

## Refinement

Refinement on  $F^2$  $R(F) = 0.0414$  $wR(F^2) = 0.1213$  $S = 1.105$ 

2335 reflections

166 parameters

H atoms riding

 $w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 0.3353P]$ ,where  $P = (F_o^2 + 2F_c^2)/3$  $\Delta\rho_{\max} = 0.495 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.381 \text{ e } \text{\AA}^{-3}$ Atomic scattering factors  
from *International Tables  
for Crystallography* (1992,  
Vol. C, Tables 4.2.6.8 and  
6.1.1.4)Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

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

	x	y	z	$U_{eq}$
O1	0.3983 (2)	0.5726 (2)	0.2975 (2)	0.0724 (6)
C2	0.3885 (2)	0.6856 (3)	0.2155 (3)	0.0689 (7)
C3	0.2765 (2)	0.6910 (3)	0.1319 (3)	0.0635 (7)
C4	0.1795 (2)	0.6364 (3)	0.1783 (3)	0.0615 (6)
C4a	0.2029 (2)	0.5680 (3)	0.2968 (3)	0.0591 (6)
C5	0.1217 (2)	0.5262 (3)	0.3588 (3)	0.0659 (7)
C6	0.1451 (2)	0.4631 (3)	0.4688 (3)	0.0651 (7)
C7	0.2535 (2)	0.4388 (3)	0.5229 (3)	0.0610 (6)
C8	0.3362 (2)	0.4778 (3)	0.4624 (3)	0.0635 (7)
C8a	0.3117 (2)	0.5423 (3)	0.3522 (3)	0.0614 (6)
C9	0.2155 (3)	0.5773 (3)	0.0671 (3)	0.0671 (7)
C10	0.4055 (3)	0.8081 (4)	0.2918 (4)	0.0863 (10)
C11	0.4779 (3)	0.6652 (5)	0.1418 (3)	0.0839 (10)
O12	0.2861 (2)	0.3780 (2)	0.6317 (2)	0.0697 (5)
C13	0.2051 (3)	0.3546 (4)	0.7053 (3)	0.0847 (10)
C14	0.26943 (8)	0.41981 (8)	0.07565 (9)	0.0867 (3)
C15	0.13757 (8)	0.60868 (10)	-0.07848 (8)	0.0845 (3)
Br16	0.04460 (3)	0.73515 (4)	0.14835 (3)	0.0753 (2)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O1—C8a	1.370 (3)	C4a—C5	1.393 (4)
O1—C2	1.465 (4)	C4a—C8a	1.402 (4)
C2—C10	1.507 (5)	C5—C6	1.367 (4)
C2—C11	1.516 (4)	C6—C7	1.392 (4)
C2—C3	1.524 (4)	C7—O12	1.355 (4)
C3—C9	1.499 (4)	C7—C8	1.389 (4)
C3—C4	1.507 (4)	C8—C8a	1.376 (4)
C4—C4a	1.473 (4)	C9—C114	1.743 (3)
C4—C9	1.520 (4)	C9—C115	1.754 (3)
C4—Br16	1.933 (3)	O12—C13	1.433 (4)
C8a—O1—C2	118.4 (2)	C8a—C4a—C4	119.7 (3)
O1—C2—C10	108.7 (3)	C6—C5—C4a	122.6 (3)
O1—C2—C11	104.2 (3)	C5—C6—C7	119.8 (3)
C10—C2—C11	112.4 (3)	O12—C7—C8	116.3 (2)
O1—C2—C3	111.7 (2)	O12—C7—C6	124.8 (3)
C10—C2—C3	109.2 (3)	C8—C7—C6	118.9 (3)
C11—C2—C3	110.7 (3)	C8a—C8—C7	120.7 (3)
C9—C3—C4	60.7 (2)	O1—C8a—C8	116.4 (2)
C9—C3—C2	126.0 (3)	O1—C8a—C4a	122.4 (3)
C4—C3—C2	118.4 (3)	C8—C8a—C4a	121.0 (3)
C4a—C4—C3	116.6 (2)	C3—C9—C4	59.9 (2)
C4a—C4—C9	120.1 (2)	C3—C9—C114	122.6 (2)
C3—C4—C9	59.4 (2)	C4—C9—C114	119.6 (2)
C4a—C4—Br16	115.0 (2)	C3—C9—C115	116.3 (2)
C3—C4—Br16	118.1 (2)	C4—C9—C115	118.9 (2)
C9—C4—Br16	116.5 (2)	C114—C9—C115	111.1 (2)
C5—C4a—C8a	116.9 (3)	C7—O12—C13	117.7 (2)
C5—C4a—C4	123.4 (2)		

Refinement was on  $F^2$  for all reflections except for one with very negative  $F_o^2$ . Isotropic H atoms were constrained to give C—H 0.93  $\text{\AA}$  (aromatic, on ring-angle external bisectors) or 0.97  $\text{\AA}$  (aliphatic, with H—C—H 109.5 $^\circ$ ) and  $U(\text{H}) = 1.2U_{eq}(\text{C})$ . All e.s.d.'s are estimated using the full covariance matrix. Data

collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, in preparation). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93* and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71614 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1073]

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**(4a*R*,8*R*,5*R*)-8-(*p*-Tolylsulfinyl)-  
2,3,4,4a,5,6,7,8-octahydro-4a-quinolinol**

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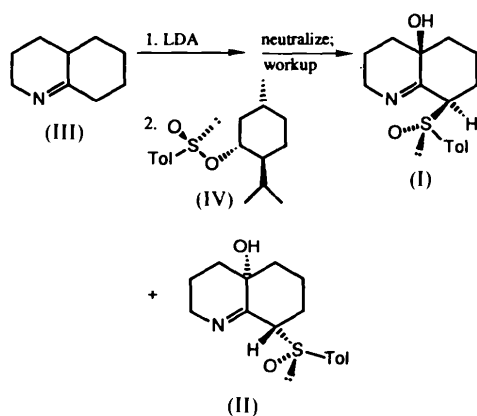
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## Abstract

The title compound,  $\text{C}_{16}\text{H}_{21}\text{NO}_2\text{S}$ , isolated from the reaction of lithiated racemic 2,3,4,4a,5,6,7,8-octahydroquinoline with 0.5 equivalents of (–)-(1*R*,2*S*,5*R*)-menthyl (SS)-*p*-toluenesulfinate, possesses the unusual conformation in which the OH and bulky *p*-toluenesulfinyl groups are in axial positions. The S=O bond distance of 1.519 (3)  $\text{\AA}$  is longer than expected because of intramolecular hydrogen bonding between the hydroxyl group and the sulfinyl O atom.

### Comment

In a study utilizing our  $\alpha$ -sulfinyl ketimine chemistry (Hua, 1992) in the asymmetric total synthesis of lycopodium alkaloids huperzine *A* and *B* (Liu, Zhu, Yu, Zhou, Han, Wu & Qi, 1986), which are used in the treatment of Alzheimer's dementia, the title compound (I) and its diastereomer (II) were synthesized. Racemic 2,3,4,4a,5,6,7,8-octahydroquinoline (III) (Cohen & Witkop, 1955) under Ar was treated with 1.1 equivalents of lithium diisopropylamide (LDA) in tetrahydrofuran at 243 K for 30 min, followed by the addition of 0.5 equivalents of (–)-(1*R*,2*S*,5*R*)-menthyl (SS)-*p*-toluenesulfinate (IV) (Phillips, 1925) while maintaining the same temperature. The mixture was then kept at 273 K for 2 h prior to neutralization. The reaction products that formed initially were flash column chromatographed which led to the separation and isolation of (I) and (II) in a ratio of 1:2. Recrystallization of (I) from ether provided single crystals suitable for X-ray analysis; m.p. 421–423 K,  $[\alpha]_D^{295} = +135.3^\circ$  ( $c = 0.6$ , CHCl<sub>3</sub>). Recrystallization of (II) from various solvents failed to provide crystals suitable for X-ray structural analysis; the white solids obtained had m.p. 443–445 K and  $[\alpha]_D^{295} = +107^\circ$  ( $c = 0.4$ , CHCl<sub>3</sub>).



When the addition of (IV) was performed at 223 K and the reaction was quenched after 20 min, only (II) was isolated. Kinetic resolution apparently took place. Evidently the toluenesulfinylated products that formed initially were autoxidized during the workup–isolation process to effect C4a hydroxylation.

Structural analysis of (I) shows that the cyclohexane ring orients in the chair conformation and the fused ketimine ring has a skew-boat conformation. The C4a-hydroxyl and C8-sulfinyl groups are both axial, and the short distance [1.81 (4) Å] between H2 of the OH and O1 of the sulfinyl is evidence of their strong hydrogen bonding. The bulky sulfinyl group having an axial orientation is uncommon. The absolute configuration at the S atom of the starting substrate (IV) was known (SS). Since this displacement reaction involves inversion of configuration

at the S atom, *S* to *R* (Hua, 1992), and the X-ray analysis definitively shows the *cis* juxtaposition of the C4a OH group with the C8 sulfinyl, the absolute configurations at S, C4a and C8 of (I) are unambiguously assigned, a task which otherwise would be difficult to perform with confidence. The chiral degradation (desulfurization) products of (I) and (II) with Raney nickel are unknown.

The structure of (II) was inferred from that of (I): since the starting quinoline (III) is a racemate, both products, having *R* and *S* configurations, respectively, at C4a, would be expected to be formed. The *cis* configuration of (II) was supported by <sup>1</sup>H NMR spectroscopy which indicated strong intramolecular hydrogen bonding between the OH group and the sulfoxide moiety [the OH resonance is shifted down field and appears as a sharp singlet, like that of (I)].

Due to the intramolecular hydrogen bonding, the S1=O1 bond of (I) is somewhat longer [1.519 (3) Å] than a normal S=O bond [1.487 (6) Å (Robinson, Hua, Wu, Miao & Meled, 1992)]. In addition, the bond angle O2–C4a–C5 [110.2 (4)°] is larger than the corresponding angle in a cyclohexane ring [107.5° (Vollhardt, 1987)].

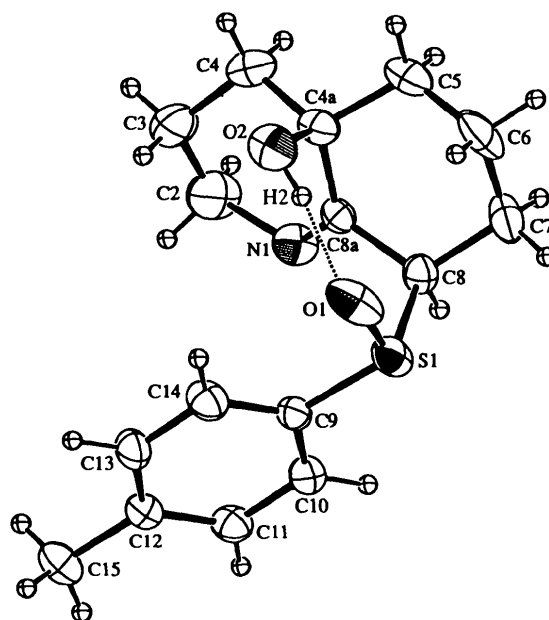


Fig. 1. Molecular configuration and atom-numbering scheme with thermal ellipsoids at the 30% probability level. H atoms are shown as isotropic spheres of arbitrary size. The dotted line represents the intramolecular hydrogen bonding.

### Experimental

#### Crystal data

C<sub>16</sub>H<sub>21</sub>NO<sub>2</sub>S  
M<sub>r</sub> = 291.41

Mo K $\alpha$  radiation  
 $\lambda = 0.71069$  Å

Monoclinic	Cell parameters from 25 reflections
$P2_1$	$\theta = 9.2-10.0^\circ$
$a = 8.866 (1) \text{ \AA}$	$\mu = 0.199 \text{ mm}^{-1}$
$b = 9.534 (1) \text{ \AA}$	$T = 296 \text{ K}$
$c = 9.245 (1) \text{ \AA}$	Equant
$\beta = 92.92 (1)^\circ$	$0.36 \times 0.30 \times 0.28 \text{ mm}$
$V = 780.4 (3) \text{ \AA}^3$	Colorless
$Z = 2$	
$D_x = 1.240 \text{ Mg m}^{-3}$	
<b>Data collection</b>	
Rigaku AFC-5S diffractometer	$R_{\text{int}} = 0.012$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25^\circ$
Absorption correction: none	$h = 0 \rightarrow 10$
1562 measured reflections	$k = 0 \rightarrow 11$
1466 independent reflections	$l = -10 \rightarrow 10$
1059 observed reflections	3 standard reflections
$[I > 3.0\sigma(I)]$	monitored every 100 reflections
	intensity variation: $-0.3\%$
<b>Refinement</b>	
Refinement on $F$	Extinction correction: none
$R = 0.030$	Atomic scattering factors from <i>International Tables for X-ray Crystallography</i> (1974, Vol. IV, Table 2.3.1)
$wR = 0.035$	Absolute configuration: the correct enantiomer was chosen on the basis of the known configuration of compound (IV)
$S = 1.40$	
1059 reflections	
183 parameters	
H-atom parameters not refined (except H2)	
$w = 4F_o^2/\sigma^2(F_o^2)$	
$(\Delta/\sigma)_{\text{max}} = 0.004$	
$\Delta\rho_{\text{max}} = 0.10 \text{ e \AA}^{-3}$	
$\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )
$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}}$
S1	0.4568 (1)	0.3182	0.5261 (1)	0.0642 (3)
O1	0.4709 (3)	0.1698 (3)	0.5849 (3)	0.080 (1)
O2	0.3547 (4)	0.1688 (3)	0.8509 (3)	0.076 (1)
N1	0.2268 (4)	0.4879 (4)	0.7677 (3)	0.064 (1)
C2	0.0996 (5)	0.4708 (7)	0.8613 (5)	0.100 (2)
C3	0.1028 (5)	0.3402 (7)	0.9505 (5)	0.095 (2)
C4	0.2574 (5)	0.3241 (6)	1.0213 (4)	0.082 (2)
C4a	0.3746 (4)	0.3077 (5)	0.9072 (3)	0.055 (1)
C5	0.5336 (5)	0.3256 (6)	0.9725 (4)	0.072 (2)
C6	0.6510 (4)	0.3203 (7)	0.8621 (5)	0.089 (2)
C7	0.6262 (5)	0.4367 (7)	0.7498 (5)	0.089 (2)
C8	0.4650 (4)	0.4387 (4)	0.6803 (4)	0.052 (1)
C8a	0.3429 (4)	0.4142 (4)	0.7870 (3)	0.042 (1)
C9	0.2651 (3)	0.3391 (4)	0.4624 (3)	0.046 (2)
C10	0.2209 (4)	0.4589 (4)	0.3894 (4)	0.055 (2)
C11	0.0741 (4)	0.4693 (4)	0.3319 (4)	0.055 (1)
C12	-0.0280 (4)	0.3619 (4)	0.3462 (4)	0.048 (1)
C13	0.0198 (4)	0.2426 (5)	0.4178 (4)	0.060 (2)
C14	0.1652 (5)	0.2287 (5)	0.4763 (4)	0.061 (2)
C15	-0.1885 (4)	0.3722 (5)	0.2830 (4)	0.068 (1)
H2	0.400 (5)	0.163 (6)	0.765 (5)	0.094

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

S1—O1	1.519 (3)	C7—C8	1.537 (5)
S1—C8	1.830 (4)	C8—C8a	1.519 (5)
S1—C9	1.781 (3)	C9—C10	1.373 (5)

O2—C4a	1.430 (5)	C9—C14	1.385 (5)
N1—C2	1.465 (5)	C10—C11	1.384 (5)
N1—C8a	1.252 (4)	C11—C12	1.378 (5)
C2—C3	1.493 (8)	C12—C13	1.373 (5)
C3—C4	1.497 (6)	C12—C15	1.513 (5)
C4—C4a	1.526 (5)	C13—C14	1.379 (5)
C4a—C5	1.515 (5)	O2—H2	0.91 (4)
C4a—C8a	1.521 (5)	H2...O1	1.81 (4)
C5—C6	1.495 (6)	O2...O1	2.715 (4)
C6—C7	1.527 (7)		
O1—S1—C8	107.9 (2)	S1—C8—C8a	114.1 (2)
O1—S1—C9	106.4 (2)	C7—C8—C8a	113.9 (3)
C8—S1—C9	100.8 (2)	N1—C8a—C4a	126.8 (3)
C2—N1—C8a	120.4 (4)	N1—C8a—C8	115.4 (3)
N1—C2—C3	115.2 (4)	C4a—C8a—C8	117.8 (3)
C2—C3—C4	108.5 (4)	S1—C9—C10	119.9 (3)
C3—C4—C4a	110.4 (3)	S1—C9—C14	119.2 (3)
O2—C4a—C4	105.7 (4)	C10—C9—C14	120.6 (3)
O2—C4a—C5	110.2 (4)	C9—C10—C11	119.2 (3)
O2—C4a—C8a	109.7 (3)	C10—C11—C12	121.3 (4)
C4—C4a—C5	111.4 (3)	C11—C12—C13	118.3 (3)
C4—C4a—C8a	109.2 (3)	C11—C12—C15	121.6 (3)
C5—C4a—C8a	110.4 (3)	C13—C12—C15	120.1 (3)
C4a—C5—C6	113.0 (3)	C12—C13—C14	121.9 (4)
C5—C6—C7	111.0 (4)	C9—C14—C13	118.7 (4)
C6—C7—C8	113.1 (3)	O2—H2...O1	172 (5)
S1—C8—C7	108.5 (3)		

The scan rate was  $6^\circ \text{ min}^{-1}$  (in  $\omega$ ). Weak reflections [ $I < 10\sigma(I)$ ] were rescanned (maximum of three rescans) and the counts accumulated to improve accuracy. The positional parameters of the hydroxyl H atom were refined; all other H atoms were placed at assumed positions ( $C-H = 0.95 \text{ \AA}$ ,  $U = 1.2 \times U_{\text{eq}}$  of the associated C atom) and fixed. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN ORTEP* (Johnson, 1965). Software used to prepare material for publication: *TEXSAN FINISH*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71607 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1077]

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## Synthesis of *N*-Benzoyl-1,3-imidazole Oximes. Structure of C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O

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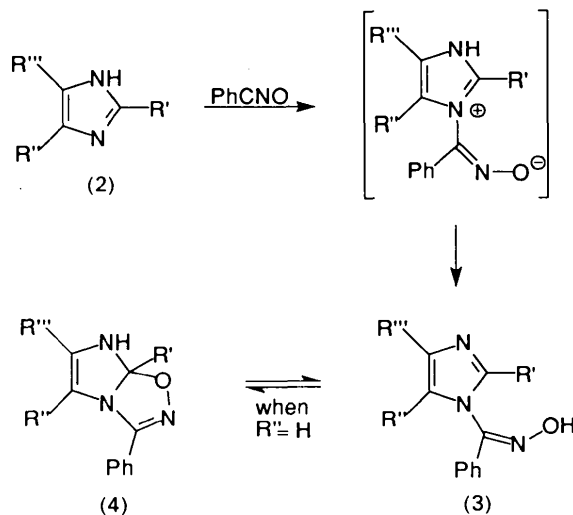
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### Abstract

In (*Z*)-1-benzoyl-5-benzyl-4-methyl-2-phenylimidazole oxime, C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O, the heterocyclic ring is planar. The dihedral angle between the phenyl directly bound to imidazole and the imidazole plane is 33.3 (1)°. The oxime fragment makes an angle of 71.9 (3)° with respect to the imidazole ring and has *Z* configuration. Crystal cohesion is due to van der Waals interactions and hydrogen bonds involving N and O atoms.

### Comment

The reaction of *N*-unsubstituted imidazoles (2) with benzonitrile oxide proceeds through a zwitterionic intermediate leading to the open (*Z*-oxime) (3) and closed (cycloadduct) (4) forms (Grassi, Foti, Risitano, Bruno, Nicolò & De Munno, 1993).



Both tautomers are present in solution when the C atom  $\alpha$  to the N atom of the C=N double bond is unsubstituted, while in the solid state only the chain-form (3) is observed. Consequently, a study was undertaken to define the solid-state structure of these compounds and in this paper we report the crystal structure of (*Z*)-1-benzoyl-5-benzyl-4-methyl-2-phenylimidazole oxime (1), which was synthesized by the reaction of 4-benzyl-3-methylisoxazol-5-one with benzonitrile oxide (Grassi, Foti, Risitano & Caruso, 1983).

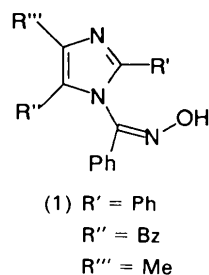


Fig. 1 shows the molecular conformation of (1) and depicts the numbering scheme. The methyl C10 and phenyl C1 atoms are 0.030 (6) and  $-0.010$  (4) Å, respectively, out of the imidazole plane. From this plane large deviations are observed for C11 [ $-0.126$  (5) Å] and C12 [ $-0.106$  (3) Å]. The deviations of each atom of the imidazole ring from the mean plane are very small (0.008 Å maximum for C8) thus indicating some  $\pi$  delocalization over this system. All the C—N bond distances in the heterocyclic ring are intermediate between the expected single- and double-bond lengths. The exocyclic angles around the N2 atom show considerable asymmetry; this asymmetry is also usual in 1,2,3-triazoles