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The Structure of Cholesterol

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Abstract

Cholesterol ($C_{27}H_{46}O$, M_r = 386·66) crystals from acetone solution are triclinic with cell parameters a = 14·172 (7), b = 34·209 (18), c = 10·481 (5) Å, α = 94·64 (4), β = 90·67 (4), and γ = 96·32 (4)°; V = 5032·6 (44) Å^3, D_x = 1·021, D_m(flotation, aqueous KCl) = 1·03 Mg m^{-3}, μ(Cu $K\alpha$, λ = 1·5418 Å) = 0·45 mm^{-1}. The space group is $P1$ and there are eight molecules in the unit cell. The structure was solved by a combination of Patterson and direct methods, and refined to R = 0·057 for 8035 observed reflections. The hydrophilic region of the bilayer structure contains parallel chains of hydrogen bonds forming a corrugated sheet. Local twofold rotational pseudosymmetry is closely obeyed by the molecules including their side chains. The latter exhibit two conformations, a fully extended, and a bent conformation.

Introduction

Although cholesterol first attracted the interest of X-ray crystallographers more than four decades ago (Bernal, Crowfoot & Fankuchen, 1940), it is only recently that the detailed crystal structures of cholesterol and some of its solvates have been determined. The reason for this delay is undoubtedly the complexity of the crystal structures, arising from a consistent tendency of cholesterol to crystallize with more than one independent molecule in the crystallographic asymmetric unit. In the monohydrate (Craven, 1976, 1979) the number of independent cholesterol molecules is eight, in the anhydrous cholesterol structure (Shieh, Hoard & Nordman, 1977*a*) and in the two forms of the hemiethanolate (Shieh, Hoard & Nordman, 1977*b*) the number is likewise eight. The lowest number so far found is in cholesterol hemimethanolate (Shieh & Nordman, 1978) where the asymmetric unit contains four cholesterol molecules.

Another remarkable feature of these cholesterol structures is the presence of local pseudosymmetry, that is, non-crystallographic symmetry which is satisfied, locally, to a remarkably high degree. Such pseudosymmetry is translational in the monohydrate and in the hemiethanolates, rotational in the anhydrous structure, and, although less closely obeyed, in the hemimethanolate.

In addition to the complexity and the pseudosymmetry, an object of interest is the characteristic bilayer nature of the structures of cholesterol crystals, with a molecular arrangement generally similar to that of cholesterol in biological membranes. We report here the fully refined structure of anhydrous cholesterol, and an account of the structure solution. An overall description of the structure and its pseudosymmetry has been published previously (Shieh, Hoard & Nordman, 1977*a*).

Experimental

Colorless, lath-shaped crystals were grown by slow evaporation of an acetone solution at room temperature. Preliminary Weissenberg and precession photographs established triclinic symmetry. All subsequent X-ray work was done on a Syntex $P\bar{1}$ diffractometer using graphite-monochromatized Cu $K\alpha$ radiation. Crystal data are given in the *Abstract*.

Diffracted intensities were collected for 10 337 unique reflections to 2θ = 100° using a crystal specimen of dimensions 0·40 × 0·28 × 0·14 mm. The intensities of three reflections ($\bar{1}12$, $03\bar{2}$ and 301) were monitored, and found to have suffered a 10% loss in the course of the data collection. All data were corrected for this decay. No absorption correction was applied.

Structure determination and refinement

With eight molecules, or 224 nonhydrogen atoms, in the asymmetric unit, and X-ray data of only moderate

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resolution, some difficulty was expected in the structure solution. Initial efforts to apply direct methods, including magic-integer approaches (White & Woolfson, 1975), were not successful.

A Patterson search (Schilling, 1970) was attempted next. The point-atom origin-removed Patterson function, exponentially damped to 0·5 at the $\sin\theta/\lambda$ limit, was computed with grid steps of approximately 0·26 Å. The search model was based on the structure of 3β-chloro-5-androsten-17β-ol (Weeks, Cooper & Norton, 1971). The two independent molecules in this structure were averaged, and local substitutions using standard bond lengths and angles were made by replacing Cl by O(3) and O by C(20). In this manner a model of the 21-atom rigid fragment of the cholesterol molecule was constructed. The 210 intrafragment vectors and their weights were calculated. A 30-vector subset was selected, with a minimum intervector separation of 0·6 Å, a minimum vector length of 2·0 Å, and a minimum vector weight of 1·3 carbon–carbon vectors.

Coarse orientation searches of the three-dimensional Euler-angle space, followed by fine searches of the eight most promising regions, yielded three 'best' peaks. These were tentatively assumed to represent three of the eight molecular orientations in the structure. Labeling the three oriented steroid fragments *A*, *F* and *H* (to conform to the designation *A*, *B*, . . ., *H* ultimately adopted for the eight molecules), the three sets of interfragment atom–atom vectors were calculated, and the three translational searches of the Patterson function carried out. If *A*, *F* and *H* represent the orientations of three molecules actually present in the structure, then the results of the three translation searches must exhibit a redundancy. This is so, because the translation vectors $A \rightarrow F$, $F \rightarrow H$ and $H \rightarrow A$ must form a closed triangle. The fact that such a closed triangle was indeed found in the translation searches, and the absence of any steric overlap among the three translated fragments, indicated that the positioning of the fragments relative to one another was correct.

It would undoubtedly have been possible to augment the structure by Patterson methods; an added fourth fragment would be subject to greater translation vector and packing constraints than the third, *etc.* Such a procedure tends to be rather cumbersome, and it is generally advantageous to apply direct methods as soon as a partial structure of sufficient phasing power has been obtained. Accordingly, an attempt was made to extend phases by *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974), starting with phases from the 63-atom partial structure composed of the three 21-atom steroid fragments. This approach was not immediately successful. The difficulty appeared to be in the last few cycles of tangent refinement, in which all the originally fixed phases were allowed to vary. At this stage a false solution represented by a single strong *E*-map peak tended to evolve. To overcome this difficulty the program was revised to increase the maximum number of input reflections and phase relationships, and to fix a certain number of phases throughout the tangent refinement. The best results were obtained as follows:

(1) The 900 highest-*E* reflections ($E_{min} = 1{\cdot}589$) were phased on the 63-atom partial structure.

(2) The phases of the 250 reflections with highest E_{calc}/E_{obs} were regarded as known phases, and used for phase recycling in *MULTAN*.

(3) The phases of those 46 reflections, in the set of 250, which had the highest phasing priority were kept fixed throughout the tangent refinement.

An *E* map calculated after one cycle of this phase-recycling scheme revealed more than 100 new atoms. The rest of the structure was found by routine Fourier and difference Fourier methods.

The structure was refined using the 8035 observed reflections for which $I \geq 2{\cdot}33\sigma_I$. Isotropic block-diagonal least-squares refinement of all 224 C and O atoms brought the *R* value to 0·125. A difference Fourier map now revealed about 70% of the H atoms. Ultimately 80% of all H atoms were found, including all eight hydroxyl H atoms. In the final cycles the C and O atoms were refined anisotropically, the eight hydroxyl H atoms isotropically, and the remaining H atoms kept fixed with thermal *B* values assigned as 1·1 times the isotropic equivalents of the *B* values of the adjacent C atoms. Least-squares weights were taken as $w = (\sigma^2 + kF_o^2)^{-1}$, where $k = 3{\cdot}7 \times 10^{-4}$ was chosen to make $w\Delta F^2$ uniformly distributed in $|F_o|$. A secondary-extinction correction of the form (Zachariasen, 1968) $\{1 + \varepsilon F_c^2(1 + \cos^4 2\theta)/[(1 + \cos^2 2\theta) \times \sin 2\theta]\}^{-0{\cdot}25}$ was applied to the F_c values. The least-squares value of the parameter ε was $4{\cdot}84 \times 10^{-6}$. The final *R* value was 0·057 for 8035 reflections.* A final difference Fourier synthesis showed no significant features.

Results and discussion

The eight independent molecules are labelled *A*, *B*, . . ., *H*, such that molecules *A*, *B*, *C* and *D* are pseudo-symmetrically related to molecules *E*, *F*, *G* and *H*, respectively (Shieh, Hoard & Nordman, 1977*a*).

The atomic parameters are listed in Table 1, with standard deviations estimated from the variance–covariance matrix of the last least-squares refinement cycle. Not included in Table 1 are the H-atom parameters.*

* Lists of structure factors, anisotropic thermal parameters, and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36003 (68 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond distances and angles, averaged over the eight independent molecules, are given in Fig. 1. Table 2 gives the average values and r.m.s. deviations of torsional angles in the rings of the steroid skeleton. The low values of the r.m.s. deviations show that the eight steroid units are closely similar; the greatest variability occurs in the torsional units 4–5–10–1 and 5–10–1–2, in a region where the planarity produced

Table 1. *Carbon and oxygen atom parameters*

Atoms are numbered conventionally as in Fig. 1; a molecule label (*A*, ..., *H*) is attached to the atom name. Positional parameters are fractional coordinates ($\times 10^4$). E.s.d.'s refer to the last significant digit in the parameter value. $B_{eq} = \frac{1}{3} \sum_i \sum_j B_{ij}\, a_i^* a_j^*\, \mathbf{a}_i . \mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)		x	y	z	B_{eq} (Å^2)
O(3)*A*	3627 (5)	4209 (1)	5421 (5)	8·9 (2)	O(3)*B*	3328 (4)	4138 (1)	603 (5)	6·8 (2)
C(1)*A*	5022 (5)	3392 (2)	4185 (6)	5·7 (2)	C(1)*B*	2453 (5)	3167 (2)	1894 (6)	5·7 (2)
C(2)*A*	4777 (6)	3807 (2)	4473 (7)	6·8 (3)	C(2)*B*	2423 (5)	3582 (2)	1482 (7)	5·9 (2)
C(3)*A*	3867 (5)	3810 (2)	5134 (7)	6·3 (2)	C(3)*B*	3360 (5)	3746 (2)	972 (6)	5·2 (2)
C(4)*A*	3894 (6)	3602 (2)	6382 (6)	6·1 (2)	C(4)*B*	3591 (5)	3489 (2)	−199 (6)	5·1 (2)
C(5)*A*	4171 (5)	3188 (2)	6100 (6)	4·9 (2)	C(5)*B*	3635 (4)	3064 (2)	157 (5)	4·5 (2)
C(6)*A*	3649 (5)	2885 (2)	6520 (6)	5·4 (2)	C(6)*B*	4394 (5)	2886 (2)	−153 (7)	5·4 (2)
C(7)*A*	3892 (5)	2466 (2)	6397 (7)	6·1 (2)	C(7)*B*	4510 (5)	2469 (2)	142 (7)	5·6 (2)
C(8)*A*	4929 (5)	2441 (2)	6017 (6)	5·4 (2)	C(8)*B*	3604 (4)	2238 (2)	532 (6)	4·7 (2)
C(9)*A*	5179 (4)	2716 (2)	4949 (6)	4·7 (2)	C(9)*B*	3060 (4)	2502 (2)	1439 (6)	4·4 (2)
C(10)*A*	5069 (5)	3155 (2)	5382 (6)	4·9 (2)	C(10)*B*	2789 (4)	2871 (2)	816 (6)	4·3 (2)
C(11)*A*	6130 (5)	2653 (2)	4326 (7)	6·4 (2)	C(11)*B*	2225 (5)	2265 (2)	2061 (7)	6·7 (2)
C(12)*A*	6262 (5)	2219 (2)	3959 (7)	6·1 (2)	C(12)*B*	2486 (6)	1904 (2)	2691 (8)	6·9 (3)
C(13)*A*	6082 (5)	1962 (2)	5087 (6)	5·6 (2)	C(13)*B*	2981 (5)	1632 (2)	1717 (7)	6·0 (2)
C(14)*A*	5076 (5)	2018 (2)	5554 (7)	5·7 (2)	C(14)*B*	3841 (5)	1880 (2)	1203 (6)	5·2 (2)
C(15)*A*	4828 (6)	1697 (2)	6458 (8)	8·1 (3)	C(15)*B*	4398 (6)	1578 (2)	457 (8)	7·5 (3)
C(16)*A*	5366 (7)	1351 (2)	5865 (9)	8·8 (3)	C(16)*B*	4251 (6)	1210 (2)	1226 (9)	8·4 (3)
C(17)*A*	5931 (6)	1510 (2)	4745 (7)	7·1 (3)	C(17)*B*	3467 (6)	1294 (2)	2262 (7)	7·2 (3)
C(18)*A*	6843 (6)	2081 (3)	6112 (8)	8·0 (3)	C(18)*B*	2256 (6)	1452 (2)	602 (7)	7·0 (3)
C(19)*A*	5922 (5)	3337 (2)	6279 (7)	6·1 (2)	C(19)*B*	1984 (5)	2766 (2)	−228 (7)	6·1 (2)
C(20)*A*	6823 (7)	1277 (3)	4501 (9)	8·8 (3)	C(20)*B*	2896 (7)	914 (2)	2632 (9)	9·1 (3)
C(21)*A*	7437 (8)	1453 (3)	3486 (11)	11·9 (4)	C(21)*B*	2134 (9)	1001 (3)	3614 (12)	12·9 (5)
C(22)*A*	6493 (8)	840 (3)	4126 (10)	11·1 (4)	C(22)*B*	3585 (9)	631 (3)	3071 (11)	12·0 (4)
C(23)*A*	7293 (10)	584 (3)	3954 (13)	14·7 (6)	C(23)*B*	3092 (11)	220 (3)	3213 (13)	15·1 (6)
C(24)*A*	6884 (17)	146 (5)	3611 (18)	23·6 (10)	C(24)*B*	3905 (12)	−71 (4)	3571 (20)	21·0 (9)
C(25)*A*	7519 (15)	−145 (5)	2963 (23)	22·3 (10)	C(25)*B*	3467 (16)	−419 (6)	3989 (22)	25·3 (12)
C(26)*A*	8285 (14)	−110 (7)	3857 (26)	27·1 (13)	C(26)*B*	3221 (26)	−691 (6)	2684 (25)	33·1 (18)
C(27)*A*	6921 (15)	−571 (4)	2568 (23)	23·4 (11)	C(27)*B*	4254 (19)	−617 (9)	4537 (39)	39·2 (21)
O(3)*C*	6358 (4)	5450 (1)	5843 (5)	7·4 (2)	O(3)*D*	6296 (4)	5512 (1)	838 (5)	7·7 (2)
C(1)*C*	7098 (5)	4452 (2)	4858 (6)	5·9 (2)	C(1)*D*	6097 (5)	4403 (2)	975 (7)	6·1 (2)
C(2)*C*	6609 (6)	4827 (2)	4761 (7)	7·0 (3)	C(2)*D*	5752 (5)	4809 (2)	754 (7)	6·5 (3)
C(3)*C*	6814 (5)	5098 (2)	5991 (6)	5·4 (2)	C(3)*D*	6574 (6)	5127 (2)	1040 (6)	6·4 (2)
C(4)*C*	7865 (5)	5198 (2)	6218 (6)	5·4 (2)	C(4)*D*	7423 (5)	5041 (2)	190 (7)	6·1 (2)
C(5)*C*	8380 (4)	4834 (2)	6263 (5)	4·3 (2)	C(5)*D*	7718 (5)	4643 (2)	327 (6)	4·7 (2)
C(6)*C*	8970 (5)	4787 (2)	7218 (6)	4·9 (2)	C(6)*D*	8612 (5)	4588 (2)	558 (6)	5·1 (2)
C(7)*C*	9544 (5)	4444 (2)	7289 (6)	5·0 (2)	C(7)*D*	9010 (5)	4209 (2)	615 (6)	4·8 (2)
C(8)*C*	9530 (4)	4186 (2)	6036 (6)	4·6 (2)	C(8)*D*	8285 (4)	3855 (2)	92 (5)	4·0 (2)
C(9)*C*	8530 (4)	4128 (2)	5461 (5)	4·2 (2)	C(9)*D*	7303 (4)	3922 (2)	617 (5)	4·1 (2)
C(10)*C*	8191 (5)	4522 (2)	5129 (6)	4·9 (2)	C(10)*D*	6926 (4)	4296 (2)	156 (5)	4·3 (2)
C(11)*C*	8416 (5)	3808 (2)	4330 (6)	5·6 (2)	C(11)*D*	6590 (5)	3545 (2)	351 (6)	5·3 (2)
C(12)*C*	8763 (5)	3417 (2)	4607 (6)	5·1 (2)	C(12)*D*	6957 (4)	3160 (2)	722 (6)	4·9 (2)
C(13)*C*	9791 (5)	3473 (2)	5106 (6)	4·7 (2)	C(13)*D*	7886 (4)	3094 (2)	61 (6)	4·3 (2)
C(14)*C*	9833 (4)	3778 (2)	6280 (5)	4·3 (2)	C(14)*D*	8559 (4)	3466 (2)	487 (6)	4·3 (2)
C(15)*C*	10830 (5)	3768 (2)	6901 (7)	6·0 (2)	C(15)*D*	9570 (5)	3355 (2)	97 (6)	5·3 (2)
C(16)*C*	10996 (5)	3326 (2)	6637 (8)	7·0 (3)	C(16)*D*	9491 (4)	2907 (2)	265 (7)	5·5 (2)
C(17)*C*	10159 (5)	3119 (2)	5701 (6)	5·4 (2)	C(17)*D*	8421 (4)	2770 (2)	541 (6)	4·7 (2)
C(18)*C*	10454 (6)	3617 (2)	4025 (7)	7·1 (3)	C(18)*D*	7767 (5)	3047 (2)	−1418 (6)	5·2 (2)
C(19)*C*	8704 (7)	4681 (2)	3945 (7)	7·9 (3)	C(19)*D*	6608 (5)	4236 (2)	−1288 (6)	5·6 (2)
C(20)*C*	10463 (5)	2780 (2)	4873 (7)	6·3 (2)	C(20)*D*	8159 (5)	2333 (2)	−11 (7)	5·5 (2)
C(21)*C*	9666 (7)	2568 (2)	3973 (8)	8·3 (3)	C(21)*D*	7107 (5)	2200 (2)	174 (8)	6·8 (3)
C(22)*C*	10913 (6)	2471 (2)	5607 (8)	7·6 (3)	C(22)*D*	8794 (5)	2069 (2)	639 (8)	7·2 (3)
C(23)*C*	10266 (7)	2279 (3)	6553 (8)	8·5 (3)	C(23)*D*	8633 (6)	1630 (2)	187 (9)	7·8 (3)
C(24)*C*	10713 (9)	1944 (3)	7177 (9)	10·8 (4)	C(24)*D*	9348 (7)	1403 (3)	881 (13)	11·7 (5)
C(25)*C*	10846 (9)	1590 (3)	6323 (10)	11·2 (4)	C(25)*D*	9110 (9)	950 (3)	692 (14)	13·5 (5)
C(26)*C*	9946 (12)	1391 (4)	5791 (16)	16·7 (7)	C(26)*D*	9222 (13)	818 (4)	−651 (18)	19·7 (8)
C(27)*C*	11342 (13)	1289 (4)	7022 (13)	17·3 (7)	C(27)*D*	9762 (10)	757 (4)	1614 (22)	20·1 (9)

Table 1 (*cont.*)

	x	y	z	B_{eq} (Å^2)		x	y	z	B_{eq} (Å^2)
O(3)*E*	6423 (4)	5799 (1)	8318 (4)	7·4 (2)	O(3)*F*	6457 (4)	5832 (1)	3491 (5)	6·8 (2)
C(1)*E*	4918 (5)	6604 (2)	7560 (6)	5·3 (2)	C(1)*F*	7475 (5)	6799 (2)	5288 (6)	5·2 (2)
C(2)*E*	5205 (5)	6182 (2)	7647 (6)	5·8 (2)	C(2)*F*	7453 (5)	6375 (2)	4680 (7)	6·2 (2)
C(3)*E*	6177 (5)	6195 (2)	8261 (6)	5·5 (2)	C(3)*F*	6487 (5)	6226 (2)	4090 (7)	6·0 (2)
C(4)*E*	6183 (5)	6410 (2)	9615 (6)	5·1 (2)	C(4)*F*	6254 (5)	6494 (2)	3060 (6)	5·3 (2)
C(5)*E*	5885 (4)	6814 (2)	9554 (6)	4·3 (2)	C(5)*F*	6244 (4)	6915 (2)	3628 (6)	4·5 (2)
C(6)*E*	6416 (5)	7122 (2)	10115 (6)	5·5 (2)	C(6)*F*	5511 (5)	7114 (2)	3456 (6)	5·3 (2)
C(7)*E*	6183 (5)	7540 (2)	10202 (7)	6·1 (2)	C(7)*F*	5407 (5)	7531 (2)	3947 (7)	6·5 (2)
C(8)*E*	5122 (5)	7566 (2)	9863 (6)	5·1 (2)	C(8)*F*	6353 (4)	7753 (2)	4459 (6)	4·8 (2)
C(9)*E*	4861 (4)	7282 (2)	8661 (6)	4·6 (2)	C(9)*F*	6899 (5)	7472 (2)	5213 (6)	5·2 (2)
C(10)*E*	4948 (4)	6850 (2)	8897 (6)	4·8 (2)	C(10)*F*	7134 (4)	7102 (2)	4388 (6)	4·6 (2)
C(11)*E*	3875 (5)	7352 (2)	8123 (7)	6·6 (2)	C(11)*F*	7772 (5)	7702 (2)	5960 (7)	6·5 (2)
C(12)*E*	3735 (6)	7776 (2)	7927 (7)	6·9 (3)	C(12)*F*	7552 (6)	8077 (2)	6765 (8)	7·5 (3)
C(13)*E*	3961 (5)	8042 (2)	9176 (7)	6·5 (2)	C(13)*F*	7078 (5)	8352 (2)	5944 (7)	5·9 (2)
C(14)*E*	4991 (5)	7988 (2)	9590 (7)	6·3 (2)	C(14)*F*	6185 (5)	8104 (2)	5336 (7)	5·6 (2)
C(15)*E*	5251 (7)	8312 (2)	10687 (9)	8·5 (3)	C(15)*F*	5614 (6)	8411 (2)	4790 (8)	7·3 (3)
C(16)*E*	4722 (7)	8674 (3)	10252 (9)	9·3 (3)	C(16)*F*	5812 (6)	8782 (2)	5756 (8)	7·9 (3)
C(17)*E*	4086 (6)	8495 (3)	9032 (8)	8·0 (3)	C(17)*F*	6590 (6)	8688 (2)	6690 (7)	7·3 (3)
C(18)*E*	3211 (7)	7947 (3)	10173 (9)	9·5 (3)	C(18)*F*	7735 (6)	8513 (2)	4958 (8)	7·1 (3)
C(19)*E*	4132 (5)	6668 (2)	9699 (7)	5·9 (2)	C(19)*F*	7898 (5)	7200 (2)	3400 (7)	5·8 (2)
C(20)*E*	3223 (7)	8723 (3)	8926 (9)	9·4 (3)	C(20)*F*	7233 (7)	9061 (2)	7231 (9)	8·6 (3)
C(21)*E*	2590 (8)	8551 (3)	7772 (12)	11·9 (4)	C(21)*F*	7963 (10)	8981 (3)	8205 (13)	13·9 (5)
C(22)*E*	3580 (10)	9162 (3)	8749 (12)	14·1 (5)	C(22)*F*	6624 (10)	9352 (3)	7850 (13)	13·7 (5)
C(23)*E*	2822 (11)	9438 (4)	8666 (14)	16·2 (6)	C(23)*F*	7093 (10)	9774 (3)	8246 (14)	15·0 (6)
C(24)*E*	3194 (15)	9853 (4)	8536 (22)	24·0 (10)	C(24)*F*	6270 (15)	10070 (4)	8719 (19)	22·0 (10)
C(25)*E*	2537 (13)	10203 (5)	8138 (24)	23·3 (11)	C(25)*F*	6652 (18)	10446 (5)	9087 (21)	24·2 (11)
C(26)*E*	1712 (15)	10118 (8)	9013 (22)	27·8 (13)	C(26)*F*	6933 (30)	10651 (8)	7841 (29)	37·8 (22)
C(27)*E*	3325 (24)	10556 (5)	7691 (27)	32·6 (17)	C(27)*F*	5878 (20)	10632 (10)	9797 (28)	37·2 (18)
O(3)*G*	3669 (3)	4485 (1)	8183 (4)	6·2 (2)	O(3)*H*	3380 (4)	4525 (1)	3089 (5)	8·1 (2)
C(1)*G*	3029 (4)	5502 (2)	7793 (6)	4·5 (2)	C(1)*H*	3681 (5)	5631 (2)	3929 (6)	5·3 (2)
C(2)*G*	3521 (5)	5126 (2)	7518 (7)	5·7 (2)	C(2)*H*	3965 (5)	5213 (2)	3544 (7)	6·2 (2)
C(3)*G*	3234 (5)	4840 (2)	8496 (6)	4·9 (2)	C(3)*H*	3131 (5)	4907 (2)	3517 (6)	5·6 (2)
C(4)*G*	2174 (5)	4756 (2)	8572 (6)	4·9 (2)	C(4)*H*	2342 (5)	5002 (2)	2600 (6)	5·7 (2)
C(5)*G*	1674 (4)	5121 (2)	8770 (5)	3·9 (2)	C(5)*H*	2076 (5)	5416 (2)	2950 (6)	5·0 (2)
C(6)*G*	1018 (4)	5155 (2)	9659 (5)	4·3 (2)	C(6)*H*	1163 (5)	5469 (2)	3144 (6)	5·2 (2)
C(7)*G*	463 (5)	5497 (2)	9879 (6)	4·7 (2)	C(7)*H*	822 (5)	5870 (2)	3428 (6)	4·8 (2)
C(8)*G*	529 (4)	5775 (2)	8806 (5)	4·1 (2)	C(8)*H*	1557 (4)	6207 (2)	3147 (5)	4·4 (2)
C(9)*G*	1582 (4)	5832 (2)	8372 (5)	3·8 (2)	C(9)*H*	2539 (4)	6132 (2)	3685 (7)	4·2 (2)
C(10)*G*	1928 (4)	5440 (2)	7845 (6)	4·2 (2)	C(10)*H*	2886 (4)	5750 (2)	3043 (6)	4·4 (2)
C(11)*G*	1724 (4)	6160 (2)	7416 (6)	4·7 (2)	C(11)*H*	3281 (4)	6495 (2)	3659 (6)	4·7 (2)
C(12)*G*	1344 (5)	6551 (2)	7915 (6)	4·9 (2)	C(12)*H*	2939 (4)	6881 (2)	4183 (6)	4·8 (2)
C(13)*G*	294 (4)	6478 (2)	8261 (6)	4·8 (2)	C(13)*H*	2021 (4)	6959 (2)	3528 (6)	4·6 (2)
C(14)*G*	202 (4)	6172 (2)	9249 (5)	4·4 (2)	C(14)*H*	1295 (4)	6597 (2)	3710 (5)	4·2 (2)
C(15)*G*	−815 (4)	6183 (2)	9744 (6)	5·1 (2)	C(15)*H*	332 (5)	6737 (2)	3340 (6)	5·3 (2)
C(16)*G*	−964 (5)	6621 (2)	9699 (7)	5·9 (2)	C(16)*H*	435 (5)	7176 (2)	3786 (6)	5·4 (2)
C(17)*G*	−116 (5)	6832 (2)	9045 (6)	4·8 (2)	C(17)*H*	1510 (4)	7297 (2)	4180 (6)	4·7 (2)
C(18)*G*	−325 (5)	6354 (2)	7059 (6)	5·7 (2)	C(18)*H*	2170 (5)	7020 (2)	2107 (6)	5·8 (2)
C(19)*G*	1504 (5)	5294 (2)	6501 (6)	5·3 (2)	C(19)*H*	3260 (5)	5805 (2)	1707 (6)	5·6 (2)
C(20)*G*	−368 (6)	7190 (2)	8359 (7)	6·8 (3)	C(20)*H*	1807 (5)	7732 (2)	3868 (6)	5·5 (2)
C(21)*G*	470 (7)	7400 (2)	7706 (8)	9·0 (3)	C(21)*H*	2867 (5)	7855 (2)	4145 (8)	6·5 (2)
C(22)*G*	−851 (5)	7478 (2)	9249 (7)	6·2 (2)	C(22)*H*	1196 (5)	7999 (2)	4684 (8)	6·7 (3)
C(23)*G*	−261 (7)	7662 (3)	10367 (8)	8·7 (3)	C(23)*H*	1331 (7)	8435 (2)	4438 (10)	9·2 (3)
C(24)*G*	−708 (8)	7978 (3)	11205 (8)	9·5 (4)	C(24)*H*	673 (6)	8670 (2)	5274 (13)	11·4 (4)
C(25)*G*	−818 (8)	8351 (3)	10565 (9)	10·5 (4)	C(25)*H*	842 (8)	9122 (3)	5223 (14)	13·3 (5)
C(26)*G*	101 (13)	8557 (4)	10262 (16)	18·2 (8)	C(26)*H*	739 (12)	9263 (4)	3942 (20)	19·6 (8)
C(27)*G*	−1321 (11)	8637 (3)	11451 (11)	15·2 (6)	C(27)*H*	287 (10)	9329 (4)	6252 (21)	19·3 (9)

by the C(5)–C(6) double bond makes the skeleton somewhat flexible. Individual values of bond lengths and angles, torsion angles and other calculated structural features have been given by Hoard (1977).

There are two distinct side-chain conformations in this structure. As shown in Fig. 2, molecules *A*, *B* and *D*, and their pseudosymmetrically related mates *E*, *F* and *H* have fully extended, all-*trans* side chains, while the pair *C* and *G* has a *gauche–trans–gauche* sequence at C(20)–C(22)–C(23)–C(24). These chain conformations are quite different from those in cholesterol monohydrate (Craven, 1979). The two distinct

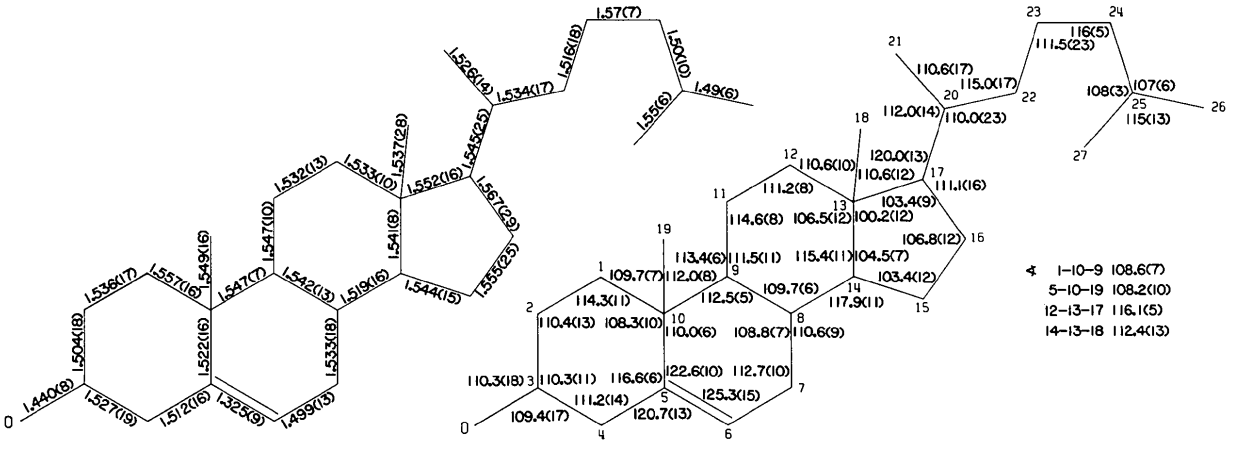

Fig. 1. Bond distances (Å) (left) and angles (°) (right), given as means and standard deviations of the eight independent values.

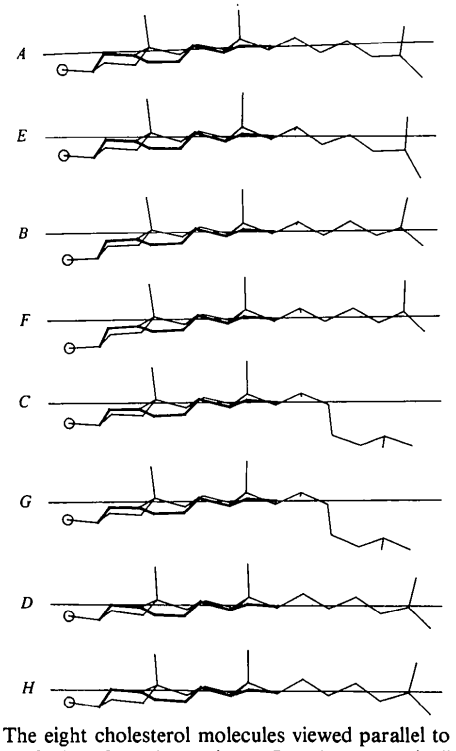

Fig. 2. The eight cholesterol molecules viewed parallel to the mean plane of the *C* and *D* rings. Pseudosymmetrically related molecules are shown next to one another.

Table 2. *Torsional angles* (°) *in the rings of the steroid skeleton, averaged over the eight molecules*

Carbon atoms		Carbon atoms	
10–1–2–3	−56 (2)	11–9–8–14	−49 (1)
1–2–3–4	58 (2)	9–8–14–13	57 (1)
2–3–4–5	−56 (2)	8–14–13–12	−61 (1)
3–4–5–10	53 (1)	14–13–12–11	56 (1)
4–5–10–1	−48 (3)	13–12–11–9	−55 (1)
5–10–1–2	49 (4)	12–11–9–8	50 (2)
10–5–6–7	1 (2)	17–13–14–15	47 (1)
5–6–7–8	13 (1)	13–14–15–16	−34 (1)
6–7–8–9	−43 (2)	14–15–16–17	8 (2)
7–8–9–10	62 (1)	15–16–17–13	21 (2)
8–9–10–5	−47 (2)	16–17–13–14	−41 (2)
9–10–5–6	16 (2)		

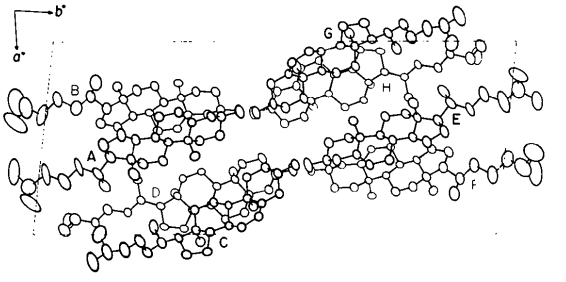

Fig. 3. One unit cell of the cholesterol structure viewed along **c** (out of page). C and O atoms are shown as 25% probability ellipsoids. The twofold rotational pseudosymmetry about the center of the triclinic cell can be recognized.

conformations in the latter structure each have one *gauche* rotation, one at C(23)–C(24), the other at C(22)–C(23).

The structure of one unit cell viewed along the *c* axis is shown in Fig. 3. The presence of a twofold symmetry axis can be recognized at the center of the cell, *i.e.* $(x,y) = (0{\cdot}5, 0{\cdot}5)$, and also at (0·0, 0·5) and (0·5, 0·0). A more detailed description of the pseudosymmetry has been given by Shieh *et al.* (1977*a*). Hydrogen bonds link the molecules into two chains along **c**. These two chains ...*AHBGA*... and ...*CFDEC*... are pseudosymmetrically related to one another. The parallel chains of hydrogen bonds in the structure form a corrugated sheet parallel to the *ac* plane. The individual hydrogen-bond chains are staggered by

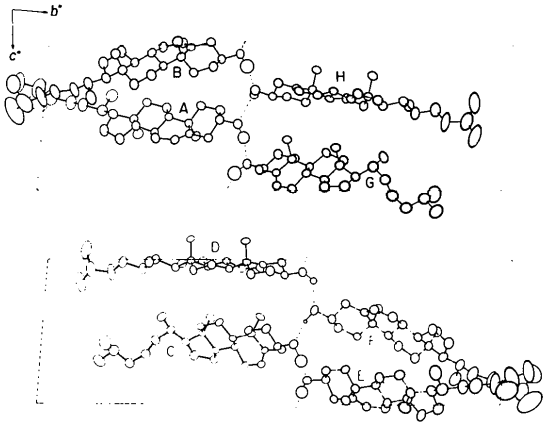

Fig. 4. One unit cell of the structure viewed along **a** (into page). The eight isotropically refined hydroxyl H atoms are shown as 25% spheres. For clarity, the two hydrogen-bonded chains are shown separately; the top figure is to be superposed on the bottom figure to give the entire cell.

±2·18 Å about the mean plane of the sheet. In this regard the structure differs from the monohydrate and the other solvates studied; in the latter structures the hydrophilic interactions are more narrowly confined to planar sheets. The hydrogen bonding is shown more clearly in Fig. 4, where the isotropically refined hydroxyl H atoms are shown.

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On Nitroguanidines. II. The Structure of *N*-Methyl-*N'*-nitroguanidine

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Abstract

The crystal and molecular structure of *N*-methyl-*N'*-nitroguanidine, $C_2H_6N_4O_2$ (M_r = 118·096), have been determined by X-ray diffraction at 115 K. The space group is $P2_1/n$ with a = 4·6320 (8), b = 10·1265 (13), c = 11·2399 (13) Å and β = 100·164 (11)° (V = 518·94 Å^3), Z = 4 and d_{calc} = 1·511 Mg m^{-3} (115 K). The observed density at 295 K is d_{obs} = 1·50 Mg m^{-3}. Full-matrix least-squares refinement converged at R = 0·047 for 3294 observed reflexions. Modifications of the weighting scheme in order to reduce polarization errors gave small but significant changes in bonding distances. The molecule is planar with an unusually long formal double C—N bond of 1·377 Å, and is interpreted as a zwitterionic structure. One of the N—O bonds is 0·02 Å longer than the other, and the difference is explained by hydrogen bonding. The crystal is built of hydrogen-bonded sheets parallel to the ($\bar{1}03$) plane, between which van der Waals interactions prevail.

Introduction

The highly conjugated guanidine moiety of the nitroguanidines forms an interesting bonding system, reflect-

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