

2,2'-Iminobis(acetamide oxime)

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Abstract. $C_4H_{11}N_5O_2$, $M_r = 161.16$, $F(000) = 344$, monoclinic, $P2_1/a$, $a = 10.458$ (4), $b = 11.388$ (4), $c = 6.208$ (2) Å, $\beta = 102.22$ (3)°, $V = 722.6$ (6) Å³, $Z = 4$, $D_m = 1.53$ (2) (pycnometer), $D_c = 1.48$ Mg m⁻³, λ (Cu $K\alpha$) = 1.54178 Å. The structure was solved using *MULTAN* and refined by the block-diagonal least-squares method. The final R value is 0.061 for 1129 observed reflections. The C–C torsion angles between the N(amine) and the N(oxime) atoms are -30.5 (5) and -80.2 (4)°.

Introduction. The Department of Analytical Chemistry of the University of Barcelona is working on the complexation of metals by molecules with oxime groups. One of these compounds is 2,2'-iminobis(acetamide oxime). The reaction mechanism of the formation of this compound depends upon the metallic ion. In order to understand the different processes of complex synthesis, it was decided to solve the structure of this compound by X-ray diffraction.

The title compound was synthesized by Eddy, Levenhagen & Ewen (1968). Colourless prismatic crystals were kindly supplied by Dr C. Mongay. They were obtained by crystallization from methanol.

A crystal $0.2 \times 0.2 \times 0.4$ mm was used for crystal data and intensity measurements on a Picker semi-automatic diffractometer. Intensities were collected with Cu $K\alpha$ radiation using the ω -scan technique with a scan interval of -0.8 to 0.8° . 1140 independent reflections were measured within the range $1 < \theta \leq 62.5^\circ$; 1129 of these were treated as observed [$I > 2.5\sigma(I)$]. Lorentz–polarization corrections were applied.

The structure was solved using the *MULTAN* system of computer programs (Main, Woolfson, Lessinger, Germain & Declercq, 1978). An E map computed with the phases from the set with the highest combined figure of merit revealed peaks for all non-hydrogen atoms. The structure was isotropically

and anisotropically refined with the *SHELX 76* computer program (Sheldrick, 1976). A difference synthesis revealed the peaks for all the H atoms, which were refined isotropically (the non-hydrogen atoms anisotropically). The refinement was terminated at $R = 0.061$ for all observed reflections, where R is defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$.*

The final atomic parameters are listed in Table 1; Fig. 1 shows a view of the molecule and the numbering of the atoms drawn by the program *PLUTO* (Motherwell & Clegg, 1978).

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35158 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final positional parameters ($\times 10^4$, for H $\times 10^3$)

	x	y	z
N(1)	3318 (3)	1027 (3)	5689 (5)
C(2)	3890 (4)	1175 (4)	8023 (6)
C(3)	5312 (4)	1498 (3)	8446 (6)
N(4)	5790 (4)	2176 (3)	10252 (6)
N(5)	5989 (3)	1114 (3)	7089 (5)
O(6)	7333 (3)	1465 (3)	7867 (5)
C(7)	1883 (4)	832 (3)	5275 (7)
C(8)	1494 (3)	-205 (3)	6523 (6)
N(9)	1083 (4)	-14 (3)	8413 (6)
N(10)	1603 (3)	-1209 (3)	5660 (5)
O(11)	1310 (3)	-2155 (2)	6980 (5)
H(N1)	376 (5)	43 (4)	531 (8)
H(C2)A	332 (4)	180 (4)	853 (7)
H(C2)B	371 (4)	48 (4)	882 (8)
H(N4)A	676 (5)	220 (4)	1090 (8)
H(N4)B	548 (5)	217 (4)	1133 (8)
H(O6)	772 (5)	141 (4)	695 (8)
H(C7)A	153 (4)	70 (4)	353 (8)
H(C7)B	140 (5)	152 (4)	554 (8)
H(N9)A	142 (5)	-51 (4)	951 (8)
H(N9)B	121 (5)	62 (5)	903 (8)
H(O11)	127 (5)	-258 (5)	607 (8)

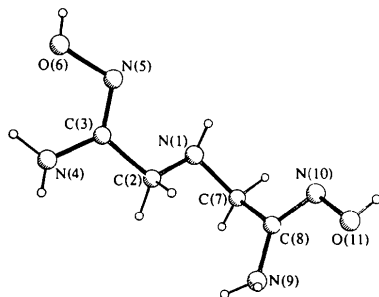


Fig. 1. View of the molecule drawn by *PLUTO*, showing numbering of the atoms

Discussion. Fig. 2 shows the bond distances, bond angles and torsion angles between the non-hydrogen atoms.

The bond distances and angles of 2,2'-iminobis(acetamide oxime) (*ibao*) differ slightly from the values obtained by Cullen & Lingafelter (1970*a*) in bis[2,2'-iminobis(acetamide oxime)]nickel(II) chloride dihydrate and in bis[2,2'-iminobis(acetamide oxime)]copper(II) chloride. However, the most interesting differences involve the C(2)–C(3) and C(7)–C(8) torsion angles; these are $-30.5(5)$ and $-80.2(4)^\circ$ in the title compound, while they range from 11.6 to 30.8° in the above-mentioned Ni and Cu complexes. This torsion angle ranges from 45 to 58° in ethylenediamine complexes (Raymond, Corfield &

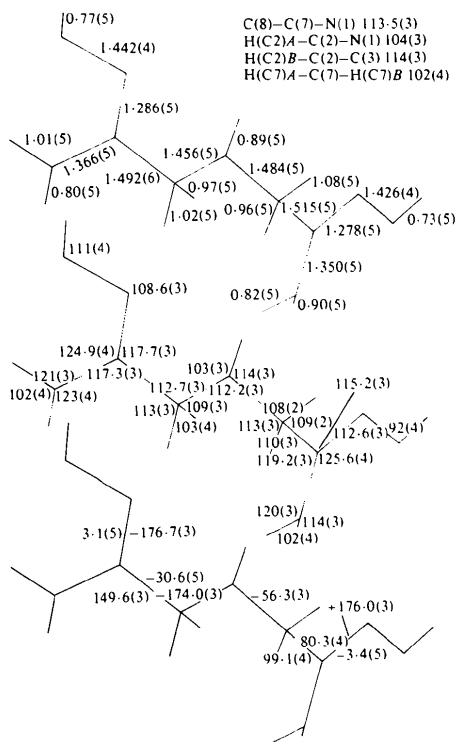


Fig. 2. Bond distances (Å), bond angles ($^\circ$) and torsion angles ($^\circ$).

Table 2. *Hydrogen-bonding geometry*

$A-B \cdots C$	d_{AC}	d_{BC}	$\angle ABC$
O(11)–H(O11) \cdots N(1) ⁱ	2.731 (4) Å	2.03 (5) Å	160 (6) $^\circ$
N(1)–H(N1) \cdots N(5) ⁱⁱ	3.158 (5)	2.35 (5)	151 (4)
O(6)–H(O6) \cdots N(10) ⁱⁱ	2.674 (4)	1.91 (5)	170 (5)

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$; (ii) $1 - x, \bar{y}, 1 - z$.

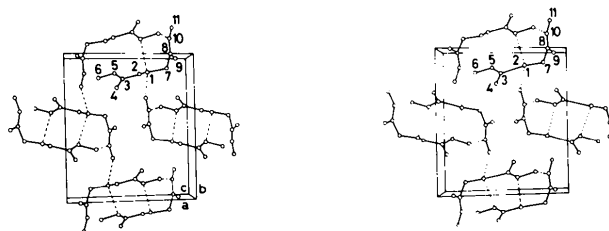


Fig. 3. Stereoview of the unit-cell contents, showing the hydrogen bonds.

Ibers, 1968; Cullen & Lingafelter, 1970*b*); it is 106° in 2-hydroxy-2-(3,4-methylenedioxyphenyl)acetamide oxime (Gozlan & Riche, 1976), while it is about 0° in the dioxime structures (Calleri, Ferraris & Viterbo, 1966, 1967*a,b*; Williams, Wolhauer & Rundle, 1959; Panattoni, Frasson & Zanotti, 1950; Hamilton, 1961; Murmann & Schlemper, 1967).

These *gauche* and *anti*-eclipsed conformations for the C(2)–C(3) and C(7)–C(8) bonds, respectively, can be explained by the hydrogen bonds of *ibao* (Fig. 3 and Table 2). The strong hydrogen bond at N(5) and N(10) indicates that the oxime N atom is a stronger coordinating agent than the amine N atoms, as was also shown by the results of Cullen & Lingafelter (1970*a*).

If the bond distances and angles of the two acetamide oxime groups in *ibao* are compared, it is possible to observe, first that the mean distances and angles are in agreement with the values mentioned in the literature [the above-mentioned structures, *International Tables for X-ray Crystallography* (1968), and *Tables of Interatomic Distances and Configuration in Molecules and Ions* (1958)], and second that the N(1)–C(2), and C(2)–C(3) distances and the C(3)–N(5)–O(6) angle are smaller than N(1)–C(7), C(7)–C(8) and C(8)–N(10)–O(11), while C(3)–N(4), C(3)–N(5), and N(5)–O(6) are longer than C(8)–N(9), C(8)–N(10) and N(10)–O(11). These differences can be explained by the double-quartet theory of Linnet (1961), according to which the C(7)–C(8) torsion angle forces the oxime-amine group at C(8) to be almost completely out of conjugation with the N(1) amine atom. The electronic resonance is therefore localized in the N(9)–C(8)–N(10)–O(11) planar group, while, at C(3), the value of the C(2)–C(3) torsion angle allows the electronic resonance to be

localized in the acetamide-oxime group. The short N(1)···N(5) intramolecular distance [2.746 (5) Å] forces an increase in the C(2)–C(3)–N(5) angle.

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17 α -Ethyanyl-17 β -hydroxy-12-methyl-4,9,11-estratrien-3-one

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Abstract. C₂₁H₂₄O₂, orthorhombic, *P*2₁2₁1, *a* = 20.140 (8), *b* = 11.134 (5), *c* = 7.458 (4) Å, *Z* = 4, *d*_x = 1.22 Mg m⁻³. The molecule is bent towards its α side. The additional 12-methyl group does not significantly affect the usual steroid conformation. The final *R* value is 0.036.

Introduction. 17 α -Ethyanyl-17 β -hydroxy-4,9,11-estratrien-3-one presents androgen and progestin properties. Its 12-methylated derivative, the title compound, has a weaker affinity for androgen and progestin receptors (Raynaud, 1979).

The crystals were obtained by slow evaporation from methanol solution. Unit-cell parameters and 1845 independent reflections were measured on an auto-

matic diffractometer, using Cu *K* α radiation.* The structure was solved by direct methods, using the *MULTAN* program (Germain, Main & Woolfson, 1971).

All the atomic parameters were refined by a least-squares procedure. The H atom positions were found on a difference Fourier map. The positional and equivalent isotropic thermal parameters of the heavy atoms are listed in Table 1. The diffusion factors used are from *International Tables for X-ray Crystallog-*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35254 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.