C4—C5—C6	117.9 (4)	C17—C18—N2	105.7 (6)
C5—C6—C7	114.2 (5)	C15—N1—N2	111.3 (4)
C6—C7—C8	129.8 (5)	C9—C10—C11	112.0 (4)
C7—C8—C9	121.4 (5)	C10—C11—C12	116.9 (4)
C7—C8—C22	123.2 (3)	O4—C20—C21	110.0 (6)
C9—C8—C22	115.3 (3)	C11—C12—C13	110.1 (4)
C8—C9—C10	111.9 (4)	O4—C20—O5	124.5 (6)
C12—C13—C14	114.2 (4)	C11—C12—C23	109.5 (4)
C12—C13—O3	109.0 (3)	O5—C20—C21	125.5 (6)
C14—C13—O3	108.1 (3)	C13—C12—C23	111.9 (4)
C3—O3—C13	110.9 (3)	C4—O4—C20	121.0 (4)
C13—C14—C1	112.5 (4)	N1—N2—C18	112.3 (5)

	(II)	Eunicin†
C1—C2—C3—C4	−166.1 (4)	−168
C2—C3—C4—C5	176.3 (5)	179
C3—C4—C5—C6	57.8 (6)	57
C4—C5—C6—C7	−102.8 (5)	−107
C5—C6—C7—C8	123.8 (5)	128
C6—C7—C8—C9	−172.7 (4)	−173
C7—C8—C9—C10	93.3 (5)	99
C8—C9—C10—C11	−71.9 (6)	−77
C9—C10—C11—C12	140.5 (4)	141
C10—C11—C12—C13	−63.6 (5)	−68
C11—C12—C13—C14	166.6 (4)	170
C12—C13—C14—C1	176.3 (3)	172
C13—C14—C1—C2	−38.8 (5)	−37
C14—C1—C2—C3	34.9 (6)	37
C1—C14—O1—C16	17.0 (4)	22
C14—O1—C16—C15	−0.4 (6)	−3
O1—C16—C15—C1	−16.2 (4)	−18
C16—C15—C1—C14	25.0 (3)	27
C15—C1—C14—O1	−26.1 (4)	−30

† E.s.d.'s for the torsion angles of eunicin are in the range 1–2°.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: local least-squares cell program. Data reduction: local data reduction program. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1984). Molecular graphics: *ORTEP*II (Johnson, 1976).

This work was partially supported by NIH grant 17562 (DvdH).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1181). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1996). C**52**, 1274-1277

(1*R*,2*S*,4*R*)-2-Benzyloxy-4-methoxy-5-(1-methylethyl)-6,8-dioxabicyclo[3.2.1]octane and (1*R*,2*S*,4*R*)-2-Benzyloxy-4-methoxy-2-methyl-6,8-dioxabicyclo[3.2.1]octane

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Abstract

The title compounds, $C_{17}H_{24}O_4$ and $C_{15}H_{20}O_4$, respectively, were obtained during studies of the relationship between structure and herbicidal activity of derivatives of levoglucosenone [Furneax *et al.* (1989). European Patent Application 0 302 599; Furneaux, Henzell & Tyler (1991). US Patent 5 047 518; Blattner, Furneaux, Mason & Tyler (1991). *Pestic. Sci.* **31**, 419–435; Furneaux, Mason & Tyler (1995). Unpublished results]. The crystal structures contain independent molecules held together by van der Waals packing forces. The pendant groups at C1 in $C_{17}H_{24}O_4$ have a minor effect on the fused dioxolane–pyranose ring conformation. The *O*-benzyl groups adopt different conformations determined by minimization of intramolecular repulsive contacts, particularly for the 4-*C*-methyl molecule, and intermolecular non-bonding contacts.

Comment

Crystals of (1*R*,2*S*,4*R*)-2-benzyloxy-4-methoxy-5-(1-methylethyl)-6,8-dioxabicyclo[3.2.1]octane, (1), and (1*R*,2*S*,4*R*)-2-benzyloxy-4-methoxy-2-methyl-6,8-dioxabicyclo[3.2.1]octane, (2), with common name 1,6-anhydro-4-*O*-benzyl-3-deoxy-4-*C*-methyl-2-*O*-methyl-β-D-*ribo*-hexopyranose, were prepared, as noted by Furneaux, Henzell & Tyler (1991), during studies of structure–activity relationships of potent herbicides based on 1,6-anhydro-4-*O*-benzyl-3-deoxy-2-*O*-methyl-

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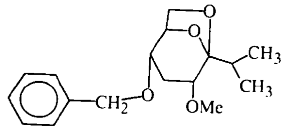
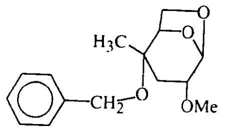


(1)



(2)

β-D-*ribo*-hexopyranose (Gainsford, Furneaux, Mason & Tyler, 1995).

The structures consist of the independent molecules shown in Figs. 1 and 2. The bond lengths and angles in the two structures are almost identical, with expected ranges (Allen *et al.*, 1987; Gainsford *et al.*, 1995). The anomeric effect (Jeffrey, Pople & Radom, 1974) is observed convincingly for the C1—O5—C5 set in both (1) and (2): mean inner, outer 1.420, 1.444 Å, respectively. Reversal of the expected trend is noted for the C1—O1—C6 set in (1) [1.441 (6), 1.422 (6) Å] compared with (2) [1.421 (8), 1.436 (8) Å]; this may be related to the influence of the 1-methylethyl substituent. Further evidence for an effect related to this substituent at C5 comes from comparing the dihedral angles in the rings: all angles are identical statistically except for C5—O5—C1—O1 [−39.2 (5) in (1), −43.2 (7)° in (2)] and C6—O1—C1—O5 [18.2 (6) in (1), 22.5 (8)° in (2)].

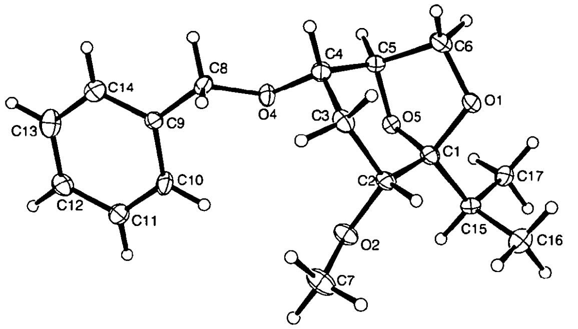


Fig. 1. View (Johnson, 1976) of $C_{17}H_{24}O_4$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level; H atoms are drawn as small circles of arbitrary radii.

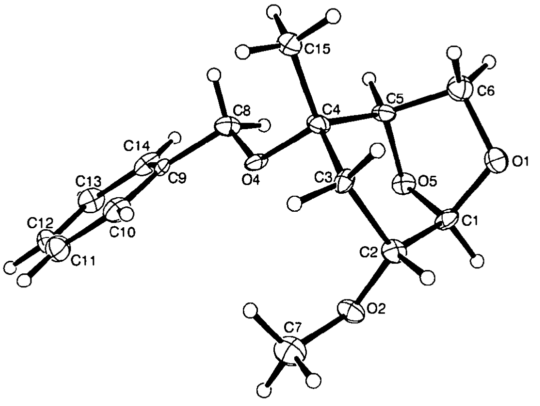


Fig. 2. View (Johnson, 1976) of $C_{15}H_{20}O_4$ showing the labelling of the non-H atoms. Displacement ellipsoids are shown at the 30% probability level; H atoms are drawn as small circles of arbitrary radii.

The 1,6-anhydro moiety five-membered ring approaches a twist (*C*2) conformation [Q = 0.409 and 0.434 Å, φ = 203.3 and 206.8° for (1) and (2), respectively (Cremer & Pople, 1975)], unlike the envelope observed in 1,6-anhydro-4-*O*-benzyl-3-deoxy-2-*O*-methyl-β-D-*ribo*-hexopyranose (Gainsford *et al.*, 1995). The glucopyranose rings are in identical, slightly flattened chair conformations [mean Q = 0.622 Å, φ = 3.6, θ = 22.2° (Cremer & Pople, 1975)] as observed previously (Gainsford *et al.*, 1995).

The molecules have only van der Waals contacts, with the benzyl groups oriented approximately along the respective longest axes. The lower density crystal, (1), has closest contacts O5···H14($-x, y-\frac{1}{2}, \frac{3}{2}-z$) 2.457 (7) and H14···H17C($-x, y+\frac{1}{2}, \frac{3}{2}-z$) 2.258 (8) Å, while the minimum contacts in (2) are longer, *e.g.* O1···H2 ($-x, y+\frac{1}{2}, \frac{1}{2}-z$) 2.533 (8) Å.

Experimental

Crystals of (1) and (2) were obtained by the process described by Furneaux, Henzell & Tyler (1991).

Compound (1)

Crystal data

$C_{17}H_{24}O_4$
M_r = 292.36
Orthorhombic
$P2_12_12_1$
a = 8.075 (3) Å
b = 8.382 (2) Å
c = 22.978 (7) Å
V = 1555.3 (8) Å^3
Z = 4
D_x = 1.249 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 24 reflections
θ = 3.59–14.62°
μ = 0.088 mm^{-1}
T = 133 (2) K
Plate
0.64 × 0.48 × 0.045 mm
Colourless

Data collection

Siemens Nicolet *R*3*m* four-circle diffractometer
ω scans
Absorption correction: none
1253 measured reflections
1206 independent reflections
969 observed reflections [$I > 2\sigma(I)$]

θ_{max} = 22.49°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 24$
3 standard reflections monitored every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.0524
$wR(F^2)$ = 0.1316
S = 1.041
1206 reflections
190 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0826P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.017
$\Delta\rho_{max}$ = 0.205 e Å^{-3}
$\Delta\rho_{min}$ = −0.249 e Å^{-3}
Extinction correction: none
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 (Å²) for (1)*

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

	x	y	z	U_{eq}
O1	0.3556 (4)	0.4257 (5)	0.57590 (14)	0.0312 (9)
O2	0.5472 (4)	0.3773 (4)	0.7178 (2)	0.0315 (10)
O4	0.1468 (4)	0.4256 (4)	0.74434 (14)	0.0290 (10)
O5	0.2737 (4)	0.2616 (4)	0.64894 (14)	0.0259 (9)
C1	0.4164 (6)	0.3367 (7)	0.6251 (2)	0.0274 (13)
C2	0.4809 (6)	0.4593 (7)	0.6687 (2)	0.0261 (13)
C3	0.3462 (6)	0.5802 (7)	0.6849 (2)	0.0296 (13)
C4	0.1724 (7)	0.5075 (7)	0.6902 (2)	0.0277 (13)
C5	0.1476 (7)	0.3823 (7)	0.6435 (2)	0.0299 (13)
C6	0.1813 (6)	0.4436 (8)	0.5821 (2)	0.0368 (15)
C7	0.6667 (7)	0.4726 (8)	0.7481 (3)	0.046 (2)
C8	0.1078 (6)	0.5309 (7)	0.7912 (2)	0.0279 (13)
C9	0.1103 (6)	0.4392 (6)	0.8473 (2)	0.0226 (12)
C10	0.2390 (7)	0.3354 (6)	0.8604 (2)	0.0309 (13)
C11	0.2457 (7)	0.2596 (7)	0.9138 (2)	0.0346 (15)
C12	0.1254 (6)	0.2870 (7)	0.9550 (2)	0.0343 (15)
C13	−0.0043 (8)	0.3889 (7)	0.9425 (2)	0.040 (2)
C14	−0.0116 (7)	0.4644 (7)	0.8889 (2)	0.0332 (14)
C15	0.5373 (6)	0.2099 (6)	0.6060 (2)	0.0274 (13)
C16	0.6877 (7)	0.2828 (8)	0.5764 (3)	0.041 (2)
C17	0.4559 (7)	0.0878 (7)	0.5656 (2)	0.0352 (15)

Table 2. *Selected geometric parameters (Å, °) for (1)*

O1—C6	1.422 (6)	C1—C15	1.510 (7)
O1—C1	1.441 (6)	C1—C2	1.525 (7)
O2—C2	1.426 (6)	C2—C3	1.532 (7)
O2—C7	1.432 (6)	C3—C4	1.535 (8)
O4—C8	1.428 (6)	C4—C5	1.513 (7)
O4—C4	1.437 (6)	C5—C6	1.525 (7)
O5—C1	1.422 (6)	C8—C9	1.501 (7)
O5—C5	1.441 (6)		
C6—O1—C1	108.2 (4)	C2—C3—C4	114.0 (4)
C2—O2—C7	111.6 (4)	O4—C4—C5	105.3 (4)
C8—O4—C4	112.9 (4)	O4—C4—C3	112.9 (4)
C1—O5—C5	103.2 (4)	C5—C4—C3	109.9 (4)
O5—C1—O1	104.8 (4)	O5—C5—C4	109.4 (4)
O5—C1—C15	108.9 (4)	O5—C5—C6	101.0 (4)
O1—C1—C15	110.8 (4)	C4—C5—C6	113.4 (5)
O5—C1—C2	108.8 (4)	O1—C6—C5	103.6 (4)
O1—C1—C2	106.4 (4)	O4—C8—C9	109.1 (4)
C15—C1—C2	116.4 (4)	C10—C9—C14	118.4 (5)
O2—C2—C1	108.9 (4)	C1—C15—C16	111.4 (4)
O2—C2—C3	113.1 (4)	C1—C15—C17	111.7 (4)
C1—C2—C3	111.2 (4)	C16—C15—C17	110.0 (4)
C5—O5—C1—O1	−39.2 (5)	C2—C3—C4—O4	78.9 (6)
C5—O5—C1—C15	−157.8 (4)	C2—C3—C4—C5	−38.3 (6)
C5—O5—C1—C2	74.4 (4)	C1—O5—C5—C4	−76.3 (5)
C6—O1—C1—O5	18.2 (6)	C1—O5—C5—C6	43.5 (5)
C6—O1—C1—C15	135.5 (5)	O4—C4—C5—O5	−64.2 (5)
C6—O1—C1—C2	−97.1 (5)	C3—C4—C5—O5	57.7 (5)
C7—O2—C2—C1	156.1 (4)	O4—C4—C5—C6	−176.0 (4)
C7—O2—C2—C3	−79.7 (5)	C3—C4—C5—C6	−54.1 (6)
O5—C1—C2—O2	69.2 (5)	C1—O1—C6—C5	8.8 (6)
O1—C1—C2—O2	−178.4 (4)	O5—C5—C6—O1	−32.0 (6)
O5—C1—C2—C3	−56.1 (5)	C4—C5—C6—O1	84.9 (6)
O1—C1—C2—C3	56.3 (5)	C4—O4—C8—C9	−171.0 (4)
C15—C1—C2—C3	−179.6 (4)	O4—C8—C9—C10	46.3 (6)
O2—C2—C3—C4	−85.2 (5)	O4—C8—C9—C14	−137.8 (5)
C1—C2—C3—C4	37.7 (6)	O5—C1—C15—C16	176.2 (4)
C8—O4—C4—C5	−159.3 (4)	C2—C1—C15—C17	176.2 (4)
C8—O4—C4—C3	80.8 (5)		

Compound (2)

Crystal data

$C_{15}H_{20}O_4$
$M_r = 264.31$
Orthorhombic
$P2_12_12_1$
$a = 5.934$ (3) Å
$b = 6.907$ (3) Å
$c = 32.751$ (18) Å
$V = 1342.3$ (12) Å^3
$Z = 4$
$D_x = 1.308$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 3.2–11.8°$
$\mu = 0.094$ mm^{-1}
$T = 133$ (2) K
Plate
0.48 × 0.21 × 0.055 mm
Colourless

Data collection

Siemens Nicolet $R3m$ four-circle diffractometer
ω scans
Absorption correction: none
1115 measured reflections
1076 independent reflections
705 observed reflections $[I > 2\sigma(I)]$

$\theta_{max} = 22.48°$
$h = -1 \rightarrow 6$
$k = 0 \rightarrow 7$
$l = 0 \rightarrow 35$
3 standard reflections monitored every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0585$
$wR(F^2) = 0.1374$
$S = 0.983$
1073 reflections
172 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.0591P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.025$
$\Delta\rho_{max} = 0.249$ e Å^{-3}
$\Delta\rho_{min} = -0.241$ e Å^{-3}
Extinction correction: none
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 (Å²) for (2)*

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

	x	y	z	U_{eq}
O1	−0.0027 (8)	0.1523 (7)	0.19987 (13)	0.0362 (14)
O2	0.3895 (7)	−0.2442 (7)	0.20321 (13)	0.0305 (13)
O4	0.1466 (7)	−0.3150 (7)	0.12065 (12)	0.0239 (12)
O5	0.2463 (7)	0.0550 (8)	0.15172 (13)	0.0267 (13)
C1	0.2024 (11)	0.0498 (12)	0.1942 (2)	0.026 (2)
C2	0.1720 (11)	−0.1585 (11)	0.2086 (2)	0.027 (2)
C3	−0.0214 (11)	−0.2522 (10)	0.1846 (2)	0.023 (2)
C4	−0.0267 (11)	−0.1982 (11)	0.1394 (2)	0.025 (2)
C5	0.0248 (12)	0.0150 (10)	0.1352 (2)	0.026 (2)
C6	−0.1203 (12)	0.1489 (12)	0.1616 (2)	0.035 (2)
C7	0.3961 (12)	−0.4452 (12)	0.2132 (2)	0.040 (2)
C8	0.1835 (11)	−0.2917 (11)	0.0784 (2)	0.030 (2)
C9	0.3458 (11)	−0.4459 (11)	0.0638 (2)	0.023 (2)
C10	0.3636 (13)	−0.6190 (11)	0.0839 (2)	0.034 (2)
C11	0.5141 (13)	−0.7591 (12)	0.0714 (2)	0.038 (2)
C12	0.6497 (13)	−0.7257 (11)	0.0384 (2)	0.033 (2)
C13	0.6336 (12)	−0.5538 (12)	0.0177 (2)	0.034 (2)
C14	0.4818 (12)	−0.4128 (12)	0.0303 (2)	0.036 (2)
C15	−0.2573 (10)	−0.2500 (11)	0.1208 (2)	0.031 (2)

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

O1—C1	1.421 (8)	C1—C2	1.524 (10)
O1—C6	1.436 (8)	C2—C3	1.533 (9)
O2—C7	1.426 (9)	C3—C4	1.529 (9)
O2—C2	1.430 (8)	C4—C5	1.510 (10)
O4—C8	1.411 (7)	C4—C15	1.540 (9)
O4—C4	1.444 (8)	C5—C6	1.530 (9)
O5—C1	1.417 (8)	C8—C9	1.514 (10)
O5—C5	1.448 (8)		

C1—O1—C6	107.2 (5)	O4—C4—C5	111.2 (6)
C7—O2—C2	113.5 (6)	O4—C4—C3	105.1 (6)
C8—O4—C4	117.6 (5)	C5—C4—C3	108.8 (6)
C1—O5—C5	101.3 (5)	O4—C4—C15	109.5 (5)
O5—C1—O1	105.8 (6)	C5—C4—C15	111.7 (6)
O5—C1—C2	110.4 (6)	C3—C4—C15	110.2 (6)
O1—C1—C2	109.2 (6)	O5—C5—C4	109.6 (6)
O2—C2—C1	104.3 (6)	O5—C5—C6	100.6 (5)
O2—C2—C3	116.0 (6)	C4—C5—C6	115.1 (6)
C1—C2—C3	109.3 (6)	O1—C6—C5	103.3 (5)
C4—C3—C2	114.1 (6)	O4—C8—C9	109.2 (6)
C5—O5—C1—O1	−43.2 (7)	C2—C3—C4—C5	−41.5 (8)
C5—O5—C1—C2	74.8 (7)	C2—C3—C4—C15	−164.3 (6)
C6—O1—C1—O5	22.5 (8)	C1—O5—C5—C4	−76.4 (7)
C6—O1—C1—C2	−96.3 (7)	C1—O5—C5—C6	45.2 (7)
C7—O2—C2—C1	−177.2 (5)	O4—C4—C5—O5	−55.1 (7)
C7—O2—C2—C3	−57.1 (8)	C3—C4—C5—O5	60.2 (7)
O5—C1—C2—O2	66.6 (7)	C15—C4—C5—O5	−177.9 (5)
O1—C1—C2—O2	−177.5 (5)	O4—C4—C5—C6	−167.6 (5)
O5—C1—C2—C3	−58.0 (7)	C3—C4—C5—C6	−52.3 (7)
O1—C1—C2—C3	57.9 (7)	C1—O1—C6—C5	6.3 (7)
O2—C2—C3—C4	−77.5 (8)	O5—C5—C6—O1	−31.8 (7)
C1—C2—C3—C4	40.0 (8)	C4—C5—C6—O1	85.9 (7)
C8—O4—C4—C5	−61.0 (7)	C4—O4—C8—C9	−171.8 (5)
C8—O4—C4—C3	−178.6 (5)	O4—C8—C9—C10	26.2 (9)
C2—C3—C4—O4	77.8 (7)	O4—C8—C9—C14	−152.5 (6)

For both compounds, data collection: *R3m Software* (Siemens, 1983); cell refinement: *R3m Software*; data reduction: *SHELXTL* (Sheldrick, 1983); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1993).

Lists of structure factors, torsion angles, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1065). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Pyrrolo-Annellated Carbazoles as Potential Antitumour-Active Compounds: Dimethyl 4-Methoxy-9-methyl-9*H*-carbazole-1,2-dicarboxylate and 5-Hydroxy-2-phenyl-10-methyl-1,2,3,10-tetrahydropyrrolo[3,4-*a*]carbazole-1,3-dione Methanol Solvate

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Abstract

The structures of the title compounds, $C_{18}H_{17}NO_5$ and $C_{21}H_{14}N_2O_3.CH_4O$, were determined. The crystal structure of the first shows significant variations between its two independent molecules; that of the second is characterized by hydrogen bonds to the co-crystallized methanol.

Comment

Selectively functionalized and annellated carbazoles as well as structurally related alkaloids are interesting target compounds for the development of antitumour and antibiotically active drugs (Chakraborty & Roy, 1991; Gribble, 1990; Pindur, 1987; Kansal & Poitier, 1986; Poitier, 1992). Due to the planar chromophore of the carbazoles, the pharmacological activity is based, first of all, on complex formation with human B-DNA (Gribble, 1990). In recent years we have synthesized a variety of functionalized carbazole and annellated carbazole derivatives in order to obtain more details on structure–activity relationships (Pindur, Haber & Erfanian-Abdoust, 1992; Pindur, Pfeuffer, Eitel, Rogge & Haber, 1991; Pindur, 1995). In this context, current molecular-modelling studies of carbazole–DNA interactions were performed (Pindur, Haber & Erfanian-Abdoust, 1992; Dräger, Haber, Erfanian-Abdoust, Pindur & Sattler, 1993; Sattler, 1994; Rehn, 1995) on the basis of molecular mechanics, molecular dynamics and quantum chemistry calculations. To obtain detailed geometrical information on the molecules interacting with DNA, X-ray analyses of the potential drugs are necessary. As a continuation of our investigations in this field, we report the crystal structures of the title compounds, (1) and (2), which will be helpful in designing new antitumour-active drugs.

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