

An oximino tautomer of 1-*n*-decyl-4-hydroxyimino-3-methyl-1*H*-pyrazol-5(4*H*)-one

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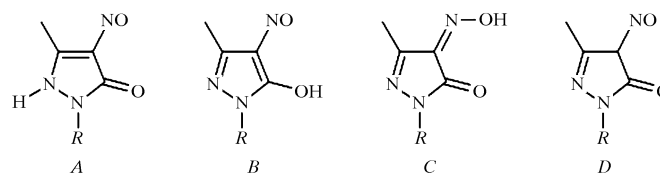
The title compound, C₁₄H₂₅N₃O₂, consists of a five-membered heterocyclic ring to which a pendant decyl group is attached. The oximino tautomeric character of the molecule is clearly defined by the distribution of well defined double bonds in the heterocycle region (one C=O and two C=N). The most conspicuous packing interaction is the strong intermolecular hydrogen bond linking the oximino OH group and the carbonyl O atom to define broad planar hydrophilic strips running along the unique *b* axis. The alkyl chains adopt a fully extended conformation and lie almost at right angles to these one-dimensional structures, defining their hydrophobic counterpart.

Comment

Pyrazolones have attracted attention because they exhibit prototropic tautomerism (Elguero, 1996; Uraev *et al.*, 2000; Gilchrist, 2001), and they have been studied extensively both in solution and in the crystalline phase (Chmutova *et al.*, 2001).

To date, most pyrazolones described are 1-aryl or 1-unsubstituted derivatives. Bartulin *et al.* (1992) showed that 3-methyl-5-pyrazolones can be alkylated easily at atom N1 with primary alkyl halides. Nitrosation of some 1-*n*-alkyl-3-methyl-5-pyrazolones was also reported (Bartulin *et al.*, 1994). Four important tautomeric structures can be envisaged for nitrosopyrazolones (see scheme below). On the basis of ¹⁵N NMR measurements for 1-ethyl-3-methyl-4-nitrosopyrazol-5-one, an equilibrium in solution between two nitroso structures, *A* and *B*, was suggested (Bartulin *et al.*, 1994). This result should be valid for any 1-*n*-alkyl homologue since they exhibit similar patterns in their ¹H and ¹³C NMR spectra. This finding was rather unexpected, because nitrosopyrazolones usually exist as oximino tautomers (structure *C*), similar to many other nitroso compounds (Wiley & Wiley, 1964; Ivanova &

Enchev, 2001; Krzan *et al.*, 2000). Unfortunately, Bartulin *et al.* (1994) did not succeed in obtaining single crystals from the compounds they reported, and the question of what the actual situation would be in the solid state remained open.



On the other hand, Barjesteh *et al.* (1996) described the crystal structure of metal complexes obtained from 1-phenyl-3-methyl- and 1,3-dimethyl-4-(hydroxyimino)pyrazol-5-one, and they suggested that the complexes have an oximino structure; however, a closer analysis of the bond lengths seems to point towards a 4-nitroso complex in both cases. The structure of 4-[(*N*-benzoyloxycarbonylvalyl)oxyimino]-3-methyl-1-phenyl-2-pyrazolin-5-one has also been described (Bertolasi *et al.*, 1978), but in this case the oximino structure is locked by the acyl group. Holzer & Hallak (2004) obtained a mixture of *E* and *Z* stereoisomers of the 4-hydroxyimino derivative by nitrosation of 3-methyl-1-phenyl-5-pyrazolone, although no crystal data were reported.

As a result of our interest in the subject and following on from the results reported by Bartulin *et al.* (1994), 1-*n*-decyl-3-methyl-5-pyrazolone was nitrosated in our laboratory and the product obtained was analysed by NMR and IR techniques.

Single-crystal X-ray structure analysis showed the product to be the title compound, (I), with a structure quite different from that observed in solution.

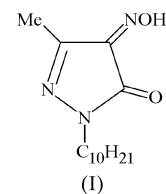


Fig. 1 is a labelled ellipsoid plot of the molecule of (I), showing the interactions with neighbouring molecules. The molecule consists of a heterocycle to which a pendant decyl group is attached. Table 1 presents selected bond lengths and angles in the heterocycle. It is apparent that the C3=O1, C2=N3 and N1=C1 distances correspond to well defined double bonds, being considerably shorter than the corresponding values in related compounds (Belmar *et al.*, 2004). The C2=N3 distance and the presence of the H atom attached to O2 (clearly visible in the difference Fourier map) confirm that the crystal structure contains the *anti*-oximino tautomer, all distances in the structure being in full agreement with the corresponding values in similar systems reported in the literature (Talberg, 1975)

In the present case, the prototropic tautomerism favours, in the solid state, the formation of the *anti* conformer, allowing the formation of a broad one-dimensional network (hereafter 'the strip') along the unique *b* axis, built up through a strong intermolecular hydrogen bond between the oximino group in

one molecule and the carbonyl group in a neighbouring molecule (Fig. 1 and Table 2).

The heterocyclic rings thus connected are almost coplanar with each other [the dihedral angle is $2.95 (1)^\circ$] and constitute

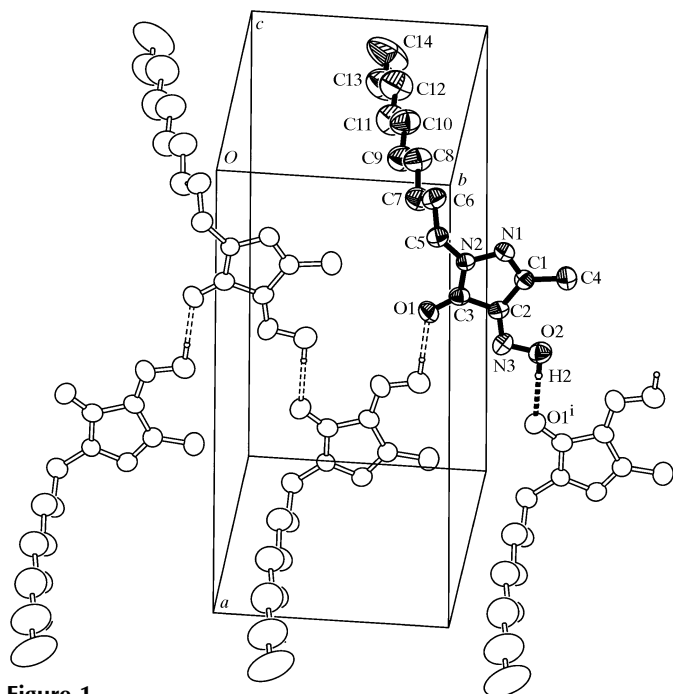


Figure 1
A displacement ellipsoid plot showing the way in which the strips are formed. Only the reference molecule in the asymmetric unit has been drawn with full 40% displacement ellipsoids, symmetry-related molecules being represented by open ellipsoids. H atoms not involved in hydrogen bonds have been omitted. (Symmetry code as in Table 2.)

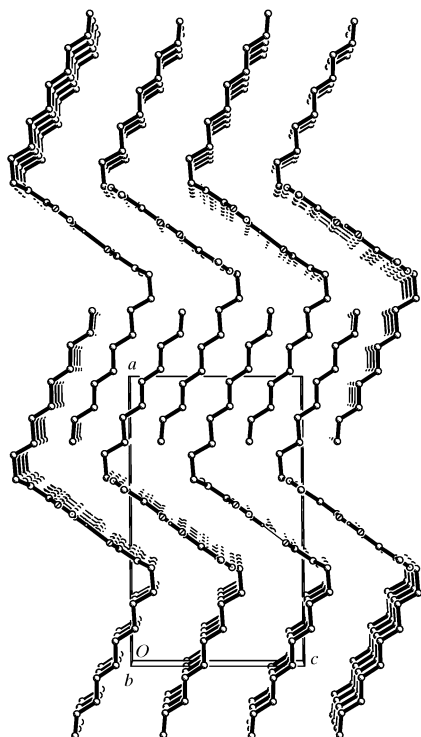


Figure 2
A packing diagram showing the stacking of strips. Note the hydrophilic core at $x \approx 0.50$ and the hydrophobic counterpart at $x \approx 1.0$

a planar core to this strip [the maximum deviation from the mean plane is $0.07 (1) \text{ \AA}$ for atom O1]. The alkyl chains adopt a fully extended conformation and lie almost at right angles to the core, their axis subtending an angle of $ca 10^\circ$ to the plane normal, in an alternating 'up and down' fashion, or, in other words, with neighbouring chains in the same strip being *trans* to each other.

Strips stack in such a way as to have the corresponding cores parallel and at a distance of $3.12 (1) \text{ \AA}$ between mean planes (Fig. 2). Rings in closest contact are related by a centre of inversion and are offset laterally so that the centre-to-centre approach, $Cg \cdots Cg(1-x, 2-y, 1-z)$, is $4.23 (1) \text{ \AA}$ (Cg is the centre of the heterocycle), with a slippage angle as large as $39.1 (1)^\circ$.

These planar strips located at $x \approx 0.50$ (Fig. 2) constitute the hydrophilic part of the structure; the alkyl chains, interdigitating parallel to each other at $x \approx 0$ and 1 , define the hydrophobic counterpart. Each one of these aliphatic segments appears surrounded in a hexagonal fashion by another six, almost parallel, neighbouring segments displaying shortest-approach $C \cdots C$ distances in the range $4.30 (1) - 5.16 (1) \text{ \AA}$.

Experimental

The title compound was obtained by nitrosation of 1-*n*-decyl-3-methyl-5-pyrazolone (Bartulin *et al.*, 1994) (yield 63%; m.p. $360 - 361 \text{ K}$). NMR measurements agreed with previous findings of two nitrosopyrazolone tautomers (*A* and *B* in scheme in *Comment*). IR spectra recorded using KBr pellets of crystals obtained by rapid evaporation of chloroform, acetone and ethanol solutions were very similar; however, little information could be extracted from them. The spectra are characterized by a strong band at 1700 cm^{-1} ($C=O$) and a medium band around 1595 cm^{-1} (NO). The fact that the ratio of $C=O$ to NO is not the same in all cases may be a consequence of different tautomer ratios. Single crystals were obtained by evaporation of an ethanol solution.

Crystal data

$C_{14}H_{25}N_3O_2$	$D_x = 1.114 \text{ Mg m}^{-3}$
$M_r = 267.37$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3987 reflections
$a = 17.948 (4) \text{ \AA}$	$\theta = 4.1 - 26.7^\circ$
$b = 8.2512 (17) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 10.762 (2) \text{ \AA}$	$T = 295 (2) \text{ K}$
$\beta = 90.461 (4)^\circ$	Prism, yellow
$V = 1593.7 (6) \text{ \AA}^3$	$0.22 \times 0.18 \times 0.14 \text{ mm}$
$Z = 4$	

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

C1—N1	1.291 (3)	C3—O1	1.218 (2)
C1—C2	1.461 (3)	C3—N2	1.340 (2)
C1—C4	1.473 (3)	N1—N2	1.403 (2)
C2—N3	1.296 (2)	N3—O2	1.349 (2)
C2—C3	1.478 (3)		
N1—C1—C2	109.47 (18)	O1—C3—C2	129.59 (19)
N1—C1—C4	121.54 (19)	N2—C3—C2	103.52 (18)
C2—C1—C4	129.0 (2)	C1—N1—N2	108.13 (16)
N3—C2—C1	135.3 (2)	C3—N2—N1	113.45 (16)
N3—C2—C3	119.25 (18)	C3—N2—C5	127.78 (17)
C1—C2—C3	105.43 (17)	N1—N2—C5	118.35 (17)
O1—C3—N2	126.88 (19)	C2—N3—O2	111.46 (17)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2\cdots O1^i$	0.86 (2)	1.81 (2)	2.671 (2)	179 (2)

Symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.**Data collection**

Bruker SMART CCD area-detector
diffractometer
 φ and ω scans
11384 measured reflections
3600 independent reflections
1831 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.059$
 $\theta_{\text{max}} = 28.0^\circ$
 $h = -22 \rightarrow 22$
 $k = -10 \rightarrow 10$
 $l = -13 \rightarrow 14$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.065$
 $wR(F^2) = 0.184$
 $S = 1.03$
3600 reflections
177 parameters

H atoms treated by a mixture of
independent and constrained
refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0861P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.10 \text{ e } \text{Å}^{-3}$

Those H atoms defined by the stereochemistry were placed at ideal positions ($Csp^2-H = 0.97 \text{ Å}$ and $Csp^3-H = 0.96 \text{ Å}$) and allowed to ride. Methyl groups were allowed to rotate about their local threefold axes. The H atom attached to O2 was found in a difference Fourier map and refined with restraints [$O-H = 0.86 (2) \text{ Å}$]. Isotropic displacement parameters for all H atoms were defined as $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{host})$, where x is 1.2 for non-methyl and hydroxy H atoms, and 1.5 for methyl H atoms. The pendant alkyl group appears highly mobile, with rather large anisotropic displacement parameters which impaired the calculation of the C—C distances, particularly for the outermost C atoms. Full use was made of the CCDC package for searching the Cambridge Structural Database (CSD; Allen, 2002).

Data collection: *SMART-NT* (Bruker, 2001); cell refinement: *SAINT-NT* (Bruker, 2000); data reduction: *SAINT-NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-NT* (Bruker, 2000); software used to prepare material for publication: *SHELXTL-NT*.

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