

Data collection

Siemens P3 four-circle diffractometer
 ω -2 θ scans
 Absorption correction: none
 2507 measured reflections
 2355 independent reflections
 2354 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$
 $\theta_{\text{max}} = 27^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 14$
 $l = -14 \rightarrow 13$
 2 standard reflections every 100 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R = 0.0305$
 $wR(F^2) = 0.0704$
 $S = 0.943$
 2354 reflections
 367 parameters
 H atoms: see below

$w = 1/[\sigma^2(F_o^2) + 0.0446P^2]$,
 $P = (F_o^2 + 2F_c^2)/3$
 $\Delta\rho_{\text{max}} = 0.160 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.155 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O2—C3	1.213 (2)	C11—C16	1.533 (2)
N1—C15	1.465 (2)	C11—C2	1.540 (3)
N1—C12	1.472 (2)		
C15—N1—C12	108.6 (1)	C16—C11—C2	112.2 (2)
C15—N1—C11	111.9 (1)	O2—C3—C4	122.4 (2)
C12—N1—C11	116.9 (2)	O2—C3—C2	122.0 (2)
N1—C11—C16	113.8 (1)	C4—C3—C2	115.6 (2)
N1—C11—C2	111.7 (1)		
N1—C11—C16—C21	-71.0 (3)	C15—N1—C11—C16	-62.1 (2)
N1—C11—C16—C17	105.8 (2)	C16—C11—C2—C3	68.3 (2)
C12—N1—C11—C16	63.9 (2)	C16—C11—C2—C1	-168.6 (2)

The structure was solved by direct phase determination and refined by full-matrix least-squares techniques on F^2 . The refinement was completed with anisotropic displacement parameters for all atoms except H atoms which were generated geometrically and refined isotropically.

Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1038). Services for accessing these data are described at the back of the journal.

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Three *trans*-2,6-Diaryl Derivatives of Oximes of *N*-Hydroxy-4-piperidone

EDUARDO DÍAZ, HÉCTOR BARRIOS AND RUBÉN A. TOSCANO

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Apartado Postal 70-213 México, DF, 04510 México. E-mail: toscano@servidor.unam.mx

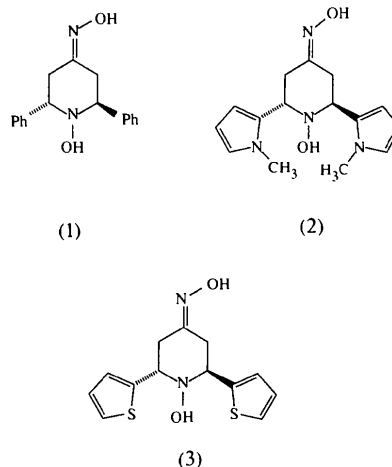
(Received 9 April 1996; accepted 19 February 1997)

Abstract

In the solid state, *trans*-2,6-diphenyl-4-(hydroxyimino)-piperidinol, C₁₇H₁₈N₂O₂, (1), *trans*-2,6-bis(1-methylpyrrol-2-yl)-4-(hydroxyimino)piperidinol, C₁₅H₂₀N₄O₂, (2), and *trans*-2,6-bis(thien-2-yl)-4-(hydroxyimino)-piperidinol, C₁₃H₁₄N₂O₂S₂, (3), adopt conformations with an axial OH substituent on the ring N atom, in contrast to the preference for an equatorial conformation in solution. Molecules of all three structures are held together in chains by hydrogen bonding.

Comment

We have previously reported a ¹H and ¹³C NMR study of the conformation of several oximes of 2,6-diaryl-piperidin-4-ones in solution (Díaz *et al.*, 1997). The crystal structures of three of these compounds, the diphenyl, (1), bis(1-methylpyrrol-2-yl), (2), and bis(thien-2-yl), (3), derivatives have been determined in order to establish their preferred conformation in the solid state.



The molecular structures of compounds (1), (2) and (3) are shown in Figs. 1, 2 and 3, respectively. In each case, the hydroxyimino group displays a twofold orientational disorder. The crystals thus comprise a mixture of two forms, differing only in the orientation

of the hydroxyl group, as in the case of the oximes of cycloundecanone and cyclododecanone (Groth, 1979).

The piperidine rings have a slightly distorted chair conformation very similar to those found by Sekar, Parthasarathy & Radhakrishnan (1990, 1993), and by Zongchao, Wilson, Arora & Dimmrock (1988) for related compounds. The orientation of the *trans* substituents at C2 and C6 is approximately the same in each case. The dihedral angle between the planes of the aromatic substituents is 65.6 (1) in (1), 65.0 (2) in (2) and 46.3 (3)° in (3).

The axial position of the OH substituent on the ring N contrasts with the preference

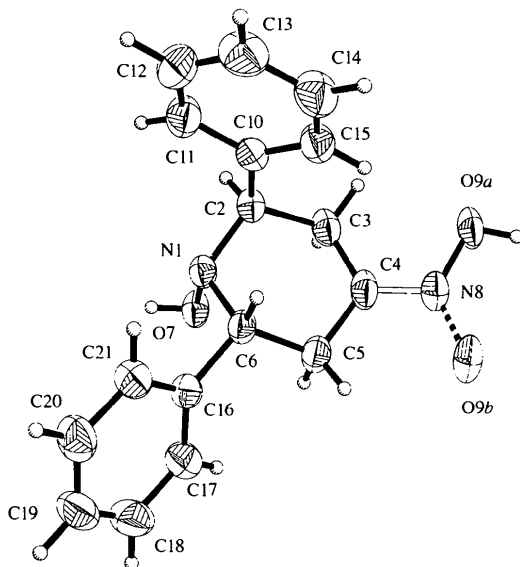


Fig. 1. Structure of (1) with displacement ellipsoids drawn at the 30% probability level.

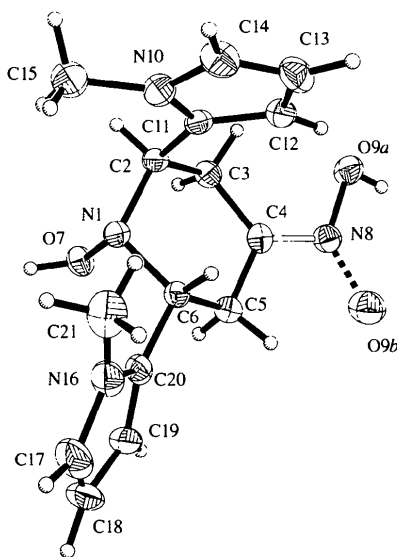


Fig. 2. Structure of (2) with displacement ellipsoids drawn at the 30% probability level.

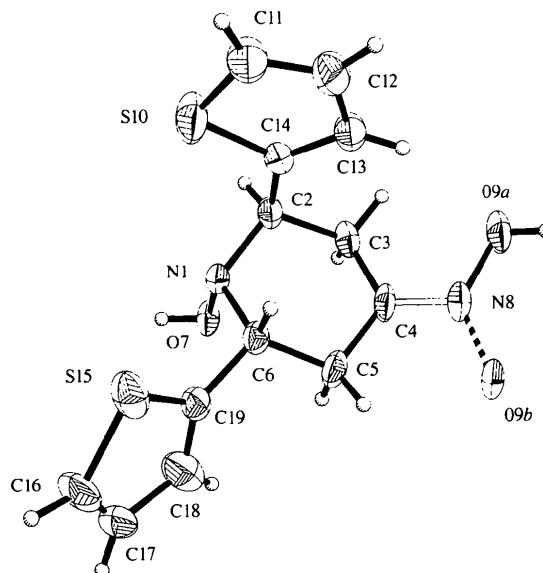


Fig. 3. Structure of (3) with displacement ellipsoids drawn at the 30% probability level.

in solution for the equatorial conformer; from NMR evidence at 203 K, the equatorial:axial ratio is 70:30% (Díaz *et al.*, 1997).

In the crystal structures, the molecules are arranged in chains by centrosymmetric pairs of O—H...N hydrogen bonds involving both the N—OH groups of the hydroxyimino and *N*-hydroxy entities alternately.

Experimental

The parent diarylidene acetones were prepared according to the method of Quilico (1962). For the preparation of compounds (1)–(3), 15.3 mmol of hydroxylamine hydrochloride and 33.9 mmol of the diarylidene acetone were successively added to a stirred solution of 64.5 mmol of potassium hydroxide in a minimum volume of 95% ethanol. The solution was refluxed until thin-layer chromatography monitoring indicated completion of the reaction. Products were purified by silica-gel column chromatography and the *cis*- and *trans* isomers (obtained in equal yields) were separated by fractional crystallization from acetone–hexane.

Compound (1)

Crystal data

$C_{17}H_{18}N_2O_2$
 $M_r = 282.33$
 Monoclinic
 $P2_1/n$
 $a = 9.890 (3) \text{ \AA}$
 $b = 10.437 (3) \text{ \AA}$
 $c = 14.790 (4) \text{ \AA}$
 $\beta = 97.75 (2)^\circ$
 $V = 1512.7 (8) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.240 \text{ Mg m}^{-3}$
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 5.1\text{--}13.3^\circ$
 $\mu = 0.660 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Irregular
 $0.30 \times 0.18 \times 0.14 \text{ mm}$
 Colourless

Data collection

Nicolet P3/F diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 2033 measured reflections
 1902 independent reflections
 1353 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

Refinement on F^2
 $R(F) = 0.050$
 $wR(F^2) = 0.128$
 $S = 1.188$
 1902 reflections
 207 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.0737P)^2 + 0.2342P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

Compound (2)**Crystal data**

C₁₅H₂₀N₄O₂
 $M_r = 288.35$
 Monoclinic
 $P2_1/c$
 $a = 10.169$ (5) Å
 $b = 14.129$ (8) Å
 $c = 10.039$ (6) Å
 $\beta = 90.67$ (4)°
 $V = 1442.3$ (14) Å³
 $Z = 4$
 $D_x = 1.328$ Mg m⁻³
 D_m not measured

Data collection

Nicolet P3/F diffractometer
 $\theta/2\theta$ scans
 Absorption correction: none
 1587 measured reflections
 1477 independent reflections
 1395 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.096$

Refinement

Refinement on F^2
 $R(F) = 0.090$
 $wR(F^2) = 0.256$
 $S = 1.130$
 1477 reflections
 207 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.2085P)^2 + 0.894P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = -0.003$

$\theta_{\text{max}} = 55.06^\circ$
 $h = 0 \rightarrow 10$
 $k = 0 \rightarrow 11$
 $l = -15 \rightarrow 15$
 2 standard reflections
 every 98 reflections
 intensity decay: 3%

$\Delta\rho_{\text{max}} = 0.140$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.194$ e Å⁻³
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.0032 (6)
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Cu $K\alpha$ radiation
 $\lambda = 1.54178$ Å
 Cell parameters from 25
 reflections
 $\theta = 5.4\text{--}14.3^\circ$
 $\mu = 0.738$ mm⁻¹
 $T = 293$ K
 Prism
 $0.52 \times 0.32 \times 0.26$ mm
 Light yellow

$\theta_{\text{max}} = 49.99^\circ$
 $h = -10 \rightarrow 10$
 $k = -14 \rightarrow 0$
 $l = 0 \rightarrow 9$
 2 standard reflections
 every 98 reflections
 intensity decay: 3%

$\Delta\rho_{\text{max}} = 0.467$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.398$ e Å⁻³
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.012 (3)
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Compound (3)**Crystal data**

C₁₃H₁₄N₂O₂S₂
 $M_r = 294.38$
 Triclinic
 $P\bar{1}$
 $a = 9.479$ (3) Å
 $b = 10.229$ (3) Å
 $c = 8.625$ (2) Å
 $\alpha = 108.98$ (2)°
 $\beta = 112.91$ (2)°
 $\gamma = 91.69$ (2)°
 $V = 716.6$ (4) Å³
 $Z = 2$
 $D_x = 1.364$ Mg m⁻³
 D_m not measured

Data collection

Nicolet P3/F diffractometer
 $\theta/2\theta$ scans
 Absorption correction:
 refined from ΔF
 (DIFABS; Walker &
 Stuart, 1983)
 $T_{\text{min}} = 0.38$, $T_{\text{max}} = 0.67$
 1592 measured reflections
 1475 independent reflections

Refinement

Refinement on F^2
 $R(F) = 0.070$
 $wR(F^2) = 0.191$
 $S = 1.100$
 1475 reflections
 226 parameters
 H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.1454P)^2 + 0.524P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.091$

Cu $K\alpha$ radiation
 $\lambda = 1.54178$ Å
 Cell parameters from 25
 reflections
 $\theta = 4.15\text{--}16.65^\circ$
 $\mu = 3.369$ mm⁻¹
 $T = 293$ (2) K
 Truncated square pyramid
 $0.40 \times 0.32 \times 0.12$ mm
 Colourless

1357 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.044$
 $\theta_{\text{max}} = 50.05^\circ$
 $h = 0 \rightarrow 9$
 $k = -10 \rightarrow 10$
 $l = -8 \rightarrow 7$
 2 standard reflections
 every 98 reflections
 intensity decay: 3%

$\Delta\rho_{\text{max}} = 0.380$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.390$ e Å⁻³
 Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.011 (3)
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 1. Hydrogen-bonding geometry (Å, °)

Compound	D—H...A	D...A	D—H...A
(1)	O7—H7...N1 ⁱ	2.831 (3)	159
	O9A—H9...N8 ⁱⁱ	2.792 (5)	156
(2)	O7—H7...N1 ⁱⁱⁱ	2.870 (4)	171
	O9A—H9...N8 ⁱ	2.835 (6)	169
(3)	O7—H7...N1 ⁱ	2.817 (4)	152
	O9A—H9...N8 ⁱⁱ	2.738 (6)	140

Symmetry codes: (i) $-x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 1 - z$; (iii) $1 - x, 1 - y, -z$; (iv) $1 - x, -y, 1 - z$.

The rather low θ_{max} values were imposed by the geometry of a diffractometer modified for macromolecular studies. Disorder contributes to the relatively high residual factors.

The oxime OH group was found to be disordered in each structure and was refined in two alternative positions with complementary occupancy factors. In the structure of (3), one of the thienyl substituents was also refined with twofold orientational disorder corresponding to 180° rotation about the C6—C19 bond, with the assistance of geometry

and displacement-parameter restraints. Distance restraints were applied to refined hydroxy H atoms; other H atoms were constrained with a riding model and $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

For all compounds, data collection: *Nicolet P3 Software* (Nicolet XRD Corporation, 1980); cell refinement: *Nicolet P3 Software*; data reduction: *Nicolet P3 Software*; program(s) used to solve structures: *SHELXTL/PC* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1113). Services for accessing these data are described at the back of the journal.

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9a-Trimethylsilyloctahydroquinolizinium Picrate

JONATHAN M. WHITE AND WAI-YING THAM

School of Chemistry, University of Melbourne, Parkville, Vic 3052, Australia. E-mail: j.white@chemistry.unimelb.edu.au

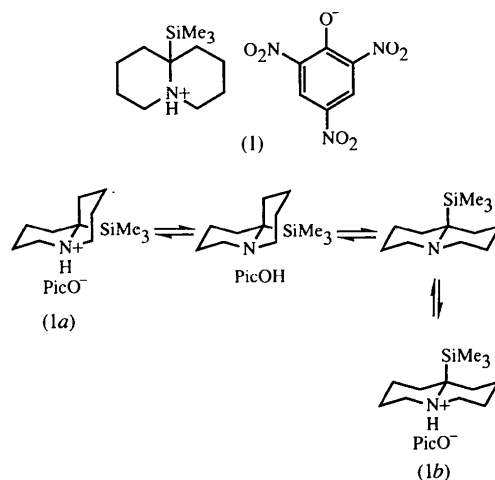
(Received 20 November 1996; accepted 22 April 1997)

Abstract

The title compound, $\text{C}_{12}\text{H}_{26}\text{NSi}^+\cdot\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, exists in the solid state in a *cis*-decalin configuration, with the trimethylsilyl substituent at a bridgehead position. There exists a hydrogen bond between the ammonium N—H and the picrate O atom [N1—H1 0.90 (3), H \cdots O1, 2.03 (3) Å and N1—H1 \cdots O1 153 (2)°].

Comment

The title compound, (1), exists in solution as a *ca* 1:1 mixture of the *cis*-, (1a), and *trans*-decalin, (1b), configurations (White & Tham, 1997); these are interconvertible by a sequence of proton transfer to the picrate anion, nitrogen inversion, then protonation again (see scheme below). The structure of (1) was determined in order to obtain information on its preferred configuration in the solid state. It was then proposed to make use of solid-state ^{13}C NMR in order to assign the signals of the *cis*–*trans* mixture in solution.



The structure of (1), as depicted in Fig. 1, shows that it adopts a *cis*-decalin configuration in the solid state. The bridgehead trimethylsilyl substituent is in an equatorial position with respect to the ring defined by atoms N1, C6, C5, C4, C3 and C2, and axial to the ring defined by N1, C6, C7, C8, C9 and C10. As a result of the axial position of the trimethylsilyl substituent, one of the methyls (C13) lies across the ring, resulting in close contacts between the H atoms attached to C13 and the axial ring H atoms attached to C8 and C10 (H13A \cdots H8B 2.25 and H13B \cdots H10A 2.21 Å). The strain arising from the close contacts results in opening of the C13—Si—C6 bond angle to 118.2 (1)°, well past the preferred tetrahedral value, presumably to minimize these repulsive interactions. The Si—C6—C7 angle,

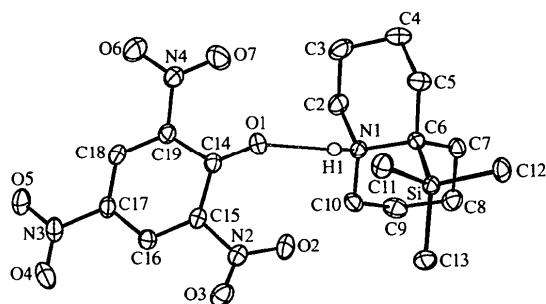


Fig. 1. ORTEP (Johnson, 1976) diagram of (1). Displacement ellipsoids are drawn at the 20% probability level.