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3-Carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-yl acetate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.051
wR factor = 0.146
Data-to-parameter ratio = 21.1

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

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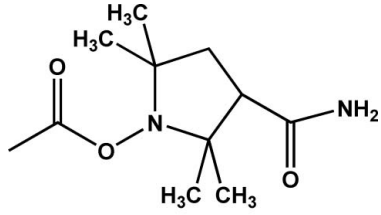
In the title compound, $C_{11}H_{20}N_2O_3$, the pyrrolidine ring adopts an envelope conformation, where the acetoxy and carbamoyl groups are equatorial. Each molecule interacts, through strong N—H···O hydrogen bonds, with two adjacent molecules.

Comment

Recently, acyl-protected hydroxylamines as spin reagents have attracted much attention because of their significant biological applications for ESR measurements of intracellular oxidative stress (Itoh *et al.*, 2000) and for ESR *in vivo* imaging (Yokoyama *et al.*, 2000; Yordanov *et al.*, 2002; Takeshita *et al.*, 2004). The synthesis of the title compound, (I), has been reported (Itoh *et al.*, 2000), but its crystal structure has, to our knowledge, not been determined so far.



(I)

The most important geometric parameters of (I) are listed in Table 1 and the structure is illustrated in Fig. 1. The pyrrolidine ring adopts an envelope conformation, in which atoms C2, C3, C4 and N1 are almost coplanar [the C2—C3—C4—N1 torsion angle is 5.67 (17)°]. The acetoxy and carbamoyl groups are equatorial due to the steric effects of the two methyl groups on C1. The sum of the angles around N1 is 329.94°, indicating sp^3 hybridization.

The crystal structure of (I) is stabilized by intermolecular N—H···O hydrogen bonds (Table 2). Atoms O2 and O3, from the acetoxy and carbamoyl groups, respectively, act as acceptors for the hydrogen bonds, with the amine of the carbamoyl group being the donor. Each molecule is thus linked to two neighbours *via* four hydrogen bonds.

Experimental

According to the method of Itoh *et al.* (2000), the reduction of 3-carbamoyl-2,2,5,5-tetramethylpyrrolidin-1-oxyl (2.78 g, 15.0 mmol) by hydrazine monohydrate (20 ml, 0.64 mol) in methanol (100 ml) yielded the hydroxylamine (2.56 g, 13.7 mmol, 92%) 3-carbamoyl-1-hydroxy-2,2,5,5-tetramethylpyrrolidine, as a colorless powder. To a solution containing the hydroxylamine (1.86 g, 10.0 mmol) and

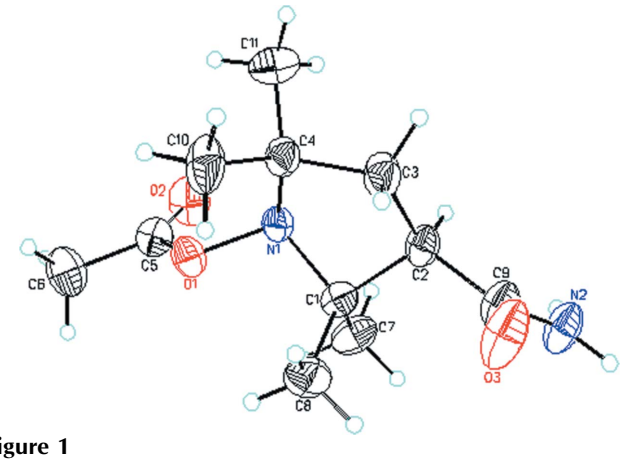


Figure 1
View of the molecular structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

triethylamine (20 ml) in 100 ml dichloromethane, acetic anhydride (20 ml, 0.21 mol) was added. The reaction mixture was stirred for 3 h at 273 K (ice bath) and then washed with water (50 ml), 3% aqueous hydrochloric acid (30 ml), water (30 ml), 5% aqueous sodium hydrogen carbonate (30 ml), and finally water (50 ml). The organic layer was dried over anhydrous magnesium sulfate and evaporated. The residue was purified by silica gel column chromatography with ethyl acetate to yield 1-acetoxy-3-carbamoyl-2,2,5,5-tetramethylpyrrolidine (2.15 g, 9.4 mmol, 94%). Single crystals suitable for X-ray analysis were obtained by recrystallization from ethyl acetate at low temperature (253 K).

Crystal data

$C_{11}H_{20}N_2O_3$
M_r = 228.29
Monoclinic, $P2_1/n$
a = 9.7037 (19) Å
b = 11.706 (2) Å
c = 12.293 (3) Å
β = 107.27 (3)°
V = 1333.4 (5) Å^3
Z = 4
D_x = 1.137 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 293 (2) K
Plate, colorless
0.61 × 0.52 × 0.21 mm

Data collection

Rigaku R-AXIS RAPID IP area-detector diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.951, T_{max} = 0.983
12633 measured reflections
3056 independent reflections
1787 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.146
S = 1.00
3056 reflections
145 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0805P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C5	1.349 (2)	N1—C4	1.491 (2)
O1—N1	1.4429 (15)	N2—C9	1.326 (2)
O2—C5	1.183 (2)	C1—C2	1.543 (2)
O3—C9	1.226 (2)	C3—C4	1.534 (2)
N1—C1	1.4769 (19)		
O1—N1—C1	109.52 (11)	C1—N1—C4	111.10 (12)
O1—N1—C4	109.32 (10)	C3—C2—C1	103.29 (12)
C9—C2—C3—C4	−154.05 (15)	C2—C3—C4—N1	5.67 (17)
O1—N1—C4—C10	23.8 (2)	N1—O1—C5—C6	−179.05 (14)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O3^{i}	0.86	2.09	2.929 (2)	164
N2—H2B···O2^{ii}	0.86	2.20	3.0359 (19)	163

Symmetry codes: (i) $-x, -y+2, -z$; (ii) $-x, -y+1, -z$.

All H atoms were positioned geometrically and refined using a riding model (C—H = 0.93–0.98 Å and N—H = 0.86 Å). For the methyl groups, U_{iso}(H) values were set equal to 1.5U_{eq}(C) and for the the other H atoms they were set to 1.2U_{eq}(C,N).

Data collection: *RAPID-AUTO* (Rigaku, 1999); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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