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The Conformation of Non-Aromatic Ring Compounds.
XCIV. The Crystal and Molecular Structure of the 3,5-Dinitrobenzoate Ester of Toxisterol *C*₁ at −170°C

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Toxisterol C_1 is an irradiation product of previtamin D. Crystals of the 3,5-dinitrobenzoate derivative, $C_{34}H_{46}O_6N_2$, are monoclinic. The lattice dimensions at −170°C are $a=8{\cdot}912$ (3), $b=7{\cdot}316$ (3), $c=24{\cdot}889$ (5) Å, $\beta=98{\cdot}93$ (5)°. The space group is $P2_1$ and $Z=2$. The structure was solved by Patterson methods, the dinitrobenzoate group serving as the known part of the molecular structure. The least-squares refinement resulted in unweighted and weighted indices $R=3{\cdot}54$ and $R_w=4{\cdot}13$%. The photo-induced rearrangement of the triene system of previtamin D has generated a closed-ring structure in which C(10) is connected to C(6) and C(5) to C(9). The result is a bicyclo[3,1,0]hexene system consisting of a cyclopropane ring C(5)–C(6)–C(10), and a nearly planar cyclopentene ring C(5)–C(6)–C(7)=C(8)–C(9). Methyl group C(19) is in the α-configuration. Ring *A* is heavily distorted and displays a half-chair conformation, while the dinitrobenzoate ester group is 3α (axially) oriented with respect to ring *A*.

Introduction

Irradiation of previtamin D_3 during extended periods (48 h or longer) below 5°C results in the formation of toxisterols (Boomsma, Jacobs, Havinga & van der Gen, 1975). From UV, IR, NMR and mass spectroscopy it was deduced that the major component C_1 of the irradiation mixture contains a [3,1,0]hexene system; the configuration of the relevant asymmetric centres 9, 10 and 6 could not, however, be settled beyond doubt. Of the four possible configurations, *i.e.* 9α,10α,6β(*H*); 9β,10α,6β(*H*); 9α,10β,6α(*H*) and 9β,10β,6α(*H*) the first seems most probable (Boomsma, 1975). A definite establishment of the configuration also reveals whether the reaction mechanism is a concerted one obeying the symmetry rules of Woodward & Hoffmann, or a multi-step mechanism.

There are two reasons why the 3,5-dinitrobenzoate ester of toxisterol C_1 was chosen for this X-ray investigation: We did not succeed in preparing single crystals of the mother compound toxisterol C_1 suitable for quantitative diffraction measurements. Introduction of an aromatic and highly polar moiety such as the 3,5-dinitrobenzoate group (DNB) very often, as in this case, enhances the crystallization process. Moreover, it has been shown that the presence of DNB with known molecular geometry facilitates the search with Patterson methods (Braun, Hornstra & Leenhouts, 1969). Accordingly the structures of the 3,5-dinitrobenzoate ester of pyrocalciferol (PCD; de Kok & Romers, 1975) and isopyrocalciferol (IPCD; de Kok, Romers & Hoogendorp, 1975) were solved.

The numbering of atoms of the title compound (hereafter DTC) is indicated in Figs. 1(*a*) and 4. Note that this accords with the numbering in previtamin D, but differs from the rules (IUPAC–IUB Commission on Biochemical Nomenclature, 1972) for numbering in the steroid system.

Experimental

The isolation of toxisterol C_1 has been described elsewhere (Boomsma, 1975). Treatment with 3,5-dinitrobenzoyl chloride gave the dinitrobenzoate ester DTC. Recrystallization from acetone/methanol yielded pale-yellow, lath-shaped monoclinic crystals. The lattice dimensions at 20°C and at −170°C (Table 1) were measured on a three-circle diffractometer using Cu *Kα* radiation ($\lambda=1{\cdot}5418$ Å). The reflexions 0*k*0 are absent for *k* odd; since DTC is optically active the space group is $P2_1$.

Table 1. *Crystal data for DTC*
(3,5-*dinitrobenzoate ester of toxisterol* C_1)

Molecular composition $C_{34}H_{46}O_6N_2$, $M=590{\cdot}7$
Two molecules per unit cell, space group $P2_1$

20°C	−170°C
$a=8{\cdot}86$ (1) Å	$a=8{\cdot}912$ (3) Å
$b=7{\cdot}31$ (1)	$b=7{\cdot}316$ (3)
$c=25{\cdot}69$ (1)	$c=24{\cdot}899$ (5)
$\beta=98{\cdot}1$ (1)°	$\beta=98{\cdot}93$ (5)°
$d_{obs}=1{\cdot}11$ g cm^{-3}	$F(000)=736$
$d_{calc}=1{\cdot}17$	μ(Cu $K\alpha$) $=6{\cdot}66$ cm^{-1}

Observed significant reflexions	1710
Reflexions less than twice the background	98
Non-observed reflexions	9

The reflexion intensities of a crystal with dimensions $0{\cdot}34\times0{\cdot}24\times0{\cdot}12$ mm were collected at −170°C with a three-circle diffractometer using Cu *Kα* radiation. The θ–2θ scanning mode was employed with a scan width varying between 1·1 and 1·6°. The maximum glancing angle θ was 50°. The radiation was monochromatized with graphite and one of the standard reflexions $0,1,\bar{1}\bar{1}$, $\bar{4}2\bar{2}$ or 322 was measured after each series of 29 reflexions. The standards were used for the calculation of a polynomial function of the exposure time in order to correct for loss in scattering power during the exposure. The intensities were reduced to structure factors in the usual way. No absorption correction was applied. An overall isotropic B value of 2·11 Å^2 was obtained from a Wilson plot.

Solution and refinement

The solution was achieved by means of the Patterson-search method using the DNB moiety as the known part of the molecule. The orientation and position of DNB in the unit cell were determined as described earlier. Since the presence of a cyclopropane ring might hamper the operation of the second part of the program (*i.e.* the search for the unknown moiety) we decided to carry on by computation of electron density maps, using the DNB group as the 'heavy atom' for the calculation of phases and taking observed structure factors as Fourier coefficients. It is worth while to mention that the *best* density map revealing 19 unknown atoms was obtained after inclusion of *all* observed structure factors. The remaining eight atoms were located in a second Fourier map. Surprisingly, a similar experience was encountered during the structure determination of IPCD.

The least-squares refinement of positional and thermal parameters was performed in the usual way as described earlier for PCD and IPCD. The initial model resulted in an R value of 18·0%. After refinement with individual isotropic B parameters, R dropped to 11·3% $[R=\sum(||F_o|-|F_c||)/\sum|F_o|,\ R_w=\{\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2\}^{1/2}]$.

The molecule contains 46 hydrogen atoms, 15 of which were found in a difference Fourier map. The remaining 31 hydrogen atoms were introduced at calculated positions. The refinement was resumed with isotropic B parameters for hydrogen atoms (4×4 blocks) and with anisotropic U_{ij} parameters for the heavy atoms (9×9 blocks). The anisotropic temperature factor is defined as $\exp[-2\pi^2\sum_{i,j}h_ih_ja_i^*a_j^*U_{ij}]$, $i,j=1,2,3$. The individual reflexions were weighted according to $w(hkl)=\sigma^{-2}(hkl)$ and only significant reflexions were included in the calculations. The final R and R_w values are 3·54 and 4·13%.†

The positional and thermal parameters of the heavy atoms are listed in Tables 2 and 3. The positional coordinates and B values of the hydrogen atoms are given in Table 4. The average estimated standard deviations are 0·0061, 0·0069, 0·0073, 0·0080 and 0·053 Å for the bond lengths N–O, C–O, C–N, C–C and C–H, respectively, and 0·5 and 0·7° for valency and torsion angles not involving hydrogen. A 40% increase in the machine-computed e.s.d.'s has been accounted for in these numbers, since the refinement was carried out in a block-diagonal approximation of the matrix of normal equations. The influence of the errors in lattice constants is negligible for these estimates.

Table 2. *Fractional coordinates* (×10^4) *of the heavy atoms*

Estimated standard deviations in the least significant digits are given in parentheses.

	x	y	z
C(1)	−4867 (4)	6722 (5)	1787 (2)
C(2)	−4237 (4)	8640 (5)	1740 (2)
C(3)	−2697 (4)	8591 (5)	1547 (2)
C(4)	−1512 (4)	7629 (5)	1958 (2)
C(5)	−2027 (4)	5868 (5)	2187 (2)
C(6)	−2988 (4)	5815 (5)	2656 (2)
C(7)	−2378 (4)	4304 (5)	3012 (2)
C(8)	−1274 (3)	3386 (5)	2812 (2)
C(9)	−895 (4)	4291 (5)	2306 (2)
C(10)	−3724 (4)	5337 (5)	2078 (2)
C(11)	809 (4)	4787 (5)	2410 (2)
C(12)	1827 (4)	3190 (7)	2637 (2)
C(13)	1359 (4)	2306 (5)	3149 (2)
C(14)	−340 (4)	1789 (5)	3011 (2)
C(15)	−656 (4)	621 (5)	3485 (2)
C(16)	846 (4)	−453 (5)	3646 (2)
C(17)	2031 (3)	392 (5)	3319 (2)
C(18)	1623 (4)	3637 (5)	3632 (2)
C(19)	−4212 (4)	3400 (5)	1929 (2)
C(20)	3669 (3)	239 (5)	3626 (2)
C(21)	4832 (4)	1059 (7)	3304 (2)
C(22)	4062 (4)	−1760 (5)	3767 (2)
C(23)	5550 (4)	−2104 (7)	4150 (2)
C(24)	5780 (4)	−4097 (7)	4293 (2)
C(25)	7146 (4)	−4627 (7)	4715 (2)
C(26)	8632 (6)	−3847 (8)	4589 (2)
C(27)	7265 (4)	−6674 (7)	4785 (2)
C(31)	−2230 (3)	6327 (5)	248 (2)
C(32)	−2853 (3)	4632 (5)	340 (2)
C(33)	−2972 (4)	3331 (5)	−65 (2)
C(34)	−2522 (4)	3664 (5)	−567 (2)
C(35)	−1921 (3)	5368 (5)	−643 (2)
C(36)	−1754 (4)	6692 (5)	−250 (2)
C(37)	−2047 (4)	7773 (5)	672 (2)
N(1)	−3659 (3)	1540 (4)	30 (1)
N(2)	−1459 (3)	5765 (5)	−1174 (1)
O(1)	−3679 (3)	364 (4)	−321 (1)
O(2)	−4163 (3)	1343 (4)	460 (1)
O(3)	−2918 (3)	7465 (4)	1054 (1)
O(4)	−1200 (2)	9078 (4)	669 (1)
O(5)	−1703 (3)	4604 (4)	−1533 (1)
O(6)	−841 (3)	7232 (4)	−1226 (1)

Molecular geometry

In addition to confirming the earlier structure elucidation (Boomsma *et al.*, 1975), the X-ray analysis of DTC establishes the configurations at carbon atoms 9, 10 and 6 to be 9α,10α,6β(*H*). This allows the conclusion that the photochemically induced formation of TCD from previtamin D proceeds *via* a non-concerted pathway (Boomsma, 1975).

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† A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31745 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Bond lengths, valency and endocyclic torsion angles are given in Fig. 1. The overall geometry is shown in Fig. 3. A few Newman projections along the bonds 10–5, 6–5, 8–9, 14–13 and 17–20 are depicted in Fig. 2(*a*), (*b*), (*c*), (*d*) and (*e*), while bond lengths and valency angles of the DNB moiety are shown in Fig. 2 (*f*) and (*g*).

The steroid nucleus

The mean value of the C(sp^3)–C(sp^3) bond lengths [1·531 (3) Å] compares favourably with the commonly observed value of 1·533 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). Since no force-field calculations are so far available it is hard to comment upon the observed spread, which ranges from 1·507 to 1·557 Å. It is, however, tempting to correlate the conspicuously short length of bond 10–19 (1·509 Å) with the exceptional connexion of rings *A* and *B via* the cyclopropane ring *P*. In contrast to normal 5α,9α,10β steroids, methyl group C(19) is 'free' and does not suffer from overcrowding effects by atoms as it would at C(2) and C(11) (see Fig. 3). The cyclopropane ring *P* is quite regular; the average of its three bond lengths (1·540 Å) approaches the ideal value of 1·533 Å.

The distribution of valency angles in the unmodified part of the molecule displays the usual characteristics and will not be commented upon here. Two valency angles in the modified part, *i.e.* 4–5–10 and 1–10–5, are exceptionally large (119·7 and 118·5°). These large values, and to a lesser degree those of the angles 2–1–10 and 3–4–5, are concomitant with the large deformation of ring *A*, which adopts the half-chair conformation

Table 3. *Thermal parameters* U_{ij} ($\times 10^3$ Å^2) *of the heavy atoms*

Estimated standard deviations in the least significant digits are given in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{21}$	$2U_{23}$	$2U_{31}$
C(1)	35 (2)	33 (2)	47 (2)	−3 (4)	1 (4)	35 (4)
C(2)	46 (3)	39 (3)	45 (2)	1 (4)	−6 (4)	29 (4)
C(3)	49 (3)	28 (2)	41 (2)	−4 (4)	−8 (4)	26 (4)
C(4)	46 (3)	32 (2)	44 (3)	−17 (4)	1 (4)	24 (4)
C(5)	34 (2)	36 (3)	33 (2)	−9 (4)	−12 (4)	22 (4)
C(6)	33 (2)	37 (3)	41 (2)	2 (4)	−19 (4)	35 (4)
C(7)	29 (2)	39 (3)	35 (2)	−14 (4)	−2 (4)	22 (4)
C(8)	20 (2)	33 (2)	40 (2)	−10 (4)	−3 (4)	20 (3)
C(9)	29 (2)	41 (3)	33 (2)	−18 (4)	−9 (4)	28 (3)
C(10)	30 (2)	31 (2)	41 (2)	0 (4)	−4 (4)	30 (4)
C(11)	27 (2)	51 (3)	42 (2)	−13 (4)	6 (4)	26 (4)
C(12)	24 (2)	64 (3)	39 (2)	−5 (4)	0 (4)	24 (4)
C(13)	21 (3)	37 (2)	36 (2)	−15 (4)	2 (4)	22 (3)
C(14)	26 (2)	36 (3)	37 (2)	−14 (4)	0 (4)	21 (3)
C(15)	24 (2)	47 (3)	56 (3)	−7 (4)	8 (5)	26 (4)
C(16)	23 (2)	32 (2)	58 (3)	−4 (4)	14 (4)	24 (4)
C(17)	21 (2)	43 (3)	37 (2)	−13 (4)	−6 (4)	22 (3)
C(18)	25 (2)	40 (3)	48 (3)	−15 (4)	−8 (4)	15 (4)
C(19)	27 (2)	34 (2)	48 (3)	−5 (4)	−9 (4)	22 (4)
C(20)	23 (2)	35 (2)	52 (3)	−5 (4)	−4 (4)	28 (4)
C(21)	25 (2)	58 (3)	79 (3)	−7 (5)	19 (5)	33 (4)
C(22)	20 (2)	47 (3)	49 (2)	−1 (4)	−3 (4)	8 (4)
C(23)	22 (2)	54 (3)	56 (3)	−9 (4)	−2 (5)	21 (4)
C(24)	24 (2)	55 (3)	40 (2)	−2 (4)	−5 (4)	12 (4)
C(25)	37 (2)	59 (3)	53 (3)	−1 (5)	−23 (5)	13 (4)
C(26)	30 (3)	89 (4)	93 (4)	−10 (5)	23 (7)	−8 (5)
C(27)	43 (3)	67 (3)	55 (3)	24 (5)	−17 (5)	3 (4)
C(31)	20 (2)	37 (2)	39 (2)	2 (4)	14 (4)	18 (3)
C(32)	19 (2)	44 (3)	35 (2)	−4 (4)	7 (4)	20 (3)
C(33)	21 (2)	37 (2)	41 (2)	9 (4)	5 (4)	10 (3)
C(34)	25 (2)	45 (3)	39 (2)	23 (4)	0 (4)	14 (3)
C(35)	23 (2)	49 (3)	36 (2)	22 (4)	17 (4)	21 (3)
C(36)	21 (2)	44 (3)	40 (2)	13 (4)	4 (4)	10 (4)
C(37)	23 (2)	38 (3)	48 (3)	7 (4)	17 (4)	9 (4)
N(1)	29 (2)	43 (2)	42 (2)	5 (3)	1 (3)	5 (3)
N(2)	39 (2)	53 (3)	46 (2)	19 (4)	18 (4)	28 (3)
O(1)	41 (2)	41 (2)	51 (2)	4 (3)	−25 (3)	14 (3)
O(2)	43 (2)	38 (2)	49 (2)	−9 (3)	9 (3)	28 (3)
O(3)	37 (2)	36 (2)	41 (2)	−17 (3)	−8 (3)	34 (3)
O(4)	31 (2)	46 (2)	53 (2)	−31 (3)	3 (3)	27 (3)
O(5)	47 (2)	71 (2)	40 (2)	13 (3)	−5 (3)	27 (3)
O(6)	67 (2)	53 (2)	61 (2)	0 (3)	26 (3)	63 (3)

Table 4. *Fractional coordinates* ($\times 10^3$) *and isotropic B values of the hydrogen atoms* ($\times 10$ Å^2)

Estimated standard deviations in the least significant digits are given in parentheses.

	x	y	z	B_{iso}
H(11)	−571 (4)	674 (5)	198 (1)	40 (9)
H(12)	−521 (4)	621 (5)	139 (1)	34 (8)
H(21)	−493 (4)	926 (5)	148 (1)	34 (8)
H(22)	−417 (4)	915 (5)	210 (1)	32 (8)
H(3)	−236 (4)	986 (5)	144 (1)	38 (8)
H(41)	−63 (4)	739 (5)	175 (1)	29 (7)
H(42)	−115 (4)	840 (5)	227 (1)	35 (8)
H(6)	−324 (3)	697 (4)	281 (1)	15 (6)
H(7)	−279 (3)	390 (5)	335 (1)	21 (6)
H(9)	−99 (3)	346 (4)	199 (1)	14 (6)
H(111)	109 (4)	513 (6)	204 (1)	44 (9)
H(112)	98 (5)	590 (6)	271 (2)	48 (9)
H(121)	172 (4)	223 (6)	231 (1)	40 (8)
H(122)	292 (4)	368 (5)	272 (1)	39 (8)
H(14)	−47 (3)	104 (5)	270 (1)	16 (6)
H(151)	−81 (4)	141 (5)	377 (1)	32 (8)
H(152)	−150 (4)	−32 (6)	337 (2)	45 (9)
H(161)	123 (3)	−36 (4)	406 (1)	17 (6)
H(162)	70 (3)	−173 (5)	358 (1)	23 (7)
H(17)	191 (3)	−28 (4)	297 (1)	6 (5)
H(181)	153 (4)	297 (5)	398 (1)	38 (8)
H(182)	96 (4)	482 (5)	355 (1)	30 (7)
H(183)	263 (3)	405 (5)	369 (1)	19 (6)
H(191)	−359 (4)	250 (5)	218 (1)	24 (7)
H(192)	−423 (4)	319 (5)	156 (1)	34 (8)
H(193)	−531 (6)	337 (7)	198 (2)	78 (14)
H(20)	375 (4)	94 (5)	400 (1)	25 (7)
H(211)	469 (4)	46 (5)	295 (1)	25 (7)
H(212)	465 (4)	237 (6)	327 (2)	49 (9)
H(213)	585 (5)	79 (7)	351 (2)	73 (13)
H(221)	400 (4)	−238 (5)	342 (1)	36 (8)
H(222)	318 (4)	−228 (6)	392 (2)	46 (9)
H(231)	641 (4)	−161 (6)	399 (1)	41 (9)
H(232)	559 (4)	−143 (5)	451 (1)	38 (8)
H(241)	488 (4)	−460 (5)	441 (1)	39 (8)
H(242)	578 (3)	−485 (5)	394 (1)	21 (7)
H(25)	703 (4)	−393 (6)	510 (1)	43 (9)
H(261)	956 (5)	−425 (7)	490 (2)	61 (11)
H(262)	883 (6)	−421 (8)	418 (2)	85 (14)
H(263)	865 (5)	−231 (7)	460 (2)	57 (10)
H(271)	804 (5)	−691 (7)	508 (2)	71 (13)
H(272)	620 (6)	−715 (8)	484 (2)	87 (15)
H(273)	739 (4)	−723 (5)	441 (1)	23 (7)
H(32)	−310 (3)	447 (5)	67 (1)	21 (6)
H(34)	−261 (4)	271 (5)	−84 (1)	30 (7)
H(36)	−136 (4)	793 (6)	−33 (1)	41 (8)

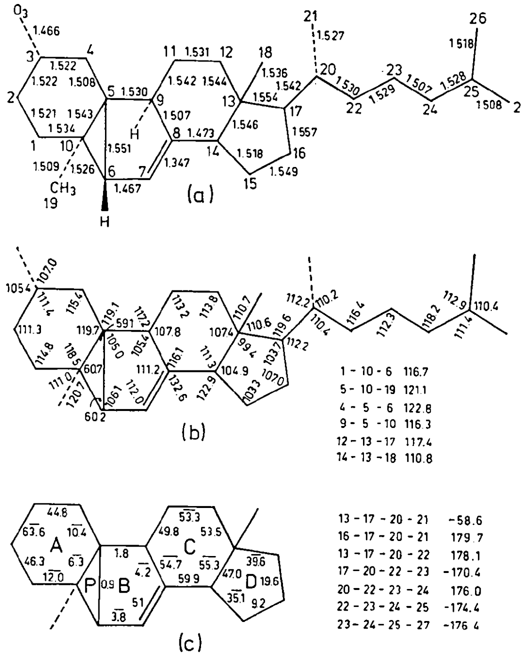

Fig. 1. (*a*) Numbering of atoms and bond lengths (Å), (*b*) valency angles (°), and (*c*) torsion angles (°) of the steroid moiety of toxisterol C_1. The standard deviations of bond lengths N–O, C–O, C–N and C–C are 0·0061, 0·0069, 0·0073 and 0·0080 Å respectively. The standard deviations of valency and torsion angles not involving hydrogen atoms are 0·5 and 0·7°.

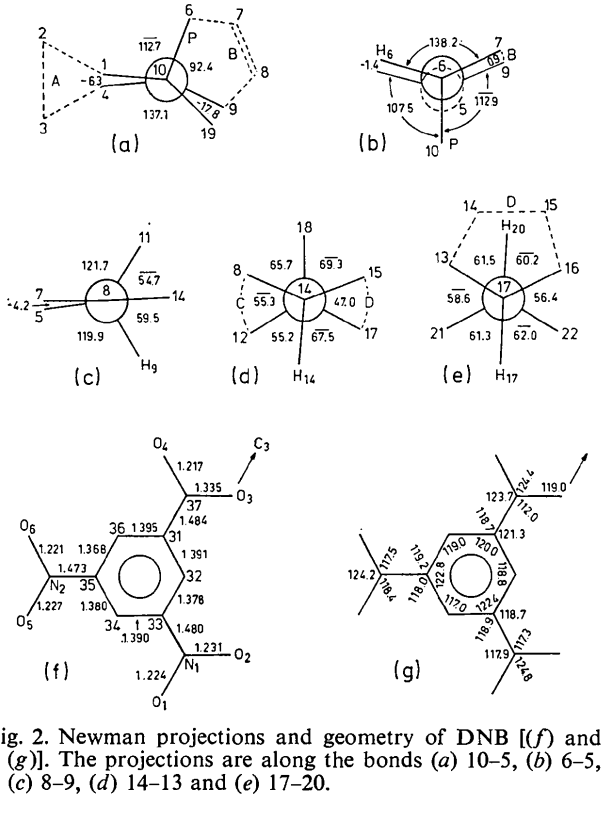

Fig. 2. Newman projections and geometry of DNB [(*f*) and (*g*)]. The projections are along the bonds (*a*) 10–5, (*b*) 6–5, (*c*) 8–9, (*d*) 14–13 and (*e*) 17–20.

of cyclohexene. From Bucourt's (1974) calculation of minimum energy conformations we estimate that an amount of 10 kcal mol^{-1} is involved in this deformation.

Ring *A* has an approximate C_2 symmetry with the diad running through the midpoints of the bonds 2–3 and 5–10. Cyclopentene ring *B* is nearly planar. Ring *C* has a chair conformation with highest puckering near C(13), C(14) and C(8), a well-known feature of many steroid molecules. Ring *D* has a $C_2(16)$–$C_s(13)$ conformation, intermediate between a half-chair and an envelope. The maximum puckering angle is $\varphi_m = 46{\cdot}8°$ and the phase angle is $\Delta = 12{\cdot}4°$.

Newman projections, Fig. 2(*a*) and (*b*), demonstrate that rings *A* and *P* and also rings *P* and *B* make angles of 113°. On the whole the steroid nucleus retains its usual elongated shape.

The 17β *side-chain*

Inspection of the additional dihedral angles listed in Fig. 1(*c*) indicates that the cholestane side-chain is quite extended, in agreement with earlier experiences (*cf.* Romers, Altona, Jacobs & de Graaff, 1974). The stretch is even better than for PCD and IPCD. The negative value (−58·6°) of dihedral angle 13–17–20–21 [see also Fig. 2(*e*)] points to the usual *S* chirality with respect to the configuration of C(20).

The 3,5-*dinitrobenzoate ester moiety*

The axial α-orientation† of the DNB group is evident from Fig. 3 and implies the overall V-shape of DTC. The V-shape can be seen best in Fig. 4. The benzene ring is quite planar, the largest deviation from its least-squares plane (Table 5) being 0·007 Å. The carboxy and nitro groups are slightly bent from this plane by amounts of 0·01, −0·02 and −0·04 Å; however, more important are the tilts about the bonds C(31)–C(37), C(33)–N(1) and C(35)–N(2) which amount to

Table 5. *Deviations* (Å) *from the least-squares plane of the benzene ring with reference to orthogonal axes* **a**, **b** *and* **c***

$$0{\cdot}8685X - 0{\cdot}3429Y + 0{\cdot}3580Z + 3{\cdot}1762 = 0$$

C(31)	0·000	C(36)	0·005	O(2)	−0·129
C(32)	−0·007	C(37)	0·010	O(3)	−0·378
C(33)	0·007	N(1)	−0·023	O(4)	0·337
C(34)	−0·001	N(2)	−0·037	O(5)	−0·130
C(35)	−0·005	O(1)	0·065	O(6)	0·045

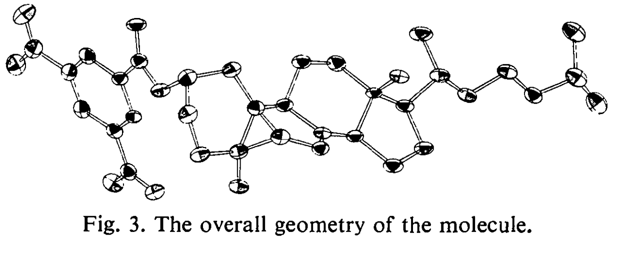

Fig. 3. The overall geometry of the molecule.

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† Note, however, that no change of configuration at C(3) has occurred.

Table 6. *Intermolecular interactions*

Distances are in Å.

(*a*) H···H interactions within 3 Å

Molecule	Operation	Number	Average	Minimum
II, III	$-1-x,\ \mp\frac{1}{2}+y,\ -z$	4	2·60	2·46
IV, V	$\mp1+x,\ y,\ z$	16	2·76	2·51
VI, VII	$\mp1+x,\ \pm1+y,\ z$	12	2·63	2·27
VIII, IX	$x,\ \mp1+y,\ z$	34	2·85	2·24
X, XI	$-x,\ \mp\frac{1}{2}+y,\ -z$	0	–	–
XII, XIII	$1-x,\ \mp\frac{1}{2}+y,\ 1-z$	16	2·67	2·41

(*b*) O···H interactions within 3 Å

Molecule	Number	Average	Minimum
II, III	4	2·85	2·77
VIII, IX	4	2·82	2·73
X, XI	10	2·78	2·69

(*c*) C···H interactions within 3·10 Å

Molecule	Number	Average	Minimum
II, III	4	3·07	2·98
IV, V	2	2·95	2·95
VI, VII	2	3·09	3·09
VIII, IX	4	3·08	3·05

(*d*) N···O and O···O interactions within 3·31 Å

Molecule	Number	Average	Minimum
II, III	4	3·21	3·13
VIII, IX	14	3·19	3·08
X, XI	8	2·99	2·79

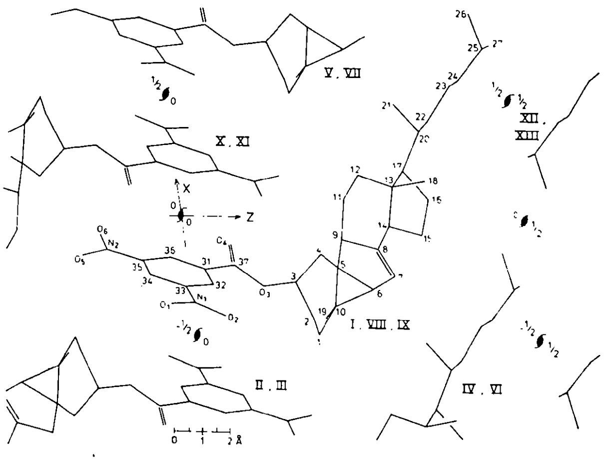

Fig. 4. Packing of the molecules in a projection along [010].

Table 7. *Intermolecular distances* (Å) *smaller than the sum of van der Waals radii*

$r_O=1\cdot55,\ r_N=1\cdot5,\ r_C=1\cdot5,\ r_H=1\cdot2$ Å.

Interaction	Molecule	Distance
H(7)····H(242)	VI	2·27
H(14)···H(42)	VIII	2·24
O(1)····H(36)	VIII	2·73
O(6)····H(121)	XI	2·69
O(5)····H(121)	XI	2·72
N(1)···O(4)	VIII	3·079
O(2)···O(4)	VIII	3·090
O(4)···C(35)	XI	2·945
O(4)···N(2)	XI	2·789

18, −4 and −4° respectively. These tilts are slightly larger than the corresponding ones for IPCD, but considerably smaller than those for PCD.

Packing

Part of the crystal structure is illustrated in Fig. 4 in a projection along [010]. In agreement with the packing of PCD and IPCD, polar forces cause clustering of the DNB groups about twofold screw axes and give rise to very short intermolecular distances between O(4) and N(1), N(2), C(35) and O(2) (see Table 7).

The reference molecule I at position x,y,z is surrounded by 12 neighbouring molecules (see Fig. 4). The lower coordination number of DTC is reflected in its lower density (1·17 g cm^{-3}). The coordination numbers of PCD and IPCD are 14 and 16 and their densities are 1·21 and 1·23 g cm^{-3} respectively. The total number of H···H contacts <3·0 Å is, however, about the same in the three structures, *i.e.* 82, 84 and 78 for DTC, PCD and IPCD respectively. The various types of interactions are tabulated in Table 6. Note that no H···H interactions are involved in the contacts between molecule I and the screw-axes-related molecules X and XI at positions $-x, \mp\frac{1}{2}+y, -z$.

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