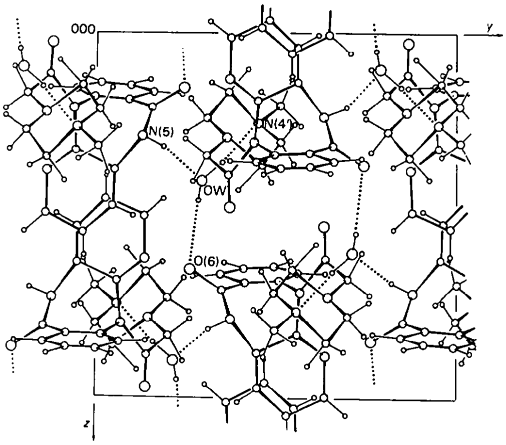

Fig. 2. A view of the crystal structure along **a** showing the packing, hydrogen bonds, and conformation of the benzodiazepine and piperazine rings.

The pyridine and benzene rings are planar in the limits of the experimental errors whereas the piperazine ring is in a chair conformation. The dihedral angle between the benzene and the pyridine ring is 60·9 (4)°.

The water molecule is involved in hydrogen bonds with the amide group of the diazepine ring, N(5)–H(5)···O(*W*)[2·800 (3)] and O(*W*)–H(*W*)2 ···O(6)[2·907 (3) Å]. N(4′) of the piperazine ring is hydrogen-bonded to the water molecule by O(*W*)–H(*W*)1···N(4′)[2·821 (3) Å]. Molecular packing is also influenced by van der Waals interactions. The relative orientation of the pyridine and piperazine ring [with a dihedral angle of 22·2 (4)°] enables a short intramolecular contact N(1)···N(1′) of 3·087 (2) Å.

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(23*R*,25*R*)- and (23*S*,25*S*)-3*β*-Methoxymethoxy-5*α*,8*α*-(3,5-dioxo-4-phenyl-1,2,4-triazole-1,2-diyl)-25-hydroxycholest-6-eno-26,23-lactone, $C_{37}H_{49}N_3O_7$

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Abstract. $M_r = 647{\cdot}8$, (23*R*,25*R*) isomer: monoclinic, $P2_1$, $a = 12{\cdot}939\ (2)$, $b = 9{\cdot}909\ (2)$, $c = 13{\cdot}517\ (2)$ Å, $\beta = 100{\cdot}46\ (1)^\circ$, $V = 1704{\cdot}3\ (5)$ Å^3, $Z = 2$, $D_x = 1{\cdot}262$ Mg m^{-3}, $F(000) = 696$, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}6$ mm^{-1}; (23*S*,25*S*) isomer: orthorhombic, $P2_12_12_1$, $a = 9{\cdot}946\ (2)$, $b = 29{\cdot}966\ (7)$, $c = 11{\cdot}189\ (2)$ Å, $V = 3334{\cdot}8\ (8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}290$ Mg m^{-3} $F(000) = 1392$, $\mu(\mathrm{Cu}\ K\alpha) = 0{\cdot}6$ mm^{-1}. The structures were determined by Patterson-search and direct methods and refined to R_w values of respectively 0·051 and 0·047 for 2650 and 3005 observed reflections. The molecules are T-shaped with the 4-phenyltriazole moiety perpen-

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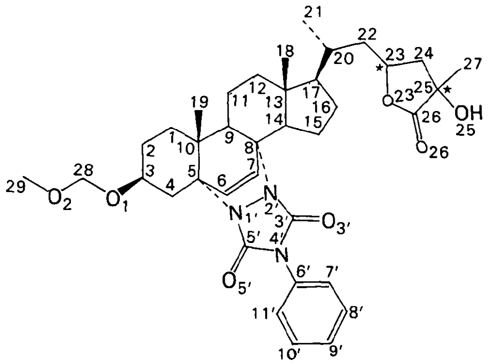
dicular to the steroid nucleus. Structural differences occur mainly within the substituents, while the conformations of the carbon skeletons are very similar, even at the centres with different configuration, with approximately *trans* arrangement for C(20) to C(27).

Introduction. In the course of the synthesis of 25-hydroxycholecalciferol-26,23-lactone, a new metabolite of vitamin D_3 developed by D. H. Williams and co-workers in this laboratory, it became necessary to determine its absolute stereochemistry at C(23) and C(25). The configurations of two diastereoisomers of the 5,8-bridged steroid lactone,



which appears as an intermediate reaction product, were therefore determined by X-ray analysis and shown to be 23*R*,25*R* (I) and 23*S*,25*S* (II). From this could be concluded that the natural metabolite has the 23*R*,25*S* stereochemistry (Morris, Williams & Norris, 1981).

Experimental. Crystals from acetone, equi-dimensional multi-faceted prisms (I) and flat needles (II); 3376 (I) and 3534 (II) unique reflections, $2\theta < 140°$, Syntex $P2_1$ diffractometer, θ–2θ scans; 2650 (I) and 3005 (II) $|F| > 3\sigma_F$ treated as observed; no absorption correction. Neither structure could be solved automatically with direct methods; recognizable fragment of 12 atoms for the 23*S*,25*S* compound obtained with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); subsequent Karle tangent expansion revealed remaining non-hydrogen atoms; refined coordinates of rigid part of (II) (altogether 25 atoms) used to solve structure of 23*R*,25*R* diastereoisomer by real-space Patterson search (Braun, Hornstra & Leenhouts, 1969); best solution could easily be expanded to the complete structure (Egert, 1983).

Isotropic refinement, unit weights, gave $R = 0{\cdot}129$ (I) and $0{\cdot}110$ (II); two cycles of anisotropic refinement gave R (I) $= 0{\cdot}090$ whereas the latter remained almost constant; 41 (I) and all 49 (II) H atoms located by difference synthesis and the 8 missing H atoms of (I) placed at calculated positions; function minimized: $\sum w|F_o - |F_c||^2$, $w = (\sigma_F^2 + kF^2)^{-1}$ ($k = 0{\cdot}0005$ and $0{\cdot}0004$, respectively); further refinement with fixed individual H temperature factors converged at $R_w = 0{\cdot}051$ (I) and $0{\cdot}047$ (II); none of the positional parameters of the non-hydrogen atoms shifted more than $0{\cdot}6$ (I) and $0{\cdot}3\sigma$ (II) in last cycle of blocked full-matrix least squares (*SHELX*76: Sheldrick, 1976); no peaks $>0{\cdot}21$ (I) and $0{\cdot}27$ e Å^{-3} (II) in final difference map; scattering factors from *International Tables for X-ray Crystallography* (1974). Parameters are listed in Tables 1 and 2.*

Table 1. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$) *for the* 23*R*,25*R* *diastereoisomer with e.s.d.'s in parentheses*

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	3761 (4)	1563	5355 (4)	64 (2)
C(2)	4888 (4)	1139 (7)	5777 (4)	71 (2)
C(3)	4919 (3)	−42 (7)	6465 (3)	59 (2)
C(4)	4198 (3)	−1216 (7)	6029 (3)	51 (2)
C(5)	3103 (3)	−799 (6)	5511 (3)	43 (1)
C(6)	2482 (4)	−1926 (6)	4924 (3)	50 (2)
C(7)	1511 (3)	−1606 (6)	4521 (3)	47 (1)
C(8)	1167 (3)	−200 (6)	4724 (3)	42 (1)
C(9)	1932 (3)	880 (6)	4422 (3)	45 (1)
C(10)	3110 (3)	432 (7)	4783 (3)	48 (1)
C(11)	1636 (4)	1323 (7)	3322 (3)	58 (2)
C(12)	469 (4)	1675 (7)	3011 (3)	54 (2)
C(13)	−222 (3)	481 (6)	3182 (3)	43 (1)
C(14)	23 (3)	156 (6)	4323 (3)	44 (1)
C(15)	−836 (3)	−786 (7)	4502 (3)	52 (1)
C(16)	−1811 (3)	−282 (7)	3778 (3)	59 (2)
C(17)	−1430 (3)	773 (7)	3066 (3)	49 (1)
C(18)	−49 (3)	−745 (7)	2523 (3)	55 (2)
C(19)	3622 (4)	−33 (7)	3896 (3)	65 (2)
C(20)	−2107 (3)	743 (7)	2013 (3)	55 (2)
C(21)	−1743 (4)	1705 (8)	1267 (4)	75 (2)
C(22)	−3280 (4)	1038 (7)	2036 (3)	58 (2)
C(23)	−4009 (4)	253 (7)	1244 (3)	64 (2)
O(23)	−4009 (3)	−1144 (6)	1631 (3)	84 (2)
C(24)	−5170 (4)	609 (7)	1033 (4)	66 (2)
C(25)	−5703 (4)	−717 (7)	745 (3)	66 (2)
O(25)	−5573 (3)	−1156 (6)	−233 (2)	92 (2)
C(26)	−4975 (5)	−1698 (8)	1389 (4)	84 (2)
O(26)	−5173 (5)	−2794 (7)	1673 (5)	152 (3)
C(27)	−6835 (4)	−836 (9)	876 (4)	84 (2)
O(1)	5972 (2)	−587 (7)	6696 (3)	82 (2)
C(28)	6404 (5)	−727 (11)	7688 (5)	113 (3)
O(2)	7464 (6)	−676 (10)	7836 (4)	174 (4)
C(29)	7648 (12)	775 (16)	7707 (14)	297 (10)
N(1')	2445 (2)	−397 (6)	6269 (2)	48 (1)
N(2')	1382 (2)	−137 (6)	5848 (2)	47 (1)
C(3')	893 (3)	393 (6)	6565 (3)	42 (1)
O(3')	5 (2)	807 (5)	6496 (2)	50 (1)
N(4')	1643 (2)	317 (6)	7443 (2)	44 (1)
C(5')	2602 (3)	−177 (6)	7263 (3)	44 (1)
O(5')	3384 (2)	−371 (6)	7894 (2)	59 (1)
C(6')	1496 (3)	869 (7)	8396 (3)	51 (1)
C(7')	650 (4)	430 (8)	8795 (3)	78 (2)
C(8')	483 (5)	998 (11)	9689 (4)	113 (4)
C(9')	1169 (6)	1973 (10)	10166 (4)	113 (4)
C(10')	1988 (6)	2404 (8)	9748 (4)	87 (3)
C(11')	2171 (4)	1800 (7)	8856 (3)	66 (2)

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* 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 38118 (46 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å^2 $\times$ 10^3) *for the 23S,25S diastereoisomer with e.s.d.'s in parentheses*

U_{eq} is one third of the trace of the orthogonalized U_{ij} tensor

	x	*y*	*z*	U_{eq}
C(1)	4340 (4)	5178 (1)	5169 (3)	41 (1)
C(2)	4674 (4)	5487 (1)	6218 (4)	48 (1)
C(3)	4824 (4)	5234 (1)	7378 (4)	40 (1)
C(4)	5731 (4)	4822 (1)	7282 (3)	35 (1)
C(5)	5492 (3)	4532 (1)	6196 (3)	31 (1)
C(6)	6533 (4)	4169 (1)	6018 (3)	38 (1)
C(7)	6323 (4)	3898 (1)	5108 (3)	36 (1)
C(8)	5034 (3)	3980 (1)	4417 (3)	30 (1)
C(9)	4935 (3)	4481 (1)	3998 (3)	31 (1)
C(10)	5394 (4)	4805 (1)	5011 (3)	32 (1)
C(11)	5616 (4)	4558 (1)	2789 (3)	42 (1)
C(12)	5155 (4)	4233 (1)	1839 (3)	42 (1)
C(13)	5455 (4)	3755 (1)	2212 (3)	33 (1)
C(14)	4699 (4)	3661 (1)	3401 (3)	31 (1)
C(15)	4856 (4)	3156 (1)	3559 (3)	42 (1)
C(16)	4734 (4)	2977 (1)	2271 (4)	45 (1)
C(17)	4828 (4)	3381 (1)	1428 (3)	37 (1)
C(18)	6974 (4)	3684 (1)	2325 (4)	46 (1)
C(19)	6775 (4)	5019 (1)	4751 (4)	44 (1)
C(20)	5508 (4)	3266 (1)	213 (3)	41 (1)
C(21)	5743 (5)	3675 (1)	−593 (4)	53 (1)
C(22)	4671 (4)	2916 (1)	−437 (4)	47 (1)
C(23)	5401 (4)	2600 (1)	−1250 (4)	51 (1)
O(23)	6186 (3)	2841 (1)	−2117 (3)	57 (1)
C(24)	4481 (4)	2300 (1)	−2007 (4)	49 (1)
C(25)	5269 (4)	2230 (1)	−3156 (4)	44 (1)
O(25)	6145 (3)	1856 (1)	−2956 (3)	63 (1)
C(26)	6151 (4)	2636 (1)	−3200 (4)	50 (1)
O(26)	6772 (3)	2776 (1)	−4034 (3)	70 (1)
C(27)	4429 (5)	2168 (2)	−4257 (4)	58 (2)
O(1)	5449 (3)	5502 (1)	8275 (2)	45 (1)
C(28)	4577 (5)	5786 (1)	8898 (4)	53 (1)
O(2)	3707 (3)	5560 (1)	9666 (3)	58 (1)
C(29)	4404 (5)	5313 (2)	10543 (4)	67 (2)
N(1′)	4176 (3)	4288 (1)	6288 (3)	32 (1)
N(2′)	3975 (3)	3964 (1)	5388 (3)	35 (1)
C(3′)	2961 (4)	3690 (1)	5706 (3)	34 (1)
O(3′)	2445 (3)	3382 (1)	5158 (2)	47 (1)
N(4′)	2569 (3)	3841 (1)	6847 (3)	34 (1)
C(5′)	3356 (3)	4200 (1)	7212 (3)	31 (1)
O(5′)	3239 (3)	4401 (1)	8156 (2)	47 (1)
C(6′)	1466 (4)	3663 (1)	7518 (3)	37 (1)
C(7′)	311 (4)	3526 (1)	6935 (4)	49 (1)
C(8′)	−738 (4)	3352 (2)	7616 (5)	60 (2)
C(9′)	−660 (5)	3331 (2)	8831 (5)	61 (2)
C(10′)	484 (5)	3475 (1)	9401 (4)	55 (1)
C(11′)	1556 (4)	3640 (1)	8757 (4)	47 (1)

Discussion. As expected, bond lengths (mean difference: 0·014 Å) and angles within the two diastereoisomers are very similar (Tables 3 and 4). The largest deviations occur in the flexible 3β substituent, which shows rather large thermal parameters in (I). There are also marked differences around the two centres with opposite configuration. A least-squares fit of the rigid parts of the molecules, *i.e.* the steroid ring system and the atoms directly bonded to it, results in a r.m.s. deviation of 0·064 Å.

Torsion angles within the steroid backbone agree well with a related structure (Allen, Cruse & Kennard, 1980) the only significant difference being the reduced puckering of ring *A* [$\bar{\omega} = 51{\cdot}3$ (I) and $51{\cdot}1°$ (II) instead of $54{\cdot}1°$]. Despite the different configurations at C(23) and C(25), the carbon chains from C(20) to C(27) exhibit similar conformations with an extended arrangement close to all-*trans* (Fig. 1); this is also

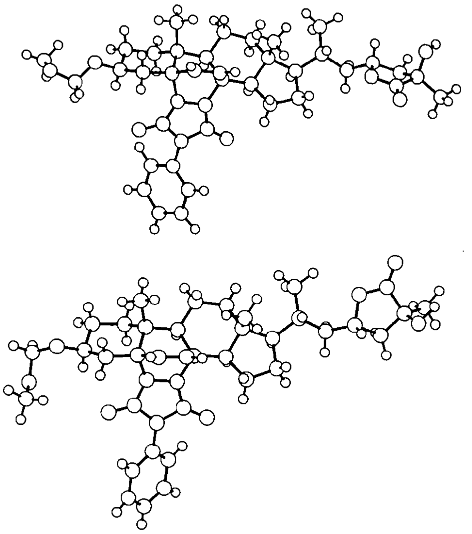

Fig. 1. Perspective views of (I) (top) and (II) (bottom) with orientations consistent with the structural formula given in the *Introduction*.

Table 3. *Bond lengths* (Å) *for* (I) *and* (II) *with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)		(I)	(II)
C(1)–C(2)	1·525 (6)	1·533 (5)	C(12)–C(13)	1·526 (8)	1·521 (5)	C(26)–O(26)	1·195 (10)	1·195 (5)
C(1)–C(10)	1·525 (6)	1·543 (5)	C(13)–C(14)	1·552 (5)	1·555 (5)	O(1)–C(28)	1·363 (7)	1·401 (5)
C(2)–C(3)	1·491 (9)	1·511 (5)	C(13)–C(17)	1·570 (6)	1·555 (5)	C(28)–O(2)	1·351 (10)	1·396 (5)
C(3)–C(4)	1·540 (8)	1·532 (5)	C(13)–C(18)	1·547 (8)	1·531 (5)	O(2)–C(29)	1·473 (19)	1·410 (6)
C(3)–O(1)	1·447 (6)	1·429 (5)	C(14)–C(15)	1·504 (7)	1·532 (5)	N(1′)–N(2′)	1·413 (4)	1·413 (4)
C(4)–C(5)	1·519 (6)	1·514 (5)	C(15)–C(16)	1·533 (6)	1·543 (5)	N(1′)–C(5′)	1·339 (5)	1·344 (4)
C(5)–C(6)	1·514 (7)	1·514 (5)	C(16)–C(17)	1·560 (8)	1·537 (5)	N(2′)–C(3′)	1·356 (6)	1·349 (5)
C(5)–C(10)	1·569 (8)	1·561 (5)	C(17)–C(20)	1·530 (5)	1·555 (5)	C(3′)–O(3′)	1·208 (5)	1·220 (4)
C(5)–N(1′)	1·500 (5)	1·502 (4)	C(20)–C(21)	1·523 (9)	1·538 (5)	C(3′)–N(4′)	1·392 (4)	1·408 (5)
C(6)–C(7)	1·314 (6)	1·319 (5)	C(20)–C(22)	1·552 (7)	1·525 (5)	N(4′)–C(5′)	1·396 (6)	1·393 (4)
C(7)–C(8)	1·503 (8)	1·517 (5)	C(22)–C(23)	1·508 (7)	1·500 (6)	N(4′)–C(6′)	1·444 (6)	1·432 (5)
C(8)–C(9)	1·561 (7)	1·576 (4)	C(23)–O(23)	1·480 (9)	1·440 (5)	C(5′)–O(5′)	1·214 (4)	1·221 (4)
C(8)–C(14)	1·523 (5)	1·522 (5)	C(23)–C(24)	1·519 (7)	1·537 (6)	C(6′)–C(7′)	1·375 (7)	1·383 (6)
C(8)–N(2′)	1·496 (4)	1·514 (4)	O(23)–C(26)	1·349 (8)	1·358 (5)	C(6′)–C(11′)	1·343 (8)	1·391 (6)
C(9)–C(10)	1·578 (6)	1·560 (5)	C(24)–C(25)	1·502 (9)	1·520 (6)	C(7′)–C(8′)	1·385 (9)	1·393 (6)
C(9)–C(11)	1·531 (6)	1·530 (5)	C(25)–O(25)	1·430 (6)	1·436 (5)	C(8′)–C(9′)	1·389 (12)	1·363 (7)
C(10)–C(19)	1·541 (7)	1·544 (5)	C(25)–C(26)	1·515 (9)	1·503 (6)	C(9′)–C(10′)	1·357 (11)	1·374 (7)
C(11)–C(12)	1·532 (6)	1·513 (5)	C(25)–C(27)	1·511 (8)	1·500 (6)	C(10′)–C(11′)	1·405 (8)	1·378 (6)

Table 4. *Bond angles* (°) *for* (I) *and* (II) *with e.s.d.'s in parentheses*

	(I)	(II)		(I)	(II)		(I)	(II)
C(2)—C(1)—C(10)	112·9 (3)	112·3 (3)	C(11)—C(12)—C(13)	111·0 (5)	110·7 (3)	O(23)—C(26)—C(25)	109·3 (6)	110·6 (3)
C(1)—C(2)—C(3)	111·4 (4)	112·0 (3)	C(12)—C(13)—C(14)	107·0 (3)	108·1 (3)	O(23)—C(26)—O(26)	122·3 (6)	121·7 (4)
C(2)—C(3)—C(4)	114·1 (4)	113·8 (3)	C(12)—C(13)—C(17)	116·3 (5)	116·5 (3)	C(25)—C(26)—O(26)	128·4 (6)	127·7 (4)
C(2)—C(3)—O(1)	110·2 (4)	111·3 (3)	C(14)—C(13)—C(17)	99·0 (3)	99·1 (3)	C(3)—O(1)—C(28)	116·9 (5)	115·0 (3)
C(4)—C(3)—O(1)	106·4 (5)	104·2 (3)	C(12)—C(13)—C(18)	111·8 (4)	110·4 (3)	O(1)—C(28)—O(2)	111·5 (6)	113·3 (3)
C(3)—C(4)—C(5)	114·8 (5)	115·2 (3)	C(14)—C(13)—C(18)	112·6 (5)	112·4 (3)	C(28)—O(2)—C(29)	101·7 (9)	112·2 (3)
C(4)—C(5)—C(6)	113·7 (5)	114·3 (3)	C(17)—C(13)—C(18)	109·5 (4)	109·9 (3)	C(5)—N(1′)—N(2′)	113·9 (3)	114·1 (3)
C(4)—C(5)—C(10)	113·0 (4)	113·0 (3)	C(8)—C(14)—C(13)	114·3 (3)	114·8 (3)	C(5)—N(1′)—C(5′)	136·6 (3)	132·6 (3)
C(6)—C(5)—C(10)	107·9 (3)	107·9 (3)	C(8)—C(14)—C(15)	119·9 (5)	120·7 (3)	N(2′)—N(1′)—C(5′)	109·5 (3)	109·1 (3)
C(4)—C(5)—N(1′)	110·8 (3)	111·2 (3)	C(13)—C(14)—C(15)	105·4 (3)	103·2 (3)	C(8)—N(2′)—N(1′)	112·9 (3)	113·1 (3)
C(6)—C(5)—N(1′)	103·9 (4)	104·8 (3)	C(14)—C(15)—C(16)	104·0 (4)	103·1 (3)	C(8)—N(2′)—C(3′)	135·9 (4)	136·7 (3)
C(10)—C(5)—N(1′)	106·9 (5)	105·0 (3)	C(15)—C(16)—C(17)	107·2 (4)	107·2 (3)	N(1′)—N(2′)—C(3′)	109·3 (3)	109·7 (3)
C(5)—C(6)—C(7)	114·6 (5)	115·8 (3)	C(13)—C(17)—C(16)	103·6 (4)	104·3 (3)	N(2′)—C(3′)—O(3′)	129·6 (3)	129·9 (3)
C(6)—C(7)—C(8)	116·1 (4)	115·3 (3)	C(13)—C(17)—C(20)	118·7 (4)	118·5 (3)	N(2′)—C(3′)—N(4′)	104·1 (3)	104·6 (3)
C(7)—C(8)—C(9)	111·4 (4)	111·0 (3)	C(16)—C(17)—C(20)	111·6 (4)	112·9 (3)	O(3′)—C(3′)—N(4′)	126·2 (4)	125·5 (3)
C(7)—C(8)—C(14)	116·8 (4)	117·7 (3)	C(17)—C(20)—C(21)	114·2 (4)	113·8 (3)	C(3′)—N(4′)—C(5′)	112·0 (3)	111·0 (3)
C(9)—C(8)—C(14)	111·7 (4)	111·2 (3)	C(17)—C(20)—C(22)	112·0 (4)	109·4 (3)	C(3′)—N(4′)—C(6′)	123·7 (4)	124·6 (3)
C(7)—C(8)—N(2′)	102·6 (4)	102·6 (3)	C(21)—C(20)—C(22)	108·5 (4)	110·6 (3)	C(5′)—N(4′)—C(6′)	123·7 (3)	124·3 (3)
C(9)—C(8)—N(2′)	103·1 (4)	101·5 (2)	C(20)—C(22)—C(23)	112·1 (4)	117·4 (3)	N(1′)—C(5′)—N(4′)	104·7 (3)	105·5 (3)
C(14)—C(8)—N(2′)	109·9 (3)	111·4 (3)	C(22)—C(23)—O(23)	105·8 (4)	110·8 (3)	N(1′)—C(5′)—O(5′)	129·4 (4)	128·8 (3)
C(8)—C(9)—C(10)	110·4 (4)	111·0 (3)	C(22)—C(23)—C(24)	118·9 (5)	114·5 (4)	N(4′)—C(5′)—O(5′)	125·9 (4)	125·6 (3)
C(8)—C(9)—C(11)	113·1 (3)	112·3 (3)	O(23)—C(23)—C(24)	102·7 (4)	104·1 (3)	N(4′)—C(6′)—C(7′)	118·3 (5)	120·0 (3)
C(10)—C(9)—C(11)	115·9 (4)	114·7 (3)	C(23)—O(23)—C(26)	110·7 (5)	111·2 (3)	N(4′)—C(6′)—C(11′)	119·5 (4)	119·5 (3)
C(1)—C(10)—C(5)	108·6 (3)	108·9 (3)	C(23)—C(24)—C(25)	103·8 (5)	103·9 (3)	C(7′)—C(6′)—C(11′)	122·2 (5)	120·5 (4)
C(1)—C(10)—C(9)	111·3 (5)	109·6 (3)	C(24)—C(25)—O(25)	112·3 (5)	106·8 (3)	C(6′)—C(7′)—C(8′)	118·4 (6)	118·4 (4)
C(5)—C(10)—C(9)	107·3 (4)	108·0 (3)	C(24)—C(25)—C(26)	101·7 (4)	102·5 (3)	C(7′)—C(8′)—C(9′)	120·0 (7)	121·3 (4)
C(1)—C(10)—C(19)	109·8 (4)	109·0 (3)	O(25)—C(25)—C(26)	99·8 (5)	106·5 (3)	C(8′)—C(9′)—C(10′)	120·4 (6)	119·7 (4)
C(5)—C(10)—C(19)	107·9 (5)	108·8 (3)	C(24)—C(25)—C(27)	116·6 (6)	115·1 (4)	C(9′)—C(10′)—C(11′)	119·3 (7)	120·7 (4)
C(9)—C(10)—C(19)	111·8 (3)	112·5 (3)	O(25)—C(25)—C(27)	111·3 (4)	111·7 (3)	C(6′)—C(11′)—C(10′)	119·5 (5)	119·3 (4)
C(9)—C(11)—C(12)	113·0 (4)	112·9 (3)	C(26)—C(25)—C(27)	113·4 (5)	113·5 (3)			

found with cholesterol (Shieh, Hoard & Nordman, 1981). The lactone rings have envelope conformations with C(23), O(23), C(25) and C(26) in the plane (Table 5) while C(24) deviates by 0·52 (1) (I) and 0·43 (1) Å (II). Their orientations with respect to the steroid ring system are comparable with that observed by Allen, Isaacs, Kennard & Motherwell (1973).

The conformations of the 3β-substituents are quite different. In (II), the dihedral angles indicate an all-*gauche* arrangement with respect to C(2) whereas the flexible chain is more extended in (I). The orientations of the 5α,8α-1,2,4-triazole rings with respect to the steroid backbone differ significantly (see Table 5), mainly because N(1′) has a planar configuration in (I) (sum of the valence angles: $\theta = 360{\cdot}0°$) but is pyramidal in (II) ($\theta = 355{\cdot}8°$), which gives rise to a small tilt of the whole substituent. In contrast to Allen *et al.* (1980) not only N(4′) [$\theta = 359{\cdot}4$ (I) and $359{\cdot}9°$ (II)] but also N(2′) [$\theta = 358{\cdot}1$ (I) and $359{\cdot}5°$ (II)] is planar in both molecules. Consistent with related structures (*cf.* Allen *et al.*, 1980), the phenyl rings are rotated in opposite senses by 53 (2) (I) and 37 (1)° (II) with respect to the dioxotriazole moiety. This arrangement seems to be a compromise between π conjugation and steric hindrance.

Table 5. *Selected dihedral angles* (°) *for* (I) *and* (II) *with e.s.d.'s in parentheses*

	(I)	(II)
C(13)—C(17)—C(20)—C(22)	179·4 (5)	−176·0 (4)
C(17)—C(20)—C(22)—C(23)	−145·5 (5)	−150·1 (4)
C(20)—C(22)—C(23)—C(24)	−168·9 (5)	−171·8 (4)
C(20)—C(22)—C(23)—O(23)	76·4 (5)	−54·4 (4)
C(22)—C(23)—C(24)—C(25)	−147·7 (6)	148·1 (4)
C(23)—C(24)—C(25)—C(27)	157·0 (7)	−149·1 (4)
O(25)—C(25)—C(26)—O(23)	91·9 (7)	−96·2 (4)
C(25)—C(26)—O(23)—C(23)	3·7 (7)	1·6 (4)
C(2)—C(3)—O(1)—C(28)	126·4 (5)	83·7 (4)
C(3)—O(1)—C(28)—O(2)	−153·7 (7)	70·5 (4)
O(1)—C(28)—O(2)—C(29)	74·6 (9)	60·0 (4)
C(6)—C(5)—N(1′)—C(5′)	131·3 (4)	106·5 (4)
C(7)—C(8)—N(2′)—C(3′)	−140·6 (5)	−111·1 (4)
C(5)—N(1′)—N(2′)—C(8)	−5·1 (4)	−8·6 (4)
C(3′)—N(4′)—C(6′)—C(7′)	57·6 (5)	−36·2 (4)
C(5′)—N(4′)—C(6′)—C(11′)	48·9 (4)	−37·8 (4)

The packing of the two diastereoisomers shows some similarities (Figs. 2 and 3). In both structures, the steroid nucleus is perpendicular to the shortest dimension (*b* in I, *a* in II). There is no stacking of aromatic rings and no unusually close contact except for

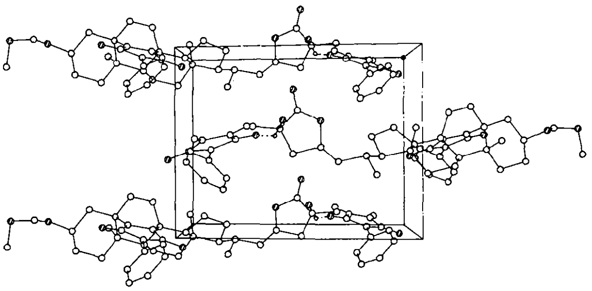

Fig. 2. Packing diagram of (I) viewed along **c** with **a** horizontal and **b** vertical. H atoms, except for the one attached to O(25), which participates in H bonding (dotted lines), are omitted. O atoms are hatched and the unit cell is outlined.

hydrogen bonding between the hydroxyl group and either of the two triazole carbonyl oxygens. In (I), O(25) interacts with O(5′) [$\Delta = 2\cdot757$ (7) Å] *via* a diagonal translation in the *ac* plane whereas (II) forms an O(25)–H···O(3′) hydrogen bond [$\Delta = 2\cdot873$ (6) Å] involving the screw axis parallel to **a**.

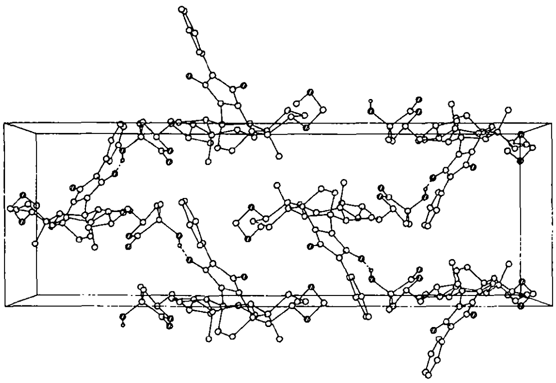

Fig. 3. Packing diagram of (II) viewed along **c** with **b** horizontal and **a** vertical. See Fig. 2 for further details.

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Structure of 1,2-Bis[(2-nitrophenyl)-*NNO*-azoxy]benzene, $C_{18}H_{12}N_6O_6$

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Abstract. $M_r = 408\cdot3$, monoclinic, space group $P2_1$, $a = 7\cdot618$ (3), $b = 11\cdot677$ (3), $c = 11\cdot267$ (4) Å, $\beta = 111\cdot13$ (2)°, $Z = 2$, $D_m = 1\cdot445$, $D_x = 1\cdot450$ Mg m^{-3}. The structure was solved by direct methods and refined to $R = 0\cdot069$ for 1214 observed reflections. The conformations around the two azoxy groups are both *trans*. The six-membered rings of the two nitrophenyl groups form dihedral angles of 1·8 and 68·1° with the benzene plane respectively.

Introduction. The title compound is a thermolysis product of 1-[(2-nitrophenyl)imino]pyridine (Tamura, Tsujimoto, Ikeda & Tomita, 1971). The colorless needle-shaped crystal from ethanol had previously been interpreted as tris(2-nitrophenyl)triaziridine by means of chemical and spectroscopic studies (Tamura *et al.*, 1971; Oae, Tsujimoto & Nakanishi, 1973). However, the present X-ray work determined it as 1,2-bis-[(2-nitrophenyl)-*NNO*-azoxy]benzene, which was recently suggested by Leuenberger, Hoesch & Dreiding (1980).

Experimental. Crystal 0·2 × 0·2 × 0·1 mm, Rigaku automated four-circle diffractometer, graphite-monochromated Cu $K\alpha$; cell constants refined with a least-squares procedure for 25 reflections; 1395 independent reflections, ω–2θ scan mode, scan speed of 2° min^{-1} with background counts for 10 s.

Lp corrections but not absorption; 1214 non-zero reflections with $|F_o| > 3\sigma|F_o|$ in the range $\sin\theta/\lambda < 0\cdot560$ Å^{-1}; structure solved by the direct method using *MULTAN* (Germain, Main & Woolfson, 1971); all non-H atoms from the *E* map with the highest combined figure of merit; refinement by block-diagonal least-squares, $w = 1$; H atoms from difference Fourier map at $R = 0\cdot100$, and introduced in subsequent refinement without constraints; in final least-squares refinement, the weighting scheme was $w = 0\cdot2$ for