Structure of 3,3'-(Trimethylenediimino)bis(3-methyl-2-butanone oxime), $C_{13}H_{28}N_4O_2$

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Abstract. $M_r = 272.4$, $I4_1cd$, $a = 15.458$ (2), $c = 13.075$ (9) Å, $U = 3124$ Å^3, $Z = 8$, $D_x = 1.163$ g cm^{-3}, $\lambda(Mo\,K\alpha) = 0.71073$ Å, $\mu = 0.47$ cm^{-1}, $F(000) = 1200$, room temperature. Full-matrix least-squares refinement of 749 reflections gave a final R value of 4.8%. The structure consists of one half molecule in an asymmetric unit with the other half related by twofold symmetry located at the central C atom of the trimethylene bridge. The two amine N atoms in the ligand are twofold-related and are suitably oriented for chelation whereas the oxime N atoms are not suitably positioned for complexation. The N—O distance [1.410 (3) Å] is significantly longer than the corresponding distance in the metal complexes of H$_2$pnao and is similar to the distance observed in H$_2$enao [3,3'-(ethylenediimino)bis(3-methyl-2-butanone oxime)]. A comparison of the structure of the title compound (H$_2$pnao) with those of H$_2$enao and their metal complexes has been made.

Introduction. Oximes and dioximes are used in gravimetric analysis and solvent extraction because of their ability to form inner-complex salts (Hedwig & Powell, 1974; Hanania & Irvine, 1962). Several metal complexes of aliphatic α-amine dioximes of types (I)–(III) have been the subject of chemical and structural studies (Hussain & Schlemper, 1979; Schlemper, Hussain & Murmann, 1981; Emsley, 1980; Anderson & Packard, 1979; Brückner, Calligaris, Nardin & Randaccio, 1969). These ligands are of interest because of their ability to form hydrogen bonds on deprotonation of the coordinated species and because the O···O distance can be varied over a significant range by a suitable choice of the size of the metal atom and the constraint in the amine bridge. Though the structures of several metal complexes of these amine dioximes are known, the dioximes themselves have not been investigated, except for H$_2$enao (Hussain & Haque, 1983). Efforts to obtain uncomplexed hydrogen-bonded species by deprotonation with a strong solution of sodium or potassium hydroxide were not successful, indicating the absence of any close proximity between the two oxime groups in these tetradentate ligands. Molecular models show that these

ligands may either have the 'twisted' form shown below with oxime groups opposite to each other and a mirror plane passing through the trimethylamine bridge or have an 'extended' configuration with a center of symmetry located at the trimethylamine bridge. Both forms are without any non-bonded interactions. The energetics as well as kinetics of complexation of these ligands should be affected by the configuration of the ligands in the free state for which structural analysis is required. The present paper describes the single-crystal structure analysis of H$_2$pnao and the results are compared with those of the H$_2$enao and coordinated α-amine dioximes.
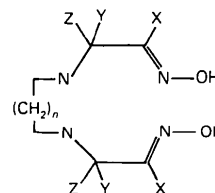
(I)	H$_2$enao	$n = 2$	$X = Y = Z = CH_3$
(II)	H$_2$pnao	$n = 3$	$X = Y = Z = CH_3$
(III)	H$_2$preh	$n = 3$	$X = Y = CH_3$ and Z = none

Experimental. Compound prepared by the method of Vassian & Murmann (1967). Colorless needle crystals of uniform morphology obtained by slow evaporation of a dilute ethanolic solution of the compound. ^{1}H NMR and IR spectra of the crystalline material were as expected. Crystal $0.25 \times 0.25 \times 0.68$ mm mounted on a glass fiber along the needle axis. Enraf–Nonius CAD-4 diffractometer controlled by a PDP 8/A computer, graphite-monochromatized Mo $K\alpha$ radiation. Monoclinic unit-cell dimensions [$a = 20.237$ (5), $b = 15.458$ (2), $c = 13.075$ (9) Å, $\beta = 130.20$ (20)°] obtained using the Nonius program *INDEX* which used the least-squares refinement of the setting angles of 25 reflections with $13 < \theta < 17°$. 4875 *hkl* and $\overline{hkl}$ reflections to $2\theta_{max} = 60.0°$ collected in *ZIGZAG* mode using ω–2θ scan method. Three standard reflections measured every 2 h; no variation in intensities. Crystal orientation monitored every 50 reflections. Background counts measured for half the total scan time by extending scan range 25% on either side of scan limit. A Delaunay reduction with *TRACER*II

suggested by a referee transformed the above mono-clinic cell to a tetragonal cell of dimensions given in the *Abstract*. Systematic extinctions in the tetragonal cell correspond to space group $I4_1cd$ (No. 110). Monoclinic data were transformed to the tetragonal data set and the structure was refined using tetragonal data. Equivalent and duplicate reflections merged, $R_{int} = 0.0075$, 1183 unique reflections, 749 with $I > 3\sigma(I)$ considered observed. Absorption corrections not applied. Coordinates of most non-hydrogen atoms obtained using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Difference Fourier map phased on O, N and C atoms found from *MULTAN* revealed positions of all non-hydrogen atoms present in an asymmetric unit with the central C atom, C(10), close to the twofold axis. C(10) treated as disordered and refined with an occupancy factor of one half. A difference Fourier map after a few cycles gave the positions of all H atoms which agreed fairly well with the calculated positions. H atom coordinates refined by holding all non-hydrogen atoms fixed. Several cycles of full-matrix least-squares refinement with anisotropic non-hydrogen atoms and H atoms at fixed positions gave final $R = 0.048$ and $R_w = 0.052$ for 138 variables and 749 observations. $\sum w(|F_o| - |F_c|)^2$ minimized, with w based on counting statistics $\{w = 0.6318/[\sigma^2|F_o| + 0.000428|F_o^2|]\}$. Largest Δ/σ in any parameter during final cycle of refinement 0.029. Highest peak in final difference maps 0.27 e Å^{-3}. Atomic scattering factors for non-hydrogen atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965); anomalous-dispersion corrections from Cromer & Liberman (1970). All calculations carried out on the IBM 3033 computer of the University of Petroleum & Minerals using *MULTAN*78 and *SHELX*76 (Sheldrick, 1976).

Discussion. Final positional parameters with B_{eq} for non-hydrogen atoms are listed in Table 1.* The atomic labeling scheme is shown in Fig. 1 and the unit-cell packing is given in Fig. 2. Bond distances and angles are included in Fig. 1 and Table 2. The structure is composed of half a molecule of H$_2$pnao per asymmetric unit with the other half related by a twofold symmetry axis located at the central C of the trimethylene bridge, *i.e.* at C(10). The chemically equivalent bond distances and angles are identical and agree well with the corresponding values found in H$_2$enao (Hussain & Haque, 1983). Some important intermolecular distances and angles are included in Table 2. The non-bonding amine N distance, N(8)—N(8'), is 3.200 Å indicating

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Table 1. *Fractional atomic positions* ($\times 10^4$) *for non-hydrogen atoms with e.s.d.'s in parentheses*

$$B_{eq} = 8\pi^2(\tfrac{1}{3} \text{trace } \bar{\mathbf{U}}).$$

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	3673 (2)	−178 (2)	−317 (3)	4.4
N(2)	3100 (2)	352 (2)	240	3.5
C(3)	2543 (2)	−64 (2)	752 (4)	3.0
C(4)	2485 (4)	−1026 (2)	775 (5)	4.7
C(5)	1911 (2)	488 (2)	1381 (3)	3.1
C(6)	2044 (3)	1452 (2)	1180 (5)	4.2
C(7)	2022 (3)	306 (4)	2525 (4)	4.7
N(8)	999 (2)	269 (2)	1123 (3)	2.9
C(9)	795 (2)	263 (3)	15 (4)	4.8
C(10)	109 (5)	−286 (4)	−310 (5)	3.8

Table 2. *Intramolecular angles* (°) *and some important intermolecular non-bonding distances* (Å)

(a) Intramolecular bonding angles

H(O1)—O(1)—N(2)	101 (2)	C(6)—C(5)—C(7)	109.3 (4)
O(1)—N(2)—C(3)	113.9 (3)	C(3)—C(5)—N(8)	110.8 (2)
N(2)—C(3)—C(4)	124.0 (3)	C(6)—C(5)—N(8)	108.1 (3)
N(2)—C(3)—C(5)	115.7 (3)	C(7)—C(5)—N(8)	106.6 (3)
C(4)—C(3)—C(5)	120.4 (3)	C(5)—N(8)—C(9)	115.2 (2)
C(3)—C(5)—C(6)	111.4 (3)	N(8)—C(9)—C(10)	117.0 (4)
C(3)—C(5)—C(7)	110.5 (3)		

(b) Some important non-bonding distances (Å)

C(10)⋯C(10')	0.947 (9)	N(8)⋯O(1$^{\text{iii}}$)	3.102 (5)
N(8)⋯N(8$^{\text{i}}$)	3.200 (5)	N(8)⋯C(10$^{\text{i}}$)	2.539 (4)
N(8)⋯O(1$^{\text{ii}}$)	2.812 (5)	C(9)⋯C(9$^{\text{i}}$)	2.588 (6)

The symmetry-related positions are the following equivalent positions relative to the reference molecule at x, y, z: (i) $-x, -y, z$; (ii) $y, \frac{1}{2}-x, \frac{1}{4}+z$; (iii) $-y, \frac{1}{2}+x, \frac{1}{4}+z$.
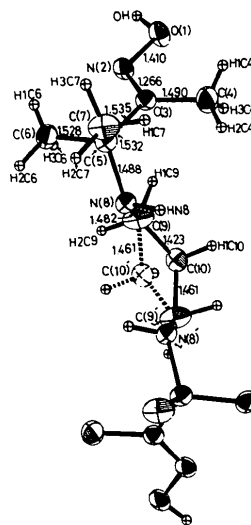C(10') is the alternative position of C(10) resulting from the disorder in this atom.

Fig. 1. The H$_2$pnao molecule with the atom-numbering scheme and bond distances (Å). The C(10) atom is disordered resulting in C(10) and C(10') in close proximity. The dotted lines shown the second position. The standard deviations in distances are as follows: all C—C 0.004–0.005, except C(9)—C(10) 0.009 Å; N—O 0.003 Å; C—N 0.004–0.005 Å.

that these N atoms are suitably oriented for the formation of a six-membered chelate ring if the ligand complexes to a metal atom.

N(8) and N(8') are 2·812 and 3·102 Å from the oxime O atom O(1) of a symmetry-related molecule. This intermolecular hydrogen-bonding contact provides a possible linkage between the H_2pnao molecules which are arranged in two mutually perpendicular columns in the unit cell. The twofold-related amine N atoms should coordinate as a first step in any complexation reaction of this ligand whereas oxime N atoms must undergo a considerable reorientation before complexation. The deprotonation process forming a short intramolecular hydrogen bond may be a driving force for such a reorientation. Intramolecular hydrogen bonding gives rise to a positive entropy change and was assessed as adding stability to these complexes (Daniel, March, Powell, Robinson & Russell, 1978). The lack of twofold symmetry in H_2enao, on the other hand, indicates that in this ligand either the complexation and the hydrogen-bond formation take place concurrently or the hydrogen-bond formation precedes the complexation. The present structure analysis also predicts that H_2pnao is capable of acting as a bidentate ligand under the reaction conditions which avoid the deprotonation step. No such complex has been reported.

A comparison of distances and angles with those of some related compounds is given in Table 3. The average N—O distance of 1·410 (3) Å is significantly longer in free H_2pnao than the corresponding distance in the coordinated ligand. Similar elongation was observed in the case of H_2enao. The N—O bond shortening in the complexes is probably the result of stronger metal—nitrogen(oxime) interactions reducing the N—O distance through inductive effects. The average C—C and C—N distances are quite normal and are similar to the corresponding distances in H_2enao. Individual distances involving H atoms are somewhat poorly defined but the average C—H, O—H and N—H distances and angles are quite normal. The main
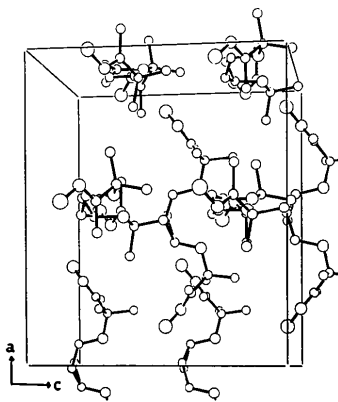
Table 3. *A comparison of some distances (Å) and angles (°) in H_2pnao with the corresponding values in related structures*

	N—O	N—C(sp^2)	O—N—C(sp^2)	Reference
[Ni(Henao)]ClO$_4$	1·349 (3)	1·296 (4)	120·9 (4)	(a)
	1·352 (3)	1·292 (4)	121·4 (4)	
[Ni(Hpnao)]Cl$_2$.H$_2$O	1·349 (6)	1·272 (6)	118·0 (4)	(b)
	1·361 (6)	1·283 (6)	117·6 (4)	
H$_2$enao	1·415 (2)	1·275 (2)	113·5 (1)	(c)
H$_2$pnao	1·410 (3)	1·266 (4)	113·9 (3)	This work

References: (a) Fair & Schlemper (1978). (b) Hussain & Schlemper (1979). (c) Hussain & Haque (1983).

difference between H_2pnao and H_2enao is the close proximity of the amine N atoms in the case of the former in contrast to the well separated amine N atoms in the latter. The chelate bite angles for the two ligands are obviously different. Both ligands are best described as having an 'extended' form with the oxime groups well apart. In both cases the formation of a strong (short) hydrogen bond is necessary for orientation of oxime N atoms in H_2pnao and oxime N as well as amine N atoms in H_2enao, in order that the ligands coordinate to the metal atom.

The IR spectrum of the free ligand in the solid state has sharp peaks at 3320, 1665 and 930 cm^{-1} for the N—H, C—N and N—O groups, respectively. Similar peaks at exactly the same wavenumbers were observed in H_2enao. In the case of the complexed H_2pnao, the above bands are broad and shifted to higher frequencies. For example, in Ni(Hpnao)Cl, a broad absorption centered at 3420 cm^{-1} was observed for N—H and an O—H—O bending peak shifted to 1800 cm^{-1} in addition to a broad region of absorption extending over the 850–1175 cm^{-1} range with a window centered about 980 cm^{-1} typically observed for the short intramolecular hydrogen bond in Hadzi (1965) type (ii) anomalous infrared spectra.

Fig. 2. Unit cell showing molecular packing.

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Structures of the *cis* and *trans* Isomers of 2,4,6-Tri-*tert*-butyl-2,4,6-trifluorocyclotrisilazane, $C_{12}H_{30}F_3N_3Si_3$

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Abstract. $M_r = 357.6$; *cis* isomer (1): trigonal, $P\bar{3}$, $a = 10.873$ (1), $c = 10.040$ (1) Å, $U = 1027.9$ Å^3, $Z = 2$, $D_x = 1.155$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 0.25$ mm^{-1}, $F(000) = 384$, $T = 291$ K, $R = 0.054$ for 1232 observed reflections; *trans* isomer (2): monoclinic, $P2_1/n$, $a = 18.077$ (4), $b = 10.569$ (2), $c = 22.015$ (6) Å, $\beta = 104.67$ (3)°, $U = 4069.0$ Å^3, $Z = 8$, $D_x = 1.167$ Mg m^{-3}, $\mu = 0.25$ mm^{-1}, $F(000) = 1536$, $T = 291$ K, $R = 0.071$ for 4421 observed reflections. (1) has crystallographic threefold rotation symmetry and a virtually planar Si_3N_3 ring [r.m.s. deviation = 0.017 (2) Å]. The two crystallographically independent molecules of (2) lie in general positions and deviations from planarity of the ring are greater [r.m.s. $\Delta = 0.086$ (3) and 0.128 (3) Å].

Introduction. A number of chain and ring silazanes built up from $-$HNSiBuF$-$ units have recently been synthesized by controlled condensation reactions of BuSiF$_3$ and LiNH$_2$ [Bu = *tert*-butyl, (CH$_3$)$_3$C] (Klingebiel & Vater, 1983). The cyclotrisilazane (BuSiFNH)$_3$ exists in two stable non-interconverting isomeric forms, the separation of which has been accomplished by fractional crystallization: the *cis* isomer is less soluble in non-polar solvents and can be selectively crystallized from a mixed solution in CH$_2$Cl$_2$ by addition of *n*-hexane.

We have investigated the structures of both isomers in order to assess the influence of the geometrical substituent distribution on the expected planarity of the Si$_3$N$_3$ ring.

Experimental. Crystals obtained from CH$_2$Cl$_2$/*n*-hexane (1) or *n*-hexane by cooling (2), 0.4 × 0.5 × 0.15 mm (1), 0.3 × 0.3 × 0.45 mm (2), mounted in capillaries, Stoe–Siemens AED diffractometer, unit-cell parameters from 2θ values of 36 (1) and 32 (2) reflections ($20 < 2\theta < 25°$), 1826 reflections with $2\theta < 55°$ and $h,k \geq 0$ (1) and 8179 reflections with $2\theta < 50°$ and $k \geq 1$ (2), profile analysis (Clegg, 1981), no significant intensity variation for 3 standard reflections, no absorption corrections, $R_{int} = 0.027$ (1) and 0.037 (2), 1581 (1) and 7144 (2) unique reflections, 1232 (1) and 4421 (2) with $F > 4\sigma(F)$; automatic multisolution direct methods, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + gF^2$, $g = 0.00068$ (1), 0.00041 (2), Bu H atoms constrained to give C$-$H $= 0.96$ Å, H$-$C$-$H $= 109.5°$, $U(H) = 1.2U_{eq}(C)$, anisotropic thermal parameters for non-H atoms, no extinction corrections, scattering factors from *International Tables for X-ray Crystallography* (1974). (1): N$-$H refined freely, 77 parameters, $R = 0.054$, $wR = 0.068$, slope of normal probability plot $= 1.51$, max. $\Delta/\sigma = 0.013$, mean $= 0.001$, largest peak in final difference map $= 0.25$ e Å^{-3}, largest hole $= -0.33$ e Å^{-3}; (2): minor disorder component for one BuSiF group with site occupation factor 0.119 (2) for Si and F; disorder of Bu group not resolved; N$-$H constrained to lie on Si$-$N$-$Si external bisector with N$-$H $= 0.62$ Å [value obtained from free refinement of (1)], $U(H) = 1.2U_{eq}(N)$, 398 parameters, $R = 0.071$, $wR = 0.073$, slope $= 1.61$, max. $\Delta/\sigma = 0.029$, mean $= 0.005$, largest peak $= 0.63$ e Å^{-3}, largest hole $=$

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