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The Conformation of Non-Aromatic Ring Compounds.
XVII.* The Crystal Structures of 2α, 3β-dichloro- and 2α, 3β-dibromo-5α-cholestane

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The isomorphous crystal structures of 2α,3β-dichloro-5α-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:

$$a=14{\cdot}99,\ b=7{\cdot}75,\ c=11{\cdot}49\ \text{Å},\ \beta=105°\ 17',\ Z=2.$$

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 2α-bromo-3β-chloro-5α-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

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

spectra. In contrast to what is found with 2β,3α-dichloro-5α-cholestane, which has its halogen atoms in axial positions, one expects no special distortion of ring *A* in the corresponding diequatorial derivatives. This would give the opportunity to investigate the conformation of the 'normally' distorted cholestane skeleton.

The numbering of the atoms (Fig. 1) is chosen in accordance with the usual chemical notation.

Experimental

2α,3β-Dibromo-5α-cholestane, $C_{27}H_{46}Br_2$, m.p. 146–148 °C, and 2α,3β-dichloro-5α-cholestane, $C_{27}H_{46}Cl_2$, m.p. 150–152 °C, were prepared by heating the corresponding 2β,3α-derivatives at ~200 °C for 1–2 hours in a nitrogen atmosphere (Hattori & Kawasaki, 1937; Alt & Barton, 1954).

Single crystals suitable for X-ray analysis were obtained by slow crystallization from ethyl acetate. The morphology and optical properties of these crystals have been previously described (Geise, Romers & Hartman, 1962). Unit-cell dimensions (Table 1) of the dibromo compound at 20 °C and at −120 °C were measured from zero level Weissenberg photographs (Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å) about [010] and [100]. The corresponding dimensions of the dichloro compound at room temperature were measured from a zero layer Weissenberg and a rotation photograph about [010]. Aluminum powder-diffraction lines ($a = 4{\cdot}0489$ Å at 20 °C) were superposed on the films for calibration purposes. A subsequent refinement of the cell dimensions of the dibromo compound at 20 °C and at −120 °C was obtained by the application of a least-squares procedure. The standard deviations are 0·007 Å in the cell edges and 4′ in the angle β. The corresponding errors are about 0·03 Å and 20′ for the other compounds. Densities were measured by the flotation method and result in an occupancy of two molecules per cell. The X-ray exposures at −120 °C were made according to the method of Kreuger (1955) and modified by Altona (1964*a*).

Systematically absent reflexions $0k0$ for k = odd indicate the space groups $P2_1$ or $P2_1/m$. The latter is ruled out, because the compounds under investigation are optically active.

The reflexion intensities of the first seven reciprocal layers about [010] and the first ten layers about [101] were recorded at room temperature with equi-inclination Weissenberg photographs (copper radiation) from two specimens (a needle and a cut crystal) of the dichloro compound. By these means, of the 2983 independent reflexions in the limiting sphere only 89 were not included. The remaining 2894 included 775 reflexions too weak to be observable. The observed intensities (2119) were estimated visually and corrected for Lorentz, polarization and spot-shape effects. The crystals chosen were sufficiently small to neglect absorption corrections ($\mu = 23{\cdot}6$ cm^{-1}).

Meanwhile the development in this laboratory of the low temperature Weissenberg technique (Altona, 1964*a*) had made sufficient progress to allow the recording of the reciprocal lattice of the dibromo compound at a temperature of −120 °C. Two cylinders with a radius of 0·007 cm were ground in the directions [010] and [100] enabling us to collect the reciprocal layers $k = 0, 1 \ldots 6$ and the layers $h = 0, 1 \ldots 10$.

In addition, Weissenberg photographs were made of $h0l$ reflexions diffracted at room temperature. There are 2936 independent reflexions within the copper limiting sphere of which 43 were outside the measuring range of the Weissenberg instrument. The number of unobserved reflexions is 370, half the number in the corresponding room-temperature data of the dichloro compound. The remaining 2523 were estimated visually by means of calibrated intensity strips. The intensities were corrected in the usual way for Lorentz, polarization and spot-shape effects. Since μR amounts to 0·28 only, no absorption corrections were made.

The structure factor moduli of the dichloro compound were put on a common scale by direct comparison of twice occurring reflexions in the zones [010] and [101]. Since the data of this latter zone were less reliable they were discarded in the refinement of the structure. The structure factors of the dibromo compound were put on a common scale by weighed correlation of reciprocal lattice lines occurring in [010] and [100] according to a least-squares procedure described by Rollett & Sparks (1960). The agreement index R_m between the two sets of scaled structure factors was

$$R_m = \Sigma\, [||F_o(1)| - |F_o(2)||] / \tfrac{1}{2}\Sigma\, |F_o(1)| + |F_o(2)| = 0{\cdot}14\,.$$

During the refinement mean values $F_m = [\frac{1}{2}|F_o(1)| + |F_o(2)|]$ were used for the reflexions occurring in both zones.

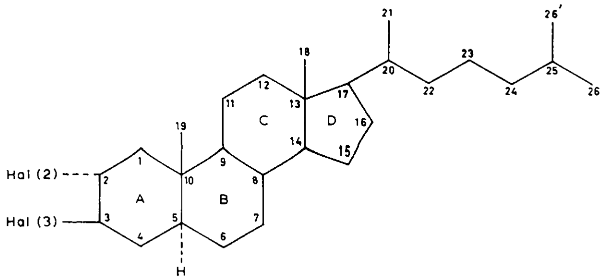

Fig. 1. The numbering of the atoms.

Table 1. *Unit-cell dimensions* (Å) *and densities* (g.cm^{-3}) *of a few 2α,3β-dihalogeno-5α-cholestanes*

Compound	*a*	*b*	*c*	β	*d*	*T*
2α,3β-Dibromo	15·05	7·77	11·50	104°30′	1·33	20 °C
2α,3β-Dibromo	14·99	7·75	11·49	105°17′		−120
2α-Bromo-3β-chloro	14·69	7·83	11·48	105°	1·23	20
2α,3β-Dichloro	14·88	7·74	11·44	105°	1·14	20

Structure determination and refinement

Nearly equal positions of the chlorine and bromine atoms in the asymmetric unit were derived from sharpened Patterson projections $P(uw)$ and $P(uv)$. The y parameter of the halogen atom attached to C(2) was arbitrarily chosen zero. An overall isotropic temperature parameter and an absolute scale factor were obtained by the method of Wilson for the $h0l$ reflexions of both steroids. The signs of about 80% of $h0l$ reflexions of of the dichloro derivative were established with the well-known isomorphous replacement technique. An electron-density projection $\varrho(x, z)$ based upon these reflexions revealed the whole molecule (Fig. 2). The methyl groups C(18) and C(19), the side chain and the chlorine atoms can be recognized in this projection, which suffers from severe overlap. Using C(18), C(19), and Cl(3) as protruding atoms of the molecule one can project an image of the molecule that covers all observed maxima in the electron-density projection.

Focusing our attention first on 2α,3β-dichloro-5α-cholestane we refined the $h0l$ reflexions of this molecule in two successive cycles of structure factor and electron-density calculations $\varrho(x, z)$ until no more signs changed. The agreement index $R(h0l)$ was 22% at this stage. The y-parameters of all atoms, except hydrogen, were next derived from a three-dimensional wire model. After two cycles of structure factors and electron-density calculations the agreement index R dropped from 43% to 28%. The phases of reflexions were considered 'reliable' if the following criteria were met (van der Helm, 1960):

$$|F_o| \geq 3;\ |F_c| \geq \tfrac{1}{2} \cdot |F_o| .$$

Further refinement was attained by the method of least squares on the Mercury computers of the Universities of Manchester and Oxford with a program devised by Rollett & Mills (1960). The weighting factor w used was given by

$$1/w = 1 + \{(|F_o| - b)/a\}^2; \quad a = 6{\cdot}0,\ b = 5{\cdot}0 .$$

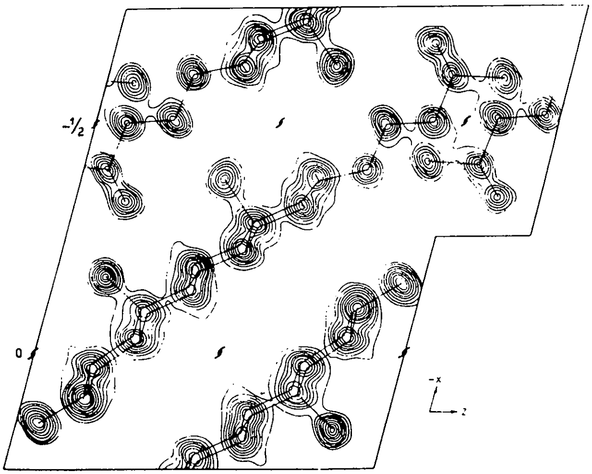

Fig. 2. Electron-density projection along the b axis of 2α,3β-dichloro-5α-cholestane. Contours are drawn at arbitrary intervals.

The scattering curves of carbon, bromine, chlorine and hydrogen were taken from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), Thomas & Umeda (1957), Dawson (1960) and McWeeny (1951), respectively. After five cycles with isotropic B's the agreement index was still high ($R = 22\%$). It is interesting to note that some side chain atoms shifted more than 1 Å during the refinement. At this stage positions of 46 hydrogen atoms were calculated, assuming bond distances C–H to be 1·08 Å and the bond angles C–C–H and H–C–H to be tetrahedral. The hydrogen positions together with their overall temperature factor ($B = 4{\cdot}0$ Å^2) were not altered during the further refinement. After three more cycles R dropped to 19·8% and no further refinement could be achieved. A difference Fourier synthesis showed no interpretable maxima or minima and a comparison between calculated and observed structure factors gave no indication of a better choice of weighting factors. It was realized that a better scaling of the different reciprocal layers $k = 0, 1 \ldots 6$ might have induced a better refinement. On the other hand the reliability of several observed intensities was rather poor and for this reason we decided to stop our attempts for better refinement of the chlorine compound. The atomic parameters and isotropic B's (except hydrogen) are given in Table 2.

The final positional parameters obtained in the refinement of the dichloro compound were used as initial parameters in the least-squares refinement of the dibromo compound. In the first two cycles an overall temperature factor $B = 3{\cdot}03$ Å^2 was applied. The constants of the weighting scheme were chosen as $a = b =$

Table 2. *Positional parameters in fractions of the cell edges and isotropic temperature parameters* (Å^2) *of 2α,3β-dichloro-5α-cholestane*

To allow easier handling of the photographs we transformed to a new unit cell, whose dimensions are: $a = 20{\cdot}99$, $b = 7{\cdot}74$, $c = 11{\cdot}44$ Å, $\beta = 136{\cdot}77°$. The positions given in this table are based upon this new cell. The transformation of indices and coordinates is given by

H (new) $= h - l$ X (new) $= x$
K (new) $= k$ Y (new) $= y$
L (new) $= l$ Z (new) $= x + z$

Atom	x	y	z	B
Cl(2)	+0·100	+0·000	+0·255	5·7
Cl(3)	+0·148	+0·380	+0·206	5·9
C(1)	−0·027	+0·168	+0·219	4·5
C(2)	+0·029	+0·191	+0·180	4·5
C(3)	+0·090	+0·360	+0·263	4·4
C(4)	+0·028	+0·510	+0·205	4·3
C(5)	−0·025	+0·490	+0·253	4·7
C(6)	−0·080	+0·651	+0·210	5·4
C(7)	−0·127	+0·632	+0·268	5·4
C(8)	−0·185	+0·471	+0·197	3·9
C(9)	−0·127	+0·306	+0·241	4·3
C(10)	−0·089	+0·325	+0·165	4·3
C(11)	−0·183	+0·136	+0·182	4·4
C(12)	−0·222	+0·121	+0·258	4·7
C(13)	−0·286	+0·281	+0·204	4·5
C(14)	−0·222	+0·442	+0·270	4·2
C(15)	−0·280	+0·589	+0·246	5·3
C(16)	−0·329	+0·500	+0·288	4·7
C(17)	−0·308	+0·305	+0·306	4·0

Table 2 (*cont.*)

Atom	*x*	*y*	*z*	*B*
C(18)	−0·372	+0·282	+0·014	4·7
C(19)	−0·167	+0·342	−0·032	4·1
C(20)	−0·389	+0·198	+0·252	4·0
C(21)	−0·373	−0·002	+0·261	5·4
C(22)	−0·398	+0·239	+0·372	5·0
C(23)	−0·494	+0·205	+0·293	4·6
C(24)	−0·500	+0·242	+0·416	4·4
C(25)	−0·596	+0·213	+0·342	5·3
C(26)	−0·591	+0·233	+0·480	5·9
C(26′)	−0·669	+0·330	+0·193	5·7
H(2)	−0·020	+0·199	+0·047	
H(3)	+0·141	+0·350	+0·402	
H(5)	+0·027	+0·471	+0·389	
H(8)	−0·243	+0·483	+0·062	
H(9)	−0·069	+0·298	+0·377	
H(14)	−0·162	+0·423	+0·406	
H(17)	−0·247	+0·280	+0·433	
H(20)	−0·454	+0·231	+0·122	
H(25)	−0·616	+0·082	+0·297	
H(1)	+0·021	+0·139	+0·356	
	−0·069	+0·050	+0·154	
H(4)	+0·068	+0·626	+0·259	
	−0·023	+0·521	+0·067	
H(6)	−0·031	+0·759	+0·279	
	−0·129	+0·679	+0·078	
H(7)	−0·077	+0·636	+0·401	
	−0·170	+0·744	+0·222	
H(11)	−0·139	+0·023	+0·225	
	−0·241	+0·128	+0·046	
H(12)	−0·164	+0·112	+0·396	
	−0·261	+0·001	+0·215	
H(15)	−0·230	+0·685	+0·344	
	−0·328	+0·631	+0·120	
H(16)	−0·298	+0·543	+0·412	
	−0·403	+0·521	+0·185	
H(22)	−0·380	+0·374	+0·411	
	−0·346	+0·168	+0·489	
H(23)	−0·546	+0·277	+0·179	
	−0·512	+0·069	+0·255	
H(24)	−0·478	+0·374	+0·461	
	−0·449	+0·166	+0·531	
H(19)	−0·211	+0·226	−0·088	
	−0·210	+0·453	−0·072	
	−0·137	+0·352	−0·079	
H(18)	−0·416	+0·172	−0·024	
	−0·413	+0·399	−0·024	
	−0·355	+0·279	−0·054	
H(21)	−0·309	−0·037	+0·388	
	−0·430	−0·070	+0·223	
	−0·370	−0·034	+0·173	
H(26)	−0·570	+0·363	+0·532	
	−0·540	+0·142	+0·584	
	−0·658	+0·205	+0·431	
H(26′)	−0·650	+0·464	+0·238	
	−0·735	+0·304	+0·145	
	−0·674	+0·313	+0·095	

6·0. Further refinement with isotropic individual *B*'s, during which hydrogen atoms were placed at calculated positions, proceeded without any difficulties. The agreement index dropped smoothly from 28% to 15·5% during five cycles.

A subsequent difference Fourier synthesis showed marked anisotropy in the thermal motion of the bromine atoms and a less pronounced anisotropy in the motion of several carbon atoms. The following refinement with anisotropic temperature parameters was performed on the X1 computer of the University of Leiden with a program devised by Mrs E. W. M. Rutten (Geise, Romers & Rutten, 1966). The hydrogen atoms were kept in fixed positions with isotropic *B*'s. The weighting factor $w=(a+F_{\min})/(a+|F_o|+b|F_o|^2)$ with $a=2, b=0{\cdot}2$ and $F_{\min}=6$ was used. $F_{\min}$ is the minimum observable value of F_o. After five cycles convergence was reached with a final *R* value of 10·1% for observed reflexions only. The largest shift in the final cycle was 0·019 Å. The average shifts were about 0·004 Å, *i.e.* less than one fifth of the standard deviation. The atomic parameters of 2α,3β-dibromo-5α-cholestane and their standard deviations are given in Table 3. The thermal parameters U_{11}, U_{22} *etc.* defined by $\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23}\}$ are listed in Table 4. The mean positional standard deviation of the carbon atoms in the dibromo compound is 0·014 Å. The mean standard deviations in the bond distances and the bond angles are 0·021 Å and 1° 24′. If we assume that the 30 C–C bonds in cholestane are chemically equivalent, one arrives at a standard deviation of 0·025 Å. (The same procedure is

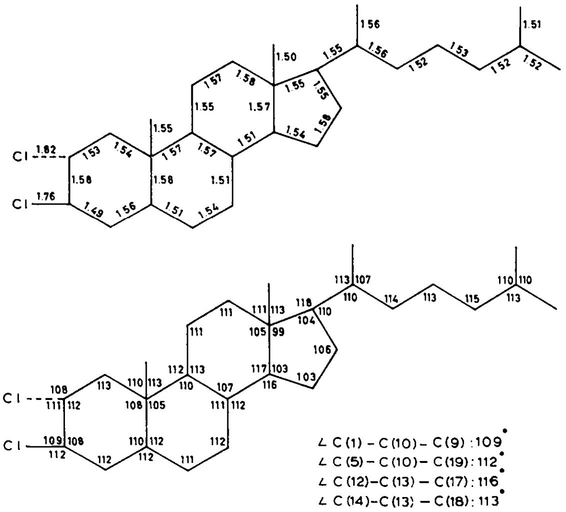

Fig. 3. Bond distances (Å) and valency angles (°) of 2α,3β-dibromo-5α-cholestane.

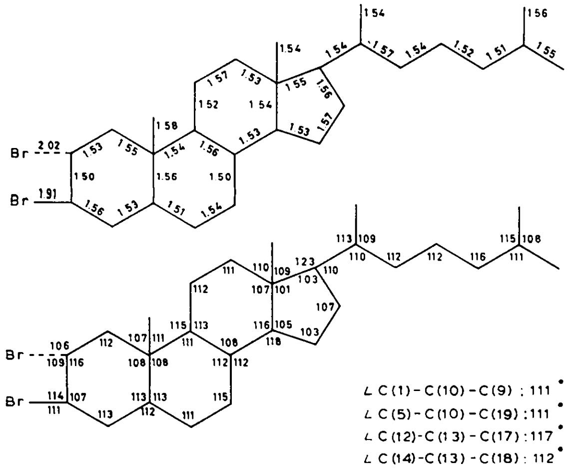

Fig. 4. Bond distances (Å) and valency angles (°) of 2α,3β-dibromo-5α-cholestane.

not allowed for the carbon bond angles, which are not chemically equivalent and exhibit significant deviations from the mean value.) The standard deviation in bond lengths and valency angles, computed with a program of J. S. Rollett, amounts to 0·035 Å and 2°, respectively. Photographic copies with calculated and observed structure factors of both compounds are on request available from the authors.

Molecular geometry and packing

Bond distances and bond angles of 2α,3β-dichloro- and 2α,3β-dibromo-5α-cholestane are summarized in Figs.

Table 3. *Positional parameters in fractions of the (first) cell edges, and their standard deviations* (Å), *of 2α,3β-dibromo-5α-cholestane*

	x	*y*	*z*	σ(*x*)	σ(*y*)	σ(*z*)
Br(2)	+0·1038	+0·0000	+0·1577	0·002	0·003	0·002
Br(3)	+0·1526	+0·4084	+0·0603	0·002	0·003	0·002
C(1)	−0·0309	+0·1780	+0·2459	0·014	0·018	0·013
C(2)	+0·0256	+0·2125	+0·1554	0·014	0·018	0·016
C(3)	+0·0871	+0·3680	+0·1790	0·012	0·017	0·013
C(4)	+0·0250	+0·5252	+0·1889	0·013	0·017	0·014
C(5)	−0·0303	+0·4993	+0·2826	0·013	0·021	0·013
C(6)	−0·0832	+0·6601	+0·2980	0·016	0·018	0·018
C(7)	−0·1336	+0·6338	+0·3970	0·015	0·019	0·016
C(8)	−0·1905	+0·4719	+0·3847	0·013	0·016	0·013
C(9)	−0·1342	+0·3095	+0·3671	0·013	0·017	0·014
C(10)	−0·0922	+0·3344	+0·2587	0·013	0·016	0·013
C(11)	−0·1868	+0·1418	+0·3662	0·013	0·015	0·015
C(12)	−0·2254	+0·1236	+0·4804	0·014	0·017	0·014
C(13)	−0·2866	+0·2776	+0·4914	0·013	0·016	0·013
C(14)	−0·2288	+0·4418	+0·4938	0·013	0·014	0·012
C(15)	−0·2859	+0·5857	+0·5295	0·014	0·018	0·015
C(16)	−0·3347	+0·4919	+0·6172	0·013	0·018	0·013
C(17)	−0·3131	+0·2960	+0·6122	0·013	0·016	0·015
C(18)	−0·3750	+0·2773	+0·3866	0·015	0·020	0·014
C(19)	−0·1707	+0·3501	+0·1365	0·014	0·018	0·013
C(20)	−0·3906	+0·1893	+0·6422	0·014	0·018	0·016
C(21)	−0·3772	−0·0058	+0·6309	0·015	0·022	0·016
C(22)	−0·3970	+0·2305	+0·7735	0·014	0·019	0·016
C(23)	−0·4948	+0·1971	+0·7876	0·013	0·020	0·016
C(24)	−0·5011	+0·2322	+0·9153	0·014	0·017	0·014
C(25)	−0·5942	+0·2010	+0·9389	0·016	0·017	0·015
C(26)	−0·6683	+0·3246	+0·8625	0·017	0·023	0·019
C(26′)	−0·5898	+0·2212	+0·0752	0·018	0·019	0·016

	x	*y*	*z*
H(2)	−0·0202	+0·2252	+0·0682
H(3)	+0·1368	+0·3505	+0·2669
H(5)	+0·0204	+0·4777	+0·3708
H(8)	−0·2479	+0·4837	+0·3063
H(9)	−0·0750	+0·3064	+0·4460
H(14)	−0·1693	+0·4241	+0·5709
H(17)	−0·2506	+0·2719	+0·6856
H(20)	−0·4559	+0·2243	+0·5751
H(25)	−0·6166	+0·0693	+0·9147
H(1)	+0·0144	+0·1458	+0·3337
	−0·0737	+0·0633	+0·2175
H(4)	+0·0702	+0·6415	+0·2151
	−0·0217	+0·5540	+0·1024
H(6)	−0·0368	+0·7702	+0·3151
	−0·1334	+0·6855	+0·2106
H(7)	−0·0842	+0·6433	+0·4848
	−0·1797	+0·7501	+0·3957
H(11)	−0·1409	+0·0322	+0·3646
	−0·2422	+0·1316	+0·2869
H(12)	−0·1689	+0·1146	+0·5619
	−0·2642	+0·0021	+0·4751
H(15)	−0·2387	+0·6831	+0·5794
	−0·3355	+0·6304	+0·4500
H(16)	−0·3095	+0·5395	+0·7063
	−0·4086	+0·5079	+0·5832
H(21)	−0·3783	+0·3662	+0·7915
	−0·3475	+0·1534	+0·8350
H(23)	−0·5451	+0·2808	+0·7259
	−0·5158	+0·0659	+0·7634
H(24)	−0·4791	+0·3653	+0·9409
	−0·4486	+0·1570	+0·9781

	x	*y*	*z*
H(19)	−0·2124	+0·2339	+0·1236
	−0·2128	+0·4609	+0·1410
	−0·1388	+0·3641	+0·0633
H(18)	−0·4156	+0·1609	+0·3936
	−0·4144	+0·3893	+0·3903
	−0·3555	+0·2702	+0·3025
H(21)	−0·3129	−0·0420	+0·6953
	−0·4335	−0·0741	+0·6539
	−0·3745	−0·0411	+0·5418
H(26)	−0·5674	+0·3551	+0·1013
	−0·5186	+0·2592	+0·1214
	−0·6350	+0·3253	+0·0864
H(26′)	−0·6469	+0·4583	+0·8887
	−0·7341	+0·3017	+0·8792
	−0·6712	+0·3072	+0·7693

3 and 4. Since most bond distances, bond angles and conformational aspects of both molecules are the same within the limits of error, we confine ourselves to a discussion of the molecular geometry of the bromine compound. The C–C bond lengths are in the range 1·49–1·58 Å and do not deviate significantly from the accepted value (1·53 Å; Bartell, 1959). The C–Br bond lengths [C(2)–Br(2) = 2·02 Å, C(3)–Br(3) = 1·91 Å] differ among each other by 0·11 Å. The possible significance of this difference is supported by a similar, though insignificant difference of 0·06 Å between the corresponding C–Cl bonds in the dichloro derivative. The C(2)–Br(2) bond distance possibly is also significantly larger than the accepted value (1·94 Å) for paraffinic C–Br bonds. So far we have found no explanation for this observed difference.

The valency bond angles show some interesting aspects. The angles within the cyclohexane rings are on the average somewhat larger (111°) than the normal tetrahedral value. Although the deviation of each angle by itself is insignificant, the deviation of the averaged value is significant indeed, because of the large number of data. The small enlargement of the valency angle is connected with a flattening of the ring system (Altona, 1964*b*). This flattening of six-membered ring systems in comparison with the ideal chair form seems to be the rule rather than the exception. It has been found in dioxane (Davis & Hassel, 1963), several dihalogenodioxanes (Altona & Romers, 1963*a*, *b*; Altona, Knobler & Romers, 1963*a*, *b*), 2,3-dichlorodithiane (Kalff & Romers, 1965) and in 2β,3α-dichloro-5α-cholestane (Geise, Romers & Rutten, 1966). The equatorial halogen atoms do not give rise to an extra distortion of ring *A* in contrast with the axially substituted chlorine atoms in the 2β,3α compound. The angle between the two C–Br vectors (74°) is only slightly larger than the ideal value (70·5°), but consistent with the flattening of the ring system. The bond angles within ring *D* are considerably smaller than 109·5°. The equatorial valencies starting from C(14) and C(13) are therefore bent towards each other, resulting in an enlargement of the angles C(12)–C(13)–C(17) and C(8)–C(14)–C(15) to about 117°.

Table 5. *Selected intermolecular distances in 2α,3β-dibromo-5α-cholestane*

The numbering of the distances corresponds to the numbering in Fig. 5.

The following notation has been used:

I	molecule at	x	y	z
II		$-x$	$y+\frac{1}{2}$	$-z$
III		$-x$	$y+\frac{1}{2}$	$-z+1$
IV		$-x-1$	$y+\frac{1}{2}$	$-z+1$
V		x	$y+1$	z

1	B(3) ··· C(2)II	3·92 Å
2	C(4) ··· Br(2)II	3·95
3	C(19) ·· Br(2)II	3·95
4	C(6) ··· C(26)IV	3·91
5	C(7) ··· C(26)IV	3·90
6	C(14) ·· Br(2)III	3·97
7	C(15) ·· Br(2)III	3·95
8	C(17) ·· Br(2)III	3·87
9	C(16) ·· Br(2)III	3·73
10	C(26) ·· C(11)IV	3·83
	C(4) ··· Br(2)V	3·91
	C(15) ·· C(21)V	3·75
	C(16) ·· C(21)V	3·95

Table 4. *Thermal parameters U_{11}, U_{22} etc. of 2α,3β-dibromo-5α-cholestane*

	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{31}$
Br(2)	+0·046	+0·061	+0·045	+0·023	+0·004	+0·043
Br(3)	+0·042	+0·074	+0·058	−0·001	+0·014	+0·056
C(1)	+0·041	+0·061	+0·029	+0·000	−0·012	+0·039
C(2)	+0·034	+0·055	+0·051	+0·007	+0·016	+0·049
C(3)	+0·023	+0·066	+0·032	−0·006	+0·013	−0·020
C(4)	+0·032	+0·048	+0·046	+0·008	+0·002	+0·020
C(5)	+0·037	+0·055	+0·042	−0·008	−0·013	+0·048
C(6)	+0·046	+0·045	+0·060	+0·011	+0·010	+0·051
C(7)	+0·047	+0·053	+0·052	−0·005	−0·011	+0·055
C(8)	+0·037	+0·049	+0·032	+0·013	+0·006	+0·027
C(9)	+0·038	+0·041	+0·042	+0·008	+0·001	+0·041
C(10)	+0·033	+0·049	+0·035	+0·013	−0·003	+0·026
C(11)	+0·037	+0·038	+0·051	−0·013	−0·001	+0·056
C(12)	+0·034	+0·047	+0·046	+0·005	+0·009	+0·037
C(13)	+0·037	+0·043	+0·032	+0·006	−0·001	+0·035
C(14)	+0·035	+0·040	+0·029	+0·015	−0·001	+0·020
C(15)	+0·042	+0·046	+0·048	+0·012	+0·003	+0·043
C(16)	+0·041	+0·036	+0·048	+0·012	−0·008	+0·046
C(17)	+0·036	+0·039	+0·051	+0·010	+0·011	+0·046
C(18)	+0·044	+0·066	+0·033	+0·000	−0·003	+0·021
C(19)	+0·035	+0·068	+0·029	+0·016	−0·006	+0·013
C(20)	+0·038	+0·043	+0·053	−0·005	−0·002	+0·031
C(21)	+0·060	+0·042	+0·061	−0·019	−0·003	+0·073
C(22)	+0·032	+0·066	+0·046	−0·004	+0·000	+0·035
C(23)	+0·024	+0·078	+0·051	−0·026	+0·007	+0·054
C(24)	+0·036	+0·057	+0·034	+0·004	−0·002	+0·034
C(25)	+0·049	+0·049	+0·044	−0·012	+0·004	+0·051
C(26)	+0·041	+0·079	+0·071	+0·020	+0·001	+0·051
C(26′)	+0·060	+0·060	+0·046	−0·001	−0·000	+0·056

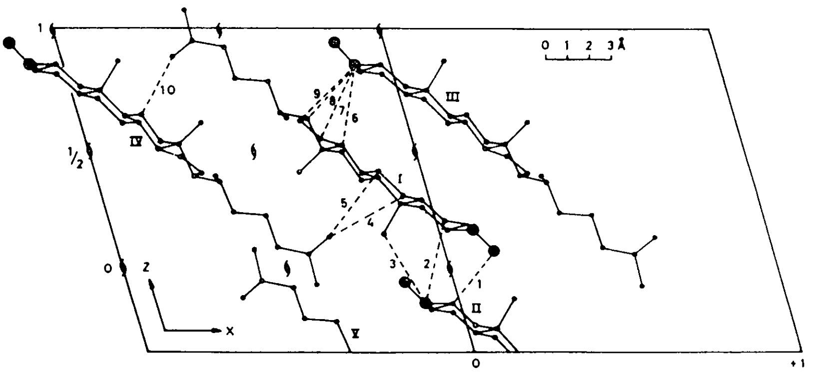

Fig. 5. View of the molecules of 2α,3β-dibromo-5α-cholestanes projected along the *b* axis. The numbered intermolecular distances are listed in Table 5.

The conformation of the side chain attached to C(17) is essentially the same as that of the one in 2β,3α-dichloro-5α-cholestane.

The molecules of 2α,3β-dihalogeno-5α-cholestane are nearly parallel to the plane (202) and this accounts for the high observed value of the structure factor $F(202)$. All intermolecular distances $\leq 4{\cdot}0$ Å are listed in Table 5. A projection of the structure along [010] is illustrated in Fig. 5. No abnormally short contacts are found. The packing of the hydrogen atoms has not been taken into account.

The structure of 2α-bromo-3β-chloro-5α-cholestane

There are four *trans*-2,3-bromo,chloro-5α-cholestanes, which fall into two groups. The halogen atoms are in axial positions in one and in equatorial positions in the other group. Chemical evidence (Alt & Barton, 1954) and measurements of electric dipole moments (Geise, 1964) distinguish between the two classes. In a previous paper on the structure of 2β,3α-dichloro-5α-cholestane (Geise, Romers & Rutten, 1966) we gave additional crystallographic evidence for the postulated structures of the two diaxial mixed compounds.

The structures of the equatorial mixed derivatives as given by Alt & Barton are supported by the crystallographic investigations described in this paper. A crystal was chosen from the compound (m.p. 134°–136°) with the postulated structure 2α-bromo-3β-chloro-5α-cholestane. A zero layer Weissenberg photograph about [010] was made with copper radiation. The *h*0*l* reflexions were estimated visually and reduced in the usual way to structure factors. The cell dimensions indicated that the compound is isomorphous with the 2α,3β-dibromo derivative. It was assumed that the atomic coordinates of the mixed and of the dibromo compound are the same. Structure factors were calculated for 2α-bromo-3β-chloro- and 2α-chloro-3β-bromo-5α-cholestane. The experimental structure factors are in good agreement with those calculated for 2α-bromo-3β-chloro-5α-cholestane and consequently, did not agree with the other postulated structure. The remaining diequatorial chlorobromo compound of melting point 156 °C is 2α-chloro-3β-bromo-5α-cholestane.

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