Structure of 3,3'-(Ethylenediimino)bis(3-methyl-2-butanone oxime), C$_{12}$H$_{26}$N$_4$O$_2$

By M. Sakhawat Hussain* and Mazhar-ul-Haque

Department of Chemistry, University of Petroleum & Minerals, Dhahran, Saudi Arabia

Abstract. $M_r = 258$, $P4_2/n$, $a = 15 \cdot 219$ (2), $c = 6 \cdot 266$ (5) Å, $U = 1451$ Å^3, $Z = 4$, $D_c = 1 \cdot 172$ g cm^{-3}, λ(Mo $K\alpha$) = 0$\cdot$7107 Å, $\mu = 0 \cdot 49$ cm^{-1}, $F(000) = 568$. Full-matrix least-squares refinement with 1190 reflections gave a final R value of 4·5%. Molecules of the title compound (H$_2$enao) are in the extended form without any intramolecular non-bonded interactions or any specific orientation of the donor atoms suitable for complexation. The N–O distance [1·415 (2) Å] is significantly longer than the corresponding distance in the metal complexes of H$_2$enao or of any other α-amine dioxime studied so far. A comparison of the distances and angles observed for the free ligand with those observed in its metal complexes is given.

Introduction. Several metal complexes of α-amine dioximes of types I and II have been studied by X-ray and neutron diffraction mainly to understand the nature of the short hydrogen bond formed by deprotonation of coordinated dioximes (Hussain & Schlemper, 1979; Ching & Schlemper, 1975; Schlemper, Hussain & Murmann, 1981). However, none of the dioxime structures themselves has ever been investigated. The uncoordinated dioximes may have either an 'extended' configuration or an orientation in which the nitrogen atoms are positioned opposite each other as shown in the idealized formula below. In the former case complexation through two nitrogens should precede wrapping of the rest of the molecule arround the metal ion so that the two oxime groups are suitably located for deprotonation and formation of a hydrogen bond. In the latter situation, complexation by simple insertion of the metal ion into the chelate cavity may precede deprotonation or both steps may occur simultaneously.

(I) H$_2$enao $n = 2$

(II) H$_2$pnao $n = 3$
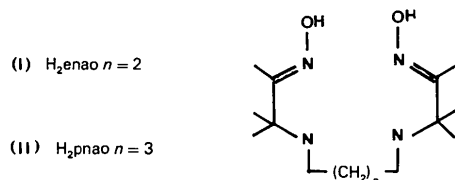
The structure of the ligand itself would provide answers to these questions. In the present paper the single-crystal structure analysis of H$_2$enao is reported and the results are compared with that of the coordinated ligand.

Experimental. The ligand was prepared by the procedure reported by Vassian & Murmann (1967). Colorless crystals of uniform morphology were obtained by slow evaporation of a dilute solution of the compound in methanol. The ^{1}H NMR and IR spectra of the crystalline material agreed well with the reported spectra. Long needle-shape crystal, 0·2 × 0·1 × 0·05mm, mounted on a glass fiber along the needle axis used for lattice constants and collection of intensity data; tetragonal unit-cell dimensions from least-squares refinement of setting angles of 25 centered reflections, $12 < 2\theta < 19°$; Enraf–Nonius CAD-4 diffractometer controlled by PDP 8/A computer, graphite-monochromatized Mo $K\alpha$ radiation; 2634 hkl and $\bar{h}kl$ to $2\theta_{max} = 60 \cdot 0°$ collected in ZIGZAG mode using ω–2θ scans; three standard reflections measured every 2 h, no significant systematic fluctuation; 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; 2111 unique reflections, 1190 with $I > 3\sigma(I)$ considered observed; 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 were carried out on the University of Petroleum and Minerals IBM 3033 computer using *SHELX* 76 (Sheldrick, 1976). Coordinates of all non-hydrogen atoms except those of methyl C atoms were obtained using automatic centrosymmetric direct-method program in *SHELX* 76. Difference Fourier map phased on O, N and three C atoms revealed positions of all non-hydrogen atoms in the asymmetric unit. A few cycles of anisotropic refinement followed by a difference Fourier synthesis gave the positions of all H atoms which agreed fairly well with the calculated positions. Several cycles of full-matrix least-squares refinement with anisotropic non-hydrogen atoms and

* To whom all correspondence should be addressed.

isotropic H atoms gave final $R = 0.045$ and $R_w = 0.061$ for 134 variables and 1190 reflections; $\sum w(|F_o| - |F_c|)^2$ minimized, with w based on counting statistics $\{w = 0.9670/[(\sigma|F_o|)^2 + 0.001362 \times |F_o^2|]\}$; largest shift in any parameter during final cycle of refinement was 0.11 times its estimated standard deviation; final difference Fourier synthesis virtually featureless. Final positional parameters for all atoms are listed in Table 1.*

Discussion. Fig. 1 shows the molecular structure with the atoms as identified in the tables. The packing of the molecules in the unit cell is shown in a stereoscopic view in Fig. 2.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38188 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* $(\times 10^4; for\ H \times 10^3)$ *and isotropic temperature factors*

Numbers in parentheses in this and all subsequent tables represent estimated standard deviations. $B_{eq} = 8\pi^2 U_{eq}$ where $U_{eq} = \frac{1}{3}$ trace U.

	x	y	z	$B_{eq}(\text{Å}^2)$
O(1)	1414 (1)	4640 (1)	−810 (3)	3·60
N(2)	1978 (1)	5201 (1)	362 (2)	2·71
C(3)	2665 (1)	4818 (1)	1058 (3)	2·45
C(4)	3258 (1)	5384 (1)	2486 (3)	2·35
N(5)	4205 (1)	5178 (1)	2227 (2)	2·22
C(6)	4547 (1)	5206 (1)	29 (3)	2·35
C(7)	2873 (2)	3869 (1)	639 (5)	4·32
C(8)	3114 (1)	6360 (1)	2038 (4)	3·06
C(9)	3040 (2)	5177 (2)	4827 (3)	3·76
H(O1)*	102 (2)	501 (2)	−123 (4)	4·03
H(N5)	432 (1)	466 (1)	281 (3)	2·13
H(1C6)	460 (1)	583 (1)	−41 (3)	3·08
H(2C6)	415 (1)	488 (1)	−104 (3)	3·16
H(1C7)	239 (2)	351 (2)	62 (6)	8·13
H(2C7)	341 (3)	370 (2)	118 (7)	9·00
H(3C7)	304 (3)	364 (3)	−84 (9)	15·87
H(1C8)	351 (2)	673 (2)	291 (4)	4·26
H(2C8)	322 (2)	649 (2)	49 (4)	4·42
H(3C8)	249 (2)	654 (1)	229 (4)	3·63
H(1C9)	315 (2)	456 (2)	517 (4)	3·87
H(2C9)	243 (2)	530 (2)	513 (4)	4·03
H(3C9)	342 (2)	550 (2)	566 (5)	4·90

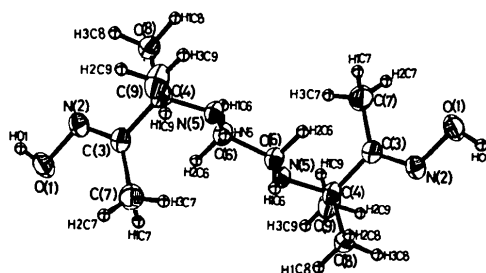* Atom H(O1) is bonded to atom O(1), atom H(1C6) to atom C(6) *etc.*

Fig. 1. Perspective view of the neutral molecule H$_2$enao showing atom labelling as identified in the tables. H atoms are illustrated with small spheres.
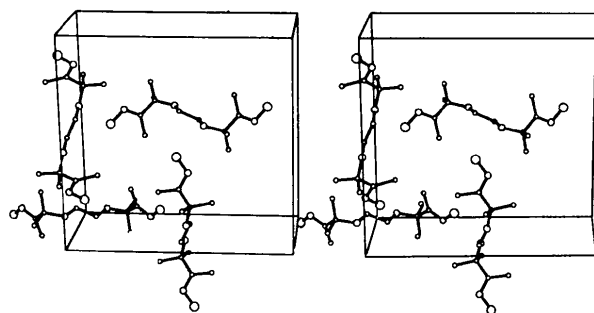

Fig. 2. Stereoscopic view of the unit cell showing molecular packing and possible intermolecular interactions. H atoms are omitted for the sake of clarity.

Table 2. *Selected bond distances* (Å) *and angles* (°)

(a) Intramolecular distances

O(1)–N(2)	1·415 (2)		C(6)–H(2C6)	1·03 (2)
N(2)–C(3)	1·275 (2)		C(7)–H(1C7)	0·92 (4)
C(3)–C(4)	1·536 (3)		C(7)–H(2C7)	0·93 (4)
C(3)–C(7)	1·502 (3)		C(7)–H(3C7)	1·02 (6)
C(4)–N(5)	1·484 (2)		C(8)–H(1C8)	0·99 (3)
C(4)–C(8)	1·527 (3)		C(8)–H(2C8)	1·01 (3)
C(4)–C(9)	1·536 (3)		C(8)–H(3C8)	1·00 (2)
N(5)–C(6)	1·473 (2)		C(9)–H(1C9)	0·99 (2)
C(6)–C(6')*	1·514 (3)		C(9)–H(2C9)	0·97 (2)
O(1)–H(O1)	0·87 (2)		C(9)–H(3C9)	0·92 (3)
N(5)–H(N5)	0·89 (2)			
C(6)–H(1C6)	0·99 (2)			

(b) Intermolecular distances

N(5)···O(1)	2·854 (3)	O(1) at position $\bar{y}, \frac{1}{4}+x, \frac{1}{4}+z$	
N(5)···O(1)	2·369 (3)	O(1) at position $y, \frac{1}{4}-x, \frac{1}{4}-z$	
H(N5)···O(1)	2·537 (4)	O(1) at position $y, \frac{1}{4}-x, \frac{1}{4}-z$	

(c) Intramolecular angles

O(1)–N(2)–C(3)	113·5 (1)		C(9)–C(4)–N(5)	105·7 (1)
N(2)–C(3)–C(7)	123·5 (2)		C(8)–C(4)–C(9)	110·1 (2)
N(2)–C(3)–C(4)	115·2 (2)		C(6)–N(5)–C(4)	116·1 (1)
C(7)–C(3)–C(4)	121·2 (2)		H(N5)–N(5)–C(4)	110 (1)
C(3)–C(4)–N(5)	112·8 (1)		H(N5)–N(5)–C(6)	110 (1)
C(3)–C(4)–C(8)	110·7 (1)		H(1C6)–C(6)–N(5)	108 (1)
C(3)–C(4)–C(9)	108·3 (2)		H(2C6)–C(6)–N(5)	113 (1)
C(8)–C(4)–N(5)	109·0 (1)		H(2C6)–C(6)–H(1C6)	109 (2)

* Related to C(6) by $-x, -y, -z$.

The asymmetric unit comprises one-half of the H$_2$enao molecule with the other half related by the center of symmetry located in the middle of the C(6)–C(6') bond. Bond distances and angles are given in Table 2, which also includes intermolecular distances less than 3·0 Å. The O(1) atom of one molecule is 2·854 Å from N(5) of the second molecule indicating some weak intermolecular hydrogen bonding, providing interlayer linkage in the unit cell with H$_2$enao moieties forming two mutually prependicular layers. Although there is ample empty space in the unit cell, the ligand crystallizes without any solvent of crystallization, unlike most of its complexes. As expected, the thermal-vibration amplitudes for the freely rotating methyl C atoms, *i.e.* C(7), C(8) and C(9), are slightly larger than for the rest of the atoms in the molecule.

The H_2enao molecules are linearly arranged in the unit cell without any intramolecular interaction or any specific orientation of amine or oxime groups in the molecule. Because of the unhindered rotation along C(6)—C(6'), the amine nitrogens attached to this bond are liable to coordinate as the first step in complexation reactions. As a result, the oxime nitrogens will be suitably oriented for complexation followed by deprotonation.

A comparison of distances and angles with those of some related compounds is given in Table 3. None of the observed values, expected to be of chemically equivalent bonds or angles, can be regarded as significantly different. The average C—C and C—N distances are quite normal and are similar to the corresponding distances in other α-amine oxime complexes. Distances involving H atoms are somewhat poorly defined, but the average C—H distance (0·98 Å) and N—H distance [0·89 (2) Å] are quite reasonable (Churchill, 1973). The H—C—H and H—C—N angles range from 108 to 113° with an average value of 110° and average deviation of 5°.

The most significant difference is in the N—O distance [1·415 (2) Å] and in the O—N—C (sp^2) angle, 113·5 (1)°. The N—O distance in the free ligand is appreciably larger (0·054 to 0·093 Å) than the corresponding distance in various complexes of α-amine dioximes. The shortening of the N—O bond in the complexes, vis-à-vis free ligand, is probably indicative of a stronger metal–nitrogen(oxime) interaction leading to relative strengthening of the N—O bond in the complexes purely through inductive effects. This is consistent with the observation (Hussain & Schlemper, 1979) that in all known α-amine oxime complexes, the metal–nitrogen(oxime) distances are always shorter than the metal–nitrogen(amine) distances.

The IR spectrum of the free ligand in the solid state has sharp bands at 3300, 1640 and 920 cm^{-1} for the $>$N—H, $>$C=N and N=O groups, respectively. All these bands are significantly shifted towards lower frequency and were observed at 3150, 1575 and 840 cm^{-1} in [Ni(Henao)]ClO_4. Such a downward shift in frequency is expected for coordinated ligand as compared to the free ligand.

Table 3. *A comparison of some distances* (Å) *and angles* (°) *in* H_2enao *with the corresponding values in related structures*

	N—O	N—C(sp^2)	O—N—C(sp^2)	Reference
[Pd(dmg)$_2$]	1·322 (4)	1·280 (4)	121·3 (2)	(a)
	1·352 (4)	1·299 (4)	121·9 (2)	
[Ni(Henao)]ClO_4	1·349 (3)	1·296 (4)	120·9 (4)	(b)
	1·352 (3)	1·292 (4)	121·4 (4)	
[Pd(Hpnao)](NO$_3$)$_2$	1·345 (5)	1·279 (6)	120·9 (4)	(c)
	1·360 (5)	1·277 (6)	120·9 (4)	
[Ni(Hpnao)]Cl$_2$.H$_2$O	1·349 (6)	1·272 (6)	118·0 (4)	(c)
	1·361 (6)	1·283 (6)	117·6 (4)	
[Ni(Henao)]NO$_3$.H$_2$O	1·360 (7)	1·286 (7)	121·1 (5)	(d)
	1·352 (7)	1·289 (7)	119·4 (5)	
H$_2$enao	1·415 (2)	1·275 (2)	113·5 (1)	This work

References: (a) Hussain, Salinas & Schlemper (1979). (b) Fair & Schlemper (1978). (c) Hussain & Schlemper (1979). (d) Ching & Schlemper (1975).

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