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The Conformation of Non-Aromatic Ring Compounds.*

XVI. The Crystal Structure of 2 β , 3 α -dichloro-5 α -cholestane (Modification β) at -120°C

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The crystal structure of 2 β ,3 α -dichloro-5 α -cholestane has been determined by comparison with the isomorphous structure of the corresponding 2 β -chloro-3 α -bromo-derivative. The unit-cell dimensions at -120°C (of the former compound) are: $a = 13.31$, $b = 10.47$, $c = 9.88$ Å; $\beta = 113^{\circ} 37'$. The space group is $P2_1$ and $Z = 2$.

The rings *A*, *B* and *C* of the steroid skeleton are in the chair form. The conformation of ring *D* is best represented by a half chair with approximate symmetry C_2 . The angle between the bonds C(2)–Cl(2) and C(3)–Cl(3), having an average length of 1.81 Å, is 157° . The mean value of the carbon bond angles (111.2°) within the cyclohexane rings deviates significantly from the ideal tetrahedral value and this deviation is connected with the flattening of the perhydrophenanthrene skeleton. The bonds C(10)–C(19) and C(13)–C(18) are not strictly parallel, but are inclined to each other at an angle of 9° , which is an indication of the slightly bent shape of the molecule. A proof of the structures and configuration of 2 β -chloro-3 α -bromo- and 2 β -bromo-3 α -chloro-5 α -cholestane is given.

Introduction

The investigation presented in this paper is a part of a series of physico-chemical and conformational studies on steroid compounds and on more simple six-membered ring systems, such as cyclohexane and dioxane derivatives. For a complete survey of this work we refer to the preceding papers of this series and to the publications cited therein.

In a preliminary communication on the optical properties, cell dimensions and space groups (Geise, Romers & Hartman, 1962) we announced the crystal structure determinations of 2 β ,3 α -dichloro- and 2 α ,3 β -dichloro-5 α -cholestane. It proved possible to obtain more accurate data at low temperature of the 2 β ,3 α -dichloro compound and of the 2 α ,3 β -dibromo derivative, the latter being isomorphous with 2 α ,3 β -dichloro-5 α -cholestane. Meanwhile the crystal structure of the synthetic steroid 4-bromo-9 β ,10 α -pregna-4,6-diene-3,20-dione was carried out and a short communication of this work appeared elsewhere (Romers, v. Heijkoop, Hesper &

* Part XIV, Kalf & Romers (1965); Part XV, Romers, v. Heijkoop, Hesper & Geise (1965).

Geise, 1965). In subsequent publications in this journal we shall discuss the crystal structures of the two $2\alpha,3\beta$ -dihalogeno-cholestanes (Geise & Romers 1966) and of the pregna-dienone (Romers, Hesper, v.Heijkoop & Geise, 1966).

In order to keep the discussion within reasonable limits, only direct crystallographic information concerning the refinement, structural parameters, bond distances, bond angles and the overall geometric shape will be presented in this paper. The conformational analysis as well as the absolute configuration of the steroids mentioned will be published elsewhere (Geise, Altona & Romers, 1966; v.Heijkoop, Geise & Romers 1966). For the same reason tables of structure factors* covering about 9000 reflexions of the four compounds are omitted. The conformational aspects of five-membered rings *D* and physico-chemical properties will be discussed elsewhere (Altona, Geise & Romers, 1966; Geise, Tieleman & Havinga, 1966).

The immediate reason for the investigation discussed in this paper was the presumption that substitution of axial hydrogen atoms by halogens at the atoms C(2) and C(3) (see Fig. 1 for the numbering of the atoms) in the cholestane molecule would effect considerable distortion of ring *A*.

Moreover, it was anticipated that the carbon-halogen vectors C(2)-Cl(2) and C(3)-Cl(3) would not be strictly antiparallel, which could, at least partly, explain the relatively high dipole moments (~ 1.3 D) observed with this class of compounds (Geise, 1964; Geise, Tieleman & Havinga 1966). Furthermore, it became possible to give a direct proof of the structure and configuration of 2β -chloro- 3α -bromo- 5α -cholestane and of the 2β -bromo- 3α -chloro derivative, because the former compound is isomorphous with one of the crystal modifications of $2\beta,3\alpha$ -dichloro- 5α -cholestane. Our results are in full agreement with those of the investigations of Barton and his coworkers (Alt & Barton, 1954; Barton & Rosenfelder, 1951), who based their proof of the structures on chemical evidence.

Experimental

$2\beta,3\alpha$ -Dichloro- 5α -cholestane, $C_{27}H_{46}Cl_2$, m.p. 110° – 112° , was prepared by adding dropwise a solution of chlorine in chloroform to a solution of 5α -cholest-2-ene in the presence of antimony trichloride (Alt & Barton, 1954). The resulting $2\beta,3\alpha$ -dichloro- and $2\alpha,3\beta$ -di-

* Photographic copies of the calculated and observed structure factors are available at the Laboratory of Organic Chemistry, University of Leiden, The Netherlands.

chlorocholestane were separated by chromatography. 2β -Chloro- 3α -bromo- 5α -cholestane was obtained by passing gaseous hydrogen chloride through a mixture of cholest-2-ene, *N*-bromosuccinimide and chloroform. The compound was purified by chromatography (m.p. 97° – 99°).

Single crystals suitable for X-ray analysis were obtained by slow crystallization from ethyl acetate. A description of the morphology and optical properties is to be found in an earlier publication (Geise, Romers & Hartman, 1962). Unit-cell dimensions (Table 1) at 20°C and at -120°C were measured from zero level Weissenberg photographs about [001] and [010], taken with copper radiation and superposed with aluminum powder diffraction lines ($a=4.0489$ Å at 20°C). The accuracy of the cell dimensions is about 0.2%. Densities were measured by the flotation method. The exposures at -120°C were made according to a technique first described by Kreuger (1955) and modified by Altona (1964). It follows from the absence of reflexions $0k0$ with $k=2n+1$ and from the observed optical activity of $2\beta,3\alpha$ -dichloro-cholestane that the space group is $P2_1$. The unit-cell contains two molecules.

The first six reciprocal layers about [001] and the first eight layers about [010] of $2\beta,3\alpha$ -dichloro- 5α -cholestane (β -modification) were recorded at -120° with the equi-inclination Weissenberg technique. There are 2908 independent reflexions within the limiting sphere, 66 of which could not be measured. The remaining 2842 reflexions, including 253 too weak to be observable, were estimated visually; these intensities were corrected for Lorentz-polarization and spot-shape effects. The linear absorption coefficient $\mu(\text{Cu } K\alpha)$ amounts to 23.6 cm^{-1} . The crystals chosen were sufficiently small and no absorption corrections were considered necessary. The structure factors were put on a common scale by correlation of common reciprocal lattice lines belonging to two zones [010] and [001]. The method used was a least-squares procedure according

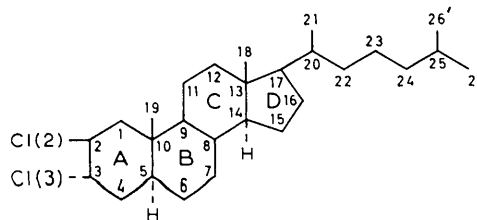


Fig. 1. The numbering of the atoms in $2\beta,3\alpha$ -dichloro- 5α -cholestane.

Table 1. Cell dimensions of some $2\beta,3\alpha$ -dihalogeno- 5α -cholestanes

Compound	Space group	Z	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β (°)	d_{exp} (g.cm ⁻³)	<i>T</i> (°C)
$2\beta,3\alpha$ -Dichloro- (β -Modification)	$P2_1$	2	13.45	10.54	10.07	113.15	1.12	20
			13.31	10.47	9.88	113.37		-120
2β -Chloro, 3α -bromo-	$P2_1$	2	13.56	10.59	10.08	112.50	1.21	20
			13.36	10.45	9.97	112.38		-120

to Rollett & Sparks (1960). The agreement index R_m between the two sets of scaled structure factors was:

$$R_m = (\sum |F_{\text{obs}1}| - |F_{\text{obs}2}|) / (\frac{1}{2} \sum |F_{\text{obs}1}| + |F_{\text{obs}2}|) = 0.12.$$

During the refinement the mean values $F_m = \frac{1}{2}(F_{\text{obs}1} + F_{\text{obs}2})$ were used for those reflexions occurring in both zones.

In order to make use of the isomorphous replacement technique (see below) the $h0l$ reflexions of 2 β -chloro,3 α -bromo-5 α -cholestane were recorded in the same way.

Structure determination and refinement

The close resemblance of the cell dimensions of 2 β ,3 α -dichloro and 2 β -chloro-3 α -bromo-cholestane indicates that the two compounds are isomorphous. The positional parameters x and z of the halogen atoms could be derived from the sharpened Patterson projections $P(u, w)$ for both compounds. The y parameters of the two chlorine atoms of the dichloro derivative were found from a similar Patterson projection $P(u, v)$.

An overall isotropic temperature parameter and the absolute scale factor were determined according to the well known method of Wilson. By means of the isomorphous replacement technique we were able to determine the signs of 75% of the $h0l$ reflexions. An electron density projection $\rho(x, z)$ of the dichloro-compound revealed the whole cholestane skeleton (Fig. 2).

The position of the bromine atom in the mixed chloro-bromo compound corresponds to that of the chlorine atom attached to C(3) in the dichloro derivative. This offered a direct proof of the structure and the configuration of 2 β -chloro-3 α -bromo-5 α -cholestane. Therefore, the structure of the other mixed chloro-bromo compound (m.p. 130°–133°) must be 2 β -bromo-

3 α -chloro-5 α -cholestane, because it was known beforehand from infrared spectra and dipole moments that the halogen atoms on C(2) and C(3) are in axial positions (Barton, Page & Shoppee, 1956; Geise 1964).

The molecule in Fig. 2 shows its flat side approximately parallel to the plane (010). The overlap is small, especially with respect to atoms belonging to the same molecule. An exception, however, is the region near the screw axes where severe overlap occurs between atoms belonging to different molecules. The $h0l$ reflexions were refined in three successive cycles of structure factor calculations and Fourier summations until an agreement index $R(h0l) = 23\%$ was attained.

The determination of the y parameters from electron density projections $\rho(x, y)$ was not very promising. On account of the severe overlap between neighbouring molecules the y parameters of all the atoms except hydrogen were derived from a three-dimensional wire model.

The y coordinate of Cl(3) was arbitrarily chosen zero and kept zero during the refinement of the structure. At this stage $R(hkl)$ was 34%. Next the $\sin \theta$ range was divided into three equal parts and the phases of reflexions were considered 'reliable' if the following criteria were satisfied (van der Helm, 1960):

$$|F_{\text{obs}}| > p; \quad |F_{\text{calc}}| \geq \frac{1}{2} \cdot |F_{\text{obs}}|.$$

The respective parameters p in the three ranges of increasing $\sin \theta$ values were chosen as 6.0, 4.5 and 3.0. This criterion is rather arbitrary, but nevertheless proved to be successful because the R index dropped to 27% after one cycle of Fourier and structure factor calculations. Further refinement was attained by the method of least squares on a Mercury computer with a program devised by Mills & Rollett (1960). The weight factor w was defined by:

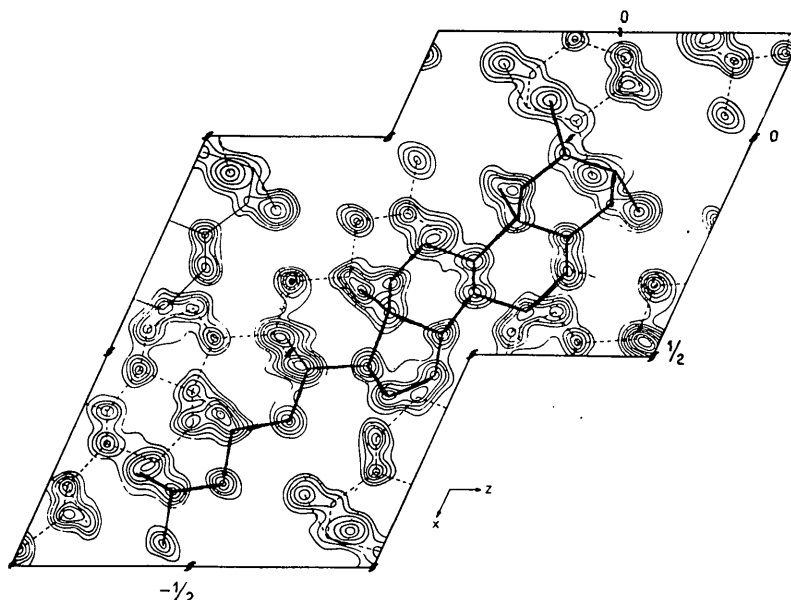


Fig. 2. Electron density, $\rho(x, z)$, of 2 β ,3 α -dichloro-5 α -cholestane. Contour lines are drawn on an arbitrary scale.

$$1/w = 1 + [(|F_{\text{obs}}| - a)/b]^2; \quad a = b = 8.$$

The scattering curves of carbon, chlorine and hydrogen respectively were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), Dawson (1960) and McWeeny (1951). After three cycles with individual isotropic temperature parameters, hydrogen positions were calculated. We assumed C-H dis-

tances to be 1.08 Å and C-C-H and H-C-H angles to be tetrahedral. The calculated hydrogen coordinates together with the overall isotropic temperature parameter ($B = 3.1 \text{ Å}^2$ for all hydrogen atoms) were not varied during the further refinement. In two more cycles the R index dropped to 14.5%. A difference Fourier synthesis based upon low angle reflexions and with hydrogen contributions not included showed that all hyd-

Table 2. *Coordinates in fractions of the cell edges and standard deviations (Å) of 2β,3α-dichlorocholestane*

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
Cl(2)	-0.0866	+0.1487	-0.0991	0.0021	0.0037	0.0025
Cl(3)	+0.1727	+0.0000	+0.2791	0.0022	0.0029	0.0024
C(1)	+0.1215	+0.0781	-0.0710	0.0080	0.0093	0.0089
C(2)	+0.0420	+0.0665	+0.0035	0.0085	0.0101	0.0096
C(3)	+0.0838	+0.1180	+0.1586	0.0081	0.0095	0.0095
C(4)	+0.1467	+0.2421	+0.1789	0.0093	0.0098	0.0095
C(5)	+0.2340	+0.2360	+0.1171	0.0080	0.0087	0.0082
C(6)	+0.3077	+0.3525	+0.1539	0.0094	0.0095	0.0093
C(7)	+0.4003	+0.3354	+0.1030	0.0092	0.0101	0.0092
C(8)	+0.3591	+0.3014	-0.0614	0.0083	0.0089	0.0087
C(9)	+0.2820	+0.1847	-0.0971	0.0075	0.0079	0.0080
C(10)	+0.1844	+0.2048	-0.0509	0.0076	0.0079	0.0077
C(11)	+0.2466	+0.1432	-0.2589	0.0074	0.0092	0.0080
C(12)	+0.3444	+0.1209	-0.3025	0.0074	0.0082	0.0080
C(13)	+0.4184	+0.2388	-0.2701	0.0075	0.0081	0.0081
C(14)	+0.4538	+0.2716	-0.1055	0.0082	0.0087	0.0085
C(15)	+0.5436	+0.3717	-0.0755	0.0089	0.0101	0.0091
C(16)	+0.6040	+0.3277	-0.1721	0.0085	0.0098	0.0092
C(17)	+0.5327	+0.2204	-0.2756	0.0078	0.0086	0.0087
C(18)	+0.3581	+0.3495	-0.3717	0.0085	0.0092	0.0091
C(19)	+0.1102	+0.3108	-0.1425	0.0090	0.0101	0.0101
C(20)	+0.5405	+0.2196	-0.4265	0.0078	0.0090	0.0088
C(21)	+0.4674	+0.1167	-0.5305	0.0082	0.0092	0.0088
C(22)	+0.6601	+0.1990	-0.4072	0.0080	0.0089	0.0088
C(23)	+0.6800	+0.2312	-0.5439	0.0087	0.0099	0.0096
C(24)	+0.8006	+0.2201	-0.5217	0.0092	0.0106	0.0102
C(25)	+0.8237	+0.2603	-0.6523	0.0107	0.0105	0.0110
C(26)	+0.9457	+0.2823	-0.6102	0.0125	0.0149	0.0137
C(26')	+0.7807	+0.1603	-0.7763	0.0124	0.0155	0.0112

Atom	x	y	z	Atom	x	y	z
H(2)	+0.024	-0.033	+0.010	H(24)	+0.852	+0.273	-0.425
H(3)	+0.015	+0.135	+0.192	H(19)	+0.829	+0.119	-0.493
H(5)	+0.286	+0.153	+0.170	H(18)	+0.079	+0.283	-0.260
H(8)	+0.314	+0.379	-0.125	H(21)	+0.156	+0.397	-0.129
H(9)	+0.331	+0.105	-0.031	H(26)	+0.042	+0.324	-0.113
H(14)	+0.496	+0.186	-0.043	H(26')	+0.343	+0.321	-0.486
H(17)	+0.565	+0.130	-0.221	H(21)	+0.407	+0.434	-0.345
H(20)	+0.512	+0.313	-0.477	H(26)	+0.280	+0.366	-0.365
H(25)	+0.783	+0.350	-0.698	H(21)	+0.493	+0.024	-0.481
H(1)	+0.179	-0.001	-0.037	H(26)	+0.383	+0.132	-0.550
H(4)	+0.077	+0.057	-0.189	H(26)	+0.477	+0.121	-0.635
H(6)	+0.184	+0.267	+0.293	H(26)	+0.986	+0.180	-0.566
H(7)	+0.092	+0.319	+0.125	H(26)	+0.980	+0.343	-0.524
H(11)	+0.342	+0.366	+0.274	H(26)	+0.966	+0.297	-0.702
H(12)	+0.260	+0.435	+0.101	H(26')	+0.823	+0.062	-0.728
H(15)	+0.451	+0.416	+0.124	H(26')	+0.797	+0.176	-0.870
H(16)	+0.454	+0.256	+0.166	H(26')	+0.694	+0.138	-0.807
H(22)	+0.192	+0.213	-0.329				
H(23)	+0.199	+0.055	-0.276				
H(23)	+0.390	+0.039	-0.246				
H(23)	+0.313	+0.101	-0.420				
H(23)	+0.598	+0.374	+0.037				
H(23)	+0.503	+0.464	-0.120				
H(23)	+0.610	+0.405	-0.241				
H(23)	+0.682	+0.290	-0.103				
H(23)	+0.713	+0.257	-0.316				
H(23)	+0.683	+0.101	-0.373				
H(23)	+0.651	+0.324	-0.582				
H(23)	+0.631	+0.166	-0.632				

rogen atoms were in positive areas (peak heights of about $0.4 \text{ e.}\text{\AA}^{-3}$), but no more accurate positions could be derived. Another difference Fourier synthesis based upon nearly all reflexions and calculated structure factors including hydrogen showed a marked anisotropy in the temperature parameters of the chlorine atoms. The anisotropy of the thermal vibrations of the carbon atoms was less pronounced but could be proved with certainty (Fig. 3).

Meanwhile new computing facilities became available and the least-squares refinement with anisotropic temperature parameters was continued on the X-1 computer of the University of Leiden. We introduced weights defined by:

$$1/w = (a + |F_{\text{obs}}| + bF_{\text{obs}}^2)/(a + F_{\text{min}}),$$

$F_{\text{min}} = 1.0$ being the overall minimum observable value of $|F_{\text{obs}}|$. The constants $a = 10.0$ and $b = 0.2$ were chosen

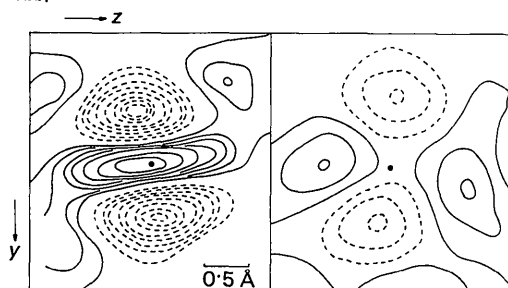


Fig. 3. Difference Fourier sections through Cl(3) (left) and C(26) (right) showing the anisotropy of the thermal motions. Contour lines are drawn on arbitrary scale; full lines indicate positive areas, dashed lines indicate negative areas.

in such a way as to make $\Sigma w(hkl)\Delta^2(hkl)$ approximately constant for all values of $|F_{\text{obs}}|$ (Cruickshank, *et al.*, 1960). Convergence was reached after five cycles. No positional shifts larger than 0.01 \AA were indicated, whereas the averaged shift was less than one fifth of the standard deviations. The final R value was 9.6% for observed reflexions only.

Results and accuracy

The positional parameters in fractions of the cell edges are listed in Table 2 and the thermal parameters defined by:

$$\exp \left\{ -2\pi^2(h^2a^*U_{11} + k^2b^*U_{22} + l^2c^*U_{33} + 2hka^*b^*U_{12} + hla^*c^*U_{13} + 2klb^*c^*U_{23}) \right\}$$

in Table 3.

The mean standard deviation in the coordinates is 0.0088 \AA . The estimated standard deviations in the cell edges are 0.002 \AA per length of 1.5 \AA . The mean standard deviations in the bond lengths and valency angles are about 0.013 \AA and 0.66° , respectively, giving rise to a 1% significance level of 0.04 \AA and 2° . No attempts were made to correct the distances for libration effects.

Discussion

The temperature parameters

By far the largest thermal motions are found at the ends of the molecule. The end of the side chain C(24), C(25), C(26) and C(26') and the two chlorine atoms Cl(2) and Cl(3) have temperature coefficients significantly higher than those of the atoms belonging to the

Table 3. Anisotropic temperature parameters of $2\beta,3\alpha$ -dichloro- 5α -cholestane

Atom	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Cl(2)	+0.021	+0.091	+0.044	+0.005	+0.029	+0.018
Cl(3)	+0.033	+0.046	+0.040	-0.007	+0.024	+0.019
C(1)	+0.023	+0.040	+0.035	-0.017	-0.013	+0.025
C(2)	+0.022	+0.051	+0.037	-0.011	-0.002	+0.023
C(3)	+0.022	+0.037	+0.047	-0.012	-0.005	+0.019
C(4)	+0.036	+0.040	+0.038	-0.001	-0.006	+0.036
C(5)	+0.027	+0.030	+0.030	+0.001	-0.008	+0.027
C(6)	+0.041	+0.036	+0.035	-0.021	-0.019	+0.038
C(7)	+0.036	+0.045	+0.035	-0.033	-0.027	+0.034
C(8)	+0.028	+0.033	+0.035	-0.016	-0.012	+0.034
C(9)	+0.022	+0.026	+0.027	-0.005	-0.003	+0.019
C(10)	+0.025	+0.026	+0.024	-0.006	-0.001	+0.022
C(11)	+0.023	+0.037	+0.032	-0.015	-0.010	+0.021
C(12)	+0.023	+0.027	+0.031	-0.006	-0.009	+0.021
C(13)	+0.022	+0.025	+0.031	-0.006	-0.009	+0.027
C(14)	+0.026	+0.031	+0.032	-0.012	-0.010	+0.020
C(15)	+0.033	+0.045	+0.032	-0.023	-0.013	+0.029
C(16)	+0.026	+0.042	+0.036	-0.013	-0.008	+0.023
C(17)	+0.024	+0.028	+0.037	-0.003	-0.003	+0.027
C(18)	+0.030	+0.033	+0.036	+0.004	+0.006	+0.026
C(19)	+0.030	+0.041	+0.049	+0.021	+0.018	+0.039
C(20)	+0.022	+0.033	+0.039	+0.005	+0.003	+0.025
C(21)	+0.031	+0.035	+0.036	-0.007	-0.015	+0.034
C(22)	+0.023	+0.038	+0.034	+0.004	-0.008	+0.024
C(23)	+0.028	+0.041	+0.044	-0.001	-0.002	+0.041
C(24)	+0.033	+0.048	+0.050	-0.002	-0.019	+0.052
C(25)	+0.048	+0.044	+0.053	-0.003	-0.002	+0.064
C(26)	+0.051	+0.084	+0.072	-0.025	-0.025	+0.078
C(26')	+0.063	+0.087	+0.043	-0.014	-0.033	+0.055

steroid skeleton. This can be understood since the packing (*vide infra*) of the side chain is not very dense. The same applies to the higher temperature parameters of C1(2) as compared with those of C1(3). The latter atom has more short intermolecular interactions with carbon atoms. The thermal motions of the carbon atoms C(5), C(9), C(10), C(13), C(17) and the atoms C(11) and C(12), that are near the mechanical centre of gravity, are low. The magnitudes and direction cosines of the principal axes of the ellipsoids of thermal motion derived from the anisotropic temperature coefficients are shown in Table 4.

The directions of maximum vibration of the carbon atoms belonging to the steroid skeleton are approximately perpendicular to the 'plane' of the rings. These direction vectors lie on the surface of a cone whose half angle amounts to 15° and whose axis makes an angle of 5° with the normal on the plane of the steroid skeleton. The directions of medium vibration (Fig. 4) are approximately perpendicular to the vectors connecting the atoms with the centre of gravity, which indicates that this part of the molecule may be considered as a rigid body.

Table 4. Magnitudes and direction cosines of the principal axes of the vibration ellipsoids, referred to orthogonal axes *abc**

l: large; m: medium; s: small

Atom	Axis	\bar{u}^2	<i>a</i>	<i>b</i>	<i>c</i> *
Cl(2)	<i>l</i>	0.095	-0.082	+0.956	+0.281
	<i>m</i>	0.043	+0.374	+0.291	-0.881
	<i>s</i>	0.021	+0.924	-0.032	+0.381
Cl(3)	<i>l</i>	0.061	-0.446	+0.698	+0.560
	<i>m</i>	0.032	-0.893	-0.392	-0.221
	<i>s</i>	0.031	+0.066	-0.599	+0.798
C(1)	<i>l</i>	0.046	+0.202	-0.846	+0.493
	<i>m</i>	0.033	+0.346	-0.410	-0.844
	<i>s</i>	0.019	+0.916	+0.341	+0.210
C(2)	<i>l</i>	0.052	+0.182	-0.983	-0.026
	<i>m</i>	0.038	+0.197	+0.011	+0.980
	<i>s</i>	0.020	+0.963	+0.184	-0.196
C(3)	<i>l</i>	0.051	-0.369	-0.019	-0.929
	<i>m</i>	0.039	-0.328	+0.938	+0.111
	<i>s</i>	0.020	+0.870	+0.346	-0.353
C(4)	<i>l</i>	0.042	+0.149	-0.784	+0.603
	<i>m</i>	0.038	-0.481	-0.591	-0.648
	<i>s</i>	0.030	-0.864	+0.193	+0.465
C(5)	<i>l</i>	0.034	-0.084	-0.740	+0.667
	<i>m</i>	0.028	-0.607	-0.493	-0.623
	<i>s</i>	0.022	-0.790	+0.458	+0.408
C(6)	<i>l</i>	0.051	+0.548	-0.624	+0.556
	<i>m</i>	0.031	+0.820	+0.269	-0.506
	<i>s</i>	0.026	+0.167	+0.733	+0.659
C(7)	<i>l</i>	0.060	+0.413	-0.774	+0.479
	<i>m</i>	0.030	+0.736	-0.026	-0.677
	<i>s</i>	0.022	+0.536	+0.632	+0.559
C(8)	<i>l</i>	0.042	+0.334	-0.654	+0.679
	<i>m</i>	0.029	+0.282	-0.619	-0.733
	<i>s</i>	0.021	-0.900	-0.436	+0.022
C(9)	<i>l</i>	0.028	—	—	—
	—	0.028	—	—	—
	<i>s</i>	0.021	+0.832	+0.418	+0.033
C(10)	<i>l</i>	0.029	+0.539	-0.709	+0.724
	<i>m</i>	0.022	—	—	—
	—	0.022	—	—	—

Table 4 (cont.)

Atom	Axis	\bar{u}^2	<i>a</i>	<i>b</i>	<i>c</i> *
C(11)	<i>l</i>	0.041	+0.252	-0.881	+0.400
	<i>m</i>	0.031	+0.441	-0.263	-0.858
	<i>s</i>	0.020	+0.861	+0.392	+0.323
C(12)	<i>l</i>	0.034	-0.099	-0.536	+0.838
	<i>m</i>	0.026	+0.616	-0.694	-0.372
	<i>s</i>	0.022	+0.781	+0.480	+0.399
C(13)	<i>l</i>	0.033	+0.137	-0.474	+0.870
	<i>m</i>	0.022	+0.112	-0.865	-0.489
	<i>s</i>	0.019	-0.984	-0.165	+0.065
C(14)	<i>l</i>	0.037	+0.121	-0.710	+0.694
	<i>m</i>	0.032	+0.700	-0.434	-0.566
	<i>s</i>	0.021	+0.704	+0.554	+0.445
C(15)	<i>l</i>	0.052	+0.417	-0.849	+0.325
	<i>m</i>	0.030	+0.369	-0.169	-0.914
	<i>s</i>	0.026	+0.830	+0.502	+0.243
C(16)	<i>l</i>	0.045	+0.220	-0.910	+0.351
	<i>m</i>	0.036	+0.423	-0.236	-0.875
	<i>s</i>	0.024	+0.879	+0.341	+0.333
C(17)	<i>l</i>	0.037	-0.081	-0.135	+0.988
	<i>m</i>	0.028	+0.215	-0.970	-0.115
	<i>s</i>	0.022	+0.973	+0.203	+0.107
C(18)	<i>l</i>	0.039	-0.069	+0.490	+0.869
	<i>m</i>	0.030	—	—	—
	—	0.030	—	—	—
C(19)	<i>l</i>	0.056	+0.166	+0.595	+0.787
	<i>m</i>	0.038	+0.436	+0.671	-0.600
	<i>s</i>	0.023	+0.885	-0.442	+0.148
C(20)	<i>l</i>	0.040	-0.140	+0.202	+0.969
	<i>m</i>	0.033	+0.200	+0.965	-0.172
	<i>s</i>	0.021	+0.970	-0.170	+0.176
C(21)	<i>l</i>	0.043	+0.156	-0.656	+0.738
	<i>m</i>	0.029	-0.555	-0.677	-0.485
	<i>s</i>	0.026	-0.818	+0.334	+0.469
C(22)	<i>l</i>	0.041	-0.221	-0.849	+0.479
	<i>m</i>	0.032	-0.052	-0.481	-0.875
	<i>s</i>	0.022	+0.974	-0.218	+0.062
C(23)	<i>l</i>	0.044	+0.150	-0.250	+0.957
	<i>m</i>	0.040	-0.025	-0.968	-0.249
	<i>s</i>	0.021	-0.988	-0.013	+0.151
C(24)	<i>l</i>	0.059	+0.098	-0.642	+0.760
	<i>m</i>	0.042	-0.340	-0.740	-0.581
	<i>s</i>	0.021	-0.936	+0.201	+0.290
C(25)	<i>l</i>	0.060	+0.478	-0.094	+0.873
	<i>m</i>	0.044	-0.004	-0.995	-0.105
	<i>s</i>	0.030	-0.878	-0.047	+0.476
C(26)	<i>l</i>	0.095	+0.222	-0.802	+0.554
	<i>m</i>	0.065	-0.155	-0.590	-0.792
	<i>s</i>	0.033	-0.963	-0.090	+0.256
C(26')	<i>l</i>	0.093	+0.110	-0.935	+0.337
	<i>m</i>	0.061	-0.905	-0.235	-0.355
	<i>s</i>	0.033	-0.411	+0.266	+0.872

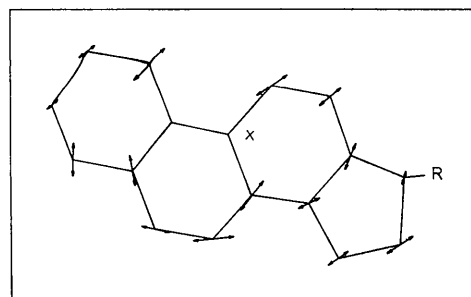


Fig. 4. Directions of medium vibration of the atoms of the steroid skeleton projected on the 'plane' of the molecule. The mechanical centre of gravity is marked with a cross.

Geometry of the molecule

The three rings *A*, *B* and *C* of the cholestane skeleton are *trans* connected and are in the chair form. The fusion between the cyclopentane ring *D* and ring *C* is *trans*. Contrary to a previous report (Geise, 1964) the conformation of the cyclopentane ring is not an envelope but a half chair with approximate symmetry C_2 instead of C_5 .

The two chlorine atoms on C(2) and C(3) are in axial positions. The side chain attached to C(17) is stretched in the 'plane' of the steroid skeleton, with both methyl groups C(21) and C(26') on the same side and nearly perpendicular to C(10)–C(19) and C(13)–C(18). A perspective view of the molecule is given in Fig. 5. Bond lengths and bond angles are summarized in Fig. 6.

There seem to be no significant deviations from the accepted values with respect to the distances. All carbon–carbon bonds are in the range 1.50–1.56 Å with a mean value of 1.532 Å. The two carbon–chlorine bonds (1.82 and 1.80 Å) are somewhat longer than the reported average C–Cl bond distance (1.767 Å; Sutton, 1958), but there are indications that the 'normal' aliphatic C–Cl bond has a length of about 1.78–1.79 Å (Bartell & Brockway, 1955; Miller, Aamodt, Dousmanis, Townes & Kraitchman, 1952; Schwendeman & Jacobs, 1962).

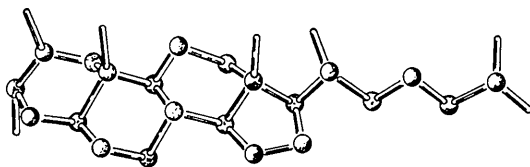


Fig. 5. A perspective view of the molecule drawn after a three-dimensional wire model based upon the final parameters.

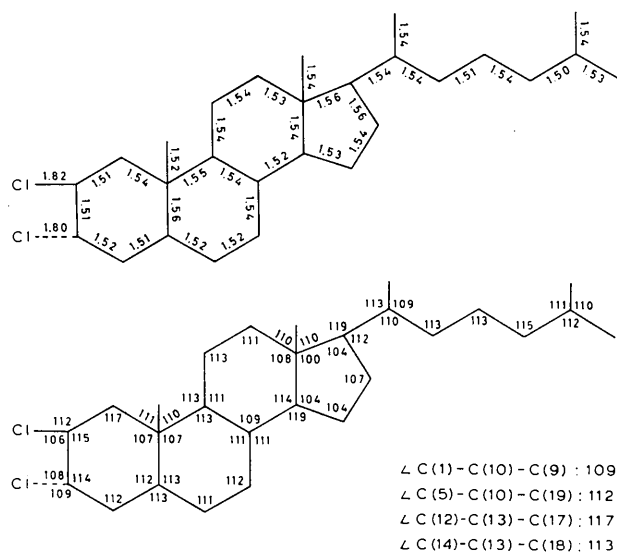


Fig. 6. Bond lengths (upper part) and bond angles (lower part) of 2β,3α-dichloro-5α-cholestane.

A consideration of the bond angles shows some interesting aspects. The average value of the angles within the cyclohexane rings (111.2°) is significantly larger than the ideal tetrahedral angle (109.5°). This implies that the perhydrophenanthrene skeleton is flattened with respect to the ideal model. The same effect has been found in other six-membered ring compounds, e.g. cyclohexane, dioxane (Davis & Hassel, 1963) and some dichlorodioxanes (Altona & Romers, 1963). The angles in the cyclopentane ring *D* are, as was expected, considerably smaller than 109.5° and this brings about, *inter alia*, an enlargement of the angle C(12)–C(13)–C(17) to 117° and of the angle C(8)–C(14)–C(15) to 119° . The angle C(2)–C(1)–C(10) has also an abnormally high value (117°), thus giving relief to the steric hindrance between the chlorine atom Cl(2) and the methyl group C(19). The two vectors C(2)–Cl(2) and C(3)–Cl(3) are not strictly antiparallel, but are at an angle of 157° . This value is slightly smaller than the 163° found for the C–Cl vectors in *trans*-2,3-dichlorodioxane-1,4 (Altona & Romers, 1963); this may arise from the flattening of the ring system coupled to an extra steric hindrance between Cl(2) and C(19). The angle of 157° gives a qualitative explanation of the rather high dipole moments found in this class of compounds. A more detailed discussion including dihedral angles and best planes will be given in a forthcoming publication.

Packing of the molecules

The molecules of 2β, 3α-dichloro-5α-cholestane* are packed approximately parallel to the plane (111). This accounts for the high value of the structure factor of

* The referee suggested that we should redefine the *a* and *c* axes in such a way as to conform the unit cells of 2β,3α-dichloro-5α-cholestane(*β* modification) and of 2β-chloro-3α-bromo-5α-cholestane with the geometric classification of steroids given by Bernal, Crowfoot & Fankuchen (1940). The transformation is given by: $a(\text{new}) = c$; $b(\text{new}) = b$; $c(\text{new}) = -c + a$. The unit-cell dimensions for the dichloro compound become: $a = 9.88$, $b = 10.47$, $c = 19.49$ Å; $\beta = 141.25^\circ$. The classification symbol is $b211$.

Table 5. Intermolecular distances up to 4.0 Å

Distance No.*	From (original mol)	to	in†	Distance
1	C(19)	Cl(3)	II	3.99 Å
2	C(19)	C(2)	II	3.92
3	C(15)	C(9)	V	3.99
4	C(16)	Cl(3)	V	3.96
5	C(22)	Cl(3)	V	3.78
6	C(23)	Cl(3)	V	3.81
7	C(24)	Cl(3)	V	3.71
8	C(22)	Cl(2)	IV	3.57
9	C(24)	Cl(2)	IV	3.91
10	C(18)	C(21)	VII	3.79
11	Cl(3)	C(21)	III	3.82
12	C(5)	C(21)	III	3.84
13	C(6)	C(21)	III	3.88
14	C(3)	C(26)	VI	3.86

* See Fig. 7.

† For the positions of the molecules I, II ... VII see Fig. 7.

the reflexion on this plane. Intermolecular distances, calculated up to a limit of 4.0 Å, are shown in Table 5. Fig. 7 shows a drawing of the structure viewed along [010]. No interactions shorter than the sum of the van der Waals radii occur. The packing is mostly supported by the protruding parts of the molecule, the chlorine atoms and the methyl groups. Most close contacts occur between molecules which are correlated by a screw axis shift of $\frac{1}{2}y$.

Calculations

The conversion of observed intensities to structure factor moduli was carried out with a data reduction program written by B. Hesper and the first author. Distances and angles were computed with a program devised by H. L. Jonkers and A. v. Loenen. The programs for molecular geometry, the calculation of hydrogen positions and some ancillary programs were made by W. Rutten and the first author. All programs mentioned above are written in ALGOL 60 language. The least-squares program used for anisotropic refinement was written by the third author. This program, written in X-1 machine code, is essentially the same as the one described by Cruickshank (1960). It uses 3×3 blocks for the positional parameters, 1×1 blocks for the isotropic temperature parameters and 6×6 blocks for the anisotropic temperature parameters. The scale factors (for different layers, if desired) are obtained from an $(n+1) \times (n+1)$ matrix, which contains the n scale factors and the over-all temperature parameter B . The difference between this B and a B' obtained from a separate 1×1 matrix of the overall temperature factor is added to the shifts resulting from the 1×1 blocks

for the individual temperature parameters (Sparks, 1960). The difference expressed in 6 anisotropic terms is added to the 6 anisotropic temperature parameters for each atom. Symmetry operations as translations and permutations are handled as described by Cruickshank. We use, however, for the alternations 8 different possibilities: xyz ; $-xyz$; $x-yz$; $xy-z$; $-x-y-z$; $x-y-z$; $-xy-z$; $-x-yz$, which are general for all space groups. Several weighting schemes (Cruickshank *et al.*, 1960; Mills & Rollett, 1960) and a possibility for individual weighting of each reflexion are available. Reflexions are read in one at a time so that no restrictions of their number exist. Storage is used in an economical way by using dynamic arrays for series of data of variable length. In the calculation of the trigonometric functions use is made of the formulae:

$$\begin{aligned}\cos(n+1)x &= 2 \cos x \cdot \cos nx - \cos(n-1)x, \\ \sin(n+1)x &= 2 \cos x \cdot \sin nx - \sin(n-1)x.\end{aligned}$$

Provisions for atoms on special positions have been made. It is possible to deal with any kind of special positions without further programming. One cycle of anisotropic refinement of 2 β ,3 α -dichloro-5 α -cholestane (2589 reflexions, 263 parameters to be refined) required about 5 hours. It is not necessary to run this in one session.

Fourier summations were calculated with a program that was written in X-1 code by the third author.

All calculations unless stated otherwise were carried out on the X-1 computer of the University of Leiden.

We wish to thank Professor Dr E. Havinga for his continuous interest in this work. Many thanks are also

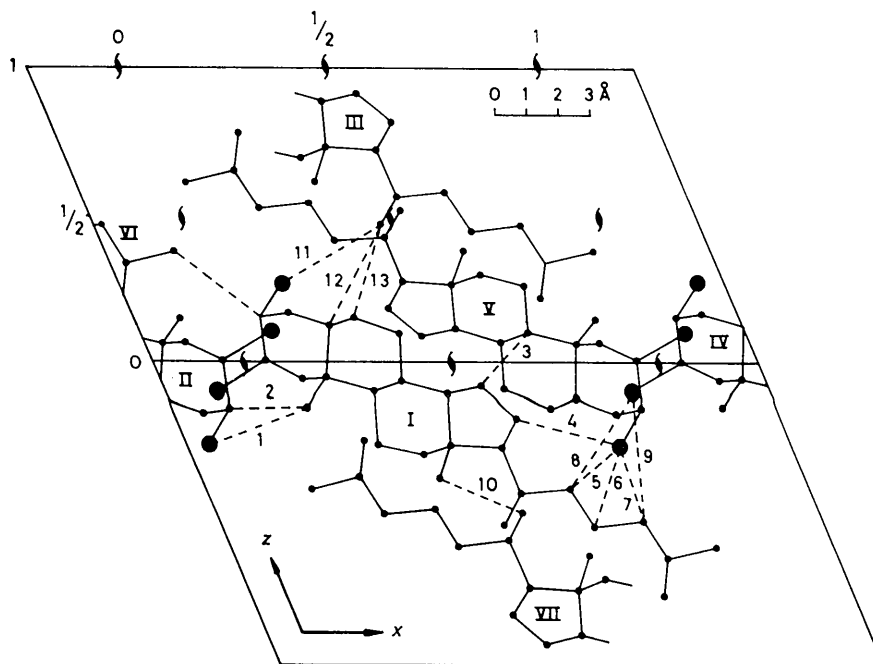


Fig. 7. The packing of the molecules viewed along the b axis. The positions of the molecules are: I x, y, z ; II $-x, y + \frac{1}{2}, -z$; III $x, y, z + 1$; IV $x + 1, y, z$; V $-x + 1, y + \frac{1}{2}, -z$; VI $x - 1, y, z + 1$; VII $-x + 1, y + \frac{1}{2}, -z + 1$.

offered to Professor D. Crowfoot-Hodgkin, who enabled one of us (H.J.G.) to use the Mercury computer of the University of Oxford. We are grateful to Dr J.S. Rollett and to the members of the staff of the Crystallography Laboratory of the University of Oxford for helpful discussions. Finally, we wish to thank the members of the Centraal Rekeninstituut of the University of Leiden for their assistance with the calculations performed on the X-1 computer.

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The Conformation of Non-Aromatic Ring Compounds.

XVII.* The Crystal Structures of 2 α , 3 β -dichloro- and 2 α , 3 β -dibromo-5 α -cholestane

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The isomorphous crystal structures of 2 α ,3 β -dichloro-5 α -cholestane and the corresponding dibromo compound were determined from a projection along [010] with the aid of room temperature data. Both structures were refined, the former with three-dimensional room-temperature data, and the latter with three-dimensional data collected at -120°C . The unit-cell dimensions of the bromo compound at -120°C are:

$$a = 14.99, b = 7.75, c = 11.49 \text{ \AA}, \beta = 105^{\circ} 17', Z = 2.$$

The space group is $P2_1$. The rings A , B and C have the chair form and ring D the conformation of a half chair with approximate symmetry C_2 . The cyclohexane rings, flatter than in the ideal model, give rise to a small enlargement of the angle between the carbon-halogen bonds. It proved possible to give crystallographic evidence for the structure of 2 α -bromo-3 β -chloro-5 α -cholestane, which is isomorphous with the compounds mentioned above.

Introduction

The present study forms part of a series of crystal structure determinations of halogen-substituted steroids (Geise, Romers & Rutten, 1966; Romers, van

Heijkoop, Hesper & Geise, 1965), dioxanes (Altona & Romers, 1963*a, b*; Altona, Knobler & Romers, 1963*a, b*) and dithianes (Kalff & Romers, 1965, 1966). The main objective of this work is to correlate the geometrical details with dipole moments, nuclear magnetic resonance spectra, infrared and ultraviolet absorption

* Part XVI, Geise, Romers & Rutten, 1966.