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1-(1-Adamantyloxy)pyridin-2(1*H*)-one

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.011 Å
Disorder in main residue
R factor = 0.082
wR factor = 0.303
Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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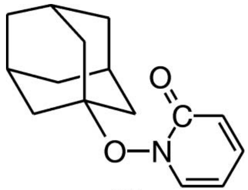
The bond angle at the bridging O atom between the two subunits of the title compound, $C_{15}H_{18}NO_2$, is 114.1 (5)°, which exceeds the values reported for structurally related 1-(alkoxy)pyridin-2(1*H*)-ones. The pyridone ring and the alkoxy substituent are located on a mirror plane so that the carbonyl O atom is disordered over two positions with occupancies of 50%.

Comment

1-(Alkoxy)pyridin-2(1*H*)-ones are O-esters of the cyclic hydroxamic acid 1-(hydroxy)pyridin-2(1*H*)-one (Walter & Schaumann, 1971). Almost a decade ago, these heterocycles were recognized as valuable models for elucidating the structural chemistry of a prominent but chemically labile class of alkoxyl radical progenitors, the 1-(alkoxy)pyridine-2(1*H*)-thiones (Beckwith & Hay, 1988; Hartung *et al.*, 1996, 1997; Hartung, 2006). Since tertiary 1-(alkoxy)pyridin-2(1*H*)-ones and the corresponding pyrdine-2(1*H*)-thiones have thus far escaped structural characterization, the title compound, (I) (Schöllkopf & Hoppe, 1972), was prepared and investigated by X-ray diffraction. The results of this study are reported here, including important and hitherto unpublished experimental details and NMR spectroscopic data.



(I)

Compound (I) crystallizes in the orthorhombic space group *Pnma*. The bond lengths of the heterocyclic core increase along the series N1—C2 < C3—C4 < C2—C3 (Table 1). Atoms C2/C2*a* and C3/C3*a* are related by the symmetry code (x, $-y + \frac{3}{2}$, z). The bond lengths and angles of the functionalized pyridine nucleus (Table 1) agree with values reported for structurally related derivatives of 1-(hydroxy)pyridin-2(1*H*)-one (Hartung *et al.*, 1996, 1997). The exception is the N1—C2—C3 angle of 115.0 (13)°, which is larger than the mean value of 112.4 (7)° for three similar structures (Hartung *et al.*, 1996, 1997). The N1—O1 distance (Table 1) is close to the mean value of 1.397 (8) Å in O-substituted derivatives of 1-(hydroxy)pyridin-2(1*H*)-one and 1.383 (8) Å in cyclic thiohydroxamates (Hartung *et al.*, 2006). The N1—O1—C5 angle of 114.1 (5)° exceeds the corresponding values in 1-(acetyloxy)pyridin-2(1*H*)-one [113.1 (1)°], 1-(cyclohexyloxy)pyri-

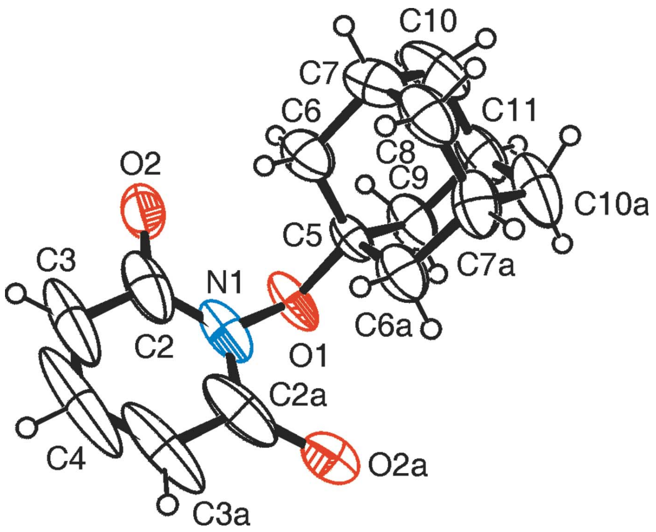


Figure 1
The molecular structure of (I) in the solid state. Displacement ellipsoids are drawn at the 40% probability level. [Symmetry code: (*a*) $x, \frac{3}{2} - y, z$.]

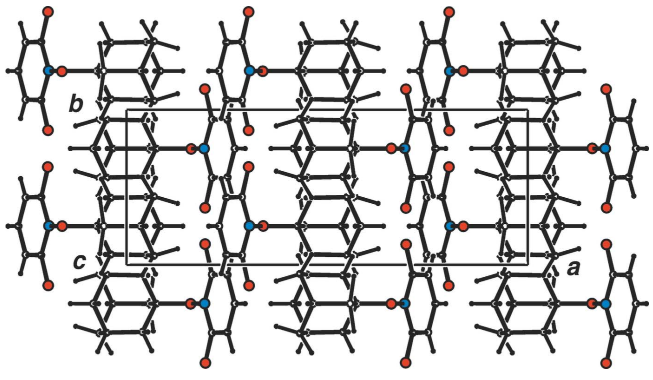


Figure 2
The packing of (I), viewed along [001].

din-2(1*H*)-one [110.2 (1)°] and 1-(1′-phenylethyl-1′-oxy)pyridin-2(1*H*)-one [111.7 (1)°] (Hartung *et al.*, 1996, 1997), which is considered to originate from the more pronounced steric congestion imposed by the tertiary substituent in (I).

The C2—N1—O1—C5 torsion angle is −94.6 (4)°. An approximately orthogonal arrangement of this subunit is a common structural motif encountered in O-esters and mixed anhydrides of hydroxamates and thiohydroxamates. It is caused by a combination of steric and Coulomb repulsion associated with substituents and orbitals at the N—O group (Hartung *et al.*, 1996, 2001). Atoms C6/C6*a*, C7/C7*a*, and C10/C10*a* of the adamantyl group are related by the symmetry code $(x, -y + \frac{3}{2}, z)$. Because the pyridone ring lies on a mirror plane, the carbonyl atom O2 is disordered over two positions with occupancies of 50%.

The C2—O2 distance is unexpectedly large for a C═O double bond (Table 1; Allen *et al.*, 1987; Hartung *et al.*, 1996), although the ^{13}C NMR chemical shift of 161.3 ($CDCl_3$) leaves no doubt of C2 being a carbonyl C atom (Kalinowski *et al.*, 1984). The ^{1}H NMR spectrum ($CDCl_3$) exhibits resonances of four lowfield-shifted protons. The spectroscopic location and multiplicity of these signals clearly point to the underlying 1-(alkoxy)pyridin-2(1*H*)-one structure outlined in the chemical formula of (I).

Packing of (I) occurs in sheets with the hydrophobic and polar entities oriented toward one another, as seen in the view along [001] in Fig. 2. The closest distance between O2 atoms from adjacent molecules is 1.55 (5) Å. Since the calculated occupancy of this atom is 50%, it is expected that the heteroatoms of one layer point in equivalent directions, thus avoiding this close contact.

Experimental

2-(1-Adamantyloxy)pyridine 1-oxide (3.00 g m, 12.3 mmol) was placed in a round-bottomed flask (5 ml) and heated under argon for 4 h at 473 ± 5 K, whereupon darkening occurred. Upon cooling to 293 K a tan solid was obtained, which was broken up and eluted with hot acetone (30 ml). The undissolved material was separated by filtration and the filtrate concentrated under reduced pressure. The remaining solid was taken up in $CHCl_3$ (10 ml) and purified by chromatography [SiO_2, $CHCl_3$–EtOH 19:1 (*v*/*v*); R_f(I) = 0.72 for $CHCl_3$–EtOH 9:1 (*v*/*v*)] to afford 1.65 g m (65%) of the title compound. Crystals suitable for X-ray diffraction were grown from a saturated solution of (I) in acetone–$CHCl_3$ (2:1 *v*/*v*), which was stored in an atmosphere of pentane vapour at 298 K. Spectroscopic analysis: ^{1}H NMR (250 MHz, $CHCl_3$, δ, p.p.m.): 1.59 (*s*, 6H), 1.94 (m_c, 6H), 2.19 (m_c, 3H), 6.00 (*dt*, J_d = 2 Hz, J_t = 7 Hz, 1H), 6.61 (*dd*, *J* = 2 and 9 Hz, 1H), 7.22 (*ddd*, *J* = 2, 7 and 9 Hz, 1H), 7.37 (*dd*, *J* = 2 and 7 Hz, 1H); ^{13}C NMR (63 MHz, $CHCl_3$, δ, p.p.m.): 31.4, 36.2, 41.5, 87.1, 104.2, 123.2, 138.5, 139.6, 161.3.

Crystal data

$C_{15}H_{18}NO_2$
$M_r = 244.30$
Orthorhombic, *Pnma*
$a = 16.982$ (3) Å
$b = 6.559$ (3) Å
$c = 11.237$ (2) Å
$V = 1251.6$ (7) Å^3
$Z = 4$
$D_x = 1.296$ Mg m^{-3}

Mo *K*α radiation
Cell parameters from 25 reflections
$\theta = 3.0$–11.1°
$\mu = 0.09$ mm^{-1}
$T = 299$ (2) K
Needle, colourless
0.70 × 0.10 × 0.03 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2132 measured reflections
1256 independent reflections
385 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.233$

$\theta_{\max} = 25.5°$
$h = 0 \rightarrow 20$
$k = -7 \rightarrow 5$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 120 min
intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.082$
$wR(F^2) = 0.303$
$S = 1.05$
1256 reflections
106 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1203P)^2 + 0.3693P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

C2—N1	1.368 (12)	C5—C9	1.540 (11)
C2—C3	1.433 (11)	C6—C7	1.537 (9)
C2—O2	1.521 (13)	C7—C8	1.495 (8)
C3—C4	1.371 (13)	C9—C11	1.568 (14)
C5—C6	1.466 (8)	C10—C11	1.515 (12)
C5—O1	1.468 (9)	N1—O1	1.387 (9)
N1—C2—C3	115.0 (13)	N1—O1—C5	114.1 (5)
C4—C3—C2	119.2 (13)		

Atoms H9, H10*A* and H10*B* were located in a difference Fourier map. Their atomic coordinates were refined and subsequently restrained, with C—H distances set to 0.97 (1)–0.98 (1) Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. All other H atoms were positioned geometrically and treated as riding, with C—H = 0.93–0.98 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. The structure was solved in $P2_1/c$, which clearly showed that atoms O2 and O2a exhibit 50% occupancy. In view of the existing mirror plane that was located in the molecule, the structure was transformed and refined in the space group *Pnma*.

Data collection: *CAD-4 Diffractometer Control Software* (Enraf–Nonius, 1993); cell refinement: *CAD-4 Diffractometer Control Software*; data reduction: *CAD-4 Diffractometer Control Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON2002* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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