Table 7. *Hydrogen bonding in* (I)–(III) [*presented as observed hydrogen bond, symmetry position of the second nonhydrogen atom with respect to the first atom, and bond distance* (Å)]

| | | |
|---|---|---|
| N(6)–H(61)···O(5′)<br>$-x, 0·5 + y, -z$<br>2·89 (1) | N(1)···H(62)–N(6)<br>$0·5 - x, -y, 0·5 + z$<br>2·94 (1) | N(1)···H(62)–N(6)<br>$0·5 - x, -y, 0·5 + z$<br>2·95 (1) |
| O(2′)–H(21′)···N(3′)<br>$-x, 0·5 + y, -z$<br>2·81 (1) | N(3)···H(53′)–O(5′)<br>$x, y, 1·0 + z$<br>2·82 (1) | N(3)···H(53′)–O(5′)<br>$x, y, 1·0 + z$<br>2·80 (1) |
| | N(6)–H(61)···N(7)<br>$0·5 - x, -y, 0·5 + z$<br>3·05 (1) | N(6)–H(61)···N(7)<br>$0·5 - x, -y, 0·5 + z$<br>3·04 (1) |
| | O(2′)–H(21′)···O<br>$2,y,z$<br>2·80 (1) | |
| | O(2′)=H(21)′···O′<br>$x,y,z$<br>2·80 (1) | |

With the nomenclature of Sundaralingam (1975), the conformation of the ribose ring in (I) and (II) may also be described as twist $^3T_2$. C(2′) and C(3′) are displaced by respectively 0·260 and 0·358 Å in (I) and 0·244 and 0·405 Å in (II) on opposite sides of the plane C(1′)O(1′)C(4′). As a result of the oxazolidine ring formation in (III), the ribose ring is markedly less puckered, its conformation being the unusual C(2′)-*exo*, with C(2′) displaced, however, only 0·272 Å from the least-squares plane of the remaining four ring atoms. Other distances from this plane are C(1′) 0·008, C(2′) –0·013, C(3′) –0·007 and C(4′) 0·012 Å.

Whereas the position of the C(5′)–O(5′) bond relative to the ribose ring is *gauche–gauche* in (II) and (III), a *gauche–trans* conformation is observed in (I). O(5′) participates in intermolecular O···H–N hydrogen bonding to N(6) in (I) but in O–H···N intermolecular hydrogen bonding to N(3) in (II) and (III), Table 7. As a result of the small value of $\chi_{CN}$ and the *gauche–gauche* position of C(5′)–O(5′), short O(5′)···C(8) intramolecular distances are observed in (II) and (III). The O(5′)···C(8) distances are 3·16 and 3·22 Å with respective O(5′)···H(8) distances of 2·28 and 2·54 Å. In contrast to the N(6) protons, the N(3′) protons in (I) and (II) do not participate in hydrogen bonding. N(3′) is intermolecularly hydrogen bonded to O(2′) in (I). With the exception of the O(2′)–H(21′)···O and O(2′)–H(21′)···O′ bonds to the disordered methanol O atoms in (II), the pattern of hydrogen bonding in (II) and (III) is identical. In both these derivatives no adenine base stacking is observed. Parallel adenine bases in (I) are related to one another at a distance of 3·53 Å by translation along **c**. There is no overlap of neighboring adenine systems. This mode of stacking (pattern I, Motherwell & Isaacs, 1972) is typical of purine nucleosides and nucleotides in the *anti* configuration with $\chi_{CN} \approx 10 \pm 20°$ (Schomburg, 1978). As a result of potential steric interaction between neighboring sugar rings no base overlap is to be expected for this stacking mode. The absence of base stacking in (II) and (III) for which the translation mode would also be expected is presumably a result of the bulkiness of the 3′-substituents, which prevents an adequate proximity of the adenine $\pi$ systems in this mode.

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# Structure of *t*-2,*c*-4,*t*-6-Trimethyl-1$\lambda^4$,3,5-trithiane *r*-1-Oxide

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## Abstract

The crystal structure of the title compound, $C_6H_{12}OS_3$, was determined by X-ray diffraction. The space group is *Pbca* with $a$ = 11·763 (2), $b$ = 19·102 (2), $c$ = 8·261 (1) Å and $Z$ = 8. The structure was refined to $R$ = 0·037 for 1834 reflections collected by diffractometry. The 1,3,5-trithiane ring takes a chair

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conformation with two of the methyl groups and the sulfoxide group equatorially oriented and one methyl group axially oriented. The trithiane ring has approximate mirror symmetry. The three non-equivalent S—C bonds are significantly different (1·835, 1·805 and 1·814 Å) owing to the effects of the substituents.

## Introduction

1,3,5-Trithiane derivatives exhibit eminent stereoselectivity in substitution reactions. In the case of the sulfoxide, in addition to the protons located on both sides of the sulfoxide group, the proton at the 4 position has a high exchange rate. Besides the two S atoms adjacent to the carbanion, the third S atom seems to contribute to the stability of the compound. From the study by ESCA (Iwamura, Fukunaga & Kushida, 1972), partial neutralization of the positive charge on the sulfoxide S atom by intramolecular charge transfer of the lone-pair electrons on the sulfide S atoms was observed. The crystal structure analysis of *t*-2,*c*-4,*t*-6-trimethyl-$1\lambda^4$,3,5-trithiane *r*-1-oxide was undertaken to elucidate the molecular structure in relation to its stereoselectivity.

## Experimental

The crystals, which were kindly supplied by Professor Ōki of the University of Tokyo, take the form of colorless, transparent prisms. The compound was obtained by oxidation of $\alpha$-trimercaptoacetaldehyde with hydrogen peroxide in acetic acid as a mixture of $\alpha$-monosulfoxides, and the crude product was recrystallized from aqueous alcohol. Crystal data are: $C_6H_{12}OS_3$, $M_r = 196{\cdot}34$, orthorhombic, *Pbca*, $Z = 8$, $a = 11{\cdot}763\ (2)$, $b = 19{\cdot}102\ (2)$, $c = 8{\cdot}261\ (1)$ Å, $U = 1856{\cdot}3\ (4)$ Å$^3$, $D_x = 1{\cdot}407$ Mg m$^{-3}$, $\mu$(Mo $K\alpha$; $\lambda = 0{\cdot}7107$ Å) = 0·710 mm$^{-1}$. A single crystal of dimensions 0·27 × 0·26 × 0·21 mm was selected for intensity-data collection. Intensities for all unique reflections within the range $2\theta < 60°$ were measured using Mo $K\alpha$ radiation on an automated Rigaku four-circle diffractometer. 1834 reflections with $|F_o| > 3\sigma(|F|)$ were regarded as observed and used for the refinement. The $\omega$–$2\theta$ scan technique was employed at a scan rate of 2° min$^{-1}$ in $\omega$ and the scan range was calculated by $1{\cdot}0° + 0{\cdot}8° \tan\theta$. The usual corrections were made for Lorentz and polarization factors, but no correction was applied for absorption or extinction.

## Structure determination

The structure was solved by the heavy-atom method. Initial coordinates for the S atoms were derived from three-dimensional sharpened Patterson maps. The positions of C and O atoms were obtained from a sulfur-phased Fourier synthesis, and subsequent difference synthesis revealed the positions of the H atoms. The refinement was carried out by the block-diagonal least-squares program *HBLS* (*UNICS*, 1967) written by Dr Ashida, based on *F* with equal weights. Anisotropic temperature factors were assigned to the non-hydrogen atoms and isotropic ones to the H atoms. Anomalous-dispersion corrections were introduced for the S atoms. The final *R* value converged to 0·037 for 1834 reflections.* At the final stage of the refinement all the parameter shifts were less than one sixth of the corresponding standard deviations. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The scattering-factor curve of Stewart, Davidson & Simpson (1965) was used for the H atoms. The atomic positional parameters and their standard deviations are listed in Table 1.

Table 1. *The final positional parameters* ($\times 10^5$ *for* S; $\times 10^4$ *for* C, O; $\times 10^3$ *for* H) *and equivalent isotropic temperature factors* ($\times 10^4$; $\times 10^3$ *for* H), *with e.s.d.'s in parentheses*

| | $x$ | $y$ | $z$ | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| S(1) | 8228 (6) | 10064 (4) | 11510 (8) | 469 (3) |
| S(3) | 22748 (6) | 13926 (4) | −17072 (9) | 538 (3) |
| S(5) | 143 (7) | 20904 (3) | −11806 (10) | 564 (3) |
| C(2) | 1699 (2) | 680 (1) | −526 (3) | 449 (13) |
| C(4) | 1010 (2) | 1745 (1) | −2658 (3) | 497 (14) |
| C(6) | −380 (2) | 1317 (1) | −65 (3) | 472 (14) |
| C(7) | 2693 (3) | 263 (2) | 159 (4) | 589 (17) |
| C(8) | 463 (2) | 1258 (1) | −3895 (3) | 668 (19) |
| C(9) | −1360 (3) | 1503 (2) | 1068 (4) | 525 (15) |
| O | 405 (2) | 361 (1) | 2008 (2) | 613 (12) |
| H(1) | 121 (2) | 40 (1) | −116 (3) | 42 (6) |
| H(2) | 131 (2) | 218 (1) | −323 (3) | 60 (8) |
| H(3) | −58 (2) | 93 (1) | −79 (3) | 50 (7) |
| H(4) | 313 (2) | 51 (1) | 71 (3) | 55 (7) |
| H(5) | 241 (3) | −8 (1) | 95 (3) | 64 (8) |
| H(6) | 311 (2) | 7 (2) | −74 (4) | 85 (10) |
| H(7) | −201 (3) | 169 (2) | 43 (4) | 98 (11) |
| H(8) | −113 (3) | 190 (2) | 183 (4) | 94 (11) |
| H(9) | −154 (3) | 114 (2) | 165 (4) | 105 (12) |
| H(10) | −18 (2) | 152 (1) | −440 (3) | 66 (8) |
| H(11) | 22 (3) | 79 (2) | −336 (4) | 91 (10) |
| H(12) | 100 (2) | 115 (1) | −484 (4) | 73 (9) |

## Description of the structure and discussion

The present trithiane compound adopts a chair conformation with two of the methyl groups and the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35380 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

sulfoxide group equatorially oriented and one methyl group axially oriented. The molecular shape and the numbering scheme are shown in Fig. 1. The plane defined by the three S atoms is given by $-0{\cdot}4455X - 0{\cdot}7109Y - 0{\cdot}5443Z + 2{\cdot}3153 = 0{\cdot}0$, where $X$, $Y$ and $Z$ are coordinates in Å referred to the crystal axes $a$, $b$ and $c$. The atomic shifts of the C and O atoms from the plane are less than 0·738 (3) Å, excluding the axial methyl C atom. The conformation of the two methyl groups at the 2 and 6 positions is equatorial and that at the 4 position, which is furthest from the O atom, is axial. Experimental evidence from PMR studies (Fukunaga, Arai, Iwamura & Ōki, 1971) indicates that the 4-equatorial proton has an exchange rate more than thirty times greater than that of the axial proton. This accounts for the relative stability of the axial methyl group at the 4 position.

The molecule has a non-crystallographic mirror plane passing through S(1)–C(4) and the pairs of bond lengths and angles related by it are nearly equal. Bond lengths and angles are tabulated in Tables 2 and 3. The S—C single-bond length in trithiane and thiaalkanes is usually 1·818 Å, which is in good agreement with the average value in this compound. However, it is evident that the S—C distances are slightly but significantly different owing to the substituted groups. The elongation of S(1)—C(2) and S(1)—C(6) (1·833–1·836 Å) seems to be mainly due to the different hybridizations of the S atoms and the induced polarization effects of $O^-$—$S^+$. Since S(1) is double-bonded to an O atom, the hybrid orbital involving the 3$d$ atomic orbitals of S is entirely different from those of S(3) and S(5). Namely, the electron clouds of S(1) tend to be more expanded because of the participation of 3$d$ orbitals, and the overlapping region of the orbitals may become further away from the S nucleus, resulting in the longer bond. If the atoms of the S—C bonds become relatively positive, the bond order would decrease giving rise to elongation of the bonds. The experimental evidence from ESCA (Iwamura, Fukunaga & Kushida, 1972) suggests the relative positiveness of the sulfoxide S atom as compared with the sulfide atoms, and also suggests the occurrence of intramolecular charge transfer from the latter to the former based on the 2$p$ binding energies of S atoms in trithiane and its 1-oxide and 1,1-dioxide derivatives. Iwamura *et al.* have proposed the occurrence of some interspacial electron transfer between the three S atoms through overlapping of 3$d$ orbitals as well as interactions through $-CH_2-$. Another possible quantum-chemical interpretation is that partial charge transfer of the lone-pair electrons of S(3) and S(5) into the anti-bonding molecular orbital of S(1)—C(2) may give rise to the relatively long bond. Shorter S—C bond lengths of 1·803–1·806 Å are observed for S(3)—C(2) and S(5)—C(6). This may be accounted for by the differences in hybridization and polarization of the S atoms. Moreover, the *gauche* effects of lone-pair electrons and hydrogen may partly contribute through the attractive force that works over a short distance between delocalized lone-pair electrons and the H atom bonded to the adjacent C atom. The difference in S—C bond lengths between $r$-4,$c$-6-dimethyl-1,3-dithiane (1·822 Å) and its oxide $r$-4,$c$-6-dimethyl-1,3-dithiane $t$-1-oxide (1·828 Å; McPhail, Onan & Koskimies, 1976) may also be accounted for by a similar concept. The average C—C bond length is 1·525 Å, which is shorter than that in trimethyltrithiane (Valle, Busetti, Mammi & Carazzolo, 1969). This hardly indicates that the deformation of the C—C

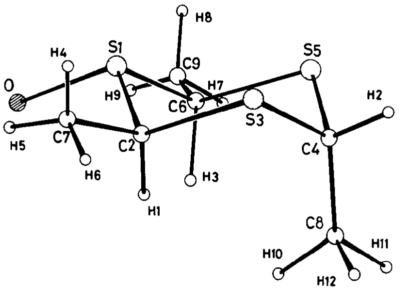

Fig. 1. The molecular structure and numbering of the atoms.

Table 2. *Bond lengths* (Å) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| S(1)–C(2) | 1·836 (3) | C(2)–C(7) | 1·524 (4) |
| S(1)–C(6) | 1·833 (3) | C(6)–C(9) | 1·527 (4) |
| S(3)–C(2) | 1·806 (3) | C(4)–C(8) | 1·525 (4) |
| S(5)–C(6) | 1·803 (4) | | |
| S(3)–C(4) | 1·812 (3) | S(1)–O | 1·504 (2) |
| S(5)–C(4) | 1·816 (3) | | |
| C(2)–H(1) | 0·94 (2) | C(8)–H(10) | 1·01 (3) |
| C(4)–H(2) | 1·03 (3) | C(8)–H(11) | 1·04 (3) |
| C(6)–H(3) | 0·98 (2) | C(8)–H(12) | 1·02 (3) |
| C(7)–H(4) | 0·84 (3) | C(9)–H(7) | 1·00 (3) |
| C(7)–H(5) | 0·98 (3) | C(9)–H(8) | 1·03 (3) |
| C(7)–H(6) | 0·97 (3) | C(9)–H(9) | 0·87 (3) |

Table 3. *Bond angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| C(2)–S(1)–C(6) | 97·5 (1) | S(1)–C(2)–S(3) | 112·3 (1) |
| C(2)–S(3)–C(4) | 101·9 (1) | S(3)–C(4)–S(5) | 111·9 (2) |
| C(4)–S(5)–C(6) | 102·2 (1) | S(5)–C(6)–S(1) | 110·3 (1) |
| S(1)–C(3)–C(7) | 109·2 (2) | C(7)–C(2)–S(3) | 107·9 (2) |
| S(1)–C(6)–C(9) | 108·8 (2) | C(9)–C(6)–S(5) | 108·4 (2) |
| S(3)–C(4)–C(8) | 114·2 (2) | C(2)–S(1)–O | 105·1 (1) |
| S(5)–C(4)–C(8) | 113·6 (2) | C(6)–S(1)–O | 105·7 (1) |
| S(1)–C(2)–H(1) | 105·6 (14) | S(5)–C(6)–H(3) | 106·0 (14) |
| S(1)–C(6)–H(3) | 110·3 (14) | S(3)–C(4)–H(2) | 103·1 (14) |
| S(3)–C(2)–H(1) | 105·6 (14) | S(5)–C(4)–H(2) | 103·4 (14) |
| C(2)–C(7)–H(4) | 112·0 (17) | C(6)–C(9)–H(9) | 108·9 (28) |
| C(2)–C(7)–H(5) | 109·7 (16) | C(4)–C(8)–H(10) | 107·1 (16) |
| C(2)–C(7)–H(6) | 108·0 (18) | C(4)–C(8)–H(11) | 110·8 (17) |
| C(6)–C(9)–H(8) | 110·4 (17) | C(4)–C(8)–H(12) | 111·5 (23) |
| C(6)–C(9)–H(7) | 109·0 (18) | | |
| H(4)–C(7)–H(5) | 103·0 (23) | H(9)–C(9)–H(7) | 113·3 (29) |
| H(5)–C(7)–H(6) | 115·2 (24) | H(10)–C(8)–H(11) | 114·1 (23) |
| H(6)–C(7)–H(4) | 108·9 (25) | H(11)–C(8)–H(12) | 108·6 (23) |
| H(7)–C(9)–H(8) | 104·5 (25) | H(12)–C(8)–H(10) | 104·6 (22) |
| H(8)–C(9)–H(7) | 108·9 (28) | | |

bonds or their valency angles is due to the steric repulsion in the present compound.

The axial methyl group is inclined towards the opposite side of the six-membered heterocyclic ring: S(3)—C(4)—C(8) is larger than the normal tetrahedral angle of 109·5° by about 5° because of steric effects. The average S—C—S angle is 111·5 (1)°, somewhat smaller than those observed in 1,3,5-trithiane and trimethyltrithiane (114·5–115·3°), but in good agreement with those in dithiane sulfoxides (110·0–112·5°; McPhail *et al.*, 1976). The C(2)—S(1)—C(6) angle at the sulfoxide S atom is 97·5°, a value expected from that in dimethyl sulfoxide (Thomas, Shoemaker & Eriks, 1966). The other two C—S—C angles average 102·1°, which is significantly larger than those in other thia derivatives. This may be attributed to the tendency to release the puckering deformation of the heterocyclic ring, and because the deformation occurs in the most flexible part of the structure. The average C—S—O angle, 105·4 (1)°, is typical for sulfoxides, and the O atom takes an in-plane conformation.

The torsion angles between the methyl groups and the sulfoxide are 60·5 and 62·3°, while that in dimethyldithiane sulfoxide is 63·9°. McPhail *et al.* reported increased ring puckering in the latter two compounds due to the introduction of a Me···O interaction. In the present compound, the dihedral angle of the ring valency part C—S(=O)—C—S is 71·5 (2)°, which is large compared to the 66·1–66·9° in trithiane. The *gauche* Me···O interaction seems to affect the valency-angle deformation within the six-membered ring.

The H atom of the equatorial methyl group is directed slightly toward the sulfoxide. The distance between the closest methyl H and the sulfoxide O atom is 2·70 Å, on average, which is nearly equal to that between the sulfoxide O atom and the H atom bonded to the ring C atom. Thus, there may be some attraction rather than repulsion between them, but the positions of the H atoms seem to be mainly determined by the staggered conformations of the C($sp^3$) atoms. The interatomic distance between the methyl C atoms and the O atoms is 3·104 Å, which is shorter than the sum of van der Waals radii. The similar distances in dithiane derivatives were attributed to steric repulsion. The facts discussed above, however, seem to indicate that the molecular geometry depends on the balance between electronic and steric effects, suggesting rather minor effects of the latter in this case.

Three S atoms form a nearly equilateral triangle with an average separation of 2·998 (1) Å. In trithiane (Fleming & Lynton, 1967), the S···S distance is 3·068 (3) Å. The significantly shorter S···S distance in the title compound suggests the possibility of overlapping of the 3$d$ orbitals of the S atoms, giving rise to electronic interactions among the S atoms with a consequent stabilization in energy. This again supports the evidence obtained by ESCA for the partial neutralization of S by the delocalization of lone-pair electrons by the use of 3$d$ orbitals.

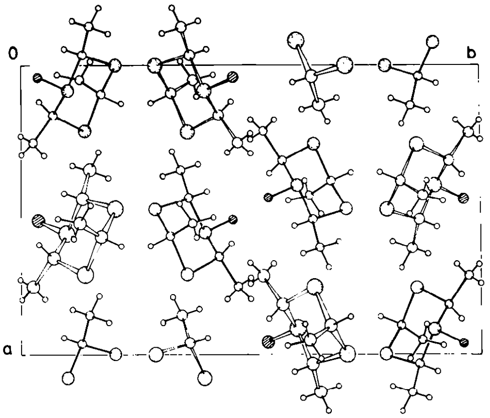

Fig. 2. The structure viewed along the $c$ axis. Dotted circles indicate S atoms and hatched circles O atoms.

The final difference Fourier maps revealed, in addition to all the bonding electrons, several peaks of 0·15 e Å$^{-3}$ around the S atoms which may be attributed to lone-pair electrons. A relatively distinct single peak, compared to those at S(3) and S(5), was observed in the vicinity of S(1) in the axial direction. Recently, the electron density distributions around S atoms have been observed in low-temperature studies of several sulfur-containing compounds: sodium thiocyanate (Bats, Coppens & Kvick, 1977), 2,5-dimercaptothiadiazole (Bats, 1976), sulfamic acid (Bats, Coppens & Koetzle, 1977), sodium sulfanilate (Bats, 1977$a$) and dicyanotrisulfane (Bats, 1977$b$). The lone-pair peaks that they observed were at about 0·6–0·8 Å from the S nuclei, with peak heights of 0·15–0·45 e Å$^{-3}$. On the whole, our observations agree well with their results. However, an accurate structure determination at low temperature seems to be desirable to enable discussion of the bonding nature of S in detail in the present compound.

Some of the closest interatomic distances not mentioned above are those between S and two methyl C atoms and between S and methine C atoms. The average values for these distances are 2·741 (3) and 3·417 (3) Å respectively. Fig. 2 shows a projection of the structure viewed along the $c$ axis. The closest intermolecular distance is O···H(6) (2·676 Å), and no significantly short distances indicating interactions other than van der Waals were observed.

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

# The Structure and Absolute Configuration of (22*R*)-3*β*-Acetoxy-5*α*,8*α*-(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

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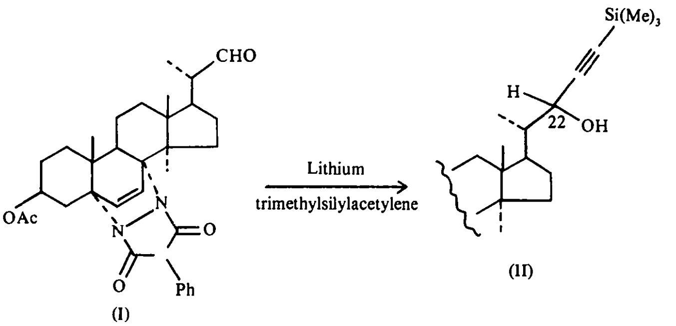
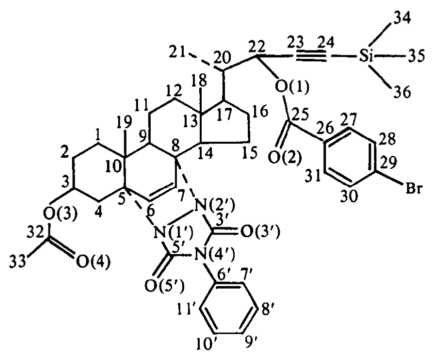
## Abstract

$C_{44}H_{52}BrN_3O_6Si$ 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 13$\beta$,14$\alpha$ half-chair. The *B* ring is forced to adopt a boat conformation by the 5$\alpha$,8$\alpha$-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).





(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), $c$ =

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