exemplified in Fig. 4(a) is distinctly better than in Fig. 4(b) with respect to the usual charge-transfer type of overlap (Prout & Kamenar, 1973); however, the distance between molecules is only 0·01 Å shorter in Fig. 4(a) than in Fig. 4(b). Although the overlap in Fig. 4(a) is reminiscent of that found in $\pi$–$\pi^*$ molecular complexes we feel that the magnitude of the distance between parallel molecules and the similarity of this distance for the two types of overlap is evidence that this merely reflects the most efficient packing of parallel molecules without any formal charge-transfer interactions.

## References

CHERIN, P. (1973). Amer. Cryst. Assoc. Summer Meeting, Univ. of Connecticut, Storrs, Connecticut, Abstract G2, p. 149.

DONOHUE, J. (1968). Structural Chemistry and Molecular Biology, edited by A. RICH & N. DAVIDSON, pp. 443–465. San Francisco: Freeman.

GRAINGER, C. T. & McCONNELL, J. F. (1969). Acta Cryst. B25, 1962–1970.

GUGGENBERGER, L. J. (1968). Inorg. Chem. 7, 2260–2264.

HAMILTON, W. C. & IBERS, J. A. (1968). Hydrogen Bonding in Solids, p. 262. New York: Benjamin.

HANSON, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). Acta Cryst. 17, 1040–1044.

JOHNSON, C. K. (1965). ORTEP. Oak Ridge National Laboratory Report ORNL-3794.

KENNARD, O., WATSON, D. G., ALLEN, F. H., ISAACS, N. W., MOTHERWELL, W. D. S., PETTERSON, R. C. & TOWN, W. G. (1972). Molecular Structures and Dimensions, Vol. A1. Utrecht: Oosthoek.

KUDER, J. E. (1972). Tetrahedron, 28, 1973–1981.

MEZ, H. C. (1968). Ber. Bunsenges. Phys. Chem. 72, 389–392.

PENDERGRASS, D. B. JR, PAUL, I. C. & CURTIN, D. Y. (1972). J. Amer. Chem. Soc. 94, 8730–8737.

PROUT, C. K. & KAMENAR, B. (1973). Molecular Complexes, Vol. 1, edited by R. FOSTER, pp. 151–207. New York: Crane & Russak.

WILLIAMS, D. E. (1964). PACK2, a Fortran Crystallographic Molecular Packing Program, USAEC Report IS-1042. PACK5 is a later-version packing program (private communication).

WILLIAMS, D. E. (1969). Acta Cryst. A25, 464–470.

# The Crystal and Molecular Structure of 3β-Hydroxy-20-oxo-5-pregnene-16α-carbonitrile

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The synthetic steroid 3β-hydroxy-20-oxo-5-pregnene-16α-carbonitrile, $C_{22}H_{31}O_2N$, is a potent inducer of liver microsomal enzymes. The structure was determined from room-temperature counter-collected data by the application of direct methods. The space group is $P2_1$ with cell dimensions $a = 12\cdot204$ (2), $b = 6\cdot300$ (1), $c = 12\cdot273$ (2) Å and $\beta = 95\cdot47$ (2)°; $D_m = 1\cdot20$, $D_x = 1\cdot207$ g cm$^{-3}$ for $Z = 2$. 1825 intensities were measured. The structure was refined by conventional least-squares techniques to an $R$ index of 3·0%. The structure packs in antiparallel chains held together by van der Waals forces. There is one OH···O hydrogen bond of 2·883 Å within the chains.

## Introduction

From extensive studies of the effect of steroids on body resistance (Selye, 1970, 1971) it has become evident that in addition to the two previously explored protective mechanisms (nervous and immunologic) there exists a third defense system with which the organism can respond, the steroidal one. In this respect the steroids are generally classified as: (a) syntoxic, if they protect against a pathogen by increasing the tolerance towards it, by suppressing non-specific inflammatory reactions against it (glucocorticoids) and (b) catatoxic, if they actually destroy the aggressor through the induction of hepatic microsomal or other enzymes.

Some catatoxic steroids are also endowed with classic hormonal activities, but the catatoxic effect does not depend on any other known pharmacological action; indeed, the synthetic steroid pregnenolone-16α-carbonitrile (PCN: Fig. 1), a very potent catatoxic steroid, is devoid of any other steroidal activity or toxic property.

We undertook the X-ray analyses of some of these

steroids in the hope of finding structural and/or conformational features that could be correlated with their activity. Here we report on the structure of PCN (Fig. 1).

## Experimental

Crystals of PCN* were grown from acetone solution by slow evaporation at room temperature. The space group was determined as $P2_1$ ($0k0$, for $k = 2n$ only) and the crystal data are: $C_{22}H_{31}O_2N$, M.W. 341·5, space group $P2_1$; $a = 12·204$ (2), $b = 6·300$ (1), $c = 12·273$ (2) Å; $\beta = 95·47$ (2)°; $V = 939·3$ Å$^3$; $F(000) = 372$; $\mu = 6·20$ cm$^{-1}$; $D_m = 1·20$ g cm$^{-3}$ (by flotation), $Z = 2$, $D_x = 1·207$ g cm$^{-3}$.

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A crystal of dimensions $0·17 \times 0·45 \times 0·20$ mm was mounted on a Picker FACS-1 four-circle diffractometer with its $b$ axis coincident with the fibre axis. The intensities of 1825 reflexions with $2\theta$ less than 127° were measured by the $\theta$–$2\theta$ scan technique with a scan rate of 1° min$^{-1}$ and a scan range of 1·7°, employing stationary-crystal stationary-counter background counts of 40 s at each end of the scan range, using Ni-filtered Cu $K\alpha$ radiation. Lorentz–polarization and absorption corrections were applied. The calculated transmission coefficients, based on a linear absorption coefficient of 6·2 cm$^{-1}$ for Cu $K\alpha$ radiation, ranged from 0·851 to 0·915.

The integrated net intensity was calculated as

$$I = N_T - 0·5(t_T/t_B)(B_1 + B_2)$$

where $N_T$ is the number of counts over the scan range, $t_T$ is the scan time and $t_B$ is the time for each background



Fig. 1. Bond distances and angles
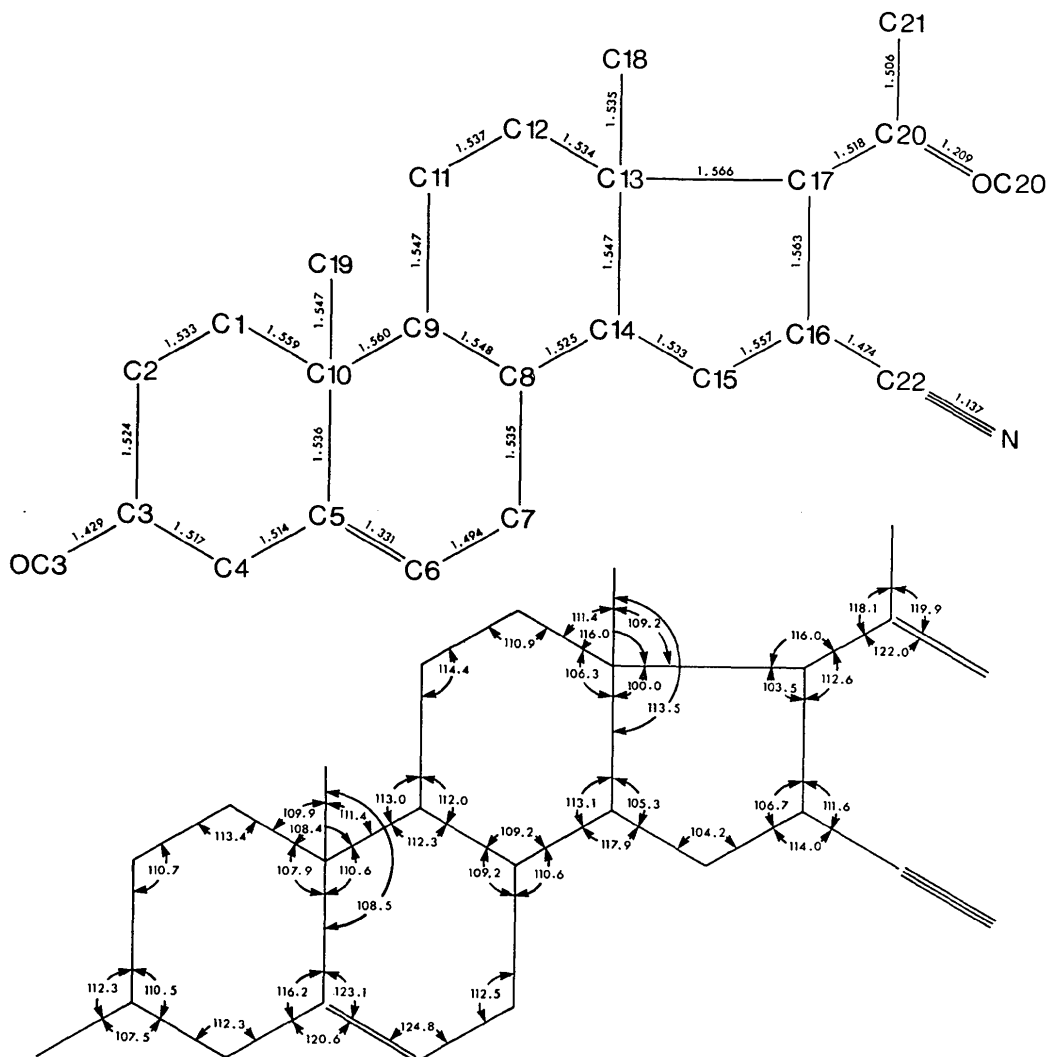
count $B_1$ and $B_2$. The standard deviations $\sigma^2(I) = 1/T^2[N_T+0\cdot25(t_T/t_B)^2(B_1+B_2)+(KN)^2+(0\cdot25)^2(N_c-N)^2]$ where $T$ is the transmission coefficient, $N$ is the net counts, $N_c$ is the net counts corrected for absorption, $K$ is a factor to account, among other things, for instrumental instability during data collection (for this case $K$ was 0·032). The last term in the brackets is a factor accounting for errors in the absorption correction. Only data for which $I > 1\cdot25\sigma(I)$ were used, which left 1762 reflexions to be entered into the least-squares refinement.

The programs used were locally modified versions of the NRC crystallographic programs (Ahmed, Hall, Pippy & Huber, 1966) and *NUCLS*, originally *ORFLS*, modified by Doedens & Ibers, further modified by J. Sygusch to include block-diagonal approximation and secondary extinction correction.

## Structure determination and refinement

The phases of the 199 largest ($E > 1\cdot5$) normalized structure factors were determined by application of the symbolic addition technique and tangent refinement using the *MULTAN* direct-phasing program (Germain, Main & Woolfson, 1971). The values of the phases that were fixed by the program for the tangent refinement were as follows: $50\bar{8}$ ($\varphi = 360°$), $51\bar{9}$ ($\varphi = 360°$), 709 ($\varphi = 360°$) to define the origin and 222 ($\varphi = \pm 45$, $\pm 135°$), $60\bar{2}$ ($\varphi = 0$, $180°$) and 056 ($\varphi = +45$, $+135°$). The enantiomorph was fixed by reflexion 056. The program generated 16 solutions and the one with the highest absolute figure of merit (1·27) was chosen.

The $E$ map calculated with these 199 reflexions revealed the positions of 15 non-hydrogen atoms. It required three Fourier maps and several preliminary

Table 1. *Positional and thermal* ($\times 10^4$) *parameters for the non-hydrogen atoms*

Thermal parameters are listed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2}+2U_{12}hka^*b^*+\ldots)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| C(1) | 7031 (2) | 7518 (3) | −678 (1) | 572 (8) | 420 (9) | 414 (7) | 54 (3) | 14 (3) | 48 (3) |
| C(2) | 6944 (2) | 7823 (3) | −1922 (1) | 574 (8) | 533 (9) | 415 (7) | 44 (4) | −2 (3) | 71 (3) |
| C(3) | 7964 (1) | 6975 (3) | −2392 (1) | 471 (7) | 557 (9) | 418 (7) | −22 (3) | 6 (3) | 51 (4) |
| C(4) | 8135 (1) | 4658 (3) | −2102 (1) | 501 (8) | 547 (9) | 405 (7) | 28 (3) | 41 (3) | 24 (4) |
| C(5) | 8163 (1) | 4265 (3) | −883 (1) | 388 (6) | 409 (8) | 393 (6) | 0 (3) | 16 (2) | 23 (3) |
| C(6) | 8998 (1) | 3227 (3) | −352 (1) | 401 (7) | 569 (9) | 479 (8) | 50 (8) | 62 (3) | 49 (4) |
| C(7) | 9101 (1) | 2753 (3) | 845 (1) | 390 (6) | 631 (9) | 469 (8) | 85 (3) | 31 (2) | 74 (4) |
| C(8) | 8008 (1) | 2997 (2) | 1349 (1) | 321 (5) | 342 (6) | 365 (6) | 25 (2) | 4 (2) | 13 (2) |
| C(9) | 7456 (1) | 5096 (2) | 949 (1) | 343 (6) | 317 (7) | 383 (6) | 15 (2) | −7 (2) | 19 (2) |
| C(10) | 7198 (1) | 5158 (2) | −318 (1) | 318 (5) | 356 (7) | 367 (6) | 6 (2) | −4 (2) | 23 (2) |
| C(11) | 6448 (1) | 5630 (3) | 1568 (1) | 455 (7) | 473 (8) | 395 (7) | 96 (3) | 11 (3) | 39 (3) |
| C(12) | 6654 (1) | 5443 (3) | 2818 (1) | 514 (7) | 377 (8) | 390 (7) | 75 (3) | 16 (3) | 9 (3) |
| C(13) | 7122 (1) | 3260 (2) | 3149 (1) | 336 (5) | 301 (6) | 329 (5) | 6 (2) | −9 (2) | 1 (2) |
| C(14) | 8196 (1) | 3023 (2) | 2593 (1) | 301 (5) | 340 (6) | 381 (6) | 7 (2) | −9 (2) | 11 (2) |
| C(15) | 8797 (1) | 1136 (3) | 3161 (1) | 442 (7) | 523 (9) | 378 (6) | 79 (3) | 5 (2) | 45 (3) |
| C(16) | 8443 (1) | 1190 (3) | 4346 (1) | 383 (6) | 381 (7) | 396 (6) | 18 (2) | −7 (2) | 30 (3) |
| C(17) | 7582 (1) | 3006 (3) | 4376 (1) | 370 (5) | 340 (7) | 351 (6) | 12 (2) | −9 (2) | −0 (2) |
| C(18) | 6285 (1) | 1494 (3) | 2847 (1) | 367 (6) | 464 (8) | 446 (7) | −43 (3) | −4 (2) | −7 (3) |
| C(19) | 6159 (1) | 3855 (4) | −690 (1) | 385 (6) | 659 (9) | 419 (7) | −53 (3) | −12 (2) | 9 (4) |
| C(20) | 6738 (1) | 2571 (3) | 5176 (1) | 443 (7) | 566 (9) | 328 (6) | 29 (3) | −0 (2) | 5 (3) |
| C(21) | 5873 (2) | 4226 (4) | 5306 (2) | 548 (8) | 711 (14) | 548 (9) | 70 (4) | 57 (3) | −13 (5) |
| C(22) | 9363 (1) | 1467 (3) | 5198 (1) | 490 (8) | 436 (9) | 487 (8) | 40 (3) | −32 (3) | 38 (3) |
| O(3) | 7893 (1) | 7141 (3) | −3557 (1) | 792 (9) | 722 (9) | 443 (6) | 27 (4) | 53 (2) | 88 (3) |
| O(20) | 6749 (1) | 596 (3) | 5705 (1) | 692 (9) | 778 (9) | 596 (7) | 82 (4) | 93 (3) | 146 (4) |
| N(22) | 10069 (2) | 1681 (4) | 5859 (2) | 727 (9) | 612 (9) | 718 (9) | 49 (4) | −158 (4) | 4 (5) |
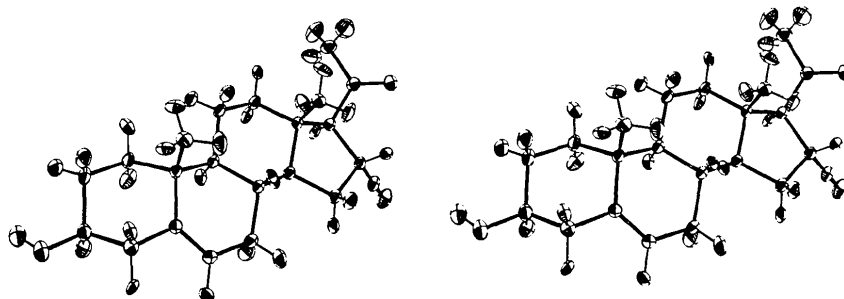


Fig. 2. A stereoscopic view of the structure showing 25 % probability ellipsoids.

cycles of full-matrix least-squares refinement, using isotropic thermal parameters and unit weights, in order to locate all non-hydrogen atoms. At this point the $R$ value was 0·135. Introducing anisotropic temperature factors and a secondary extinction correction reduced $R$ to 0·095. A three-dimensional difference Fourier map revealed the positions of ten hydrogen atoms. Inclusion of these in the refinement and a calculation of a second difference Fourier map revealed the positions of the remaining hydrogen atoms. Refinement was continued using the block-diagonal least-squares approximation in blocks of $9 \times 9$. Inclusion and refinement of the hydrogen positions as well as isotropic temperature factors for hydrogen atoms reduced $R$ to 0·032. At this stage a counting-statistics
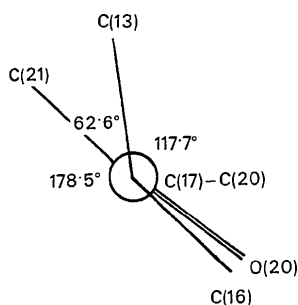
weighting scheme was introduced giving $R = 0·031$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2} = 0·042$. Allowing the hydrogen atoms also to refine anisotropically gave $R = 0·030$ and $R_w = 0·038$ (observed data, 1762 reflexions) and $R_w = 0·038$ (including unobserved data, 1816 reflexions). A difference Fourier map at this point showed no peak higher than 0·11 e Å$^{-3}$. The final secondary extinction parameter $g$ (Åsbrink & Werner, 1966), was $0·21(3) \times 10^4$. The function $\sum w(|F_o| - |F_c|)^2/N$, where $N$ is the number of reflexions in the particular range, showed no significant variation with $|F_o|$, $h$ (the slowest varying index during data collection) or $\sin \theta/\lambda$. Average and maximum shifts in the final least-squares refinement were 0·2$\sigma$ and 0·4$\sigma$ respectively. Tables 1 and 2 show the final positional and thermal parameters for the non-hydrogen and hydrogen atoms respectively. The scattering factors for all non-hydrogen atoms are from Cromer & Waber (1965) and for hydrogen from Stewart, Davidson & Simpson (1965).* No attempt was made to determine the absolute configuration of the molecule. However, the configuration that appears in Fig. 2, and the parameters reported in Tables 1 and 2, correspond to the absolute



Fig. 3. Newman projection down the C(17)–C(20) bond.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30756 (19 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Positional and thermal* ($\times 10^3$) *parameters for the hydrogen atoms*

Thermal parameters are listed in the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

| | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| H(1$A$) | 772 (2) | 831 (5) | −34 (2) | 60 (16) | 50 (17) | 93 (21) | 1 (7) | −7 (7) | 2 (8) |
| H(1$B$) | 636 (2) | 808 (5) | −39 (2) | 71 (16) | 76 (20) | 48 (14) | 1 (8) | 12 (6) | 8 (7) |
| H(2$A$) | 682 (2) | 935 (5) | −213 (2) | 70 (15) | 70 (19) | 47 (14) | 9 (7) | 5 (6) | 5 (7) |
| H(2$B$) | 628 (2) | 700 (5) | −230 (2) | 59 (14) | 76 (20) | 41 (12) | −1 (7) | −5 (5) | 4 (7) |
| H(3) | 862 (2) | 785 (5) | −206 (2) | 53 (13) | 79 (20) | 51 (14) | 3 (7) | −2 (5) | 4 (7) |
| H(4$A$) | 882 (2) | 408 (4) | −240 (2) | 58 (13) | 42 (14) | 48 (13) | 16 (6) | 7 (5) | 8 (5) |
| H(4$B$) | 748 (2) | 384 (4) | −250 (2) | 55 (12) | 51 (15) | 32 (10) | −4 (6) | 2 (4) | 4 (5) |
| H(6) | 960 (2) | 275 (4) | −79 (2) | 35 (10) | 81 (18) | 31 (10) | 3 (6) | 4 (4) | 8 (5) |
| H(7$A$) | 971 (2) | 380 (6) | 129 (2) | 65 (16) | 85 (21) | 66 (18) | 1 (8) | −2 (6) | 5 (9) |
| H(7$B$) | 940 (2) | 131 (5) | 98 (2) | 91 (18) | 71 (19) | 40 (13) | 8 (8) | 10 (6) | 11 (6) |
| H(8) | 751 (1) | 178 (3) | 109 (1) | 42 (10) | 35 (11) | 19 (8) | −1 (4) | 3 (3) | −1 (4) |
| H(9) | 802 (2) | 619 (3) | 109 (2) | 45 (11) | 31 (12) | 35 (10) | −6 (5) | −3 (4) | 1 (4) |
| H(11$A$) | 620 (2) | 712 (4) | 136 (2) | 62 (14) | 67 (18) | 48 (13) | 12 (7) | 2 (5) | 8 (6) |
| H(11$B$) | 584 (2) | 466 (4) | 130 (2) | 54 (13) | 57 (16) | 40 (12) | 3 (6) | −5 (5) | −1 (5) |
| H(12$A$) | 721 (2) | 648 (4) | 314 (2) | 67 (15) | 35 (14) | 69 (16) | 7 (6) | −2 (6) | 7 (6) |
| H(12$B$) | 597 (2) | 568 (4) | 312 (2) | 75 (15) | 57 (16) | 30 (11) | 14 (6) | 15 (5) | 9 (5) |
| H(14) | 861 (1) | 430 (4) | 279 (1) | 43 (11) | 43 (13) | 22 (9) | −5 (5) | −1 (4) | 0 (4) |
| H(15$A$) | 956 (2) | 127 (4) | 315 (2) | 42 (12) | 68 (17) | 54 (14) | 3 (6) | −1 (5) | 18 (7) |
| H(15$B$) | 857 (2) | −26 (4) | 277 (2) | 64 (14) | 51 (15) | 31 (11) | 8 (6) | −0 (5) | 0 (5) |
| H(16) | 809 (1) | −16 (4) | 451 (2) | 28 (9) | 51 (14) | 43 (12) | 3 (5) | −0 (4) | 5 (5) |
| H(17) | 798 (2) | 428 (4) | 460 (2) | 57 (13) | 48 (15) | 39 (11) | 12 (6) | −5 (5) | 2 (5) |
| H(18$A$) | 607 (2) | 132 (4) | 207 (2) | 74 (16) | 57 (17) | 36 (12) | −8 (7) | 3 (5) | 0 (6) |
| H(18$B$) | 562 (2) | 169 (5) | 319 (2) | 40 (12) | 101 (24) | 65 (16) | −12 (8) | 7 (5) | 2 (8) |
| H(18$C$) | 656 (2) | 17 (4) | 312 (2) | 62 (15) | 45 (17) | 105 (23) | 6 (7) | −8 (7) | 12 (7) |
| H(19$A$) | 623 (2) | 238 (6) | 946 (2) | 73 (18) | 101 (28) | 68 (18) | −5 (9) | −8 (7) | 22 (9) |
| H(19$B$) | 604 (2) | 356 (4) | 853 (2) | 34 (10) | 57 (17) | 42 (12) | 3 (5) | 5 (4) | −5 (6) |
| H(19$C$) | 552 (1) | 468 (5) | 949 (2) | 24 (10) | 80 (19) | 49 (12) | −4 (6) | −3 (4) | −8 (6) |
| H(21$A$) | 377 (2) | 41 (5) | 466 (3) | 64 (18) | 90 (28) | 132 (30) | 2 (9) | 17 (9) | 6 (11) |
| H(21$B$) | 556 (3) | 405 (7) | 595 (2) | 110 (25) | 129 (33) | 78 (22) | 15 (13) | 20 (9) | 8 (12) |
| H(21$C$) | 528 (2) | 421 (6) | 467 (2) | 93 (21) | 88 (24) | 49 (16) | 13 (10) | −10 (7) | −5 (8) |
| H(O3) | 237 (3) | 333 (6) | 371 (2) | 104 (23) | 87 (24) | 73 (20) | −14 (10) | 15 (8) | −16 (9) |

configuration as determined by the synthesis* of the compound.

## Thermal vibration analysis†

The shapes and orientations of the thermal vibration ellipsoids are shown in Fig. 2. When the thermal motion of the molecule is analysed in terms of the rigid-body motion of the steroid nucleus, C(1)–C(17), plus C(18) and C(19), we find that the molecule does in fact behave very nearly as a rigid body. The root-mean-square differences (Table 3) between the $U_{ij}$ terms calculated from the anisotropic $\beta_{ij}$ terms and those calculated from rigid-body parameters are only 0·002 Å² for the above-mentioned 19 atoms. The other substituent groups, however, have a small amount of additional independent motion. The rigid-body motions are principally translational, and are almost isotropic with an average amplitude of translation of 0·18 Å. Rotational motion (Table 4) is limited by the close packing of the irregularly shaped molecules, and amounts to only 5·5° about the long axis of the molecule. The positional parameters were corrected for the librational motion (Schomaker & Trueblood, 1968) and these corrected parameters were used in all intramolecular geometry calculations not involving hydrogen atoms. This correction resulted in a systematic lengthening of the bonds by an average of 0·003 Å, the largest correction being 1σ.

## Discussion

The interatomic distances and angles which are presented in Fig. 1 are normal. A wide range of C($sp^3$)–C($sp^3$) bond lengths is found with values ranging from 1·517 (5) to 1·566 (5) Å. This is most likely the result of (a) interaction between non-bonded neighbouring substituents, (b) the effect of ring closure and (c) the effect of electron-withdrawing substituents. It will be noticed that the longest bonds [C(13)–C(17) = 1·566, C(16)–C(17) = 1·563, C(9)–C(10) = 1·560 Å are

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* Dr P. Kourounakis, private communications.
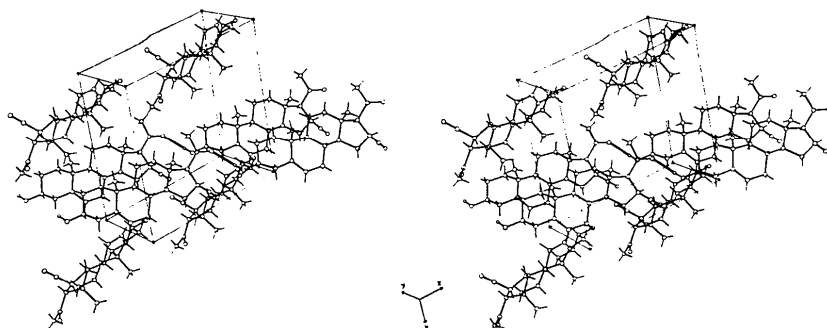† All rigid-body calculations were carried out by use of Schomaker & Trueblood's (1968) program.

between carbon atoms which have non-hydrogen substituents (larger non-bonded interactions) some of which are electron withdrawing (methyl group, CN,

Table 3. *Differences between $U_{ij}$ derived from the input $B_{ij}$ and those calculated from the rigid-body parameters*

The atoms are numbered in the same order as in Fig. 1. The differences are × 10⁴ Å².

$$\sigma(U) = \left[\frac{\sum(\Delta U_{ij})^2}{114-20}\right]^{1/2} = 0{\cdot}0022 \text{ Å}^2.$$

| | | | | | |
|---|---|---|---|---|---|
| 1 | −1 | −10 | −7 | 5 | 15 | 9 |
| 2 | 2 | −7 | −14 | −7 | −13 | 17 |
| 3 | −19 | 21 | 1 | −14 | 0 | −1 |
| 4 | 19 | 20 | 5 | 33 | 25 | −11 |
| 5 | 5 | −31 | −2 | −27 | −4 | 1 |
| 6 | −31 | −43 | 28 | −44 | 25 | −16 |
| 7 | 20 | 27 | 14 | 22 | −7 | 24 |
| 8 | 2 | 17 | −14 | 17 | 0 | 9 |
| 9 | 5 | 3 | 8 | 9 | −2 | 22 |
| 10 | −19 | −32 | −8 | −3 | 2 | 15 |
| 11 | 24 | 23 | −5 | 33 | −4 | 23 |
| 12 | −11 | −5 | −4 | −6 | −7 | −6 |
| 13 | 11 | −7 | −33 | −15 | −9 | 6 |
| 14 | −2 | 3 | −2 | −3 | −3 | −4 |
| 15 | 36 | 38 | −59 | 7 | −22 | −9 |
| 16 | −7 | −37 | −10 | −33 | −8 | −8 |
| 17 | −27 | 28 | −11 | 17 | 3 | 2 |
| 18 | −8 | −16 | 70 | 16 | −7 | −36 |
| 19 | 4 | 8 | 43 | −8 | 16 | −38 |

Table 4. *Rigid-body vibration parameters for the nuclei,* C(1)–C(19)

Standard deviations are given in parentheses.

Components of the tensors T, L and S (× 10⁴)

| T (Å²) | 309 (8) | 9 (7) | −45 (5) |
|---|---|---|---|
| | | 312 (9) | 10 (6) |
| | | | 371 (5) |
| L (rad²) | 7 (1) | 4 (1) | −10 (1) |
| | | 14 (1) | −25 (1) |
| | | | 83 (3) |
| S (Å × rad) | 6 (3) | 12 (1) | 3 (1) |
| | 3 (1) | 5 (3) | 8 (2) |
| | 8 (2) | 4 (2) | −11 (22) |

Magnitudes of principal axes

| T (Å) | 0·20 | 0·18 | 0·17 |
|---|---|---|---|
| L (°) | 5·5 | 1·5 | 1·3 |



Fig. 4. A stereoscopic view of the molecular packing (*ORTEP* program by C. K. Johnson).

## Table 5. *Torsion angles in the rings*

The sign convention for the direction of the torsion angle is that of Klyne & Prelog (1960). $\varphi_{A-B}$ is the torsion angle about the $A$–$B$ bond, in which the other two atoms required to define the angle are those attached to either end of the bond and are in the ring in question.

| Ring $A$ | | Ring $B$ | | Ring $C$ | | Ring $D$ | |
|---|---|---|---|---|---|---|---|
| Bond | $\varphi_{A-B}$ | Bond | $\varphi_{A-B}$ | Bond | $\varphi_{A-B}$ | Bond | $\varphi_{A-B}$ |
| C(1)–C(2) | −57·8° | C(5)–C(6) | 1·3° | C(8)—C(9) | −49·7° | C(13)–C(14) | 44·7° |
| C(2)–C(3) | 57·4 | C(6)–C(7) | 16·8 | C(9)—C(11) | 48·3 | C(14)–C(15) | −30·8° |
| C(3)–C(4) | −54·2 | C(7)–C(8) | −46·4 | C(11)–C(12) | −53·4 | C(15)–C(16) | 4·3 |
| C(4)–C(5) | 52·0 | C(8)–C(9) | 61·1 | C(12)–C(13) | 58·5 | C(16)–C(17) | 23·0 |
| C(5)–C(10) | −48·9 | C(9)–C(10) | −42·7 | C(13)–C(14) | −64·4 | C(13)–C(17) | −40·6 |
| C(1)–C(10) | 51·5 | C(5)–C(10) | 11·8 | C(8)—C(14) | 59·9 | | |

C=O). Bonds C(9)–C(10) and C(13)–C(17) are also the longest in the dexamethasome acetate structure (Terzis & Theophanides, 1975). The C(16)–C(22) distance of 1·474 Å compares well with other $sp^3$–$sp$ C–C bonds (Kornblau & Hughes, 1964). All C–H bond lengths vary between 0·94 and 1·04 Å with standard deviations between 0·04 and 0·06 Å. The O(3)–H(O3) distance is 0·83 (4) Å. The tetrahedral angles involving hydrogen atoms vary between 103 and 115° with standard deviations of 3–5°. The H(6)–C(6)–C(5) and H(6)–C(6)–C(7) angles are 117 and 118° respectively. A table of these bond lengths and angles is available.* As shown by the intraring torsional angles in Table 5, the $A$ and $C$ rings have chair conformations and the $B$ ring has a half-chair conformation. The $D$-ring conformation is intermediate between a half chair and a C(13) or $\beta$-envelope, as shown by the parameters $\Delta = 23·4$ and $\varphi_m = 45·7$ (Altona, Geise & Romers, 1968) and the torsional angles in Table 5. The C(17) side-chain orientation, which may be observed in Fig. 2, resembles the orientation in similar structures. However, as shown in the Newman projection (Fig. 3) O(20) and C(16) are almost eclipsed (torsional angle O(20)–C(20)–C(17)–C(16) = −1·2°). In ten structures having 17(H) and 21(H$_3$) substituents this angle varies from −6 to −30° (average = 17°).† The conformation in the present structure is outside this range and is probably influenced by the intermolecular hydrogen bond O(20)···H–O(3) (2·883 Å, 168°) (Fig. 4).

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* This table has been deposited with the structure factors (see footnote on page 793).
† We thank Dr W. L. Duax for this information.

### References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). NRC Crystallographic Programs for the IBM 360 system. *World List of Crystallographic Computer Programs*, 2nd ed., Appendix, p. 52. Utrecht: Oosthoek.

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **B18**, 104–109.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* **A27**, 368–376.

Klyne, W. & Prelog, V. (1960). *Experientia*, **16**, 521–523.

Kornblau, M. J. & Hughes, R. E. (1964). *Acta Cryst.* **17**, 1033–1036.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.

Selye, H. (1970). *Rev. Canad. Biol.* **29**, 49.

Selye, H. (1971). *Hormones and Resistance.* Berlin–Heidelberg–New York: Springer-Verlag.

Stewart, J., Davidson, R. & Simpson, A. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Terzis, A. & Theophanides, T. (1975). *Acta Cryst.* **B31**, 796–801.

Åsbrink, S. & Werner, P. E. (1966). *Acta Cryst.* **20**, 407–410.