7) Å, however, exceeds the sum of two Cl van der Waals radii (1.75 Å; Bondi, 1964).

Experimental

A solution of 4-(4-chlorophenyl)-*N*-(pentenyloxy)-1,3-thiazole-2(3*H*)-thione (Hartung *et al.*, 1999) (124 mg, 0.395 mmol) in C_6H_6 (3 ml) and $BrCCl_3$ (1 ml) was photolyzed (λ = 350 nm) for 1 h at 298 K. The reaction mixture was concentrated under reduced pressure (Hartung *et al.*, 2003). The residue was crystallized from petroleum ether/CH_2Cl_2 to provide 107 mg (78%) of the title compound, (I), as colorless needles (m.p. 375 K). Calculated: C 34.81, H 1.46, N 4.06, S 18.58%; found: C 35.78, H 2.06, N 3.94, S 17.88%. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.42 (m_c, 2H), 7.84 (*s*, 1H), 7.89 (m_c, 2H); ^{13}C NMR (63 MHz, $CDCl_3$): δ 96.7 (CCl_3), 120.8, 127.8, 129.1, 131.8, 134.8, 154.8 (C2), 156.7.

Crystal data

$C_{10}H_5Cl_4NS_2$
M_r = 345.07
Monoclinic, $P2_1$
a = 10.353 (3) Å
b = 6.107 (1) Å
c = 10.882 (2) Å
β = 102.23 (2)°
V = 672.4 (3) Å^3
Z = 2
D_x = 1.704 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 4.5–14.0°
μ = 1.16 mm^{-1}
T = 303 (2) K
Needle, colorless
0.75 × 0.13 × 0.05 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω/2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.865, T_{max} = 0.943
2883 measured reflections
1444 independent reflections
1165 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 26.0°
$h = -12 \rightarrow 12$
$k = -7 \rightarrow 0$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.085
S = 1.08
1444 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0505P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.708 (4)	C4—C5	1.362 (7)
S1—C5	1.684 (5)	C4—C6	1.474 (5)
S2—C2	1.761 (4)	C9—Cl1	1.730 (5)
S2—C12	1.817 (4)	C12—Cl4	1.762 (5)
N3—C2	1.289 (6)	C12—Cl2	1.762 (4)
N3—C4	1.365 (6)	C12—Cl3	1.764 (4)
C2—N3—C4	109.9 (4)	C5—C4—C6	126.1 (4)
C5—S1—C2	88.7 (2)	C4—C5—S1	110.9 (4)
C2—S2—C12	101.1 (2)	Cl4—C12—Cl2	110.5 (2)
N3—C2—S1	116.0 (3)	Cl4—C12—Cl3	107.9 (2)
N3—C2—S2	125.2 (3)	Cl2—C12—Cl3	109.2 (3)
S1—C2—S2	118.8 (3)	Cl4—C12—S2	112.6 (3)
C5—C4—N3	114.6 (4)		

All H atoms were refined as riding [C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C)].

Data collection: *CAD-4 Diffractometer Control Software* (Nonius, 1993); cell refinement: *CAD-4 Diffractometer Control Software*; data reduction: *CAD-4 Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON2003* (Spek, 2003) and *ORTEP-3 for Windows* (Farrugia, 1997, 2005); software used to prepare material for publication: *SHELXL97*.

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