

Fig. 2. Molecular packing of the title compound in the unit cell viewed down the *a* axis.

around N(12) is $348.4(6)^\circ$, a 'pyramidal' value intermediate between those for $sp^2(360^\circ)$ and $sp^3(328.4^\circ)$ hybridization (Ammon, Mazzocchi, Regan & Colicelli, 1979). The plane through C(13), N(12) and C(16) makes an angle of $145.6(2)^\circ$ with the plane of the benzene ring.

The molecular packing viewed along *a* is shown in Fig. 2. There is a close intramolecular C—H...O contact involving the carbonyl oxygen with C(15)...O(11) 2.684(4), H(C15)...O(11) 2.25(4) Å and C(15)—H(C15)...O(11) $109(2)^\circ$ (Taylor & Kennard, 1982). The crystal structure is stabilized by van der Waals interactions.

The concept that two molecular conformations exist in the excited state, one fully planar and the other with the donor group perpendicular to the acceptor [due to a twist around the $\dot{N}-C(sp^2)$ bond], is said to be responsible for the dual band laser emission. This is not applicable for the title compound since: (i) the plane of the donor group [the alkylamino group constituting N(12), C(13) and C(16)] is not coplanar with that of the acceptor group and (ii) the donor group can never become perpendicular to the acceptor as the twist around $\dot{N}-C(sp^2)$ is restricted by cyclization. The structural investigation indicates that the geometry around

N(12) is nearly pyramidal. In the excited state, this pyramidal geometry may be in equilibrium with a trigonal planar form and these two forms may be responsible for the dual emission by the title compound. If such conformational changes are responsible for the dual emission here, then the concept is applicable for the alkylaminocoumarins, where a transition from planar to pyramidal geometry around N is also possible.

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Structure of an Unusually Non-Polar Hydroxy Ether

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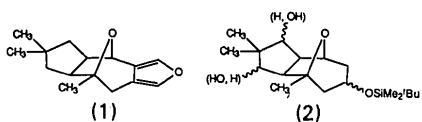
Abstract. (1*R**,3*R**,7*S**,9*S**)-1,4,4-Trimethyl-9-(*tert*-butyldimethylsilyloxy)-*exo*-11-oxatricyclo[5.3.1.0^{2,6}]-

undecan-3-ol, C₁₉H₃₆O₃Si, *M_r* = 340.90, orthorhombic, *Pbca*, *a* = 10.411(3), *b* = 13.275(3), *c* = 29.085(10) Å, *V* = 4019(2) Å³, *Z* = 8, *D_x*(130 K) = 1.13 g cm⁻³, λ(Mo *K*α) = 0.71069 Å, μ = 1.24 cm⁻¹,

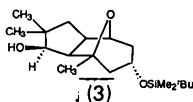
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$F(000) = 1504$, $T = 130$ K, $R = 0.077$ for 1005 observed reflections with $I > 3\sigma(I)$. The compound, whose connectivity was not readily apparent from spectroscopic and chemical information alone, possesses a tricyclic framework containing an O-bridged bicyclo[3.2.1]octane fused in a *cis-exo* manner to a cyclopentanol ring. Most noteworthy is the considerably lower polarity of this compound relative to its opposite cyclopentanol stereoisomer. The close proximity [2.78 (1) Å] of the bridging O atom in the [3.2.1] system to the hydroxyl O atom on the five-membered ring is suggestive of an intramolecular hydrogen bond, although the H atom could not be located.

Introduction. In the course of a study aimed at the synthesis of a sesquiterpene natural product, furan-ether B (1), we explored methods for the removal of extraneous hydroxyl groups from a series of isomeric molecules of the general formula (2). These molecules were obtained as a mixture of regio- and stereoisomers as a result of the use of a relatively unselective cycloaddition process to generate the ring system, and later through reduction of a ketone on the five-membered ring. As none of the regio- or stereochemical features is present in the final target molecule, our original hope was to carry the entire isomer mixture through all the steps of the synthesis, finally arriving at the single natural product at the end of the sequence.



In the course of attempts to deoxygenate (2), we isolated a relatively non-polar material possessing only very weak absorption in the region of the infrared spectrum characteristic of the hydroxyl OH stretching frequencies. However, proton NMR still showed downfield signals which could be associated with the CH proton of a secondary alcohol. As a result of these ambiguous data, together with a general desire to establish a firm reference for our spectroscopic assignments relating to regio- and stereochemistry in this series, an X-ray crystal structure determination was carried out, resulting in the structure (3). The compounds were isolated as racemic mixtures; for convenience just one stereoisomer is shown for each.



Experimental. Compound (3), colorless plates obtained by recrystallization from methanol-water, crystal dimensions 0.05 × 0.25 × 0.25 mm (it was not possible to obtain larger crystals); Syntex P2₁ diffractometer, modified LT-1 low-temperature apparatus, $T = 130$ K, Mo $K\alpha$ radiation, graphite monochromator; cell dimensions from least-squares fit of 13 reflections with $21 < 2\theta < 39^\circ$; space group *Pbca* (No. 61) based on conditions $0kl$, $k = 2n$; $h0l$, $l = 2n$; $hk0$, $h = 2n$; no absorption correction (range of absorption correction factors 1.00–1.03); data collected to $2\theta_{\max} = 45^\circ$ with hkl ranges 0 to 11, 0 to 14 and 0 to 30, respectively; ω scans, 1.2° range, $10.0^\circ \text{ min}^{-1}$, $\pm 1.0^\circ$ offset for backgrounds; two check reflections monitored every 200 reflections showed no decay; 3039 reflections measured, 2606 independent data, 1005 observed [$I > 3\sigma(I)$] used in the solution and refinement (based on F); structure solved by direct methods; full-matrix least-squares refinement, 122 parameters; H atoms included at calculated positions using a riding model with C—H 0.96 Å; all atoms with isotropic thermal parameters, those of H atoms fixed at $U = 1.2U_C$; Si was assigned anisotropic thermal parameters in the final cycles of refinement; $R = 0.077$, $wR = 0.065$, $w = [\sigma^2(F_o)]^{-1}$, $S = 1.76$, $(\Delta/\sigma)_{\max} = 0.148$ for rotation of the methyl group at C(17); $\Delta\rho_{\max}$ in final difference map was $0.43 \text{ e } \text{Å}^{-3}$ and of no chemical significance; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV); computer programs from the *SHELXTL* (version 5) package (Sheldrick, 1985). The final atomic coordinates and thermal parameters are given in Table 1 and bond distances and bond angles are listed in Table 2.*

Discussion. The structure of (3) (Fig. 1) consists of discrete molecules containing the *exo*-11-oxatricyclo-[5.3.1.0^{2,6}]undecane ring system, essentially an 8-oxabicyclo[3.2.1]octane fused in a *cis-exo* manner to a cyclopentane ring. The stereochemical configurations at C(3) and C(8), and the *syn* regiochemical relationship between the methyl group at C(1), *i.e.* C(13), and the hydroxyl group represented by O(3), are clearly defined as well.

Two previous examples of compounds containing this ring system have been subjected to structural analysis (La Belle, Knudsen, Olmstead, Hope, Yanuck & Schore, 1985) in addition to two compounds containing the simpler 8-oxabicyclo[3.2.1]octane system (Olmstead, Hope, Sampath & Schore,

* H-atom coordinates, anisotropic thermal parameters and lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53256 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) for $\text{C}_{19}\text{H}_{36}\text{O}_3\text{Si}$

	x	y	z	U_{eq}
Si	7603 (3)	7592 (2)	1357 (1)	24 (1)
O(1)	6261 (6)	7031 (5)	1510 (2)	22 (2)
O(2)	3123 (6)	6335 (5)	2110 (2)	22 (2)
O(3)	1780 (7)	4876 (6)	1619 (2)	39 (2)
C(1)	4153 (9)	5601 (7)	1998 (3)	15 (3)
C(2)	5424 (9)	6063 (7)	2152 (3)	23 (3)
C(3)	5715 (10)	7108 (8)	1963 (3)	26 (3)
C(4)	4503 (9)	7757 (7)	1943 (3)	27 (3)
C(5)	3328 (9)	7130 (8)	1788 (3)	27 (3)
C(6)	3578 (8)	6582 (7)	1328 (3)	14 (2)
C(7)	3990 (9)	5518 (7)	1483 (3)	17 (3)
C(8)	2873 (8)	4854 (9)	1309 (3)	31 (3)
C(9)	2498 (13)	5321 (7)	850 (3)	26 (3)
C(10)	2406 (10)	6443 (7)	1004 (3)	26 (3)
C(11)	3526 (10)	5175 (9)	478 (3)	31 (3)
C(12)	1175 (11)	4961 (10)	669 (4)	46 (4)
C(13)	3929 (10)	4639 (8)	2277 (4)	36 (3)
C(14)	7476 (14)	8971 (7)	1497 (4)	40 (3)
C(15)	8981 (10)	7044 (9)	1664 (4)	35 (3)
C(16)	7710 (11)	7404 (8)	721 (3)	24 (3)
C(17)	9008 (11)	7795 (9)	540 (4)	40 (4)
C(18)	7657 (14)	6253 (8)	613 (4)	43 (3)
C(19)	6591 (10)	7931 (9)	468 (4)	37 (3)

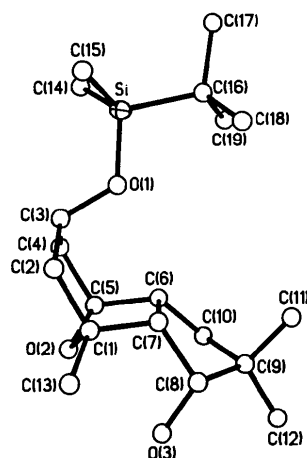


Fig. 1. ($1R^*$, $3R^*$, $7S^*$, $9S^*$)-1,4,4-trimethyl-9-(*tert*-butyldimethylsilyloxy)-*exo*-11-oxatricyclo[5.3.1.0^{2,6}]undecan-3-ol, $\text{C}_{19}\text{H}_{36}\text{O}_3\text{Si}$.

1984). In all of those a trigonal (ketone) carbon rather than a tetrahedral carbon atom is present at the position labeled C(3) in Fig. 1, and in the tricyclics the cyclopentane ring is present as a nearly planar enone rather than the saturated ring in (3). As a result, (3) presents a more folded structure overall than the previously studied systems, with the pyran ring containing C(1)—C(5) and O(2) being much more noticeably chair-like. Most significant is the puckering in the direction of a half-chair conformation about C(8) and C(10) in the cyclopentane ring. Internal ring angles at these atoms are C(7)—C(8)—C(9) 104.3 (8) and C(6)—C(10)—C(9) 103.9 (8)°. At C(9), which contains *gem*-dimethyl substitution, the

Table 2. Bond lengths (\AA) and angles ($^\circ$) for $\text{C}_{19}\text{H}_{36}\text{O}_3\text{Si}$

Si—O(1)	1.645 (7)	Si—C(14)	1.880 (10)
Si—C(15)	1.840 (11)	Si—C(16)	1.870 (9)
O(1)—C(3)	1.437 (12)	O(2)—C(1)	1.486 (12)
O(2)—C(5)	1.428 (12)	O(3)—C(8)	1.453 (11)
C(1)—C(2)	1.526 (13)	C(1)—C(7)	1.513 (12)
C(1)—C(13)	1.532 (14)	C(2)—C(3)	1.523 (14)
C(3)—C(4)	1.529 (14)	C(4)—C(5)	1.547 (14)
C(5)—C(6)	1.545 (13)	C(6)—C(7)	1.542 (13)
C(6)—C(10)	1.552 (13)	C(7)—C(8)	1.544 (13)
C(8)—C(9)	1.524 (13)	C(9)—C(10)	1.559 (13)
C(9)—C(11)	1.533 (15)	C(9)—C(12)	1.550 (17)
C(16)—C(17)	1.541 (16)	C(16)—C(18)	1.561 (15)
C(16)—C(19)	1.545 (15)	O(2)···O(3)	2.78 (1)
			(Non-bonding)
O(1)—Si—C(14)	108.8 (5)	O(1)—Si—C(15)	110.6 (4)
C(14)—Si—C(15)	109.5 (6)	O(1)—Si—C(16)	104.9 (4)
C(14)—Si—C(16)	110.4 (5)	C(15)—Si—C(16)	112.5 (5)
Si—O(1)—C(3)	123.5 (6)	C(1)—O(2)—C(5)	103.5 (7)
O(2)—C(1)—C(2)	107.3 (7)	O(2)—C(1)—C(7)	100.6 (7)
C(2)—C(1)—C(7)	114.7 (8)	O(2)—C(1)—C(13)	108.7 (7)
C(2)—C(1)—C(13)	108.2 (8)	C(7)—C(1)—C(13)	116.6 (8)
C(1)—C(2)—C(3)	115.6 (8)	O(1)—C(3)—C(2)	110.2 (8)
O(1)—C(3)—C(4)	109.4 (8)	C(2)—C(3)—C(4)	111.3 (8)
C(3)—C(4)—C(5)	111.1 (8)	O(2)—C(5)—C(4)	108.9 (7)
O(2)—C(5)—C(6)	104.2 (8)	C(4)—C(5)—C(6)	111.9 (8)
C(5)—C(6)—C(7)	103.1 (7)	C(5)—C(6)—C(10)	116.7 (7)
C(7)—C(6)—C(10)	106.7 (7)	C(1)—C(7)—C(6)	104.7 (7)
C(1)—C(7)—C(8)	116.7 (8)	C(6)—C(7)—C(8)	102.6 (7)
O(3)—C(8)—C(9)	112.1 (7)	O(3)—C(8)—C(9)	109.6 (8)
C(7)—C(8)—C(9)	104.3 (8)	C(8)—C(9)—C(10)	98.7 (7)
C(8)—C(9)—C(11)	112.8 (9)	C(10)—C(9)—C(11)	111.5 (9)
C(8)—C(9)—C(12)	113.6 (9)	C(10)—C(9)—C(12)	109.7 (10)
C(11)—C(9)—C(12)	110.1 (8)	C(6)—C(10)—C(9)	103.9 (8)
Si—C(16)—C(17)	110.2 (7)	Si—C(16)—C(18)	109.1 (7)
C(17)—C(16)—C(18)	106.9 (9)	Si—C(16)—C(19)	111.5 (7)
C(17)—C(16)—C(19)	110.3 (8)	C(18)—C(16)—C(19)	108.7 (9)
O(2)···O(3)—C(8)	86.4 (7)		

internal ring angle is highly compressed, 98.7 (7)°, as expected. The overall result is to force a short non-bonded distance of 2.78 (1) Å between the bridging oxygen, O(2), and the hydroxyl oxygen, O(3). There are no other abnormalities in the structure and no short intermolecular distances.

Tricyclic hydroxy ether (3) exhibits unusually low polarity, as well as attenuated O—H stretching absorption in the infrared compared with the stereoisomer in which the configuration of the hydroxy group is reversed, removing it from the vicinity of the bridging O atom. Indeed, the polarity of (3) is comparable to that of the cyclopentanone from which (3) and its stereoisomer are prepared by reduction. Reactivity at the O—H bond of (3) is also considerably reduced relative to its stereoisomer: (3) is isolated unchanged while its isomer is completely consumed in reactions in which isomer mixtures are subjected to attempted hydroxyl removal *via* a sequence of, first, inorganic ester formation with $\text{ClPO}(\text{NMe}_2)_2$ and, second, dissolving metal reduction using Li and amines (Ireland, Muchmore & Hengartner, 1972). In fact, it was from just such experiments that (3), freed from all its other regio-

and stereoisomers, was first isolated in pure form. The hydroxyl H atom in (3) was not located despite the fact that considerable effort was made to do so. However, the closest contact to another molecule for the hydroxyl O(3) atom is 2.58 Å to H(4B), and its closest contact to another O atom is 4.91 Å to O(2'). Thus there is very little likelihood that this hydroxyl group is involved in any sort of intermolecular interaction. On the other hand, it is well situated for intramolecular hydrogen bonding and given the considerable driving force expected for such an interaction it is plausible that such an interaction is responsible for the anomalous properties and behavior of this compound.

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Structures of Two Isomeric Dihydropyridine Derivatives with S Substituents: Solid-State Allyl Migration

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Abstract. Ethyl 5-cyano-1,4-dihydro-2-methyl-4-phenyl-6-allylthio-3-pyridinecarboxylate, (I), C₁₉H₂₀N₂O₂S, *M_r* = 340.43, melting-point range = 358–360 K, monoclinic, *C*2/*c*, *a* = 17.071 (4), *b* = 7.277 (2), *c* = 29.065 (6) Å, β = 104.96 (2)°, *V* = 3488 (17) Å³, *Z* = 8, *D_x* = 1.296 g cm⁻³, λ = 0.71069 Å, μ = 1.58 cm⁻¹, *F*(000) = 1440, *T* = 140 (5) K, *R* = 0.059, *wR* = 0.069 for 299 variables and 2201 unique reflections for which *I* > 3σ(*I*). On heating continuously at 328 K (I) undergoes a solid-state transformation, forming a product (II) melting in the range 452–453 K whose cell parameters are *a* = 17.117 (8), *b* = 7.272 (4), *c* = 29.599 (11) Å, β = 108.63 (4)°, *V* = 3491 (42) Å³, *Z* = 8, *D_x* = 1.295 g cm⁻³, λ = 0.71069 Å. Ethyl 5-cyano-1,4,5,6-tetrahydro-2-methyl-4-phenyl-5-allyl-6-thioxo-3-pyridinecarboxylate, (III), C₁₉H₂₀N₂O₂S, *M_r* = 340.43, melting point = 451 K, monoclinic, *P*2₁/*c*, *a*

= 11.797 (1), *b* = 12.274 (2), *c* = 13.068 (3) Å, β = 104.07 (1)°, *V* = 1835 (6) Å³, *Z* = 4, *D_x* = 1.232 g cm⁻³, λ = 0.71069 Å, μ = 1.49 cm⁻¹, *F*(000) = 720, *T* = 295 (2) K, *R* = 0.036, *wR* = 0.038 for 325 variables and 1707 unique reflections for which *I* > 3σ(*I*). The ethyl group of the ethoxycarbonyl substituent in (III) is disordered over two positions. (I) and (III) differ in the position of the allyl group and in the conformation of the ethoxycarbonyl substituent. It is proposed that the (I) → (II) solid-state transformation involves the migration of the propylene chain of the allylthio substituent to the same position it occupies in (III), that the molecular structure of (II) therefore resembles that of (III) and that the molecular packing of (II) resembles that of (I). The molecular structure and the packing of (I), and the relative configuration of the propylene chain in (III), indicate two mechanisms for allyl migration: an intermolecular transfer or an intramolecular Cope rearrangement.

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