BATS, J. W., COPPENS, P. & KOETZLE, T. F. (1977). *Acta Cryst.* B**33**, 37–45.
BATS, J. W., COPPENS, P. & KVICK, Å. (1977). *Acta Cryst.* B**33**, 1534–1542.
FLEMING, J. E. & LYNTON, H. (1967). *Can. J. Chem.* **45**, 353–357.
FUKUNAGA, M., ARAI, K., IWAMURA, H. & ŌKI, M. (1971). *Bull. Chem. Soc. Jpn*, **45**, 302.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
IWAMURA, H., FUKUNAGA, M. & KUSHIDA, K. (1972). *J. Chem. Soc. Chem. Commun.* pp. 450–451.
MCPHAIL, A. T., ONAN, K. D. & KOSKIMIES, J. (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 1004–1008.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
THOMAS, R., SHOEMAKER, C. B. & ERIKS, K. (1966). *Acta Cryst.* **21**, 12–20.
UNICS (1967). Edited by T. SAKURAI. The Crystallographic Society of Japan.
VALLE, G., BUSETTI, V., MAMMI, M. & CARAZZOLO, G. (1969). *Acta Cryst.* B**25**, 1621–1636.

Acta Cryst. (1980). B**36**, 2337–2341

The Structure and Absolute Configuration of (22*R*)-3β-Acetoxy-5α,8α-(3,5-dioxo-4-phenyl-1*H*,2*H*-1,2,4-triazole-1,2-diyl)-24-trimethylsilylchol-6-en-23-yn-22-yl *p*-Bromobenzoate at 279 ± 1 K

BY FRANK H. ALLEN, WILLIAM B. T. CRUSE AND OLGA KENNARD*

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

(*Received* 19 *March* 1980; *accepted* 28 *April* 1980)

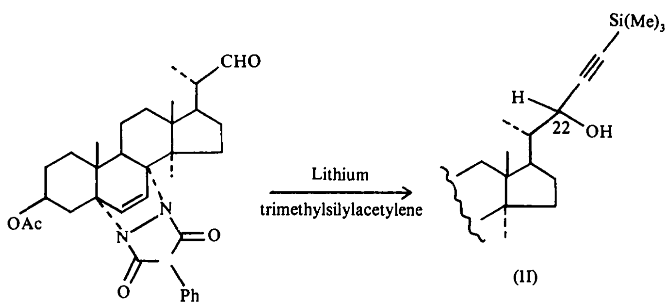
Abstract

$C_{44}H_{52}BrN_3O_6Si$ is orthorhombic, $P2_12_12_1$. Experimental measurements were made at 279 ± 1 K: a = 10·585 (2), b = 18·659 (3), c = 21·945 (3) Å, D_x = 1·267 Mg m^{-3}, Z = 4; 2901 unique reflexion intensities with $F > 3\sigma(F)$. The structure was refined to R = 0·053. The absolute side-chain stereochemistry is established as 20(*S*),22(*R*). The *A* and *C* rings are in the chair conformation, the *D* ring approximates a 13β,14α half-chair. The *B* ring is forced to adopt a boat conformation by the 5α,8α-diazo bridge. The triazole ring is a shallow half-chair and makes a dihedral angle of 42·1 (5)° with the 4′-phenyl ring.

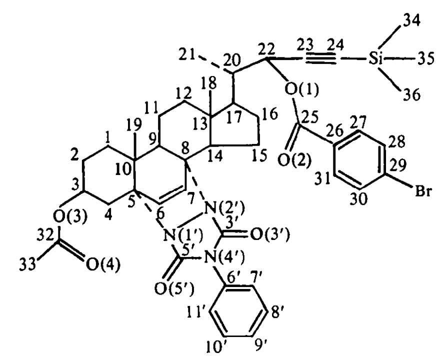
Introduction

A projected synthesis of vitamin D_3, chirally labelled with deuterium at C(24), is being developed by Dr D. H. Williams and co-workers in this laboratory. In the course of this work it was necessary to know the absolute configuration at C(22) of the diastereoisomeric alcohols (II), obtained by reaction of lithium trimethylsilylacetylene on the aldehyde (I). This paper reports the X-ray analysis of the 22-*p*-bromobenzoate derivative of (II); the atomic nomenclature used in the analysis is depicted in (III).

* External Staff, Medical Research Council.



(I) (II)



(III)

Experimental

Crystal data

$C_{44}H_{52}BrN_3O_6Si$, M_r = 826·9, orthorhombic, $P2_12_12_1$, a = 10·585 (2), b = 18·659 (3), c =

0567-7408/80/102337-05$01.00

21·945 (3) Å, U = 4335·2 Å^3, Z = 4, D_x = 1·267 Mg m^{-3}, Cu $K\alpha$ (λ = 1·54178 Å), μ(Cu $K\alpha$) = 18·0 mm^{-1}; colourless platy acicular crystals from acetone. Cell parameters were obtained by least squares from 2θ values for 15 strong high-order reflexions measured on a diffractometer at 279 ± 1 K.

Intensity data

Intensities were measured at 279 ± 1 K on a Syntex $P2_1$ diffractometer with graphite-monochromated Cu $K\alpha$ radiation and a cooling device developed by Cruse, Kennard & Raithby (1980). One octant of data was measured to 2θ (max.) = 120° with a θ–2θ scan at a minimum scan speed of 1·4° (2θ) min^{-1}. The scan range was ±1° about the α_1–α_2 doublet, with backgrounds measured for 0·25 total scan time at each end of the range. The crystal size was 0·25 × 0·06 × 0·12 mm. Intensities were corrected for Lorentz and polarization effects, and also for absorption with the empirical method of Sheldrick (1979). Of the 3627 unique independent reflexions, 2901 had $F > 3\sigma(F)$ and were considered observed.

Structure analysis and refinement

The positions of Br and Si were established from a Patterson map. The structure was developed initially by successive Fourier syntheses, only strong peaks in chemically sensible positions being added at each stage. The process yielded a well defined steroid ring nucleus and the 5α,8α-diazo bridge; the bromobenzoyloxy, 3β-acetoxy and 4′-phenyl groups were also apparent in plausible positions. There was, however, no significant electron density at the positions expected for the carbonyl groups of the dioxotriazole moiety and Si failed to link with the established fragment. An attempt was made to develop the Br, Si phases by tangent expansion. The E map yielded a fragment which was recognizable as the steroid B ring, parts of the A and C rings and a *complete* bridging dioxotriazole moiety. It was also noted that atomic sites common to the Fourier and direct fragments had comparable coordinates, confirming that the structure was correctly placed in the unit cell. One cycle of isotropic full-matrix least-squares refinement on a composite molecule assembled from the two fragments reduced R from 0·39 to 0·23. A subsequent difference synthesis revealed the C(23)—C(24) acetylenic link and three methyl groups.

Refinement proceeded, first with isotropic then anisotropic thermal parameters, to R = 0·079 with a unitary weighting scheme. H atoms were now included in calculated positions and the C—H geometry was constrained in subsequent refinements with C—C(sp^2)—H = 120, H—C(sp^3)—H = 109·5° and C—H = 1·08 Å. Separate overall isotropic thermal parameters were applied to the methyl and non-methyl H atoms. Final refinement used the cascade method (Rivera & Sheldrick, 1978). Four reflexions obviously in error were omitted and a weighting scheme of the form $w = 1/[\sigma^2(F_o) + 0{\cdot}0004F_o^2]$ gave mean $w\Delta^2$

Table 1. *Atomic coordinates* (×10^4) *and* U_{eq} (Å^2 ×10^3) [U_{eq} *is calculated as* $(U_{11}.U_{22}.U_{33})^{1/3}$]

	x	y	z	U_{eq}
Br(1)	438 (1)	−7066 (1)	−4675 (1)	141 (1)
Si(1)	8513 (2)	−8660 (1)	−2628 (1)	83 (1)
C(1)	−2306 (6)	−8374 (3)	221 (3)	80 (4)
C(2)	−3341 (6)	−8367 (3)	701 (3)	85 (4)
C(3)	−3933 (5)	−9106 (3)	750 (3)	76 (4)
C(4)	−2982 (5)	−9687 (3)	864 (2)	72 (4)
C(5)	−1897 (5)	−9683 (3)	402 (2)	61 (3)
C(6)	−855 (6)	−10221 (3)	519 (2)	72 (4)
C(7)	56 (5)	−10245 (3)	108 (2)	63 (3)
C(8)	−126 (5)	−9744 (3)	−431 (2)	60 (3)
C(9)	−344 (5)	−8951 (2)	−200 (2)	62 (3)
C(10)	−1283 (5)	−8934 (3)	347 (2)	66 (3)
C(11)	864 (5)	−8536 (3)	−92 (3)	77 (4)
C(12)	1729 (6)	−8555 (3)	−638 (3)	77 (4)
C(13)	2083 (5)	−9329 (3)	−798 (3)	68 (4)
C(14)	879 (4)	−9761 (3)	−934 (2)	56 (3)
C(15)	1403 (5)	−10467 (3)	−1167 (3)	72 (4)
C(16)	2555 (5)	−10220 (3)	−1564 (3)	73 (4)
C(17)	2753 (5)	−9431 (3)	−1426 (2)	65 (4)
C(18)	2902 (5)	−9662 (3)	−286 (3)	85 (4)
C(19)	−613 (6)	−8769 (3)	955 (2)	85 (4)
C(20)	4166 (5)	−9210 (3)	−1487 (3)	74 (4)
C(21)	4444 (6)	−8414 (3)	−1303 (3)	95 (5)
C(22)	4554 (5)	−9342 (3)	−2162 (3)	73 (4)
C(23)	5889 (5)	−9163 (3)	−2295 (3)	81 (4)
C(24)	6931 (5)	−8991 (3)	−2426 (3)	96 (5)
C(25)	3455 (5)	−9149 (3)	−3099 (3)	75 (4)
C(26)	2675 (5)	−8636 (3)	−3454 (3)	67 (4)
C(27)	2227 (6)	−8859 (3)	−4018 (3)	87 (5)
C(28)	1552 (7)	−8402 (4)	−4377 (3)	101 (5)
C(29)	1309 (6)	−7725 (3)	−4169 (3)	91 (4)
C(30)	1693 (6)	−7482 (3)	−3602 (3)	80 (4)
C(31)	2375 (5)	−7962 (3)	−3245 (3)	77 (4)
C(32)	−5927 (7)	−8817 (4)	1216 (3)	111 (6)
C(33)	−6704 (8)	−8912 (4)	1775 (4)	162 (8)
C(34)	9011 (8)	−8058 (4)	−2028 (4)	147 (7)
C(35)	9633 (5)	−9407 (3)	−2698 (3)	88 (5)
C(36)	8332 (7)	−8166 (5)	−3359 (4)	149 (7)
O(1)	3753 (3)	−8893 (2)	−2540 (2)	76 (3)
O(2)	3788 (5)	−9724 (2)	−3278 (2)	109 (5)
O(3)	−4799 (4)	−9144 (2)	1266 (2)	98 (3)
O(4)	−6234 (5)	−8458 (3)	780 (2)	137 (5)
N(1′)	−2387 (4)	−9865 (2)	−222 (2)	60 (3)
N(2′)	−1427 (4)	−9917 (2)	−676 (2)	57 (3)
C(3′)	−1817 (5)	−10404 (3)	−1108 (2)	56 (3)
N(4′)	−3020 (4)	−10618 (2)	−934 (2)	56 (3)
C(5′)	−3341 (5)	−10345 (3)	−365 (2)	59 (3)
O(3′)	−1270 (3)	−10574 (2)	−1576 (2)	65 (3)
O(5′)	−4312 (3)	−10461 (2)	−89 (2)	79 (4)
C(6′)	−3806 (5)	−11085 (3)	−1287 (2)	58 (3)
C(7′)	−3898 (5)	−10986 (3)	−1910 (3)	71 (4)
C(8′)	−4659 (6)	−11444 (4)	−2256 (3)	85 (5)
C(9′)	−5318 (6)	−11985 (4)	−1976 (3)	96 (5)
C(10′)	−5220 (6)	−12071 (4)	−1342 (3)	92 (5)
C(11′)	−4458 (5)	−11615 (3)	−1000 (3)	72 (4)

values which varied only slightly with sin θ or $|F_o|$. The final $R = 0·053$ and $R_w = \sum w^{1/2}\Delta/\sum w^{1/2}|F_o| = 0·054$. The thermal parameters for Br and some other terminal atoms are rather high and show marked anisotropy, but attempts to interpret a difference map in terms of disordered sites were not successful. Final positions for the non-H atoms are in Table 1;* derived bond lengths, valence angles and selected torsion angles* are in Tables 2, 3 and 4. All calculations were carried out with *SHELX* (Sheldrick, 1979).

Absolute configuration

The enantiomer chosen for refinement employed the accepted absolute stereochemistry of the 5α-cholane skeleton; the chirality at C(22) is *R*. This assignment was confirmed by calculating generalized weighted R_G factors (Hamilton, 1965) for the present structure ($R_G^+ = 0·059$) and its inverse ($R_G^- = 0·065$), with $+if''$ anomalous-dispersion corrections in each case. The second enantiomer has <0·5% significance and may be

* Lists of structure factors, anisotropic thermal parameters, H atom positions and a full list of torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35372 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å)

Br(1)–C(29)	1·896 (8)	Si(1)–C(24)	1·839 (7)
Si(1)–C(34)	1·810 (10)	Si(1)–C(35)	1·837 (7)
Si(1)–C(36)	1·859 (10)	C(1)–C(2)	1·520 (9)
C(1)–C(10)	1·530 (8)	C(2)–C(3)	1·519 (8)
C(3)–C(4)	1·501 (8)	C(3)–O(3)	1·459 (7)
C(4)–C(5)	1·532 (7)	C(5)–C(6)	1·514 (8)
C(5)–C(10)	1·546 (7)	C(5)–N(1′)	1·503 (6)
C(6)–C(7)	1·322 (8)	C(7)–C(8)	1·519 (7)
C(8)–C(9)	1·582 (6)	C(8)–C(14)	1·533 (7)
C(8)–N(2′)	1·513 (6)	C(9)–C(10)	1·558 (7)
C(9)–C(11)	1·513 (8)	C(10)–C(19)	1·541 (8)
C(11)–C(12)	1·509 (8)	C(12)–C(13)	1·531 (8)
C(13)–C(14)	1·538 (7)	C(13)–C(17)	1·562 (8)
C(13)–C(18)	1·549 (8)	C(14)–C(15)	1·519 (7)
C(15)–C(16)	1·567 (8)	C(16)–C(17)	1·519 (7)
C(17)–C(20)	1·557 (7)	C(20)–C(21)	1·567 (9)
C(20)–C(22)	1·556 (9)	C(22)–C(23)	1·481 (7)
C(22)–O(1)	1·452 (7)	C(23)–C(24)	1·185 (8)
C(25)–C(26)	1·486 (8)	C(25)–O(1)	1·353 (7)
C(25)–O(2)	1·195 (7)	C(26)–C(27)	1·388 (9)
C(26)–C(31)	1·377 (8)	C(27)–C(28)	1·363 (9)
C(28)–C(29)	1·367 (9)	C(29)–C(30)	1·386 (9)
C(30)–C(31)	1·391 (8)	C(32)–C(33)	1·488 (12)
C(32)–O(3)	1·346 (8)	C(32)–O(4)	1·213 (9)
N(1′)–N(2′)	1·426 (6)	N(1′)–C(5′)	1·386 (6)
N(2′)–C(3′)	1·378 (6)	C(3′)–O(3′)	1·221 (6)
N(4′)–C(3′)	1·389 (6)	N(4′)–C(5′)	1·390 (6)
N(4′)–C(6′)	1·432 (6)	C(5′)–O(5′)	1·214 (6)
C(6′)–C(7′)	1·385 (8)	C(6′)–C(11′)	1·360 (8)
C(7′)–C(8′)	1·399 (9)	C(8′)–C(9′)	1·373 (9)
C(9′)–C(10′)	1·405 (10)	C(10′)–C(11′)	1·392 (10)

Table 3. *Bond angles* (°)

C(24)–Si(1)–C(34)	107·3 (4)	C(24)–Si(1)–C(35)	110·7 (3)
C(34)–Si(1)–C(35)	110·1 (3)	C(24)–Si(1)–C(36)	106·3 (3)
C(34)–Si(1)–C(36)	110·5 (4)	C(35)–Si(1)–C(36)	111·8 (3)
C(2)–C(1)–C(10)	113·0 (5)	C(1)–C(2)–C(3)	109·8 (5)
C(2)–C(3)–C(4)	113·0 (5)	C(2)–C(3)–O(3)	111·1 (5)
C(4)–C(3)–O(3)	104·9 (4)	C(3)–C(4)–C(5)	112·9 (4)
C(4)–C(5)–C(6)	115·5 (4)	C(4)–C(5)–C(10)	111·8 (4)
C(6)–C(5)–C(10)	107·9 (4)	C(4)–C(5)–N(1′)	110·1 (4)
C(6)–C(5)–N(1′)	104·9 (4)	C(10)–C(5)–N(1′)	106·1 (4)
C(5)–C(6)–C(7)	115·9 (5)	C(6)–C(7)–C(8)	114·8 (5)
C(7)–C(8)–C(9)	110·1 (4)	C(7)–C(8)–C(14)	117·4 (4)
C(9)–C(8)–C(14)	110·6 (4)	C(7)–C(8)–N(2′)	105·1 (4)
C(9)–C(8)–N(2′)	100·4 (4)	C(14)–C(8)–N(2′)	111·8 (4)
C(8)–C(9)–C(10)	111·0 (4)	C(8)–C(9)–C(11)	113·9 (4)
C(10)–C(9)–C(11)	114·2 (4)	C(1)–C(10)–C(5)	109·5 (4)
C(1)–C(10)–C(9)	109·0 (4)	C(5)–C(10)–C(9)	108·1 (4)
C(1)–C(10)–C(19)	110·2 (4)	C(5)–C(10)–C(19)	107·9 (4)
C(9)–C(10)–C(19)	112·1 (4)	C(9)–C(11)–C(12)	112·1 (5)
C(11)–C(12)–C(13)	110·7 (5)	C(12)–C(13)–C(14)	109·6 (4)
C(12)–C(13)–C(17)	115·3 (5)	C(14)–C(13)–C(17)	98·1 (4)
C(12)–C(13)–C(18)	110·5 (5)	C(14)–C(13)–C(18)	113·1 (4)
C(17)–C(13)–C(18)	109·7 (4)	C(8)–C(14)–C(13)	115·1 (4)
C(8)–C(14)–C(15)	121·0 (4)	C(13)–C(14)–C(15)	102·6 (4)
C(14)–C(15)–C(16)	102·6 (4)	C(15)–C(16)–C(17)	106·3 (4)
C(13)–C(17)–C(16)	103·4 (4)	C(13)–C(17)–C(20)	118·7 (4)
C(16)–C(17)–C(20)	111·8 (4)	C(17)–C(20)–C(21)	114·1 (5)
C(17)–C(20)–C(22)	107·1 (4)	C(21)–C(20)–C(22)	110·2 (5)
C(20)–C(22)–C(23)	113·8 (5)	C(20)–C(22)–O(1)	107·4 (4)
C(23)–C(22)–O(1)	108·3 (5)	C(22)–C(23)–C(24)	176·2 (7)
Si(1)–C(24)–C(23)	176·1 (6)	C(26)–C(25)–O(1)	112·3 (4)
C(26)–C(25)–O(2)	124·6 (5)	O(1)–C(25)–O(2)	123·1 (5)
C(25)–C(26)–C(27)	117·7 (5)	C(25)–C(26)–C(31)	122·7 (5)
C(27)–C(26)–C(31)	119·5 (5)	C(26)–C(27)–C(28)	120·4 (6)
C(27)–C(28)–C(29)	119·0 (6)	Br(1)–C(29)–C(28)	119·7 (5)
Br(1)–C(29)–C(30)	117·2 (5)	C(28)–C(29)–C(30)	123·1 (6)
C(29)–C(30)–C(31)	116·6 (6)	C(26)–C(31)–C(30)	121·2 (6)
C(33)–C(32)–O(3)	111·7 (6)	C(33)–C(32)–O(4)	124·7 (7)
O(3)–C(32)–O(4)	123·6 (6)	C(22)–O(1)–C(25)	116·8 (4)
C(3)–O(3)–C(32)	118·1 (5)	C(5)–N(1′)–N(2′)	113·9 (4)
C(5)–N(1′)–C(5′)	127·1 (4)	N(2′)–N(1′)–C(5′)	108·4 (4)
C(8)–N(2′)–N(1′)	112·7 (3)	C(8)–N(2′)–C(3′)	131·2 (4)
N(1′)–N(2′)–C(3′)	108·2 (4)	N(2′)–C(3′)–N(4′)	105·9 (4)
N(2′)–C(3′)–O(3′)	127·5 (5)	N(4′)–C(3′)–O(3′)	126·3 (5)
C(3′)–N(4′)–C(5′)	111·5 (4)	C(3′)–N(4′)–C(6′)	123·9 (4)
C(5′)–N(4′)–C(6′)	124·5 (4)	N(1′)–C(5′)–N(4′)	105·2 (4)
N(1′)–C(5′)–O(5′)	128·2 (5)	N(4′)–C(5′)–O(5′)	126·2 (5)
N(4′)–C(6′)–C(7′)	119·6 (5)	N(4′)–C(6′)–C(11′)	119·1 (5)
C(7′)–C(6′)–C(11′)	121·3 (5)	C(6′)–C(7′)–C(8′)	119·7 (6)
C(7′)–C(8′)–C(9′)	119·9 (6)	C(8′)–C(9′)–C(10′)	119·4 (6)
C(9′)–C(10′)–C(11′)	120·5 (6)	C(6′)–C(11′)–C(10′)	119·3 (5)

Table 4. *Intra-annular torsion angles* (°) *for steroid rings A, B, C, D and for the diazo rings* B_1 [N(1′), N(2′), C(5)–C(8)] *and* B_2 [N(1′), N(2′), C(5), C(8)–C(10)]

Ring *A*		Ring *C*		Ring *D*	
Bond	ω(obs.)	Bond	ω(obs.)	Bond	ω(obs.)
1–2	−56·8 (6)	8–9	−44·9 (6)	13–14	51·5 (5)
2–3	54·1 (6)	9–11	52·2 (6)	14–15	−39·2 (5)
3–4	−52·7 (6)	11–12	−59·2 (6)	15–16	11·0 (5)
4–5	51·8 (6)	12–13	58·9 (6)	16–17	20·8 (5)
5–10	−52·6 (6)	13–14	−54·4 (6)	17–13	−43·8 (5)
10–1	56·4 (6)	14–8	46·6 (6)		

Ring *B*		Ring B_1		Ring B_2		Theoretical*
Bond	ω(obs.)	Bond	ω(obs.)	Bond	ω(obs.)	ω(theor.)
10–5	60·7 (5)	1′–5	−51·5 (5)	10–5	−51·2 (5)	±38
5–6	−57·2 (6)	5–6	55·6 (6)	5–1′	62·6 (5)	∓40
6–7	−2·3 (7)	6–7	−2·3 (7)	1′–2′	−2·6 (6)	0
7–8	54·0 (6)	7–8	−53·4 (6)	2′–8	−59·4 (6)	±40
8–9	−44·1 (5)	8–2′	55·0 (5)	8–9	66·4 (6)	∓38
9–10	−11·0 (5)	1′–2′	−2·6 (6)	9–10	−11·0 (5)	0

* Theoretical values for unsubstituted boat form of cyclohexene from Bucourt & Hainaut (1965).

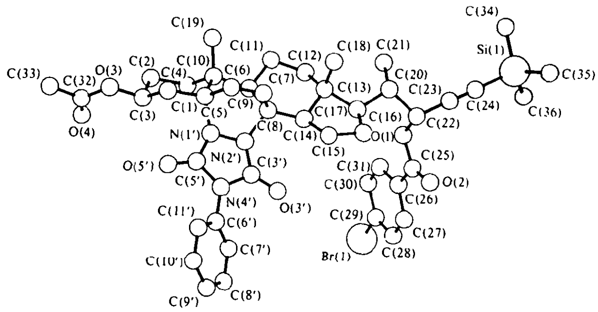


Fig. 1. Perspective view of a single molecule of (III) showing the correct absolute configuration.

rejected. Fig. 1, a perspective view of (III), therefore depicts the correct absolute chirality at all asymmetric centres.

Table 6. *Details of some mean planes in the molecule*

Equations of planes, in the form $aX + bY + cZ + d = 0$, refer to orthogonal axes. Atomic deviations are in Å × 10^3.

Plane 1: dioxotriazole moiety

$a = -0\cdot4494, b = 0\cdot7434, c = -0\cdot4954, d = -12\cdot3328$

N(1′) 31 (6), N(2′) −6 (6), C(3′) −25 (6), N(4′) 62 (6), C(5′) −25 (6), O(3′) −24 (6), O(5′) −12 (6)

Plane 2: 4′-phenyl ring

$a = 0\cdot7746, b = -0\cdot6185, c = -0\cdot1323, d = 10\cdot0346$

C(6′) 5 (7), C(7′) −5 (7), C(8′) 1 (7), C(9′) 2 (8), C(10′) −2 (7), C(11′) −2 (7)

Plane 3: phenyl group of bromobenzoyloxy moiety

$a = 0\cdot8470, b = 0\cdot3364, c = -0\cdot4116, d = 0\cdot0796$

C(26) 21 (7), C(27) −11 (7), C(28) −6 (7), C(29) 13 (7), C(30) −3 (7), C(31) −14 (7)

Discussion

Fig. 1 shows that the steroid nucleus is slightly concave towards the 5α,8α-dioxotriazole bridge, which forces ring *B* to adopt a boat conformation. Individual ring conformations are described by the intra-annular torsion angles (ω) listed in Table 4.

Ring *A* is an almost perfect chair; the mean torsion angle [$\bar{\omega}$ = 54·1 (6)°] compares well with the 55·9° reported by Geise, Buys & Mijlhoff (1971) for free cyclohexane and with the 55·8° obtained from energy-minimization studies by Bucourt & Hainaut (1965). The maximum deviation from $\bar{\omega}$ is 2·7°, indicating a symmetric ring; this is confirmed by the asymmetry parameters (Duax & Norton, 1975) which range from $\Delta C_s^1 = 1\cdot0°$ to $\Delta C_2^{2,3} = 4\cdot4°$.

Ring *C* is also a chair, but shows marked asymmetry due to the fusion of the boat-form ring *B*. Ring *C* is flattened in the fusion area C(8), C(9), C(14) with compensatory puckering in the area C(11), C(12), C(13). The value of $\bar{\omega}$ [52·7 (6)°] indicates only slight overall flattening, but maximum deviations from the mean of −7·8 and +6·5° and $\Delta C_2^{9,11}$ = 13·3° indicate the extent of the distortion.

The five-membered *D* ring has values of φ_m and Δ (Altona, Geise & Romers, 1968) of 51·8 and 11·8°. The conformation thus approximates a 13β,14α half-chair, commonly found in steroids (Duax & Norton, 1975).

The 5α,8α-diazo bridging of the cyclohexene ring *B* gives rise to two further six-membered rings, denoted in Tables 4 and 5 as B_1 (containing the diazo bridge and Δ^6 bond) and B_2 [diazo bridge and C(9)—C(10) single bond]. All three rings are boats and show considerably increased puckering in comparison with the theoretical ω values of Bucourt & Hainaut (1965). Ring *B* is highly puckered in the area of the tetrasubstituted C(5) and C(10); the steric strain is reduced to some extent on the opposite side of the ring by the presence of the trisubstituted C(9). Rings *B* and B_2 are markedly distorted from *mm* symmetry as shown by the asymmetry parameters in Table 5; ring B_1, in which the diazo bridge and the C(6)—C(7) ethylenic linkage form the base plane of the boat, is highly symmetric. The conformations of rings *B*, B_1 and B_2 are compared (Table 5, and references cited therein) with three recent structure determinations (PBAZHT, PTCODT, PZPCOD) in which cyclohexene is bridged by a dioxotriazole moiety, and one (PTZCUO) in which cyclohexane is similarly bridged. Comparison structures were located and analysed with the database and program system of the Cambridge Crystallographic

Table 5. *Conformational comparison* (°) *for rings* *B*, B_1, B_2

E.s.d.'s of torsion angles are in the range 0·7–0·9° for PBAZHT, 1·2–1·5° for PTCODT and PZPCOD and 0·5–0·7° for PTZCUO.

	This work (III)	PBAZHT[(a)]	PTCODT[(b)]	PZPCOD[(c)]	PTZCUO[(d)]
Ring *B*					
$\bar{\omega}$	38·2 (6)	36·7	38·9	37·6	41·5
ΔC_s^5	7·9	2·5	4·2	2·8	4·8
$\Delta C_s^{6,7}$	11·9	1·6	4·1	1·7	6·0
Ring B_1					
$\bar{\omega}$	36·7 (6)	39·1	38·8	37·9	39·6
ΔC_s^5	2·6	3·8	6·0	3·4	4·2
$\Delta C_s^{6,7}$	2·9	5·0	6·0	5·7	4·8
Ring B_2					
$\bar{\omega}$	42·2 (6)	42·3	41·7	41·5	40·8
ΔC_s^5	9·1	2·9	4·8	6·0	5·2
$\Delta C_s^{6,7}$	11·0	5·0	6·0	3·1	5·9

(*a*) 12-Phenyl-3,4:5,6-dibenzo-10,12,14-triazapentacyclo[7.5.2.C^{2,7}.0^{2,8}.0^{10,14}]hexadeca-3,5,15-triene-11,13-dione (Pauly, Fischer & Durr, 1979).
(*b*) 5-Phenyl-15-thia-3,5,7-triazapentacyclo[7.4.3.2^{2,8}.0^{1,9}.0^{3,7}]octadec-17-ene-4,6,15-trione (Kaftory, 1978*a*).
(*c*) 5-Phenyl-3,5,7-triazapentacyclo[7.4.3.2^{2,8}.0^{1,9}.0^{3,7}]octadec-17-ene-4,6-dione (Kaftory, 1978*b*).
(*d*) 4-Phenyl-2,4,6-triazatricyclo[5.2.2.0^{2,6}]undecane-3,5-dione (van der Ende, Offereins & Romers, 1974).

Data Centre (Allen *et al.*, 1979). The substitution patterns of all four comparison systems are considerably less complex than that in (III). Whilst the mean puckering parameters ($\bar{\omega}$) are comparable for each ring, the distortion of rings B, B_2 in (III) from ideal *mm* symmetry is apparently a result of the complex substitution. In the three cyclohexene structures the asymmetry parameters all fall in the narrow range 1·6–6·0° (mean 4·1°), while in (III) the range is 2·6–11·9° with a mean of 7·6°. In the bridged cyclohexene systems (columns 1–4, Table 5) the most flexible ring (B_2) has the highest degree of puckering. In the bridged cyclohexane (PTZCUO) all three rings have identical conformations within experimental error.

The dioxotriazole system is not planar (Table 6). The 1,2,4-triazine ring adopts a shallow N(4′), C(5′) half-chair conformation with Δ, φ_m (Altona, Geise & Romers, 1968) at 2·0, 8·7°. N(4′) has a planar configuration [sum of valence angles, θ = 359·9 (5)°] while N(1′), N(2′) are pyramidal [θ = 349·4 (5), 352·1 (5)°]. These values compare well with those obtained for the structures cited in Table 5 where Δ values range from 0 to 12·6° and φ_m from 8·6 to 12·4°. In each case N(4′) is planar and N(1′), N(2′) are pyramidal save for PTCODT (Table 5). The 4′-phenyl group (plane 2, Table 6) makes an angle of 42·1° with the dioxotriazole moiety; values in the structures cited in Table 5 range from 45 to 75·3°. Intra-annular C—N distances average to 1·386 (6) Å, with individual values all within 1·5σ of the mean. The exocyclic N(4′)—C(6′) is considerably longer at 1·432 (6) Å, a feature common to the other structures cited.

The Si—C(Me) distances range from 1·810 (10) to 1·859 (10) with a mean of 1·835 (10) Å; the Si—C(*sp*) distance is 1·839 (7) Å. These values are slightly longer than comparable means of 1·82 (1) and 1·82 (1) Å in the highly conjugated 1,8-bis(trimethylsilyl)octatetrayne (Coles, Hitchcock & Walton, 1975), but the Si—C(*sp*) distance in (III) is identical to the mean of two such distances in a Co complex of trimethylsilylpropynylidene (Fritch, Vollhardt, Thompson & Day, 1979). The mean Si—C(Me) distance is, however, significantly shorter than some recently reported means for trimethylsilyl of 1·868 (10) (Lu, Hseu & Lee, 1977), 1·863 (8) (Collins & Davis, 1978) and 1·86 and 1·89 Å (Leroy, Courseille, Daney & Bouas-Laurent, 1976).

A view of the molecular packing along a is in Fig. 2. The steroid nucleus and extended C(17) side chain are approximately parallel to c. The packing arrangement in the bc plane is dictated by van der Waals interactions, particularly between the terminal bromophenyl group and the 4′-phenyldioxotriazole system in a molecule related by the 2_1 axis parallel to b, and between the terminal 3β-acetoxy group and the carbonyl O(2) of molecules related by the 2_1 axis parallel to c.

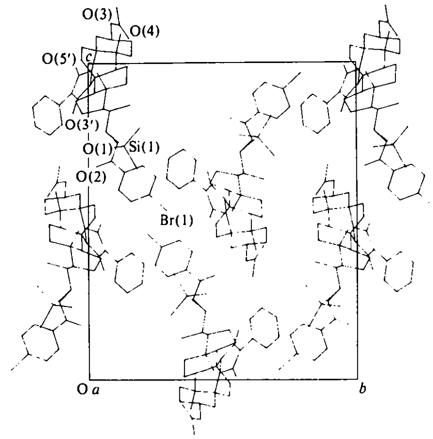


Fig. 2. Molecular packing of (III) viewed along a.

We thank Dr D. H. Williams and Dr J. Meadows for suggesting the problem and for the crystals, the Science Research Council for provision of the diffractometer and the Medical Research Council for financial support. Illustrations were prepared with *PLUTO* developed by Dr W. D. S. Motherwell.

References

Allen, F. H., Bellard, S., Brice, M. D., Cartwright, B. A., Doubleday, A., Higgs, H., Hummelink, T., Hummelink-Peters, B. G., Kennard, O., Motherwell, W. D. S., Rodgers, J. R. & Watson, D. G. (1979). *Acta Cryst.* B**35**, 2331–2339.

Altona, C., Geise, H. J. & Romers, C. (1968). *Tetrahedron*, **24**, 13–32.

Bucourt, R. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

Coles, B. F., Hitchcock, P. B. & Walton, D. R. M. (1975). *J. Chem. Soc. Dalton Trans.* pp. 442–448.

Collins, R. C. & Davis, R. E. (1978). *Acta Cryst.* B**30**, 288–289.

Cruse, W. B. T., Kennard, O. & Raithby, P. R. (1980). In preparation.

Duax, W. L. & Norton, D. A. (1975). *Atlas of Steroid Structure.* London: Plenum.

Ende, C. van der, Offereins, B. & Romers, C. (1974). *Acta Cryst.* B**30**, 1947–1952.

Fritch, J. R., Vollhardt, K. P. C., Thompson, M. R. & Day, V. W. (1979). *J. Am. Chem. Soc.* **101**, 2768–2770.

Geise, H. J., Buys, H. R. & Mijlhoff, F. C. (1971). *J. Mol. Struct.* **9**, 447–452.

Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.

Kaftory, M. (1978*a*). *Acta Cryst.* B**34**, 303–305.

Kaftory, M. (1978*b*). *Acta Cryst.* B**34**, 300–303.

Leroy, F., Courseille, C., Daney, M. & Bouas-Laurent, H. (1976). *Acta Cryst.* B**32**, 2792–2796.

Lu, T. H., Hseu, T. H. & Lee, T. J. (1977). *Acta Cryst.* B**33**, 913–916.

Pauly, K. H., Fischer, K. & Durr, H. (1979). *Cryst. Struct. Commun.* **8**, 115–119.

Rivera, A. V. & Sheldrick, G. M. (1978). *Acta Cryst.* B**34**, 3374–3376.

Sheldrick, G. M. (1979). Private communication.