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3-Ethynyl-2,2,5,5-tetramethyl-1-oxyl-3-pyrroline

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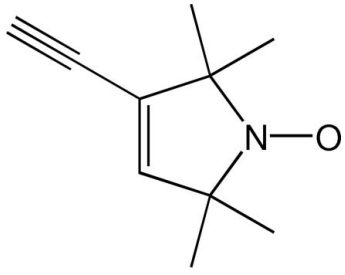
Key indicators: single-crystal X-ray study; T = 167 K; mean σ(C–C) = 0.002 Å; R factor = 0.062; wR factor = 0.157; data-to-parameter ratio = 27.3.

The five-membered ring of the title compound, $C_{10}H_{14}NO$, is almost planar [mean deviation from best plane = 0.006 (1) Å]. The N—O bond is in the plane of the five-membered ring. The molecule is positioned about a pseudo-mirror plane at y = 0.375. In the crystal, molecules are connected by intermolecular C—H···O contacts into layers parallel to (010).

Related literature

For the preparation of the title compound, see: Schiemann *et al.* (2007). For its application as a spin label, see: Schiemann *et al.* (2007); Piton *et al.* (2007). For the crystal structure of a related compound, see: Fritscher *et al.* (2002).



Experimental

Crystal data

$C_{10}H_{14}NO$ M_r = 164.22
Monoclinic, $P2_1/c$
a = 7.9326 (15) Å
b = 19.058 (4) Å
c = 6.5989 (11) Å
β = 104.333 (14)°
V = 966.6 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 167 K
0.60 × 0.55 × 0.07 mm

Data collection

Siemens SMART 1K CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
T_{min} = 0.870, T_{max} = 0.995
16848 measured reflections
3301 independent reflections
2214 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.157
S = 1.19
3301 reflections
121 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O1^{i}	0.975 (19)	2.441 (18)	3.3907 (18)	164.6 (14)
C6—H6A···O1^{ii}	0.98 (2)	2.20 (2)	3.174 (2)	171.2 (17)

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

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2152).

References

Fritscher, J., Beyer, M. & Schiemann, O. (2002). *Chem. Phys. Lett.* **364**, 393–401.
Piton, N., Mu, Y., Stock, G., Prisner, T. F., Schiemann, O. & Engels, J. W. (2007). *Nucleic Acids Res.* **35**, 3128–3143.
Schiemann, O., Piton, N., Plackmeyer, J., Bode, B. E., Prisner, T. F. & Engels, J. W. (2007). *Nat. Protoc.* **2**, 904–923.
Sheldrick, G. M. (2000). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

supplementary materials

Acta Cryst. (2009). E**65**, o1848 [**doi:10.1107/S1600536809026725**]

3-Ethynyl-2,2,5,5-tetramethyl-1-oxyl-3-pyrroline

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Comment

For EPR measurements of RNA, DNA or proteins, the occurrence of paramagnetic species is required. The title compound is a nitroxide spin label compound. Its synthesis has been reported by Schiemann *et al.* (2007). The application for DNA and RNA labeling has been described by Schiemann *et al.* (2007) and Piton *et al.* (2007). Here we report the crystal structure of the compound.

The molecular structure of the title compound is shown in Fig. 1. The five-membered ring is almost planar: the mean deviation from the best plane is 0.006 (1) Å. The molecule approximately has mirror symmetry and is positioned about a pseudo-mirror plane at y = 0.375. The N atom is planar and deviates by only 0.006 (2)Å from the plane through C1, C4 and O1. A related molecule with a very similar conformation of the 3-ethynyl-2,2,5,5-tetramethyl-1-oxyl-3-pyrroline group has been reported by Fritscher *et al.* (2002).

The molecules are connected by intermolecular C—H···O contacts to layers parallel to [0 1 0] (Fig. 2 and Table 1).

Experimental

The preparation of the title compound has been reported by Schiemann *et al.* (2007). Crystals were obtained by recrystallization from ethanol.

Refinement

The H atoms at C2 and C6 were taken from a difference Fourier synthesis and were refined with isotropic thermal parameters. The remaining H atoms were geometrically positioned using: C_{methyl}—H=0.98Å and $U_{iso}(H)=1.5U_{eq}(C_{methyl})$. The torsion angles about the *C*—C_{methyl} bonds were refined for the methyl groups

Figures

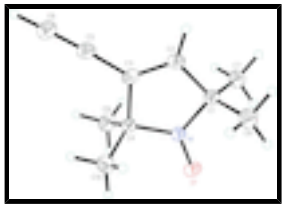

Fig. 1. The structure of the title compound shown with 50% probability displacement ellipsoids. The H atoms are drawn as small spheres of arbitrary radius.

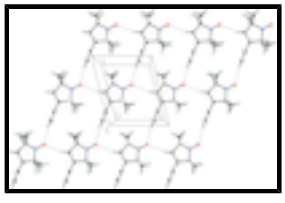

Fig. 2. A hydrogen bonded layer of molecules, viewed down the *b* axis. Intermolecular C—H···O contacts are shown as dashed lines.

3-Ethynyl-2,2,5,5-tetramethyl-1-oxyl-3-pyrroline

Crystal data

$C_{10}H_{14}NO$	F_{000} = 356
M_r = 164.22	D_x = 1.129 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 130 reflections
a = 7.9326 (15) Å	θ = 3–23º
b = 19.058 (4) Å	μ = 0.07 mm^{-1}
c = 6.5989 (11) Å	T = 167 K
β = 104.333 (14)º	Plate, yellow
V = 966.6 (3) Å^3	0.6 × 0.55 × 0.07 mm
Z = 4	

Data collection

Siemens SMART 1K CCD diffractometer	3301 independent reflections
Radiation source: normal-focus sealed tube	2214 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.035
T = 167 K	θ_{max} = 32.4º
ω scans	θ_{min} = 2.1º
Absorption correction: multi-scan (SADABS; Sheldrick, 2000)	h = −11→11
T_{min} = 0.870, T_{max} = 0.995	k = −27→28
16848 measured reflections	l = −9→9

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.062	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.157	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.35P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.19	$(\Delta/\sigma)_{max}$ = 0.005
3301 reflections	$\Delta\rho_{max}$ = 0.44 e Å^{-3}
121 parameters	$\Delta\rho_{min}$ = −0.23 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.62303 (13)	0.37389 (6)	0.53230 (15)	0.0287 (3)
N1	0.54492 (14)	0.37427 (7)	0.33858 (17)	0.0219 (2)
C1	0.63968 (16)	0.37208 (8)	0.1714 (2)	0.0208 (3)
C2	0.48802 (18)	0.37338 (8)	−0.0187 (2)	0.0230 (3)
C3	0.33449 (17)	0.37599 (8)	0.0304 (2)	0.0213 (3)
C4	0.35322 (16)	0.37802 (8)	0.2659 (2)	0.0203 (3)
C5	0.16502 (18)	0.37655 (8)	−0.1101 (2)	0.0257 (3)
C6	0.0205 (2)	0.37657 (10)	−0.2191 (2)	0.0326 (3)
C7	0.7461 (2)	0.30471 (8)	0.1866 (3)	0.0286 (3)
H7A	0.6683	0.2641	0.1719	0.043*
H7B	0.8307	0.3028	0.3228	0.043*
H7C	0.8077	0.3040	0.0750	0.043*
C8	0.7560 (2)	0.43669 (9)	0.1864 (3)	0.0298 (3)
H8A	0.6849	0.4792	0.1763	0.045*
H8B	0.8146	0.4360	0.0719	0.045*
H8C	0.8433	0.4363	0.3206	0.045*
C9	0.2700 (2)	0.31455 (9)	0.3439 (2)	0.0302 (4)
H9A	0.3192	0.2714	0.3017	0.045*
H9B	0.1441	0.3153	0.2833	0.045*
H9C	0.2933	0.3162	0.4967	0.045*
C10	0.2884 (2)	0.44689 (9)	0.3368 (3)	0.0315 (4)
H10A	0.3487	0.4862	0.2898	0.047*
H10B	0.3119	0.4475	0.4897	0.047*
H10C	0.1629	0.4512	0.2764	0.047*
H2A	0.503 (2)	0.3735 (9)	−0.161 (3)	0.029 (4)*
H6A	−0.098 (3)	0.3781 (10)	−0.308 (3)	0.045 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0254 (5)	0.0447 (6)	0.0133 (4)	0.0007 (5)	−0.0005 (3)	−0.0003 (5)
N1	0.0177 (5)	0.0338 (6)	0.0135 (5)	0.0002 (5)	0.0025 (4)	0.0002 (5)

C1	0.0185 (5)	0.0273 (7)	0.0171 (5)	−0.0002 (5)	0.0050 (4)	0.0001 (6)
C2	0.0253 (6)	0.0288 (7)	0.0142 (5)	−0.0006 (6)	0.0039 (4)	−0.0005 (5)
C3	0.0216 (6)	0.0239 (6)	0.0159 (5)	−0.0007 (5)	−0.0001 (4)	0.0000 (5)
C4	0.0162 (5)	0.0274 (7)	0.0165 (5)	0.0000 (5)	0.0027 (4)	−0.0013 (5)
C5	0.0252 (6)	0.0334 (8)	0.0176 (6)	−0.0015 (6)	0.0034 (5)	−0.0006 (6)
C6	0.0262 (7)	0.0466 (10)	0.0229 (7)	−0.0002 (7)	0.0019 (5)	−0.0017 (7)
C7	0.0248 (7)	0.0312 (8)	0.0298 (8)	0.0050 (6)	0.0065 (6)	−0.0030 (6)
C8	0.0288 (7)	0.0351 (9)	0.0260 (8)	−0.0081 (6)	0.0081 (6)	0.0007 (6)
C9	0.0278 (7)	0.0388 (9)	0.0241 (8)	−0.0073 (6)	0.0065 (6)	0.0054 (6)
C10	0.0292 (8)	0.0379 (9)	0.0266 (8)	0.0085 (7)	0.0053 (6)	−0.0071 (7)

Geometric parameters (Å, °)

O1—N1	1.2752 (14)	C6—H6A	0.97 (2)
N1—C4	1.4787 (16)	C7—H7A	0.9800
N1—C1	1.4815 (17)	C7—H7B	0.9800
C1—C2	1.5079 (18)	C7—H7C	0.9800
C1—C7	1.526 (2)	C8—H8A	0.9800
C1—C8	1.527 (2)	C8—H8B	0.9800
C2—C3	1.336 (2)	C8—H8C	0.9800
C2—H2A	0.975 (19)	C9—H9A	0.9800
C3—C5	1.4317 (18)	C9—H9B	0.9800
C3—C4	1.5248 (18)	C9—H9C	0.9800
C4—C10	1.525 (2)	C10—H10A	0.9800
C4—C9	1.527 (2)	C10—H10B	0.9800
C5—C6	1.193 (2)	C10—H10C	0.9800
O1—N1—C4	122.07 (11)	C1—C7—H7B	109.5
O1—N1—C1	122.43 (11)	H7A—C7—H7B	109.5
C4—N1—C1	115.50 (10)	C1—C7—H7C	109.5
N1—C1—C2	99.88 (10)	H7A—C7—H7C	109.5
N1—C1—C7	110.43 (12)	H7B—C7—H7C	109.5
C2—C1—C7	112.54 (12)	C1—C8—H8A	109.5
N1—C1—C8	109.81 (12)	C1—C8—H8B	109.5
C2—C1—C8	112.67 (12)	H8A—C8—H8B	109.5
C7—C1—C8	111.00 (12)	C1—C8—H8C	109.5
C3—C2—C1	112.74 (12)	H8A—C8—H8C	109.5
C3—C2—H2A	124.7 (11)	H8B—C8—H8C	109.5
C1—C2—H2A	122.5 (11)	C4—C9—H9A	109.5
C2—C3—C5	127.55 (13)	C4—C9—H9B	109.5
C2—C3—C4	112.53 (11)	H9A—C9—H9B	109.5
C5—C3—C4	119.92 (12)	C4—C9—H9C	109.5
N1—C4—C3	99.34 (10)	H9A—C9—H9C	109.5
N1—C4—C10	109.88 (12)	H9B—C9—H9C	109.5
C3—C4—C10	112.29 (12)	C4—C10—H10A	109.5
N1—C4—C9	110.37 (12)	C4—C10—H10B	109.5
C3—C4—C9	112.47 (12)	H10A—C10—H10B	109.5
C10—C4—C9	111.82 (13)	C4—C10—H10C	109.5
C6—C5—C3	176.86 (16)	H10A—C10—H10C	109.5
C5—C6—H6A	178.2 (12)	H10B—C10—H10C	109.5

C1—C7—H7A	109.5		
O1—N1—C1—C2	179.84 (13)	C1—N1—C4—C3	1.46 (17)
C4—N1—C1—C2	−1.06 (17)	O1—N1—C4—C10	62.65 (18)
O1—N1—C1—C7	61.15 (17)	C1—N1—C4—C10	−116.46 (14)
C4—N1—C1—C7	−119.74 (13)	O1—N1—C4—C9	−61.12 (18)
O1—N1—C1—C8	−61.57 (17)	C1—N1—C4—C9	119.77 (13)
C4—N1—C1—C8	117.54 (13)	C2—C3—C4—N1	−1.34 (17)
N1—C1—C2—C3	0.11 (17)	C5—C3—C4—N1	178.28 (14)
C7—C1—C2—C3	117.23 (15)	C2—C3—C4—C10	114.75 (15)
C8—C1—C2—C3	−116.35 (15)	C5—C3—C4—C10	−65.63 (18)
C1—C2—C3—C5	−178.76 (15)	C2—C3—C4—C9	−118.07 (15)
C1—C2—C3—C4	0.82 (19)	C5—C3—C4—C9	61.54 (18)
O1—N1—C4—C3	−179.43 (13)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2A···O1^{i}	0.975 (19)	2.441 (18)	3.3907 (18)	164.6 (14)
C6—H6A···O1^{ii}	0.98 (2)	2.20 (2)	3.174 (2)	171.2 (17)

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) *x*−1, *y*, *z*−1.

Fig. 1

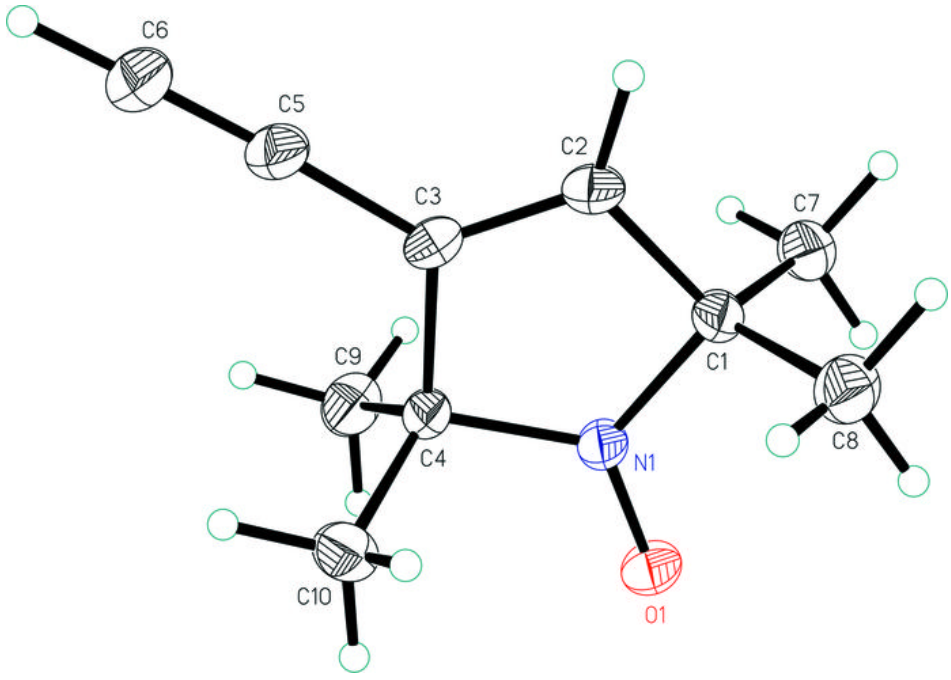

Fig. 2