

The Conformation of Non-Aromatic Ring Compounds.
XCIII. The Crystal and Molecular Structure of the 3,5-Dinitrobenzoate Ester of
Isopyrocalciferol at -170°C

BY A. J. DE KOK, C. ROMERS AND J. HOOGENDORP

Gorlaeus Laboratoria, X-ray and Electron Diffraction Section, Rijksuniversiteit Leiden, Leiden, The Netherlands

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The 3,5-dinitrobenzoate ester of isopyrocalciferol, 9β -ergosta-5,7,22-trien- 3β -ol 3',5'-dinitrobenzoate, is monoclinic, space group $P2_1$, $Z=2$, with $a=18.364$ (5), $b=5.955$ (5), $c=14.568$ (5) Å and $\beta=94.03$ (5) $^{\circ}$ at -170°C . The structure was solved by means of the least-squares method using Mo $K\alpha$ reflexion intensities recorded at -170°C with a three-circle diffractometer. With the exception of valency angles 3-4-5 (108.3°), 1-10-5 (105.4°) and 9-10-19 (106.4°) no unusual bond distances or angles are observed. The conformations of ring *A* (chair) and ring *D* (half-chair), are about equal to those of pyrocalciferol. Owing to the reversed ($9\beta,10\beta$) configuration as compared with the $9\alpha,10\alpha$ configuration occurring in pyrocalciferol the conformations of rings *B* and *C* are quite different: *B* is irregular and *C* is a boat.

Introduction

Isopyrocalciferol is a byproduct of the heating of previtamin D, the main heating product being pyrocalciferol. The structure of the 3,5-dinitrobenzoate ester of the latter compound (PCD) has been reported (de Kok & Romers, 1975). Three $\Delta^{5,7}$ steroids with $9\alpha,10\beta$ (ergosterol; Braun, Hornstra, Knobler, Romers & Rutten, 1973), $9\beta,10\alpha$ (lumisterol; de Kok & Romers, 1974) and $9\alpha,10\alpha$ (pyrocalciferol) configurations have been investigated in this laboratory.

The title compound (hereinafter IPCD) having the $9\beta,10\beta$ configuration [Fig. 1(a)] is the fourth stereoisomer differing in configuration at atoms C(9) and C(10). The systematic name of IPCD is 9β -ergosta-5,7,22-trien- 3β -ol 3',5'-dinitrobenzoate. The numbering of atoms is indicated in Fig. 1(a) and (d).

Experimental

Monoclinic colourless crystals of IPCD were obtained by recrystallization from light petroleum in the form of plates with main faces {100}. The lattice dimensions at 20°C and at -170°C were measured manually on a

three-circle diffractometer using Mo $K\alpha$ radiation ($\lambda=0.7107$ Å), see Table 1. The reflexions $0k0$ are absent for k odd; since IPCD is optically active the space group is $P2_1$.

The reflexion intensities of a crystal with dimensions $0.56 \times 0.22 \times 0.07$ mm were collected at -170°C with a three-circle diffractometer using graphite-mono-chromatized Mo $K\alpha$ radiation. The θ - 2θ scanning mode with scan width varying between 0.8° and 1.3° was employed. By means of one of three standard reflexions ($4\bar{1}2$, $\bar{2}23$ and $\bar{2}05$) measured after each series of 19 reflexions a polynomial correction function of the time was obtained in order to correct for loss of scattering power during the exposure.

In all, 4890 symmetry-independent reflexions were measured. These reflexions were classified in three groups: 2810 significant reflexions having counts $>2\sigma$ (background), 198 non-significant reflexions having counts $<2\sigma$ and 1882 reflexions not registered by the pulse-height discriminator. Since the linear absorption coefficient for Mo $K\alpha$ radiation (Table 1) is very small no absorption correction was applied. The intensities were reduced to structure factors in the usual way. An overall isotropic B value of 1.82 Å² was obtained from a Wilson plot.

Table 1. *Crystal data of IPCD*

$\text{C}_{35}\text{H}_{46}\text{O}_6\text{N}_2$, $M=590.7$, $Z=2$, space group $P2_1$	
20°	-170°
$a=18.550$ (5) Å	$a=18.364$ (5) Å
$b=6.040$ (8)	$b=5.955$ (5)
$c=14.565$ (8)	$c=14.568$ (5)
$\beta=93.48^{\circ}$	$\beta=94.03$ (5) $^{\circ}$
$d_{\text{obs}}=1.19$ g cm ⁻³	
$d_{\text{calc}}=1.23$ (-170°)	
$F(000)=736$	
$\mu(\text{Mo } K\alpha)=0.85$ cm ⁻¹	

Observed significant reflexions: 2810
 Reflexions less than twice the background: 198
 Non-observed reflexions within $\theta=30^{\circ}$: 1882

Solution of the structure

Attempts to solve the structure with direct methods using the program of Motherwell & Isaacs (1971) were not successful, although further stages of the analysis indicated that part of the structure (the 3,5-dinitrobenzoate moiety) could have been recognized. The Patterson-search method of Braun, Hornstra & Leenhouts (1969), using as known part a planar model of the 3,5-dinitrobenzoate group as described for PCD, produced the correct orientation and position of this ester group, but failed to recognize the unknown part

of the structure, the steroid moiety. In a second attempt the non-planar 3,5-dinitrobenzoate group observed in PCD was introduced as the known part of the search. Again only the orientation and position of this group were established by the program. The average values of the positional coordinates of the ten atoms which had the best agreement in both attempts were next used as shifts for the calculation of a composite Patterson function. This function was obtained by taking the sum of the corresponding grid points of the shifted Patterson functions. The Fourier coefficients of the Patterson functions were normalized E^2 values.

Ring *D* and the ergostane tail C(13)···C(27) were recognized together with the ester group C(31)···C(37), N(1), N(2), O(1)···O(6). Structure factors calculated for this part of the molecule resulted in an agreement of $R=33\%$. The atoms still lacking were located in a difference Fourier map.

It is worth mentioning that the structure could have been solved from Fourier maps based on calculated phases from the earlier mentioned ten atoms. The electron density was, of course, highest at the position of the ten introduced atoms, but among the 15 next highest density regions only one peak was false. Surprisingly, the density map based on all observed struc-

ture factors (2810) gave the best result, while the solution based upon 400 structure factors having the most reliable phases was most unsatisfactory.

The refinement of atomic positions, vibrational parameters and the location of hydrogen atoms was a matter of routine and will not be described in detail. By means of minimization of block-diagonal least squares R and R_w dropped to values of 4.59 and 4.31% respectively (see de Kok & Romers (1975) for the definition of R and R_w).

The positional and vibrational parameters of the heavy atoms are listed in Tables 2 and 3. The positions and isotropic B values of the hydrogen atoms are in Table 4.

Discussion of the structure

Bearing in mind the block-diagonal approximation to the matrix of normal equations and applying the same

Table 2. Fractional coordinates ($\times 10^4$) of the heavy atoms

Estimated standard deviations in units of the last decimal are given in parentheses.

	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
C(1)	-1311 (2)	-4421 (7)	4297 (2)
C(2)	-743 (2)	-3779 (7)	3608 (2)
C(3)	-989 (2)	-1860 (7)	2995 (2)
C(4)	-1254 (2)	176 (7)	3526 (3)
C(5)	-1811 (2)	-634 (7)	4176 (2)
C(6)	-2510 (2)	-164 (7)	4027 (3)
C(7)	-3082 (2)	-1392 (7)	4478 (3)
C(8)	-2905 (2)	-2876 (7)	5143 (2)
C(9)	-2119 (2)	-3005 (7)	5552 (2)
C(10)	-1531 (2)	-2396 (7)	4873 (2)
C(11)	-1989 (2)	-5178 (7)	6086 (3)
C(12)	-2507 (2)	-5452 (7)	6871 (2)
C(13)	-3279 (2)	-4524 (5)	6640 (2)
C(14)	-3425 (2)	-4418 (7)	5579 (2)
C(15)	-4241 (2)	-4069 (8)	5415 (3)
C(16)	-4569 (2)	-5242 (7)	6239 (3)
C(17)	-3926 (2)	-5993 (7)	6906 (2)
C(18)	-3354 (2)	-2128 (7)	7045 (3)
C(19)	-864 (2)	-1500 (7)	5468 (3)
C(20)	-4115 (2)	-5986 (7)	7918 (2)
C(21)	-3467 (2)	-6554 (7)	8590 (2)
C(22)	-4725 (2)	-7631 (7)	8079 (3)
C(23)	-5413 (2)	-7140 (7)	8184 (3)
C(24)	-5989 (2)	-8795 (8)	8441 (3)
C(25)	-6441 (2)	-7859 (7)	9209 (3)
C(26)	-6951 (3)	-5941 (10)	8904 (3)
C(27)	-5949 (2)	-7155 (8)	10042 (3)
C(28)	-6470 (2)	-9582 (10)	7610 (3)
C(31)	412 (2)	-984 (7)	1309 (2)
C(32)	706 (2)	1028 (7)	1628 (2)
C(33)	1264 (2)	1973 (7)	1165 (2)
C(34)	1529 (2)	1020 (7)	387 (2)
C(35)	1219 (2)	-969 (7)	95 (2)
C(36)	663 (2)	-1995 (7)	532 (2)
C(37)	-180 (2)	-2168 (7)	1785 (2)
O(1)	1375 (2)	4885 (5)	2226 (2)
O(2)	2069 (2)	4953 (5)	1080 (2)
O(3)	-371 (1)	-1011 (5)	2510 (1)
O(4)	-438 (1)	-3931 (5)	1522 (1)
O(5)	1232 (1)	-3920 (5)	-946 (2)
O(6)	1954 (1)	-1114 (5)	-1133 (2)
N(1)	1591 (2)	4107 (5)	1516 (2)
N(2)	1491 (2)	-2084 (5)	-726 (2)

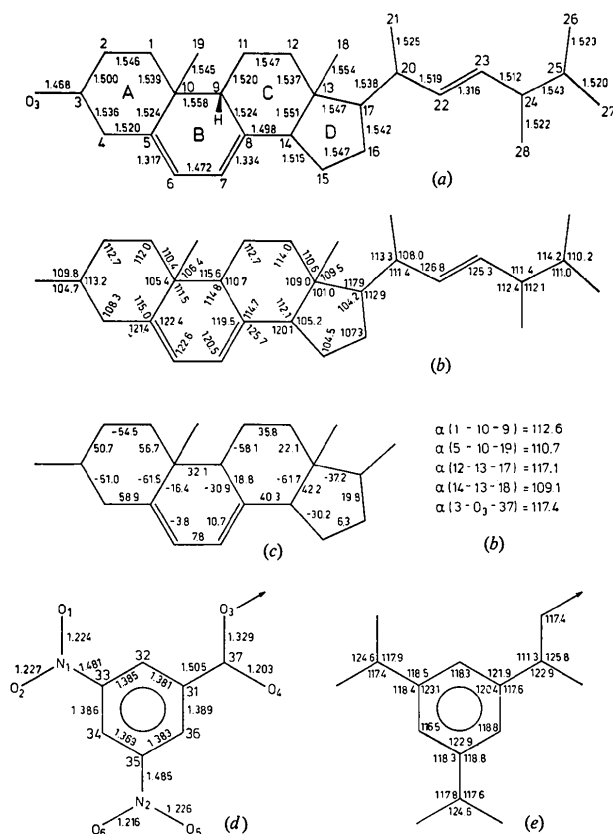


Fig. 1. (a) Bond distances (Å) and numbering of atoms of the steroid moiety. (b) Valency angles (°). (c) Torsion angles (°). (d) Bond distances and numbering of the DNB moiety. (e) Valency angles of the DNB moiety.

procedure as discussed for pyrocalciferol we arrive at respective average e.s.d.'s of 0.008, 0.007, 0.065, 0.006, 0.005 and 0.05 Å for the bond lengths C-C(tail), C-C(elsewhere), C-N, C-O, N-O and C-H, and to average e.s.d.'s of 0.4° and 0.6° for valency and torsion angles not involving hydrogen.

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

Estimated standard deviations in units of the last decimal are given in parentheses.

	U_{11}	U_{22}	U_{33}	$2U_{21}$	$2U_{23}$	$2U_{31}$
C(1)	24 (2)	12 (2)	20 (2)	3 (3)	5 (3)	11 (3)
C(2)	24 (2)	14 (2)	25 (2)	6 (3)	2 (3)	18 (3)
C(3)	21 (2)	17 (2)	19 (2)	-12 (3)	-3 (3)	11 (3)
C(4)	25 (2)	15 (2)	26 (2)	11 (3)	7 (3)	19 (3)
C(5)	25 (2)	11 (2)	24 (2)	2 (3)	-1 (3)	15 (3)
C(6)	33 (2)	17 (2)	25 (2)	7 (4)	7 (4)	14 (3)
C(7)	20 (2)	31 (2)	25 (2)	8 (4)	4 (4)	8 (3)
C(8)	20 (2)	14 (2)	21 (2)	4 (3)	0 (3)	12 (3)
C(9)	17 (2)	15 (2)	20 (2)	1 (3)	-1 (3)	5 (3)
C(10)	18 (2)	13 (2)	18 (2)	-3 (3)	-2 (3)	10 (3)
C(11)	22 (2)	27 (2)	24 (2)	-4 (4)	9 (4)	11 (3)
C(12)	18 (2)	21 (2)	21 (2)	-1 (3)	5 (3)	6 (3)
C(13)	17 (2)	12 (2)	19 (2)	-2 (3)	-3 (3)	7 (3)
C(14)	17 (2)	16 (2)	22 (2)	0 (3)	4 (3)	2 (3)
C(15)	24 (2)	40 (3)	27 (2)	-15 (4)	17 (4)	2 (3)
C(16)	20 (2)	37 (2)	29 (2)	-10 (4)	19 (4)	0 (3)
C(17)	22 (2)	12 (2)	22 (2)	-2 (3)	-2 (3)	8 (3)
C(18)	28 (2)	13 (2)	28 (2)	1 (3)	0 (4)	19 (3)
C(19)	24 (2)	35 (3)	24 (2)	-24 (4)	-4 (4)	2 (3)
C(20)	17 (2)	16 (2)	23 (2)	6 (3)	1 (3)	8 (3)
C(21)	25 (2)	32 (2)	20 (2)	3 (4)	3 (4)	12 (3)
C(22)	26 (2)	20 (2)	23 (2)	0 (3)	7 (3)	17 (3)
C(23)	29 (2)	24 (2)	28 (2)	-7 (4)	10 (4)	14 (3)
C(24)	28 (2)	31 (2)	31 (2)	-3 (4)	16 (4)	17 (3)
C(25)	28 (2)	34 (3)	33 (2)	-5 (4)	27 (4)	25 (3)
C(26)	41 (3)	59 (4)	70 (3)	26 (5)	64 (6)	55 (5)
C(27)	49 (3)	36 (3)	37 (2)	-20 (5)	7 (5)	31 (4)
C(28)	48 (3)	61 (4)	38 (3)	-48 (6)	10 (5)	10 (4)
C(31)	18 (2)	17 (2)	18 (2)	0 (3)	13 (3)	-3 (3)
C(32)	19 (2)	17 (2)	16 (2)	1 (3)	1 (3)	1 (3)
C(33)	17 (2)	14 (2)	22 (2)	-3 (3)	4 (3)	-13 (3)
C(34)	12 (2)	24 (2)	23 (2)	0 (3)	14 (4)	-1 (3)
C(35)	18 (2)	24 (2)	15 (2)	6 (3)	1 (3)	5 (3)
C(36)	19 (2)	13 (2)	20 (2)	-1 (3)	-1 (3)	-2 (3)
C(37)	18 (2)	22 (2)	20 (2)	-1 (3)	7 (3)	1 (3)
O(1)	39 (2)	21 (1)	29 (1)	-13 (3)	-7 (3)	5 (2)
O(2)	28 (1)	25 (2)	42 (2)	-23 (3)	9 (3)	10 (3)
O(3)	21 (1)	14 (1)	21 (1)	-5 (2)	0 (2)	16 (2)
O(4)	31 (1)	22 (1)	24 (1)	-21 (3)	-4 (3)	17 (2)
O(5)	27 (1)	33 (2)	33 (2)	-12 (3)	-21 (3)	9 (2)
O(6)	23 (1)	39 (2)	37 (2)	-4 (3)	-6 (3)	31 (2)
N(1)	23 (2)	21 (2)	28 (3)	-3 (3)	9 (3)	-6 (3)
N(2)	16 (1)	32 (2)	21 (2)	9 (3)	4 (3)	10 (2)

Bond lengths, valency and endocyclic torsion angles are presented in Fig. 1 (*a-e*).

The overall geometry is depicted in Fig. 2. Unlike the folded structure of PCD, the shape of IPCD is

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

Estimated standard deviations in units of the last decimal are given in parentheses.

	X/a	Y/b	Z/c	B (ISO)
H(2A)	-63 (2)	-481 (8)	326 (3)	39 (10)
H(2B)	-26 (2)	-336 (8)	394 (3)	36 (9)
H(1A)	-175 (2)	-512 (6)	393 (2)	10 (6)
H(1B)	-106 (2)	-562 (6)	475 (2)	16 (7)
H(3)	-137 (2)	-218 (6)	257 (2)	13 (7)
H(4A)	-144 (2)	100 (7)	308 (2)	23 (8)
H(4B)	-80 (1)	70 (6)	387 (2)	6 (6)
H(6)	-266 (2)	73 (6)	357 (2)	15 (7)
H(7)	-360 (2)	-121 (6)	422 (2)	10 (6)
H(9)	-205 (2)	-195 (5)	601 (2)	4 (6)
H(11A)	-212 (2)	-635 (9)	560 (3)	50 (11)
H(11B)	-147 (2)	-539 (6)	638 (2)	12 (7)
H(12A)	-252 (2)	-700 (7)	712 (2)	26 (8)
H(12B)	-226 (2)	-494 (7)	744 (2)	27 (8)
H(14)	-328 (2)	-592 (6)	543 (2)	14 (7)
H(15A)	-432 (2)	-229 (7)	542 (2)	22 (8)
H(15B)	-446 (2)	-450 (7)	479 (2)	24 (8)
H(16A)	-491 (2)	-416 (8)	655 (3)	33 (9)
H(16B)	-487 (2)	-655 (6)	608 (2)	16 (7)
H(17)	-377 (2)	-726 (6)	674 (2)	15 (7)
H(18A)	-300 (2)	-130 (6)	677 (2)	5 (6)
H(18B)	-326 (2)	-222 (6)	774 (2)	12 (6)
H(18C)	-382 (2)	-162 (6)	694 (2)	13 (7)
H(19A)	-48 (2)	-123 (7)	508 (2)	25 (8)
H(19B)	-66 (2)	-277 (6)	597 (2)	9 (6)
H(19C)	-104 (2)	-19 (7)	580 (2)	25 (8)
H(20)	-436 (1)	-450 (6)	798 (2)	6 (6)
H(21A)	-326 (2)	-801 (7)	842 (2)	18 (7)
H(21B)	-361 (2)	-675 (7)	920 (2)	25 (8)
H(21C)	-301 (2)	-538 (7)	865 (3)	31 (9)
H(22)	-460 (2)	-909 (9)	810 (3)	57 (12)
H(23)	-563 (2)	-564 (7)	810 (2)	34 (9)
H(24)	-570 (2)	-1020 (6)	871 (2)	16 (7)
H(25)	-680 (2)	-913 (7)	937 (2)	22 (8)
H(26A)	-664 (2)	-469 (8)	868 (3)	35 (9)
H(26B)	-719 (3)	-524 (12)	950 (4)	89 (17)
H(26C)	-731 (2)	-630 (8)	834 (2)	33 (9)
H(27A)	-565 (2)	-850 (7)	1014 (2)	25 (8)
H(27B)	-623 (2)	-702 (7)	1063 (2)	29 (8)
H(27C)	-563 (2)	-585 (9)	992 (3)	60 (12)
H(28A)	-693 (2)	-1086 (9)	778 (3)	56 (12)
H(28B)	-616 (2)	-1010 (7)	715 (3)	32 (9)
H(28C)	-669 (3)	-823 (11)	731 (3)	77 (15)
H(32)	53 (2)	174 (6)	217 (2)	13 (7)
H(34)	194 (2)	167 (6)	13 (2)	12 (7)
H(36)	47 (2)	-339 (6)	32 (2)	7 (6)

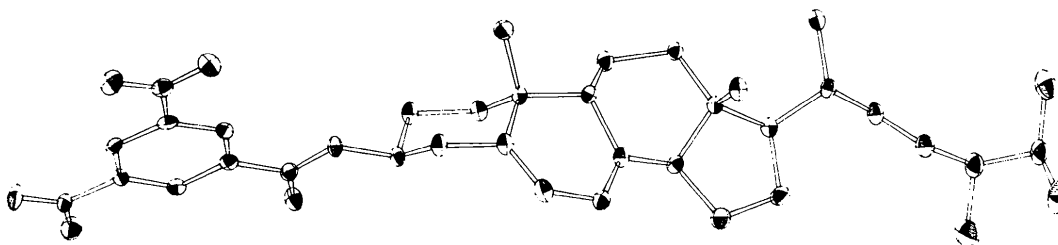


Fig. 2. An ORTEP projection of the molecule (Johnson, 1967).

elongated. The main difference in molecular shape is caused by the different linkage between ester and steroid moieties in the two molecules; the linkage C(3)–O(3) with respect to ring *A* being axial in pyrocalciferol and equatorial in isopyrocalciferol.

A number of Newman projections are shown in Fig. 3. Geometric entities not given in Fig. 1 and 3 are listed in Table 5. The corresponding entities of pyrocalciferol are also included in this table.

The steroid nucleus

The mean value of the C(*sp*³)–C(*sp*³) bond lengths [1.536 (3) Å] agrees with the commonly observed value of 1.533 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). Only the bonds C(9)–C(10) and C(2)–C(3) deviate more than three times the standard deviation from the observed average value. In agreement with earlier experiences the large value for C(9)–C(10) and the small value of C(2)–C(3) next to the ester linkage are quite regular. The 'inner' valency angle $\alpha(1-10-5)$ is surprisingly small: its value (105.4°) is considerably smaller than the corresponding value of pyrocalciferol (111.3°).

Ring *A* is a slightly distorted chair. Its mean puckering (55.7°) agrees with the values observed by

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31107 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

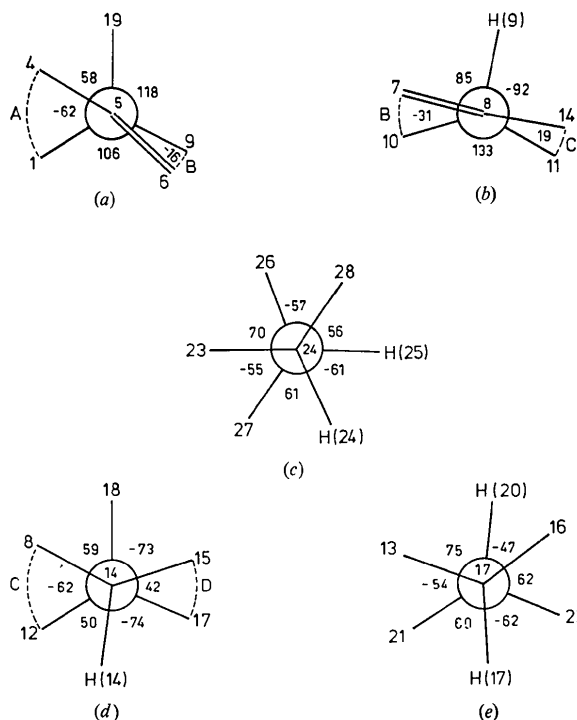


Fig. 3. Newman projections along 5–10 (a), 8–9 (b), 24–25 (c) 14–13 (d), 17–20 (e).

Table 5. *Molecular entities of IPCD not indicated in Fig. 1*

Numbers in parentheses are e.s.d.'s in units of the last decimal. The corresponding values of PCD are also listed.

Mean distances	IPCD	PCD
C(<i>sp</i> ³)–C(<i>sp</i> ³) single	1.536 (3) Å	1.541 (2) Å
C(<i>sp</i> ³)–C(<i>sp</i> ²) single	1.516 (4)	1.514 (2)
C(<i>sp</i> ²)=C(<i>sp</i> ²) double	1.322 (6)	1.326 (3)
C(<i>sp</i> ²)–C(<i>sp</i> ²) single	1.472	1.456
C(<i>sp</i> ²)–C(<i>sp</i> ²) aromatic	1.382 (3)	1.387 (2)
C(<i>sp</i> ³)–H saturated	0.99 (1)	1.00 (1)
C(<i>sp</i> ²)–H otherwise	0.95 (2)	0.93 (2)
Mean bond angles		
$\alpha[C-C(sp^3)-C]$ saturated with exclusion of ring <i>D</i> and quaternary carbon atoms	111.9 (5)°	111.9 (5)°
$\alpha[H-C(sp^3)-C]$ no specification	108.7 (6)	111.8 (2)
$\alpha[H-C(sp^3)-H]$ no specification	108.0 (12)	105.0 (4)

Least-squares plane of the benzene ring, with reference to orthogonal axes *a*, *b* and *c** (IPCD):
 $-0.6393x + 0.5038y - 0.5809z + 1.7938 = 0$

Deviations from least-squares plane (Å)

	IPCD	PCD		IPCD	PCD
C(31)	-0.004	0.008	O(1)	-0.088	0.304
C(32)	0.006	-0.004	O(2)	0.010	0.395
C(33)	-0.005	-0.003	O(3)	-0.028	-0.306
C(34)	0.003	0.006	O(4)	-0.057	-0.190
C(35)	-0.002	-0.003	O(5)	-0.092	-0.421
C(36)	0.002	-0.004	O(6)	0.048	0.508
C(37)	-0.035	0.066	N(1)	-0.022	0.047
			N(2)	-0.017	0.014

Geise, Buys & Mijlhoff (1971), 55.9°, and by Bastiansen, Fernholt, Seip, Kambara & Kuchitsu (1973), 54.9°. In contrast to the other $\Delta^{5,7}$ steroids, e.g. ergosterol, lumisterol and pyrocalciferol, the largest puckering of ring *A* in IPCD is observed near the juncture C(5)–C(10), connecting rings *A* and *B*. In all investigated $\Delta^{5,7}$ steroids of the vitamin D series the symmetry of ring *A* (D_{3d} in the ideal case) is degraded towards C_s with a mirror plane running through the midpoints of bond C(2)–C(3) and C(5)–C(10).

The conformation of ring *B* containing two double bonds is irregular. One would expect a 1–3 diplanar geometry as observed for ergosterol, lumisterol and pyrocalciferol. However, the torsion angle about the double bond C(7)–C(8) (10.7°) is too large for the designation 'dipolar' proposed by Bucourt. The sign of the torsion angle about C(6)–C(7) agrees with the Cotton effect observed by Jacobs (1972). Ring *B* has an approximate C_s symmetry with the mirror plane running through the atoms C(6) and C(9).

Ring *C* has a boat conformation which was predicted several years ago by Jacobs & Havinga (1965). Using the pseudorotation formula of Buys & Geise (1968) and designating the torsion angles about the bonds 8–14, 8–9 ... 13–14 as $\varphi_0, \varphi_1-\varphi_5$ we found $\Delta = -50.3^\circ$ and $\varphi_m = 60^\circ$.

Accordingly the conformation is intermediate between a twist boat and a boat.

Ring *D* has a $C_s(13)-C_2(16)$ conformation, *e.g.* an intermediate form between an envelope with C(13) as flap and a half-chair with a dyad running through C(16). Its phase angle Δ is 17.9° and $\varphi_m = 52.3^\circ$. The large maximum puckering angle φ_m indicates that ring *D* is substantially more puckered than the corresponding rings of ergosterol, lumisterol and pyrocalciferol (46.2° , 45.9° and 47.5°).

The geometry of the *A/B*, *B/C* and *C/D* junctures is depicted in the Newman projections of Fig. 3(*a*), (*b*) and (*d*). We note that the torsion angles $\varphi(1-10-5-4)$ and $\varphi(9-10-5-6)$ have equal signs whereas the torsion angles $\varphi(7-8-9-10)$ and $\varphi(14-8-9-11)$ are of opposite sign, and mention that the corresponding pairs of torsion angles of PCD have opposite and equal signs respectively. The case of equal signs of torsion angles about a juncture of *trans*-connected rings was discussed by Jacobs (1972). It can be seen in Fig. 3(*d*) and (*e*) that the antiplanar configuration of H(14) and C(18) and of H(17) and H(20) is not perfect. The deviations from the ideal case are about 9° . Given *e.s.d.*'s of $\sim 4^\circ$ in dihedral angles involving hydrogen atoms this deviation is significant on a 95% confidence level.

The 17 β -side chain

The dihedral angles defining the conformation of the side chain have already been tabulated [Table 7, de Kok & Romers (1975)]. It appears that the ergostane side chains of pyro- and isopyrocalciferol are folded in the same way. According to the Cahn-Ingold-Prelog rules (1966) the chain has *R*-chirality at C(20) and C(24).

The 3,5-dinitrobenzoate ester moiety

The benzene nucleus is quite planar; the deviations of carbon atoms C(31) \cdots C(36) from the least-squares plane (see Table 5), are less than 0.006 \AA . C(37), N(1), N(2), O(1) \cdots O(6) deviate at most 0.09 \AA from this plane. These deviations are significant although much smaller than for the corresponding ester group of PCD. The small non-planarity of this group in IPCD is accomplished by (i): a bending of the two nitro groups and the carboxyl group out of the benzene plane, the out-of-plane deviations of N(1), N(2) and C(37) being -0.02 , -0.017 and -0.033 \AA , respectively and (ii) a tilt of $+2.7^\circ$, -3.7° and $+0.6^\circ$ of these groups about the axes N(1)-C(33), N(2)-C(35) and C(37)-C(31), respectively. The different degrees of planarity of this group in IPCD and PCD are probably correlated with the different overall shape and packing of these molecules.

Packing

Fig. 4 illustrates the packing of molecules in the lattice. The total length of the elongated molecule measured from O(6) to C(26) amounts to 22.9 \AA . It is interesting to note that the vector from O(6) to C(26) has two components larger than *b* and *c* and one component nearly equal to *a*.

Intermolecular interactions of the type $H \cdots H$ and $O \cdots H$ within 3.0 \AA are given in Table 6.

The molecules are tightly packed and surrounded by 16 neighbours. The ester groups are clustered around the screw axis at $x=0, z=0$, resulting in many interactions between O(4), O(5) and O(6) of the reference molecule I at x, y, z and atoms O(3), C(37), C(35), O(6) and N(2) of molecules II, III, X and XI at $x, -1+y, z$; $x, 1+y, z$; $-x, -\frac{1}{2}+y, -z$ and $-x, \frac{1}{2}+y, -z$, see Table 7. On the other hand the remaining part of the molecule is perhaps slightly less densely packed than PCD; we observe a total number of 78 $H \cdots H$ contacts $< 3.0 \text{ \AA}$ with a mean value of 2.74 \AA in the structure of IPCD and of 84 such contacts with mean value 2.72 \AA in PCD. The calculated densities at

Table 6. Intermolecular interactions within 3.0 \AA

The reference molecule is I at x, y, z .

Molecule operation		Number of	Average	Minimum
(a) $H \cdots H$ interactions		inter-	distance	distance
		actions		
II	$x, -1+y, z$	10	2.73 \AA	2.60 \AA
III	$x, 1+y, z$	10	2.73 \AA	2.60 \AA
IV	$-x, -\frac{1}{2}+y, 1-z$	9	2.76 \AA	2.54 \AA
V	$-x, \frac{1}{2}+y, 1-z$	9	2.76 \AA	2.54 \AA
VIII	$-1-x, -\frac{1}{2}+y, 1-z$	7	2.70 \AA	2.45 \AA
IX	$-1-x, \frac{1}{2}+y, 1-z$	7	2.70 \AA	2.45 \AA
X	$-1-x, 1\frac{1}{2}+y, 1-z$	1	2.89 \AA	
XI	$-1-x, -1\frac{1}{2}+y, 1-z$	1	2.89 \AA	
XIV	$-1-x, -\frac{1}{2}+y, 2-z$	10	2.74 \AA	2.59 \AA
XV	$-1-x, \frac{1}{2}+y, 2-z$	10	2.74 \AA	2.59 \AA
XVI	$-1+x, -1+y, 1-z$	2	2.66 \AA	2.64 \AA
XVII	$1+x, 1+y, -1+z$	2	2.66 \AA	2.64 \AA
(b) $O \cdots H$ interactions				
IV	$-x, -\frac{1}{2}+y, 1-z$	3	2.98 \AA	2.98 \AA
V	$-x, \frac{1}{2}+y, 1-z$	3	2.98 \AA	2.98 \AA
VI	$-x, 1\frac{1}{2}+y, 1-z$	2	2.74 \AA	2.54 \AA
VII	$-x, -1\frac{1}{2}+y, 1-z$	2	2.74 \AA	2.54 \AA
XVI	$-1+x, -1+y, 1+z$	3	2.69 \AA	2.63 \AA
XVII	$1+x, 1+y, -1+z$	3	2.69 \AA	2.63 \AA

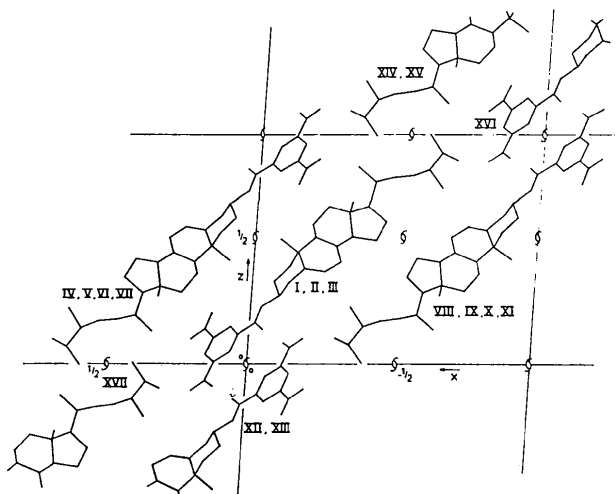


Fig. 4. A projection of the structure along $[010]$.

Table 7. Intra- and intermolecular distances (Å) between atoms of the ester group less than or equal to the sum of the van der Waals radii: $r_H=1.2$, $r_C=1.5$, $r_N=1.7$ and $r_O=1.55$ Å

Intermolecular interaction	Symmetry operation		
O(5)–O(3)	$-x, -\frac{1}{2}+y, -z$	2.96	
O(5)–C(37)	$-x, -\frac{1}{2}+y, -z$	2.94	
O(4)–O(6)	$-x, -\frac{1}{2}+y, -z$	3.09	
O(4)–N(2)	$-x, -\frac{1}{2}+y, -z$	2.88	
O(4)–C(35)	$-x, -\frac{1}{2}+y, -z$	2.93	
O(6)–H(25)	$1+x, 1+y, -1+z$	2.63	
O(6)–H(28A)	$1+x, 1+y, -1+z$	2.68	
O(2)–H(21A)	$-x, 1\frac{1}{2}+y, 1-z$	2.56	
O(2)–H(26B)	$1+x, 1+y, -1+z$	2.75	
O(3)–O(5)	$-x, \frac{1}{2}+y, -z$	2.96	
O(6)–O(4)	$-x, \frac{1}{2}+y, -z$	3.09	
N(2)–O(4)	$-x, \frac{1}{2}+y, -z$	2.88	
Intramolecular interactions			
O(5)–H(36)	2.40	O(4)–C(3)	2.73
O(4)–H(36)	2.53	O(6)–H(34)	2.48
O(4)–H(3)	2.59	O(2)–H(34)	2.40
O(4)–H(2A)	2.63	O(1)–H(32)	2.42
O(4)–C(2)	3.13	O(3)–H(32)	2.41

–170°C are 1.235 and 1.232 g cm⁻³ for IPCD and PCD. The observed intra- and intermolecular interactions in the two structures do not give a decisive answer as to why the ester group in IPCD is more planar than in PCD. Conversely, the question arises why is the ester group in the pyrocalciferol structure not planar? We recalculated the inter- and intramolecular distances of PCD with a model in which the two nitro groups were put at positions coplanar with the benzene ring. Comparison of calculated intermolecular distances of the assumed planar ester structure (Table 8) with the observed values indicates that a planar 3,5-dinitrobenzoate ester group in the crystal structure of PCD is unacceptable. With one exception, the calculated distances are shorter than the observed values and significantly shorter than the sum of the van der Waals radii ($r_O=1.55$, $r_N=1.2$ and $r_C=1.5$ Å). We may conclude that the difference in planarity of the 3,5-dinitrobenzoate groups in the two structures is a packing effect.

Table 8. Intermolecular interactions of O(1), O(4), O(5) and O(6) in a planar 3,5-dinitrobenzoate ester group in the structure of PCD

The third entry refers to the calculated values (Å) in the assumed structure, the fourth to the observed values.

Symmetry operation	l_{calc}	l_{obs}	
O(6)–H(18A)	$-x, \frac{1}{2}+y, -z$	2.63	< 3.00
O(6)–H(18C)	$-x, \frac{1}{2}+y, -z$	2.61	< 3.00
O(6)–C(18)	$-x, \frac{1}{2}+y, -z$	2.98	3.40
O(4)–H(17)	$-x, \frac{1}{2}+y, 1-z$	2.77	2.62
O(1)–H(21A)	$-x, \frac{1}{2}+y, 1-z$	2.82	< 3.00
O(6)–H(6)	$x, 1+y, z$	2.27	2.67
O(6)–H(7)	$x, 1+y, z$	2.50	2.86
O(6)–C(6)	$x, 1+y, z$	2.59	3.08
O(6)–C(7)	$x, 1+y, z$	2.71	3.18
O(1)–H(15B)	$x, 1+y, z$	2.55	2.73

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