organic compounds

1,2-Bis[(pyridin-2-ylmethyl)sulfanyl]-ethane and its dimorphic hydro-chloride salt

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Although having been described as a liquid in the literature for 41 years, 1,2-bis[(pyridin-2-ylmethyl)sulfanyl]ethane, $C_{14}H_{16}N_2S_2$, (I), has now been obtained as monoclinic crystals via a new and convenient method of purification. Molecules of (I) are located on crystallographic inversion centres and are held together by C—H$\cdots$N and C—H$\cdots$S interactions, resulting in the formation of a three-dimensional network structure. In addition, two polymorphs of the corresponding hydrochloride salt, 2-[({2-[(pyridin-1-ium-2-ylmethyl)sulfanyl]ethyl}sulfanyl)-methyl]pyridin-1-ium dichloride, $C_{14}H_{18}N_2S_2^{2+}\cdot2Cl^-$, (II) and (III), have been isolated. Molecules of (II) and (III) have similar conformations and are located on inversion centres. Both polymorphs form three-dimensional networks through N—H$\cdots$Cl, C—H$\cdots$Cl and C—H$\cdots$S interactions. The structure of (III) displays voids of 35 Å^3.

Comment

The synthesis of 1,2-bis[(pyridin-2-ylmethyl)sulfanyl]ethane, (I), was first reported by Livingstone & Nolan (1970). It was prepared by deprotonation of ethane-1,2-dithiol using sodium ethoxide, followed by a reaction with 2-picolyl chloride. The product was obtained as an oil, which the authors did not distil. More recent publications (Sarkar et al., 2009) also describe the compound as an oil, and when it was prepared in our laboratory we initially also obtained a golden-brown viscous oil. However, the second batch we prepared crystallized abruptly after 11 d; the crystallization occurred at ambient temperature after a small amount had been withdrawn from the bottle with a syringe. In the preceding days, the sample had been subjected to the same procedure numerous times, without nucleation. The crystallization of approximately 5 g was complete within 2 min and was accompanied by the evolution of heat. Nearly colourless crystals of (I), with a melting point of 324 K, could be separated from a small amount of brown oily residue by washing with a small amount of benzene. The crystallization of (I)

therefore proved to be a perfect mode of purification. All subsequent syntheses of this compound in our laboratory have invariably yielded a crystalline product within hours (Dunitz & Bernstein, 1995).
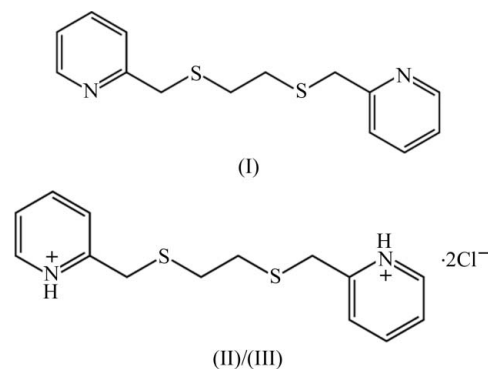
Xylitol [systematic name: (2R,3R,4S)-pentane-1,2,3,4,5-pentaol] is another compound with a similar history. It was first obtained as a syrup in 1891, independently by Fischer & Stahel (1891) and Bertrand (1891); it was not until 1942 that crystalline xylitol was reported (Wolfrom & Kohn, 1942). Interestingly, crystalline xylitol was first obtained as a meta-stable hygroscopic form (monoclinic, m.p. 334 K). In 1943, a high-melting form (orthorhombic, m.p. 367 K) was reported (Carson et al.,1943), but the monoclinic form has been very difficult to obtain (Kim & Jeffrey, 1969) and its crystal structure is still not available in the Cambridge Structural Database (Version 5.32, May 2011 update; Allen, 2002).

A single crystal of (I) could be separated from the solid mass, and we report herein its crystal structure. The molecular conformation about the central CH$_2$—CH$_2$ bond in (I) is anti, and the molecule is located on an inversion centre (Fig. 1). There are two sets of intermolecular hydrogen bonds involving the adjacent aromatic atoms H5 and H4, viz. C5—H5$\cdots$S1^{ii} and C4—H4$\cdots$N1^i (see Table 1 for geometric details and symmetry codes). These intermolecular interactions result in the formation of a three-dimensional hydrogen-bonded network structure. Since the molecules of (I) are centrosymmetric, each molecule forms eight interactions with eight adjacent molecules. The two molecules accepting hydrogen bonds from atoms H5 and H4 stack parallel to the crystallographic a axis, and so do the molecules accepting hydrogen
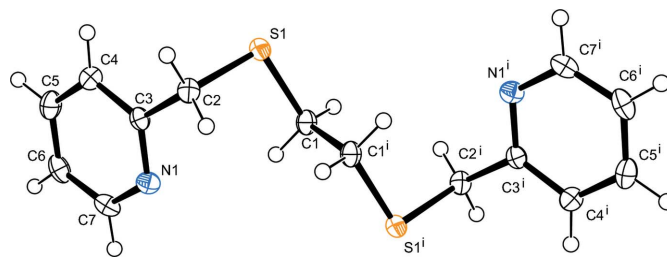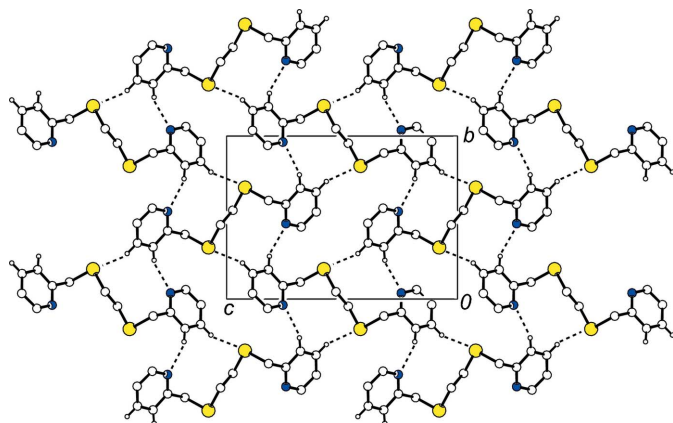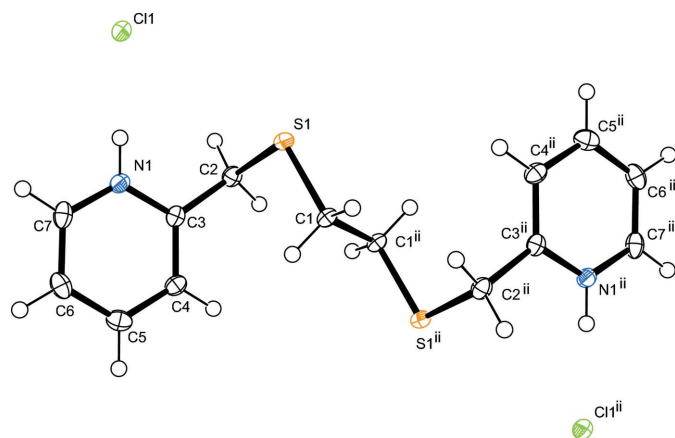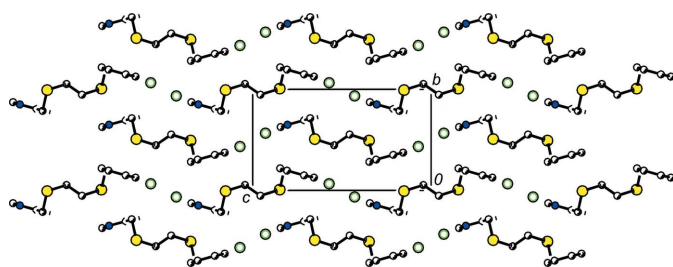

Figure 1
The molecular structure of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) −x, −y + 1, −z.]

Figure 2
The hydrogen-bonded network structure of (I), viewed along the *a* axis. H atoms not involved in C—H···S and C—H···N interactions (dashed lines) have been omitted for clarity.
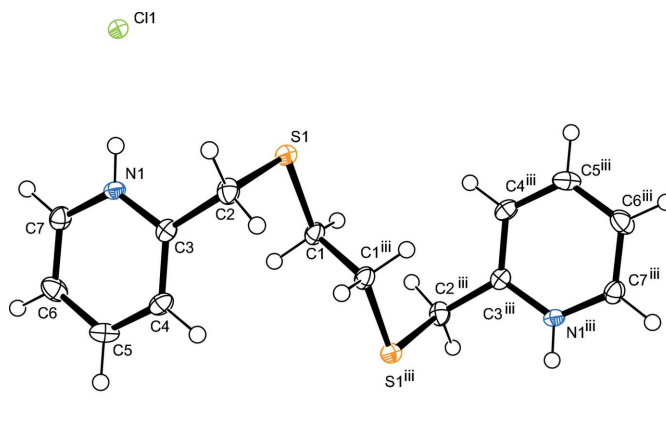

Figure 3
The molecular structure of (II), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (ii) $-x + 1, -y, -z + 2$.]

Figure 4
The crystal packing of (II), viewed along the *a* axis. H atoms have been omitted for clarity.

bonds from atoms H5 and H4 at $(-x, -y + 1, -z)$. Thus, the crystal structure is built up by stacks along the *a* axis (Fig. 2). There are no intermolecular interactions within the stacks.

Compound (I) was prepared in order to use it as a ligand in the formation of transition metal complexes. Two attempts to prepare complexes with vanadium(IV) and molybdenum(V) failed and led to the crystallization of the dihydrochloride salt, 2-[({2-[(pyridin-1-ium-2-ylmethyl)sulfanyl]ethyl}sulfanyl)-methyl]pyridin-1-ium dichloride, which was obtained as two different polymorphs, (II) and (III). In the first case, (II) was

Figure 5
The molecular structure of (III), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (iii) $-x + 1, -y, -z + 1$.]

prepared intentionally by the addition of dilute hydrochloric acid to render (I) water soluble. In the second case, hydrochloride salt (III) was obtained due to the release of hydrogen chloride as a result of hydrolysis of the molybdenum(V) chloride used as reactant. We have made no attempt to establish the reproducibility of the formation of these polymorphs, neither have we conducted any studies on the crystallization of pure 2-[({2-[(pyridin-1-ium-2-ylmethyl)sulfanyl]-ethyl}sulfanyl)methyl]pyridin-1-ium dichloride. A higher density and more efficient packing in (II) than in (III) make it probable, however, that (II) would be the more favoured polymorph (Burger & Ramberger, 1979).

The molecular conformation of (II) (Fig. 3) is similar to that found in (I). Both adopt an *anti* conformation about the central CH_2—CH_2 bond and both have molecules located on inversion centres. The difference between the two molecular structures is the conformation about the C2—C3 bond. In (I), the S1—C2—C3—N1 torsion angle is 94.16 (12)°, while the corresponding torsion angle in (II) is −79.25 (15)°. The shortest intermolecular distance in (II) is the N1—H1N···Cl1 hydrogen bond (Table 2). In addition, there are three sets of C—H···Cl interactions and one set of C—H···S interactions. The C—H···S interactions, involving atoms H2*A* and S1($-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$), are the only short interactions between adjacent cations; the cationic molecules are mainly held together by interactions with the chloride ions. The intermolecular interactions in (II) result in the formation of a three-dimensional network structure (Fig. 4).

The molecular conformation found in polymorph (III) (Fig. 5) is very similar to that found in (II), with the molecules located on crystallographic inversion centres. As in the case of (II), the shortest intermolecular contact in (III) is the N—H···Cl interaction (Table 3). In addition, there are five sets of C—H···Cl interactions involving all four aromatic H atoms and atom H1*B*. There is also a short C—H···S contact involving atoms H2*B* and S1($-x + \frac{1}{2}, y + \frac{1}{2}, z$). As in the cases of (I) and (II), these interactions give rise to the formation of a three-dimensional network structure.
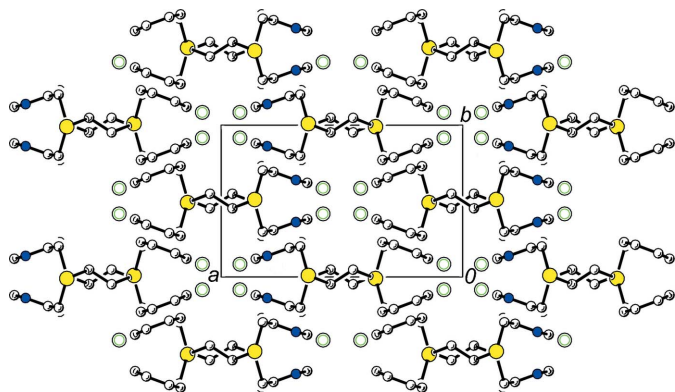
Figure 6
The crystal packing of (III), viewed along the *c* axis. H atoms have been omitted for clarity.
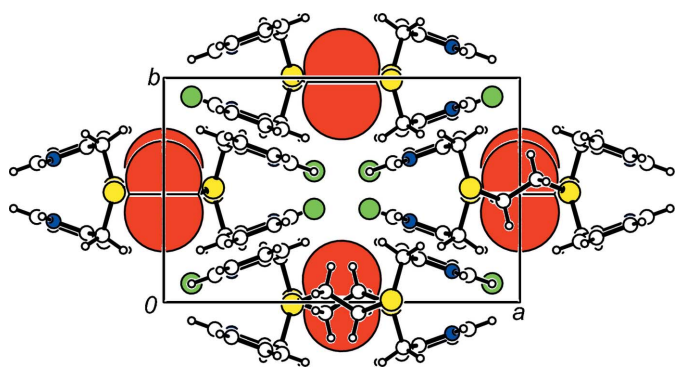

Figure 7
The location of voids (shaded; red in the electronic version of the paper) in the unit cell of (III).

One obvious difference between the crystal packing of (II) and (III) is the twofold axis parallel to the *b* axis in (III), which gives an alternating orientation of molecules when viewed along the *c* axis (Fig. 6).

The most remarkable feature in the crystal structure of (III) is, however, the presence of voids (Fig. 7), each with a volume of 35 Å^3, corresponding to *ca* 4.3% of the unit-cell volume (Spek, 2009). The presence of voids larger than approximately 25 Å^3 is generally considered rare (Atwood, Barbour & Jerga, 2002; Atwood, Barbour *et al.*, 2002). These voids are only slightly smaller than the volume typically occupied by a water molecule (*ca* 45 Å^3) but no significant electron density was observed within the voids. The largest peak in the difference Fourier map is located close to the C2—S1 bond. The voids are not likely to have arisen from the loss of cocrystallized solvent molecules, since the crystals were mounted at low temperature only minutes after being removed from the mother liquor. This time is probably too short for a quantitative loss of a molecule such as water, which would be expected to form strong hydrogen bonds with the other constituents in the crystal structure, while cocrystallized diethyl ether would most likely have left a far larger void. Other recent examples of small organic molecules crystallizing with voids include guanidinium 2-phenylacetate, with voids of 86.5 Å^3 (Smith &

Wermuth, 2010), (2*E*,4*E*)-1-(6-chloro-2-methyl-4-phenyl-3-quinolyl)-5-phenylpenta-2,4-dien-1-one, with voids of 35 Å^3 (Loh *et al.*, 2010), and diammonium biphenyl-4,4′-disulfonate, with voids of 43 Å^3 (Smith *et al.*, 2008).

Experimental

For the preparation of (I), sodium (6.4 g, 0.28 mol) was dissolved in absolute ethanol (200 ml) at 303–313 K under a nitrogen atmosphere. The solution was cooled on ice and ethane-1,2-dithiol (5.1 ml, 0.061 mol) was added. After 20 min, a solution of 2-chloromethyl-pyridinium chloride (19.68 g, 0.12 mol) in absolute ethanol (140 ml) was added slowly. The solution was stirred for 30 min at ambient temperature, refluxed for 4 h under a nitrogen atmosphere and finally stirred at ambient temperature overnight. Water (50 ml) was added and the ethanol was allowed to evaporate. The residue was extracted with dichloromethane (3 × 100 ml). The combined organic phases were washed with water (100 ml) and evaporated to leave a brown oil, which crystallized within hours. The crystalline mass was washed rapidly with a few millilitres of ice-cooled benzene to give almost colourless crystalline (I) (yield 12.1 g, 67%; m.p. 324.4–324.8 K). A second crop was recovered from the filtrate. The product can be recrystallized from hot benzene. The spectroscopic data for compound (I) are given in the archived CIF.

For the preparation of (II), vanadyl perchlorate hydrate (0.11 g, *ca* 0.4 mmol) and 1,2-bis[(pyridin-2-ylmethyl)sulfanyl]ethane (0.11 g, 0.4 mmol) were added to distilled water (5 ml). Hydrochloric acid (4.0 *M*) was added dropwise until a clear-blue solution was obtained. Colourless crystals of (II) formed after a few days upon slow evaporation of the solvent.

For the preparation of (III), molybdenum(V) chloride (0.11 g, 0.4 mmol) was dissolved in acetone (1.5 ml) and solid 1,2-bis[(pyridin-2-ylmethyl)sulfanyl]ethane (0.11 g, 0.4 mmol) was added. The precipitate which formed was filtered off, washed with acetone (5 ml) and dissolved in dimethyl sulfoxide (3 ml). The solution was filtered and divided into three equal parts in three vials, and diethyl ether vapour was diffused into each solution. In each vial, colourless crystals of (III) and a red microcrystalline by-product formed after a few days.

Compound (I)

Crystal data

C$_{14}$H$_{16}$N$_2$S$_2$	$V = 687.56$ (6) Å^3
$M_r = 276.41$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 4.6910$ (2) Å	$\mu = 0.37$ mm^{-1}
$b = 10.1688$ (6) Å	$T = 120$ K
$c = 14.5806$ (8) Å	$0.36 \times 0.20 \times 0.18$ mm
$\beta = 98.679$ (2)°	

Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer	14018 measured reflections
	1213 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	1141 reflections with $I > 2\sigma(I)$
$T_{min} = 0.829$, $T_{max} = 0.936$	$R_{int} = 0.023$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$	114 parameters
$wR(F^2) = 0.059$	All H-atom parameters refined
$S = 1.08$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
1213 reflections	$\Delta\rho_{min} = -0.16$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C4—H4$\cdots$N1^i	0.950 (17)	2.695 (17)	3.6042 (17)	160.4 (12)
C5—H5$\cdots$S1^{ii}	0.950 (17)	2.959 (16)	3.8045 (14)	149.0 (12)

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

Table 2
Hydrogen-bond geometry (Å, °) for polymorph (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N$\cdots$Cl1	0.90 (2)	2.10 (2)	2.9992 (14)	175.7 (17)
C1—H1A$\cdots$Cl1^i	0.99	2.82	3.6428 (16)	141
C2—H2A$\cdots$S1^{ii}	0.99	2.85	3.8286 (15)	168
C4—H4$\cdots$Cl1^{iii}	0.95	2.73	3.6376 (16)	161
C6—H6$\cdots$Cl1^{iv}	0.95	2.80	3.7298 (16)	168
C7—H7$\cdots$Cl1^v	0.95	2.63	3.5517 (16)	165

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

Table 3
Hydrogen-bond geometry (Å, °) for polymorph (III).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1N$\cdots$Cl1	0.85 (2)	2.19 (2)	3.0293 (15)	175 (2)
C1—H1B$\cdots$Cl1^i	0.99	2.76	3.6022 (16)	143
C2—H2B$\cdots$S1^{ii}	0.99	2.95	3.7522 (17)	139
C4—H4$\cdots$Cl1^{iii}	0.95	2.80	3.7405 (17)	171
C5—H5$\cdots$Cl1^{iv}	0.95	2.74	3.6385 (17)	158
C6—H6$\cdots$Cl1^v	0.95	2.80	3.6084 (17)	143
C7—H7$\cdots$Cl1^{vi}	0.95	2.61	3.5298 (17)	162

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

Polymorph (II)

Crystal data

$C_{14}H_{18}N_2S_2^{2+}\cdot2Cl^-$	$V = 850.47$ (9) Å^3
$M_r = 349.32$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 7.8247$ (5) Å	$\mu = 0.62$ mm^{-1}
$b = 7.8382$ (5) Å	$T = 100$ K
$c = 14.1408$ (9) Å	$0.22 \times 0.20 \times 0.06$ mm
$\beta = 101.297$ (3)°	

Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer	15273 measured reflections
	1687 independent reflections
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1996)	1499 reflections with $I > 2\sigma(I)$
$T_{min} = 0.620$, $T_{max} = 0.745$	$R_{int} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.060$	
$S = 1.07$	
1687 reflections	$\Delta\rho_{max} = 0.28$ e Å^{-3}
95 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}

Polymorph (III)

Crystal data

$C_{14}H_{18}N_2S_2^{2+}\cdot2Cl^-$	$V = 1748.7$ (2) Å^3
$M_r = 349.32$	$Z = 4$
Orthorhombic, $Pbcn$	Mo $K\alpha$ radiation
$a = 13.6599$ (9) Å	$\mu = 0.60$ mm^{-1}
$b = 8.5928$ (6) Å	$T = 100$ K
$c = 14.8979$ (11) Å	$0.24 \times 0.10 \times 0.06$ mm

Data collection

Bruker Nonius X8 APEXII CCD area-detector diffractometer	32186 measured reflections
	1711 independent reflections
Absorption correction: multi-scan $SADABS$ (Sheldrick, 1996)	1558 reflections with $I > 2\sigma(I)$
$T_{min} = 0.652$, $T_{max} = 0.745$	$R_{int} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.082$	
$S = 1.07$	
1711 reflections	$\Delta\rho_{max} = 0.76$ e Å^{-3}
95 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

The H atoms in (I) were located in a difference Fourier map and refined freely. In (II) and (III), the N-bound H atoms were located in difference Fourier maps and refined freely. The C-bound H atoms in (II) and (III) were included in calculated positions and refined using a riding model, with C—H = 0.95 (aromatic) or 0.99 Å (methylene), and with $U_{iso}(H) = 1.5U_{eq}(C)$.

For all compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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