

S-Ethyl N-(4-chlorobenzoyl)dithio-carbamate: sheets built from π -stacked hydrogen-bonded chains

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Molecules of the title compound, $C_{10}H_{10}ClNOS_2$, are linked into $C(4)$ chains by an $N-H\cdots O$ hydrogen bond [$H\cdots O = 2.16$ Å, $N\cdots O = 3.013$ (3) Å and $N-H\cdots O = 176^\circ$], and the chains are linked into sheets by a centrosymmetric π - π stacking interaction.

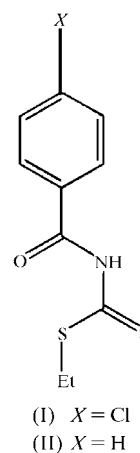
Comment

S-Alkyl *N*-aroyldithiocarbamates are utilized in the preparation of *S,S*-dialkyl *N*-aroyliminodithiocarbonates, which are themselves useful intermediates for organic synthesis (Augustín *et al.*, 1980). We report here the molecular and supramolecular structures of the title compound, (I) (Fig. 1), which differ in several respects from those of the unsubstituted analogue (II) (Low *et al.*, 2004). Compound (I) crystallizes in space group $P2_1/c$ with $Z' = 1$, whereas (II) crystallizes in $C2/c$ with $Z' = 2$. While the corresponding bond distances and angles in (I) and (II) are very similar, the molecular conformations adopted by the *S*-ethyl substituent are different. For the independent molecules in (II), the $C-S-C$ torsion angles are both close to 180° , but in (I) this angle is only 82.5 (3) $^\circ$ (Fig. 1).

The most striking difference between (I) and (II) lies in their supramolecular aggregations. In (I), this is dominated by a nearly linear $N-H\cdots O$ hydrogen bond (Table 1), which gives rise to a $C(4)$ chain (Bernstein *et al.*, 1995) running parallel to the $[001]$ direction and generated by the c -glide plane at $y = \frac{1}{4}$ (Fig. 2). There is also a short intermolecular $C-H\cdots O$ contact involving the same two molecules (Table 1),

but this is probably just an adventitious consequence of the $N-H\cdots O$ hydrogen bond. A second $[001]$ chain, related to the first by inversion, is generated by the c -glide plane at $y = \frac{3}{4}$.

The $[001]$ chains in (I) are weakly linked into sheets by an aromatic π - π stacking interaction. The aryl rings of the molecules at (x, y, z) and $(1-x, 1-y, 1-z)$, which form parts of the chains along $y = \frac{1}{4}$ and $y = \frac{3}{4}$, respectively, are strictly parallel; the interplanar spacing is 3.464 (2) Å and the ring-centroid separation is 3.865 (2) Å, corresponding to a ring-centroid offset of 1.714 (2) Å. Propagation of this interaction then links the $[001]$ chains into a (100) sheet (Fig. 3); there are no direction-specific interactions between adjacent sheets.



There is a $Cl\cdots Cl$ contact involving molecules at (x, y, z) and $(1-x, 2-y, 1-z)$, with a $Cl\cdots Cl$ distance of 3.135 (2) Å and a $C-Cl\cdots Cl$ angle of 165.5 (2) $^\circ$; however, these two molecules lie in the same (100) sheet. The $Cl\cdots Cl$ distance is certainly shorter than the sum of the van der Waals radii (3.52 Å) given by Bondi (1964); however, the sum of the

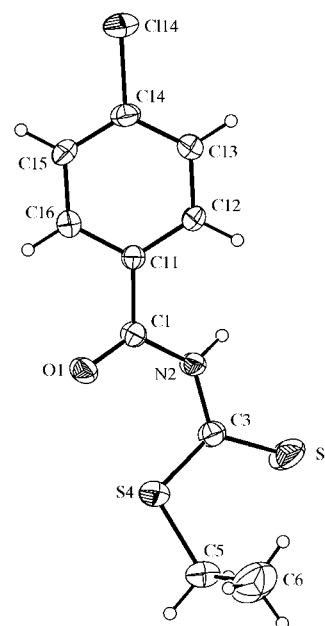


Figure 1
The molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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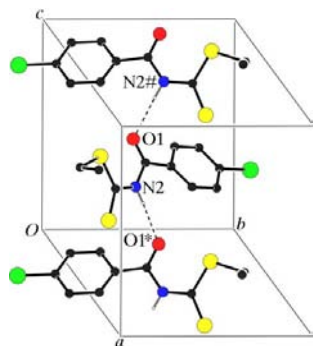


Figure 2
Part of the crystal structure of (I), showing the formation of a hydrogen-bonded C(4) chain along [001]. For clarity, H atoms bonded to C atoms have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, 1 - y, -\frac{1}{2} + z)$ and $(x, 1 - y, \frac{1}{2} + z)$, respectively.

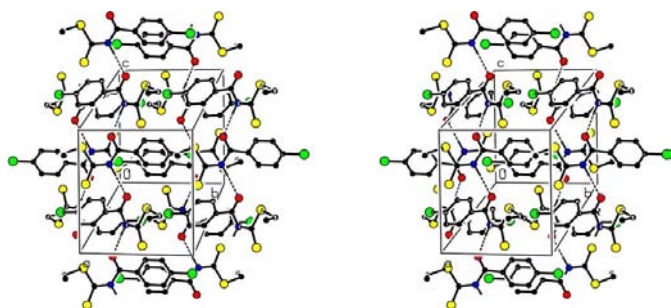


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of a (100) sheet of π -stacked [001] chains. For clarity, H atoms bonded to C atoms have been omitted.

minor radii in the polar flattening model (Nyburg & Faerman, 1985) is only 3.16 Å, so this contact may be of limited significance. Nonetheless, the C—Cl...Cl angle is consistent with the results of a database analysis (Ramasubbu *et al.*, 1986), which showed that such angles fall into two clusters, one around 90° and the other around 180°.

By contrast, the hydrogen bonding in (II) does not involve the O atom at all; instead, the primary aggregation is dominated by the formation, by means of pairs of N—H...S hydrogen bonds, of two independent $R_2^2(8)$ dimers, one generated by inversion and the other generated by a twofold screw axis. These two independent dimers are then linked into chains by a single C—H... π (arene) hydrogen bond. Thus, the types of intermolecular interaction manifested in the supramolecular aggregation in (I) and (II) are entirely different; it is striking that the introduction of a remote substituent is associated with such a difference in the nature of the hydrogen bonding.

Experimental

4-Chlorobenzoyl chloride (5.5 ml, 0.043 mol) was added to a solution of potassium thiocyanate (4.1 g, 0.043 mol) in acetonitrile (75 ml); this mixture was heated under reflux for 15 min to afford 4-chlorobenzoyl isothiocyanate, which was not isolated. After cooling the intermediate solution to 273 K under an inert atmosphere, ethanethiol (35 ml, 0.47 mol) was added, and this mixture was then stirred at

room temperature for 27 h. Ice-water was added and the title compound was extracted with ethyl acetate (3 × 25 ml). The combined organic extracts were dried over anhydrous sodium sulfate and the solvent was then removed under reduced pressure. The resulting yellow solid was recrystallized from ethanol to give crystals of (I) suitable for single-crystal X-ray diffraction (yield 89%, m.p. 398 K).

Crystal data

$C_{10}H_{10}ClNOS_2$
 $M_r = 259.76$
 Monoclinic, $P2_1/c$
 $a = 14.4020$ (7) Å
 $b = 9.1110$ (14) Å
 $c = 9.7040$ (13) Å
 $\beta = 108.484$ (8)°
 $V = 1207.6$ (3) Å³
 $Z = 4$

$D_x = 1.429$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2756 reflections
 $\theta = 5.0$ – 27.5 °
 $\mu = 0.63$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.41 \times 0.28 \times 0.23$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (EvalCCD; Duisenberg *et al.*, 2003)
 $T_{\min} = 0.781$, $T_{\max} = 0.868$
 22 106 measured reflections

2756 independent reflections
 1334 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.136$
 $\theta_{\text{max}} = 27.5$ °
 $h = -18 \rightarrow 18$
 $k = -11 \rightarrow 11$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.139$
 $S = 1.00$
 2756 reflections
 137 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0655P)^2 + 0.0228P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.35$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.33$ e Å⁻³

Table 1

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2...O1 ⁱ	0.86	2.16	3.013 (3)	176
C12—H12...O1 ⁱ	0.93	2.50	3.070 (3)	120

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

The space group $P2_1/c$ was uniquely assigned from the systematic absences. All H atoms were located from difference maps and then treated as riding atoms, with C—H distances of 0.93 (aromatic), 0.96 (CH₃) and 0.97 Å (CH₂), and N—H distances of 0.86 Å, and with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Data collection: COLLECT (Hooft, 1999); cell refinement: DIRAX/LSQ (Duisenberg *et al.*, 2000); data reduction: EvalCCD (Duisenberg *et al.*, 2003); program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: OSCAIL (McArdle, 2003) and SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXL97 and PRPKAPPA (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1793). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Augustín, M., Richter, M. & Salas, S. (1980). *J. Prakt. Chem.* **322**, 55–68.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Duisenberg, A. J. M., Hooft, R. W. W., Schreurs, A. M. M. & Kroon, J. (2000). *J. Appl. Cryst.* **33**, 893–898.
- Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
- Ferguson, G. (1999). *PRPKAPPA*. University of Guelph, Canada.
- Hooft, R. W. W. (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Low, J. N., Cobo, J., Insuasty, H., Estrada, M., Cortés, E. & Glidewell, C. (2004). *Acta Cryst.* **C60**, o483–o485.
- McArdle, P. (2003). *OSCAIL for Windows*. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
- Nyburg, S. C. & Faerman, C. H. (1985). *Acta Cryst.* **B41**, 274–279.
- Ramasubbu, N., Parthasarathy, R. & Murray-Rust, P. (1986). *J. Am. Chem. Soc.* **108**, 4308–4314.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.