

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 $B_{\text{iso}}(\text{H}) = 1.3B_{\text{eq}}(\text{C})$.

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: *ORTEPII* (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.

References

- Beurskens, P. T. (1984). *DIRDIF. Direct Methods for Difference Structures – an Automatic Procedure for Phase Extension and Refinement of Difference Structure Factors*. Technical Report 1984/1. Crystallography Laboratory, Toernooiveld, 6525 ED Nijmegen, The Netherlands.
- Castañeda-Acosta, J., Fronczek, F. R. & Fischer, N. H. (1991). *Acta Cryst.* **C47**, 2702–2704.
- Castañeda-Acosta, J., Fronczek, F. R. & Fischer, N. H. (1992). *Acta Cryst.* **C48**, 179–181.
- Cox, P. J., Sim, G. A. & Herz, W. (1975). *J. Chem. Soc. Perkin Trans. 2*, pp. 459–463.
- Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Fischer, N. H., Olivier, E. J. & Fischer, H. D. (1979). *Progress in the Chemistry of Organic Natural Products*, Vol. 38, edited by W. Herz, H. Grisebach & G. B. Kirby. Vienna: Springer.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Korp, J. D., Bernal, I., Fischer, N. H., Leonard, C., Lee, I.-Y. & LeVan, N. (1982). *J. Heterocycl. Chem.* **19**, 181–187.
- Parodi, F. J., Fronczek, F. R. & Fischer, N. H. (1989). *J. Nat. Prod.* **52**, 554–566.
- Schmalle, H. W., Klaska, K. H. & Jarchow, O. (1977). *Acta Cryst.* **B33**, 2213–2217.
- Seaman, F. C., Malcolm, A. J., Fronczek, F. R., Lee, I.-Y. & Fischer, N. H. (1984). *Phytochemistry*, **23**, 817–822.
- Yao, J.-X. (1981). *Acta Cryst.* **A37**, 642–644.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1996). **C52**, 1266–1268

A Kryptoracemic Hydroperoxide

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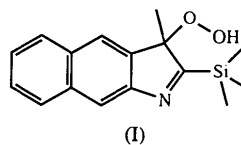
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Abstract

2-Trimethylsilyl-3-methyl-3*H*-benz[*f*]indol-3-yl hydroperoxide, C₁₆H₁₉NO₂Si, crystallizes in space group *P*2₁ 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.

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

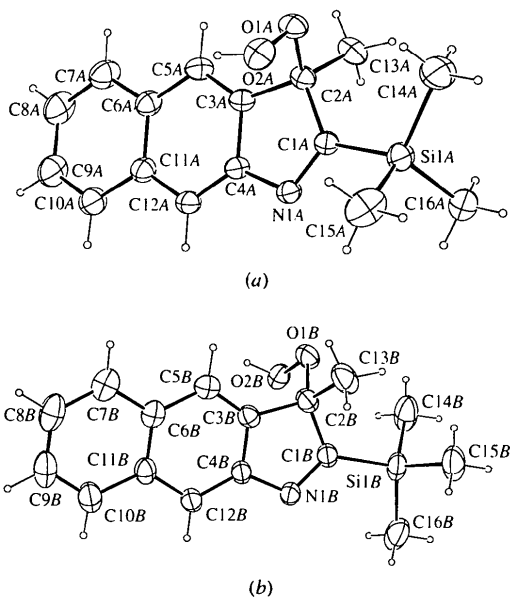


Fig. 1. The two independent enantiomeric molecules, (a) molecule A and (b) molecule B, with ellipsoids at the 30% probability level and H atoms represented by circles of arbitrary radii.

Cambridge Structural Database (CSD) (Allen, Kennard & Taylor, 1983) yielded 39 structures containing this substructure, with $R < 0.10$, coordinates reported, and the O—O distance not obviously shortened by large displacement parameters. The O—O distances of this set ranged from 1.42 (1) to 1.48 (1) Å, with a mean value of 1.462 Å. Reference codes for these 39 structures are included in the supplementary material. A search of the CSD for the benzindole substructure found in the present compound yielded no hits.

Packing is illustrated in Fig. 2. Intermolecular interactions are seen to be dominated by OOH···N hydrogen bonds, forming chains of alternating A and B molecules in the c direction. In the O2A—H2OA···N1B($x, y, z -$

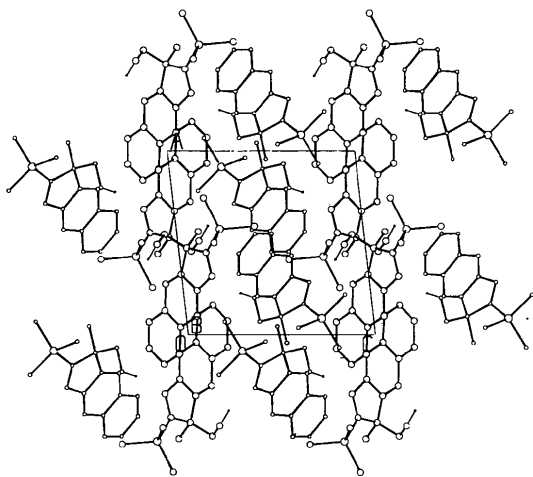


Fig. 2. Projection of the structure down the symmetry axis. Molecule A is represented by larger circles.

1) hydrogen bond, the O···N distance is 2.763 (3) Å and the angle about H is 161 (3)°. Values for the O2B—H2OB···N1A interaction are 2.813 (3) Å and 162 (3)°. The kryptoracemic nature of the packing would seem to be related to the inability of the molecule to form these hydrogen bonds utilizing glide planes.

Experimental

The compound was prepared by Pd-catalyzed cyclization between 1-trimethylsilylpropyne and 3-bromo-2-aminonaphthalene. TLC chromatography over silica gel, eluting with hexane–ethyl acetate (3:1), yielded the title compound with $R_f = 0.65$ and m.p. = 389 K. Crystals for the X-ray analysis were grown by slow evaporation of the eluent.

Crystal data

$C_{16}H_{19}NO_2Si$
 $M_r = 285.42$
 Monoclinic
 $P2_1$
 $a = 9.734 (1) \text{ \AA}$
 $b = 17.075 (1) \text{ \AA}$
 $c = 9.764 (1) \text{ \AA}$
 $\beta = 96.40 (1)^\circ$
 $V = 1612.8 (4) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.176 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 $\lambda = 1.54184 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 20\text{--}25^\circ$
 $\mu = 1.28 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Prism
 $0.38 \times 0.25 \times 0.23 \text{ mm}$
 Golden yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\theta/2\theta$ scans
 Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.894$, $T_{\max} = 0.998$
 6931 measured reflections
 6562 independent reflections

5807 observed reflections [$I > 3\sigma(I)$]
 $R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 74.88^\circ$
 $h = 0 \rightarrow 12$
 $k = -21 \rightarrow 21$
 $l = -12 \rightarrow 11$
 3 standard reflections
 frequency: 120 min
 intensity decay: 5.4%

Refinement

Refinement on F
 $R = 0.041$
 $wR = 0.048$
 $S = 2.146$
 5807 reflections
 369 parameters
 H atoms: see below
 $w = 4F_o^2 / [\sigma^2(F_o^2) + 0.0004F_o^4]$
 $(\Delta/\sigma)_{\text{max}} = 0.020$

$\Delta\rho_{\text{max}} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.11 \text{ e \AA}^{-3}$
 Extinction correction: isotropic (Zachariasen, 1963)
 Extinction coefficient: $0.17 (2) \times 10^{-5}$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	U_{eq}
Si1A	0.57600 (6)	1.00000	0.23086 (7)	0.0546 (2)
O1A	0.5467 (2)	0.88827 (9)	-0.0659 (1)	0.0516 (4)
O2A	0.4903 (2)	0.9637 (1)	-0.1125 (2)	0.0619 (5)

N1A	0.3159 (2)	0.9352 (1)	0.1602 (2)	0.0453 (4)	O1A—C2A—C13A	104.3 (2)	O1B—C2B—C13B	104.1 (2)
C1A	0.4455 (2)	0.9287 (1)	0.1430 (2)	0.0434 (5)	C1A—C2A—C3A	100.9 (2)	C1B—C2B—C3B	101.2 (2)
C2A	0.4719 (2)	0.8621 (1)	0.0434 (2)	0.0432 (5)	C1A—C2A—C13A	112.3 (2)	C1B—C2B—C13B	114.1 (2)
C3A	0.3257 (2)	0.8358 (1)	-0.0022 (2)	0.0418 (5)	C3A—C2A—C13A	113.1 (2)	C3B—C2B—C13B	113.3 (2)
C4A	0.2380 (2)	0.8807 (1)	0.0729 (2)	0.0416 (5)	C2A—C3A—C4A	106.9 (2)	C2B—C3B—C4B	107.1 (2)
C5A	0.2733 (2)	0.7797 (1)	-0.0903 (2)	0.0504 (6)	C2A—C3A—C5A	132.5 (2)	C2B—C3B—C5B	131.8 (2)
C6A	0.1274 (2)	0.7669 (1)	-0.1106 (2)	0.0508 (6)	C4A—C3A—C5A	120.6 (2)	C4B—C3B—C5B	121.1 (2)
C7A	0.0668 (3)	0.7091 (2)	-0.2016 (3)	0.0699 (8)	N1A—C4A—C3A	110.7 (2)	N1B—C4B—C3B	110.8 (2)
C8A	-0.0731 (3)	0.6967 (2)	-0.2171 (3)	0.0782 (9)	N1A—C4A—C12A	127.2 (2)	N1B—C4B—C12B	127.5 (2)
C9A	-0.1584 (3)	0.7438 (2)	-0.1467 (3)	0.0772 (8)	C3A—C4A—C12A	122.1 (2)	C3B—C4B—C12B	121.6 (2)
C10A	-0.1040 (2)	0.8008 (2)	-0.0596 (3)	0.0646 (7)	C3A—C5A—C6A	119.8 (2)	C3B—C5B—C6B	119.5 (2)
C11A	0.0402 (2)	0.8135 (1)	-0.0362 (2)	0.0495 (6)	C5A—C6A—C7A	122.2 (2)	C5B—C6B—C7B	121.8 (2)
C12A	0.0982 (2)	0.8712 (1)	0.0569 (2)	0.0482 (5)	C5A—C6A—C11A	119.0 (2)	C5B—C6B—C11B	119.3 (2)
C13A	0.5616 (2)	0.7977 (2)	0.1134 (3)	0.0606 (7)	C7A—C6A—C11A	118.8 (2)	C7B—C6B—C11B	118.9 (2)
C14A	0.7462 (3)	0.9897 (2)	0.1629 (3)	0.095 (1)	C6A—C7A—C8A	121.1 (3)	C6B—C7B—C8B	121.0 (2)
C15A	0.5003 (4)	1.0978 (2)	0.1922 (3)	0.084 (1)	C7A—C8A—C9A	119.9 (3)	C7B—C8B—C9B	119.9 (3)
C16A	0.5919 (3)	0.9785 (2)	0.4173 (3)	0.0747 (9)	C8A—C9A—C10A	120.7 (2)	C8B—C9B—C10B	121.6 (3)
Si1B	0.08680 (8)	1.04709 (5)	0.72225 (7)	0.0705 (2)	C9A—C10A—C11A	121.4 (2)	C9B—C10B—C11B	120.5 (2)
O1B	0.0701 (2)	0.9705 (1)	0.3884 (2)	0.0640 (5)	C3A—C11A—C10A	118.1 (2)	C6B—C11B—C10B	118.0 (2)
O2B	0.1987 (2)	1.0127 (1)	0.3733 (2)	0.0598 (4)	C6A—C11A—C12A	120.0 (2)	C6B—C11B—C12B	119.8 (2)
N1B	0.2843 (2)	0.9318 (1)	0.6767 (2)	0.0525 (5)	C10A—C11A—C12A	121.9 (2)	C10B—C11B—C12B	122.2 (2)
C1B	0.1647 (2)	0.9609 (1)	0.6334 (2)	0.0540 (6)	C4A—C12A—C11A	118.6 (2)	C4B—C12B—C11B	118.6 (2)
C2B	0.0965 (2)	0.9179 (2)	0.5038 (2)	0.0549 (6)				
C3B	0.2041 (2)	0.8573 (1)	0.4832 (2)	0.0494 (5)				
C4B	0.3133 (2)	0.8681 (1)	0.5884 (2)	0.0481 (5)				
C5B	0.2068 (2)	0.7987 (1)	0.3906 (2)	0.0548 (6)				
C6B	0.3227 (2)	0.7479 (1)	0.3982 (2)	0.0540 (6)				
C7B	0.3288 (3)	0.6839 (2)	0.3064 (3)	0.0708 (8)				
C8B	0.4391 (3)	0.6347 (2)	0.3172 (3)	0.0820 (9)				
C9B	0.5491 (3)	0.6481 (2)	0.4160 (3)	0.0821 (8)				
C10B	0.5496 (3)	0.7092 (2)	0.5057 (3)	0.0721 (8)				
C11B	0.4348 (2)	0.7606 (1)	0.5012 (2)	0.0539 (6)				
C12B	0.4278 (2)	0.8223 (1)	0.5983 (2)	0.0544 (6)				
C13B	-0.0440 (3)	0.8831 (2)	0.5204 (3)	0.084 (1)				
C14B	0.0369 (4)	1.1226 (2)	0.5914 (3)	0.111 (1)				
C15B	-0.0687 (3)	1.0143 (3)	0.7989 (3)	0.107 (1)				
C16B	0.2150 (4)	1.0829 (2)	0.8614 (3)	0.096 (1)				

Table 2. Selected geometric parameters (Å, °)

Si1A—C1A	1.894 (2)	Si1B—C1B	1.909 (3)
Si1A—C14A	1.861 (3)	Si1B—C14B	1.841 (3)
Si1A—C15A	1.847 (3)	Si1B—C15B	1.849 (4)
Si1A—C16A	1.847 (3)	Si1B—C16B	1.844 (3)
O1A—O2A	1.453 (2)	O1B—O2B	1.465 (3)
O1A—C2A	1.430 (3)	O1B—C2B	1.442 (3)
O2A—H2O _A	0.95 (3)	O2B—H2O _B	0.95 (3)
N1A—C1A	1.296 (3)	N1B—C1B	1.293 (3)
N1A—C4A	1.423 (3)	N1B—C4B	1.435 (3)
C1A—C2A	1.536 (3)	C1B—C2B	1.547 (3)
C2A—C3A	1.511 (3)	C2B—C3B	1.502 (3)
C2A—C13A	1.518 (3)	C2B—C13B	1.516 (4)
C3A—C4A	1.411 (3)	C3B—C4B	1.406 (3)
C3A—C5A	1.350 (3)	C3B—C5B	1.351 (3)
C4A—C12A	1.361 (3)	C4B—C12B	1.357 (3)
C5A—C6A	1.428 (3)	C5B—C6B	1.419 (3)
C6A—C7A	1.413 (3)	C6B—C7B	1.418 (4)
C6A—C11A	1.421 (3)	C6B—C11B	1.415 (3)
C7A—C8A	1.369 (4)	C7B—C8B	1.359 (4)
C8A—C9A	1.391 (4)	C8B—C9B	1.378 (4)
C9A—C10A	1.361 (4)	C9B—C10B	1.362 (4)
C10A—C11A	1.413 (3)	C10B—C11B	1.418 (4)
C11A—C12A	1.415 (3)	C11B—C12B	1.424 (3)
C1A—Si1A—C14A	110.9 (1)	C1B—Si1B—C14B	108.2 (1)
C1A—Si1A—C15A	104.9 (1)	C1B—Si1B—C15B	109.6 (2)
C1A—Si1A—C16A	107.3 (1)	C1B—Si1B—C16B	108.7 (1)
C14A—Si1A—C15A	111.3 (2)	C14B—Si1B—C15B	109.2 (2)
C14A—Si1A—C16A	110.7 (1)	C14B—Si1B—C16B	112.6 (2)
C15A—Si1A—C16A	111.6 (1)	C15B—Si1B—C16B	108.7 (2)
O2A—O1A—C2A	107.7 (1)	O2B—O1B—C2B	107.8 (1)
O1A—O2A—H2O _A	103 (1)	O1B—O2B—H2O _B	93 (1)
C1A—N1A—C4A	109.2 (2)	C1B—N1B—C4B	108.9 (2)
Si1A—C1A—N1A	120.0 (2)	Si1B—C1B—N1B	122.4 (2)
Si1A—C1A—C2A	127.7 (1)	Si1B—C1B—C2B	125.6 (2)
N1A—C1A—C2A	112.2 (2)	N1B—C1B—C2B	112.0 (2)
O1A—C2A—C1A	112.1 (2)	O1B—C2B—C1B	111.5 (2)
O1A—C2A—C3A	114.5 (2)	O1B—C2B—C3B	113.0 (2)

The structure with the opposite direction of the polar axis was refined under identical circumstances, yielding $R = 0.046$, $wR = 0.054$ and $S = 2.433$. The better refinement is reported. The structure was solved by direct methods. C—H H atoms were visible in difference maps, but were placed in calculated positions, with C—H = 0.95 Å and $B_{iso}(H) = 1.3B_{eq}(C)$. Hydroperoxy H atoms were refined with isotropic displacement parameters.

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 solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (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 have been deposited with the IUCr (Reference: TA1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Allen, F. H., Kennard, O. & Taylor, R. (1983). *Acc. Chem. Res.* **16**, 146–153.
- Bernal, I. (1995a). ACA Annual Meeting, Montreal, Quebec, Canada. Abstract 4a.1.c.
- Bernal, I. (1995b). Private communication.
- Enraf-Nonius (1977). *CAD-4 Operations Manual*. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.