rotation about the orthonormal x axis of +15°.* The figures were produced using a modified version of the program *PLUTO* written by S. Motherwell, G. P. Jones and P. J. Pauling (unpublished).

All computations were carried out on the University College London IBM 360/651, the University of London CDC 6600 and our GT 44. The programs for the GT 44 were written by Douglas Richardson.

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* The orthonormal axes are defined as $x_o = a^*$, $y_o = c \times a^*$, $z_o = c$.

Table 5. *Selected torsion angles* (°) *for non-hydrogen atoms*

N(1)–C(3)–C(4)–C(5)	−139	O(1)–C(7)–C(8)–O(3)	175
C(1)–N(1)–C(3)–C(4)	−51	O(1)–C(7)–C(8)–C(9)	−67
C(2)–N(1)–C(3)–C(4)	73	O(1)–C(7)–C(8)–C(15)	54
C(3)–C(4)–C(5)–C(6)	120	C(7)–C(8)–C(9)–C(10)	76
C(4)–C(5)–C(6)–O(1)	−158	C(7)–C(8)–C(15)–C(16)	179
C(5)–C(6)–O(1)–C(7)	88	C(9)–C(8)–C(15)–C(20)	177
C(6)–O(1)–C(7)–C(8)	−171		

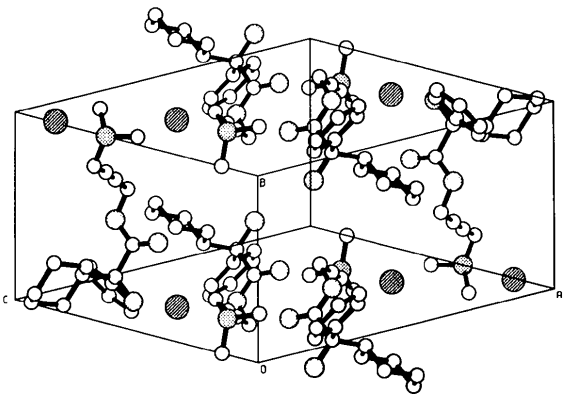

Fig. 2. Molecular packing viewed down the c axis with rotation about the orthonormal Y axis of 45° and rotation about the orthonormal X axis of 15°.

References

BAKER, R. W. & PAULING, P. J. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 1247–1249.

BUSING, W. R., ELLISON, R. D., LEVY, H. A., KING, S. P. & ROSEBURY, R. T. (1968). Report ORNL-143. Oak Ridge National Laboratory, Tennessee.

CLARKE, P. J., PAULING, P. J. & PETCHER, T. J. (1975). *J. Chem. Soc. Perkin Trans.* 2, pp. 774–778.

CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

INCH, T. D. & BRIMBLECOMBE, R. W. (1971). *J. Pharm. Pharmacol.* **23**, 813–815.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KARLE, J. & HAUPTMAN, H. (1953). *Acta Cryst.* **6**, 131–141.

KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635–651.

Acta Cryst. (1979). B**35**, 1123–1128

Pseudosymmetry in Cholesterol Monohydrate

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Abstract

Cholesterol monohydrate ($C_{27}H_{47}O.H_2O$) is triclinic, space group $P1$, with $a = 12{\cdot}39$ (3), $b = 12{\cdot}41$ (3), $c = 34{\cdot}36$ (6) Å, $\alpha = 91{\cdot}9$ (1), $\beta = 98{\cdot}1$ (1), $\gamma = 100{\cdot}8$ (1)° and has eight molecules each of cholesterol and water in the unit cell. There are systematic absences in X-ray reflections hkl when h, k are both odd, and the diffraction symmetry is almost $2/m$. The crystal structure has a bilayer arrangement of cholesterols. Each side of the bilayer has a subcell containing two cholesterol molecules. The two similar subcells have repeats $(a, b/2)$ and $(a/2, b)$ with a common c direction. At the interface between subcell regions, which consists of a layer of hydrogen-bonded hydroxyl groups and water molecules, there is local twofold symmetry.

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Introduction

The crystal structure determination of cholesterol monohydrate has been reported, its biological significance discussed and a possible epitaxical relationship with hydroxyapatite has been pointed out (Craven, 1976). Crystallographic aspects of the structure of cholesterol monohydrate are now described in more detail.

Cholesterol monohydrate is of interest because of its crystallographic pseudosymmetry. By this is meant that the true space group is augmented by space-group operations, which apply at least approximately to a localized region of the structure. Pseudosymmetry also occurs in the crystal structures of cholesterol (Shieh, Hoard & Nordman, 1977*a*), cholesterol hemimethanolate (Shieh & Nordman, 1978), the triclinic and monoclinic forms of cholesterol hemiethanolate (Shieh, Hoard & Nordman, 1977*b*; Shieh & Nordman, 1977) and sodium cholesteryl sulfate dihydrate (Pascher & Sundell, 1977). There are considerable differences in the nature of the pseudosymmetry in this series of crystal structures.

Pseudosymmetry in the diffraction pattern

The crystal structure of cholesterol monohydrate was determined using a crystal grown from slow evaporation of an acetone–water solution at room temperature. The X-ray data were measured on a computer-controlled diffractometer with Cu $K\alpha$ graphite-monochromated radiation (λ = 1·5418 Å). Unit-cell parameters were obtained by least-squares fit to the diffractometer angle data for eight reflections. The Niggli reduced cell, a = 12·39 (3), b = 12·41 (3), c = 34·36 (6) Å, α = 91·9 (1), β = 98·1 (1), γ = 100·8 (1)°, contains $8(C_{27}H_{46}O).8H_2O$. The corresponding reciprocal lattice is shown in Fig. 1. X-ray intensities were measured for all reflections with $\sin\theta/\lambda < 0{\cdot}5$ Å^{-1} in a hemisphere of reciprocal space. Of 10 157 independent reflections, only 2495 were obtained with intensity $I > 2\sigma(I)$. The high proportion of weak intensities was due to the large atomic thermal vibrations (overall isotropic B = 7·6 Å^2) and to a remarkable systematic absence of reflections *hhl* with h and k both odd (Fig. 1). The strongest such intensity was $4\sigma(I)$, and all but 15 were less than $2\sigma(I)$. None of these was used in the structure determination. The diffraction symmetry was triclinic ($\bar{1}$) but was unusual in being approximately monoclinic ($2/m$). The pseudo-mirror plane ('*m*' in Fig. 1) coincides with the *hhl* net, so that the pseudo-twofold axis ('2' in Fig. 1) is parallel to the crystal axis [1$\bar{1}$0], which happens to be within 0·1° of the reciprocal lattice vector 44$\bar{1}$. A comparison of observed structure amplitudes in the rows 20*l*, 02*l* (Fig. 2) which are related by the pseudomirror plane, shows significant differences. However, in other rows, such as 2$\bar{2}$*l* (Fig. 2), the pseudosymmetry is striking.

Following Bogren & Larsson (1963) it was considered whether the crystal might be twinned on (001). This might explain the systematic absences in *hkl* which are inconsistent with those of any Bravais lattice, and also the pseudomonoclinic symmetry. Twinning would require the observed reciprocal lattice (Fig. 1) to be a superposition of two identical lattices with common c^*. The two cells which are indicated by shaded faces in Fig. 1 and which are related by the pseudomirror might appear to be identical, but this is not so. They are similar, but nonsuperposable because of differences in cell angles.

The crystal structure was assumed to consist of two subcell regions with a common c direction having translations (a, $b/2$) in the first region and ($a/2$, b) in the second. The first subcell region would then

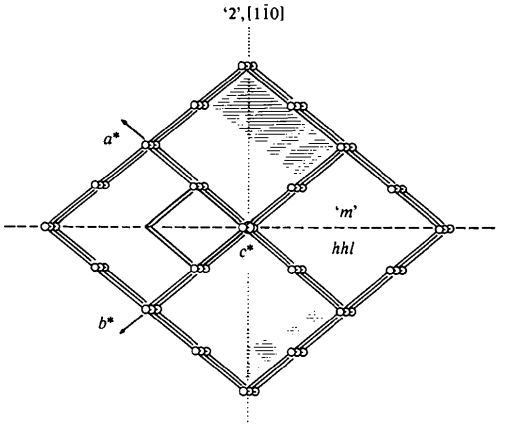

Fig. 1. The reciprocal lattice for cholesterol monohydrate. The small cell which is outlined is the true triclinic reciprocal cell, with translations a^*, b^*, c^*. Omitted rows (h, k both odd) are those with systematically-absent reflections.

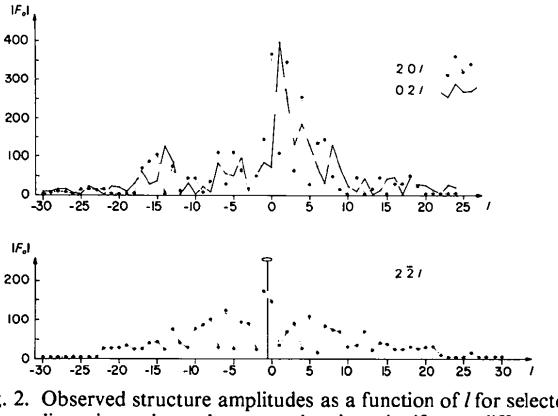

Fig. 2. Observed structure amplitudes as a function of l for selected row lines in reciprocal space, showing significant differences between 20*l* and 02*l*, but remarkable pseudosymmetry in the row 2$\bar{2}$*l*.

contribute no diffracted intensity to reflections *hkl* with *k* odd and the second would contribute nothing to those with *h* odd, thus explaining the systematic absences.

Pseudosymmetry in the crystal structure

There has been no further refinement since the earlier report (Craven, 1976). The final carbon and oxygen parameters are in Table 1.* These give $R = \sum |\Delta| / \sum |F_o| = 0{\cdot}12$, where $\Delta = |F_o| - |F_c|$ and the summation is with respect to the 2480 reflections with $I > 2\sigma$ which were used in the refinement. Because the structure determination was carried out at low resolution ($d_{min} = 1{\cdot}0$ Å), the atom positional parameters have high e.s.d.'s (0·04 Å).†

In each of the pairs of molecules (*A*,*B*), (*C*,*D*), (*E*,*F*) and (*G*,*H*) there are no significant differences from an exact subcell translational symmetry. Thus in Table 1, atoms at (*x*,*y*,*z*) in molecules *A* and *E* correspond to atoms at (x, $\frac{1}{2}+y$, z) in molecules *B* and *F* respectively, and atoms at (*x*,*y*,*z*) in molecules *C* and *G* correspond to atoms at ($\frac{1}{2}+x$, y, z) in molecules *D* and *H*.

The nearly-equivalent subcell regions (*ABEF*) and (*CDGH*) have an interface at the puckered layer of hydrogen-bonded hydroxyl groups and water molecules which is parallel to the (001) crystal face. In order to be compatible with both subcell regions, the interfacing layer should have the repeat translations (*a*/2, *b*/2). The hydrogen-bonding layer repeats in this way [Fig. 2 in Craven (1976)] but not as regularly as in the cholesterol subcells. Another consequence of interfacing the cholesterol subcell regions is the development of local twofold symmetry axes which pass through the hydrogen-bonding region and are parallel to [110]. Each of these local symmetry elements relates only two molecules, such as (*A*,*G*) or (*F*,*D*) which are shown in Fig. 3.* The symmetry operation consists of 180° rotation about the symmetry axis, coupled with a translation of 2·5 Å parallel to the [1$\bar{1}$0] direction. The local symmetry is effective for the steroid framework, but the relationship is progressively lost in the side chain from atom C(17) towards the end of the molecule. Thus the molecular arrangement is very similar in the two cholesterol subcells represented by (*A*,*F*) and (*D*,*G*) in Fig. 3, except in the side-chain region. The differences in the conformations of the side chains are compared more directly in Fig. 4. Sawzik & Craven (1979) have compared the conformations of the steroid frameworks in cholesterol monohydrate and in eight cholesteryl ester molecules. The fragments C(1) to C(19) from two molecules were superposed and the best fit determined by least squares (Nyburg, 1974). For the molecules *A*, *C*, *E*, *G*, taken in pairs, the r.m.s. displacements of corresponding atoms range from 0·15 to 0·11 Å, with the worst fit between *A* and *E*. The conformational differences are slight, but possibly significant. For all twelve molecules taken in pairs, r.m.s. displacements ranged from 0·20 to 0·05 Å.

* The generated hydrogen atom parameters and a table of observed and calculated structure amplitudes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34210 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Within experimental error, the values of bond lengths and angles agree with those accurately determined for cholesteryl acetate (Sawzik & Craven, 1979).

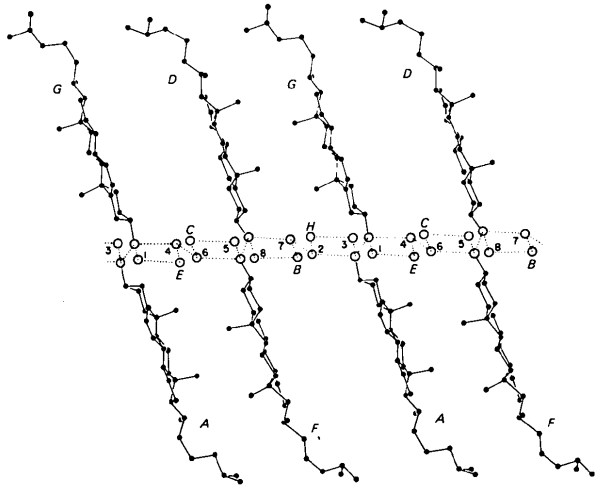

Fig. 3. A partial structure in projection down the [1$\bar{1}$0] axis. Local twofold symmetry relates molecules *A* to *G* and *F* to *D*. Open circles are oxygen atoms which are denoted by numbers for water and letters for cholesterol oxygens.

Discussion

Pseudosymmetry appears to be a common feature in those cholesterol crystal structures which have hydro-

* Atomic coordinates in Å can be obtained for an orthogonal system with axes [1$\bar{1}$0], c^* and [1$\bar{1}$0] × c^* by postmultiplying the matrix (9·451, −9·567, −2·398/0, 0, 33·953/−7·904, −7·904, 4·694) by the fractional atomic coordinates in Table 1. This transformation was used in preparing Fig. 3.

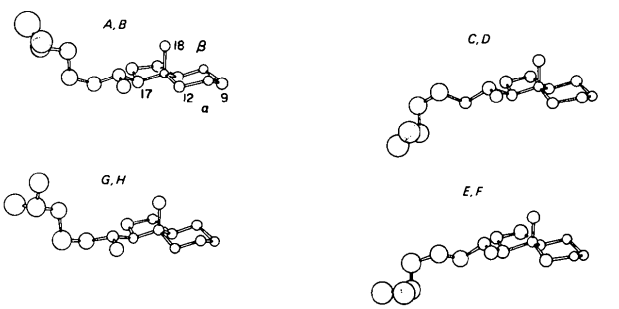

Fig. 4. Conformations of the side chains at atom C(17). There is a common orientation for the steroid skeleton, which is shown in part. Carbon atoms are represented as 25% probability spheres.

Table 1. *Atomic parameters for cholesterol monohydrate*

Water oxygen atoms are labelled *W*. Cholesterol carbon and oxygen atoms are labelled with a letter denoting the molecule and a number which conforms to the chemical nomenclature. Positional parameters are fractional coordinates ($\times 10^3$). E.s.d.'s for positional and isotropic thermal parameters are given in parentheses and refer to the least significant digit in the parameter value. Positional parameters without e.s.d.'s were derived from inspection of the electron-density map.

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
W(1)	32 (3)	602 (3)	522 (1)	10 (1)	*W*(5)	979 (3)	806 (3)	491 (1)	12 (1)
W(2)	528 (3)	621 (3)	518 (1)	11 (1)	*W*(6)	12 (3)	111 (3)	521 (1)	13 (1)
W(3)	482 (3)	304 (3)	488 (1)	11 (1)	*W*(7)	497 (3)	819 (3)	489 (1)	12 (1)
W(4)	980 (3)	305 (3)	493 (1)	12 (1)	*W*(8)	532 (2)	115 (2)	526 (1)	8 (1)
A(OH)	360 (3)	426 (2)	528 (1)	9 (1)	*B*(OH)	355 (3)	925 (3)	526 (1)	10 (1)
A(1)	250 (4)	407 (3)	624 (1)	8 (1)	*B*(1)	256 (4)	904 (3)	624 (1)	9 (1)
A(2)	253 (3)	429 (3)	584 (1)	7 (1)	*B*(2)	250 (3)	930 (3)	582 (1)	7 (1)
A(3)	368 (4)	416 (4)	572 (1)	10 (1)	*B*(3)	367 (5)	909 (4)	569 (2)	12 (2)
A(4)	369 (3)	282 (3)	573 (1)	7 (1)	*B*(4)	364 (3)	787 (3)	571 (1)	7 (1)
A(5)	370 (4)	264 (4)	619 (1)	10 (1)	*B*(5)	370 (4)	765 (4)	617 (1)	10 (2)
A(6)	441 (3)	216 (3)	638 (1)	6 (1)	*B*(6)	445 (3)	717 (3)	637 (1)	5 (1)
A(7)	449 (3)	186 (3)	679 (1)	5 (1)	*B*(7)	446 (3)	688 (3)	677 (1)	5 (1)
A(8)	350 (3)	197 (3)	697 (1)	5 (1)	*B*(8)	353 (3)	703 (3)	698 (1)	5 (1)
A(9)	305 (3)	303 (3)	679 (1)	8 (1)	*B*(9)	309 (4)	803 (4)	681 (1)	7 (1)
A(10)	276 (3)	291 (3)	635 (1)	5 (1)	*B*(10)	276 (3)	794 (3)	635 (1)	5 (1)
A(11)	208 (3)	317 (3)	703 (1)	5 (1)	*B*(11)	206 (3)	816 (3)	702 (1)	6 (1)
A(12)	232 (3)	319 (3)	750 (1)	9 (1)	*B*(12)	236 (4)	822 (3)	747 (1)	7 (1)
A(13)	278 (3)	221 (3)	764 (1)	4 (1)	*B*(13)	279 (3)	722 (3)	763 (1)	5 (1)
A(14)	373 (4)	212 (3)	740 (1)	8 (1)	*B*(14)	374 (4)	711 (4)	739 (1)	9 (1)
A(15)	428 (3)	121 (3)	764 (1)	7 (1)	*B*(15)	424 (3)	620 (3)	763 (1)	6 (1)
A(16)	398 (4)	127 (4)	806 (1)	9 (1)	*B*(16)	410 (4)	632 (4)	806 (1)	9 (1)
A(17)	333 (4)	225 (3)	807 (1)	8 (1)	*B*(17)	334 (4)	726 (4)	805 (1)	8 (1)
A(18)	186 (3)	122 (3)	754 (1)	7 (1)	*B*(18)	182 (3)	621 (3)	753 (1)	6 (1)
A(19)	174 (3)	211 (3)	624 (1)	7 (1)	*B*(19)	166 (4)	712 (3)	621 (1)	8 (1)
A(20)	258 (4)	208 (4)	836 (1)	10 (1)	*B*(20)	259 (4)	713 (4)	838 (1)	10 (2)
A(21)	191 (4)	296 (4)	838 (2)	11 (1)	*B*(21)	195 (5)	799 (4)	838 (2)	11 (2)
A(22)	336 (5)	204 (5)	876 (2)	13 (2)	*B*(22)	335 (5)	707 (5)	877 (2)	12 (2)
A(23)	264 (5)	184 (5)	915 (2)	15 (2)	*B*(23)	260 (5)	684 (5)	912 (2)	14 (2)
A(24)	183	81	908	17 (2)	*B*(24)	180	584	909	16 (2)
A(25)	143	62	951	22 (3)	*B*(25)	142	560	950	23 (3)
A(26)	30	80	952	29 (4)	*B*(26)	30	575	946	29 (4)
A(27)	130	−56	960	38 (6)	*B*(27)	135	442	960	36 (5)
C(OH)	163 (3)	−1 (3)	488 (1)	12 (1)	*D*(OH)	659 (3)	1 (3)	484 (1)	11 (1)
C(1)	244 (4)	−7 (4)	386 (1)	10 (1)	*D*(1)	750 (4)	1 (4)	385 (1)	10 (1)
C(2)	237 (4)	−37 (4)	430 (1)	10 (1)	*D*(2)	730 (4)	−35 (4)	428 (2)	11 (2)
C(3)	189 (4)	53 (4)	446 (1)	10 (1)	*D*(3)	689 (4)	57 (4)	446 (1)	10 (2)
C(4)	77 (3)	65 (3)	426 (1)	5 (1)	*D*(4)	576 (3)	64 (3)	424 (1)	6 (1)
C(5)	101 (3)	94 (3)	385 (1)	6 (1)	*D*(5)	600 (3)	97 (3)	383 (1)	6 (1)
C(6)	58 (3)	184 (3)	366 (1)	7 (1)	*D*(6)	560 (4)	185 (4)	365 (1)	8 (1)
C(7)	64 (3)	219 (3)	327 (1)	7 (1)	*D*(7)	561 (3)	216 (3)	327 (1)	7 (1)
C(8)	87 (3)	126 (3)	300 (1)	7 (1)	*D*(8)	588 (3)	129 (3)	298 (1)	7 (1)
C(9)	175 (3)	71 (3)	322 (1)	5 (1)	*D*(9)	675 (3)	74 (3)	321 (1)	6 (1)
C(10)	152 (3)	23 (3)	362 (1)	5 (1)	*D*(10)	649 (3)	25 (3)	359 (1)	6 (1)
C(11)	223 (3)	−6 (3)	296 (1)	7 (1)	*D*(11)	726 (4)	−2 (3)	295 (1)	7 (1)
C(12)	257 (4)	46 (3)	256 (1)	8 (1)	*D*(12)	757 (4)	49 (3)	254 (1)	10 (1)
C(13)	162 (3)	95 (3)	236 (1)	6 (1)	*D*(13)	664 (3)	96 (3)	234 (1)	5 (1)
C(14)	130 (3)	179 (3)	263 (1)	6 (1)	*D*(14)	633 (3)	179 (3)	262 (1)	6 (1)
C(15)	58 (3)	241 (3)	237 (1)	7 (1)	*D*(15)	557 (4)	243 (4)	236 (1)	8 (1)
C(16)	105 (4)	246 (4)	199 (1)	9 (1)	*D*(16)	607 (4)	246 (4)	199 (1)	9 (1)
C(17)	197 (3)	174 (3)	204 (1)	6 (1)	*D*(17)	694 (3)	169 (3)	203 (1)	7 (1)
C(18)	66 (4)	6 (3)	219 (1)	8 (1)	*D*(18)	565 (4)	4 (4)	217 (1)	8 (1)
C(19)	68 (4)	−87 (4)	350 (1)	11 (1)	*D*(19)	568 (4)	−84 (4)	349 (2)	10 (2)
C(20)	203 (4)	122 (4)	159 (1)	10 (1)	*D*(20)	706 (4)	127 (4)	160 (2)	10 (2)
C(21)	270 (4)	46 (4)	163 (1)	9 (1)	*D*(21)	776 (4)	47 (4)	162 (1)	9 (1)
C(22)	255 (4)	225 (4)	136 (1)	9 (1)	*D*(22)	746 (5)	226 (5)	135 (2)	13 (2)
C(23)	234	195	88	17 (2)	*D*(23)	734 (4)	198 (4)	92 (2)	11 (2)
C(24)	280	298	69	19 (3)	*D*(24)	788 (6)	301 (6)	70 (2)	19 (3)
C(25)	406	333	83	21 (3)	*D*(25)	908 (7)	336 (7)	78 (3)	22 (3)
C(26)	445	250	55	29 (4)	*D*(26)	942 (9)	252 (9)	51 (3)	28 (4)
C(27)	445	440	63	28 (4)	*D*(27)	955	445	62	28 (4)

Table 1 (*cont.*)

	x	*y*	*z*	*B* (Å²)		*x*	*y*	*z*	*B* (Å²)
E(OH)	844 (3)	428 (3)	529 (1)	10 (1)	*F*(OH)	835 (3)	930 (3)	528 (1)	11 (1)
E(1)	864 (4)	302 (3)	630 (1)	8 (1)	*F*(1)	858 (4)	802 (4)	627 (1)	8 (1)
E(2)	895 (3)	335 (3)	586 (1)	8 (1)	*F*(2)	890 (4)	835 (4)	585 (1)	8 (1)
E(3)	808 (4)	391 (4)	568 (1)	11 (2)	*F*(3)	807 (4)	891 (4)	566 (2)	11 (2)
E(4)	792 (3)	491 (3)	593 (1)	6 (1)	*F*(4)	785 (3)	987 (3)	589 (1)	6 (1)
E(5)	763 (3)	458 (3)	631 (1)	5 (1)	*F*(5)	762 (3)	956 (3)	630 (1)	6 (1)
E(6)	684 (3)	496 (3)	648 (1)	6 (1)	*F*(6)	679 (3)	994 (3)	647 (1)	6 (1)
E(7)	664 (3)	486 (3)	686 (1)	7 (1)	*F*(7)	662 (4)	985 (3)	686 (1)	7 (1)
E(8)	755 (3)	443 (3)	716 (1)	6 (1)	*F*(8)	752 (3)	945 (3)	713 (1)	6 (1)
E(9)	804 (3)	361 (3)	693 (1)	5 (1)	*F*(9)	802 (3)	858 (3)	690 (1)	5 (1)
E(10)	851 (3)	401 (3)	656 (1)	7 (1)	*F*(10)	849 (4)	902 (3)	653 (1)	7 (1)
E(11)	884 (3)	310 (3)	718 (1)	5 (1)	*F*(11)	890 (3)	811 (3)	717 (1)	5 (1)
E(12)	852 (4)	270 (4)	758 (1)	9 (1)	*F*(12)	850 (4)	771 (4)	756 (1)	9 (1)
E(13)	817 (3)	360 (3)	779 (1)	6 (1)	*F*(13)	817 (3)	859 (3)	779 (1)	6 (1)
E(14)	725 (3)	392 (3)	753 (1)	6 (1)	*F*(14)	722 (3)	892 (3)	750 (1)	6 (1)
E(15)	661 (5)	462 (4)	778 (2)	12 (2)	*F*(15)	657 (5)	953 (5)	776 (2)	13 (2)
E(16)	666 (4)	403 (4)	816 (1)	10 (1)	*F*(16)	665 (4)	901 (4)	815 (2)	10 (2)
E(17)	739 (4)	310 (4)	813 (1)	9 (1)	*F*(17)	747 (4)	812 (4)	812 (1)	8 (1)
E(18)	902 (4)	447 (3)	793 (1)	8 (1)	*F*(18)	905 (4)	950 (4)	794 (1)	9 (1)
E(19)	963 (4)	491 (3)	666 (1)	8 (1)	*F*(19)	960 (4)	990 (4)	664 (1)	8 (1)
E(20)	804 (4)	299 (4)	852 (1)	9 (1)	*F*(20)	806 (4)	795 (4)	853 (2)	9 (1)
E(21)	888 (4)	226 (4)	852 (1)	11 (2)	*F*(21)	887 (5)	725 (5)	852 (2)	11 (2)
E(22)	709 (5)	240 (5)	875 (2)	15 (2)	*F*(22)	710	744	877	15 (2)
E(23)	746	222	915	18 (2)	*F*(23)	755	722	918	18 (3)
E(24)	656	183	945	23 (3)	*F*(24)	660	685	946	22 (3)
E(25)	595	75	932	22 (3)	*F*(25)	595	579	936	23 (3)
E(26)	682	11	954	26 (4)	*F*(26)	685	510	955	26 (4)
E(27)	515	62	966	28 (4)	*F*(27)	520	565	965	29 (4)
G(OH)	169 (3)	475 (3)	488 (1)	11 (1)	*H*(OH)	663 (3)	477 (3)	485 (1)	11 (1)
G(1)	146 (3)	596 (3)	387 (1)	7 (1)	*H*(1)	644 (4)	599 (3)	386 (1)	8 (1)
G(2)	138 (3)	591 (3)	431 (1)	8 (1)	*H*(2)	643 (4)	594 (3)	430 (1)	7 (1)
G(3)	165 (4)	486 (3)	443 (1)	8 (1)	*H*(3)	664 (4)	490 (4)	442 (1)	8 (1)
G(4)	281 (3)	483 (3)	441 (1)	8 (1)	*H*(4)	785 (4)	485 (4)	440 (1)	9 (1)
G(5)	290 (3)	485 (3)	396 (1)	7 (1)	*H*(5)	796 (4)	493 (3)	394 (1)	7 (1)
G(6)	338 (4)	415 (4)	375 (1)	9 (1)	*H*(6)	841 (4)	425 (4)	376 (1)	9 (1)
G(7)	355 (4)	424 (4)	333 (1)	9 (1)	*H*(7)	852 (4)	423 (4)	332 (1)	9 (1)
G(8)	338 (3)	531 (3)	313 (1)	6 (1)	*H*(8)	834 (4)	532 (4)	314 (1)	8 (1)
G(9)	240 (3)	570 (3)	331 (1)	5 (1)	*H*(9)	741 (3)	578 (3)	329 (1)	6 (1)
G(10)	260 (3)	588 (3)	375 (1)	6 (1)	*H*(10)	763 (3)	590 (3)	374 (1)	6 (1)
G(11)	220 (3)	676 (3)	308 (1)	6 (1)	*H*(11)	718 (3)	678 (3)	308 (1)	6 (1)
G(12)	199 (3)	659 (3)	265 (1)	6 (1)	*H*(12)	699 (3)	664 (3)	263 (1)	6 (1)
G(13)	302 (3)	629 (3)	249 (1)	6 (1)	*H*(13)	801 (4)	630 (3)	249 (1)	7 (1)
G(14)	311 (3)	520 (3)	273 (1)	6 (1)	*H*(14)	819 (4)	527 (3)	271 (1)	7 (1)
G(15)	403 (3)	476 (3)	249 (1)	6 (1)	*H*(15)	900 (3)	477 (3)	247 (1)	7 (1)
G(16)	377 (4)	514 (3)	206 (1)	9 (1)	*H*(16)	877 (4)	515 (4)	206 (1)	8 (1)
G(17)	286 (3)	589 (3)	208 (1)	5 (1)	*H*(17)	788 (3)	586 (3)	207 (1)	6 (1)
G(18)	405 (4)	723 (4)	260 (1)	10 (1)	*H*(18)	908 (4)	724 (4)	257 (1)	9 (1)
G(19)	345 (3)	686 (3)	393 (1)	8 (1)	*H*(19)	842 (4)	691 (4)	391 (1)	9 (1)
G(20)	282 (3)	659 (3)	175 (1)	7 (1)	*H*(20)	783 (4)	658 (4)	171 (1)	8 (1)
G(21)	200 (4)	727 (4)	174 (2)	12 (2)	*H*(21)	700 (5)	730 (5)	172 (2)	12 (2)
G(22)	287 (5)	606 (5)	134 (2)	15 (2)	*H*(22)	781 (5)	605 (5)	133 (2)	14 (2)
G(23)	283 (7)	674 (7)	95 (2)	20 (3)	*H*(23)	792 (7)	666 (7)	95 (2)	19 (3)
G(24)	402 (5)	752 (5)	101 (2)	15 (2)	*H*(24)	896 (5)	750 (5)	101 (2)	15 (2)
G(25)	405	830	65	21 (3)	*H*(25)	904	827	63	20 (3)
G(26)	445	765	35	25 (4)	*H*(26)	950	764	37	26 (4)
G(27)	490	930	77	22 (3)	*H*(27)	995	930	76	21 (3)

gen bonding or ionic interactions involving polar C(3) substituents as well as a packing together of nonpolar cholesteryl groups. However, the crystal structures and the pseudosymmetry can be quite different from those of cholesterol monohydrate.

In the crystal structure of anhydrous cholesterol (Shieh, Hoard & Nordman, 1977*a*) which is triclinic, with space group *P*1 and has eight cholesterols in the unit cell, the molecules are hydrogen bonded in two separate chains ...*AHBGA*... and ...*CFDEC*.... Each

molecule in one chain is related to a molecule in the other chain by one of a series of parallel axes of local twofold symmetry. Thus, each molecule *A* is related to a molecule *E*, *H* to *D*, *B* to *F* and *G* to *C*. The pseudosymmetry, which applies to complete molecules, involves a rotation of 180° coupled with a translation of about 2·8 Å parallel to the axis. There is no subcell translational symmetry as in cholesterol monohydrate. Within a group of molecules such as *ABCD*, which are unrelated by pseudosymmetry, the molecular long axes make angles ranging from 4 to 36°, and the least-squares planes through the tetracyclic systems make dihedral angles ranging from 3 to 88°. This complex packing arrangement allows hydrogen bonding of the hydroxyl groups with an average O···O distance of 2·87 Å. When the cholesterol molecules are packed nearly parallel, as in cholesterol monohydrate, infinite hydrogen-bonded chains cannot form because the average hydroxyl O···O distance would be too large (>3·0 Å). The more regular packing of cholesterols in the monohydrate becomes possible in the presence of the water molecules which form hydrogen-bonding bridges between cholesteryl hydroxyl groups.

The crystal structure of sodium cholesteryl sulfate dihydrate (Pascher & Sundell, 1977) is triclinic with space group *P*1 and two cholesteryl sulfates (*A* and *B*) in the unit cell. Molecules *A* pack with each other to form one side of a bilayer structure, while molecules *B* form the other side. The packing of the tetracyclic systems of the *A* and *B* molecules is very similar, but differs from that of cholesterol in the monohydrate. There is no sublattice translational symmetry. However, there are axes of local twofold symmetry as in cholesterol monohydrate. These axes pass through the bilayer interface region of the structure and relate the tetracyclic system of each molecule *A* with a molecule *B*. The pseudosymmetry consists of a rotation of 180° about the crystal axis [1$\bar{1}$0], coupled with a translation of 2·0 Å. The pseudosymmetry does not apply either to the tail groups C(23) through C(27) which have different conformations in *A* and *B*, or to the polar region of the structure, consisting of the sulfate groups, sodium ions and water molecules.

The nature of the pseudosymmetry in other related crystal structures has yet to be described in detail. However, in the three structures which have been discussed, it appears that the efficient packing of bulky cholesterol molecules with each other imposes steric requirements which are quite different from those of hydrogen bonding or ionic interactions. Complexity and pseudosymmetry may come from the need to reconcile these two different aspects of the structure within the same unit cell.

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References

BOGREN, H. & LARSSON, K. (1963). *Biochim. Biophys. Acta*, **75**, 65–69.

CRAVEN, B. M. (1976). *Nature (London)*, **260**, 727–729.

NYBURG, S. C. (1974). *Acta Cryst.* B**30**, 251–253.

PASCHER, I. & SUNDELL, S. (1977). *Acta Chem. Scand. Ser. A*, **31**, 767–774.

SAWZIK, P. & CRAVEN, B. M. (1979). *Acta Cryst.* B**35**, 895–901.

SHIEH, H. S., HOARD, L. G. & NORDMAN, C. E. (1977*a*). *Nature (London)*, **267**, 287–289.

SHIEH, H. S., HOARD, L. G. & NORDMAN, C. E. (1977*b*). Am. Crystallogr. Assoc. Abstracts of Winter Meeting, Asilomar, California, p. 30.

SHIEH, H. S. & NORDMAN, C. E. (1977). Am. Crystallogr. Assoc. Abstracts of Summer Meeting, Michigan State Univ., p. 84.

SHIEH, H. S. & NORDMAN, C. E. (1978). Am. Crystallogr. Assoc. Abstracts of Winter Meeting, Univ. of Oklahoma, p. 22.