$S = 1.208$
1742 reflections
244 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.00223(F_o)^2]$

Extinction correction: Larson (1967)
Extinction coefficient: 0.00062 (3)
Atomic scattering factors from *SHELXTL-Plus* (Sheldrick, 1991)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C(1)	1.0563 (4)	0.1689 (4)	0.8590 (3)	0.064 (2)
C(2)	1.1222 (5)	0.2827 (3)	0.8749 (3)	0.071 (2)
C(3)	1.0307 (5)	0.3702 (3)	0.8424 (2)	0.051 (1)
C(4)	0.8553 (5)	0.3693 (3)	0.8533 (2)	0.049 (1)
C(5)	0.7914 (4)	0.2499 (3)	0.8482 (2)	0.042 (1)
C(6)	0.6219 (5)	0.2388 (3)	0.8671 (2)	0.053 (1)
C(7)	0.5574 (4)	0.1333 (3)	0.8389 (2)	0.052 (1)
C(8)	0.6468 (4)	0.0314 (3)	0.8574 (2)	0.040 (1)
C(9)	0.8245 (4)	0.0478 (3)	0.8534 (2)	0.039 (1)
C(10)	0.8884 (4)	0.1570 (3)	0.8818 (2)	0.043 (1)
C(11)	0.9036 (4)	−0.0532 (3)	0.8841 (2)	0.054 (1)
C(12)	0.8316 (4)	−0.1613 (3)	0.8595 (3)	0.052 (1)
C(13)	0.6537 (4)	−0.1597 (3)	0.8592 (2)	0.041 (1)
C(14)	0.6023 (4)	−0.0657 (3)	0.8145 (2)	0.044 (1)
C(15)	0.5932 (4)	−0.1193 (3)	0.9278 (2)	0.044 (1)
C(16)	0.4265 (5)	−0.1489 (3)	0.9429 (2)	0.051 (1)
C(17)	0.5982 (4)	−0.2717 (3)	0.8388 (2)	0.049 (1)
C(18)	0.8282 (6)	0.4260 (3)	0.9217 (2)	0.064 (2)
C(19)	0.7785 (6)	0.4383 (3)	0.7979 (2)	0.063 (2)
C(20)	0.8788 (6)	0.1594 (3)	0.9605 (2)	0.065 (2)
C(21)	0.3541 (4)	−0.3178 (3)	0.8901 (2)	0.045 (1)
C(22)	0.1856 (5)	−0.2966 (4)	0.8750 (3)	0.060 (2)
C(23)	0.3819 (5)	−0.4389 (3)	0.9026 (2)	0.061 (2)
O(1)	1.0927 (4)	0.4387 (3)	0.8087 (2)	0.080 (1)
O(2)	0.6030 (3)	−0.0023 (2)	0.9253 (1)	0.047 (1)
O(3)	0.4066 (3)	−0.2641 (2)	0.9489 (1)	0.051 (1)
O(4)	0.4346 (3)	−0.2790 (2)	0.8318 (1)	0.047 (1)

Table 2. *Geometric parameters* (*Å*, °)

C(1)—C(2)	1.546 (6)	C(2)—C(3)	1.484 (6)
C(3)—C(4)	1.535 (6)	C(4)—C(5)	1.574 (5)
C(5)—C(6)	1.522 (5)	C(6)—C(7)	1.521 (6)
C(7)—C(8)	1.520 (5)	C(8)—C(9)	1.554 (5)
C(1)—C(10)	1.530 (5)	C(5)—C(10)	1.568 (5)
C(9)—C(10)	1.559 (5)	C(9)—C(11)	1.545 (5)
C(11)—C(12)	1.548 (5)	C(12)—C(13)	1.541 (5)
C(8)—C(14)	1.515 (5)	C(13)—C(14)	1.522 (5)
C(13)—C(15)	1.536 (5)	C(15)—C(16)	1.519 (6)
C(13)—C(17)	1.515 (5)	C(4)—C(18)	1.540 (6)
C(4)—C(19)	1.538 (6)	C(10)—C(20)	1.558 (5)
C(21)—C(22)	1.512 (5)	C(21)—C(23)	1.531 (5)
C(3)—O(1)	1.202 (5)	C(8)—O(2)	1.456 (4)
C(15)—O(2)	1.443 (4)	C(16)—O(3)	1.434 (4)
C(21)—O(3)	1.413 (5)	C(17)—O(4)	1.426 (4)
C(21)—O(4)	1.429 (5)		
C(2)—C(1)—C(10)	112.2 (3)	C(6)—C(7)—C(8)	115.5 (3)
C(2)—C(3)—C(4)	117.6 (3)	C(7)—C(8)—C(14)	112.8 (3)
C(4)—C(3)—O(1)	121.7 (4)	C(7)—C(8)—O(2)	108.9 (3)
C(3)—C(4)—C(18)	105.7 (3)	C(14)—C(8)—O(2)	103.0 (3)
C(3)—C(4)—C(19)	109.0 (3)	C(8)—C(9)—C(11)	108.3 (3)
C(18)—C(4)—C(19)	108.0 (3)	C(1)—C(10)—C(5)	108.3 (3)
C(4)—C(5)—C(10)	117.7 (3)	C(5)—C(10)—C(9)	106.6 (3)
C(5)—C(6)—C(7)	109.9 (3)	C(5)—C(10)—C(20)	112.4 (3)
C(7)—C(8)—C(9)	112.6 (3)	C(9)—C(11)—C(12)	113.0 (3)
C(9)—C(8)—C(14)	109.1 (3)	C(12)—C(13)—C(14)	107.7 (3)
C(9)—C(8)—O(2)	110.1 (3)	C(14)—C(13)—C(15)	99.5 (3)
C(8)—C(9)—C(10)	116.5 (3)	C(14)—C(13)—C(17)	116.5 (3)
C(10)—C(9)—C(11)	113.3 (3)	C(8)—C(14)—C(13)	101.6 (3)
C(1)—C(10)—C(9)	108.3 (3)	C(13)—C(15)—C(16)	114.8 (3)
C(1)—C(10)—C(20)	110.1 (3)	C(16)—C(15)—O(2)	107.6 (3)
C(9)—C(10)—C(20)	111.0 (3)	C(13)—C(17)—O(4)	113.5 (3)
C(11)—C(12)—C(13)	113.2 (3)	C(22)—C(21)—O(3)	113.1 (3)
C(12)—C(13)—C(15)	109.9 (3)	C(22)—C(21)—O(4)	104.8 (3)
C(12)—C(13)—C(17)	107.9 (3)	O(3)—C(21)—O(4)	110.5 (3)
C(15)—C(13)—C(17)	114.9 (3)	C(16)—O(3)—C(21)	115.7 (3)
C(1)—C(2)—C(3)	111.9 (4)	C(13)—C(15)—O(2)	105.9 (3)
C(2)—C(3)—O(1)	120.7 (4)	C(15)—C(16)—O(3)	111.6 (3)
C(3)—C(4)—C(5)	110.2 (3)	C(22)—C(21)—C(23)	110.6 (3)
C(5)—C(4)—C(18)	115.3 (3)	C(23)—C(21)—O(3)	105.8 (3)
C(5)—C(4)—C(19)	108.6 (3)	C(23)—C(21)—O(4)	112.2 (3)
C(4)—C(5)—C(6)	114.0 (3)	C(8)—O(2)—C(15)	109.3 (2)
C(6)—C(5)—C(10)	110.3 (3)	C(17)—O(4)—C(21)	115.3 (3)

The H atoms in the CH and CH_2 groups were allowed to ride on the bonded C atom and refined.

Data collection: *SHELXTL-Plus* (Sheldrick, 1991). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXTL-Plus*, *PARST* (Nardelli, 1983).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1039). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1-Phenyl-4-imidazolidinone (Z)-Oxime

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Abstract

The treatment of 4-nitroimidazoles with an excess of sodium borohydride in the presence of sodium methoxide yields the (*Z*)-oximes of 4-imidazolidinones. The title compound, 1-phenyl-4-imidazolidinone (*Z*)-

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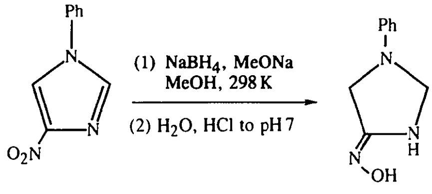
oxime, $C_9H_{11}N_3O$, is a coplanar molecule despite the saturation of the hetero ring.

Comment

Interest in the antiprotozoal, antiviral and radio-sensing behavior of certain nitroimidazoles (Moss, Paniucci, McClelland & Rauth, 1988) and their derivatives has led to an interest in the chemical and bio-reduction of nitroarenes.

Reactions of nitroarenes with nucleophiles, *e.g.* nucleophilic substitution of the H atom (Makosza, 1992) or ring transformations of nitroheteroarenes following nucleophilic attack, may involve reduction of the nitro group (Suwinski, Salwinska, Swierczek & Pawlus, 1994). Nitroarenes reduced with sodium borohydride usually yield azoxy or azo compounds (Hutchins, Lamson, Rua, Milewski & Maryanoff, 1971). In other cases, treatment of aromatic nitro compounds with $NaBH_4$ has resulted in either the reduction of the ring to cyclohexane leaving the nitro group untouched or in cleavage of the nitro group (Kaplan, 1964). In contrast, the reduction of an aliphatic nitro compound containing an α-H atom may be stopped at the oxime stage (Patai, 1970).

We have effected hydride reduction of a nitroheteroarene [4-nitro-1-phenylimidazole, (I)] to a (*Z*)-oxime, (II). The solid-state structure of 1-phenyl-4-imidazolidinone (*Z*)-oxime, (II), shows all the non-H atoms to be coplanar (standard deviation 0.03 Å). Despite the planarity of the derivatized imidazole ring, bond distances attest to its saturation; N3—C2 1.45 (1) and N3—C4 1.44 (1) Å compared with the corresponding distances of 1.372 (3) and 1.373 (3) Å observed in 1,4-dinitroimidazole (Grimmett, Hua, Chang, Foley & Simpson, 1989). The shortened N1—C5 distance of 1.32 (1) Å, however, indicates delocalization of the unshared pair of electrons on the N1 atom due to conjugation with the C5═N4 double bond. Intermolecular hydrogen bonding is observed in the solid involving the O1 and N1 atoms as donors and the O1, N4 and N1 atoms as acceptors.



(I) (II)

Other 1-alkyl- and 1-aryl-4-nitroimidazoles behave like 4-nitro-1-phenylimidazole. The reduction of 1-substituted 2-methyl-4-nitroimidazoles produces the respective oximes, but in lower yields because of byproduct formation (probably oximes of imidazolidone derivatives). 1-Substituted 5-methyl-4-nitroimidazoles, unstable in the presence of strong bases, do not undergo such reductions.

Compound (II) has also been obtained by the hydride reduction of 4-nitro-1-phenylimidazole in ethylene glycol at 298 K, though the reaction was slow and the yield of reduced product lower (68%). A mixture of the oxime of 2-methyl-1-phenyl-4-imidazolidinone and a byproduct was obtained from 2-methyl-4-nitro-1-phenylimidazole, but no reduction of 5-methyl-4-nitro-1-phenylimidazole (stable in ethylene glycol) was observed under similar conditions. These results suggest that hydride reduction begins with attack of the hydride ion on position 5 of the imidazole ring.

A similar reduction (nitro to nitroso) in 4-nitroimidazoles has recently been observed in reactions of 1-aryl-4-nitroimidazoles with nucleophiles (Makosza, 1992; Suwinski, Swierczek & Glowiak, 1993). Catalytic hydrogenation of 4-nitroimidazoles leads to unstable 4-aminoimidazoles (Suwinski & Walczak, 1994).

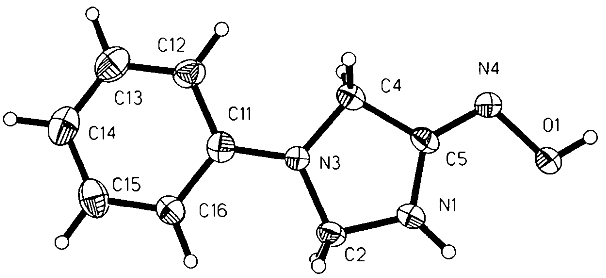


Fig. 1. Projection view of 1-phenyl-4-imidazolidinone (*Z*)-oxime. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

4-Nitro-1-phenylimidazole was added to a solution of sodium methoxide in methanol followed by the addition of sodium borohydride. The resulting solution was stirred at 298 K until the original organic material disappeared (thin-layer chromatography) and was then neutralized with concentrated HCl. The solvent was reduced in volume at low pressure, diluted with water and the resulting precipitate was recrystallized from MeOH (94% yield). Found: C 61.64, H 6.35, N 23.64%; M^+ 177; calculated for $C_9H_{11}N_3O$: C 61.90, H 6.26, N 23.71%; M^+ 177; ^{1}H NMR (DMSO-d_6): δ 3.88 (*s*, 2H), 4.56 (*s*, 2H), 6.38–7.31 (*m*, 6H), 8.94 (*s*, 1H).

Crystal data

$C_9H_{11}N_3O$
$M_r = 177.2$
Monoclinic
$P2_1/c$
$a = 15.312(3)$ Å
$b = 5.024(1)$ Å
$c = 12.514(3)$ Å
$\beta = 112.23(3)°$
$V = 891.1(1)$ Å^3
$Z = 4$
$D_x = 1.321$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 31 reflections
$\theta = 9.881$–$24.521°$
$\mu = 0.091$ mm^{-1}
$T = 298$ K
Needle
$0.30 \times 0.15 \times 0.10$ mm
Colorless

Data collection

Syntex $P4$ four-circle diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2204 measured reflections
1554 independent reflections
512 observed reflections [$F > 4.0\sigma(F)$]
$R_{\rm int} = 0.066$
$\theta_{\rm max} = 27.5°$
$h = -18 \rightarrow 17$
$k = -5 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections monitored every 97 reflections intensity decay: 0.0001%

Refinement

Refinement on F
$R = 0.0470$
$wR = 0.0475$
$S = 1.06$
512 reflections
119 parameters
$w = 1/[\sigma^2(F) + 0.0008F^2]$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: none
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 (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y†	z	$U_{\rm eq}$
O1	0.5038 (3)	0.069 (1)	0.3570 (4)	0.043 (3)
N1	0.4001 (4)	0.294 (1)	0.4548 (5)	0.046 (4)
C2	0.3328 (5)	0.435 (2)	0.4922 (6)	0.039 (4)
N3	0.2928 (5)	0.623 (2)	0.3985 (5)	0.046 (4)
C4	0.3254 (5)	0.587 (2)	0.3056 (6)	0.039 (4)
N4	0.4442 (5)	0.278 (1)	0.2938 (5)	0.036 (3)
C5	0.3959 (5)	0.365 (2)	0.3516 (7)	0.032 (4)
C11	0.2214 (6)	0.793 (2)	0.3926 (7)	0.039 (4)
C12	0.1789 (6)	0.964 (2)	0.2987 (7)	0.051 (4)
C13	0.1084 (6)	1.140 (2)	0.2973 (8)	0.059 (5)
C14	0.0779 (7)	1.150 (2)	0.3877 (9)	0.059 (5)
C15	0.1167 (6)	0.976 (2)	0.4782 (9)	0.062 (5)
C16	0.1876 (6)	0.805 (2)	0.4829 (7)	0.046 (5)

† The small b cell dimension is reflected in high errors in the y atomic coordinates.

Table 2. *Selected geometric parameters (Å, °)*

C11—N3	1.37 (1)	N4—O1	1.421 (8)
C11—C12	1.40 (1)	C4—C5	1.51 (1)
C11—C16	1.41 (2)	C5—N1	1.32 (1)
C12—C13	1.39 (2)	C5—N4	1.29 (1)
C13—C14	1.38 (2)	N1—C2	1.47 (1)
C14—C15	1.37 (2)	N3—C2	1.45 (1)
C15—C16	1.37 (2)	N3—C4	1.44 (1)
C4—N3—C2	113.8 (7)	C12—C11—N3	122.5 (9)
N3—C4—C5	101.6 (7)	C16—C11—N3	120.8 (8)
C4—C5—N1	109.8 (8)	C11—C12—C13	120.8 (10)
C4—C5—N4	121.1 (8)	C12—C13—C14	121.1 (9)
N1—C5—N4	129.1 (7)	C13—C14—C15	118.6 (10)
C5—N1—C2	113.7 (7)	C14—C15—C16	121.5 (11)
N3—C2—N1	100.9 (7)	C11—C16—C15	121.1 (9)
C5—N4—O1	108.9 (6)	C11—N3—C4	123.3 (7)
C12—C11—C16	116.7 (9)	C11—N3—C2	122.3 (8)

The H atom associated with the oxime O1 atom was located from a difference Fourier synthesis and the remaining H atoms were placed in sites with idealized geometry. All H atoms were included in least-squares cycles with fixed positional and isotropic displacement parameters. A variable scan rate was used, with a scan width of 0.6° below $K\alpha_1$ and 0.6° above $K\alpha_2$ to a maximum 2θ value of 60°. Refinement was completed using full-matrix least-squares methods.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXS86*. Molecular graphics: *XP* (Siemens, 1990).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PA1215). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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L-Isoleucine, Redetermination at 120 K

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Abstract

This redetermination of L-isoleucine, $C_6H_{13}NO_2$, forms part II in the series of crystal structures of hydrophobic amino acids. Standard deviations for bond lengths between heavy atoms are down to 0.002 Å. Detailed parameters for the hydrogen-bonding pattern are given.

Comment

The hydrophobic amino acids, except L-alanine, crystallize in monoclinic space groups with alternating hydro-

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