

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

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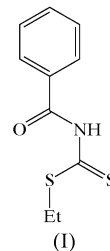
The title compound, C₁₀H₁₁NOS₂, crystallizes with $Z' = 2$ in space group $C2/c$. The molecules are linked by two N—H \cdots S hydrogen bonds [H \cdots S = 2.60 and 2.62 Å, N \cdots S = 3.350 (2) and 3.490 (2) Å, and N—H \cdots S = 143 and 172°] into two distinct types of $R_2^2(8)$ dimer, *viz.* one generated by inversion and the other by a twofold rotation axis. A single C—H $\cdots\pi$ (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, RSH, react smoothly with aroylisothiocyanates, ArCONCS, to give *S*-alkyl *N*-aroyldithiocarbamates, (ArCO)NHC(=S)SR, 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.



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 \cdots S hydrogen bonds (Table 2) are markedly different.

Although the N \cdots 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 \cdots S, N \cdots S and N—H \cdots 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

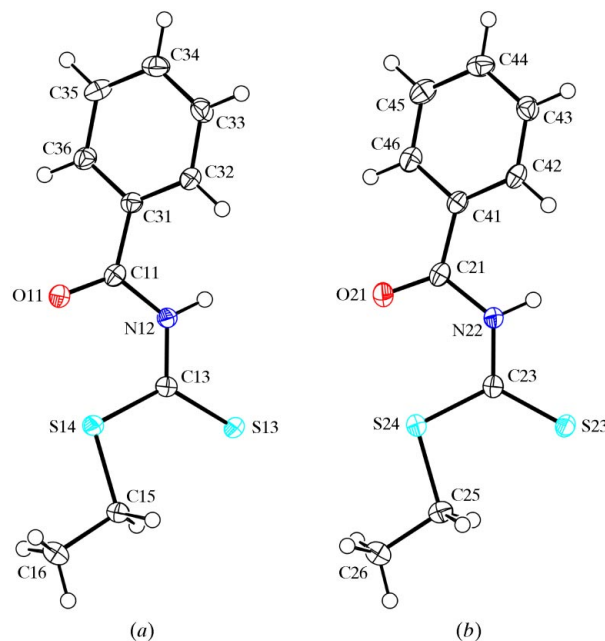


Figure 1

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.

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

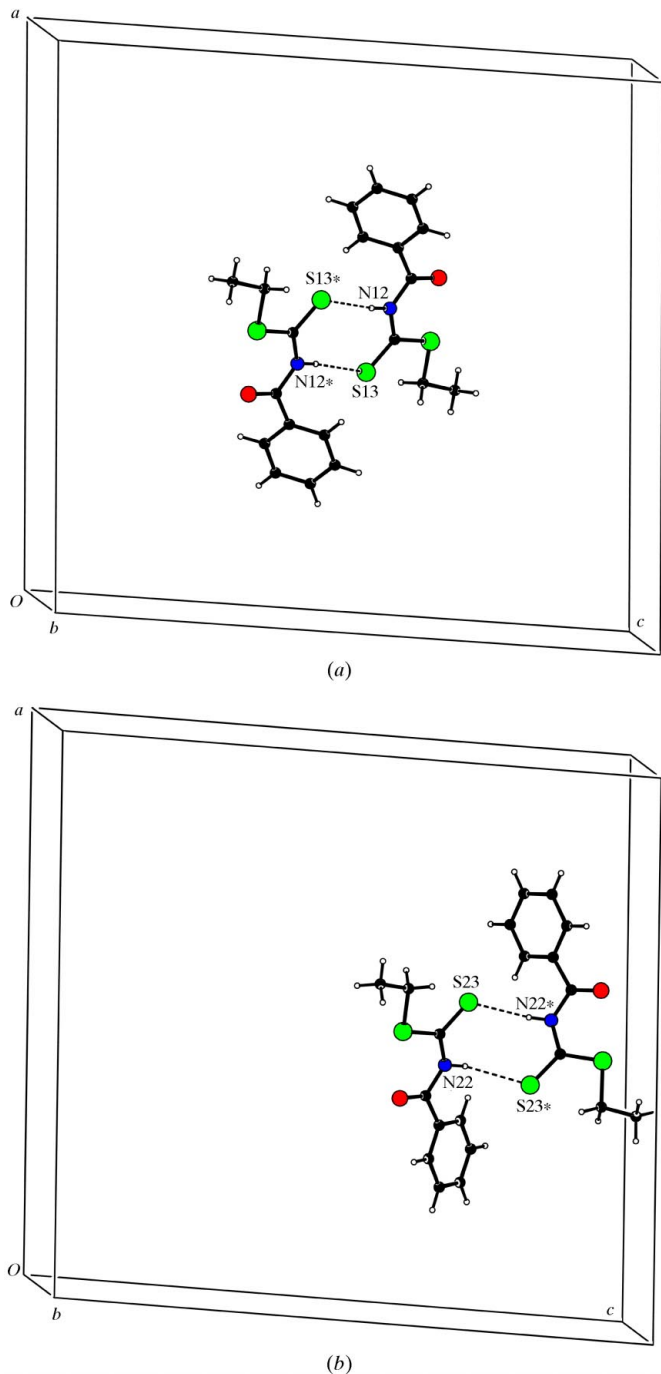


Figure 2
The two independent hydrogen-bonded dimers in the structure of (I), showing (a) that generated by inversion, where atoms marked with an asterisk (*) are at the symmetry position $(1 - x, 1 - y, 1 - z)$, and (b) that generated by rotation, where atoms marked with an asterisk (*) are at the symmetry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

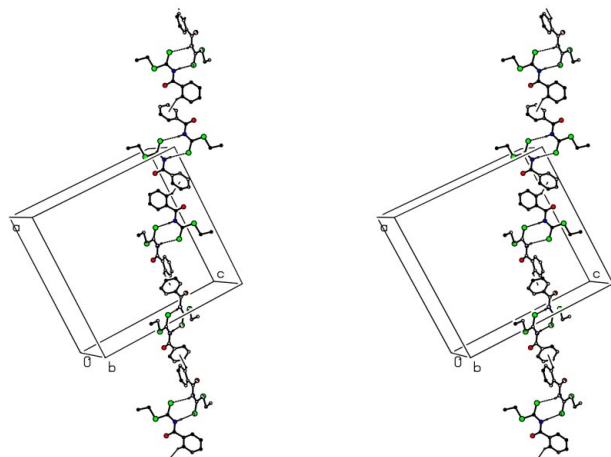


Figure 3
A stereoview of part of the crystal structure of (I), showing the formation of the [201] chain of rings linking the two types of $R_2^2(8)$ dimer.

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.

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

$C_{10}H_{11}NOS_2$
 $M_r = 225.34$
 Monoclinic, $C2/c$
 $a = 21.8190$ (5) Å
 $b = 8.4596$ (2) Å
 $c = 23.1792$ (5) Å
 $\beta = 94.5140$ (14)°
 $V = 4265.15$ (17) Å³
 $Z = 16$

$D_x = 1.404$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4840 reflections
 $\theta = 3.1$ – 27.5°
 $\mu = 0.46$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.20 \times 0.20 \times 0.16$ mm

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 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.067$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -28 \rightarrow 28$
 $k = -10 \rightarrow 10$
 $l = -30 \rightarrow 29$

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 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{Å}^{-3}$

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, °).

Cg1 is the centroid of the C31—C36 ring.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N12—H12 \cdots S13 ⁱ	0.88	2.62	3.490 (2)	172
N22—H22 \cdots S23 ⁱⁱ	0.88	2.60	3.350 (2)	143
C46—H46 \cdots Cg1 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 $C2/c$ and Cc as possible space groups; $C2/c$ 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 (CH₃) or 0.99 Å (CH₂), an N—H distance of 0.88 Å, and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Data collection: *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 *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the EPSRC X-ray Crystallographic Service, University of Southampton, England; the authors thank the staff for all their help and advice. JNL thanks NCR Self-Service, Dundee, for grants that have provided computing facilities for this work. JC thanks the Consejería de Educación y Ciencia (Junta de Andalucía, Spain) and the Universidad de Jaén for financial support. HI, ME and EC thank COLCIENCIAS and UDENAR (Universidad de Nariño) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1733). Services for accessing these data are described at the back of the journal.

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supporting information

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$c = 23.1792$ (5) Å

$\beta = 94.5140$ (14)°

$V = 4265.15$ (17) Å³

$Z = 16$

$F(000) = 1888$

$D_x = 1.404$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 4840 reflections

$\theta = 3.1$ – 27.5 °

$\mu = 0.46$ mm⁻¹

$T = 120$ K

Block, colourless

$0.20 \times 0.20 \times 0.16$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: rotating anode

Graphite monochromator

φ scans, and ω scans with κ offsets

Absorption correction: multi-scan

(*SORTAV*; Blessing, 1995, 1997)

$T_{\min} = 0.902$, $T_{\max} = 0.929$

33304 measured reflections

4840 independent reflections

3569 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.067$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 3.1$ °

$h = -28 \rightarrow 28$

$k = -10 \rightarrow 10$

$l = -30 \rightarrow 29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.089$

$S = 1.01$

4840 reflections

255 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.8703P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.38 \text{ e } \text{\AA}^{-3}$

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
S13	0.43471 (2)	0.36946 (6)	0.54420 (2)	0.02042 (12)
S14	0.49163 (2)	0.24080 (5)	0.65662 (2)	0.01954 (12)
O11	0.60744 (6)	0.34703 (16)	0.66461 (6)	0.0243 (3)
N12	0.55035 (6)	0.40915 (17)	0.58096 (6)	0.0175 (3)
C11	0.60505 (8)	0.4030 (2)	0.61624 (8)	0.0188 (4)
C13	0.49451 (8)	0.3452 (2)	0.59213 (8)	0.0163 (4)
C15	0.41451 (8)	0.1605 (2)	0.64882 (8)	0.0208 (4)
C16	0.40314 (9)	0.0795 (2)	0.70572 (9)	0.0276 (5)
C31	0.65977 (8)	0.4715 (2)	0.59075 (8)	0.0180 (4)
C32	0.67309 (8)	0.4399 (2)	0.53411 (8)	0.0212 (4)
C33	0.72637 (8)	0.5011 (2)	0.51352 (8)	0.0252 (4)
C34	0.76538 (9)	0.5960 (2)	0.54910 (9)	0.0266 (4)
C35	0.75195 (8)	0.6278 (2)	0.60514 (9)	0.0260 (5)
C36	0.69969 (8)	0.5635 (2)	0.62660 (8)	0.0219 (4)
S23	0.56865 (2)	0.73412 (6)	0.69753 (2)	0.02289 (13)
S24	0.51204 (2)	0.84877 (6)	0.58307 (2)	0.02053 (12)
O21	0.39103 (6)	0.77129 (15)	0.58351 (6)	0.0244 (3)
N22	0.45330 (6)	0.69264 (18)	0.66186 (6)	0.0184 (3)
C21	0.39665 (8)	0.7034 (2)	0.62979 (8)	0.0188 (4)
C23	0.50920 (8)	0.7543 (2)	0.64916 (8)	0.0174 (4)
C25	0.59095 (8)	0.9172 (2)	0.58779 (9)	0.0253 (4)
C26	0.59880 (9)	1.0212 (2)	0.53514 (8)	0.0253 (4)
C41	0.34413 (8)	0.6283 (2)	0.65692 (8)	0.0185 (4)
C42	0.35075 (8)	0.5093 (2)	0.69847 (8)	0.0206 (4)
C43	0.29949 (8)	0.4416 (2)	0.71982 (8)	0.0232 (4)
C44	0.24097 (8)	0.4920 (2)	0.70002 (9)	0.0254 (4)
C45	0.23416 (9)	0.6117 (2)	0.65953 (9)	0.0274 (5)
C46	0.28515 (9)	0.6793 (2)	0.63742 (9)	0.0239 (4)
H12	0.5507	0.4606	0.5480	0.021*
H15A	0.3842	0.2462	0.6405	0.025*
H15B	0.4106	0.0835	0.6166	0.025*
H16A	0.4356	0.0015	0.7152	0.041*
H16B	0.3631	0.0262	0.7019	0.041*
H16C	0.4034	0.1586	0.7366	0.041*
H32	0.6459	0.3769	0.5097	0.025*
H33	0.7362	0.4781	0.4752	0.030*
H34	0.8014	0.6391	0.5347	0.032*
H35	0.7785	0.6937	0.6291	0.031*
H36	0.6912	0.5822	0.6656	0.026*

H22	0.4525	0.6558	0.6973	0.022*
H25A	0.6001	0.9785	0.6238	0.030*
H25B	0.6195	0.8261	0.5881	0.030*
H26A	0.5904	0.9588	0.4998	0.038*
H26B	0.6410	1.0615	0.5368	0.038*
H26C	0.5700	1.1102	0.5350	0.038*
H42	0.3907	0.4745	0.7122	0.025*
H43	0.3043	0.3604	0.7481	0.028*
H44	0.2058	0.4442	0.7143	0.031*
H45	0.1942	0.6479	0.6467	0.033*
H46	0.2801	0.7602	0.6090	0.029*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S13	0.0160 (2)	0.0259 (3)	0.0189 (3)	-0.00182 (18)	-0.00175 (18)	0.00254 (19)
S14	0.0168 (2)	0.0220 (3)	0.0197 (3)	-0.00085 (18)	0.00062 (18)	0.00365 (19)
O11	0.0206 (7)	0.0314 (8)	0.0203 (7)	-0.0020 (6)	-0.0019 (5)	0.0058 (6)
N12	0.0163 (7)	0.0184 (8)	0.0176 (8)	-0.0008 (6)	0.0004 (6)	0.0032 (6)
C11	0.0172 (9)	0.0181 (9)	0.0208 (10)	0.0030 (7)	-0.0005 (7)	-0.0022 (8)
C13	0.0175 (8)	0.0131 (9)	0.0187 (9)	0.0004 (7)	0.0033 (7)	-0.0030 (7)
C15	0.0188 (9)	0.0233 (10)	0.0206 (10)	-0.0025 (8)	0.0033 (8)	0.0001 (8)
C16	0.0284 (10)	0.0289 (12)	0.0263 (11)	-0.0041 (9)	0.0073 (9)	0.0049 (9)
C31	0.0149 (8)	0.0173 (9)	0.0215 (10)	0.0023 (7)	0.0000 (7)	0.0032 (8)
C32	0.0184 (9)	0.0239 (10)	0.0206 (10)	-0.0004 (8)	-0.0016 (7)	0.0009 (8)
C33	0.0237 (10)	0.0326 (12)	0.0199 (11)	0.0022 (8)	0.0052 (8)	0.0011 (8)
C34	0.0185 (9)	0.0287 (11)	0.0330 (12)	-0.0014 (8)	0.0050 (8)	0.0043 (9)
C35	0.0168 (9)	0.0268 (11)	0.0339 (12)	-0.0033 (8)	-0.0007 (8)	-0.0044 (9)
C36	0.0173 (9)	0.0264 (11)	0.0221 (10)	0.0020 (8)	0.0011 (8)	-0.0029 (8)
S23	0.0169 (2)	0.0346 (3)	0.0169 (3)	0.00119 (19)	0.00015 (18)	0.0016 (2)
S24	0.0201 (2)	0.0246 (3)	0.0168 (2)	-0.00065 (18)	0.00092 (18)	0.00270 (19)
O21	0.0258 (7)	0.0264 (7)	0.0202 (7)	-0.0023 (6)	-0.0023 (6)	0.0047 (6)
N22	0.0176 (7)	0.0219 (8)	0.0156 (8)	-0.0004 (6)	0.0008 (6)	0.0008 (6)
C21	0.0203 (9)	0.0167 (9)	0.0188 (10)	0.0017 (7)	-0.0026 (7)	-0.0049 (8)
C23	0.0204 (9)	0.0159 (9)	0.0159 (9)	0.0018 (7)	0.0011 (7)	-0.0032 (7)
C25	0.0190 (9)	0.0292 (11)	0.0276 (11)	-0.0015 (8)	0.0013 (8)	0.0031 (9)
C26	0.0272 (10)	0.0235 (11)	0.0258 (11)	-0.0014 (8)	0.0060 (8)	0.0018 (8)
C41	0.0193 (9)	0.0181 (10)	0.0178 (10)	-0.0002 (7)	-0.0012 (7)	-0.0042 (7)
C42	0.0201 (9)	0.0208 (10)	0.0200 (10)	0.0007 (8)	-0.0043 (8)	-0.0039 (8)
C43	0.0268 (10)	0.0222 (10)	0.0201 (10)	-0.0018 (8)	0.0002 (8)	-0.0005 (8)
C44	0.0201 (9)	0.0289 (11)	0.0281 (11)	-0.0033 (8)	0.0065 (8)	-0.0062 (9)
C45	0.0196 (10)	0.0282 (11)	0.0339 (12)	0.0043 (8)	-0.0006 (8)	-0.0019 (9)
C46	0.0236 (10)	0.0226 (10)	0.0247 (11)	0.0011 (8)	-0.0034 (8)	0.0001 (8)

Geometric parameters (Å, °)

C11—O11	1.214 (2)	C21—O21	1.214 (2)
C11—N12	1.394 (2)	C21—N22	1.394 (2)

C11—C31	1.491 (3)	C21—C41	1.492 (3)
N12—C13	1.376 (2)	N22—C23	1.379 (2)
N12—H12	0.88	N22—H22	0.88
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)
C15—C16	1.524 (3)	C25—C26	1.525 (3)
C15—H15A	0.99	C25—H25A	0.99
C15—H15B	0.99	C25—H25B	0.99
C16—H16A	0.98	C26—H26A	0.98
C16—H16B	0.98	C26—H26B	0.98
C16—H16C	0.98	C26—H26C	0.98
C31—C32	1.393 (3)	C41—C42	1.393 (3)
C31—C36	1.393 (3)	C41—C46	1.398 (3)
C32—C33	1.391 (3)	C42—C43	1.383 (3)
C32—H32	0.95	C42—H42	0.95
C33—C34	1.393 (3)	C43—C44	1.389 (3)
C33—H33	0.95	C43—H43	0.95
C34—C35	1.380 (3)	C44—C45	1.381 (3)
C34—H34	0.95	C44—H44	0.95
C35—C36	1.390 (3)	C45—C46	1.385 (3)
C35—H35	0.95	C45—H45	0.95
C36—H36	0.95	C46—H46	0.95
O11—C11—N12	121.93 (17)	O21—C21—N22	121.70 (17)
O11—C11—C31	122.69 (16)	O21—C21—C41	123.10 (16)
N12—C11—C31	115.37 (16)	N22—C21—C41	115.19 (16)
C13—N12—C11	127.21 (15)	C23—N22—C21	128.55 (16)
C13—N12—H12	115.2	C23—N22—H22	114.6
C11—N12—H12	117.6	C21—N22—H22	116.0
N12—C13—S13	119.11 (13)	N22—C23—S23	118.39 (13)
N12—C13—S14	116.96 (13)	N22—C23—S24	117.17 (13)
S13—C13—S14	123.93 (10)	S23—C23—S24	124.44 (11)
C13—S14—C15	101.57 (8)	C23—S24—C25	101.18 (9)
C16—C15—S14	107.20 (13)	C26—C25—S24	107.59 (13)
C16—C15—H15A	110.3	C26—C25—H25A	110.2
S14—C15—H15A	110.3	S24—C25—H25A	110.2
C16—C15—H15B	110.3	C26—C25—H25B	110.2
S14—C15—H15B	110.3	S24—C25—H25B	110.2
H15A—C15—H15B	108.5	H25A—C25—H25B	108.5
C15—C16—H16A	109.5	C25—C26—H26A	109.5
C15—C16—H16B	109.5	C25—C26—H26B	109.5
H16A—C16—H16B	109.5	H26A—C26—H26B	109.5
C15—C16—H16C	109.5	C25—C26—H26C	109.5
H16A—C16—H16C	109.5	H26A—C26—H26C	109.5
H16B—C16—H16C	109.5	H26B—C26—H26C	109.5
C32—C31—C36	120.16 (17)	C42—C41—C46	119.29 (17)
C32—C31—C11	122.14 (16)	C42—C41—C21	123.90 (16)

C36—C31—C11	117.62 (17)	C46—C41—C21	116.77 (17)
C33—C32—C31	119.60 (17)	C43—C42—C41	120.27 (17)
C33—C32—H32	120.2	C43—C42—H42	119.9
C31—C32—H32	120.2	C41—C42—H42	119.9
C32—C33—C34	120.00 (18)	C42—C43—C44	120.19 (18)
C32—C33—H33	120.0	C42—C43—H43	119.9
C34—C33—H33	120.0	C44—C43—H43	119.9
C35—C34—C33	120.29 (18)	C45—C44—C43	119.78 (18)
C35—C34—H34	119.9	C45—C44—H44	120.1
C33—C34—H34	119.9	C43—C44—H44	120.1
C34—C35—C36	120.08 (18)	C44—C45—C46	120.52 (18)
C34—C35—H35	120.0	C44—C45—H45	119.7
C36—C35—H35	120.0	C46—C45—H45	119.7
C35—C36—C31	119.82 (18)	C45—C46—C41	119.93 (18)
C35—C36—H36	120.1	C45—C46—H46	120.0
C31—C36—H36	120.1	C41—C46—H46	120.0
O11—C11—N12—C13	-5.6 (3)	O21—C21—N22—C23	1.4 (3)
C31—C11—N12—C13	175.14 (16)	C41—C21—N22—C23	-177.70 (16)
C11—N12—C13—S13	178.96 (14)	C21—N22—C23—S23	175.75 (14)
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)
S13—C13—S14—C15	6.04 (14)	S23—C23—S24—C25	-2.88 (15)
C13—S14—C15—C16	-174.12 (13)	C23—S24—C25—C26	-173.31 (13)
O11—C11—C31—C32	135.8 (2)	O21—C21—C41—C42	158.22 (18)
N12—C11—C31—C32	-45.0 (2)	N22—C21—C41—C42	-22.7 (3)
O11—C11—C31—C36	-41.0 (3)	O21—C21—C41—C46	-19.8 (3)
N12—C11—C31—C36	138.22 (17)	N22—C21—C41—C46	159.28 (16)
C36—C31—C32—C33	-0.2 (3)	C46—C41—C42—C43	0.5 (3)
C11—C31—C32—C33	-176.96 (17)	C21—C41—C42—C43	-177.46 (17)
C31—C32—C33—C34	-1.3 (3)	C41—C42—C43—C44	-0.1 (3)
C32—C33—C34—C35	1.1 (3)	C42—C43—C44—C45	-1.0 (3)
C33—C34—C35—C36	0.8 (3)	C43—C44—C45—C46	1.6 (3)
C34—C35—C36—C31	-2.3 (3)	C44—C45—C46—C41	-1.2 (3)
C32—C31—C36—C35	2.0 (3)	C42—C41—C46—C45	0.1 (3)
C11—C31—C36—C35	178.91 (17)	C21—C41—C46—C45	178.24 (17)

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N12—H12 \cdots S13 ⁱ	0.88	2.62	3.490 (2)	172
N22—H22 \cdots S23 ⁱⁱ	0.88	2.60	3.350 (2)	143
C46—H46 \cdots Cg1 ⁱⁱⁱ	0.95	2.85	3.678 (2)	146

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