P2—O22	1,508 (2)	C2—C3	1,382 (3)
P2—O32	1,570 (2)	C3—C4	1,381 (4)
P2—O42	1,572 (2)	C4—C5	1,378 (4)
P1···P2	4,213 (1)	C5—C6	1,380 (4)
P1···P2^{i}	4,262 (1)		
O11—P1—O21	116,9 (1)	O32—P2—O42	106,3 (1)
O11—P1—O31	109,8 (1)	C6—C1—C2	120,6 (2)
O21—P1—O31	109,4 (1)	C6—C1—N1	119,3 (2)
O11—P1—O41	108,7 (1)	C2—C1—N1	120,1 (2)
O21—P1—O41	106,5 (1)	C3—C2—C1	119,8 (2)
O31—P1—O41	104,8 (1)	C3—C2—N2	119,8 (2)
O12—P2—O22	118,11 (9)	C1—C2—N2	120,3 (2)
O12—P2—O32	111,11 (9)	C4—C3—C2	119,5 (2)
O22—P2—O32	104,97 (9)	C5—C4—C3	120,3 (2)
O12—P2—O42	106,21 (9)	C4—C5—C6	120,3 (2)
O22—P2—O42	109,55 (9)	C1—C6—C5	119,3 (2)

Codes de symétrie: (i) $1 + x, y, z$; (ii) $1 - x, -y, 1 - z$.

Tableau 3. *Distances et liaisons hydrogène* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O31—HO31···O21^{i}	0,76 (3)	1,82 (3)	2,584 (2)	173 (4)
O41—HO41···O22^{ii}	0,85 (3)	1,83 (3)	2,667 (2)	171 (3)
O32—HO32···O21	0,85 (4)	1,72 (4)	2,568 (2)	174 (3)
O42—HO42···O11^{iii}	0,80 (4)	1,75 (4)	2,546 (2)	172 (4)
N1—H1N1···O22^{iv}	0,90 (3)	1,95 (3)	2,825 (3)	163 (3)
N1—H2N1···O42^{v}	0,92 (4)	1,99 (4)	2,845 (3)	154 (3)
N1—H3N1···O11^{vi}	0,89 (4)	2,12 (4)	2,840 (3)	137 (3)
N2—H1N2···O22^{iv}	0,82 (3)	2,06 (3)	2,818 (3)	152 (3)
N2—H2N2···O41^{vii}	0,90 (3)	2,22 (3)	2,923 (3)	135 (2)
N2—H3N2···O12^{v}	1,02 (4)	1,64 (4)	2,652 (3)	177 (3)

Codes de symétrie: (i) $1-x, -y, 1-z$; (ii) $1+x, y, z$; (iii) $1-x, -y, -z$; (iv) $1+x, y, 1+z$; (v) $x, y, 1+z$; (vi) $2-x, -y, 1-z$; (vii) $1-x, 1-y, 1-z$.

La largeur de scan est $(0{,}7 + 0{,}35\mathrm{tg}\theta)^\circ$. Les intensités ont été corrigées des facteurs de Lorentz et de polarisation. La structure a été résolue par les méthodes directes (*SHELXS*86; Sheldrick, 1990) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993).

Collection des données: *CAD*-4 *Software* (Enraf–Nonius, 1989). Affinement des paramètres de la maille: *CAD*-4 *Software*. Réduction des données: *MolEN* (Fair, 1990). Le dessin de la structure a été obtenu à l'aide du programme *ORTEP*II (Johnson, 1976).

Les listes des facteurs de structure, des facteurs d'agitation thermique anisotrope, des coordonnées des atomes d'hydrogène et des distances et angles des atomes d'hydrogène ont été déposées au dépôt d'archives de l'UICr (Référence: DU1120). On peut en obtenir des copies en s'adressant à: The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, Angleterre.

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Stereochemistry of Hydroxylation Reactions on Polycyclic Pyrans

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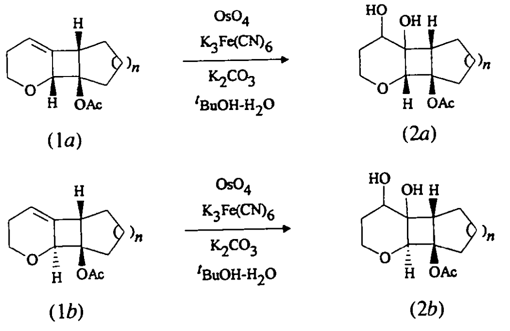
Abstract

The configurations at the ring junctions of the tricyclic pyrans (1*RS*,2*SR*,6*RS*,7*RS*,8*RS*)-6,7-dihydroxy-3-oxatricyclo[6.6.0.0^{2,7}]tetradec-1-yl acetate, $C_{15}H_{24}O_5$, and (1*RS*,2*RS*,6*SR*,7*SR*,8*RS*)-6,7-dihydroxy-3-oxatricyclo[6.6.0.0^{2,7}]tetradec-1-yl acetate monohydrate, $C_{15}H_{24}O_5.H_2O$, indicate that, in the reactions leading to these compounds, hydroxylation always takes place on the less hindered side of the substrate, and that the heterocycle exerts greater steric hindrance than the carbocycle. The structures and conformations of the two stereoisomers and their hydrogen bonding are discussed.

Comment

During our studies on the chemistry of new polycyclic pyrans (Jamart-Grégoire, Mercier-Girardot, Ianelli, Nardelli & Caubère, 1995), we had to consider the bishydroxylation of compound (1) and the stereochemistry of the glycols (2) obtained according to the scheme below [isomers have *a* or *b* appended to the compound identifier, *e.g.* (1*a*) and (1*b*)].

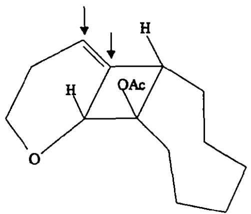


(1*a*) (2*a*)

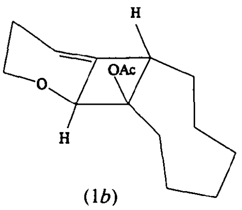
(1*b*) (2*b*)

None of the usual spectroscopic data allowed us to define the structures of (2). Therefore, we undertook the X-ray crystal structure analysis of two representative compounds (2*a*) and (2*b*) (n = 4), for which suitable single crystals were obtained.

Besides the knowledge of the molecular structures of (2), the results of these analyses led to the interesting mechanistic conclusion that the hydroxylations always take place on the less hindered side of the substrate (1) (see scheme below) and that in (1*b*) the steric hindrance generated by the heterocyclic part of the molecule is much more important than that generated by the carbocycle.

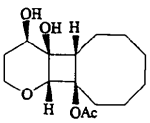


(1*a*)

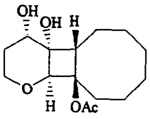


(1*b*)

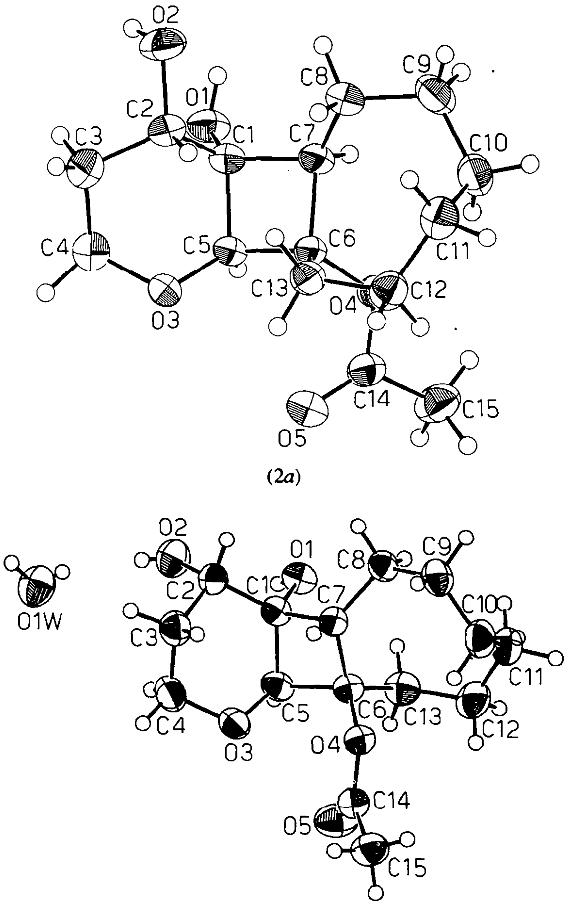
The crystals of the two compounds not only differ in molecular configuration, but also because compound (2*b*) crystallizes with a water molecule and this, through hydrogen bonding, influences both molecular conformation and packing. As shown in Fig. 1, the configuration is *cis-syn-cis* for compound (2*a*) and *cis-anti-cis* for (2*b*). For the same *S* configuration at C2 and *S*,*R* at the C1—C5 junction (using the atom labelling of Fig. 1), the configuration at the C6—C7 junction is opposite in the two compounds: *S*,*S* for (2*a*) and *R*,*R* for (2*b*). The enantiomers of these two molecules are also present in the crystals, both space groups being centrosymmetric.



(2*a*)



(2*b*)



(2*a*)

(2*b*)

Fig. 1. *ORTEP* (Johnson, 1965) drawings of the molecules of compounds (2*a*) and (2*b*). Ellipsoids are drawn at the 50% probability level.

The conformations about the C1—C2, C1—C5 and C6—C7 bonds and the orientation of the acetyl substituents are described by the torsion angles quoted in Tables 2 and 4, which show that the C1—O1 bond is synclinal to C2—O2 in both compounds [more open in compound (2*a*)], and anticlinal and antiperiplanar to C5—O3 in compounds (2*a*) and (2*b*), respectively; C6—O4 is anticlinal to C7—C8 in both compounds.

The parameters in Table 5 allow direct comparison of puckering, conformation and relative position of the rings. The total puckering amplitude of ring *A* is remarkably reduced in compound (2*b*) where O3 is involved in a short non-bonded repulsive interaction [O3···O4 = 2.671 (2) Å], whereas it acts as a weak proton acceptor [C13—H132···O3 = 2.53 (2) Å] in (2*a*); also, the different position of the O2—H hydroxy group in the two compounds may influence the puckering of these rings.

The cyclooctane rings in (2*a*) and (2*b*) have similar puckering amplitudes and conformations, as shown by the respective average bond distances, endocyclic bond angles and torsion angles: $\langle d(\text{C—C})\rangle$ = 1.538 (6), 1.531 (5) Å, $\langle\alpha\rangle$ = 116.8 (9), 117.5 (10)°, $\langle|\tau|\rangle$ = 74.5, 67.7°. These values agree fairly well with the averages of those calculated by Hendrickson (1967) for the boat-chair (BC) [++−+/−−+−] conformation of unsubstituted cyclooctane, $\langle\alpha\rangle$ = 116.2, $\langle|\tau|\rangle$ = 69.2°, for which the sum of the non-bonded energies is 46.4 kJ mol^{-1}.

The orientation of the acetyl substituent is defined by the C7—C6—O4—C14 torsion angle whose values (see Tables 2 and 4) indicate that the O4—C14 bond is antiperiplanar to the C6—C7 bond in both molecules. The non-bonded energy profiles, calculated by rotating the acetyl group about the C6—O4 bond in the free molecule, show a well defined minimum for the conformation found experimentally in the crystals of both compounds. This finding indicates that intramolecular steric hindrance imposes the observed orientation of that substituent, while the orientation of the carbonyl plane about the C14—O4 bond is essentially determined by the intermolecular hydrogen bonds involving the O5 atom (see Tables 2 and 4).

The orientation of the two hydroxyl groups is determined by the hydrogen bonds (see Tables 2 and 4) that they form with the tetrahydropyran and carbonyl O atoms of adjacent molecules in (2*a*), while for (2*b*) their interaction with the water molecule is more important. As shown in Fig. 2, the molecules in crystals of (2*b*) are packed in layers parallel to the *ac* plane, with sheets of hydrophobic and hydrophilic contacts at $b = 0$ and $b = \frac{1}{2}$, respectively.

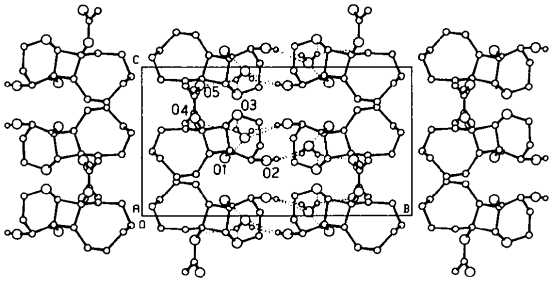


Fig. 2. *PLUTO* (Motherwell & Clegg, 1976) projection of the unit-cell contents of compound (2*b*). For clarity, only the H atoms involved in hydrogen bonding are represented.

A Schomaker & Trueblood (1968) **TLS** rigid-body analysis using the *THMV* program (Trueblood, 1984), shows a satisfactory agreement between the observed and calculated U_{ij} parameters: wR_U is 0.115 and 0.099 for (2*a*) and (2*b*), respectively, improving to 0.092 and 0.069, respectively, if internal motions are considered according to Dunitz & White (1973).

Experimental

Compounds (2*a*) and (2*b*) were obtained by esterification (Hogle, Treglich & Vorbroggen, 1972) followed by bishydroxylation (Minato, Yamamoto & Tsuji, 1990) of the (1*RS*,2*RS*,8*SR*) and (1*RS*,2*SR*,8*SR*) isomers of 3-oxatricyclo[6.6.0.0^{2,7}]tetradec-6-en-1-ol, respectively, synthesized by Jamart-Grégoire, Mercier-Girardot, Ianelli, Nardelli & Caubère (1995).

Compound (2*a*)

Crystal data

$C_{15}H_{24}O_5$
$M_r = 284.35$
Monoclinic
$P2_1/n$
$a = 17.631$ (7) Å
$b = 11.843$ (4) Å
$c = 6.984$ (1) Å
$\beta = 92.36$ (3)°
$V = 1457.1$ (8) Å^3
$Z = 4$
$D_x = 1.296$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 30 reflections
$\theta = 24$–40°
$\mu = 0.792$ mm^{-1}
$T = 293$ (2) K
Tablet
0.36 × 0.24 × 0.19 mm
Colourless

Data collection

Siemens AED diffractometer
Profile data from θ–2θ scans
Absorption correction: none
2997 measured reflections
2771 independent reflections
2219 observed reflections [$I > 2\sigma(I)$]
$R_{\text{int}} = 0.0451$

$\theta_{\max} = 70.08°$
$h = -21 \rightarrow 21$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 8$
1 standard reflection monitored every 50 reflections intensity variation: within statistical fluctuation

Refinement

Refinement on F^2
$R(F) = 0.056$
$wR(F^2) = 0.1553$
$S = 1.112$
2765 reflections
278 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.1121P)^2 + 0.3606P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 0.74$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.043 (3)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2*a*)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O1	0.74624 (9)	0.9071 (1)	0.3417 (2)	0.0473 (5)
O2	0.8391 (1)	0.9653 (1)	0.0309 (3)	0.0566 (6)
O3	0.75458 (8)	0.6479 (1)	0.1430 (2)	0.0507 (5)
O4	0.56444 (7)	0.7436 (1)	0.0780 (2)	0.0394 (4)
O5	0.58704 (9)	0.5609 (1)	0.1390 (3)	0.0553 (5)
C1	0.7345 (1)	0.8572 (1)	0.1585 (3)	0.0374 (5)
C2	0.8081 (1)	0.8555 (2)	0.0505 (3)	0.0422 (6)
C3	0.8642 (1)	0.7742 (2)	0.1501 (4)	0.0558 (8)
C4	0.8262 (1)	0.6734 (2)	0.2371 (5)	0.0685 (11)
C5	0.7029 (1)	0.7365 (1)	0.1751 (3)	0.0377 (6)
C6	0.6419 (1)	0.7621 (1)	0.0147 (3)	0.0359 (5)
C7	0.6611 (1)	0.8904 (1)	0.0410 (3)	0.0374 (6)
C8	0.6673 (1)	0.9682 (2)	−0.1313 (3)	0.0440 (6)
C9	0.5911 (1)	1.0112 (2)	−0.2142 (4)	0.0540 (7)
C10	0.5356 (1)	0.9186 (2)	−0.2768 (3)	0.0497 (7)
C11	0.5676 (1)	0.8311 (2)	−0.4147 (3)	0.0506 (7)
C12	0.5860 (1)	0.7153 (2)	−0.3272 (3)	0.0470 (6)
C13	0.6526 (1)	0.7064 (2)	−0.1785 (3)	0.0415 (6)
C14	0.5444 (1)	0.6404 (2)	0.1342 (3)	0.0414 (6)
C15	0.4634 (1)	0.6368 (2)	0.1889 (5)	0.0581 (8)

Table 2. *Selected geometric parameters* (Å, °) *for* (2*a*)

O1—C1	1.416 (2)	C3—C4	1.510 (3)
O2—C2	1.419 (2)	C5—C6	1.550 (3)
O3—C5	1.414 (2)	C6—C13	1.521 (3)
O3—C4	1.431 (3)	C6—C7	1.566 (2)
O4—C14	1.335 (2)	C7—C8	1.523 (3)
O4—C6	1.470 (2)	C8—C9	1.528 (3)
O5—C14	1.205 (2)	C9—C10	1.522 (3)
C1—C2	1.527 (3)	C10—C11	1.537 (3)
C1—C5	1.541 (2)	C11—C12	1.531 (3)
C1—C7	1.555 (3)	C12—C13	1.539 (3)
C2—C3	1.526 (3)	C14—C15	1.494 (3)

C5—O3—C4	109.4 (2)	O4—C6—C5	112.2 (2)
C14—O4—C6	119.1 (1)	C13—C6—C5	116.7 (2)
O1—C1—C2	110.9 (2)	O4—C6—C7	107.9 (13)
O1—C1—C5	111.0 (2)	C13—C6—C7	119.5 (2)
C2—C1—C5	110.0 (2)	C5—C6—C7	88.02 (13)
O1—C1—C7	117.3 (2)	C8—C7—C1	119.0 (2)
C2—C1—C7	116.7 (2)	C8—C7—C6	121.1 (2)
C5—C1—C7	88.7 (13)	C1—C7—C6	89.3 (13)
O2—C2—C3	112.2 (2)	C7—C8—C9	114.2 (2)
O2—C2—C1	111.9 (2)	C10—C9—C8	114.4 (2)
C3—C2—C1	109.3 (2)	C9—C10—C11	114.7 (2)
C4—C3—C2	113.1 (2)	C12—C11—C10	115.5 (2)
O3—C4—C3	112.3 (2)	C11—C12—C13	118.3 (2)
O3—C5—C1	116.0 (2)	C6—C13—C12	116.8 (2)
O3—C5—C6	117.6 (2)	O5—C14—O4	123.4 (2)
C1—C5—C6	90.4 (1)	O5—C14—C15	124.9 (2)
O4—C6—C13	110.6 (2)	O4—C14—C15	111.6 (2)
O1—C1—C2—O2	−57.2 (2)	C2—C1—C5—C6	−103.6 (2)
O1—C1—C2—C3	67.7 (2)	C5—C6—C7—C1	14.2 (1)
C7—C1—C2—O2	80.7 (2)	O4—C6—C7—C8	−109.2 (2)
C5—C1—C2—C3	−55.5 (2)	C13—C6—C7—C1	−105.6 (2)
O1—C1—C5—O3	−105.5 (2)	C13—C6—C7—C8	18.3 (3)
C2—C1—C5—O3	17.6 (2)	C14—O4—C6—C7	−156.4 (2)
C7—C1—C5—C6	14.4 (1)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O2	0.81 (3)	2.57 (3)	2.857 (3)	103 (2)
O1—H1O···O3^{i}	0.81 (3)	2.10 (3)	2.854 (2)	155 (3)
O2—H2O···O5^{i}	0.88 (3)	1.98 (3)	2.837 (3)	167 (3)

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

Compound (2*b*)

Crystal data

$C_{15}H_{24}O_5.H_2O$
$M_r = 302.37$
Monoclinic
$C2/c$
$a = 20.355\ (7)$ Å
$b = 16.648\ (5)$ Å
$c = 9.181\ (2)$ Å
$\beta = 97.14\ (4)°$
$V = 3087\ (2)$ Å^3
$Z = 8$
$D_x = 1.301$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 30 reflections
$\theta = 20–39°$
$\mu = 0.787$ mm^{-1}
$T = 293\ (2)$ K
Small prism
0.51 × 0.38 × 0.29 mm
Pale yellow

Data collection

Siemens AED diffractometer
$\theta–2\theta$ scans
Absorption correction: none
5759 measured reflections
2939 independent reflections
2282 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0291$

$\theta_{\max} = 70.21°$
$h = -24 \rightarrow 17$
$k = -20 \rightarrow 20$
$l = -11 \rightarrow 8$
1 standard reflection monitored every 50 reflections intensity variation: within statistical fluctuation

Refinement

Refinement on F^2
$R(F) = 0.0374$
$wR(F^2) = 0.1024$
$S = 1.123$
2938 reflections
291 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0679P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.002$

$\Delta\rho_{\max} = 0.30$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0090 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2*b*)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
O1	0.51540 (5)	0.30739 (7)	0.3948 (1)	0.0456 (3)
O2	0.54946 (7)	0.46060 (8)	0.3763 (2)	0.0639 (5)
O3	0.65079 (5)	0.35294 (6)	0.6833 (1)	0.0506 (3)
O4	0.67687 (4)	0.19642 (6)	0.6624 (1)	0.0420 (3)
O5	0.63825 (6)	0.21556 (8)	0.8795 (1)	0.0659 (4)
O1*W*	0.58124 (6)	0.61840 (8)	0.4723 (2)	0.0648 (4)
C1	0.58294 (6)	0.32503 (8)	0.4432 (2)	0.0385 (4)
C2	0.60337 (7)	0.40489 (8)	0.3808 (2)	0.0443 (4)
C3	0.66337 (8)	0.4383 (1)	0.4755 (2)	0.0529 (6)
C4	0.65379 (9)	0.4347 (1)	0.6357 (2)	0.0552 (6)
C5	0.59534 (7)	0.31097 (8)	0.6114 (2)	0.0417 (4)
C6	0.61518 (6)	0.22300 (8)	0.5797 (1)	0.0389 (4)
C7	0.62693 (6)	0.25042 (8)	0.4228 (1)	0.0372 (4)
C8	0.60885 (8)	0.19991 (9)	0.2863 (2)	0.0434 (4)
C9	0.65474 (9)	0.1292 (1)	0.2683 (2)	0.0532 (5)
C10	0.65932 (9)	0.0675 (1)	0.3920 (2)	0.0574 (6)
C11	0.5934 (1)	0.0389 (1)	0.4367 (2)	0.0606 (6)
C12	0.5773 (1)	0.0728 (1)	0.5827 (2)	0.0597 (6)
C13	0.55983 (7)	0.1619 (1)	0.5911 (2)	0.0500 (5)
C14	0.68151 (8)	0.19406 (9)	0.8097 (2)	0.0473 (5)
C15	0.7472 (1)	0.1617 (1)	0.8745 (2)	0.0610 (6)

Table 4. *Selected geometric parameters* (Å, °) *for* (2*b*)

O1—C1	1.422 (2)	C3—C4	1.509 (2)
O2—C2	1.433 (2)	C5—C6	1.556 (2)
O3—C5	1.419 (2)	C6—C13	1.531 (2)
O3—C4	1.433 (2)	C6—C7	1.558 (2)
O4—C14	1.345 (2)	C7—C8	1.516 (2)
O4—C6	1.453 (2)	C8—C9	1.525 (2)
O5—C14	1.206 (2)	C9—C10	1.525 (3)
C1—C2	1.526 (2)	C10—C11	1.527 (3)
C1—C5	1.551 (2)	C11—C12	1.528 (3)
C1—C7	1.556 (2)	C12—C13	1.530 (3)
C2—C3	1.514 (2)	C14—C15	1.494 (2)
C5—O3—C4	112.8 (1)	O4—C6—C5	114.6 (1)
C14—O4—C6	118.8 (1)	C13—C6—C5	113.7 (1)
O1—C1—C2	111.1 (1)	O4—C6—C7	110.5 (1)
O1—C1—C5	108.2 (1)	C13—C6—C7	117.2 (1)
C2—C1—C5	119.1 (1)	C5—C6—C7	88.3 (1)
O1—C1—C7	110.2 (1)	C8—C7—C1	117.3 (1)
C2—C1—C7	117.6 (1)	C8—C7—C6	123.5 (1)
C5—C1—C7	88.5 (1)	C1—C7—C6	88.0 (1)
O2—C2—C3	109.8 (1)	C7—C8—C9	115.4 (1)
O2—C2—C1	109.4 (1)	C10—C9—C8	114.9 (1)
C3—C2—C1	110.0 (1)	C9—C10—C11	115.8 (2)
C4—C3—C2	110.6 (1)	C10—C11—C12	114.4 (2)
O3—C4—C3	110.6 (1)	C11—C12—C13	118.6 (1)
O3—C5—C1	114.2 (1)	C12—C13—C6	117.6 (1)
O3—C5—C6	109.9 (1)	O5—C14—O4	124.1 (1)
C1—C5—C6	88.3 (1)	O5—C14—C15	124.9 (2)
O4—C6—C13	111.0 (1)	O4—C14—C15	111.0 (1)
O1—C1—C2—O2	37.1 (2)	C7—C1—C5—C6	−19.6 (1)
C5—C1—C2—O2	−89.6 (2)	O1—C1—C5—O3	−157.7 (1)
C5—C1—C2—C3	31.1 (2)	C5—C6—C7—C1	−19.6 (1)
C7—C1—C2—C3	−73.9 (2)	O4—C6—C7—C8	102.9 (1)
C2—C1—C5—O3	−29.6 (2)	C13—C6—C7—C1	96.3 (1)
O1—C1—C5—C6	91.2 (1)	C13—C6—C7—C8	−25.5 (2)
C7—C1—C5—O3	91.5 (1)	C14—O4—C6—C7	159.8 (1)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···O1*W*	0.62 (5)	2.22 (5)	2.821 (2)	162 (6)
O1*W*—H2OW···O2	0.87 (7)	2.25 (7)	2.821 (2)	123 (6)
O1—H1O···O1*W*^{i}	0.83 (4)	1.91 (4)	2.735 (2)	173 (4)
O1*W*—H1OW···O5^{ii}	0.84 (3)	2.43 (2)	3.156 (2)	146 (2)
O1*W*—H1OW···O3^{ii}	0.84 (3)	2.50 (3)	3.194 (2)	141 (2)

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

Table 5. *Conformation of the rings and dihedral angles (°) between the ring planes*

Q_T = total puckering amplitude (Å) (Cremer & Pople, 1975), DAP = minimum displacement asymmetry parameter (Nardelli, 1983*b*), BC = boat-chair, T = twist, S = sofa. *A*, *B* and *C* denote the six-, four- and eight-membered rings, respectively.

	Q_T	DAP	Conformation
Compound (2*a*)			
A	0.731 (2)	*D*2(C3) = 0.0461 (8)	T
B	0.0503 (5)		
C	1.205 (2)	*DS*(C8) = 0.0867 (8)	BC
Compound (2*b*)			
A	0.512 (2)	*DS*(C1) = 0.0274 (9)	S
B	−0.0695 (3)		
C	1.192 (2)	*DS*(C8) = 0.0468 (7)	BC

Dihedral angles	*A*/*B*	*B*/*C*	*A*/*C*
(2*a*)	135.3 (1)	114.0 (1)	155.6 (1)
(2*b*)	114.7 (1)	126.4 (1)	147.5 (1)

The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure.

Both structures were solved by direct methods and refined by anisotropic full-matrix least squares. All the H atoms were found from the $\Delta\rho$ maps and refined isotropically. The H2O*W* atom of compound (2*b*) was found too near the O1*W* atom [0.62 (5) Å], so its position was corrected by shifting it along the H2O*W*—O1*W* direction at an ZO1*W*—H2O*W* distance equal to that found for O1*W*—H1O*W*.

The calculations were carried out on the ENCORE91 and GOULD–POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma), and on a COMPAQ-486c portable computer.

For both compounds, data collection: local programs; cell refinement: *LQPARM* (Nardelli & Mangia, 1984); data reduction: local programs. Program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990) for (2*a*); *SIR*88 (Burla, *et al.*, 1988) for (2*b*). For both compounds, program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965); *PLUTO* (Motherwell & Clegg, 1976); software used to prepare material for publication: *PARST* (Nardelli, 1983); *PARSTCIF* (Nardelli, 1991).

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3-Methyl-6-(4-methylpiperazin-1-yl)-11*H*-pyrido[2,3-*b*][1,4]benzodiazepine

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Abstract

The synthesis and crystal structure of $C_{18}H_{21}N_5$ has been undertaken as part of a study of dopamine receptors. The diazepine ring has a boat conformation. The four C atoms of the outer ring junctions are almost coplanar; the maximum deviation from their mean plane