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Hydrogen-bonded layered structures in two bis(*tert*-butyldimethylsilyloxy)-substituted cyclic diol derivatives

C. Foces-Foces[a]* and M. López-Rodríguez[b]

[a]Instituto Rocasolano, CSIC, Departamento de Cristalografía, Serrano 119, E-28006 Madrid, Spain, and [b]Instituto de Bioorgánica, Universidad de La Laguna, Avda. Astrofísico Fco. Sánchez 2, E-38206 La Laguna, Tenerife, Spain
Correspondence e-mail: cfoces@iqfr.csic.es

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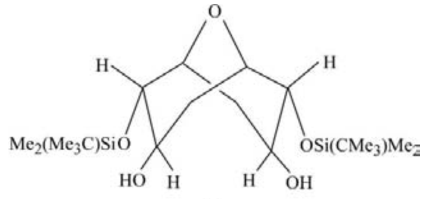
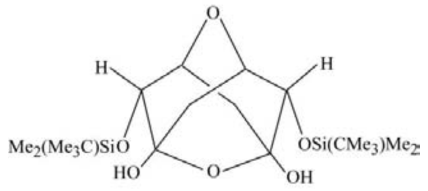
2,6-Bis(*tert*-butyldimethylsilyloxy)-9-oxabicyclo[3.3.1]nonane-3,7-diol, $C_{20}H_{42}O_5Si_2$, (I), and 4,8-bis(*tert*-butyldimethylsilyloxy)-2,6-dioxatricyclo[3.3.1^{3,7}]decane-1,3-diol, $C_{20}H_{40}O_6Si_2$, (II), form layered structures that differ in the way the molecules are connected within each layer. The endocyclic O atom common to both structures plays an active role in the hydrogen-bonding network, whereas the second oxygen bridge in (II) does not participate in any interaction. This work reports the first structural analysis of two bis(*tert*-butyldimethylsilyloxy)-substituted cyclic diol derivatives and provides insight into the influence of small changes in the molecular structure on the supramolecular aggregation. The unbalanced hydrogen-bond acceptor/donor ratio, greater in (II) than in (I), does not result in the inclusion of water molecules in the structure.

Comment

Compounds (I) and (II) were synthesized as intermediate products within a project related to the synthesis of universal templates for the resolution of racemic mixtures of secondary alcohols (Carrasco *et al.*, 2001; López-Rodríguez & Foces-Foces, 2007). A search of the Cambridge Structural Database (Version 5.29, January 2008 update; Allen 2002) for bicyclic ether-bridged derivatives with *tert*-butyldimethylsilyloxy side substituents (OTBS hereinafter) gave just two oxabicyclic structures [refcodes WAXXIC (Takahashi *et al.*, 2000) and KEKPIA (Paquette & Zhang, 2006)] with only one OTBS side substituent and a different relative disposition of the two hydroxy groups. In the latter, apart from a bulky methoxybenzyloxy substituent, the OTBS substituent displays a quasi-axial disposition, in contrast to the equatorial configuration in the former and in the present compounds (Fig. 1). Furthermore, only one dioxatricycle derivative has been reported (OXADMN; 1,3,5,7-tetramethoxy-2,6-dioxatricyclo[3.3.1^{3,7}]decane; Kanters & Hulscher, 1968). Considering these facts, the structural characterizations of compounds (I) and (II) were undertaken, and the effect of including a second oxygen bridge on the molecular structure, the conformational changes and the associated packing features were analysed.



(I)



(II)

Both compounds crystallize with two independent molecules in the asymmetric unit. The superposition of the two molecules is shown in Fig. 2. The major discrepancies between the two compounds concern the orientation of the hydroxy H atom and the substituents at the Si atoms with respect to the central core (Tables 1 and 3). The C atoms of the methyl and *tert*-butyl groups at Si1 and Si2 (atoms C11–C14 and C17–C20, respectively, for molecules *A* and *B*) adopt anticlinal and antiperiplanar conformations in (I), while in (II) the synclinal conformation is also observed. The main differences in the core between (I) and (II) are due to the inclusion of an additional ether bridge between atoms C3 and C7 [atom O6 in Fig. 1(*b*)] that results in the shortening of the C3$\cdots$C7 distance [2.413 (2) and 2.420 (2) Å in (II*A*) and (II*B*) *versus*

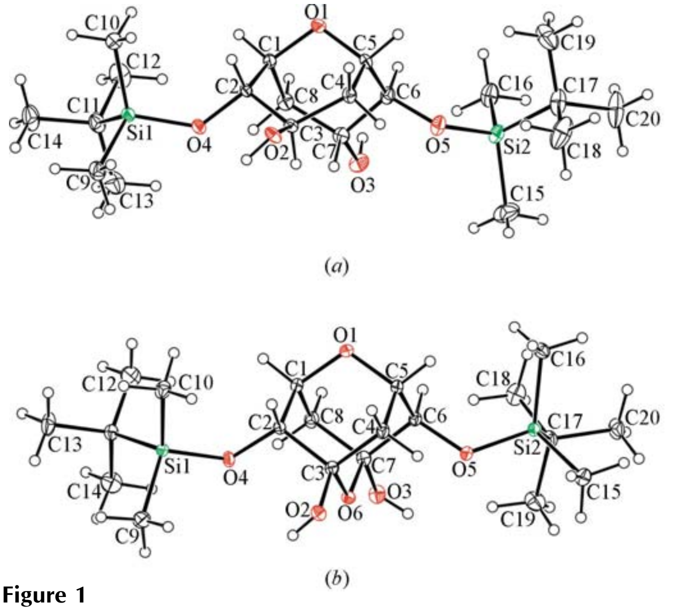


Figure 1
The molecular structures of (*a*) compound (I) and (*b*) compound (II). Only molecule *A* is represented, showing displacement ellipsoids at the 30% probability level.

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3.133 (11) Å in WAXXIC and 3.187 (4) and 3.182 (4) Å in (I*A*) and (I*B*), respectively] followed by an increase in the puckering of the O1/C1–C5 and O1/C1/C5–C8 rings of the core [with total puckering amplitudes of 0.625 (1) *versus* 0.557 (6) Å on average in (II) and (I), respectively (Cremer & Pople, 1975)]. Significant differences in the C—OH distances and in the C—C—C angles around atoms C3 and C7 have also been observed (Tables 1 and 3).

The crystal structures are characterized by two-dimensional hydrogen-bonding networks, although the supramolecular aggregations differ from each other. In (I), each independent molecule is engaged in similar hydrogen-bond interactions, forming sheets of only molecules *A* (Fig. 3*a*) or molecules *B* parallel to the *bc* plane. One hydroxy group, O2, acts as a donor and an acceptor of hydrogen bonds, while the other, O3, acts as a donor only. The former links molecules (hydroxy-to-ether contacts) along the *c* axis into *C*(6) chains (Bernstein *et al.*, 1995) that are connected through hydroxy-to-hydroxy contacts, resulting in sheets of $R_4^4(16)$ and $R_4^4(28)$ edge-fused rings (Table 2 and Fig. 3*a*).

In contrast to this situation, in (II), the two independent molecules and their symmetry-related molecules are associated into one layer through different hydrogen bonds (Table 4 and Fig. 3*b*). The four hydroxy groups are in different environments. Whereas both hydroxy groups in molecule *B* act as hydrogen-bond donors to O atoms, in molecule *A*, atom O2 acts simultaneously as a donor and an acceptor, and hydroxy atom O3 seems to be not sterically accessible and does not participate in any hydrogen-bonding interactions either as a donor or as an acceptor. Similar *C*(6) chains to that in (I) but involving alternately molecules *A* and *B* are observed along the *c* axis. The O3—H3O group of molecule *B* connects these chains into sheets of $R_4^4(24)$ and $R_8^8(40)$ edge-fused rings (Table 4 and Fig. 3*b*). The other O6 bridge, in both molecules *A* and *B*, is not engaged in any hydrogen-bond

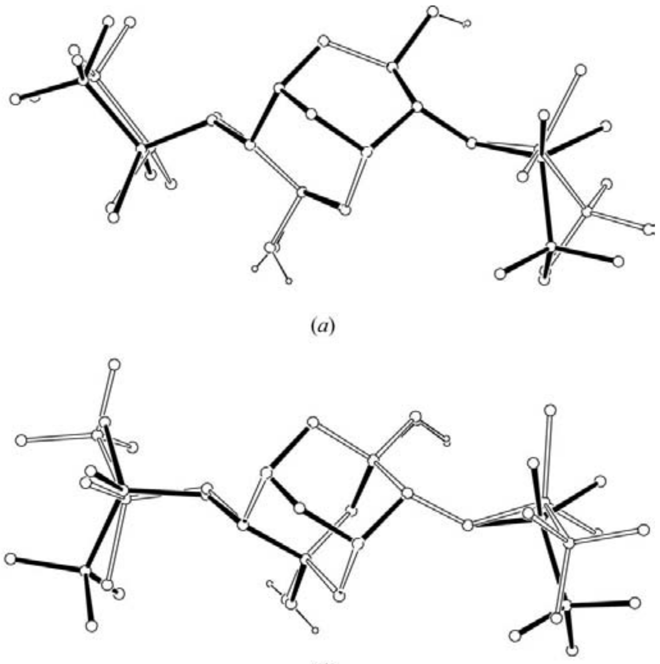

Figure 2
Superposition of the two independent molecules in (*a*) (I) and (*b*) (II), using atoms O1, C1 and C5 as common reference. In both compounds, molecule *A* is represented with filled bonds.

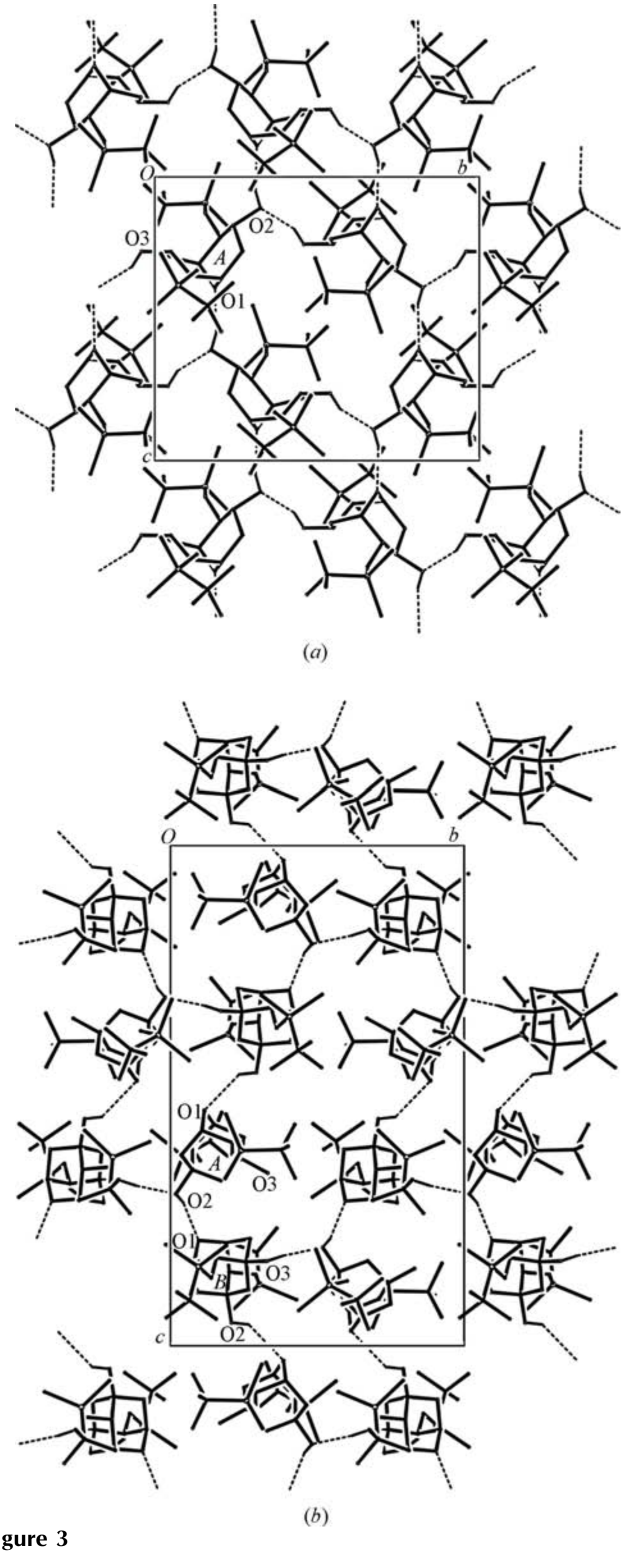

Figure 3
Comparison of the supramolecular aggregation of (*a*) molecules *A* in (I) and (*b*) molecules *A* and *B* in (II). H atoms not involved in the hydrogen-bond interactions have been omitted for clarity.

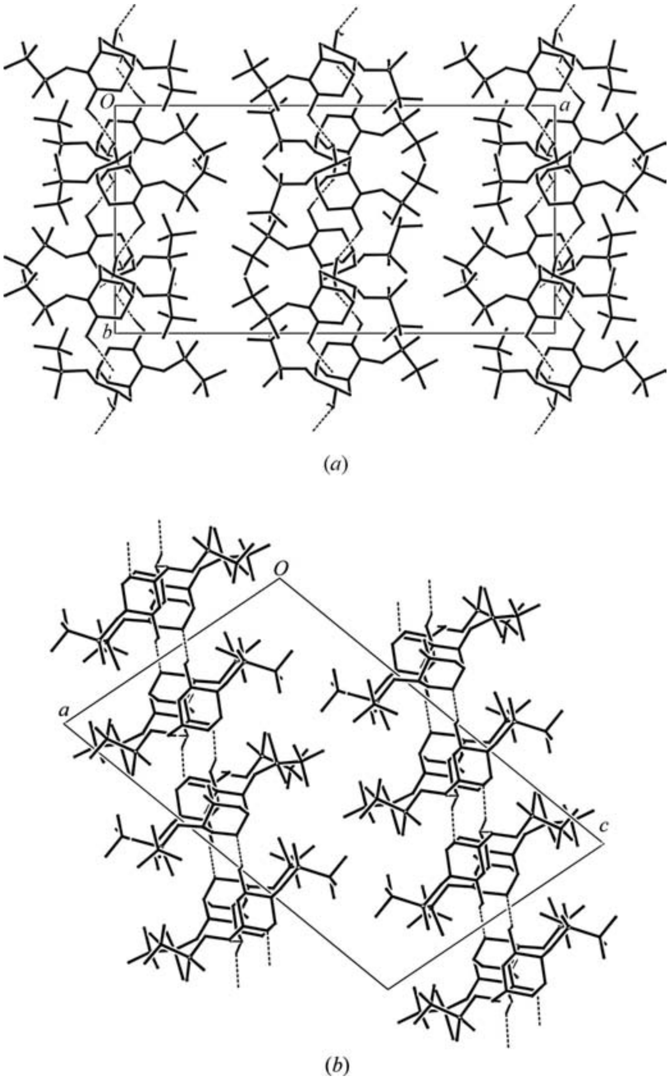

Figure 4
(*a*) Packing diagram of compound (I), showing the alternation of sheets formed by molecules *B*, *A* and *B*, respectively. (*b*) Packing diagram of compound (II), showing two single sheets related by translation. H atoms not involved in the hydrogen-bond interactions have been omitted for clarity.

contact. The crystal structures are built up of sheets of molecules *A* or molecules *B* that stack alternately by translation in the [100] direction in (I) (Fig. 4*a*), while in (II) the single sheet (molecules *A* and *B*) extends by translation along [100] (Fig. 4*b*).

The volumes per atom in (I) and (II) differ, with a value of 23.2 Å^3 per non-H atom for (I) and 21.4 Å^3 for (II), reflecting the differences in the hydrogen-bonding motifs.

Experimental

Compounds (I) and (II) were obtained as intermediate products in the synthesis of universal templates for the resolution of racemic mixtures of secondary alcohols (Carrasco *et al.*, 2001). Both compounds were crystallized from a carbon tetrachloride/isopropyl ether mixture (50%). No structural phase transition was detected when cooling the samples from room temperature to 150 K.

Compound (I)

Crystal data

$C_{20}H_{42}O_5Si_2$
M_r = 418.72
Monoclinic, $P2_1/c$
a = 27.7623 (6) Å
b = 14.3663 (3) Å
c = 12.6076 (2) Å
β = 93.491 (1)°

V = 5019.10 (17) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.17 mm^{-1}
T = 150 (2) K
0.60 × 0.37 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*PLATON*; Spek, 2003)
$T_{\min}$ = 0.907, $T_{\max}$ = 0.968

33413 measured reflections
10858 independent reflections
9400 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.059

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.157
S = 1.10
10858 reflections

492 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 1.03 e Å^{-3}
$\Delta\rho_{\min}$ = −0.35 e Å^{-3}

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

O2*A*—C3*A*	1.436 (3)	O2*B*—C3*B*	1.434 (3)
O3*A*—C7*A*	1.432 (3)	O3*B*—C7*B*	1.429 (3)
C2*A*—C3*A*—C4*A*	111.8 (2)	C2*B*—C3*B*—C4*B*	111.4 (2)
C6*A*—C7*A*—C8*A*	109.2 (2)	C6*B*—C7*B*—C8*B*	109.6 (2)
C1*A*—C2*A*—O2*A*—H2*OA*	−146.1	C1*B*—C2*B*—O2*B*—H2*OB*	−141.0
C6*A*—C7*A*—O3*A*—H3*OA*	−71.1	C6*B*—C7*B*—O3*B*—H3*OB*	−136.6
C1*A*—C2*A*—O4*A*—Si1*A*	−97.8 (2)	C1*B*—C2*B*—O4*B*—Si1*B*	−99.2 (2)
C2*A*—O4*A*—Si1*A*—C9*A*	−121.7 (2)	C2*B*—O4*B*—Si1*B*—C9*B*	−67.5 (2)
C2*A*—O4*A*—Si1*A*—C10*A*	−1.2 (2)	C2*B*—O4*B*—Si1*B*—C10*B*	51.9 (3)
C2*A*—O4*A*—Si1*A*—C11*A*	120.6 (2)	C2*B*—O4*B*—Si1*B*—C11*B*	171.8 (2)
C5*A*—C6*A*—O5*A*—Si2*A*	−140.1 (2)	C5*B*—C6*B*—O5*B*—Si2*B*	−146.3 (2)
C6*A*—O5*A*—Si2*A*—C15*A*	−119.1 (2)	C6*B*—O5*B*—Si2*B*—C15*B*	−106.0 (2)
C6*A*—O5*A*—Si2*A*—C16*A*	2.7 (3)	C6*B*—O5*B*—Si2*B*—C16*B*	16.5 (2)
C6*A*—O5*A*—Si2*A*—C17*A*	121.8 (2)	C6*B*—O5*B*—Si2*B*—C17*B*	135.4 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*A*—H2O*A*···O1*A*$^{\rm i}$	0.84	2.05	2.841 (2)	157
O3*A*—H3O*A*···O2*A*$^{\rm ii}$	0.84	2.13	2.892 (3)	151
O2*B*—H2O*B*···O1*B*$^{\rm i}$	0.84	1.92	2.740 (2)	165
O3*B*—H3O*B*···O2*B*$^{\rm iii}$	0.84	2.00	2.823 (3)	167

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

Compound (II)

Crystal data

$C_{20}H_{40}O_6Si_2$
M_r = 432.70
Monoclinic, $P2_1/n$
a = 15.0964 (17) Å
b = 13.6368 (15) Å
c = 24.291 (2) Å
β = 106.676 (9)°

V = 4790.3 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.18 mm^{-1}
T = 150 (2) K
0.60 × 0.60 × 0.50 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*PLATON*; Spek, 2003)
$T_{\min} = 0.900$, $T_{\max} = 0.916$
36437 measured reflections
10345 independent reflections
8213 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.112$
$S = 1.05$
10345 reflections
509 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.25$ e Å^{-3}

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

O2*A*—C3*A*	1.401 (2)	O2*B*—C3*B*	1.393 (2)
O3*A*—C7*A*	1.390 (2)	O3*B*—C7*B*	1.388 (2)
C4*A*—C3*A*—C2*A*	107.8 (1)	C4*B*—C3*B*—C2*B*	107.1 (1)
C8*A*—C7*A*—C6*A*	108.3 (2)	C6*B*—C7*B*—C8*B*	107.9 (1)
C1*A*—C2*A*—O2*A*—H2*OA*	−111	C1*B*—C2*B*—O2*B*—H2*OB*	−112
C6*A*—C7*A*—O3*A*—H3*OA*	54	C6*B*—C7*B*—O3*B*—H3*OB*	−155
C1*A*—C2*A*—O4*A*—Si1*A*	−108.7 (2)	C1*B*—C2*B*—O4*B*—Si1*B*	−127.8 (1)
C2*A*—O4*A*—Si1*A*—C9*A*	−117.9 (2)	C2*B*—O4*B*—Si1*B*—C9*B*	−153.4 (1)
C2*A*—O4*A*—Si1*A*—C10*A*	1.7 (2)	C2*B*—O4*B*—Si1*B*—C10*B*	−32.8 (2)
C2*A*—O4*A*—Si1*A*—C11*A*	122.6 (1)	C2*B*—O4*B*—Si1*B*—C11*B*	88.0 (2)
C5*A*—C6*A*—O5*A*—Si2*A*	−95.7 (2)	C5*B*—C6*B*—O5*B*—Si2*B*	−109.2 (1)
C6*A*—O5*A*—Si2*A*—C15*A*	160.0 (1)	C6*B*—O5*B*—Si2*B*—C15*B*	−68.7 (2)
C6*A*—O5*A*—Si2*A*—C16*A*	39.7 (2)	C6*B*—O5*B*—Si2*B*—C16*B*	52.2 (2)
C6*A*—O5*A*—Si2*A*—C17*A*	−82.0 (1)	C6*B*—O5*B*—Si2*B*—C17*B*	171.3 (1)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*A*—H2O*A*···O1*B*	0.84	2.14	2.922 (2)	154
O2*B*—H2O*B*···O1*A*$^{\rm i}$	0.84	2.46	3.164 (2)	142
O3*B*—H3O*B*···O2*A*$^{\rm ii}$	0.84	1.97	2.801 (2)	171
C6*A*—H6*A*···O2*B*$^{\rm iii}$	1.00	2.60	3.463 (2)	144

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

All H atoms were located in difference Fourier maps and were subsequently refined using a riding model [C—H = 0.98 (CH_3), 0.99 (CH_2) or 1.00 Å (CH), O—H = 0.84 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C,O)].

For both compounds, data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3255). Services for accessing these data are described at the back of the journal.

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