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Structure of a Synthetic Hexahydrobenzofuran Subunit, $C_{16}H_{22}O_7$, Related to the Avermectins

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Abstract. Methyl 6,7-diacetoxy-6-methyl-3-methyleneperhydrobenzofuran-4-carboxylate, $C_{16}H_{22}O_7$, $M_r = 326{\cdot}35$, monoclinic, $P2_1$, $a = 7{\cdot}5763\,(18)$, $b = 10{\cdot}2792\,(14)$, $c = 11{\cdot}3512\,(16)$ Å, $\beta = 108{\cdot}23\,(2)^\circ$, $V = 839{\cdot}64$ Å^3, $D_x = 1{\cdot}29$ Mg m^{-3}, $Z = 2$, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1{\cdot}54178$ Å, $T = 293$ K, $\mu(\mathrm{Cu}\ K\bar{\alpha}) = 0{\cdot}813$ mm^{-1}, $F(000) = 348$, $R = 0{\cdot}064$ for 1322 observed reflections. The title compound is constituted of a five-membered ring of the envelope type containing an O atom. To this ring is fused a cyclohexane ring in the chair conformation. There are four substituents attached to the six-membered ring: a methoxycarbonyl group in equatorial position at C(2), an axial methyl and an equatorial acetoxy group at C(4) and another acetoxy also in axial position at C(5).

Introduction. The avermectin group of macrolide antiparasitic agents contains a hexahydrobenzofuran ring system with an unusual substitution pattern (Davies & Green, 1986). Several synthetic approaches to this subunit have been reported recently (Jung & Street, 1984; Prashad & Fraser-Reid, 1985; Kozikowski & Maloney Huss, 1985; Grimmins & Lever, 1986; Ireland & Obrecht, 1986; Jung, Street &

Usui, 1986; Hanessian, Beaulieu & Dubé, 1986) as well as the synthesis of avermectin B_{1a} (Hanessian, Ugolini, Dubé, Hodges & André, 1986; Hanessian, Ugolini, Hodges, Beaulieu, Dubé & André, 1987; Hanessian, Dubé & Hodges, 1987). Conformational aspects play an important role in this class of compound and the orientation of the carbonyl-containing substituent at C(2) of the hexahydrobenzofuran subunit is primordial for biological activity. It was therefore important to obtain an X-ray crystal-structure analysis for one of the synthetic intermediates in order to establish configurational and conformational features.

Experimental. Crystals of $C_{16}H_{22}O_7$ were recrystallized from ether/ethyl acetate solution. Crystal bound by {001}, {101}, {010}, dimensions 0·05 × 0·15 × 0·24 mm. Unit-cell dimensions from 25 well centered reflections in the range $40 \leq 2\theta \leq 50°$. Nonius CAD-4 diffractometer, graphite-monochromatized Cu $K\bar{\alpha}$ radiation, ω–2θ scan, $\Delta\omega = (1\cdot00 + 0\cdot14\tan\theta)°$, $2\theta_{\max} = 150\cdot0°$, $0 \leq h \leq 9$, $0 \leq k \leq 12$, $-14 \leq l \leq 13$. Orientation monitored every 200 measurements, intensity checked every hour using seven standard reflections, largest intensity fluctuation 3·0%. Use of the FLAT option, 1829 measured reflections, 1324 such that $I \geq 1\cdot96\sigma(I)$ retained for structure determination and refinement. Lp correction, no absorption correction.

The structure was solved by direct methods (*MULTAN*80).* Block-diagonal least-squares refinement, all non-hydrogen atoms anisotropic. The H atoms, found on difference Fourier synthesis, kept at ideal positions (C—H = 0·95 Å, $B_{\rm iso} = 4\cdot5$ Å^2). Only one or two H atoms on C(12), C(43) and C(53) were clearly visible on the difference Fourier synthesis. From these, the positions of the others were computed with C—H = 0·95 Å and ideal tetrahedral angles, $B_{\rm iso} = 5\cdot5$ Å^2. The positional parameters of the H atoms were not refined, but were recalculated after each least-squares cycle. Function minimized $\sum w(|F_o| - |F_c|)^2$. In the last cycles, two reflections were given zero weights. A mechanical failure occurred as 020 and $20\bar{1}$ were measured. Final $R = 0\cdot0638$, $wR = 0\cdot0581$ [weights derived from the counting statistics $w = 1/\sigma^2(F)$] and $S = 2\cdot207$ for 208 refined parameters. Maximum $(\Delta/\sigma) = 0\cdot32$, average $(\Delta/\sigma) = 0\cdot11$, residual electron density fluctuation on final difference Fourier synthesis −0·26 and +0·25 e Å^{-3}.

The scattering curves for the non-hydrogen atoms were taken from Cromer & Mann (1968) and those for the H atoms from Stewart, Davidson & Simpson (1965). Real and imaginary parts of anomalous dispersion of O from Cromer & Liberman (1970).

Table 1. *Final atomic coordinates, e.s.d.'s* (× 10^4) *and* U_{eq} *values* (Å^2 × 10^3)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O(6)	10727 (5)	1548	6650 (4)	54
O(11)	3774 (6)	−894 (5)	4110 (4)	66
O(12)	4222 (5)	1071 (4)	3423 (4)	63
O(41)	6940 (5)	−831 (4)	8676 (3)	45
O(42)	8696 (6)	217 (5)	10388 (4)	70
O(51)	9731 (5)	−675 (4)	7558 (3)	39
O(52)	12265 (6)	−447 (6)	9211 (4)	94
C(1)	4487 (7)	182 (6)	4299 (5)	42
C(2)	5687 (7)	676 (5)	5544 (5)	35
C(3)	5847 (7)	−304 (6)	6574 (5)	36
C(4)	6965 (7)	248 (6)	7833 (5)	38
C(5)	8948 (7)	534 (6)	7824 (5)	36
C(6)	8925 (7)	1493 (6)	6788 (5)	40
C(7)	7593 (7)	1190 (6)	5498 (5)	35
C(8)	8795 (8)	346 (6)	4973 (5)	45
C(8′)	10727 (8)	869 (8)	5571 (6)	62
C(9)	8378 (10)	−564 (8)	4167 (7)	76
C(12)	3081 (11)	734 (9)	2201 (6)	104
C(42)	7757 (8)	−692 (8)	9915 (5)	55
C(43)	7265 (11)	−1790 (8)	10564 (5)	78
C(44)	6049 (8)	1442 (7)	8183 (5)	52
C(52)	11434 (8)	−1034 (7)	8305 (5)	56
C(53)	12024 (9)	−2261 (7)	7845 (6)	62

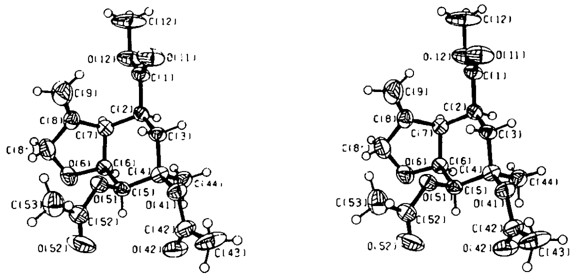

Fig. 1. Stereoview of the molecule of $C_{16}H_{22}O_7$.

Discussion. Structure-factor calculations were performed for each configuration by changing x,y,z into $\bar{x},\bar{y},\bar{z}$. The configuration with the smaller values of R, wR and S corresponds to the set of atomic coordinates presented in Table 1.* For the other configuration, $R = 0\cdot0640$, $wR = 0\cdot0582$ and $S = 2\cdot212$. The atomic numbering adopted is given on the stereoview of the molecule shown in Fig. 1. The bond distances, angles and torsion angles of interest are given in Table 2.

The five-membered ring exhibits the usual envelope conformation in which C(6), O(6), C(8′) and C(8) are

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* The programs used here are modified versions of *NRC*-2, data reduction, *NRC*-10, bond distances and angles, *NRC*-22, mean planes (Ahmed, Hall, Pippy & Huber, 1973), *FORDAP*, Fourier and Patterson maps (A. Zalkin, unpublished), *NUCLS*, least-squares refinement (Doedens & Ibers, 1967), *MULTAN*80, multisolution program (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *ORTEP*, stereodrawings (Johnson, 1965).

* Lists of anisotropic temperature factors, the structure factors and the calculated atomic coordinates of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44735 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å), *bond angles* (°), *torsion angles* (°) *and their e.s.d.'s*

C(6)—O(6)	1·423 (7)	C(1)—O(11)	1·220 (8)
O(6)—C(8′)	1·410 (8)	C(1)—O(12)	1·319 (7)
C(8′)—C(8)	1·507 (9)	O(12)—C(12)	1·429 (8)
C(8)—C(7)	1·509 (8)	C(4)—O(41)	1·469 (7)
C(7)—C(6)	1·528 (7)	O(41)—C(42)	1·355 (6)
C(6)—C(5)	1·530 (8)	C(42)—C(43)	1·459 (11)
C(5)—C(4)	1·534 (8)	C(42)—O(42)	1·195 (9)
C(4)—C(3)	1·525 (7)	C(4)—C(44)	1·523 (9)
C(3)—C(2)	1·519 (8)	C(5)—O(51)	1·449 (7)
C(2)—C(7)	1·554 (8)	O(51)—C(52)	1·355 (7)
C(8)—C(9)	1·277 (10)	C(52)—C(53)	1·486 (10)
C(2)—C(1)	1·509 (7)	C(52)—O(52)	1·189 (8)
C(6)—O(6)—C(8′)	109·7 (4)	C(5)—C(4)—O(41)	111·2 (4)
O(6)—C(8′)—C(8)	107·7 (5)	C(44)—C(4)—O(41)	109·8 (5)
C(8′)—C(8)—C(7)	103·8 (5)	C(3)—C(4)—C(44)	112·3 (5)
C(8)—C(7)—C(6)	101·3 (5)	C(5)—C(4)—C(44)	112·0 (5)
C(7)—C(6)—O(6)	105·7 (4)	C(4)—C(5)—O(51)	107·6 (4)
C(7)—C(6)—C(5)	116·8 (5)	C(6)—C(5)—O(51)	107·4 (4)
C(6)—C(5)—C(4)	110·7 (4)	C(2)—C(1)—O(11)	125·0 (5)
C(5)—C(4)—C(3)	108·9 (4)	C(2)—C(1)—O(12)	112·2 (5)
C(4)—C(3)—C(2)	111·2 (4)	O(11)—C(1)—O(12)	122·8 (5)
C(3)—C(2)—C(7)	113·6 (4)	C(1)—O(12)—C(12)	117·9 (5)
C(2)—C(7)—C(6)	112·3 (4)	C(4)—O(41)—C(42)	120·1 (5)
C(8)—C(7)—C(2)	120·0 (5)	O(41)—C(42)—C(43)	109·7 (6)
O(6)—C(6)—C(5)	109·2 (4)	O(41)—C(42)—O(42)	124·3 (6)
C(7)—C(8)—C(9)	131·3 (6)	C(43)—C(42)—O(42)	126·0 (6)
C(8′)—C(8)—C(9)	124·9 (6)	C(5)—O(51)—C(52)	118·4 (4)
C(7)—C(2)—C(1)	112·1 (4)	O(51)—C(52)—C(53)	110·1 (5)
C(3)—C(2)—C(1)	112·2 (5)	O(51)—C(52)—O(52)	123·1 (6)
C(3)—C(4)—O(41)	102·3 (4)	C(53)—C(52)—O(52)	126·8 (6)
O(6)—C(8′)—C(8)—C(7)	20·9 (6)	C(2)—C(3)—C(4)—O(41)	179·7 (4)
C(8′)—C(8)—C(7)—C(6)	−31·9 (6)	C(6)—C(5)—C(4)—O(41)	170·3 (4)
C(8)—C(7)—C(6)—O(6)	32·9 (5)	C(7)—C(6)—C(5)—O(51)	68·0 (6)
C(7)—C(6)—O(6)—C(8′)	−21·1 (6)	C(3)—C(4)—C(5)—O(51)	−58·7 (5)
C(6)—O(6)—C(8′)—C(8)	0·2 (6)	C(2)—C(1)—O(12)—C(12)	−179·0 (5)
C(7)—C(2)—C(3)—C(4)	55·1 (6)	O(11)—C(1)—O(12)—C(12)	−1·4 (9)
C(2)—C(3)—C(4)—C(5)	−62·6 (6)	C(4)—O(41)—C(42)—C(43)	169·9 (5)
C(3)—C(4)—C(5)—C(6)	58·4 (6)	C(4)—O(41)—C(42)—O(42)	−8·4 (9)
C(4)—C(5)—C(6)—C(7)	−49·2 (6)	C(5)—O(51)—C(52)—C(53)	−177·3 (5)
C(5)—C(6)—C(7)—C(2)	40·5 (7)	C(5)—O(51)—C(52)—O(52)	4·8 (9)
C(6)—C(7)—C(2)—C(3)	−42·6 (6)	C(42)—O(41)—C(4)—C(5)	66·2 (6)
C(3)—C(2)—C(7)—C(8)	76·1 (6)	C(42)—O(41)—C(4)—C(3)	−177·7 (5)
C(5)—C(6)—C(7)—C(8)	−88·8 (6)	C(52)—O(51)—C(5)—C(6)	110·5 (5)
C(4)—C(5)—C(6)—O(6)	−169·0 (4)	C(52)—O(51)—C(5)—C(4)	−130·3 (5)
C(2)—C(7)—C(6)—O(6)	162·2 (4)	O(12)—C(1)—C(2)—C(7)	−56·0 (6)
O(6)—C(8′)—C(8)—C(9)	−162·2 (7)	O(12)—C(1)—C(2)—C(3)	174·8 (5)
C(6)—C(7)—C(8)—C(9)	151·5 (8)	C(3)—C(4)—O(41)—C(42)	−177·7 (5)
C(9)—C(8)—C(7)—C(2)	27·3 (10)	C(44)—C(4)—O(41)—C(42)	−58·3 (6)
C(8)—C(7)—C(2)—C(1)	−52·3 (7)	O(11)—C(1)—C(2)—C(3)	−2·7 (8)
C(4)—C(3)—C(2)—C(1)	−176·5 (5)	O(11)—C(1)—C(2)—C(7)	126·5 (6)
C(6)—C(7)—C(2)—C(1)	−171·1 (5)	O(51)—C(5)—C(4)—O(41)	53·3 (5)
C(2)—C(3)—C(4)—C(44)	62·1 (6)	O(51)—C(5)—C(4)—C(44)	176·5 (4)
C(6)—C(5)—C(4)—C(44)	−66·4 (6)	O(51)—C(5)—C(6)—O(6)	−51·8 (5)

coplanar [plane (1)] and the atom C(7) is at the flap. This atom is 0·527 (6) Å away from plane (1). The dihedral angle between planes (1) and (2) [defined by the atoms C(8), C(7) and C(6)] is 33·2°.

Atom C(9) is at −0·321 (8) Å from plane (1) and at −0·459 (8) Å from plane (2). The angle C(7)—C(8)—C(9) = 131·3 (6)° is larger than C(8′)—C(8)—C(9) = 124·9 (6)°, probably because of the strain arising from the junction of the two ring systems and the presence of the substituent at C(2).

The five-membered ring is *cis*-fused to the cyclohexane ring. The torsion angles C(5)—C(6)—C(7)—C(2) and O(6)—C(6)—C(7)—C(8) are 40·5 (7) and 32·9 (5)° respectively.

The cyclohexane ring has the chair conformation. However, it deviates slightly from the ideal conformation; the atoms C(2), C(3), C(5) and C(6) are nearly coplanar [plane (3)] while atoms C(7) and C(4) are displaced to opposite sides of plane (3) by +0·518 (6) and −0·723 (6) Å respectively. The flattening of the ring at C(7) is apparent in the C(5)—C(6)—C(7)—C(2) and C(6)—C(7)—C(2)—C(3) torsion angles of 40·5 (7) and −42·6 (6)° respectively. The four other endocyclic torsion angles have an average of 56·2°; this value is close to that calculated by Bucourt & Hainault (1965). The mean value of the ring valency angles is 112·2°. The dihedral angle between the mean plane (3) of the cyclohexane ring and plane (1) of the five-membered ring is 112·5°.

The methoxycarbonyl group at C(2) is in an equatorial position, C(6)—C(7)—C(2)—C(1) = −171·1 (5) and C(4)—C(3)—C(2)—C(1) = −176·5 (5)°. The group of atoms constituted of O(11), O(12), C(1), C(12) and C(2) is planar [plane (4)]. This plane makes an angle of only 30·1° with plane (3) of the cyclohexane ring.

The methyl group at C(4) is in an axial position, C(2)—C(3)—C(4)—C(44) = −62·1 (6) and C(6)—C(5)—C(4)—C(44) = −66·4 (6)°, while the acetoxy group at C(4) is in an equatorial position, C(2)—C(3)—C(4)—O(41) = 179·7 (4) and C(6)—C(5)—C(4)—O(41) = 170·3 (4)°. The acetoxy group at C(5) is also axial, C(7)—C(6)—C(5)—O(51) = 68·0 (6) and C(3)—C(4)—C(5)—O(51) = −58·7 (5)°. The groups of atoms O(41), O(42), C(42), C(43), C(4) [plane (5)] and O(51), O(52), C(52), C(53), C(5) [plane (6)] are each quasi-coplanar. The acetoxy group at C(5) [plane (6)] is not quite perpendicular to plane (3) of the cyclohexane ring; the dihedral angle between these two planes is 73·6°. The two acetoxy groups are in different conformations.

The sequence of atoms extending from C(12) through the six-membered ring to C(43) is in a fully extended conformation.

The C—O single-bond distance, C(12)—O(12) = 1·429 (8) Å, is shorter than C(5)—O(51) = 1·449 (7) or C(4)—O(41) = 1·469 (7) Å. This confirms the finding of Allen & Kirby (1984) who observed that the C—O*R* bond distances are related to the degree of substitution at C. Thus, the C—O distance is shortest for methyl derivatives, and the more the C is substituted, the longer the C—O bond is. In our case, the C(4)—O(41) bond distance is longest while it is shortest in the case of the C(12)—O(12) bond.

The molecules are held together by van der Waals forces. The closest approaches are observed between O(6) and C(9) at 3·244 (8) Å, and also between O(11) and C(7) at 3·247 (7) Å.

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Structure of N^2-*p*-Nitrophenylbenzamidine

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Abstract. $C_{13}H_{11}N_3O_2$, $M_r = 241{\cdot}3$, monoclinic, $C2/c$, $a = 20{\cdot}885$ (3), $b = 5{\cdot}7616$ (6), $c = 19{\cdot}603$ (2) Å, $\beta = 94{\cdot}791$ (8)°, $V = 2350{\cdot}7$ (5) Å^3, $Z = 8$, $D_m = 1{\cdot}35$, $D_x = 1{\cdot}362$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1{\cdot}54178$ Å, $\mu(\text{Cu } K\alpha) = 0{\cdot}694$ mm^{-1}, $F(000) = 1008$, room temperature, $R = 0{\cdot}046$ for 1016 observed reflexions. The N^1—C and N^2=C bonds are different [1·355 (5) and 1·280 (5) Å respectively]. The N^1 and *p*-nitrophenyl substituents at the C=N^2 double bond are in *cis* configuration. The N^1—C—N^2 angle [125·9 (3)°] is different from that found in *trans* benzamidine derivatives (about 118°). The *p*-nitrophenyl and phenyl rings are twisted by 78·9 (4) and 21·2 (4)° relative to the amidine fragment.

Introduction. This work is part of a series of structural studies on the amidine system carried out in this laboratory.† We are looking for the changes induced in the geometry of the amidine group by different substituents and for factors controlling the *cis–trans* isomerism around the C=N^2 bond. Also, we would like to find out how the disposition of the side groups relative to the central amidine groups depends on the character and dimensions of those groups.

Experimental. The title compound was synthetized by one of us (JO). Prismatic yellow crystals obtained from absolute ethanol, D_m by flotation, space group from Weissenberg photographs, crystal 0·1 × 0·1 × 0·25 mm, Syntex $P2_1$ diffractometer, cell parameters from least-squares treatment of setting angles of 15 reflexions with $14 \leq 2\theta \leq 20°$. 1513 reflexions measured in the range: h: 0→22, k: 0→6, l: −21→+21. No significant intensity variation for two standard reflexions recorded every 1·5 h. Maximum value of $2\theta = 115°$. Peak profile analysis according to Lehmann & Larsen (1974), 1017 observed reflexions with $I \geq 2\sigma(I)$. Structure solved by direct methods using *SHELX*76 (Sheldrick, 1976) program. Full-matrix least-squares refinement on F, H atoms from $\Delta\rho$ map, anisotropic thermal parameters for non-H atoms,

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† Previous paper: Ciszak, Gdaniec & Kosturkiewicz (1987).

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