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S-Ethyl *N*-benzoyldithiocarbamate: two independent hydrogen-bonded $R_2^2(8)$ dimers of different symmetry linked into chains by a C—H···π(arene) interaction

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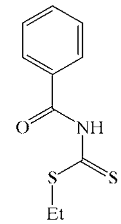
The title compound, $C_{10}H_{11}NOS_2$, crystallizes with $Z' = 2$ in space group $C2/c$. The molecules are linked by two N—H···S hydrogen bonds [H···S = 2.60 and 2.62 Å, N···S = 3.350 (2) and 3.490 (2) Å, and N—H···S = 143 and 172°] into two distinct types of $R_2^2(8)$ dimer, *viz.* one generated by inversion and the other by a twofold rotation axis. A single C—H···π(arene) hydrogen bond links the two types of dimer into chains.

Comment

It has been shown (Elmore *et al.*, 1956; Nash *et al.*, 1969) that alkanethiols, *R*SH, react smoothly with aroylisothiocyanates, ArCONCS, to give *S*-alkyl *N*-aroyldithiocarbamates, (ArCO)NHC(=S)S*R*, in good yields. We report here the molecular and supramolecular structures of the title compound, (PhCO)NHC(=S)SEt, (I), which is an important intermediate in the preparation of *S*,*S*-dialkyl *N*-aroylimino-dithiocarbonates used in the synthesis of many organic compounds (Augustín *et al.*, 1980). We have modified the reported method for the synthesis of *S*-methyl *N*-benzoyldithiocarbamate (Elmore *et al.*, 1956), so enhancing the yield from 49 to 87%.

The title compound crystallizes in space group $C2/c$, with $Z' = 2$ (Fig. 1). The bond lengths (Table 1), which are normal for their types (Allen *et al.*, 1987), are, in general, almost identical in the two independent molecules, as are the overall molecular conformations. However, the two torsion angles defining the orientation of the benzene rings relative to the rest of the nearly planar molecular skeletons differ by 22°. This fact alone suffices to preclude the possibility of any additional symmetry.



(I)

Such a possibility is also ruled out by the observation that each type of molecule forms a hydrogen-bonded dimer but that these have different symmetries. For molecules of type 1 (Fig. 1*a*), atom N12 in the molecule at (x, y, z) acts as a hydrogen-bond donor to thione atom S13 in the molecule at ($1-x$, $1-y$, $1-z$), so generating a centrosymmetric $R_2^2(8)$ dimer (Bernstein *et al.*, 1995) centred at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) (Fig. 2*a*). However, for molecules of type 2 (Fig. 1*b*), atom N22 at (x, y, z) acts as a donor to thione atom S23 at ($1-x$, y, $\frac{3}{2}-z$), so that this $R_2^2(8)$ dimer (Fig. 2*b*) lies across the twofold rotation axis along ($\frac{1}{2}$, y, $\frac{3}{4}$). The dimensions of the two independent N—H···S hydrogen bonds (Table 2) are markedly different.

Although the N···S distance is above the sum of the conventional van der Waals radii (3.3 Å; Bondi, 1964), an analysis (Allen *et al.*, 1997) of hydrogen bonds having a secondary amine donor and a thione-type S atom as the acceptor, using data retrieved from the Cambridge Structural Database (Allen, 2002), indicated mean H···S, N···S and N—H···S parameters of 2.46 (1) Å, 3.40 (1) Å and 158 (1)°, respectively, in such bonds involving the neutral species R^1R^2C=S as an acceptor, and 2.51 (1) Å, 3.44 (1) Å and

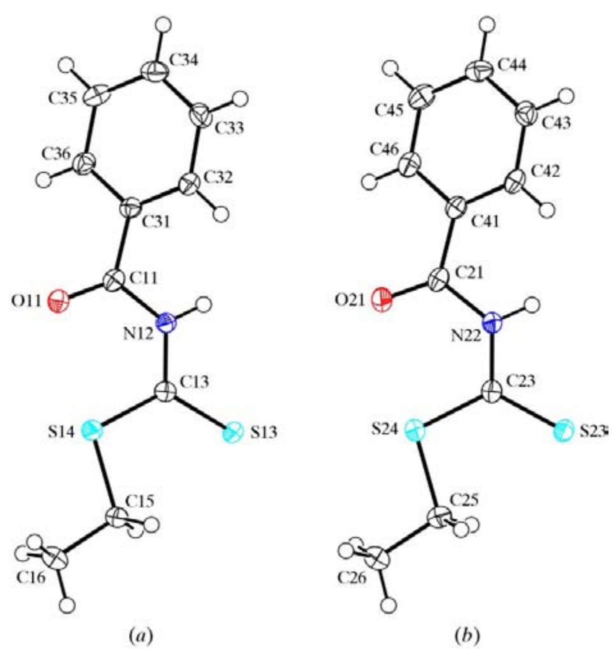


Figure 1
The two independent molecules in (I), showing the atom-labelling scheme in (*a*) the type 1 molecule and (*b*) the type 2 molecule. Displacement ellipsoids are drawn at the 30% probability level.

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158 (1)°, respectively, in such bonds involving neutral thioureas as an acceptor. Accordingly, the N—H···S interactions in (I) appear to be fairly typical of such hydrogen bonds.

Each unit cell contains four dimers of each type, and the two types are linked into chains by a single C—H···π(arene) hydrogen bond. Atoms C46 in the type 2 molecules at (x, y, z) and ($1 - x$, y, $\frac{3}{2} - z$) lie in the dimer across the twofold axis along ($\frac{1}{2}$, y, $\frac{3}{4}$). These atoms act as hydrogen-bond donors, respectively, to the C31–C36 rings in the type 1 molecules at ($-\frac{1}{2} + x, \frac{1}{2} + y, z$) and ($\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$), which are themselves components of the type 1 dimers centred at (0, 1, $\frac{1}{2}$) and (1, 1, 1), respectively. Within these type 1 dimers, the molecules at ($\frac{1}{2} - x$, $\frac{3}{2} - y$, $1 - z$) and ($\frac{1}{2} + x$, $\frac{3}{2} - y$, $\frac{1}{2} + z$) similarly accept hydrogen bonds from atoms C46 in the type 2 molecules at ($1 - x$, $2 - y$, $1 - z$) and ($1 + x$, $2 - y$, $\frac{1}{2} + z$), respectively, which themselves lie in the type 2 dimers across the rotation axes along ($\frac{1}{2}$, $-y$, $\frac{1}{4}$) and ($\frac{3}{2}$, $-y$, $\frac{5}{4}$). Propagation of this single C—H···π(arene) hydrogen bond by inversion and rotation thus links dimers of the two types into a chain of rings running parallel to the [201] direction (Fig. 3). Four chains pass through each unit cell, but there are no direction-specific interactions between adjacent chains.

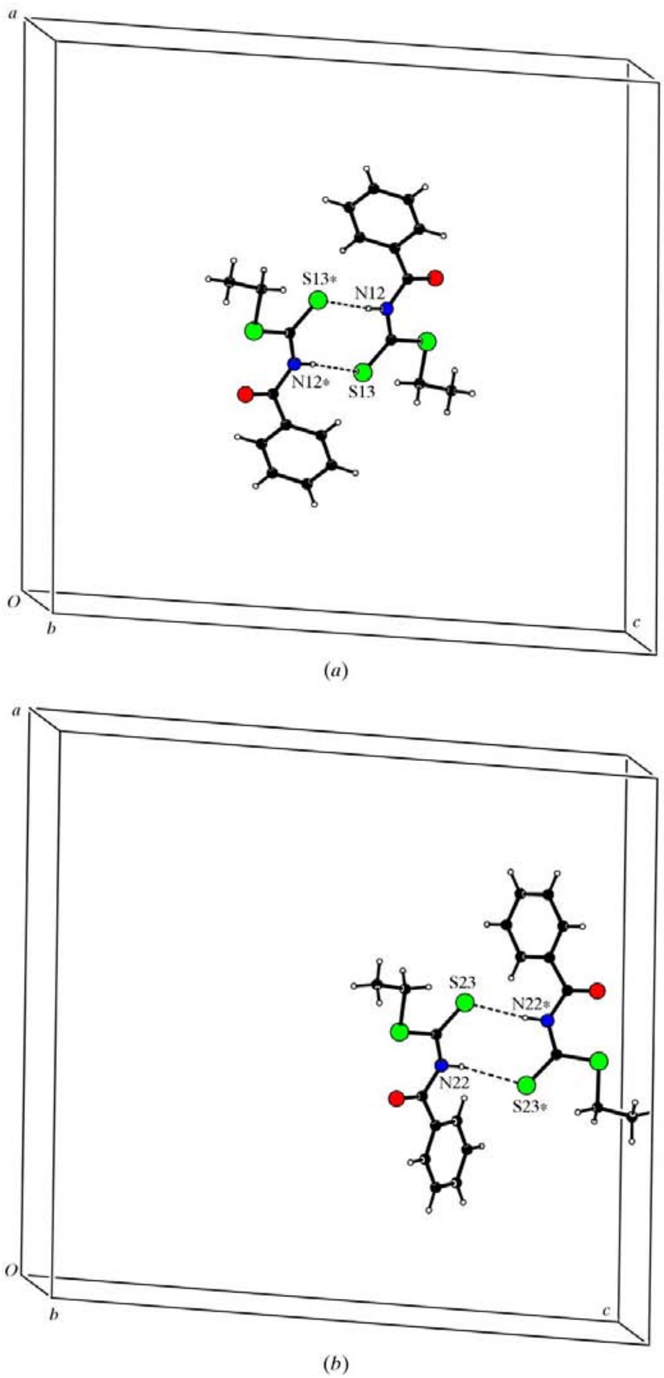

Figure 2
The two independent hydrogen-bonded dimers in the structure of (I), showing (*a*) that generated by inversion, where atoms marked with an asterisk (*) are at the symmetry position ($1 - x$, $1 - y$, $1 - z$), and (*b*) that generated by rotation, where atoms marked with an asterisk (*) are at the symmetry position ($1 - x$, y, $\frac{3}{2} - z$).

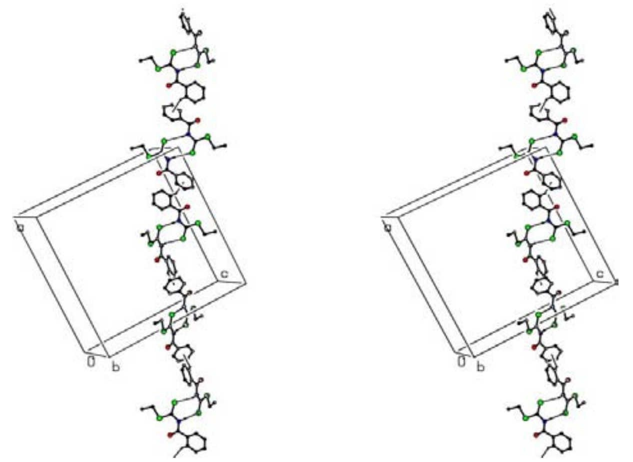

Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of the [201] chain of rings linking the two types of $R_2^2(8)$ dimer.

Experimental

Benzoyl chloride (5 ml, 0.043 mol) was added to a solution of potassium thiocyanate (4.1 g, 0.043 mol) in acetonitrile (75 ml) and this mixture was heated under reflux for 15 min to afford benzoyl isothiocyanate. The mixture was cooled 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 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 87%, m.p. 348 K; literature (Nash *et al.*, 1969) m.p. 352–353 K, yield 49%].

Crystal data

$C_{10}H_{11}NOS_2$	D_x = 1.404 Mg m^{-3}
M_r = 225.34	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 4840 reflections
a = 21.8190 (5) Å	θ = 3.1–27.5°
b = 8.4596 (2) Å	μ = 0.46 mm^{-1}
c = 23.1792 (5) Å	T = 120 (2) K
β = 94.5140 (14)°	Block, colourless
V = 4265.15 (17) Å^3	0.20 × 0.20 × 0.16 mm
Z = 16	

Data collection

Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)
$T_{min} = 0.902$, $T_{max} = 0.929$
33 304 measured reflections
4840 independent reflections
3569 reflections with $I > 2\sigma(I)$
$R_{int} = 0.067$
$\theta_{max} = 27.5°$
$h = -28 \rightarrow 28$
$k = -10 \rightarrow 10$
$l = -30 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.089$
$S = 1.01$
4840 reflections
255 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.8703P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C11—O11	1.214 (2)	C21—O21	1.214 (2)
C11—N12	1.394 (2)	C21—N22	1.394 (2)
N12—C13	1.376 (2)	N22—C23	1.379 (2)
C13—S13	1.6586 (18)	C23—S23	1.6552 (18)
C13—S14	1.7414 (19)	C23—S24	1.7333 (19)
S14—C15	1.8103 (18)	S24—C25	1.8116 (18)
C31—C11—N12—C13	175.14 (16)	C41—C21—N22—C23	−177.70 (16)
C11—N12—C13—S14	−1.6 (2)	C21—N22—C23—S24	−4.1 (2)
N12—C13—S14—C15	−173.39 (13)	N22—C23—S24—C25	176.92 (14)
C13—S14—C15—C16	−174.12 (13)	C23—S24—C25—C26	−173.31 (13)
N12—C11—C31—C32	−45.0 (2)	N22—C21—C41—C42	−22.7 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*1 is the centroid of the C31–C36 ring.

D—H···A	D—H	H···A	D···A	D—H···A
N12—H12···S13^{i}	0.88	2.62	3.490 (2)	172
N22—H22···S23^{ii}	0.88	2.60	3.350 (2)	143
C46—H46···*Cg*1^{iii}	0.95	2.85	3.678 (2)	146

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, y, \frac{3}{2} - z$; (iii) $x - \frac{1}{2}, \frac{1}{2} + y, z$.

The systematic absences permitted *C*2/*c* and *Cc* as possible space groups; *C*2/*c* was selected and confirmed by the structure analysis. All H atoms were located from difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH_3) or 0.99 Å (CH_2), an N—H distance of 0.88 Å, and U_{iso}(H) values of $1.2U_{eq}$(C,N) or $1.5U_{eq}(C_{methyl})$.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *PRPKAPPA* (Ferguson, 1999).

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