C(6)	0.7629 (2)	0.03190 (4)	0.1665 (3)	0.0185 (4)
C(7)	0.7390 (2)	0.00035 (4)	0.3338 (3)	0.0184 (4)
C(8)	0.7566 (2)	−0.03184 (4)	0.1694 (3)	0.0185 (4)
C(9)	0.7315 (2)	−0.06341 (4)	0.3348 (3)	0.0183 (4)
C(10)	0.7481 (2)	−0.09552 (4)	0.1699 (3)	0.0215 (4)
C(11)	0.7212 (2)	−0.12701 (4)	0.3342 (4)	0.0274 (5)

Table 2. *Selected geometric parameters (Å, °)*

N(1)—C(1)	1.494 (2)	C(6)—C(7)	1.522 (2)
C(1)—C(2)	1.514 (2)	C(7)—C(8)	1.524 (2)
C(2)—C(3)	1.525 (2)	C(8)—C(9)	1.521 (2)
C(3)—C(4)	1.520 (2)	C(9)—C(10)	1.521 (2)
C(4)—C(5)	1.524 (2)	C(10)—C(11)	1.519 (2)
C(5)—C(6)	1.526 (2)		
N(1)—C(1)—C(2)	111.3 (1)	C(5)—C(6)—C(7)	113.8 (1)
C(1)—C(2)—C(3)	111.7 (1)	C(6)—C(7)—C(8)	113.8 (1)
C(2)—C(3)—C(4)	113.3 (1)	C(7)—C(8)—C(9)	113.9 (1)
C(3)—C(4)—C(5)	113.8 (1)	C(8)—C(9)—C(10)	113.9 (1)
C(4)—C(5)—C(6)	113.6 (1)	C(9)—C(10)—C(11)	113.8 (1)
N(1)—C(1)—C(2)—C(3)	179.4 (1)		
C(1)—C(2)—C(3)—C(4)	−170.0 (1)		
C(2)—C(3)—C(4)—C(5)	178.1 (1)		
C(3)—C(4)—C(5)—C(6)	−177.9 (1)		
C(4)—C(5)—C(6)—C(7)	179.4 (1)		
C(5)—C(6)—C(7)—C(8)	−179.9 (1)		
C(6)—C(7)—C(8)—C(9)	−179.6 (1)		
C(7)—C(8)—C(9)—C(10)	179.7 (1)		
C(8)—C(9)—C(10)—C(11)	−179.4 (1)		

Table 3. *Contact distances (Å)*

Cl(1)···N(1)	3.209 (1)	O(1)···N(1)	2.845 (2)
Cl(1)···N(1^{i})	3.235 (2)	Cl(1)···O(1^{iii})	3.180 (1)
Cl(1)···N(1^{ii})	3.353 (1)	Cl(1)···O(1^{iv})	3.226 (1)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1+z$; (ii) $x, y, 1+z$; (iii) $x-\frac{1}{2}, \frac{1}{2}-y, z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, 1+z$.

The crystal used for analysis was cooled with an Oxford Cryostream system (Cosier & Glazer, 1986).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1038). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Guaianolide 11*β**H*,13-Dihydromicheliolide

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Abstract

The lactone ring of the guaianolide-class sesquiterpene lactone [3*S*-(3α,3aα,9α,9aα,9b*β*)]-3a,4,5,7,8,9,9a,9b-octahydro-9-hydroxy-3,6,9-trimethylazuleno[4,5-*b*]furan-2-(3*H*)-one, $C_{15}H_{22}O_3$, is *trans*-fused to the seven-membered ring. Two molecules are present in the asymmetric unit; they differ only slightly in conformation. The seven-membered ring is in the chair conformation, with the local mirror bisecting the double bond. The lactone is in the envelope conformation, while the other five-membered ring adopts the half chair. The two independent molecules form a hydrogen-bonded dimer, with O···O distances 2.907 (3) and 2.966 (2) Å.

Comment

11*βH*,13-Dihydromicheliolide, (1), is the major compound obtained from the BF_3-mediated rearrangement of 11*βH*,13-dihydroparthenolide (Parodi, Fronczek & Fischer, 1989). The crystal structure of (1) was determined in order to confirm the relative configurations of the five asymmetric C atoms, and to compare its conformation and hydrogen bonding with those of micheliolide (Castañeda-Acosta, Fronczek & Fischer, 1991). The two independent molecules of the asymmetric unit have very similar conformations. The 17 endocyclic torsion angles of the two exhibit a mean difference of 3.4°, with the largest deviation, about C9—C10, of 8.4 (2)°. The most notable conformational difference between the two molecules involves the OH group, in which the O—H bond is *anti* to C3 in the *A* molecule and *anti* to C5 in

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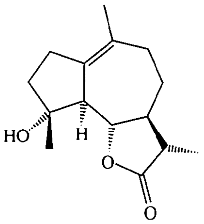
the *B* molecule, in order to maximize hydrogen-bonding interactions, as described below. The overall conformation is similar to that of micheliolide (Castañeda-Acosta *et al.*, 1991), except for that of the lactone ring, which is a half chair in micheliolide. Bond distances for the two independent molecules (Table 2) agree well. The r.m.s. difference in the 20 intramolecular distances is 0.006 Å, and the largest individual difference is 0.012 (4) Å for O3—C4.



(1)

The two independent molecules form hydrogen-bonded dimers, as illustrated in Fig. 1. OH group O3*A* donates an intermolecular hydrogen bond to OH group O3*B*, with an O···O distance of 2.907 (3) Å and an angle about H of 164 (4)°. The OH group of the *B* molecule is involved in an intermolecular interaction which may be viewed as a bifurcated hydrogen bond. Its shortest contact [2.966 (2) Å] is to O1*A*; however, the angle about H is 140 (3)°. The H atom points more nearly at the carbonyl O atom O2*A*, with an O—H···O angle of 166 (3)° and a O···O distance of 3.406 (3) Å.

It may be noted that there exists an alternate possible mode of hydrogen-bonded dimer formation, namely that with the two OH groups with switched donor and acceptor identities, and O3*A* donating a bifurcated interaction to O1*B* and O2*B*. That mode is not utilized in this structure; however, micheliolide exhibits similar dimer formation, and the two modes coexist with disordered H-atom positions (Castañeda-Acosta *et al.*, 1991). The two molecules are not independent, but are related by a twofold axis in that case.

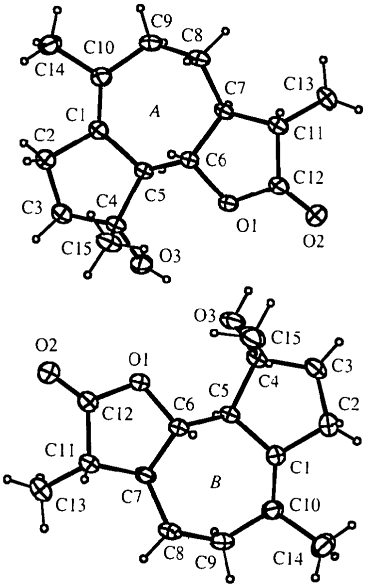


Fig. 1. The two independent molecules, with ellipsoids at the 40% probability level and H atoms represented with arbitrary radii.

Fig. 2 illustrates the packing, which features an approximate 2_1 screw axis parallel to the *a* axis at $y = 0.83$, $z = 0.05$. The screw axis is inexact, with the mean deviation of the 18 heavy atoms in molecule *A* and their equivalents in molecule *B* of 1.40 Å. The largest difference, 3.43 Å, is for O3, as a result of the difference in hydrogen bonding. The approximate screw axis is much more exact when atoms in the vicinity of O3 are excluded. The 14 atoms remaining when C3, C4, C15 and O3 are excluded exhibit a mean deviation of 0.95 Å.

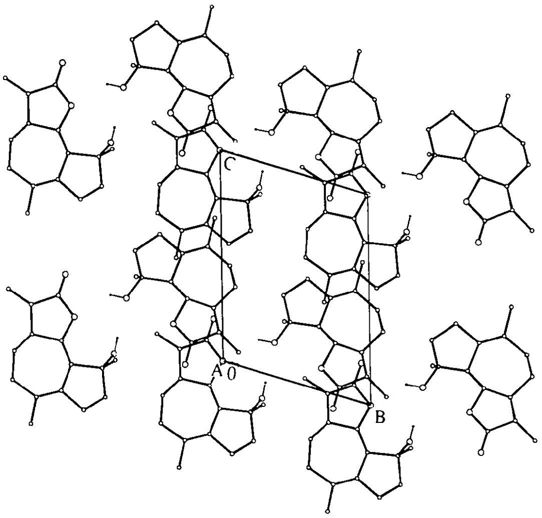


Fig. 2. Projection of the structure down the *a* axis, illustrating the approximate 2_1 screw axis.

The structures of several closely related compounds have been reported. These include arteglasin A (Schmalle, Klaska & Jarchow, 1977), berlandin (Cox, Sim & Herz, 1975), 3α-epoxypumilin (Seaman, Malcolm, Fronczek, Lee & Fischer, 1984), 9α-thiophenoxy-11*β**H*,13-dihydromicheliolide (Castañeda-Acosta, Fronczek & Fischer, 1992), and pumilin (Korp *et al.*, 1982).

Experimental

Compound (1) was prepared by the BF_3-mediated rearrangement of 11*β**H*,13-dihydroparthenolide (Parodi, Fronczek & Fischer, 1989). Crystals were grown from ethyl acetate–hexane.

Crystal data

$C_{15}H_{22}O_3$	Mo $K\alpha$ radiation
$M_r = 250.34$	$\lambda = 0.71073$ Å

Triclinic
$P1$
$a = 8.5033\,(8)$ Å
$b = 8.8856\,(6)$ Å
$c = 10.773\,(1)$ Å
$\alpha = 101.29\,(1)^\circ$
$\beta = 97.70\,(1)^\circ$
$\gamma = 118.42\,(1)^\circ$
$V = 677.2\,(3)$ Å^3
$Z = 2$
$D_x = 1.228$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 9$–13°
$\mu = 0.078$ mm^{-1}
$T = 299$ K
Needle fragment
$0.75 \times 0.52 \times 0.42$ mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3099 measured reflections
3099 independent reflections
2776 observed reflections $[I > 2\sigma(I)]$

$\theta_{\max} = 27.5^\circ$
$h = 0 \rightarrow 11$
$k = -11 \rightarrow 10$
$l = -13 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F
$R = 0.040$
$wR = 0.048$
$S = 2.72$
2776 reflections
331 parameters
H atoms: see below
$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0004F_o^4]$
$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.06$ e Å^{-3}
Extinction correction: isotropic (Zachariasen, 1963)
Extinction coefficient: $0.13\,(2) \times 10^{-5}$

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)
Absolute configuration: assumed to correspond to accepted absolute configuration of sesquiterpene lactones from higher plants (Fischer, Olivier & Fischer, 1979)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

$U_{\rm iso}$ for H atoms; $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
O1*A*	0.0000	0.0000	0.0000	0.0467 (5)
O2*A*	−0.0228 (3)	−0.0571 (2)	0.1897 (2)	0.0669 (7)
O3*A*	−0.0534 (2)	0.2618 (2)	−0.1212 (2)	0.0527 (5)
C1*A*	−0.0774 (3)	−0.0988 (2)	−0.3707 (2)	0.0362 (6)
C2*A*	−0.0151 (3)	0.0525 (3)	−0.4327 (2)	0.0483 (7)
C3*A*	−0.0274 (4)	0.1977 (3)	−0.3402 (2)	0.0503 (7)
C4*A*	0.0209 (3)	0.1812 (2)	−0.2044 (2)	0.0417 (6)
C5*A*	−0.0845 (3)	−0.0262 (2)	−0.2315 (2)	0.0340 (5)
C6*A*	−0.0123 (3)	−0.0924 (2)	−0.1327 (2)	0.0351 (6)
C7*A*	−0.1314 (3)	−0.2894 (2)	−0.1422 (2)	0.0359 (6)
C8*A*	−0.1095 (3)	−0.4125 (3)	−0.2490 (2)	0.0483 (7)
C9*A*	−0.1974 (4)	−0.4276 (3)	−0.3868 (3)	0.0553 (8)
C10*A*	−0.1213 (3)	−0.2644 (3)	−0.4352 (2)	0.0396 (6)
C11*A*	−0.0736 (3)	−0.2906 (2)	−0.0035 (2)	0.0422 (6)
C12*A*	−0.0305 (3)	−0.1085 (3)	0.0763 (2)	0.0452 (7)
C13*A*	−0.2097 (4)	−0.4446 (3)	0.0382 (3)	0.0605 (9)
C14*A*	−0.1045 (3)	−0.3047 (3)	−0.5735 (2)	0.0483 (7)
C15*A*	0.2281 (4)	0.2694 (3)	−0.1507 (3)	0.0553 (8)
O1*B*	0.4020 (2)	0.6677 (2)	0.1061 (2)	0.0508 (5)
O2*B*	0.4767 (3)	0.7420 (3)	−0.0721 (2)	0.0864 (9)
O3*B*	0.0829 (2)	0.3534 (2)	0.1612 (2)	0.0534 (6)
C1*B*	0.3384 (3)	0.7353 (3)	0.4525 (2)	0.0399 (6)
C2*B*	0.2845 (4)	0.5835 (3)	0.5131 (3)	0.0611 (9)
C3*B*	0.1521 (4)	0.4166 (3)	0.3989 (3)	0.0575 (8)
C4*B*	0.2282 (3)	0.4567 (3)	0.2817 (2)	0.0414 (6)
C5*B*	0.2876 (3)	0.6567 (2)	0.3034 (2)	0.0352 (6)
C6*B*	0.4410 (3)	0.7632 (2)	0.2438 (2)	0.0367 (6)
C7*B*	0.4691 (3)	0.9435 (2)	0.2378 (2)	0.0360 (6)
C8*B*	0.5605 (3)	1.0892 (3)	0.3682 (2)	0.0444 (7)
C9*B*	0.4385 (4)	1.0557 (3)	0.4624 (3)	0.0524 (8)
C10*B*	0.4050 (3)	0.9061 (3)	0.5216 (2)	0.0426 (7)
C11*B*	0.5693 (3)	0.9756 (3)	0.1310 (2)	0.0445 (7)
C12*B*	0.4810 (4)	0.7872 (3)	0.0405 (2)	0.0539 (8)
C13*B*	0.5613 (5)	1.1050 (3)	0.0614 (3)	0.069 (1)
C14*B*	0.4356 (4)	0.9589 (4)	0.6690 (3)	0.0586 (9)
C15*B*	0.3829 (4)	0.4192 (3)	0.2768 (3)	0.0581 (8)
H3O*A*	0.006 (4)	0.288 (4)	−0.040 (3)	0.08 (1)
H3O*B*	0.056 (4)	0.244 (4)	0.153 (3)	0.09 (1)

Table 2. *Selected geometric parameters (Å, °)*

O1*A*—C6*A*	1.465 (2)	O1*B*—C6*B*	1.462 (3)
O1*A*—C12*A*	1.343 (3)	O1*B*—C12*B*	1.350 (3)
O2*A*—C12*A*	1.198 (3)	O2*B*—C12*B*	1.191 (3)
O3*A*—C4*A*	1.430 (3)	O3*B*—C4*B*	1.442 (3)
O3*A*—H3O*A*	0.88 (3)	O3*B*—H3O*B*	0.87 (4)
C1*A*—C2*A*	1.517 (3)	C1*B*—C2*B*	1.515 (4)
C1*A*—C5*A*	1.533 (3)	C1*B*—C5*B*	1.530 (3)
C1*A*—C10*A*	1.340 (3)	C1*B*—C10*B*	1.343 (3)
C2*A*—C3*A*	1.524 (4)	C2*B*—C3*B*	1.518 (3)
C3*A*—C4*A*	1.520 (4)	C3*B*—C4*B*	1.522 (4)
C4*A*—C5*A*	1.559 (3)	C4*B*—C5*B*	1.555 (3)
C4*A*—C15*A*	1.512 (4)	C4*B*—C15*B*	1.508 (5)
C5*A*—C6*A*	1.507 (4)	C5*B*—C6*B*	1.515 (3)
C6*A*—C7*A*	1.521 (3)	C6*B*—C7*B*	1.519 (3)
C7*A*—C8*A*	1.522 (4)	C7*B*—C8*B*	1.513 (3)
C7*A*—C11*A*	1.513 (3)	C7*B*—C11*B*	1.514 (4)
C8*A*—C9*A*	1.520 (4)	C8*B*—C9*B*	1.516 (4)
C9*A*—C10*A*	1.513 (4)	C9*B*—C10*B*	1.509 (4)
C10*A*—C14*A*	1.505 (4)	C10*B*—C14*B*	1.514 (4)
C11*A*—C12*A*	1.516 (3)	C11*B*—C12*B*	1.511 (3)
C11*A*—C13*A*	1.512 (3)	C11*B*—C13*B*	1.513 (5)
C6*A*—O1*A*—C12*A*	110.3 (1)	C6*B*—O1*B*—C12*B*	109.4 (2)
C4*A*—O3*A*—H3O*A*	108 (2)	C4*B*—O3*B*—H3O*B*	103 (2)
C2*A*—C1*A*—C5*A*	107.8 (2)	C2*B*—C1*B*—C5*B*	108.5 (2)
C2*A*—C1*A*—C10*A*	122.6 (2)	C2*B*—C1*B*—C10*B*	123.6 (2)
C5*A*—C1*A*—C10*A*	129.5 (2)	C5*B*—C1*B*—C10*B*	127.7 (2)
C1*A*—C2*A*—C3*A*	104.5 (2)	C1*B*—C2*B*—C3*B*	103.9 (2)
C2*A*—C3*A*—C4*A*	104.8 (2)	C2*B*—C3*B*—C4*B*	104.5 (2)
O3*A*—C4*A*—C3*A*	107.6 (2)	O3*B*—C4*B*—C3*B*	110.6 (2)
O3*A*—C4*A*—C5*A*	111.5 (2)	O3*B*—C4*B*—C5*B*	107.5 (2)
O3*A*—C4*A*—C15*A*	111.1 (2)	O3*B*—C4*B*—C15*B*	110.0 (2)
C3*A*—C4*A*—C5*A*	101.8 (2)	C3*B*—C4*B*—C5*B*	102.7 (2)
C3*A*—C4*A*—C15*A*	111.4 (2)	C3*B*—C4*B*—C15*B*	111.1 (3)
C5*A*—C4*A*—C15*A*	113.0 (2)	C5*B*—C4*B*—C15*B*	114.6 (2)
C1*A*—C5*A*—C4*A*	104.4 (2)	C1*B*—C5*B*—C4*B*	104.3 (2)
C1*A*—C5*A*—C6*A*	112.8 (2)	C1*B*—C5*B*—C6*B*	112.5 (1)
C4*A*—C5*A*—C6*A*	115.5 (1)	C4*B*—C5*B*—C6*B*	116.3 (2)
O1*A*—C6*A*—C5*A*	109.9 (2)	O1*B*—C6*B*—C5*B*	110.9 (1)
O1*A*—C6*A*—C7*A*	103.1 (2)	O1*B*—C6*B*—C7*B*	102.9 (2)
C5*A*—C6*A*—C7*A*	116.8 (2)	C5*B*—C6*B*—C7*B*	116.1 (2)
C6*A*—C7*A*—C8*A*	112.9 (2)	C6*B*—C7*B*—C8*B*	114.9 (2)
C6*A*—C7*A*—C11*A*	102.4 (1)	C6*B*—C7*B*—C11*B*	101.5 (2)
C8*A*—C7*A*—C11*A*	115.8 (2)	C8*B*—C7*B*—C11*B*	117.1 (2)
C7*A*—C8*A*—C9*A*	113.2 (3)	C7*B*—C8*B*—C9*B*	113.0 (2)
C8*A*—C9*A*—C10*A*	119.7 (2)	C8*B*—C9*B*—C10*B*	117.8 (3)
C1*A*—C10*A*—C9*A*	127.0 (2)	C1*B*—C10*B*—C9*B*	124.8 (2)
C1*A*—C10*A*—C14*A*	119.9 (2)	C1*B*—C10*B*—C14*B*	120.8 (2)
C9*A*—C10*A*—C14*A*	112.9 (2)	C9*B*—C10*B*—C14*B*	114.2 (2)
C7*A*—C11*A*—C12*A*	101.8 (2)	C7*B*—C11*B*—C12*B*	101.5 (2)
C7*A*—C11*A*—C13*A*	116.9 (2)	C7*B*—C11*B*—C13*B*	117.3 (3)
C12*A*—C11*A*—C13*A*	113.7 (2)	C12*B*—C11*B*—C13*B*	113.1 (2)
O1*A*—C12*A*—O2*A*	120.9 (2)	O1*B*—C12*B*—O2*B*	122.2 (2)
O1*A*—C12*A*—C11*A*	109.8 (2)	O1*B*—C12*B*—C11*B*	109.8 (2)
O2*A*—C12*A*—C11*A*	129.4 (2)	O2*B*—C12*B*—C11*B*	128.0 (3)

The structure was solved by direct methods using *RANTAN* (Yao, 1981) and *DIRDIF* (Beurskens, 1984). An *E* map generated using *RANTAN* contained a recognizable fragment of one of the two independent molecules. *DIRDIF* was used to expand this fragment to the full structure. The OH H atoms were refined with isotropic displacement parameters, while others were placed in calculated positions guided by difference maps, with C—H 0.95 Å and $B_{\rm iso}$(H) = 1.3$B_{\rm eq}$(C).

Data collection: CAD-4 diffractometer system (Enraf–Nonius, 1977). Cell refinement: CAD-4 diffractometer system. Data reduction: *PROCESS* in *MolEN* (Fair, 1990). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *CIF IN* in *MolEN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with a stereodrawing of the packing, have been deposited with the IUCr (Reference: BK1193). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Kryptoracemic Hydroperoxide

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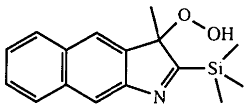
Abstract

2-Trimethylsilyl-3-methyl-3*H*-benz[*f*]indol-3-yl hydroperoxide, $C_{16}H_{19}NO_2Si$, crystallizes in space group $P2_1$ with two independent molecules of opposite handedness in the asymmetric unit. The two differ by a 60° rotation of the trimethylsilyl group with respect to the indole ring. The hydroperoxide O—O distances in the two molecules are 1.453 (2) and 1.465 (3) Å. The hydroperoxide groups form intermolecular hydrogen bonds of O···N(indole) lengths 2.763 (3) and 2.813 (3) Å.

Comment

Of the several outcomes of crystallization from a racemic solution, one possibility is the formation of a kryptoracemate, in which the space group is enantiomorphic, but the asymmetric unit contains racemic pairs. This is by far the least common, according to Bernal (1995*a*), who finds less than three dozen examples. In most of the known cases, the two enantiomeric molecules are related by a pseudocenter (Bernal, 1995*b*). The present structure, (I), has no pseudocenters and the two molecules differ in conformation, primarily in the rotation of the trimethylsilyl group about the Si—C(indole) bond. In the *A* molecule, illustrated in Fig. 1(*a*), the C14*A* methyl group is approximately eclipsed by a C atom of the indole ring, the C2*A*—C1*A*—Si1*A*—C14*A* torsion angle being 8.1 (3)°. In the *B* molecule, the C16*B* methyl group is almost eclipsed by the N atom of the indole, forming the torsion angle C16*B*—Si1*B*—C1*B*—N1*B* of 4.9 (3)°. The disposition of the hydroperoxy group with respect to the ring system is similar in the two molecules, with C13—C2—O1—O2 torsion angles of −163.7 (2) for *A* and 174.6 (2)° for *B*. The mean difference between the 22 bond distances in the two molecules is 0.007 Å, and the largest individual difference is 0.020 (4) Å for Si—C14.



(I)

The hydroperoxide O—O distances, 1.453 (2) for *A* and 1.465 (3) Å for *B*, are typical. A search of the