

to the c_{hex} axis is altered from $BCBC\dots$ to $ABCABC\dots$. As a result, each layer type (A , B or C) will contain molecules with either of the phase II orientations. To overcome this asymmetry, the molecule on each site is allowed to occupy either of these two orientations. A small rotation yields the two orientations around the $[111]_{\text{cub}}$ direction of the phase I structure. Further, the four diagonals of a face-centred cube must be threefold axes. Thus, on each site, two molecular orientations are allowed around each of the four $\langle 111 \rangle_{\text{cub}}$ directions, symmetrically equivalent to the two around $[111]_{\text{cub}}$. This produces the phase I structure. It is seen, therefore, that the structures of the two phases are simply related.

Recently, Reynolds (1974) presented a theoretical analysis of the plastic phase transformation in TEDA. At the time of publication, neither the solution to the phase II molecular conformation problem, nor a determination of the phase I structure was available (Nimmo & Lucas, 1976*a,b*). Thus Reynolds assumed a conformation for the molecule; in fact he chose the correct conformation. He approximated the crystal behaviour by using models for the orientational disordering, and predicted a structure for phase I from that of phase II. Although no precise structural description is given, his predicted structure appears to be in agreement with the experimentally determined one (Nimmo & Lucas, 1976*a,b*) both in terms of the equilibrium positions of the molecule around the f.c.c. lattice sites, and the occurrence of hindered molecular reorientations.

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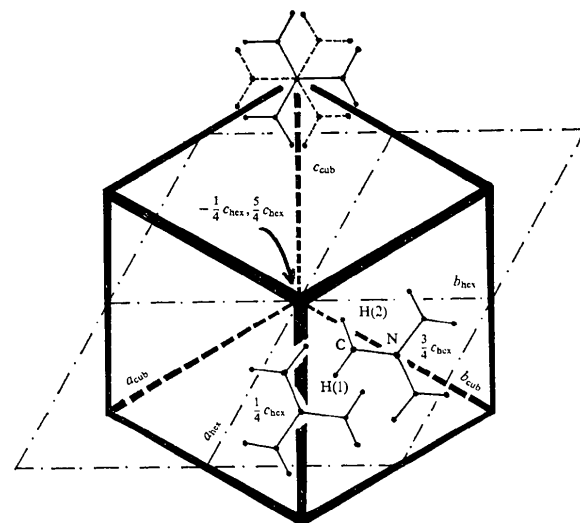


Fig. 1. The relation between the hexagonal (approximately h.c.p.) and f.c.c. unit cells appropriate to phases II and I of TEDA respectively. The cube is viewed along its $[111]_{\text{cub}}$ direction (centre of the diagram and out of the page), which is coincident with the c_{hex} axis; the cube origin is located at $-\frac{1}{4}c_{\text{hex}}$. The phase II structure is illustrated in the hexagonal unit cell at the lower right of the diagram (heights refer to the centroids of the two molecules). The two orientations of the molecule (centred on a f.c.c. lattice site) around the $[111]_{\text{cub}}$ direction for phase I are shown at the top of the diagram. There are two such orientations about each of the other $\langle 111 \rangle_{\text{cub}}$ directions, symmetrically related to those shown; the molecule on each lattice site undergoes hindered reorientations between these eight orientations.

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The crystal structure of 3 α ,5 β -dibromocholestane. By S. GORTER, *Gorlaeus Laboratories, X-ray and Electron Diffraction Section, University of Leiden, P.O. Box 75, Leiden, The Netherlands*

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Crystals of 3 α ,5 β -dibromocholestane are orthorhombic: $a=28.513(3)$, $b=7.003(1)$, $c=13.225(2)$ Å, $Z=4$, space group $P2_12_12_1$. The structure was determined by Patterson methods, using 1359 diffractometer-measured reflexions (Cu $K\alpha$ radiation). The refined structure ($R=4.74\%$) does not show unusual features in bond lengths, valency or torsion angles. However, the side chain displays an unusual conformation: it is folded about the bonds 20–22 and 23–24.

In a solution of chloroform saturated with hydrogen bromide the steroid 3 β -hydroxy-5 α ,6 β -dibromocholestane can be converted at room temperature into a mixture of mainly two compounds (Warmerdam & van der Gen, 1976): 3 α ,5 β -dibromo- and 3 β ,5 α -dibromocholestane. Due to loss of hydrogen bromide in the mass spectrometer experiments the composition of the reaction products

could not be settled beyond doubt and it was decided to carry out a diffraction analysis of the former compound.

Orthorhombic colourless needles were obtained by recrystallization from acetone: $a=28.513(3)$, $b=7.003(1)$, $c=13.225(2)$ Å at 20°C; space group $P2_12_12_1$; $D_{\text{exp}}=1.30$ g cm $^{-3}$, $Z=4$. 1359 symmetry-independent reflexion intensities larger than twice the standard deviation were meas-

Table 1. Fractional coordinates and vibrational parameters ($\text{\AA}^2 \times 10^3$) of the heavy atoms of $3\alpha,5\beta$ -dibromocholestane. E.s.d.'s are given in parentheses in units of the last decimal. The temperature factor is defined as $\exp(-2\pi^2 \sum_{i,j=1,2,3} a_i^* a_j^* h_i h_j U_{ij})$.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Br(1)	0.22571 (4)	0.0938 (2)	1.12464 (8)	94 (1)	100 (1)	49 (1)	6 (1)	5 (1)	15 (1)
Br(2)	0.15311 (4)	-0.1653 (3)	0.80918 (10)	73 (1)	130 (2)	92 (1)	-37 (1)	0 (1)	-6 (1)
C(1)	0.2165 (4)	0.3468 (19)	0.9117 (8)	59 (7)	67 (11)	66 (6)	13 (7)	15 (7)	17 (6)
C(2)	0.1908 (3)	0.2112 (24)	0.8459 (7)	43 (6)	106 (14)	51 (6)	23 (7)	11 (8)	-7 (5)
C(3)	0.1859 (4)	0.0180 (21)	0.8960 (7)	59 (7)	81 (13)	50 (6)	-26 (7)	-2 (7)	10 (5)
C(4)	0.2330 (4)	-0.0620 (19)	0.9271 (8)	71 (8)	56 (11)	54 (6)	-8 (7)	13 (7)	1 (5)
C(5)	0.2608 (3)	0.0781 (20)	0.9907 (7)	54 (6)	65 (12)	47 (6)	2 (7)	-11 (8)	8 (5)
C(6)	0.3082 (4)	-0.0073 (20)	1.0213 (8)	87 (8)	66 (11)	60 (6)	5 (7)	14 (7)	-2 (6)
C(7)	0.3433 (3)	-0.0091 (21)	0.9312 (7)	61 (6)	79 (13)	51 (6)	24 (7)	-11 (8)	-10 (5)
C(8)	0.3470 (3)	0.1836 (18)	0.8835 (7)	44 (5)	45 (10)	55 (6)	10 (6)	13 (7)	-2 (5)
C(9)	0.2984 (3)	0.2615 (19)	0.8505 (6)	37 (5)	58 (10)	47 (5)	7 (5)	1 (6)	-10 (4)
C(10)	0.2650 (3)	0.2792 (19)	0.9445 (7)	50 (6)	42 (11)	46 (6)	-2 (6)	7 (7)	1 (5)
C(11)	0.3010 (3)	0.4400 (26)	0.7879 (7)	44 (5)	57 (10)	69 (6)	12 (6)	4 (8)	5 (5)
C(12)	0.3363 (3)	0.4265 (18)	0.6986 (7)	50 (5)	59 (9)	68 (6)	-1 (5)	21 (7)	3 (5)
C(13)	0.3840 (3)	0.3642 (20)	0.7357 (7)	36 (5)	56 (11)	61 (6)	5 (6)	2 (8)	-3 (4)
C(14)	0.3786 (3)	0.1776 (18)	0.7896 (7)	44 (5)	50 (11)	53 (6)	11 (6)	-7 (7)	-10 (5)
C(15)	0.4297 (3)	0.1021 (20)	0.8023 (8)	51 (5)	77 (10)	88 (7)	21 (6)	4 (8)	-18 (5)
C(16)	0.4544 (3)	0.1703 (20)	0.7067 (8)	48 (5)	100 (12)	83 (7)	15 (7)	-16 (8)	11 (6)
C(17)	0.4202 (3)	0.3052 (18)	0.6481 (6)	40 (5)	88 (10)	39 (5)	1 (6)	-3 (6)	1 (4)
C(18)	0.4058 (3)	0.5167 (19)	0.8011 (7)	60 (6)	81 (11)	59 (6)	-6 (7)	1 (8)	5 (5)
C(19)	0.2847 (4)	0.4231 (20)	1.0198 (8)	84 (8)	61 (11)	65 (7)	4 (8)	0 (7)	5 (6)
C(20)	0.4455 (4)	0.4588 (23)	0.5922 (8)	56 (6)	128 (14)	75 (7)	-13 (8)	-14 (9)	-1 (6)
C(21)	0.4121 (4)	0.5869 (26)	0.5301 (26)	64 (7)	160 (16)	93 (8)	-19 (9)	44 (10)	12 (6)
C(22)	0.4839 (4)	0.3893 (30)	0.5199 (9)	66 (8)	197 (18)	85 (8)	-2 (10)	19 (12)	-1 (7)
C(23)	0.4708 (4)	0.2536 (28)	0.4391 (9)	67 (7)	195 (19)	88 (8)	-3 (10)	-20 (12)	-9 (7)
C(24)	0.5095 (5)	0.2018 (28)	0.3666 (9)	147 (14)	208 (22)	78 (9)	4 (15)	-4 (13)	2 (10)
C(25)	0.5515 (4)	0.1098 (22)	0.3994 (8)	75 (8)	141 (16)	72 (7)	-3 (9)	-19 (10)	7 (6)
C(26)	0.5347 (7)	-0.0962 (26)	0.4272 (14)	$B=12.5 (6) \text{\AA}^2$					
C(27)	0.5864 (5)	0.1042 (36)	0.3192 (12)	$B=13.6 (6) \text{\AA}^2$					

ured on a diffractometer using graphite-monochromatized Cu $K\alpha$ radiation. θ - 2θ scanning was employed between $\theta=5$ and 50° . Due to radiation damage the crystal slowly deteriorated during the measurement. A number of standard reflexions were used to correct for loss in scattering. For the same reason, however, an absorption correction could not be made.

Conventional Patterson methods produced the molecular structure, while block-diagonal least-squares refinement [anisotropic for Br and C, but isotropic for C(26) and C(27), fixed isotropic B 's and fixed positions for H atoms] resulted in weighted 6.75% and unweighted 4.74% R values. Some evidence for disorder of the tail atoms C(25), C(26) and C(27) was observed.

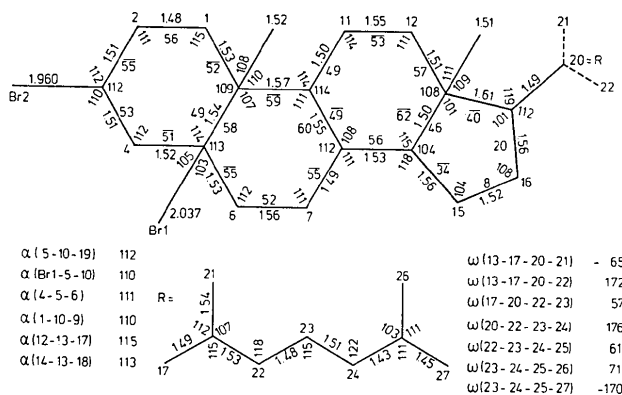


Fig. 1. Bond lengths (\AA), valency (α) and torsion (ω) angles ($^\circ$) of $3\alpha,5\beta$ -dibromocholestane.

The positional and vibrational parameters together with their e.s.d.'s are collected in Table 1.* The $\sigma(\text{C-C})$ values vary between 0.015 and 0.027 \AA , $\sigma(\text{C-Br})=0.011 \text{\AA}$. The molecular geometry of the molecule (Fig. 1) does not deviate significantly from the picture one expects on the basis of the average molecular entities for 5β -androstanone (Romers, Altona, Jacobs & de Graaff, 1974). Contrary to the fully stretched side chains observed in nine cholestanes (*cf.* Romers *et al.*) the side chain of $3\alpha,5\beta$ -dibromocholestane is folded about the bonds 20-22 and 23-24.

The full set of crystallographic data and atomic parameters will be forwarded to the Medical Foundation of Buffalo in order to include these data in the *Atlas of Steroid Structures* (Duax & Norton, 1975) and no further publication is intended.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31998 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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