avermectins possess a disaccharide side chain. In contrast to L-oleandrose of avermectin, cytovaricin has a β-D-cymarosyl side chain.

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The Structure of Tetrazole Steroid Analogues.
III. Structure of 4,6-Diaza-A,B-bishomocholest-4a-eno[4,3-d][6,7-d]bistetrazole (HS-649), C27H42N8*

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Abstract. $M_r = 478.7$, monoclinic, space group $C2$, $a = 35.537$ (4), $b = 7.494$ (1), $c = 10.319$ (1) Å, $\beta = 101.25$ (1)°, $V = 2695.2$ Å^3, $Z = 4$, $D_x = 1.179$, $D_m = 1.143$ (6) Mg m^{-3}, $\lambda(\text{Cu } K\alpha) = 1.54178$ Å. Final $R = 0.054$ for 2318 observed reflexions. The molecule exhibits a bowing in the α-direction.

Introduction. The bistetrazolo steroids 3,6-diaza-A,B-bishomocholest-4a-eno[3,4-d] [6,7-d] (HS-650) and 4,6-diaza-A,B-bishomocholest-4a-eno[4,3-d] [6,7-d] (HS-649) are produced when cholest-4-ene-3,6-dione is treated with excess of hydrazoic acid and boron trifluoride in benzene (Singh & Bhutani, 1978). Our previous paper (Husain, Tickle, Palmer, Singh & Bhutani, 1982) described the crystal and molecular geometry of HS-650 and in the present paper a similar analysis of HS-649 is reported, together with a comparative study of the two.

Experimental. The synthesis has been described by Singh & Bhutani (1978). Good quality tabular, transparent crystals grown from a mixture of acetone and water at room temperature are monoclinic, b axis parallel to the needle axis. Consideration of preliminary X-ray photographs led to assignment of space group C2. Intensities and accurate cell parameters were measured on a Hilger & Watts Y290 four-circle diffractometer, Ni-filtered Cu Kα radiation, $2\theta < 140°$. A floating window (Tickle, 1975) employing the $\omega/2\theta$ scanning mode was used to measure 5886 reflexions, including two symmetry equivalents. Absorption corrections (North, Phillips & Mathews, 1968; Tickle, 1979) were applied. Data set consisted of 2700 unique reflexions with a merging $R = 0.0249$.

Many attempts were made to determine the crystal structure of HS-649 by direct methods using the programs MULTAN 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), YZARC (Declercq, Germain & Woolfson, 1979) and SHELX 76 (Sheldrick, 1976), but all met with failure. The structure was

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solved using vector verification (Braun, Hornstra & Leenhouts, 1969), a Patterson search procedure similar to that of Nordman (1966). The program *VEC*1 (Ladd, 1973) implemented on the CDC 6600 computer at ULCC attempts to fit the vectors of a rigid molecular fragment of known geometry to the interatomic vectors in the Patterson function. A modified sum function is used to assess the measure of fit (MOF).

A 17-atom model constituting rings *B*-homo, *C*, *D* and the tetrazole ring T_2 was obtained from the crystal structure of HS-650 (Husain, 1981). A sharpened Patterson map was calculated at intervals of *a*/240, *b*/48 and *c*/70. The vector model was then fitted as follows:

(1) Rotation search at 9° intervals to find possible orientations of the model in Patterson space.

(2) Translation search, using vectors between 2·8–6·0 Å, to position each of the possible orientations of the model in the unit cell.

(3) Optimization, or fine adjustment of the positions of the 30 best parameter sets generated in stages (1) and (2).

Stages (1), (2) and (3) take into account Laue and space-group symmetry operations and include an intermolecular-distance test. The possible parameter sets were assessed according to both the value of the MOF, which is expected to be the smallest for the best fit, and the percentage reduction in MOF, during optimization. Using the program *SHELX* 76 structure factors were calculated from the fractional coordinates of the 17-atom fragment obtained from the best set in *VEC*1. A Sim-weighted difference electron density map revealed 16 more peaks corresponding to possible non-H atoms. The resulting 33-atom model was refined isotropically, by full-matrix least squares for four cycles after which $R = 0.21$. A second difference electron density map yielded the two remaining atoms to complete the model. Anisotropic full-matrix least-squares refinement of the model gave $R = 0.09$. The H atoms were then geometrically positioned and allowed to ride on the corresponding C atoms, with their isotropic thermal parameters refining individually. Weights were applied to the final least-squares cycle as: $w = 0.5982[\sigma^2(|F|) + 0.005432|F|^2]^{-1}$.

Secondary extinction observed for low $(\sin\theta/\lambda)$ reflexions was accounted for by refining an extinction parameter whose final value was 8.42 (1) × 10^{-3}; final $R = 0.059$, $R_w = 0.074$ and $R_g = 0.092$ for all 2700 reflexions and $R_o = 0.054$, $R_{wo} = 0.063$ and $R_{go} = 0.079$ for 2318 observed reflexions with $I > 3\sigma(I)$; $F(000) = 1040$, scattering factors taken from *International Tables for X-ray Cystallography* (1974).

Discussion. The final atomic coordinates of the non-H atoms together with their e.s.d.'s and equivalent

isotropic thermal parameters are given in Table 1.* The H atoms are numbered according to the C atoms to which they are bonded. Intramolecular bond lengths, bond angles and torsion angles are shown in Fig. 1. Ring-junction torsion angles are given in Table 2 for comparison with HS-650 (Husain *et al.*, 1982).

As in the structure of 3,6-diaza-*A*,*B*-bishomo-cholest-4a-eno[3,4-*d*][6,7-*d*]bistetrazole (HS-650), the

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Table 1. *Refined positional parameters with e.s.d.'s in parentheses and equivalent isotropic thermal parameters for non-*H *atoms*

	x	*y*	*z*	$U_{eq}(\text{Å}^2)$
C(1)	−0·2052 (1)	0·3083 (5)	−0·3142 (3)	0·0652
C(2)	−0·2250 (1)	0·2039 (7)	−0·4353 (4)	0·0766
C(3)	−0·2660 (1)	0·1770 (6)	−0·4346 (4)	0·0753
N(4')	−0·2800 (1)	0·1287 (5)	−0·3270 (3)	0·0670
N(3')	−0·3193 (1)	0·1103 (7)	−0·3624 (4)	0·0890
N(2')	−0·3274 (1)	0·1499 (9)	0·4868 (5)	0·1056
N(1')	−0·2949 (1)	0·1942 (7)	0·5345 (4)	0·0950
C(4a)	−0·2630 (1)	0·1005 (5)	−0·1951 (4)	0·0607
C(5)	−0·2268 (1)	0·1330 (4)	−0·1346 (3)	0·0499
N(4'')	−0·2203 (1)	0·0971 (4)	0·0041 (3)	0·0547
N(3'')	−0·2382 (1)	0·1884 (5)	0·0887 (3)	0·0698
N(2'')	−0·2230 (1)	0·1279 (6)	0·2064 (3)	0·0774
N(1'')	−0·1960 (1)	0·0028 (5)	0·1989 (3)	0·0671
C(7)	−0·1945 (1)	−0·0141 (5)	0·0729 (3)	0·0522
C(7a)	−0·1707 (1)	−0·1374 (5)	0·0105 (3)	0·0536
C(8)	−0·1435 (1)	−0·0490 (4)	·0·0706 (3)	0·0453
C(9)	−0·1640 (1)	0·0432 (5)	−0·2006 (3)	0·0498
C(10)	−0·1917 (1)	0·2023 (5)	−0·1824 (3)	0·0522
C(11)	·0·1338 (1)	0·1045 (6)	−0·2804 (3)	0·0643
C(12)	−0·1067 (1)	−0·0432 (5)	−0·3072 (3)	0·0620
C(13)	−0·0864 (1)	−0·1361 (5)	−0·1823 (3)	0·0476
C(14)	−0·1179 (1)	−0·1988 (4)	−0·1070 (3)	0·0449
C(15)	−0·0965 (1)	−0·3199 (5)	0·0011 (3)	0·0510
C(16)	−0·0668 (1)	−0·4157 (5)	−0·0668 (3)	0·0552
C(17)	−0·0677 (1)	0·3196 (5)	−0·2000 (3)	0·0531
C(18)	−0·0572 (1)	·0·0097 (5)	−0·0968 (3)	0·0579
C(19)	−0·1716 (1)	0·3415 (5)	−0·0834 (4)	0·0633
C(20)	−0·0281 (1)	−0·3261 (6)	−0·2408 (3)	0·0598
C(21)	−0·0274 (1)	−0·2199 (8)	−0·3662 (5)	0·0903
C(22)	−0·0156 (1)	−0·5197 (7)	−0·2532 (4)	0·0665
C(23)	0·0235 (1)	−0·5448 (7)	0·2909 (4)	0·0708
C(24)	0·0362 (1)	−0·7366 (7)	−0·2875 (5)	0·0775
C(25)	0·0728 (2)	−0·7804 (9)	−0·3252 (8)	0·1247
C(26)	0·0999 (2)	−0·6578 (16)	−0·3464 (14)	0·1799
C(27)	0·0842 (2)	−0·9735 (9)	0·3146 (6)	0·1002

Table 2. *Inter-ring torsion angles* (°)

E.s.d.'s are 0·4–0·6°.

Rings		
A–B	C(1)–C(10)–C(5)– N(4'')	−156·8
	C(9)–C(10)–C(5)–C(4a)	−101·1
B–C	C(10)–C(9)–C(8)–C(14)	+180·0
	C(11)–C(9)–C(8)–C(7a)	−172·8
C–D	C(12)–C(13)–C(14)–C(15)	+169·5
	C(17)–C(13)–C(14) C(8)	+180·0
A–T₁	C(2)–C(3)–N(4')–N(3')	−178·2
	N(1')–C(3)–N(4')–C(4a)	−176·5
B–T₂	C(5)–N(4'')–C(7)–N(1'')	+176·3
	C(7a)–C(7)–N(4'')–N(3'')	+178·2

Fig. 1. (a) Bond lengths (Å) with e.s.d.'s subscripted, (b) bond angles (°) with e.s.d.'s subscripted.

Fig. 2. Stereoview down the C(14)—C(12) bond exhibiting a cis-like conformation.

Fig. 1. (cont.) (c) Selected torsion angles (°) with e.s.d.'s in the range 0·4—1·0°.

dihedral angle at ring junction *A,B* is about 53° in HS-649 which corresponds to a bowing of the molecule in the α-direction (Fig. 2). Ring *A* has a 'butterfly' conformation similar to ring *B* in HS-665 (Husain, Palmer, Singh, Bhardwaj & Paul, 1981). Ring *B* has only one direction with noticeably dominant mirror symmetry, between C(9) and C(7)—N(4''). Ring *C* has a highly symmetrical chair conformation while ring *D* adopts a distorted 13α,14β half-chair conformation with $\Delta C_2^{16} = 6\cdot93°$. The fusion of the tetrazoles with the steroid nucleus has resulted in partial delocalization observed in shortened C—C and C—N bond lengths subtending angles > 120°. Several C—C bond lengths in the cholesteryl side chain exhibit apparent shortening associated with high thermal parameters: C(25)—C(26) = 1·381 (13) Å with U_{33} of C(26) > 0·45 Å². E.s.d.'s are, as expected, quite high in the cholesteryl side chain which has an extended conformation with chain length C(17)···C(25) = 6·4 Å. There are no intermolecular contact distances less than 3·6 Å. The crystal packing is similar to that of HS-650 ($P2_12_12_1$, $Z = 8$) which mimics a $C222_1$ arrangement.

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1,8-Dinitro-4,5-dihydroxyanthraquinone,* $C_{14}H_6N_2O_8$

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Abstract. $M_r = 330.21$, monoclinic, $P2_1/a$, $a = 15.664$ (8), $b = 12.056$ (7), $c = 6.704$ (5) Å, $\beta = 94.20$ (5)°, $V = 1262.62$ Å^3, $D_x = 1.737$, $D_m = 1.717$ Mg m^{-3}, $Z = 4$, $\lambda(Cu\,K\alpha) = 1.5418$ Å, $\mu(Cu\,K\alpha) = 1.29$ mm^{-1}, $F(000) = 672$, $R = 0.044$ for 1862 observed $[I > 3\sigma(I)]$ reflexions. The structure comprises discrete molecules with two internal hydrogen bonds per molecule, and the two nitro groups are inclined by 83.83 (5) and 62.88 (5)° to the anthraquinone nucleus.

Introduction. This work was undertaken as part of a study of the distortions from planarity of a number of substituted anthraquinones which might yield correlations between structure and chemical reactivity. Several of the results of these structure determinations have already been published (Bailey, 1958; Bailey & Brown, 1967*a,b c*; Brown & Mitchell, 1982).

Experimental. Sample obtained from Imperial Chemical Industries Limited (Organics Division), acicular crystals suitable for X-ray diffraction measurements grown from phenol solution, strongly pleochroic, showing purple and brown shading; unit-cell dimensions obtained initially from rotation photographs, and more accurately from high-angle reflexions on Weissenberg photographs by a least-squares analysis of the $\alpha_1\alpha_2$ separations; crystal $2.0 \times 0.2 \times 0.2$ mm for collecting intensity data; Nonius integrating Weissenberg camera at University College London; multiple-film photographs taken about **b** (zero level) and **c** (zero and five levels), intensities derived from a combination of visual and optical measurements using a Joyce–Loebl microdensitometer; 2316 measured reflexions; structure solved by a combination of a sharpened three-dimensional Patterson synthesis and manually derived $\sum_2$ relationships; signs of 171 independent structure amplitudes thereby obtained, the resulting E map showing all the non-hydrogen atoms; parameters refined by least-squares calculations using B_{ij} and $w = 1/F$ until shifts were all less than 0.5σ; positional parameters for the six H atoms obtained from a difference Fourier map, and these, together with their B_{iso}, were refined until the shifts were less than σ; $R_w = 0.058$; scattering factors from *International Tables for X-ray Crystallography* (1962); computer programs used included some local compilations on the IBM 360/65 at University College London, but were mainly those of the NRC series (Ahmed, Hall, Pippy & Huber, 1970) implemented on the ICL 1905E at the London Polytechnics Computer Unit.

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* IUPAC nomenclature: 1,8-dihydroxy-4,5-dinitroan-thra-quinone.