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Bipodal 1,1′-acyl-3,3,3′,3′-tetraalkylbis(thiourea) ligands with flexible C_3, C_4 and C_6 spacer groups

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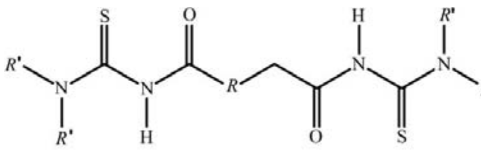
In the structures of 3,3,3′,3′-tetraethyl-1,1′-(propane-1,3-diyldicarbonyl)bis(thiourea), $C_{15}H_{28}N_4O_2S_2$, (I), 3,3,3′,3′-tetraethyl-1,1′-(butane-1,4-diyldicarbonyl)bis(thiourea), $C_{16}H_{30}N_4O_2S_2$, (II), and 3,3,3′,3′-tetrabutyl-1,1′-(hexane-1,6-diyldicarbonyl)bis(thiourea), $C_{26}H_{50}N_4O_2S_2$, (III), compound (I) displays resonance-assisted hydrogen bonding, (II) exhibits an inversion centre, and both (II) and (III) are characterized by intermolecular hydrogen bonds between the carbonyl O atoms and thioamide H atoms, leading to chains of hydrogen-bonded molecules throughout the structures. The accurate structural data for these molecules is expected to assist in molecular modelling and other studies currently in progress.

Comment

N,*N*-Dialkyl-*N*′-aryl(aroyl)thioureas coordinate to a diverse array of transition metal ions, usually in an *S*,*O*-bidentate manner, although several examples of coordination through the S atom and an S,N-donor-atom set have been reported (Koch *et al.*, 2001). In view of the interesting practical applications of metal complexes of this class of ligands, a considerable number of both ligands and metal complexes have been studied, and several have been structurally characterized (Sacht *et al.*, 2000; Hernandez *et al.*, 2005). Potentially 'bipodal' derivatives of *N*,*N*-dialkyl-*N*′-aroylthioureas in which two potentially *S*,*O*-chelating acylthiourea motifs are linked through a 'spacer' *R* (see scheme) were reported as early as 1965 (Goerdeler & Stadelbauer, 1965). More recently, work on bipodal derivatives based on *para*-substituted phenyl ring spacers [as in 3,3,3′,3′-tetraethyl-1,1′-terephthaloylbis(thiourea) or 3,3,3′,3′-tetra-*n*-butyl-1,1′-terephthaloylbis(thiourea)] has shown that, with d^8 metal ions, such ligands form almost exclusively 3:3 metallamacrocycles of Ni^{II} (Köhler *et al.*, 1986), Pt^{II} (Koch *et al.*, 1999) and Pd^{II} (Koch *et al.*, 2001). In this context, we showed that the corresponding *meta*-substituted phenyl ligands [3,3,3′,3′-tetraethyl-1,1′-isophthaloylbis(thiourea)] undergo 'self-assembly' with d^8 metal ions to form exclusively the corresponding 2:2 metallamacrocycles, largely as a result of the strong tendency of these ligands to form *cis*-coordinated metal complexes (Koch *et al.*, 1999). The pyridine adducts of 2:2 and 3:3 nickel(II) complexes of 3,3,3′,3′-tetraethyl-1,1′-terephthaloylbis(thiourea) show some interesting host–guest chemistry in the solid state (Hallale *et al.*, 2005). Recently, the corresponding diiodidoplatinum(IV) adducts were prepared and characterized after electrochemically induced oxidative addition of I_2 to the corresponding 2:2 and 3:3 Pt^{II} complexes of 3,3,3′,3′-tetraethyl-1,1′-isophthaloylbis(thiourea) and 3,3,3′,3′-tetraethyl-1,1′-terephthaloylbis(thiourea) (Westra *et al.*, 2005). A similar bipodal ligand with a 2,6-substituted pyridine ring as spacer and its Ag^{I} coordination polymer has been described (Schröder *et al.*, 2000). In all these bipodal ligands the *spacer unit* was a planar 'rigid' phenyl or pyridyl ring.



(I) $R = (CH_2)_2$, $R' = -CH_2CH_3$
(II) $R = (CH_2)_3$, $R' = -CH_2CH_3$
(III) $R = (CH_2)_5$, $R' = -CH_2CH_2CH_2CH_3$

As part of our continuing interest in such bipodal ligands, we have prepared a series of *N*,*N*-dialkyl-*N*′-(acyl)thioureas with *flexible* C_3, C_4 and C_6 spacers and report here the crystal and molecular structures of 3,3,3′,3′-tetraethyl-1,1′-glutaroylbis(thiourea), (I), 3,3,3′,3′-tetraethyl-1,1′-adipoylbis(thiourea), (II), and 3,3,3′,3′-tetrabutyl-1,1′-suberoylbis(thiourea), (III). König *et al.* (1987) reported the synthesis of a variety of 3,3,3′,3′-tetraalkyl-1,1′-alkanedioylbis(thioureas) and the Ni^{II}, Cu^{II}, Pd^{II} and Pt^{II} metal complexes of 3,3,3′,3′-tetraethyl-1,1′-adipoylbis(thiourea), although no structural characterization was carried out.

In view of the nomenclature and atom-numbering schemes of compounds of this type reported in the literature historically being inconsistent, we here follow an atom-numbering scheme for molecules (I)–(III) to correspond to the bipodal molecules with rigid 'spacers' as reported by Westra *et al.* (2005), as this method offers the most clarity.

Compound (I) crystallizes in the $P2_1/n$ space group and the molecule adopts a conformation such that the two acylthiourea motifs are at an approximate right angle to one another, owing to the flexible nature of the spacer group (Fig. 1). The donor O and S atoms in each acylthiourea unit assume opposing orientations indicated by the O—C(O)—N—C(O)—C(S) and S—C(S)—N—C(S)—C(O) torsion angles (Table 1). Table 1 shows that the N—C bond lengths are all shorter than the average C—N single bond length of 1.472 (5) Å (Allen *et al.*, 1987), but follow the expected order in which the thioamide N1—C12 bond length is relatively the

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longest, followed by the amide N1—C11 bond; the second thioamide N2—C12 bond is the shortest. This trend is consistent with that generally observed for a variety of related simple *N*,*N*-dialkyl-*N*′-benzoylthioureas (Koch *et al.*, 1995; Dillen *et al.*, 2006).

In the crystal structure, molecules of (I) are linked by two intermolecular hydrogen bonds (Table 2) between the S atom of one molecule and the thioamide H atom of a neighbouring molecule (Fig. 2). The acylthiourea unit consists of a donor–acceptor pair connected by a 'resonant π system', evident from the shortening of the amide and thioamide C—N bonds. This leads to one molecule being hydrogen bonded to two others, as shown in Fig. 2, and this type of hydrogen-bond formation represents an example of π-bond co-operativity or resonance-assisted hydrogen bonding (Steiner, 2002). This, to the best of our knowledge, is the first time that hydrogen bonding of this type has been reported for these compounds. Similar observations have been made for the closely related *N*,*N*-diethyl-*N*′-benzoylselenourea (Bruce *et al.*, 2007).

The relative orientations of the acylthiourea units are such that, if a plane is defined by C11/C1–C3/C31 along the length of the spacer group, the O atom of one acylthiourea unit is above the plane and the corresponding S atom below, while in the second acylthiourea unit, the O atom is below the plane while the corresponding S atom lies above the plane.

Compound (II) crystallizes in the $P\overline{1}$ space group, exhibiting an inversion centre located midway between atoms C2 and C2′, resulting in only half the molecule appearing in the asymmetric unit. The remainder of the molecule can be generated with the symmetry operator ($-x$, $-y$, $-z$ + 1) and the whole molecule is shown in Fig. 3. The C—N bond lengths of (II) (Table 3) are similar to those in (I) in that the C—N bond lengths in the acylthiourea unit are all shorter than the average C—N single bond length of 1.472 (5) Å and are consistent with the trend described previously for (I). It is noteworthy that the molecule of (II) with the C_4 flexible spacer assumes an approximately linear conformation in the solid state, in contrast to that of (I) in which the molecule with the C_3 spacer is significantly 'bent'. Moreover, the relative *anti* orientations of the S and O donor atoms in (I) are not observed in (II), for which the O1—C11—N1—C12 [7.1 (4)°] and S1—C12—N1—C11 [45.5 (3)°] torsion angles are substantially different from the corresponding angles [12.6 (4) and 125.7 (2)°] in (I). This is most likely due to the involvement of the O-atom donor in the intramolecular hydrogen bond exhibited by (II) (see below).

The intermolecular hydrogen-bonding pattern observed for (II) is quite different from that seen in (I). In (II) the thioamide H atoms (H1 and H1′) hydrogen bond to the carbonyl O atoms (O1 and O1′) of a neighbouring molecule (Table 4), as shown in Fig. 4, thus precluding the formation of resonance-

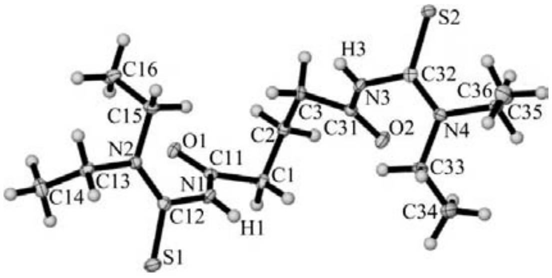

Figure 1
The molecular structure of (I), with the atomic numbering shown. Displacement ellipsoids are drawn at the 50% probability level.

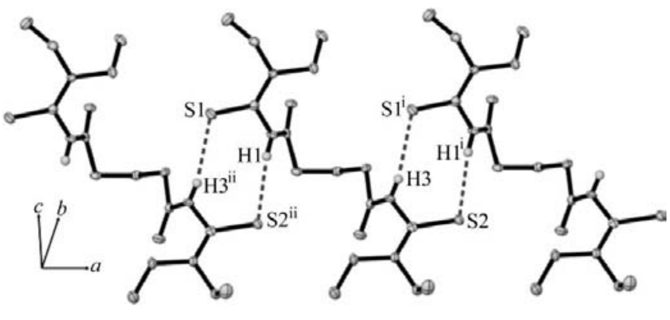

Figure 2
A view of the structure of (I), showing the intermolecular N—H···S hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level. H atoms, except H1 and H3, have been omitted for clarity. [Symmetry codes: (i) x + 1, y, z; (ii) x − 1, y, z.]

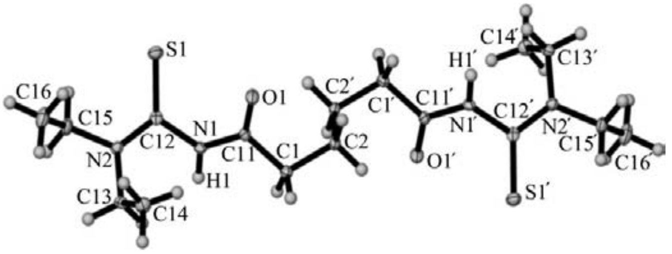

Figure 3
The molecular structure of (II), with the atomic numbering shown. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $-x$, $-y$, $-z$ + 1.]

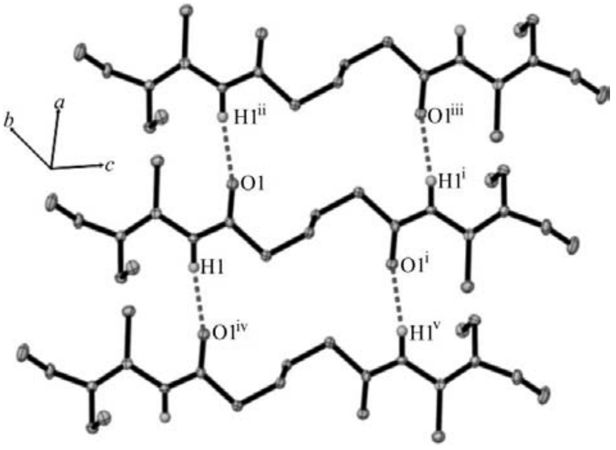

Figure 4
The structure of (II), showing intermolecular N—H···O hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level. H atoms, except H1, have been omitted for clarity. [Symmetry codes: (i) $-x$, $-y$, $-z$ + 1; (ii) x + 1, y, z; (iii) $-x$ + 1, $-y$, $-z$ + 1; (iv) x − 1, y, z; (v) $-x$ − 1, $-y$, 1 − z.]

assisted hydrogen bonding as observed in the crystal structure of (I).

Despite crystallizing in the same space group as (II), the molecule of (III) with the C_6 spacer does not exhibit an inversion centre, the whole molecule being contained in the asymmetric unit (Fig. 5). The overall conformation that molecule (III) adopts differs from that of both (I) and (II); while the C_6 spacer of the molecule remains reasonably linear, the molecule assumes an overall U shape with the two butyl groups of the terminal thioamide units extending above and below this conformation (Fig. 5). As for the previous compounds, the relative orientations of the S and O donor atoms of the acylthiourea groups on either side of the C_6 spacer differ in that the carbonyl O atom of one acylthiourea residue is situated above the C11/C1–C6/C61 plane, while the other carbonyl O atom is below the plane. In each case, the S atom of the thiocarbonyl group has an *anti* orientation relative to that of the carbonyl O atom, as indicated by the torsion angles in Table 5. This is reminiscent of (I) and different from (II), which interestingly exhibits similar hydrogen bonding.

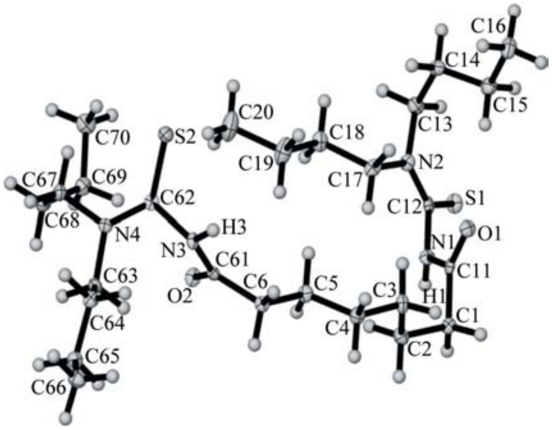

Figure 5

The molecular structure of (III), with the atomic numbering shown. Displacement ellipsoids are drawn at the 50% probability level.

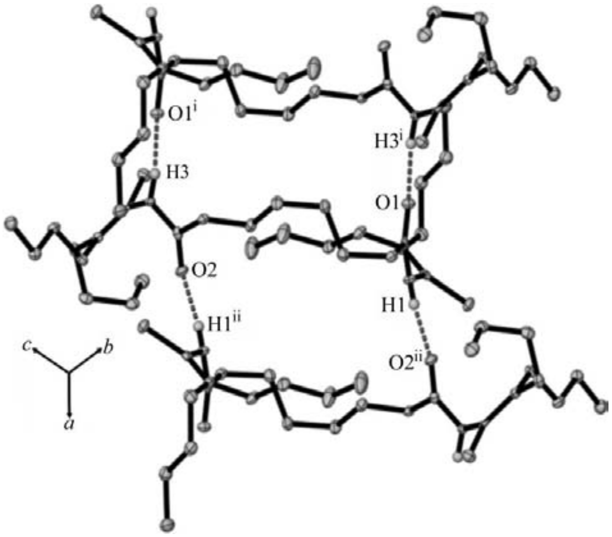

Figure 6

The structure of (III), showing intermolecular N—H···O hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 50% probability level. H atoms, except H1, have been omitted for clarity. [Symmetry codes: (i) $-x + 1, -y + 1, -z$; (ii) $-x + 2, -y + 1, -z$.]

Similar to (I), the C—N bond lengths in each chelate ring are not identical to the corresponding C—N bonds in the second ring; however, they are all shorter than the average single C—N bond length of 1.472 (5) Å, and the trend described for (I) is maintained here. Intermolecular hydrogen bonding (Table 6) between the carbonyl O atom of one molecule and thioamide H atom of a neighbouring molecule is evident, and the molecular arrangement in this compound is similar to that in (II), in that each molecule has two hydrogen bonds to each neighbour on either side of the central molecule, as shown in Fig. 6.

Experimental

All reactions were carried out under an inert N_2 atmosphere. All reagents and solvents were commercially available and used without further purification, except for the acetone which was distilled prior to use. One molar equivalent of the appropriate acid dichloride in acetone was added dropwise to two molar equivalents of KSCN in acetone. The mixture was heated under reflux for 45 min, after which it was cooled to room temperature and the dropwise addition of two molar equivalents of the appropriate secondary amine in acetone followed. The mixture was heated under reflux for a further 45 min and cooled to room temperature, with subsequent addition of water (*ca* 15–25% *v*/*v*) to dissolve the KCl which formed as a by-product. Slow evaporation of the acetone afforded a crystalline product and recrystallization from water/acetone solutions (variable ratio of 5–20% *v*/*v*) yielded crystals suitable for analysis. Analysis for (I) (yield 53%, m.p. 392.6–393.4 K). ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (*s*, 2H, –NH–), 3.96 [*br s*, 4H, $–N(CH_2CH_3)_2$], 3.61 [*br s*, 4H, $–N(CH_2CH_3)_2$], 2.39 (*t*, 4H, $–CH_2—CH_2—CH_2–$), 2.19 (*m*, 2H, $–CH_2—CH_2—CH_2–$), 1.30 [*m*, 12H, $–N(CH_2CH_3)_2$]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.4 (CS), 170.6 (CO), 47.6 [$–N(CH_2CH_3)_2$], 47.3 [$–N(CH_2CH_3)_2$], 34.7 [$CH_2—CH_2—CH_2$], 24.0 ($–CH_2—CH_2—CH_2–$), 13.4 [$–N(CH_2CH_3)_2$], 11.2 [$–N(CH_2CH_3)_2$]. Analysis for (II) (yield 58%, m.p. 394.7–395.5 K). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (*s*, 2H, –NH–), 3.94 [*br s*, 4H, $–N(CH_2CH_3)_2$], 3.53 [*br s*, 4H, $–N(CH_2CH_3)_2$], 2.40 [*t*, 4H,

Table 1

Selected geometric parameters (Å, °) for (I).

S1—C12	1.687 (3)	O2—C31	1.208 (3)
O1—C11	1.215 (3)	N2—C12	1.319 (3)
N1—C11	1.373 (3)	N3—C31	1.390 (3)
N1—C12	1.411 (3)	N3—C32	1.406 (3)
S2—C32	1.682 (3)	N4—C32	1.326 (3)
C12—N1—C11—O1	12.6 (4)	C32—N3—C31—O2	26.3 (4)
C11—N1—C12—S1	125.7 (2)	C31—N3—C32—S2	113.9 (2)

Table 2

Hydrogen-bond geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···S2^{ii}	0.82 (3)	2.58 (3)	3.393 (2)	173 (3)
N3—H3···S1^{i}	0.77 (3)	2.60 (3)	3.344 (2)	165 (2)

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

–CH_2—$(CH_2)_2$—CH_2–], 1.74 [*q*, 4H, –CH_2—$(CH_2)_2$—CH_2–], 1.29 [*s*, 12H, –$N(CH_2CH_3)_2$]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.9 (CS), 169.8 (CO), 47.6 [$N(CH_2CH_3)_2$], 36.3 [CH_2—$(CH_2)_2$—CH_2], 24.2 [CH_2—$(CH_2)_2$—CH_2], 13.2 [$N(CH_2CH_3)_2$], 11.6 [$N(CH_2CH_3)_2$]. Analysis for (III) (yield 76.1%, m.p. 353.2–355.2 K. ^1H NMR (400 MHz, $CDCl_3$): δ 8.82 (*s*, 2H, –NH–), 3.88 [*br t*, 4H, –$N(CH_2CH_2CH_2CH_3)_2$], 3.44 [*br t*, 4H, –$N(CH_2CH_2CH_2CH_3)_2$], 2.34 [*t*, 4H, –CH_2—$(CH_2)_4$—CH_2–], 1.67 [*m*, 12H, –CH_2—$(CH_2)_4$—CH_2– and –$N(CH_2CH_2CH_2CH_3)_2$], 1.36 [*m*, 12H, –CH_2—$(CH_2)_4$—CH_2– and –$N(CH_2CH_2CH_2CH_3)_2$], 0.92 [*m*, 12H, –$N(CH_2CH_2CH_2CH_3)_2$]. ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.5 (CS), 169.9 (CO), 53.1 [–$N(CH_2CH_2CH_2CH_3)_2$], 52.9 [–$N(CH_2CH_2CH_2CH_3)_2$], 36.1 [–CH_2—$(CH_2)_4$—CH_2–], 30.0 [–$N(CH_2CH_2CH_2CH_3)_2$], 28.4 [–$N(CH_2CH_2CH_2CH_3)_2$], 28.0 [–CH_2—$(CH_2)_4$—CH_2–], 24.8 [–CH_2—$(CH_2)_4$—CH_2–], 20.0 [–$N(CH_2CH_2CH_2CH_3)_2$], 13.8 [–$N(CH_2CH_2CH_2CH_3)_2$], 13.7 [–$N(CH_2CH_2CH_2CH_3)_2$].

Compound (I)

Crystal data

$C_{15}H_{28}N_4O_2S_2$
M_r = 360.53
Monoclinic, $P2_1/n$
a = 7.1475 (18) Å
b = 27.999 (7) Å
c = 9.387 (2) Å
β = 93.026 (5)°
V = 1875.9 (8) $Å^3$
Z = 4
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 100 (2) K
0.22 × 0.21 × 0.18 mm

Data collection

Bruker APEX-I CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.937, T_{max} = 0.948
10628 measured reflections
3685 independent reflections
2845 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.129
S = 1.05
3685 reflections
220 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.66 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.47 e $Å^{-3}$

Compound (II)

Crystal data

$C_{16}H_{30}N_4O_2S_2$
M_r = 374.56
Triclinic, $P\overline{1}$
a = 4.8287 (9) Å
b = 6.3977 (12) Å
c = 15.661 (3) Å
α = 85.532 (3)°
β = 86.985 (3)°
γ = 81.894 (3)°
V = 477.09 (16) $Å^3$
Z = 1
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 100 (2) K
0.47 × 0.21 × 0.05 mm

Data collection

Bruker APEX-I CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.874, T_{max} = 0.985
4902 measured reflections
1847 independent reflections
1611 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.156
S = 1.16
1847 reflections
111 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.90 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.30 e $Å^{-3}$

Table 3
Selected geometric parameters (Å, °) for (II).

S1—C12	1.666 (3)	N1—C12	1.421 (3)
O1—C11	1.223 (3)	N2—C12	1.336 (4)
N1—C11	1.353 (3)		
C12—N1—C11—O1	7.1 (4)	C11—N1—C12—S1	45.5 (3)

Table 4
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1^{iv}	0.88	2.05	2.921 (3)	170.5

Symmetry code: (iv) $x - 1, y, z$.

Table 5
Selected geometric parameters (Å, °) for (III).

S1—C12	1.673 (2)	O2—C61	1.229 (3)
O1—C11	1.223 (3)	N2—C12	1.330 (3)
N1—C11	1.383 (3)	N3—C61	1.363 (3)
N1—C12	1.408 (3)	N3—C62	1.423 (3)
S2—C62	1.667 (2)	N4—C62	1.331 (3)
C12—N1—C11—O1	9.0 (4)	C62—N3—C61—O2	−10.6 (4)
C11—N1—C12—S1	122.3 (2)	C61—N3—C62—S2	−106.2 (2)

Table 6
Hydrogen-bond geometry (Å, °) for (III).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H3···O1^{i}	0.85 (2)	2.09 (2)	2.902 (3)	160 (2)
N1—H1···O2^{ii}	0.82 (2)	2.01 (2)	2.828 (3)	172 (2)

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

Compound (III)

Crystal data

$C_{26}H_{50}N_4O_2S_2$
M_r = 514.82
Triclinic, $P\overline{1}$
a = 9.3206 (15) Å
b = 10.6717 (17) Å
c = 15.537 (2) Å
α = 105.164 (3)°
β = 97.767 (3)°
γ = 92.111 (3)°
V = 1473.7 (4) $Å^3$
Z = 2
Mo $K\alpha$ radiation
μ = 0.21 mm^{-1}
T = 100 (2) K
0.41 × 0.37 × 0.05 mm

Data collection

Bruker APEX-I CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.961, T_{max} = 0.990
10961 measured reflections
5709 independent reflections
3751 reflections with $I > 2\sigma(I)$
R_{int} = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.053
$wR(F^2)$ = 0.085
S = 0.87
5709 reflections
319 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.36 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.28 e $Å^{-3}$

H atoms involved in hydrogen bonding were located from a difference electron-density map and all other H atoms were placed in geometrically calculated positions. H atoms bonded to N atoms in compounds (I) and (III) were refined freely (refined distances are given in Tables 2 and 6). All other H atoms were treated as riding [C—H = 0.99 (for $-CH_2$) or 0.98 Å (for $-CH_3$), N—H = 0.88 Å, and $U_{iso}(H) = 1.2U_{eq}(C,N)$ for $-CH_2$ and amine or $1.5U_{eq}(C)$ for $-CH_3$ H atoms].

For all compounds, data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *X-SEED*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR3036). Services for accessing these data are described at the back of the journal.

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