

Monoclinic pseudosymmetry in 2-phenoxybenzenesulfonamide, a triclinic structure having $Z' = 4$, and spontaneous resolution in monoclinic *N*-methyl-2-phenoxybenzenesulfonamide

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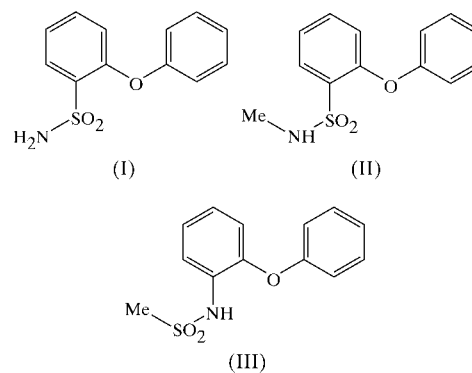
2-Phenoxybenzenesulfonamide, $C_{12}H_{11}NO_3S$, (I), crystallizes in space group $P\bar{1}$ with $Z' = 4$, but the structure closely mimics the monoclinic space group $P2_1/b$ with $Z' = 2$. The molecules of (I) are linked by a combination of $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds into two independent chains of centrosymmetric edge-fused $R_2^2(18)$ and $R_6^6(34)$ rings. *N*-Methyl-2-phenoxybenzenesulfonamide, $C_{13}H_{13}NO_3S$, (II), crystallizes in space group $P2_1$ with $Z' = 1$, and is an example of spontaneous resolution. The molecules are linked by $N-H\cdots O$ and $C-H\cdots O$ hydrogen bonds into chains of spiro-fused $R_2^2(12)$ rings, and these chains are linked into sheets by a single $C-H\cdots\pi(\text{arene})$ hydrogen bond.

Comment

We report here the structure of two closely related sulfonamides, namely 2-phenoxybenzenesulfonamide, (I), and its *N*-methyl analogue, (II), which both show interesting crystallization characteristics.

Compound (I) crystallizes in space group $P\bar{1}$ with four independent molecules in the asymmetric unit (Fig. 1). The choice of the asymmetric unit in cases where $Z' > 1$ allows some flexibility, but for (I) the asymmetric unit has been selected such that the molecules labelled *A* and *C* act as hydrogen-bond donors to molecules *B* and *D*, respectively, within the asymmetric unit. The bond lengths and angles present no unusual values, but the orientation of the sulfonamide groups relative to the adjacent arene rings is very similar in all four molecules (Table 1). These orientations are probably controlled in part by the intramolecular $N-H\cdots O$

hydrogen bonds (Table 2), each of which generates an $S(6)$ motif (Bernstein *et al.*, 1995).



The overall molecular conformations, which can be defined in terms of five independent torsion angles for each molecule, indicate the occurrence of pseudosymmetry. The values of these torsion angles (Table 1) show that for the selected asymmetric unit, molecules *A* and *D* form an approximately enantiomorphous pair and molecules *B* and *C* form a second such pair independent of the first. Detailed scrutiny of the atomic coordinates shows that those for molecule *D* are approximately related to those for molecule *A* by the transformation $(x - 1, y - \frac{1}{2}, \frac{3}{2} - z)$, while those of molecule *B* are similarly related to those of molecule *C* by the related transformation $(x, y - \frac{1}{2}, \frac{3}{2} - z)$. Overall, therefore, there is a pseudo *b*-glide plane at $z = \frac{3}{4}$. The unit-cell dimensions rule out any symmetry higher than triclinic, and the absence of any additional symmetry was confirmed by examination of the refined structure using *PLATON* (Spek, 2003). However, the structure exhibits a close mimicry of space group $P2_1/b$, an

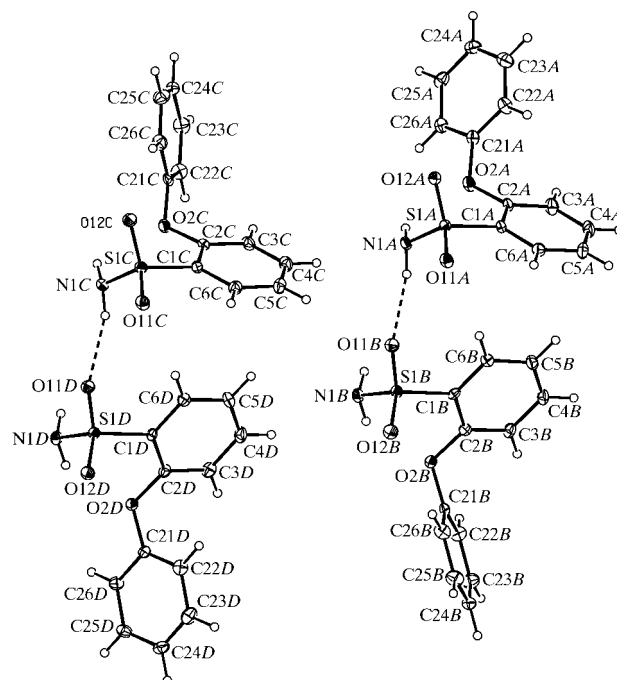


Figure 1

The four independent molecules in (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

alternative to the conventional setting, $P2_1/c$, of space group No. 14. Consistent with this mimicry, the intensities of the $00l$ reflections are, in general, much weaker when l is odd than when l is even, although there is no obviously consistent pattern amongst the $hk0$ reflections.

The molecules of (I) are linked by a combination of N—H···O and C—H···O hydrogen bonds (Table 2) into two independent but very similar chains of edge-fused rings, one built from molecules of types *A* and *B* only, the other from molecules of types *C* and *D* only. It is necessary to discuss only one of these in any detail. Within the asymmetric unit, atom N1*A* acts as hydrogen-bond donor, *via* atom H11*A*, to atom O11*B*. In a similar manner, atom N1*B* at (x, y, z) acts as donor, *via* atom H11*B*, to atom O11*A* at $(x - 1, y, z)$. In this manner, a $C_2^2(8)$ chain built from type *A* and *B* molecules and running parallel to the $[100]$ direction is generated by translation. Within this chain, there is an intermolecular C—H···O contact, which is possibly more an adventitious contact consequent upon the N—H···O hydrogen bonds than a structurally significant hydrogen bond. Two antiparallel chains of *A* and *B* molecules, related to one another by inversion, run through each unit cell and these are linked by a single C—H···O hydrogen bond. Atom C25*B* at (x, y, z) acts as hydrogen-bond donor to atom O12*B* at $(1 - x, 1 - y, 1 - z)$, and propagation of this interaction by translation and inver-

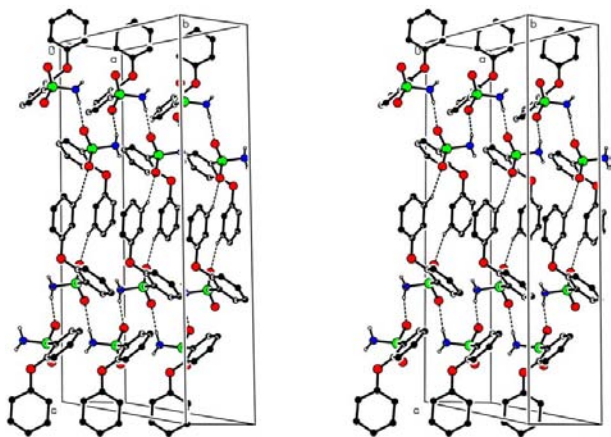


Figure 2
A stereoview of part of the crystal structure of (I), showing the formation of a $[100]$ chain of edge-fused $R_2^2(18)$ and $R_6^6(34)$ rings built from molecules of types *A* and *B* only. For the sake of clarity, H atoms bonded to C atoms but not involved in the hydrogen-bonding motif shown have been omitted

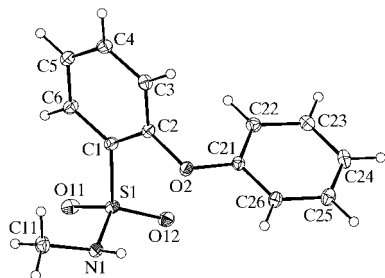


Figure 3
The molecule of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

tion generates a chain of centrosymmetric edge-fused rings along $(x, \frac{1}{2}, \frac{1}{2})$, with $R_2^2(18)$ rings centred at $(n + \frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ ($n =$ zero or integer) and $R_6^6(34)$ rings centred at $(n, \frac{1}{2}, \frac{1}{2})$ ($n =$ zero or integer) (Fig. 2).

The molecules of types *C* and *D* form an entirely similar chain of edge-fused rings running along the line $(x, 0, 1)$. Hence, in projection down a , there is a chain of *A* and *B* type molecules at the cell centre and chains of *C* and *D* type molecules at the cell vertices. However, there are no direction-specific interactions between adjacent chains. Despite the large number of independent aryl groups in the structure of (I), this contains neither C—H··· π (arene) hydrogen bonds nor aromatic π – π stacking interactions.

The *N*-methyl analogue, (II) (Fig. 3), of (I) crystallizes in the chiral space group $P2_1$ with $Z' = 1$. The molecular conformation of (II), as judged from the leading torsion angles (Table 1) bears no particularly close resemblance to those in (I), and there are no intramolecular hydrogen bonds in (II). The resulting molecular point group is C_1 , so that the molecules are chiral. Accordingly, each crystal of (II) contains only a single enantiomorph, in contrast with the crystals of (I). Since the bulk sample of (II) is racemic, the crystallization represents an example of spontaneous resolution to form a conglomerate, rather than a racemate as in (I).

The molecules of (II) are linked into sheets by a combination of three hydrogen bonds (Table 3) and it is convenient to analyse the sheet formation in terms of its two one-dimensional substructures. Atoms N1 and C26 in the molecule at (x, y, z) act as hydrogen-bond donors to, respectively, atoms O11 and O12, both in the molecule at $(1 + x, y, z)$, so generating by translation a $C(4)C(8)[R_2^2(12)]$ chain of rings running parallel to the $[100]$ direction (Fig. 4). In addition, atom C4 at (x, y, z) acts as hydrogen-bond donor to the monosubstituted ring C21–C26 in the molecule at $(x, 1 + y, z)$, so generating by

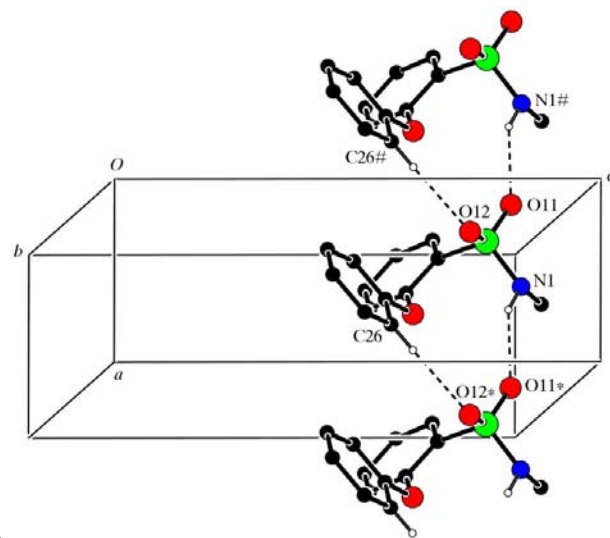


Figure 4
Part of the crystal structure of (II), showing the formation of a $[100]$ chain of spiro-fused $R_2^2(12)$ rings. For the sake of clarity, H atoms bonded to C atoms but not involved in the hydrogen-bonding motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(1 + x, y, z)$ and $(x - 1, y, z)$, respectively.

translation a chain running parallel to the [010] direction (Fig. 5). The combination of the [100] and [010] chains generates an (001) sheet (Fig. 6). Two such sheets pass through each unit cell, one each in the domains $-0.02 < z < 0.49$ and $0.51 < z < 1.02$, but there are no direction-specific interactions between adjacent sheets.

The $C(4)$ chain motif in (II) is very characteristic of simple sulfonamides (Vorontsova, 1966; Cotton & Stokely, 1970; Klug, 1970; Brink & Mattes, 1986; Lightfoot *et al.*, 1993;

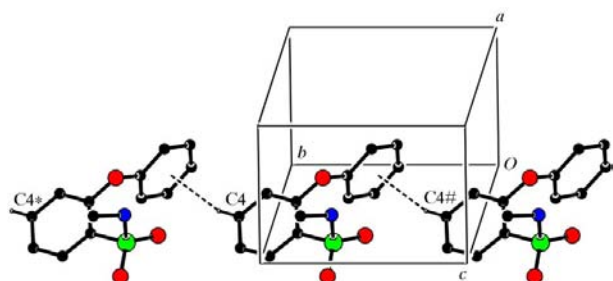


Figure 5
Part of the crystal structure of (II), showing the formation of a C—H... π (arene) chain along [010]. For the sake of clarity, H atoms not involved in the hydrogen-bonding motif shown have been omitted. Atoms marked with an asterisk (*) or a hash (#) are at the symmetry positions $(x, 1 + y, z)$ and $(x, y - 1, z)$, respectively.

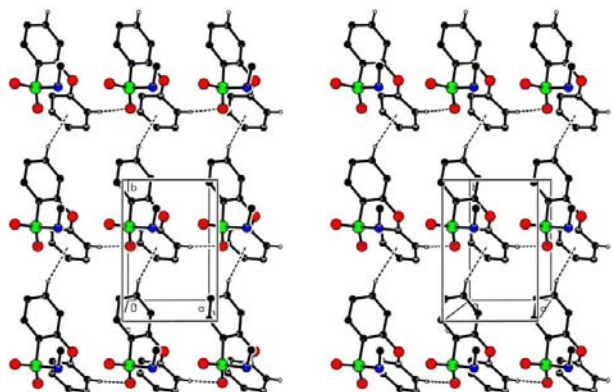


Figure 6
A stereoview of part of the crystal structure of (II), showing the formation of an (001) sheet by combination of the [100] and [010] chains. For the sake of clarity, H atoms not involved in the hydrogen-bonding motifs shown have been omitted.

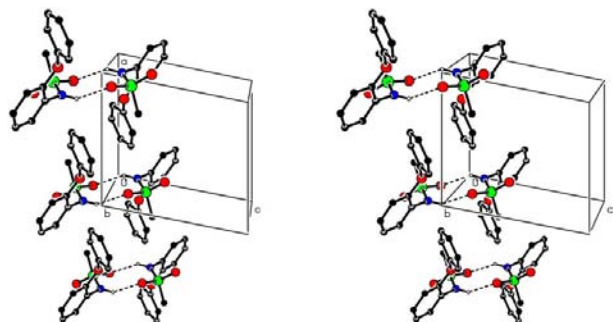


Figure 7
A stereoview of part of the crystal structure of (III) (Chandramohan & Ravikumar, 1999), showing the formation of a π -stacked [110] chain of centrosymmetric hydrogen-bonded dimers. The original atom coordinates have been used. For the sake of clarity, H atoms not involved in the hydrogen-bonding motif shown have been omitted.

Tremayne *et al.*, 1999, 2002; Clark *et al.*, 2003). The related $C_2^2(8)$ motif arises in (I) because two independent molecules participate in the formation of a single chain. On the other hand, the other hydrogen-bond motif most characteristic of sulfonamides, the $R_2^2(8)$ ring (Klug, 1968; Blaschette *et al.*, 1986; Tremayne *et al.*, 1999, 2002; Kelly *et al.*, 2002; Clark *et al.*, 2003), is absent from the structures of both (I) and (II). However, in compound (III) [Cambridge Structural Database (Allen, 2002) refcode SUTYOU; Chandramohan & Ravikumar, 1999], which is an isomer of (II), pairs of N—H...O hydrogen bonds generate centrosymmetric $R_2^2(8)$ rings, as noted in the original report. In addition, however, the resulting dimers are linked into [110] chains by a single aromatic π - π stacking interaction (Fig. 7).

Experimental

Samples of (I) and (II) were prepared by the reaction of 2-phenoxybenzenesulfonyl chloride (Neale *et al.*, 1965) with an aqueous ammonia solution for (I) or with an aqueous methylamine solution for (II). Crystals suitable for single-crystal X-ray diffraction were grown from solutions in ethanol. M.p. for (I): 388–389 K [literature value 386–388 K (Abramovitch *et al.*, 1978)]; m.p. for (II): 354–357 K.

Compound (I)

Crystal data

$C_{12}H_{11}NO_3S$
 $M_r = 249.28$
 Triclinic, $P\bar{1}$
 $a = 5.2539(2) \text{ \AA}$
 $b = 16.2090(8) \text{ \AA}$
 $c = 26.5417(9) \text{ \AA}$
 $\alpha = 84.850(2)^\circ$
 $\beta = 88.951(2)^\circ$
 $\gamma = 87.607(2)^\circ$
 $V = 2248.98(16) \text{ \AA}^3$

$Z = 8$
 $D_x = 1.472 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 9651 reflections
 $\theta = 3.1\text{--}27.4^\circ$
 $\mu = 0.28 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
 Block, colourless
 $0.22 \times 0.16 \times 0.12 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.926$, $T_{\max} = 0.967$
 22 883 measured reflections

9651 independent reflections
 4912 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.071$
 $\theta_{\max} = 27.4^\circ$
 $h = -6 \rightarrow 6$
 $k = -20 \rightarrow 20$
 $l = -34 \rightarrow 33$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.203$
 $S = 1.05$
 9651 reflections
 614 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0812P)^2 + 1.7227P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.64 \text{ e \AA}^{-3}$

Table 1

Selected torsion angles ($^\circ$) for (I) and (II).

Parameter	(I, $n = A$)	(I, $n = B$)	(I, $n = C$)	(I, $n = D$)	(II, $n = \text{nil}$)
$C21n-O2n-C2n-C1n$	132.0 (4)	-130.1 (4)	132.5 (4)	-130.6 (4)	101.8 (3)
$C2n-O2n-C21n-C22n$	-26.3 (6)	-98.4 (5)	96.5 (5)	23.7 (6)	-6.1 (4)
$C2n-C1n-S1n-N1n$	51.5 (4)	-50.2 (4)	50.4 (4)	-50.6 (4)	66.5 (3)
$C2n-C1n-S1n-O11n$	166.2 (3)	-165.4 (3)	165.4 (3)	-165.8 (3)	-179.0 (2)
$C2n-C1n-S1n-O12n$	-66.1 (4)	66.3 (4)	-67.0 (4)	66.0 (4)	-48.6 (3)
$C1-S1-N1-C11$					61.3 (2)

Compound (II)

Crystal data

$C_{13}H_{13}NO_3S$
 $M_r = 263.30$
 Monoclinic, $P2_1$
 $a = 5.3804$ (2) Å
 $b = 7.9959$ (4) Å
 $c = 14.4462$ (7) Å
 $\beta = 95.226$ (2)°
 $V = 618.91$ (5) Å³
 $Z = 2$

$D_x = 1.413$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 2703 reflections
 $\theta = 2.9$ – 27.5 °
 $\mu = 0.26$ mm⁻¹
 $T = 120$ (2) K
 Block, colourless
 $0.22 \times 0.10 \times 0.08$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans, and ω scans with κ offsets
 Absorption correction: multi-scan (SORTAV; Blessing, 1995, 1997)
 $T_{\min} = 0.951$, $T_{\max} = 0.979$
 7538 measured reflections

2703 independent reflections
 2548 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.116$
 $\theta_{\text{max}} = 27.5$ °
 $h = -6 \rightarrow 6$
 $k = -10 \rightarrow 10$
 $l = -18 \rightarrow 17$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.145$
 $S = 1.05$
 2703 reflections
 164 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 0.5323P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.21$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.48$ e Å⁻³
 Absolute structure: Flack (1983), with 1188 Friedel pairs
 Flack parameter = 0.20 (11)

Table 2

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1A-H12A \cdots O2A$	0.88	2.33	2.897 (5)	122
$N1B-H12B \cdots O2B$	0.88	2.19	2.894 (4)	137
$N1C-H12C \cdots O2C$	0.88	2.37	2.871 (4)	117
$N1D-H12D \cdots O2D$	0.88	2.20	2.915 (4)	138
$N1A-H11A \cdots O11B$	0.88	2.13	2.950 (4)	156
$N1B-H11B \cdots O11A^i$	0.88	2.08	2.945 (4)	165
$N1C-H11C \cdots O11D$	0.88	2.14	2.947 (4)	153
$N1D-H11D \cdots O11C^i$	0.88	2.07	2.931 (4)	165
$C25B-H25B \cdots O12B^{ii}$	0.95	2.47	3.371 (6)	157
$C25C-H25C \cdots O12C^{iii}$	0.95	2.42	3.320 (6)	158
$C26A-H26A \cdots O12A^i$	0.95	2.52	3.410 (5)	156
$C26D-H26D \cdots O12D^i$	0.95	2.46	3.378 (5)	161

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

Table 3

Hydrogen-bonding geometry (Å, °) for (II).

Cg1 is the centroid of ring C21–C26.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O11^i$	0.88	2.21	2.953 (3)	141
$C26-H26 \cdots O12^i$	0.95	2.43	3.377 (4)	174
$C4-H4 \cdots Cg1^{ii}$	0.95	2.83	3.741 (3)	161

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

Crystals of (I) are triclinic and space group $P\bar{1}$ was selected and confirmed by the subsequent structure analysis. For (II), the systematic absences permitted $P2_1$ and $P2_1/m$ as possible space groups. Consideration of the unit-cell volume led to the selection of $P2_1$, which was confirmed by the successful structure analysis. All H atoms were located in difference maps and then treated as riding atoms, with C–H distances of 0.95 (aromatic) or 0.98 Å (methyl) and N–H distances of 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or

$1.5U_{\text{eq}}(\text{C})$ for the methyl group. Examination of the refined structure of (I) using the ADDSYM option in PLATON (Spek, 2003) revealed no possible additional symmetry, but scrutiny of the reflection data suggested the possibility of twinning about c^* . Following the use of the TWINROT option in PLATON to generate a HKLF 5-type reflection file, modified to take into account possible reflection overlap, further refinement led to significant reductions in the R indices, although with only trivial changes to the atomic coordinates and hence to the derived geometric parameters, and indicated a twin fraction of ca 8.8 (2)%. The correct absolute configuration of (II) was established by means of the Flack parameter (Flack, 1983).

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement and data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); structure solution: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); structure refinement: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1716). Services for accessing these data are described at the back of the journal.

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