

The Structure of Tetrazole Steroid Analogues.

I.* The Structure of 17 β -(5-Methyltetrazol-1-yl)-7 α -aza-*B*-homoandrost-5-eno[7 α ,7-*d*]-tetrazol-3 β -yl Acetate (HS-665)†

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Abstract

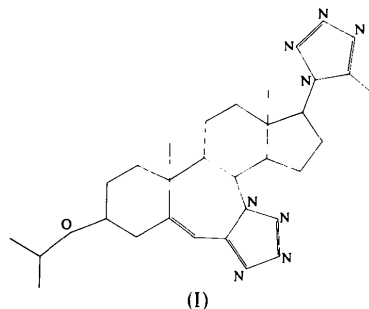
The crystal structure of the novel synthetic molecule 17 β -(5-methyltetrazol-1-yl)-7 α -aza-*B*-homoandrost-5-eno[7 α ,7-*d*]tetrazol-3 β -yl acetate (HS-665), C₂₃H₃₂N₈O₂, has been determined by X-ray diffraction using direct methods. Crystals are monoclinic, *P*2₁, with *a* = 6.414 (1), *b* = 23.668 (3), *c* = 7.779 (1) Å, β = 100.08 (1)°, *Z* = 2, and the structure was refined by least-squares analysis to *R*_o = 0.039 for 1790 reflections measured on a four-circle diffractometer. Rings *A* (chair) and *D* (envelope) are in their usual steroid conformations while ring *C*, which is usually chair, is a strained chair/sofa having lost most of its pseudo-symmetry, and the heterocyclic seven-membered ring *B*-homo has a distorted sofa or 'butterfly-like' conformation with two predominantly planar 'wings' of four atoms each. Both tetrazole rings are planar. The molecule is slightly curled with two shallow convex surfaces: one, convex towards the α face, formed by rings *A*, *B*-homo and the fused tetrazole ring *T*₁; the other, convex towards the β face, formed by rings *B*-homo, *C* and *D*. The curvature of the molecule results in a short C(18)···C(19) distance of 3.887 Å compared with the normal value of around 4.6 Å.

Introduction

The interest in steroidal tetrazoles or, in fact, any modified steroid, lies in the potential changes in pharmaceutical and biological properties which such modifications may bring about (Mechoulam, 1968). It is well known that the addition of heterocyclic rings

such as pyrazoles, triazoles or pyridines, for example, can cause striking changes in the physiological activity of a steroid drug (Clinton, Manson, Stonner, Beyler, Potts & Arnold, 1959; Zhungietu & Dorofeenko, 1967). With this in mind several tetrazolo-steroids have been synthesized as described, for example, by Singh, Mathur & Sharma (1972), Singh, Bhutani, Malhotra & Paul (1978) and Singh, Kapoor & Paul (1979). Since the tetrazole group is generally observed to be inert in biological systems, the chemical and structural changes induced by its presence may prove to be useful factors in drug design. At present, methods for producing the chemical modifications are still under development. The work described here is the first of a series of crystallographic structure determinations undertaken to verify the chemical structures and investigate and characterize the molecular geometry and conformational features of members of the series of compounds prepared by Singh and co-workers. Several other X-ray analyses in the series have now been completed in this laboratory (Palmer, Lisgarten & Chattopadhyay, 1981; Husain & Palmer, 1981).

The compound HS-665, the X-ray analysis of which is described here, is a bistetrazole steroid, C₂₃H₃₂N₈O₂ (I), prepared by Singh, Bhardwaj & Paul (1977) by subjecting 3 β -acetoxy-pregn-5-ene-7,20-dione to the Schmidt (1924) reaction. HS-665 corresponds to



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† Alternative description: 1 β -(5-Methyltetrazol-1-yl)tetrazolo[5,1-*g*][7 α]aza-*B*-homoandrost[5]en-10 β -yl acetate.

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fraction *C* resulting from this reaction, having the proposed structural formula indicated in (I). Ring *B* is a modified heterocyclic seven-membered ring (denoted *B*-homo) resulting from the incorporation of tetrazole ring *T*₁ fused to the steroid nucleus. Tetrazole group *T*₂ is appended to ring *D* via the C(17)–N(1'') bond. One objective of the crystallographic analysis was to verify the bonding assignments shown in (I).

Experimental

Slow cooling of a solution of HS-665 in a methanol-ethanol mixture produced clear wedge-shaped crystals which were characterized optically and X-ray photographically as monoclinic, *P*2₁. The unit-cell parameters were determined by least-squares refinement of the θ , χ and φ values of eight reflections measured accurately on a Hilger & Watts Y290 four-circle diffractometer using Cu *K* α radiation (Tickle, 1979). Intensities were measured on the same instrument by step-scanning in the ω -2 θ mode to a limit of 2 θ = 140°. A total of 5057 reflections were measured which reduced to a unique set of 2138 of which 1790 with $I_o > 3\sigma(I_o)$ were classified as observed. Lorentz and polarization factors were applied in the usual manner. Semi-empirical absorption corrections were applied ($\mu_{\text{CuK}\alpha} = 0.619 \text{ mm}^{-1}$, $\mu_r = 0.06$ to 0.35) using the method of North, Phillips & Mathews (1968) modified according to Kopfmann & Huber (1968) whereby the transmission coefficient is calculated as the geometric rather than the arithmetic mean of the transmission coefficients of the incident and reflected beams (Tickle, 1979). The measured density $D_m = 1.292(3) \text{ Mg m}^{-3}$ corresponds to $Z = 2$; $D_c = 1.291 \text{ Mg m}^{-3}$.

Structure determination and refinement

The structure was solved by direct methods using *MULTAN* 78 (Main, 1978), a more recent version of the program described by Germain, Main & Woolfson (1971). Overall scale and temperature factors derived by the program using a Wilson (1942) plot technique [see also, for example, Ladd & Palmer (1980) and Rogers (1980)] were used to convert $|F|$ values to $|E|$ values. 500 reflections with $|E| > 1.0$ and a further 50 weak ψ_0 reflections with $|E| < 0.2$ were used to generate 32 phase sets. Set 3 was selected for further analysis on the strength of the figures of merit [see, for example, Ladd & Palmer (1980)], which were as follows: ABS FOM = 1.05 (fourth highest), PSI ZERO = 1.55 (lowest), RESID (R_{Karle}) = 24.77 (lowest) and COMBINED FOM = 2.07 (highest). The *E* map calculated from phase set 3 contained 29 high peaks in stereochemically reasonable positions and isotropic full-matrix least-squares refinement of this

Table 1. Refined positional parameters ($\times 10^4$, for H $\times 10^3$) and isotropic thermal parameters with e.s.d.'s in parentheses

	For non-H atoms $U_{\text{iso}} = (U_1 U_2 U_3)^{1/3}$.			
	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} (Å ²)
C(1)	7506 (7)	1999 (2)	3825 (5)	0.059 (3)
C(2)	7532 (8)	1405 (2)	4639 (6)	0.065 (3)
C(3)	5939 (7)	1042 (2)	3523 (6)	0.063 (3)
C(4)	6414 (9)	1014 (2)	1672 (7)	0.071 (4)
C(5)	6424 (6)	1593 (2)	870 (5)	0.054 (3)
C(6)	5110 (7)	1666 (2)	-668 (6)	0.064 (3)
C(7)/C(5')	4755 (7)	2143 (2)	-1820 (5)	0.060 (3)
N(1')	3131 (6)	2177 (2)	-3144 (5)	0.071 (3)
N(2')	3379 (6)	2669 (2)	-3955 (5)	0.071 (3)
N(3')	5071 (6)	2934 (2)	-3203 (4)	0.060 (2)
N(7a)/N(4')	5959 (5)	2598 (1)	-1852 (3)	0.052 (2)
C(8)	7933 (6)	2761 (2)	-638 (4)	0.047 (2)
C(9)	7569 (5)	2652 (1)	1268 (4)	0.046 (2)
C(10)	7924 (5)	2021 (2)	1897 (4)	0.049 (2)
C(11)	8824 (6)	3056 (1)	2653 (4)	0.053 (3)
C(12)	9252 (6)	3652 (1)	2058 (4)	0.050 (3)
C(13)	10179 (5)	3630 (1)	372 (4)	0.047 (2)
C(14)	8467 (5)	3366 (1)	-1032 (4)	0.048 (2)
C(15)	9232 (7)	3495 (2)	-2768 (4)	0.059 (3)
C(16)	10515 (7)	4043 (2)	-2447 (6)	0.064 (3)
C(17)	10402 (6)	4201 (1)	-526 (5)	0.059 (3)
C(18)	12267 (6)	3291 (2)	635 (6)	0.061 (3)
C(19)	10227 (6)	1830 (2)	1870 (6)	0.066 (3)
N(1'')	12206 (5)	4547 (2)	274 (4)	0.058 (2)
N(2'')	14205 (5)	4429 (2)	51 (6)	0.075 (3)
N(3'')	15411 (6)	4806 (2)	909 (6)	0.081 (3)
N(4'')	14256 (6)	5173 (2)	1698 (5)	0.074 (3)
C(5'')	12253 (6)	5014 (2)	1277 (5)	0.065 (3)
C(5''')	10402 (10)	5285 (3)	1788 (10)	0.089 (4)
O(1')	6108 (5)	470 (0)	4214 (4)	0.071 (2)
C(2')	4347 (8)	158 (2)	3917 (7)	0.086 (4)
C(3')	4797 (10)	-439 (2)	4542 (7)	0.089 (5)
O(2')	2672 (8)	310 (2)	3186 (8)	0.072 (3)
H(11)	602 (9)	221 (2)	369 (6)	0.067 (12)
H(12)	857 (6)	226 (2)	454 (5)	0.045 (9)
H(21)	730 (6)	143 (2)	588 (5)	0.056 (10)
H(22)	899 (9)	123 (2)	462 (7)	0.071 (13)
H(3)	435 (7)	116 (2)	345 (5)	0.055 (9)
H(41)	552 (7)	75 (2)	84 (5)	0.067 (12)
H(42)	795 (8)	83 (2)	185 (6)	0.062 (10)
H(6)	427 (10)	136 (3)	-96 (7)	0.086 (17)
H(8)	900 (6)	251 (2)	-94 (4)	0.040 (8)
H(9)	595 (6)	272 (1)	123 (4)	0.040 (8)
H(111)	1031 (6)	290 (2)	317 (5)	0.040 (8)
H(112)	811 (7)	308 (2)	352 (6)	0.056 (10)
H(121)	1032 (7)	382 (2)	295 (5)	0.054 (9)
H(122)	792 (6)	387 (2)	185 (5)	0.041 (8)
H(14)	723 (6)	357 (2)	-107 (4)	0.041 (8)
H(151)	1008 (7)	321 (2)	-306 (6)	0.066 (11)
H(152)	791 (6)	356 (2)	-378 (4)	0.048 (8)
H(161)	1212 (9)	397 (2)	-253 (6)	0.080 (14)
H(162)	1010 (8)	435 (2)	-331 (7)	0.077 (13)
H(17)	903 (7)	442 (2)	-42 (6)	0.063 (11)
H(181)	1199 (8)	291 (2)	92 (6)	0.065 (12)
H(182)	1290 (9)	331 (2)	-36 (8)	0.065 (11)
H(183)	1337 (7)	344 (2)	152 (6)	0.074 (15)
H(191)	1127 (11)	211 (3)	277 (8)	0.120 (20)
H(192)	1037 (8)	177 (2)	59 (6)	0.079 (13)
H(193)	1067 (8)	144 (2)	249 (7)	0.083 (14)
H(51'')	933 (14)	511 (4)	115 (10)	0.156 (24)
H(52'')	1045 (16)	562 (5)	211 (13)	0.167 (23)
H(53'')	1023 (14)	517 (4)	312 (15)	0.171 (23)

Table 1 (cont.)

	x	y	z	U_{iso} (Å ²)
H(31')	365 (19)	-58 (5)	507 (15)	0.202 (23)
H(32')	565 (20)	-51 (6)	583 (18)	0.213 (23)
H(33')	521 (23)	-64 (6)	370 (18)	0.231 (23)

trial structure gave $R = 0.256$, the missing four non-H atoms being located on a difference map. Further isotropic refinement gave $R = 0.135$.

Anisotropic block-diagonal least-squares refinement of the non-H parameters converged at $R = 0.086$. A difference electron density map calculated at this stage revealed 30 of the 32 H atoms. The remaining two H atoms were positioned geometrically using ideal bond lengths and angles, and similar calculations were used to check the assigned coordinates of the other H atoms. Three cycles of block-diagonal least squares in which positional parameters were varied for all atoms and with anisotropic temperature factors for the non-H atoms and isotropic temperature factors for the H atoms gave final values of $R = 0.048$, $R_w = 0.060$, $R_G = 0.073$, for 2138 reflections and $R_o = 0.039$, $R_w = 0.046$, $R_G = 0.059$ for 1790 reflections with $I > 3\sigma(I)$, where $R_w = \sum w^{1/2} |\Delta| / \sum w^{1/2} |F_o|$, $R_G = (\sum w \Delta^2 / \sum w |F_o|^2)^{1/2}$, $\Delta = |F_o| - |F_c|$. The number of parameters in the three refinement blocks was 188, 125 and 114 respectively. The weighting scheme used in the final cycle of least squares was $w = 1.0 / [\sigma^2(F) + 0.005356 |F|^2]$. No significant variation in the distribution of $\sum w \Delta^2$ with $\sin \theta$ or $(|F|/|F_{max}|)^{1/2}$ was observed.* The final difference electron density map contained no region with density greater than 0.16 e \AA^{-3} . Positional and isotropic thermal parameters are given in Table 1.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35672 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

The atom-numbering scheme is shown in Fig. 1, in which, for convenience, alternative numbers are quoted for atoms C(7) and N(7a) in tetrazole ring T_1 ; these alternatives, C(5') for C(7) and N(4') for N(7a), both conform to steroid nomenclature. H atoms are numbered according to the bonded C atoms. Bond lengths and bond angles are shown in Fig. 1, and selected torsion angles in Fig. 2. Selected least-squares planes and dihedral angles are presented in Table 2.

The average of the 22 C—C bond lengths is 1.529 \AA . As discussed below, four of these bonds (marked with an asterisk in Fig. 1) have low values and three (marked with a double asterisk) have high values. The length of the double bond C(5)=C(6) = $1.345 (6) \text{ \AA}$ is close to the expected value; the two adjacent bonds C(6)—C(7) = $1.435 (7) \text{ \AA}$ and C(7)—N(7a) = $1.329 (5) \text{ \AA}$ both show partial double-bond character.

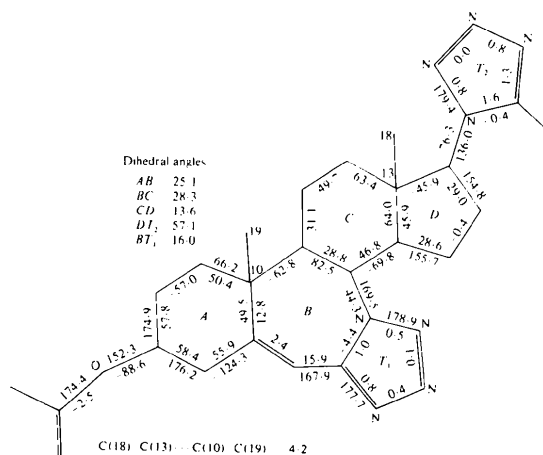


Fig. 2. Selected torsion angles ($^\circ$) in HS-665. E.s.d.'s in torsion angles range from 0.09 to 0.12 $^\circ$.

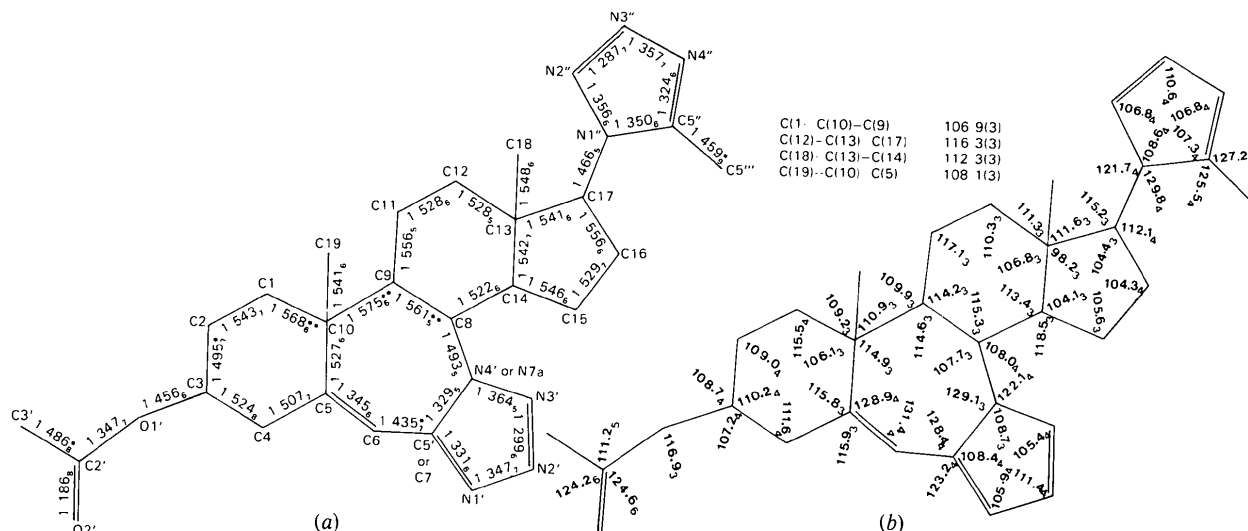


Fig. 1. (a) Bond lengths (Å). Short bonds are indicated *, long bonds **. The atom-numbering scheme is also shown. (b) Bond angles ($^\circ$). E.s.d.'s are given as subscripts.

Table 2. *Least-squares planes*

(a) Coefficients in the equation $pX' + qY' + rZ' = s$ of the least-squares planes. [The equations are defined with regard to orthogonal axes $X'(a^*)$, $Y'(b)$, $Z'(c)$ expressed in Å.]

Plane	p	q	r	s
T_1	0.5346	-0.4719	-0.7011	0.5841
T_2	0.1178	-0.5803	-0.8057	-6.2790
B_1	0.7203	-0.1448	-0.6784	2.4643
B_2	0.5358	-0.4539	-0.7123	0.7099
$B_3 T_1$	0.5470	-0.4814	-0.6849	0.5237
D	0.8304	-0.5308	0.1697	-0.0879

(b) Distances (Å) of atoms from least-squares planes (asterisks indicate atoms not included in the calculation of the planes; e.s.d.'s are 0.004–0.008 Å).

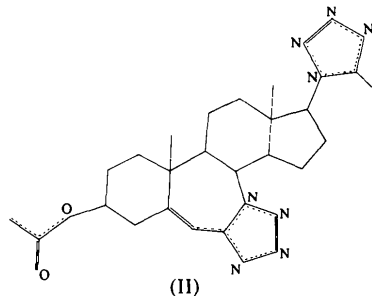
Plane T_1		Plane B_1	
C(7)	-0.005	C(6)	0.030
N(1')	0.004	C(5)	-0.058
N(2')	-0.001	C(10)	0.050
N(3')	-0.002	C(9)	-0.023
N(7a)/N(4')	0.004		
Plane T_2		Plane B_2	
N(1'')	0.006	C(6)	0.007
N(2'')	-0.003	C(7)	-0.016
N(3'')	-0.002	N(7a)/N(4')	0.026
N(4'')	0.006	C(8)	-0.006
C(5'')	-0.007		
C(5''')	-0.030	Plane $B_3 T_1$	
		C(5)	-0.092
		C(6)	0.092
		C(7)	0.013
		N(1')	-0.006
		N(2')	-0.030
		N(3')	-0.018
		N(7a)/N(4')	0.019
		C(8)	0.021
		C(9)*	-1.024
		C(10)*	-0.491
Plane D			
C(14)	-0.001		
C(15)	0.001		
C(16)	-0.001		
C(17)	0.001		
C(13)*	0.726		

(c) Dihedral angles ($^\circ$) between planes (e.s.d.'s are 0.4–0.8 $^\circ$)

Plane 1	Plane 2	Plane 1	Plane 2	Plane 1	Plane 2	
A	B	B	C	T_1	T_2	103.2
A	T_1	B	D	C	D	13.6
A	C	B	T_2	C	T_2	70.5
A	D	T_1	C	D	T_2	57.1
A	T_2	T_1	D	B_1	B_2	20.9
B	T_1					

Consequently, atoms C(5), C(6), C(7) and C(8) in ring B together with N(1'), N(2'), N(3') and N(7a) in the tetrazole ring T_1 form an approximately planar region (plane $B_3 T_1$ in Table 2). In the same region angles C(5)–C(6)–C(7) = 131.4 (4), C(6)–C(7)–N(7) = 128.4 (4) and C(10)–C(5)–C(6) = 128.9 (4) $^\circ$ are very open. Associated with the aromatic-like tetrazole ring T_2 the bond C(5'')–C(5''') = 1.459 (9) Å also exhibits partial double-bond character. The four atoms of the acetate group are planar, C(2')–C(3') = 1.486 (8) and O(1')–C(2') = 1.347 (7) Å both being partial double

bonds. In ring A the bond C(2)–C(3) = 1.495 (7) Å is short, presumably a consequence of the acetyl group on C(3). The slight but significant lengthening of the bonds in the chain C(1)–C(10)–C(9)–C(8) linking rings A , B and C is probably due to strain imposed by the additional bond in ring B . Of the five C–N bonds in the molecule only one, the linkage bond C(17)–N(1'') = 1.466 (5) Å between rings D and T_2 , is a true single bond. This value compares well with the average C–N bond length of 1.475 (4) Å in the alkaloid methyl-warifteine (Borkakoti & Palmer, 1978). The average of the four other ring C–N bond lengths is 1.334 Å, all being within 2σ of this value. The expected value for a single N–N bond is approximately 1.44 Å and for a double N=N bond approximately 1.24 Å (Kennard, Watson, Allen, Isaacs, Motherwell, Pettersen & Town, 1972). The two bonds N(2'')=N(3'') = 1.287 (7) and N(2')=N(3') = 1.299 (6) Å thus closely exhibit double-bond character. The average value of the four other ring N–N distances is 1.345 Å; as all are within 1σ of this value, they are thus partial double bonds. Both tetrazole rings are flat (Table 2) and, according to the above discussion, exhibit delocalization of bonds shown in the revised chemical structure (II). The average value of the C–H bond lengths is 0.99 Å, of the C–C–H bond angles 109.0 $^\circ$ and of the H–C–H angles 106 $^\circ$.



Ring A is in the usual chair conformation, all asymmetry parameters (Duax & Norton, 1975) ΔC_5 and ΔC_2 being small. Ring D is in the usual envelope conformation with $\Delta C_5^{C(13)} = 0.14^\circ$. Due to the strain imposed by the modified ring B -homo, ring C , which is usually in the chair conformation, has become flattened at the C(9) position and has adopted a half-chair conformation having a pseudo twofold axis across C(9)–C(13) with $\Delta C_2^{C(9)} = 1.19^\circ$. The conformation of ring B -homo may be described in terms of two approximately planar groups of four atoms each, B_1 and B_2 respectively in Table 2, with a dihedral angle of 20.9 $^\circ$ (Table 2). We propose the term 'butterfly' for such a conformation, atom C(6) forming the 'head', C(8)–C(9) the 'tail' and planes B_1 , B_2 the 'wings'. All asymmetry parameters in ring B -homo are high, the smallest being $\Delta C_2^{C(6)} = 16.5^\circ$ and $\Delta C_5^{C(9)} = 21.5^\circ$. The overall shape of the molecule may be described in terms of the dihedral angles between the least-squares

Table 3. *Close contacts* (Å)

Atom 1	Atom 2	Symmetry operation for atom 2	Type of contact*
C(3')	N(4'')	$2-x, -\frac{1}{2}+y, 1-z$	3.233 (8) <i>H to T</i>
C(4)	N(4'')	$2-x, -\frac{1}{2}+y, -z$	3.258 (8) <i>H to T</i>
O(1')	N(4'')	$2-x, -\frac{1}{2}+y, 1-z$	3.297 (8) <i>H to T</i>
C(5'')	N(3'')	$-1+x, y, z$	3.349 (8) <i>T to T</i>
C(4)	C(5'')	$2-x, -\frac{1}{2}+y, -z$	3.503 (8) <i>H to T</i>

* '*H to T*' = 'head to tail', i.e. *A* ring end in contact with *D* ring end. '*T to T*' = 'tail to tail', i.e. *D* ring end in contact with *D* ring end.

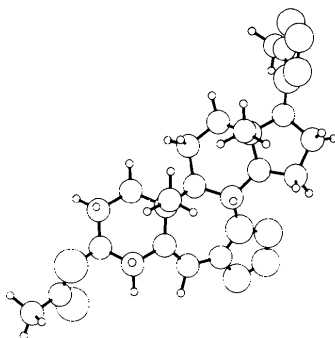
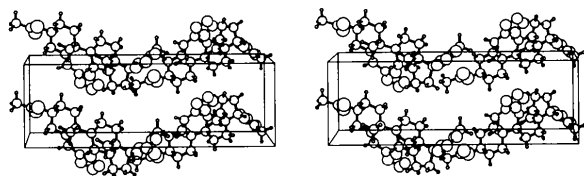


Fig. 3. View approximately perpendicular to the plane of the molecule.

Fig. 4. Packing of the molecules viewed along *a*.

planes calculated for the non-planar rings *A*, *B*, *C* and *D*, and the planar rings *T*₁ and *T*₂ (Table 2). Rings *A*, *B* and *T*₁ form a shallow surface convex towards the α face of the molecule which, extended, includes C(2')=O(2'). Rings *B*, *C* and *D* also form a shallow surface but convex towards the β face which, extended, contains tetrazole ring *T*₂. This unusual curvature results in a shortening of the distance C(18)···C(19) to 3.887 (4) Å, compared to the usual value of around 4.6 Å. The longitudinal molecular twist is small, the pseudo-torsion angle C(18)–C(13)···C(10)–C(19) being -4.2° . A view of the molecule approximately perpendicular to the plane of the molecule is shown in Fig. 3. Table 3 lists the shortest intermolecular contacts and the packing of the molecules is illustrated in Fig. 4.

Computations were undertaken on the IBM 360 computer at University College, London (data reduction and *MULTAN*), and on the University of London CDC 6600 computer (structure determination and refinement using the *SHELX* program package, Sheldrick, 1978).

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