

Hydrogen-bonding patterns in two aroylthiocarbamates and two aroylimidothiocarbonates

Henry Insuasty,^a Edison Castro,^a Edison Sánchez,^a Justo Cobo^b and Christopher Glidewell^{c*}

^aDepartamento de Química, Universidad de Nariño, Ciudad Universitaria Torobajo, AA 1175, Pasto, Colombia, ^bDepartamento de Química Inorgánica y Orgánica, Universidad de Jaén, 23071 Jaén, Spain, and ^cSchool of Chemistry, University of St Andrews, Fife KY16 9ST, Scotland
Correspondence e-mail: cg@st-andrews.ac.uk

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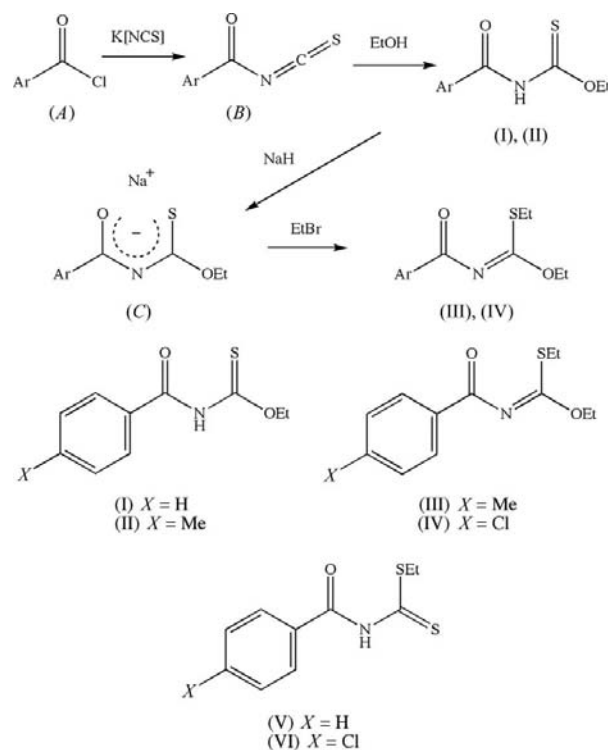
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In *O*-ethyl *N*-benzoylthiocarbamate, C₁₀H₁₁NO₂S, the molecules are linked into sheets by a combination of two-centre N—H···O and C—H···S hydrogen bonds and a three-centre C—H···(O,S) hydrogen bond. A combination of two-centre N—H···O and C—H···O hydrogen bonds links the molecules of *O*-ethyl *N*-(4-methylbenzoyl)thiocarbamate, C₁₁H₁₃NO₂S, into chains of rings, which are linked into sheets by an aromatic π – π stacking interaction. In *O,S*-diethyl *N*-(4-methylbenzoyl)imidothiocarbonate, C₁₃H₁₇NO₂S, pairs of molecules are linked into centrosymmetric dimers by pairs of symmetry-related C—H··· π (arene) hydrogen bonds, while the molecules of *O,S*-diethyl *N*-(4-chlorobenzoyl)imidothiocarbonate, C₁₂H₁₄ClNO₂S, are linked by a single C—H···O hydrogen bond into simple chains, pairs of which are linked by an aromatic π – π stacking interaction to form a ladder-type structure.

Comment

O,S-Dialkyl aroylimidothiocarbonates are structural analogues of *S,S*-dialkyl aroylimidothiocarbonates, which have been widely used as synthetic starting materials (Augustín *et al.*, 1980; Sato *et al.*, 1981; Fukada *et al.*, 1985, 1986, 1990; Insuasty *et al.*, 2006, 2008). We report here the structures of two *O*-ethyl aroylthiocarbamates, (I) and (II) (Figs. 1*a* and 1*b*), and two *O,S*-diethyl aroylimidothiocarbonates, (III) and (IV) (Figs. 1*c* and 1*d*), and we compare these structures with those of two closely related *S*-ethyl aroyldithiocarbamates, (V) and (VI) (see scheme) (Low *et al.*, 2004, 2005). The structure of (I) has been briefly reported previously [Cambridge Structural Database (Allen, 2002) refcode GIFSUK; Arslan *et al.*, 2007], but the authors' primary concern was the comparison of the experimental geometry and vibrational frequencies with those calculated from first principles at various levels of

theory. The hydrogen bonding was described extremely briefly in terms of only an N—H···O interaction. Accordingly, we have thought it worthwhile to report here a more complete description of the hydrogen bonding in (I).



Compounds (I) and (II) were prepared by the addition of ethanol to the corresponding intermediate aroylisothiocyanate, (B) (see scheme), itself prepared by reaction of potassium thiocyanate with the aroyl chloride, (A). Deprotonation of the *O*-ethyl aroylthiocarbamates yields the ionic intermediate, (C), reaction of which with bromoethane gives (III) and (IV). The corresponding reactions of the appropriate aroylisothiocyanate, (B), with ethanethiol rather than with ethanol produces the dithiocarbamate esters (V) and (VI) (Low *et al.*, 2004, 2005). It is interesting to note that in the conversion of (A) to (B), the thiocyanate anion reacts with the aroyl chloride exclusively *via* the harder N terminus, while in the formation of (III) and (IV) from (C), this anionic component of (C) reacts with bromoethane exclusively at the softer S centre.

Despite the close pairwise similarities between the molecular constitutions within the pairs of compounds (I) and (II), (III) and (IV), and (V) and (VI), and the overall similarities within the group comprised of (I), (II), (V) and (VI), no two of these compounds are isomorphous. Thus, for example, while compounds (I) and (II) crystallize in the space groups *Pna*2₁ and *P2*₁/*c*, respectively, both with *Z'* = 1, their close analogues (V) and (VI) crystallize in, respectively, *C2*/*c* with *Z'* = 2 and *P2*₁/*c* with *Z'* = 1. The unit-cell dimensions of (II) and (VI), which could well have been isomorphous and isostructural are, in fact, significantly different, particularly for the cell repeat distance *a* and the cell angle β . Also, (III) and (IV), which

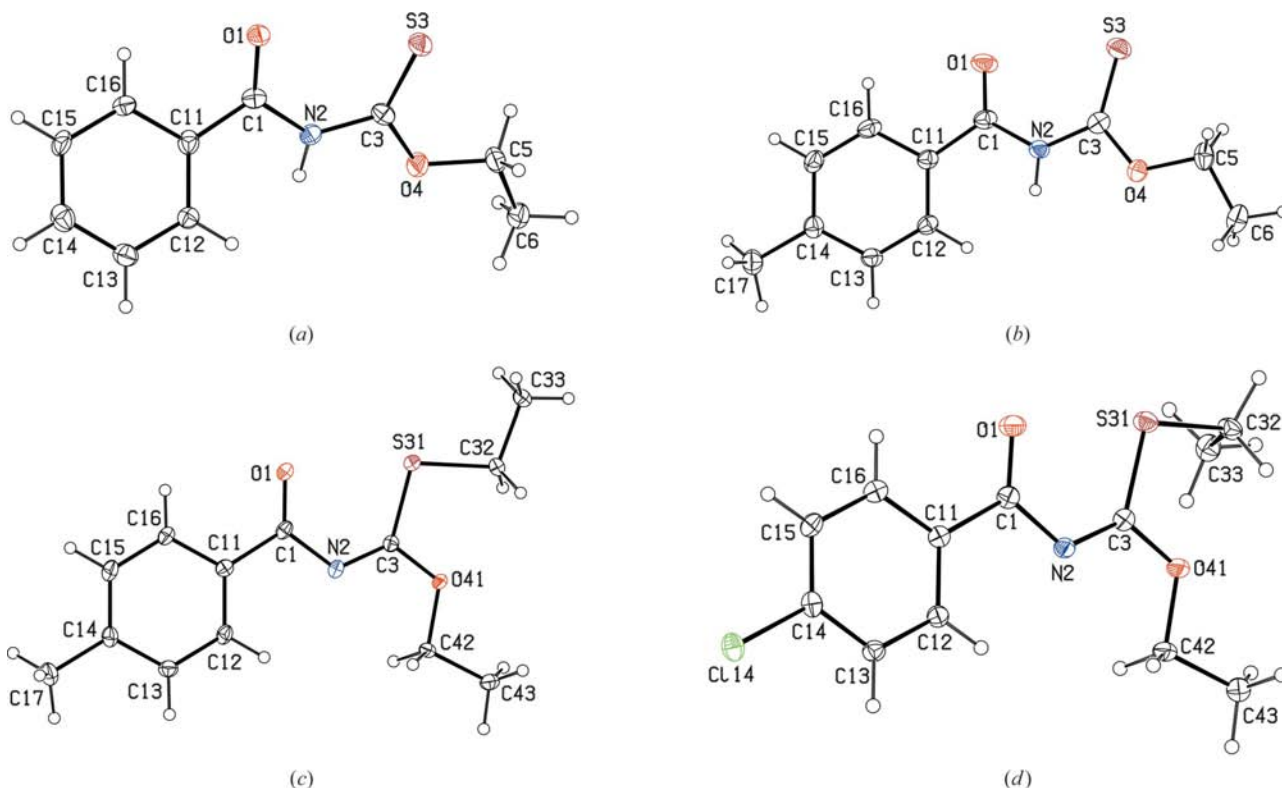


Figure 1

The molecular structures of (a) (I), (b) (II), (c) (III) and (d) (IV), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

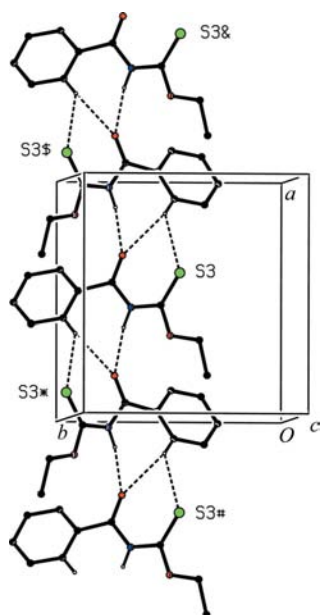
might plausibly have been expected to be isomorphous, crystallize with triclinic unit cells in which the real and reduced cell angles are very different: the cell angles in (III) are all significantly greater than 90° , while those in (IV) are all well below 90° . Hence the unit cell for (III) can be assigned as belonging to type II, designation 4R (Buerger, 1956), while that of (IV) can be assigned as type I, designation 1R.

In thiocarbamate esters (I) and (II), the molecular skeletons adopt chain-extended conformations which, apart from the aryl substituents, are close to planarity, as shown by the leading torsion angles (Table 1). The most striking feature of the conformations of thiocarbonates (III) and (IV) is the orientation of the *S*-ethyl groups (Figs. 1c and 1d). Whereas in (III) this ethyl group is almost coplanar with the rest of the skeleton, in (IV) this unit is almost orthogonal to the rest of the molecule (Table 1). Also, whereas in thiocarbamate esters (I) and (II) the formal C=O and C=S double bonds are mutually *cisoid*, in dithiocarbamate esters (V) and (VI) (Low *et al.*, 2004, 2005) these units adopt a *transoid* arrangement (*cf.* scheme).

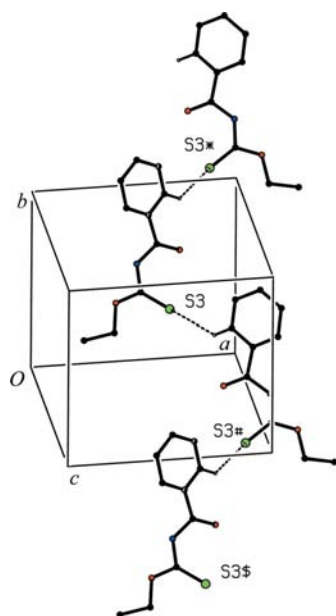
In each of compounds (I)–(IV), the C–O bond distances involving atom O3, namely C3–O4 in (I) and (II), and C3–O41 in (III) and (IV), are all the same within experimental uncertainty. In addition, the N2–C3 bonds in (I) and (II) are long for their type (Allen *et al.*, 1997a). These observations, taken together, indicate that in (I) and (II) there is very little electronic delocalization from atoms N2 and O4 on to atom S3. By contrast, the C=S bond distances are 1.6586 (18) and

1.6552 (18) Å in (V), where $Z' = 2$ (Low *et al.*, 2004), and 1.631 (3) Å in (VI) (Low *et al.*, 2005), typical of such distances in compounds containing $>N-C(=S)-S-$ fragments (Allen *et al.*, 1997a) and consistent with the occurrence of conjugative delocalization. In (III) and (IV), the C–N distances provide a clear distinction between the formal C1–N2 single bonds and the formal N2=C3 double bonds. Despite the apparent lack of any significant polarization of the electronic structures in (I) and (II), the bond angles at atoms C1, N2 and C3 are certainly consistent with a strongly repulsive nonbonded interaction between atoms O1 and S3. A similar pattern of bond angles is apparent in (III) and (IV).

The supramolecular aggregation in (I) and (II) is dominated by a combination of N–H...O and C–H...O hydrogen bonds, utilizing the same acceptor O1 atom in each compound (Table 2). These interactions are augmented, in the case of (I) only, by two C–H...S interactions. In (I), molecules related by the *a*-glide plane at $y = \frac{3}{4}$ are linked by a combination of a two-centre N–H...O hydrogen bond and a weaker three-centre C–H...O(S) hydrogen bond to form a ribbon containing alternating $R_1^2(6)$ (Bernstein *et al.*, 1995) and $R_2^1(7)$ rings and running parallel to the [100] direction (Fig. 2). A second C–H...S interaction links molecules related by the *n*-glide plane at $x = \frac{3}{4}$ into a simple $C(7)$ chain running parallel to the $[01\bar{1}]$ direction (Fig. 3). The combination of the ribbon along [100] and the chain along $[01\bar{1}]$ generates a hydrogen-bonded sheet parallel to (011), but there are no direction-specific interactions between adjacent sheets. In particular,

**Figure 2**

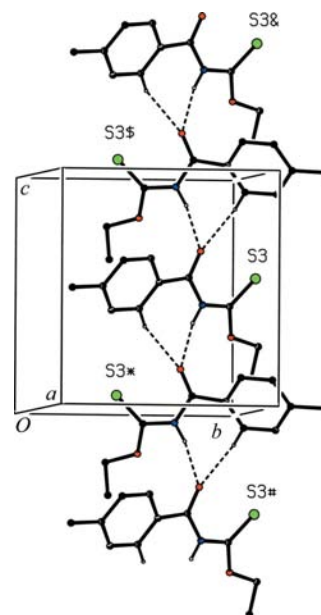
Part of the crystal structure of (I), showing the formation of a ribbon along [100] containing $R_1^2(6)$ and $R_2^1(7)$ rings. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash symbol (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(-\frac{1}{2} + x, \frac{3}{2} - y, z)$, $(-1 + x, y, z)$, $(\frac{1}{2} + x, \frac{3}{2} - y, z)$ and $(1 + x, y, z)$, respectively.

**Figure 3**

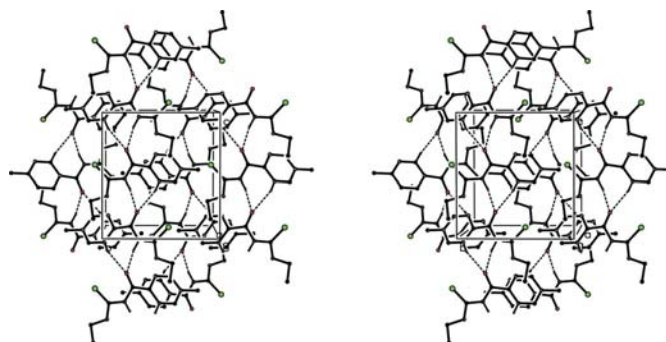
Part of the crystal structure of (I), showing the formation of a $C(7)$ chain along [011]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash symbol (#) or a dollar sign (\$) are at the symmetry positions $(\frac{3}{2} - x, \frac{1}{2} + y, -\frac{1}{2} + z)$, $(\frac{3}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z)$ and $(x, -1 + y, 1 + z)$, respectively.

both $C-H \cdots \pi(\text{arene})$ hydrogen bonds and aromatic $\pi-\pi$ stacking interactions are absent from the crystal structure of (I).

In (II), a combination of $N-H \cdots O$ and $C-H \cdots O$ hydrogen bonds, similar to the corresponding combination in (I), links molecules related by the c -glide plane at $y = \frac{3}{4}$ into a

**Figure 4**

Part of the crystal structure of (II), showing the formation of a chain of $R_2^1(7)$ rings along [001]. For the sake of clarity, H atoms not involved in the motifs shown have been omitted. Atoms marked with an asterisk (*), a hash symbol (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions $(x, \frac{3}{2} - y, -\frac{1}{2} + z)$, $(x, y, -1 + z)$, $(x, \frac{3}{2} - y, \frac{1}{2} + z)$ and $(x, y, 1 + z)$, respectively.

**Figure 5**

A stereoview of part of the crystal structure of (II), showing the π -stacking of hydrogen-bonded chains along [001] to form a sheet parallel to (100). For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

chain of $R_2^1(7)$ rings running parallel to the [001] direction (Fig. 4). The closest intermolecular contacts between atom S3 and the H atoms in (II) corresponding to the $C-H \cdots S$ interactions in (I) all have $H \cdots S$ distances well in excess of 3 Å, and hence they cannot be regarded as structurally significant. Although significant $C-H \cdots S$ interactions are absent from the crystal structure of (II), the hydrogen-bonded chains are linked by an aromatic $\pi-\pi$ stacking interaction. The aryl rings in the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are parallel by symmetry, with an interplanar spacing of 3.479 (2) Å. The corresponding ring-centroid separation is 3.746 (2) Å and the ring-centroid offset (slippage) is 1.389 (2) Å. The effect of this stacking interaction is to link the hydrogen-bonded chains into a sheet parallel to (100) (Fig. 5).

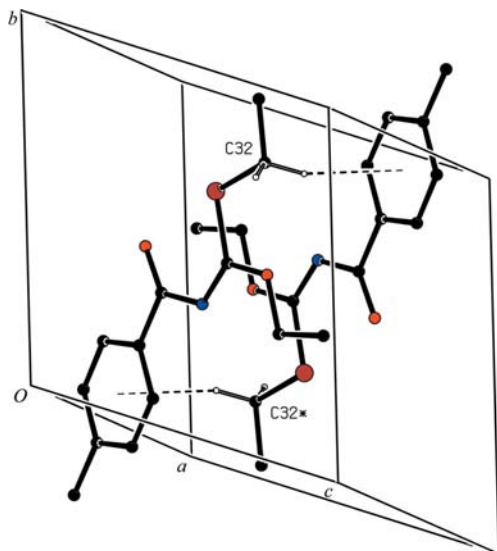


Figure 6

Part of the crystal structure of (III), showing the formation of a centrosymmetric dimer by means of symmetry-related C—H... π (arene) hydrogen bonds. For the sake of clarity, H atoms bonded to C atoms which are not involved in the motif shown have been omitted. The atom marked with an asterisk (*) is at the symmetry position ($1 - x, 1 - y, 1 - z$).

Since no N—H bonds are present in (III) and (IV), the modes of supramolecular aggregation in these compounds necessarily differ substantially from those observed in (I) and (II). In (III), a single C—H... π (arene) hydrogen bond links pairs of molecules into centrosymmetric dimers (Fig. 6). However, π – π stacking interactions are absent and there are no direction-specific interactions between the dimeric units. By contrast, the crystal structure of (IV) contains no C—H... π (arene) hydrogen bonds, but instead chains built from C—H...O hydrogen bonds are linked in pairs to form a ladder-type structure, in which molecules related by translation form $C(6)$ chains running parallel to the [100] direction. The aryl rings of the molecules at (x, y, z) and $(1 - x, 1 - y, 1 - z)$ are strictly parallel, with an interplanar spacing of 3.428 (2) Å. The ring-centroid separation and offset are 3.787 (2) and 1.609 (2) Å, respectively, so that pairs of antiparallel $C(6)$ chains are weakly linked (Fig. 7).

It is of interest briefly to compare the supramolecular aggregation in (V) and (VI) (Low *et al.*, 2004, 2005) with that in (I)–(IV). Compound (V) crystallizes with $Z' = 2$ in space group $C2/c$ (Low *et al.*, 2004) and each type of molecule independently forms a cyclic $R_2^2(8)$ dimer. These dimers are built using two symmetry-related N—H...S hydrogen bonds, with the thione-type S atoms as the acceptors in both types of dimer. One type of dimer contains molecules related by inversion and the other contains molecules related by a twofold rotation axis, and the two independent types of dimer are linked into chains by a single C—H... π (arene) hydrogen bond. It is striking that there is no participation by the amidic O atom in the hydrogen bonding in (V). In compound (VI), on the other hand, where $Z' = 1$ (Low *et al.*, 2005), a combination of N—H...O and C—H...O hydrogen bonds generates a

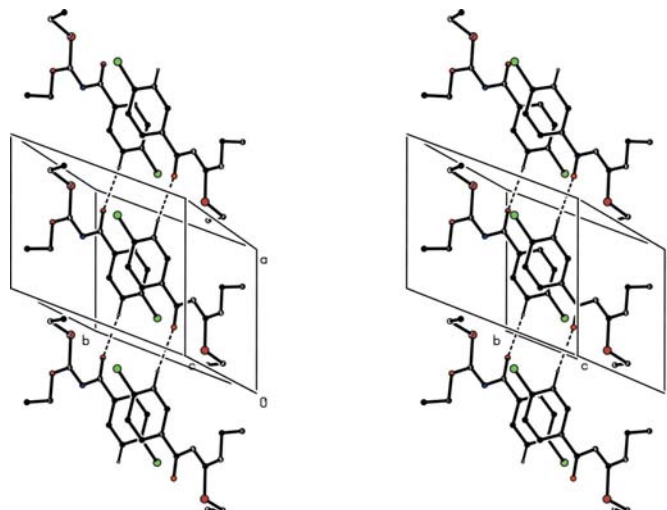


Figure 7

A stereoview of part of the crystal structure of (IV), showing a π -stacked pair of antiparallel hydrogen-bonded chains along [100]. For the sake of clarity, H atoms not involved in the motif shown have been omitted.

chain of $R_2^1(7)$ rings along [001], and chains of this type are linked into a sheet by a single aromatic π – π stacking interaction. Thus, while (II) and (VI) are not isomorphous, and while their molecules adopt different conformations, nonetheless their crystal structures exhibit very similar patterns of intermolecular interaction.

The only hydrogen bonds in this series of compounds, *viz.* (I)–(VI), which involve S atoms as the acceptors utilize the thione-type S atoms in (I) and (V); the two-coordinate S atoms in compounds (III)–(VI) do not participate in any hydrogen-bond formation. This observation is certainly consistent with the deductions drawn from database analyses (Allen *et al.*, 1997*a,b*) that, while thione-type S atoms can in some circumstances act as effective hydrogen-bond acceptors, two-coordinate S atoms are, in general, very poor acceptors.

Experimental

For the synthesis of (I) and (II), the appropriate aroyl chloride (0.043 mol) was added to a solution of potassium thiocyanate (0.043 mol) in acetonitrile (75 ml). This mixture was heated under reflux for 15 min to afford the corresponding aroyl isothiocyanate, which was not isolated. After cooling the intermediate solution to 273 K under an inert atmosphere, dry ethanol (0.47 mol) was added, and this mixture was then stirred at ambient temperature for 24 h. Ice-water was added to the reaction mixture and the resulting light-green solid was collected by filtration, washed with water, dried under reduced pressure and finally crystallized by slow evaporation, at ambient temperature and in air, of a solution in *n*-hexane, to give crystals suitable for single-crystal X-ray diffraction. For (I): yield 95%, m.p. 345 K; for (II): yield 92%, m.p. 331 K.

For the synthesis of (III) and (IV), a slight excess of sodium hydride (60% suspension in oil, 0.020 mol) was added under an inert atmosphere to an ice-cold solution of the corresponding *O*-ethyl aroylimidothiocarbonate (0.010 mol) in *N,N*-dimethylformamide (6 ml). This mixture was stirred for 45 min at ambient temperature, and then bromoethane (0.012 mol) was added slowly and the stirring was continued for a further 30 min. Ice-water was added to the

reaction mixture and the resulting colourless solid was collected by filtration, washed with water, dried under reduced pressure and finally crystallized by slow evaporation, at ambient temperature and in air, of a solution in dry ethanol, to give crystals suitable for single-crystal X-ray diffraction. For (III): yield 94%, m.p. 333 K; for (IV): yield 95%, m.p. 373 K.

Compound (I)

Crystal data

$C_{10}H_{11}NO_2S$ $V = 1017.65 (16) \text{ \AA}^3$
 $M_r = 209.27$ $Z = 4$
 Orthorhombic, $Pna2_1$ Mo $K\alpha$ radiation
 $a = 9.9418 (8) \text{ \AA}$ $\mu = 0.29 \text{ mm}^{-1}$
 $b = 9.3619 (5) \text{ \AA}$ $T = 120 \text{ K}$
 $c = 10.9337 (13) \text{ \AA}$ $0.50 \times 0.42 \times 0.41 \text{ mm}$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer 13852 measured reflections
 1889 independent reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003) 1284 reflections with $I > 2\sigma(I)$
 $T_{\min} = 0.868$, $T_{\max} = 0.890$ $R_{\text{int}} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$ H-atom parameters constrained
 $wR(F^2) = 0.130$ $\Delta\rho_{\max} = 0.45 \text{ e \AA}^{-3}$
 $S = 1.14$ $\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$
 1889 reflections Absolute structure: Flack (1983),
 128 parameters with 890 Bijvoet pairs
 1 restraint Flack parameter: 0.08 (17)

Compound (II)

Crystal data

$C_{11}H_{13}NO_2S$ $V = 1099.6 (2) \text{ \AA}^3$
 $M_r = 223.29$ $Z = 4$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 12.2845 (14) \text{ \AA}$ $\mu = 0.27 \text{ mm}^{-1}$
 $b = 9.1431 (17) \text{ \AA}$ $T = 120 \text{ K}$
 $c = 9.7897 (4) \text{ \AA}$ $0.34 \times 0.30 \times 0.24 \text{ mm}$
 $\beta = 90.182 (7)^\circ$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer 11469 measured reflections
 2026 independent reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003) 1334 reflections with $I > 2\sigma(I)$
 $T_{\min} = 0.918$, $T_{\max} = 0.937$ $R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$ 138 parameters
 $wR(F^2) = 0.134$ H-atom parameters constrained
 $S = 1.07$ $\Delta\rho_{\max} = 0.31 \text{ e \AA}^{-3}$
 2026 reflections $\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$

Compound (III)

Crystal data

$C_{13}H_{17}NO_2S$ $\gamma = 107.307 (11)^\circ$
 $M_r = 251.35$ $V = 629.19 (17) \text{ \AA}^3$
 Triclinic, $P\bar{1}$ $Z = 2$
 $a = 7.2470 (16) \text{ \AA}$ Mo $K\alpha$ radiation
 $b = 8.8870 (7) \text{ \AA}$ $\mu = 0.25 \text{ mm}^{-1}$
 $c = 10.737 (1) \text{ \AA}$ $T = 120 \text{ K}$
 $\alpha = 100.691 (7)^\circ$ $0.42 \times 0.33 \times 0.26 \text{ mm}$
 $\beta = 99.984 (13)^\circ$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer 2460 independent reflections
 2064 reflections with $I > 2\sigma(I)$
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003)
 $T_{\min} = 0.889$, $T_{\max} = 0.938$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.060$ 158 parameters
 $wR(F^2) = 0.167$ H-atom parameters constrained
 $S = 1.18$ $\Delta\rho_{\max} = 0.71 \text{ e \AA}^{-3}$
 2460 reflections $\Delta\rho_{\min} = -0.46 \text{ e \AA}^{-3}$

Compound (IV)

Crystal data

$C_{12}H_{14}ClNO_2S$ $\gamma = 69.548 (15)^\circ$
 $M_r = 271.75$ $V = 633.7 (2) \text{ \AA}^3$
 Triclinic, $P\bar{1}$ $Z = 2$
 $a = 7.8028 (14) \text{ \AA}$ Mo $K\alpha$ radiation
 $b = 9.480 (2) \text{ \AA}$ $\mu = 0.46 \text{ mm}^{-1}$
 $c = 9.860 (2) \text{ \AA}$ $T = 120 \text{ K}$
 $\alpha = 69.545 (13)^\circ$ $0.52 \times 0.45 \times 0.29 \text{ mm}$
 $\beta = 75.683 (14)^\circ$

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer 14986 measured reflections
 2363 independent reflections
 Absorption correction: multi-scan (SADABS; Sheldrick, 2003) 1707 reflections with $I > 2\sigma(I)$
 $T_{\min} = 0.778$, $T_{\max} = 0.879$ $R_{\text{int}} = 0.051$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$ 156 parameters
 $wR(F^2) = 0.119$ H-atom parameters constrained
 $S = 1.12$ $\Delta\rho_{\max} = 0.49 \text{ e \AA}^{-3}$
 2363 reflections $\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I)–(IV).

	(I)	(II)	(III)	(IV)
C1–O1	1.206 (5)	1.208 (3)	1.210 (4)	1.220 (3)
C1–N2	1.385 (5)	1.370 (3)	1.379 (4)	1.382 (3)
N2–C3	1.384 (6)	1.377 (3)	1.283 (4)	1.281 (3)
C3–S3	1.615 (4)	1.615 (3)		
C3–O4	1.325 (5)	1.324 (3)		
C3–S31			1.730 (4)	1.733 (3)
C3–O41			1.321 (4)	1.326 (3)
O1–C1–N2	122.4 (4)	122.3 (3)	125.7 (3)	125.1 (3)
C1–N2–C3	127.3 (4)	127.1 (2)	120.0 (3)	119.2 (2)
N2–C3–S3	127.4 (3)	128.5 (2)		
N2–C3–S31			128.3 (3)	127.9 (2)
C12–C11–C1–N2	19.3 (6)	−21.4 (4)	8.3 (5)	8.9 (4)
C11–C1–N2–C3	−162.4 (4)	179.0 (2)	177.9 (3)	176.1 (2)
C1–N2–C3–O4	−179.9 (4)	−171.7 (2)		
N2–C3–O4–C5	−174.4 (4)	−177.8 (2)		
C3–O4–C5–C6	−171.0 (4)	−171.3 (2)		
C1–N2–C3–S31			1.3 (5)	0.7 (4)
C1–N2–C3–O41			−178.8 (3)	−179.6 (2)
N2–C3–C31–C32			178.1 (3)	−172.7 (3)
C3–S31–C32–C33			−179.4 (3)	78.7 (2)
N2–C3–O41–C42			−1.3 (5)	3.2 (4)
C3–O41–C42–C43			−178.4 (3)	−172.5 (2)

Table 2

Hydrogen bonds and short intermolecular contacts (Å, °) for (I)–(IV).

Cg1 is the centroid of the C11–C16 ring.

Compound	D–H···A	D–H	H···A	D···A	D–H···A
(I)	N2–H2···O1 ⁱ	0.88	2.05	2.921 (4)	170
	C12–H12···S3 ⁱ	0.95	2.83	3.606 (4)	139
	C12–H12···O1 ⁱ	0.95	2.51	3.192 (5)	129
	C16–H16···S3 ⁱⁱ	0.95	2.86	3.576 (5)	134
(II)	N2–H2···O1 ⁱⁱⁱ	0.88	2.03	2.896 (3)	167
	C12–H12···O1 ⁱⁱⁱ	0.95	2.32	3.075 (3)	136
(III)	C32–H32B···Cg1 ^{iv}	0.99	2.62	3.554 (5)	158
(IV)	C13–H13···O1 ^v	0.95	2.45	3.345 (4)	156

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

All H atoms were located in difference maps and then treated as riding atoms in geometrically idealized positions, with C–H = 0.95 (aromatic), 0.98 (CH₃) or 0.99 Å (CH₂) and N–H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{carrier})$, where $k = 1.5$ for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms. For (I), the correct orientation of the structure with respect to the polar-axis direction was established by means of the Flack x parameter (Flack, 1983), $x = 0.08$ (17), and the Hooft y parameter (Hooft *et al.*, 2008), $y = 0.03$ (5), for 99.6% coverage of the Bijvoet pairs. Compound (III) was handled as a nonmerohedral twin, in which the two twin components are related by the matrix (1.000, 0.557, 0.320/0.000, –1.000, 0.000/0.000, 0.000, –1.000). Using the original reflection file (15150 measured reflections, $R_{\text{int}} = 0.0581$), a modified file (2460 reflections, $R_{\text{int}} = 0.0000$) was prepared using the TwinRotMat option in *PLATON* (Spek, 2009) and then used in conjunction with the HKLF 5 option in *SHELXL97* (Sheldrick, 2008), giving twin fractions of 0.268 (5) and 0.732 (5).

For all compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DIRAX/LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) for (I); *SIR2004* (Burla *et al.*, 2005) for (II), (III) and (IV). For all compounds, program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3214). Services for accessing these data are described at the back of the journal.

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