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Structure of 3β,20β-Diacetoxy-11β-hydroxymethyl-5α-pregnane: an Unusual Hydrogen-Bonding Scheme*

By F. R. Ahmed and C. P. Huber

Division of Biological Sciences, National Research Council of Canada, Ottawa, Canada K1A 0R6

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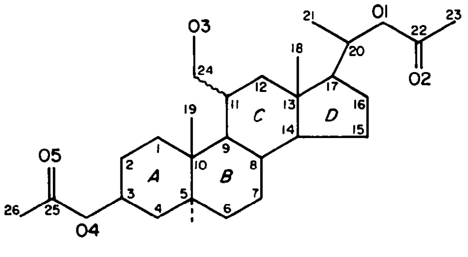
Abstract. $C_{26}H_{42}O_5$, $M_r = 434{\cdot}62$, monoclinic, $P2_1$, $a = 21{\cdot}776\,(5)$, $b = 6{\cdot}119\,(2)$, $c = 19{\cdot}864\,(8)$ Å, $\beta = 111{\cdot}69\,(5)°$, $V = 2459{\cdot}4$ Å^3, $Z = 4$, $D_m = 1{\cdot}178$, $D_x = 1{\cdot}174$ Mg m^{-3}, $\lambda(\text{Cu}\,K\alpha_1) = 1{\cdot}54056$ Å, $\mu = 0{\cdot}599$ mm^{-1}, $F(000) = 952$, $T = 297$ K, final $R = 0{\cdot}048$ for 3267 observed reflections. The two independent molecules of the asymmetric unit have the same 11β-hydroxymethyl configuration and the same absolute configuration. There are differences in conformation of the C(3) and, to a lesser extent, C(17) side chains in the two molecules, resulting from the intermolecular hydrogen bonding and different packing environments. Intermolecular hydrogen bonds O—H···O link the molecules into bundles of three interwound helices of pitch 3*b* along *y*.

Introduction. The title compound (1) and its derivatives are considered to be useful intermediates for the synthesis of products of biological interest. The compound was synthesized from an 11-methylene steroid, 3β,20β-diacetoxy-11-methylene-5α-pregnane, by oxidative hydroboration (Engel, Lourdusamy, Baroan, Ibrahim & Bończa-Tomasewski, 1984; Engel, Baroan, Ibrahim, Le Van, Lourdusamy & Mukherjee, 1985). It seemed important to determine unequivocally the configuration of the 11-hydroxymethyl substituent thus formed, not only because of the importance of the stereochemistry of 11-substituents on biological activities, but also because the catalytic reduction of the 11-methylene steroid which had afforded compound (1), and its 12-oxo derivative, had led, rather unexpectedly, not to 11β-methylated but to 11α-methylated products (Engel *et al.*, 1984).



(1)

Experimental. Crystals in the shape of thin needles were obtained from ether/hexane and their density was measured by flotation in aqueous KI solution. The X-ray measurements were carried out on an Enraf–Nonius CAD-4 diffractometer using Ni-filtered Cu radiation and a crystal 0·03 × 0·10 × 0·87 mm. The cell parameters were derived by a least-squares fit of the θ values for 17 reflections with $26 \le \theta \le 38°$. Intensities up to $\theta = 65°$ for $h = -25$ to 25, $k = 0$ to 7, $l = 0$ to 23, were measured by ω–2θ scans for $\Delta\omega = (1{\cdot}0 + 0{\cdot}14\tan\theta)°$ plus 50% for the backgrounds. Three standard reflections measured every hour of radiation time varied within ±5% of the mean values. Of the 4626 unique reflections scanned, 3267 were observed with $I \ge 2{\cdot}0\sigma(I)$. The net intensities were

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* NRCC publication No. 26377.

corrected for scale variation and the Lp effect, but not for absorption.

Table 1. *Fractional coordinates* [$\times 10^4$; O(13) *and* H $\times 10^3$] *and equivalent isotropic temperature factors* (Å^2)

$$B_{\rm eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
Molecule I				
C(1)	2470 (2)	6432	3790 (2)	4·2
C(2)	3222 (2)	6594 (9)	4050 (3)	4·6
C(3)	3534 (2)	6202 (9)	4858 (2)	4·6
C(4)	3323 (2)	4038 (9)	5060 (2)	4·5
C(5)	2583 (2)	3877 (8)	4799 (2)	4·1
C(6)	2347 (2)	1750 (9)	5034 (2)	4·7
C(7)	1620 (2)	1727 (10)	4867 (2)	5·0
C(8)	1191 (2)	2369 (8)	4083 (2)	4·2
C(9)	1468 (2)	4411 (8)	3827 (2)	3·9
C(10)	2221 (2)	4241 (8)	3972 (2)	3·8
C(11)	1015 (2)	5301 (8)	3078 (2)	4·0
C(12)	292 (2)	5459 (9)	3025 (2)	4·3
C(13)	16 (2)	3413 (8)	3247 (2)	4·0
C(14)	491 (2)	2787 (8)	4003 (2)	4·5
C(15)	103 (3)	1093 (10)	4263 (3)	5·8
C(16)	−620 (3)	1839 (11)	3912 (3)	6·0
C(17)	−634 (2)	3718 (9)	3382 (3)	5·1
C(18)	−77 (2)	1500 (9)	2697 (3)	4·8
C(19)	2387 (2)	2397 (8)	3537 (2)	4·4
C(20)	−1270 (2)	3781 (10)	2738 (3)	5·6
C(21)	−1866 (3)	4308 (14)	2932 (4)	8·3
C(22)	−1492 (3)	5256 (14)	1542 (3)	7·7
C(23)	−1343 (3)	7228 (16)	1144 (3)	9·0
C(24)	1070 (2)	4185 (10)	2413 (2)	4·9
C(25)	4605 (2)	7581 (10)	5582 (3)	5·2
C(26)	5328 (3)	7176 (12)	5789 (3)	6·6
O(1)	−1214 (2)	5533 (7)	2258 (2)	5·8
O(2)	−1815 (3)	3738 (13)	1274 (3)	13·3
O(3)	606 (2)	5249 (11)	1782 (2)	7·8*
O(4)	4247 (2)	6226 (6)	5071 (2)	5·2
O(5)	4355 (2)	8918 (8)	5847 (3)	9·1
O(13)	147 (1)	487 (3)	215 (1)	7·9 (6)*
Molecule II				
C(1)	7068 (2)	4518 (8)	8217 (2)	4·1
C(2)	7796 (2)	4393 (9)	8320 (2)	4·6
C(3)	8215 (2)	4152 (9)	9113 (2)	4·4
C(4)	8020 (2)	2136 (10)	9431 (2)	4·9
C(5)	7290 (2)	2234 (9)	9312 (2)	4·2
C(6)	7084 (2)	292 (10)	9660 (3)	5·3
C(7)	6388 (2)	550 (11)	9622 (3)	5·4
C(8)	5869 (2)	1081 (8)	8873 (2)	4·0
C(9)	6119 (2)	2952 (7)	8506 (2)	3·7
C(10)	6824 (2)	2530 (8)	8511 (2)	3·6
C(11)	5580 (2)	3804 (8)	7797 (2)	3·7
C(12)	4928 (2)	4323 (8)	7910 (2)	3·8
C(13)	4668 (2)	2465 (8)	8242 (2)	3·7
C(14)	5228 (2)	1774 (8)	8945 (2)	4·1
C(15)	4894 (3)	241 (10)	9308 (2)	5·2
C(16)	4184 (2)	1179 (9)	9091 (2)	5·0
C(17)	4141 (2)	3089 (8)	8554 (2)	4·3
C(18)	4407 (2)	535 (9)	7714 (2)	4·6
C(19)	6868 (2)	493 (9)	8064 (3)	4·7
C(20)	3432 (2)	3431 (9)	8033 (2)	4·6
C(21)	2955 (3)	3995 (13)	8400 (3)	6·7
C(22)	3015 (2)	5372 (10)	6897 (2)	4·7
C(23)	3115 (2)	7346 (11)	6515 (3)	5·5
C(24)	5482 (2)	2363 (9)	7131 (2)	4·2
C(25)	9254 (2)	5705 (10)	9216 (2)	5·4
C(26)	9945 (3)	5198 (13)	9269 (3)	7·4
O(1)	3463 (1)	5278 (6)	7577 (1)	4·5
O(2)	2596 (2)	4025 (9)	6649 (2)	7·9
O(3)	4907 (2)	3037 (6)	6533 (2)	5·7
O(4)	8910 (2)	3912 (7)	9217 (2)	5·6
O(5)	9033 (2)	7511 (7)	9177 (2)	6·4
H(O3)	477 (3)	178 (12)	621 (3)	11·0 (18)

* Disordered with occupancies 0·86 (1) and 0·29 (1) for O(3) and O(13) respectively. H(24,2) is also disordered with positions very close to O(3) and O(13); for this reason we expected the sum of the occupancy factors to be approximately 1·125 (for O+H) instead of the refined value of 1·15.

Structure determination was by direct methods with the aid of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). The $|E|$ distribution statistics were indicative of a non-centrosymmetric space group. Structure determination was attempted in space groups $P2$ and $P2_1$ but only the latter produced a recognizable steroid skeleton for each of the two independent molecules. The model was then developed by two weighted and one unweighted Fourier maps. 79 H atoms were located from difference maps after partial refinement. Five H atoms belonging to molecule I were not located: the three on C(23), that on O(3), and one of the pair on C(24). A relatively large electron density peak (0·81 e Å^{-3}) at 1·24 (2) Å from C(24) in molecule I was attributed to an overlap of the missing H(24,2), and a partial disorder of O(3). Hence, O(3) was assumed to be disordered in two positions with different occupancies which were allowed to refine. Only the position with the higher occupancy was assigned anisotropic thermal parameters. The position with the lower occupancy is identified as O(13) in the tables.

Refinement was by block-diagonal least squares minimizing $\sum w(|F_o| - |F_c|)^2$, with $w = \{1 + [(|F_o| - 20)/20]^2\}^{-1}$ in the final cycles, excluding as well as the unobserved reflections the three strong ones ($\bar{1}11$, 012 and $\bar{1}03$) which showed extinction effects. At convergence, $R = 0·048$ for the 3267 observed reflections, $wR = 0·050$, $S = 0·73$, mean $(\Delta/\sigma) = 0·13$ for the 881 parameters, and maximum $(\Delta/\sigma) = 0·50$ (0·97 for H). The residual electron density in the final difference map was within $\pm 0·14$ e Å^{-3}. Scattering factors for the non-H atoms were from *International Tables for X-ray Crystallography* (1974), H from Stewart, Davidson & Simpson (1965). Computations employed the NRC program system (Ahmed, Hall, Pippy & Huber, 1973) and *ORTEP* (Johnson, 1976). The refined atomic parameters are listed in Table 1.*

Discussion. The *ORTEP* drawings presented in Fig. 1 show that the two independent molecules have the same absolute configuration, and that in both the 11-hydroxymethyl substituent has the β-configuration. This is in agreement with the stereochemistry tentatively suggested by Engel *et al.* (1984), and corresponds to the usually observed stereochemical course of hydroborations of olefins, from the less hindered side of the molecule, as well as to the results of certain catalytic hydrogenations in acidic media of 11-methylene steroids, which lead to 11β-methyl adducts (Elks, 1960; Kirk & Petrow, 1961). It contrasts, however, with the

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* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms, and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43151 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

result of catalytic hydrogenation of 3β,20β-diacetoxy-11-methylene-5α-pregnane, the same compound from which oxidative hydroboration led to the title compound. The former reaction, as well as the hydrogenation of the corresponding 12-oxo derivative, led to 11α-methylated products (Engel *et al.*, 1984, 1985).

The two molecules, shown in Fig. 1, are not exactly identical if the orientations of the side-chain substituents are taken into consideration. They exhibit some flexibility depending on the intermolecular packing environments. While the differences in torsional angles along the C(17) side chain of the two molecules are less than 8°, in the C(3) side chain the differences are much larger (*cf.* Fig. 1). The C(2)—C(3)—O(4)—C(25) changes by 43° from molecule I to molecule II. In molecule I the C(9)—C(11)—C(24)—O(3) angle differs by 90° for the two disordered positions of O(3).

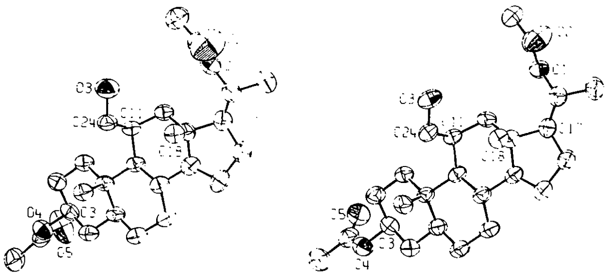

Fig. 1. Similar views of molecules I (left) and II (right) with the thermal ellipsoids drawn at 50% probability. All H atoms and the position of O(3) in molecule I with the lower occupancy have been excluded.

Bond lengths and valence angles for molecules I and II are listed in Table 2. Corresponding bond lengths in the two molecules are comparable except for the terminal C(22)—C(23) bond where a difference of 0·056 (14) Å is observed. The largest differences among corresponding valence angles, of the order 2·1 (6)–3·3 (6)°, are associated with the side-chain substituents as indicated in Table 2.

In both molecules, all the ring junctions are *trans*. Rings *A*, *B* and *C* are in the chair form, while the *D* rings are in the twist form with parameters $q_2 = 0{\cdot}44$, 0·48 Å and $\varphi_2 = 278$, 282° for molecules I and II respectively (Cremer & Pople, 1975). As might be expected, both molecules are somewhat bent because of repulsions

Table 2. *Bond lengths* (Å) *and valence angles* (°)

	I	II		I	II
C(1)—C(2)	1·527 (7)	1·524 (7)	C(12)—C(13)	1·523 (7)	1·524 (7)
C(1)—C(10)	1·539 (7)	1·527 (7)	C(13)—C(14)	1·524 (6)	1·535 (6)
C(2)—C(3)	1·513 (7)	1·508 (5)	C(13)—C(17)	1·546 (7)	1·540 (6)
C(3)—C(4)	1·504 (8)	1·516 (8)	C(13)—C(18)	1·562 (7)	1·542 (7)
C(3)—O(4)	1·451 (6)	1·457 (7)	C(14)—C(15)	1·542 (8)	1·522 (8)
C(4)—C(5)	1·503 (6)	1·519 (7)	C(15)—C(16)	1·537 (9)	1·553 (8)
C(5)—C(6)	1·534 (7)	1·523 (8)	C(16)—C(17)	1·552 (8)	1·562 (7)
C(5)—C(10)	1·553 (5)	1·549 (5)	C(17)—C(20)	1·499 (8)	1·522 (6)
C(6)—C(7)	1·493 (7)	1·498 (7)	C(20)—C(21)	1·519 (9)	1·513 (8)
C(7)—C(8)	1·542 (6)	1·534 (7)	C(20)—O(1)	1·469 (7)	1·465 (6)
C(8)—C(9)	1·553 (7)	1·559 (6)	C(22)—C(23)	1·541 (12)	1·485 (8)*
C(8)—C(14)	1·495 (7)	1·515 (7)	C(22)—O(1)	1·335 (7)	1·344 (4)
C(9)—C(10)	1·560 (7)	1·553 (7)	C(22)—O(2)	1·168 (11)	1·193 (7)
C(9)—C(11)	1·549 (6)	1·553 (6)	C(24)—O(3)	1·442 (6)	1·432 (6)
C(10)—C(19)	1·543 (6)	1·554 (7)	C(25)—C(26)	1·494 (8)	1·501 (8)
C(11)—C(12)	1·542 (7)	1·550 (7)	C(25)—O(4)	1·319 (7)	1·329 (7)
C(11)—C(24)	1·531 (6)	1·538 (6)	C(25)—O(5)	1·206 (8)	1·196 (7)
C(2)—C(1)—C(10)	113·8 (4)	113·6 (4)	C(12)—C(13)—C(14)	107·2 (4)	107·6 (4)
C(1)—C(2)—C(3)	110·7 (4)	110·1 (4)	C(12)—C(13)—C(17)	115·8 (4)	116·1 (4)
C(2)—C(3)—C(4)	111·2 (4)	111·1 (4)	C(12)—C(13)—C(18)	112·1 (4)	112·3 (4)
C(2)—C(3)—O(4)	108·7 (4)	110·7 (4)	C(14)—C(13)—C(17)	101·0 (4)	99·3 (3)
C(4)—C(3)—O(4)	109·3 (4)	107·2 (4)*	C(14)—C(13)—C(18)	111·5 (4)	112·2 (4)
C(3)—C(4)—C(5)	111·1 (4)	109·9 (4)	C(17)—C(13)—C(18)	108·7 (4)	108·8 (4)
C(4)—C(5)—C(6)	112·8 (4)	111·4 (4)	C(8)—C(14)—C(13)	116·2 (4)	116·2 (4)
C(4)—C(5)—C(10)	114·6 (4)	114·5 (4)	C(8)—C(14)—C(15)	120·9 (4)	119·4 (4)
C(6)—C(5)—C(10)	110·3 (4)	111·5 (4)	C(13)—C(14)—C(15)	104·0 (4)	104·0 (4)
C(5)—C(6)—C(7)	112·8 (4)	110·9 (4)	C(14)—C(15)—C(16)	104·2 (5)	104·0 (4)
C(6)—C(7)—C(8)	114·8 (4)	116·1 (5)	C(15)—C(16)—C(17)	106·7 (5)	105·6 (4)
C(7)—C(8)—C(9)	111·9 (4)	110·5 (4)	C(13)—C(17)—C(16)	103·8 (4)	102·9 (3)
C(7)—C(8)—C(14)	111·4 (4)	110·0 (4)	C(13)—C(17)—C(20)	118·1 (4)	118·7 (4)
C(9)—C(8)—C(14)	109·4 (4)	109·4 (4)	C(16)—C(17)—C(20)	112·2 (5)	110·9 (4)
C(8)—C(9)—C(10)	113·3 (4)	113·0 (3)	C(17)—C(20)—C(21)	113·3 (5)	114·1 (4)
C(8)—C(9)—C(11)	114·3 (4)	113·1 (3)	C(17)—C(20)—O(1)	107·5 (4)	105·0 (4)*
C(10)—C(9)—C(11)	117·0 (4)	118·4 (4)	C(21)—C(20)—O(1)	107·1 (5)	108·6 (4)
C(1)—C(10)—C(5)	106·8 (4)	107·3 (4)	C(23)—C(22)—O(1)	110·4 (6)	111·1 (4)
C(1)—C(10)—C(9)	109·7 (4)	110·4 (4)	C(23)—C(22)—O(2)	126·5 (7)	125·8 (5)
C(1)—C(10)—C(19)	109·3 (4)	108·5 (4)	O(1)—C(22)—O(2)	123·1 (7)	123·1 (5)
C(5)—C(10)—C(9)	107·0 (3)	107·3 (4)	C(11)—C(24)—O(3)	107·2 (4)	110·5 (4)*
C(5)—C(10)—C(19)	110·8 (4)	109·7 (4)	C(26)—C(25)—O(4)	111·8 (5)	112·3 (5)
C(9)—C(10)—C(19)	113·2 (4)	113·5 (4)	C(26)—C(25)—O(5)	126·3 (6)	124·3 (5)
C(9)—C(11)—C(12)	111·1 (4)	111·3 (4)	O(4)—C(25)—O(5)	121·9 (5)	123·3 (5)
C(9)—C(11)—C(24)	116·6 (4)	113·9 (4)*	C(20)—O(1)—C(22)	119·0 (5)	118·2 (3)
C(12)—C(11)—C(24)	111·9 (4)	113·5 (4)	C(3)—O(4)—C(25)	119·7 (4)	118·2 (4)
C(11)—C(12)—C(13)	115·5 (4)	114·6 (4)			

* Values which differ significantly between molecules I and II.

between the three β- and axial substituents on C(10), C(11) and C(13). The angles between the normals to rings *B* and *C* are 9·6 (6)° in molecule I and 11·6 (6)° in II; the angles between the normals to rings *A* and *D* are 26·2 (6)° in I and 26·7 (6)° in II. Pairs of the three axial substituents are splayed by amounts between 19·5 (5) and 25·0 (5)° in the two molecules.

Molecules I and II and their equivalents are interconnected by hydrogen bonds, from O(3) of I (in either of its disordered positions) to O(5) of II and from O(3) of II to O(5) of I, with O···O distances of 2·857 (7) Å [2·84 (2) Å for the position with the lower occupancy] and 2·906 (6) Å respectively. The H atom attached to O(3) of II was located at O(3)—H = 0·98 (7) Å and O(3)—H···O(5) = 158 (6)°, but that attached to O(3) of I was not located because of the disorder. The C(24)—O(3)···O(5) angle has values 92·2 (3), 97·5 (9) and 102·9 (3)° for $O(3)_I$, $O(13)_I$, and $O(3)_{II}$ respectively. The hydrogen bonds link the molecules into bundles of three interwound helices of pitch 3*b* in the *y* direction, as illustrated schematically in Fig. 2. The first helix connects molecules

$$\mathrm{I}(x,y,z)\cdots\mathrm{II}(x,y+1,z)\cdots\mathrm{I}'(1-x,y+\tfrac{3}{2},1-z)\cdots\mathrm{II}'(1-x,y+\tfrac{5}{2},1-z)\cdots\mathrm{I}(x,y+3,z),$$

the second

$$\mathrm{II}(x,y,z)\cdots\mathrm{I}'(1-x,y+\tfrac{1}{2},1-z)\cdots\mathrm{II}'(1-x,y+\tfrac{3}{2},1-z)\cdots\mathrm{I}(x,y+2,z)\cdots\mathrm{II}(x,y+3,z),$$

and the third

$$\mathrm{I}'(1-x,y-\tfrac{1}{2},1-z)\cdots\mathrm{II}'(1-x,y+\tfrac{1}{2},1-z)\cdots\mathrm{I}(x,y+1,z)\cdots\mathrm{II}(x,y+2,z)\cdots\mathrm{I}'(1-x,y+\tfrac{5}{2},1-z).$$

The helices are separated by normal van der Waals distances, as are adjacent bundles, and the unit-cell contents are identical, except for the disorder of O(3).

The fact that the pitch of a single helix is 3*b* requires that each bundle be composed of three helices, differently situated with respect to a given unit cell, but equivalent if one considers translation by one or two unit cells. The 3*b* pitch seems to arise because all four molecules (the two independent ones and the two related to them by 2_1 symmetry) are involved in each helix, and because the tilt of the molecules with respect to the *b* axis results in each molecule, with its hydrogen bond at one end, taking up approximately 0·75*b*.

This hydrogen-bonding scheme is very unusual; we are not aware of any other comparable example. In an attempt to find one, a search was made of the NBS Crystal Data database for steroids with space group $P2_1$ and $Z = 4$, resulting in 93 unique 'hits'. In no case was such a packing arrangement described. It is, of course, possible that an example exists in some space group/chemical class/*Z* combination, possibly unrecognized by the author(s), as packing arrangements are not always examined. However, the whole process was time-consuming enough to discourage us from widening our search.

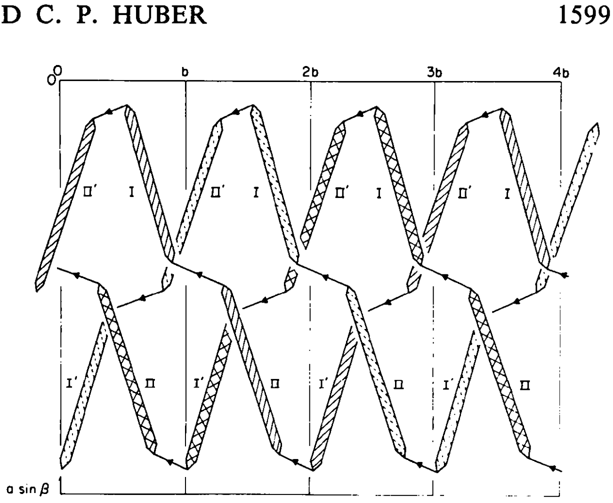

Fig. 2. Schematic drawing of the helices formed by the intermolecular hydrogen bonds. Each ribbon represents one molecule starting at O(3) (the donor atom) and ending at O(5) (the acceptor). Each hydrogen bond is drawn as a solid line with an arrow from O(3) to the nearest O(5). Molecules I and II are at (x, $y \pm n$, z), while I′ and II′ are their equivalents at ($1 - x$, $\frac{1}{2} + y \pm n$, $1 - z$) where n is an integer.

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