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2-Methoxy-3-methyl-6-oxo-4-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosylamino)-1,6-dihydropyrimidine-5-carbaldehyde 0.065-hydrate and 2-methylsulfanyl-6-oxo-4-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosylamino)-1,6-dihydropyrimidine-5-carbaldehyde: hydrogen-bonded structures in one or three dimensions

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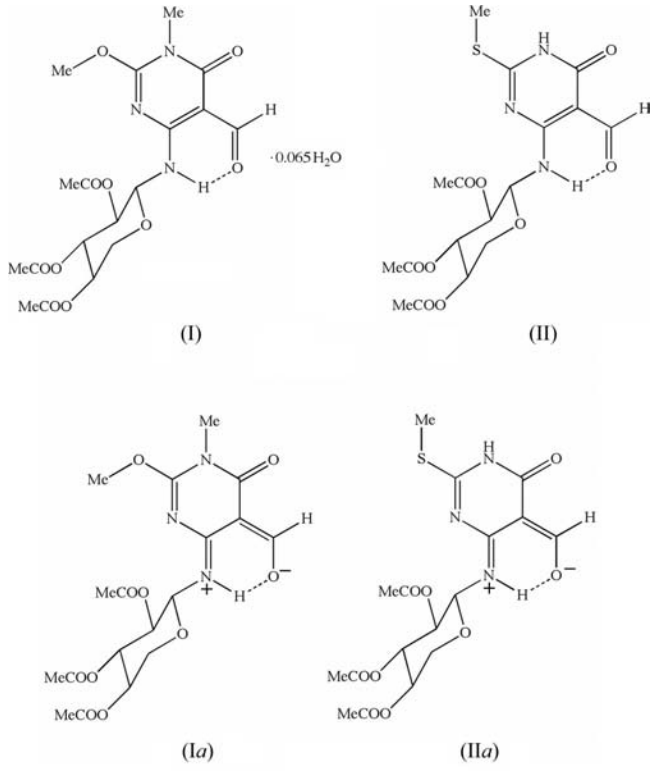
The organic components of 2-methoxy-3-methyl-6-oxo-4-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosylamino)-1,6-dihydropyrimidine-5-carbaldehyde 0.065-hydrate, $C_{18}H_{23}N_3O_{10}\cdot 0.065H_2O$, (I), which crystallizes with $Z' = 2$ in the space group $P2_12_12_1$, are linked into a three-dimensional framework structure by a combination of four C—H···O hydrogen bonds. In 2-methylsulfanyl-6-oxo-4-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosylamino)-1,6-dihydropyrimidine-5-carbaldehyde, $C_{17}H_{21}N_3O_9S$, (II), where the pyrimidine fragment is disordered with two different conformations for the methylsulfanyl substituent, molecules are linked into chains of rings by a combination of N—H···O and C—H···O hydrogen bonds.

Comment

5-Substituted aminopyrimidine derivatives are useful intermediates for the preparation of fused pyrimidine systems, and we have previously reported the preparation of 5-formyl-6-glycosylaminopyrimidines under Vilsmeier–Haack conditions (Negrillo *et al.*, 1988). We report here the structures of two representative examples of 6-oxo-4-(2,3,4-tri-*O*-acetyl-β-D-xylopyranosylamino)-1,6-dihydropyrimidine-5-carbaldehydes, *viz*. (I) and (II) (Figs. 1 and 2), of which (I) is a partial hydrate containing 0.065 (3) molecules of water per molecule of the organic component. Compounds (I) and (II) both crystallize in the space group $P2_12_12_1$, but with Z' values of 2 and 1, respectively, so that their unit-cell dimensions show no obvious simple relationship to one another. In compound (II), the pyrimidine component is disordered, and this disorder was modelled using two sets of sites with refined occupancies of 0.899 (2) and 0.101 (2); an unexpected feature of the disorder is that the methylsulfanyl substituent adopts different conformations in the two disorder components.



The xylopyranose rings in both compounds adopt almost perfect chair conformations, with all of the non-H substituents occupying equatorial sites, giving the absolute configuration in (II) as (*x*1*R*,*x*2*R*,*x*3*S*,*x*4*R*), where *x* = 2 or 4, with the absolute configuration in (I) set to be identical. The pyrimidine rings are all planar despite the heavy degree of substitution. The formyl groups are all oriented so that intramolecular N—H···O hydrogen bonds (Tables 2 and 4) can form; these interactions may play a role in controlling the orientation of the formyl group (Cobo *et al.*, 2008). The methoxy C atoms in (I) are oriented on the same side of the pyrimidine ring as the formyl O atom, whereas in (II) the methylsulfanyl C atom is oriented to the opposite side in the major component and to the same side in the minor component (Tables 1 and 3, and Figs. 1 and 2); no simple explanation for these differences was obvious. The bond lengths within the pyrimidine systems (Tables 1 and 3) provide some evidence for the polarization of the electronic structures. In particular, the formyl C—O distances are all long for their type (Allen *et al.*, 1987), as are the exocyclic C—N bonds, while the C—C bonds linking the formyl unit to the ring are all long, suggesting the importance of the polarized forms (I*a*) and (II*a*) (see scheme). The intramolecular N—H···O hydrogen bonds can thus be regarded as charge-assisted hydrogen bonds (Gilli *et al.*, 1994).

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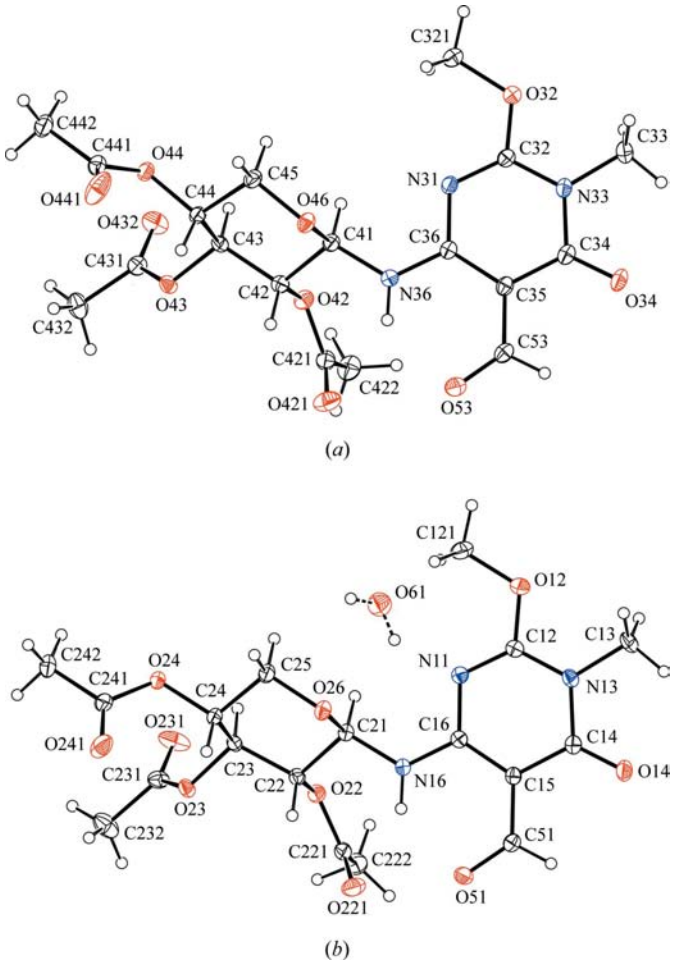

Figure 1
The independent components of compound (I), showing the atom-labelling scheme for (*a*) a type 1 molecule together with the partially occupied water site, and (*b*) a type 2 molecule. Displacement ellipsoids are drawn at the 30% probability level.

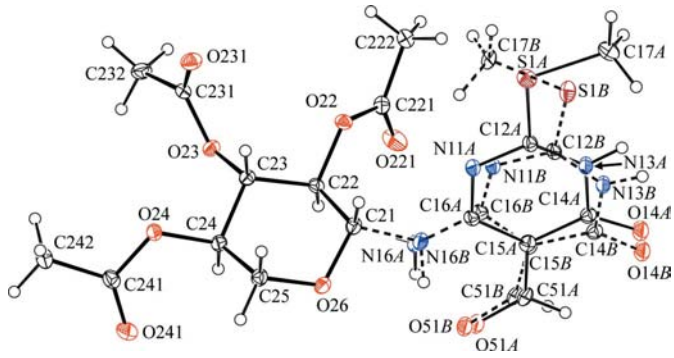

Figure 2
The molecular structure of compound (II), showing the major and minor orientations of the pyrimidine unit, together with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

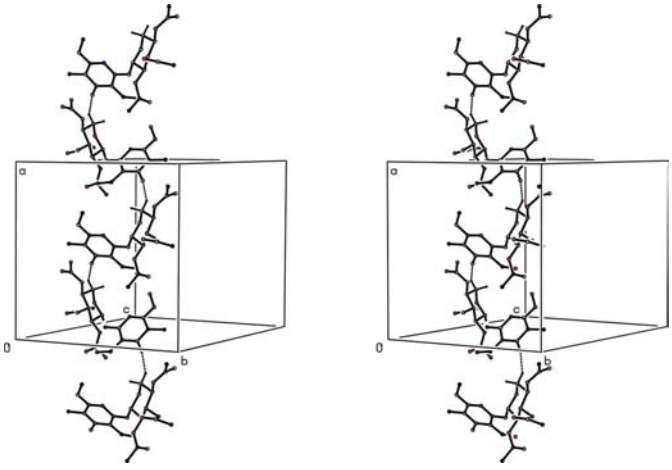

Figure 3
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of type 2 molecules running parallel to [100]. For the sake of clarity, the partial water molecule and H atoms not involved in the motif shown have been omitted.

In compound (I), the organic components are linked by four C—H···O hydrogen bonds (Table 2) to form a three-dimensional framework structure of some complexity; however, the formation of this framework can readily be analysed in terms of three distinct one-dimensional substructures. One of the hydrogen bonds links the two molecules within the selected asymmetric unit, while the other three give rise, in various combinations, to the three substructures, The simplest of the substructures, along [100], depends on just one hydrogen bond and involves only the type 2 molecules, containing atom N31 (Fig. 1). Atom C45 at (x, y, z) acts as hydrogen-bond donor to atom O34 at ($\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$), so linking type 2 molecules related by the 2_1 screw axis along (x, $\frac{1}{4}$, $\frac{1}{2}$) into a $C(9)$ (Bernstein *et al.*, 1995) chain running parallel to the [100] direction (Fig. 3).

In a somewhat similar manner, the substructure along [010] involves only the type 1 molecules, containing atom N11 (Fig. 1), but now two hydrogen bonds are involved. Atoms C24 and C51 at (x, y, z) act as hydrogen-bond donors, respectively, to atom O14 at ($1-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$) and O241 at ($1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$), so linking type 1 molecules related by the 2_1 screw axis along ($\frac{1}{2}$, y, $\frac{3}{4}$) into a $C(10)C(12)[R_2^2(10)]$ chain of rings running parallel to the [010] direction (Fig. 4). The final substructure, along [001], involves both types of molecule and all four of the C—H···O hydrogen bonds (Fig. 5). The combination of the chains parallel to [100], [010] and [001] suffices to link all of the molecules of (I) into a continuous framework structure.

The hydrogen-bonded structure of compound (II) is much simpler than that of (I) and involves only two hydrogen bonds, one each of the N—H···O and C—H···O types (Table 4). The same pattern of hydrogen bonds is evident for both components of the disordered pyrimidine unit, so that the disorder has no effect on the supramolecular aggregation. Atoms N13*n* and C22*n* (*n* = *A* or *B*) at (x, y, z) act as hydrogen-bond donors, respectively, to atom O221 at ($1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$) and O14*n* at ($1-x$, $-\frac{1}{2}+y$, $\frac{3}{2}-z$), thereby linking molecules related by the 2_1 screw axis along ($\frac{1}{2}$, y, $\frac{3}{4}$) into a $C(8)C(11)[R_2^2(9)]$ chain of rings running parallel to the [010] direction (Fig. 6).

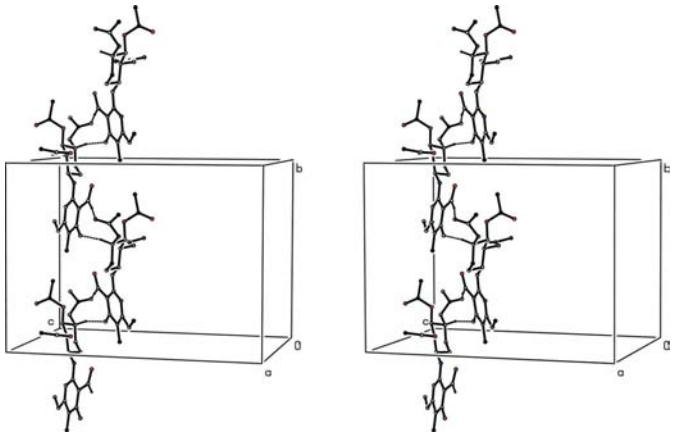

Figure 4
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain of rings built from type 1 molecules and running parallel to [010]. For the sake of clarity, the partial water molecule and H atoms not involved in the motif shown have been omitted.

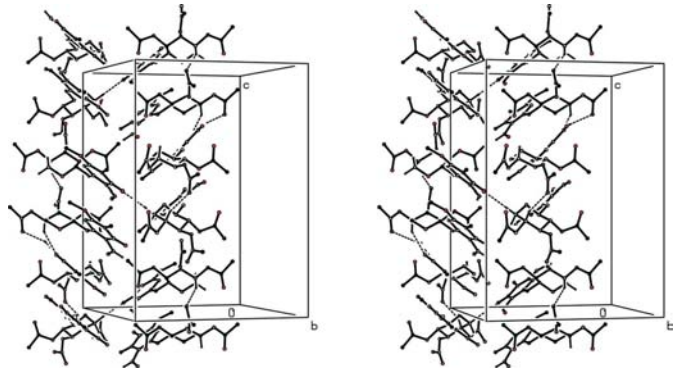

Figure 5
A stereoview of part of the crystal structure of compound (I), showing the formation of a hydrogen-bonded chain, including both of types of molecule and running parallel to [001]. For the sake of clarity, the partial water molecule and H atoms not involved in the motif shown have been omitted.

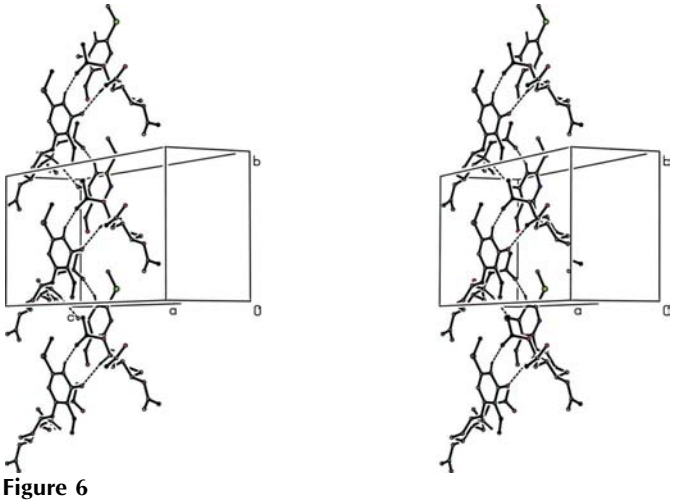

Figure 6
A stereoview of part of the crystal structure of compound (II), showing the formation of a hydrogen-bonded chain of rings running parallel to [010]. For the sake of clarity, the minor orientation of the disordered pyrimidine unit and H atoms not involved in the motifs shown have been omitted.

There are thus both similarities and differences between the chains of rings along [010] formed in compound (II) and by the type 1 molecules in compound (I). Each chain is formed from molecules related by the 2_1 screw axis along $(\frac{1}{2}, y, \frac{3}{4})$ and each is built from two hydrogen bonds acting in the two opposite directions along [010]. However, in (I), these hydrogen bonds are both of the C—H···O type, while in (II) there is one each of the N—H···O and C—H···O types, although the same two acceptor O atoms are involved in both structures. The use of different donor atoms in the two structures necessarily leads to different hydrogen-bond motifs and to different graph-set descriptors, *viz.* $C(10)C(12)[R_2^2(10)]$ in (I) and $C(8)C(11)[R_2^2(9)]$ in (II).

Experimental

Samples of (I) and (II) were prepared according to the published procedure of Negrillo *et al.* (1988) and were recrystallized from ethanol.

Compound (I)

Crystal data

$C_{18}H_{23}N_3O_{10}\cdot 0.065H_2O$
$M_r = 442.57$
Orthorhombic, $P2_12_12_1$
$a = 14.3816\ (2)$ Å
$b = 14.7626\ (2)$ Å
$c = 20.1025\ (3)$ Å
$V = 4267.96\ (10)$ Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 120\ (2)$ K
$0.22 \times 0.20 \times 0.18$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.975$, $T_{max} = 0.980$
70888 measured reflections
5407 independent reflections
4925 reflections with $I > 2\sigma(I)$
$R_{int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.088$
$S = 1.08$
5407 reflections
581 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

N11—C12	1.304 (2)	N31—C32	1.303 (2)
C12—N13	1.351 (3)	C32—N33	1.352 (2)
N13—C14	1.413 (2)	N33—C34	1.417 (3)
C14—C15	1.439 (3)	C34—C35	1.437 (3)
C15—C16	1.411 (3)	C35—C36	1.405 (3)
C16—N11	1.362 (2)	C36—N31	1.364 (2)
C12—O12	1.328 (2)	C32—O32	1.325 (2)
C14—O14	1.223 (2)	C34—O34	1.226 (2)
C15—C51	1.432 (3)	C35—C53	1.432 (3)
C51—O51	1.241 (2)	C53—O53	1.232 (3)
C16—N16	1.345 (2)	C36—N36	1.350 (2)
N11—C12—O12—C121	5.9 (3)	N31—C32—O32—C321	2.6 (3)
C16—C15—C51—O51	−0.5 (3)	C36—C35—C53—O53	1.4 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
N16—H16···O51	0.88	2.03	2.707 (2)	133
N36—H36···O53	0.88	2.06	2.725 (2)	132
C24—H24···O14^{i}	1.00	2.34	3.237 (3)	148
C44—H44···O231	1.00	2.28	3.213 (3)	155
C45—H45B···O34^{ii}	0.99	2.38	3.245 (3)	145
C51—H51···O241^{iii}	0.95	2.54	3.442 (3)	159

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

Compound (II)

Crystal data

$C_{17}H_{21}N_3O_9S$
M_r = 443.44
Orthorhombic, $P2_12_12_1$
a = 6.92940 (10) Å
b = 10.7415 (2) Å
c = 26.4825 (5) Å
V = 1971.15 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 120 (2) K
0.44 × 0.35 × 0.30 mm

Data collection

Bruker–Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.885, T_{max} = 0.936
12812 measured reflections
4482 independent reflections
4065 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.096
S = 1.14
4482 reflections
327 parameters
40 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter: −0.02 (7)

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

N11A—C12A	1.325 (2)	C12A—S1A	1.746 (2)
C12A—N13A	1.352 (2)	C14A—O14A	1.230 (2)
N13A—C14A	1.403 (3)	C15A—C51A	1.436 (3)
C14A—C15A	1.425 (3)	C51A—O51A	1.236 (3)
C15A—C16A	1.412 (2)	C16A—N16A	1.335 (3)
C16A—N11A	1.364 (2)		
N11A—C12A—S1A—C17A	−176.7 (2)	N11B—C12B—S1B—C17B	−11 (2)
C16A—C15A—C51A—O51A	3.9 (7)	C16B—C15B—C51B—O51B	−20 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
N13A—H13A···O221^{i}	0.88	2.11	2.942 (2)	157
N13B—H13B···O221^{i}	0.88	1.96	2.780 (9)	155
N16A—H16A···O51A	0.88	1.92	2.645 (6)	139
N16B—H16B···O51B	0.88	2.01	2.68 (6)	132
C22—H22···O14A^{ii}	1.00	2.31	3.304 (2)	171
C22—H22···O14B^{ii}	1.00	2.52	3.468 (15)	159

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

With the exception of the H atoms of the water component in (I) and the H atoms in the minor component of the pyrimidine unit in (II), all H atoms were located in difference maps. Those which could not be located directly were included in calculated positions, and then all H atoms bonded to C or N atoms were treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (formyl), 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (aliphatic C—H) and N—H = 0.88 Å, and with U_{iso}(H) = kU_{eq}(carrier), where k = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and k = 1.2 for all other H atoms. For the partial water component of (I), the O—H and H···H distances were subject to the restraints 0.84 (1) and 1.34 (1) Å, respectively, and the refined occupancy was 0.065 (3) molecules of water per molecule of the organic component. For (II), all atoms apart from those of the sugar moiety were included in the disorder model, with the bond distances and one-angle nonbonded distances in the minor B component constrained to have the same values as the corresponding distances in the major A component, subject to an s.u. value of 0.005 Å, while the distances N16n—C16n (n = A or B) were both subject to the distance constraint 1.40 (2) Å. In addition, it was necessary to constrain corresponding atoms in the two components to have the same anisotropic displacement parameter components, apart from atoms S1n and C17n, which were subject to rigid-bond restraints, *via* DELU and ISOR, with s.u. values of 0.015 and 0.010 Å^2, respectively. Subject to these conditions, the refined occupancies for the two disorder components were 0.899 (2) and 0.101 (2). For (II), the correct absolute configuration was established by means of the Flack x parameter (Flack, 1983) of −0.02 (7) and the Hooft y parameter (Hooft *et al.*, 2008) of −0.003 (31), calculated in each case for 1900 Bijvoet pairs from a possible maximum of 1911, *i.e.* 99.4% coverage. In the absence of significant resonant scattering in (I), it was not possible to determine the absolute configuration directly; accordingly, the Friedel-equivalent reflections were merged prior to the final refinements and the absolute configuration was set by reference to that in (II).

For both compounds, data collection: *COLLECT* (Hooft, 1999); cell refinement: *DIRAX*/*LSQ* (Duisenberg *et al.*, 2000); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); 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: GG3202). Services for accessing these data are described at the back of the journal.

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