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The 3,3,5,5[$^{2}H_{4}$]-4-methacrylamido-2,2,6,6-tetra([$^{2}H_{3}$]methyl)piperidin-1-yloxyl radical

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The main features of the crystal structure of the title radical, $C_{13}H_{7}D_{16}N_{2}O_{2}$, are N—H$\cdots$O and C—H$\cdots$O hydrogen bonds, which are responsible for the formation of chains of molecules in the [001] direction.

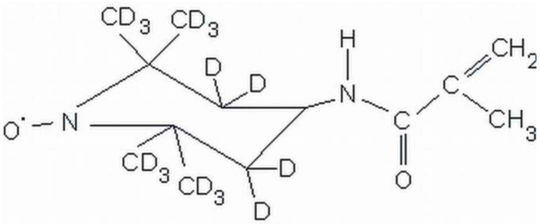
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.109
Data-to-parameter ratio = 11.6

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

Comment

The title compound, (I), can be assigned to aminoxyl radicals belonging to the group of stable radicals. They have been widely used as spin labels for electron spin resonance measurements (Pilar *et al.*, 1999), or as reagents for redox (Naik *et al.*, 1998) or polymerization reactions (Hawker *et al.*, 1997).



(I)

An overall view of the molecule of (I) is shown in Fig. 1. The piperidine ring adopts a chair conformation. The C2/C3/C5/C6 plane forms angles of 32.1 (1)° with the C2/N1/C6 plane and 51.8 (1)° with the C3/C4/C5 plane. This geometry fits well with the average geometry of piperidine rings resulting from 114 hits found in the Cambridge Structural Database (Version 5.26; Allen, 2002).

The second part of the molecule, the short methacrylamide chain, is in an equatorial position with respect to the piperidine ring. Theoretically, it should be planar. However, stress induced by hydrogen bonds results in a rotation between the amide group and the C13=C14 double bond of 15.3 (1)°. The amide group remains planar, the C4—N10—C11—O12 torsion angle being 3.8 (2)°.

The crystal packing diagram in Fig. 2 shows the network of hydrogen bonds that join molecules of (I) into a chain in the [001] direction. They connect the nitroxyl O atom with three H atoms of a neighbouring molecule. The arrangement of these hydrogen bonds is shown in detail in Fig. 3. The strongest hydrogen bond, with an H$\cdots$O distance of 2.14 (2) Å, is directed towards the amino group. Two other hydrogen bonds, towards the methacryloyl group and the CH_{2} group of the ring, are significantly longer, with H$\cdots$O = 2.55 and 2.47 (2) Å, respectively.

Atom O12 is coordinated by very weak hydrogen bonds to atoms C17, C14 and C15, with C$\cdots$O distances of 3.373 (2),

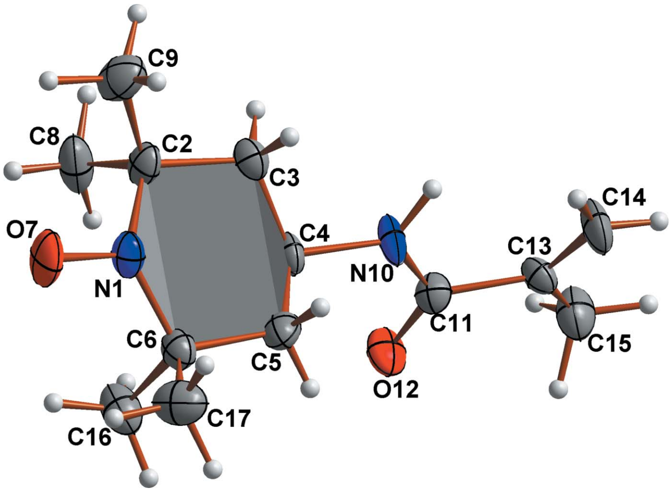


Figure 1
The structure of the title compound, showing the atom-numbering scheme and the chair conformation of the ring of the piperidine derivative. Displacement ellipsoids are drawn at the 50% probability level.

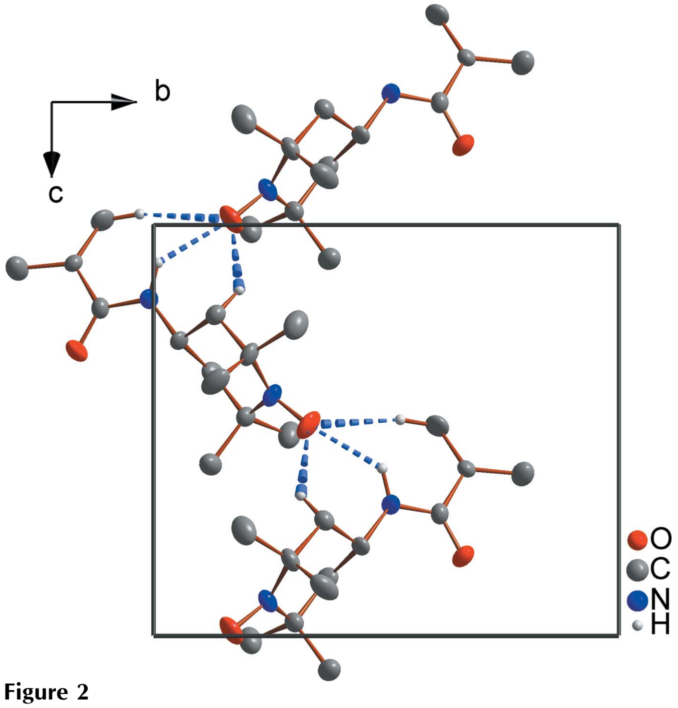


Figure 2
Part of the crystal structure of (I), showing the molecular packing and formation of a chain of molecules along the [001] direction. Dashed lines indicate hydrogen bonds.

3.438 (2), and 3.464 (2) Å, respectively. These bonds connect the [001]-direction chains and give rise to three-dimensional connectivity through the whole crystal structure. Details of all hydrogen bonds are given in Table 1.

Experimental

3,3,5,5[$^2H_4$]-4-Methacrylamido-2,2,6,6-tetra([$^2H_3$]methyl)piperidine (1.0 g), sodium ethylendiamintetraacetate (0.1 g) and sodium tungstate(IV) dihydrate (0.1 g) were dissolved in methanol (5 ml) and water (3 ml) with the addition of 30% hydrogen peroxide (1.7 ml).

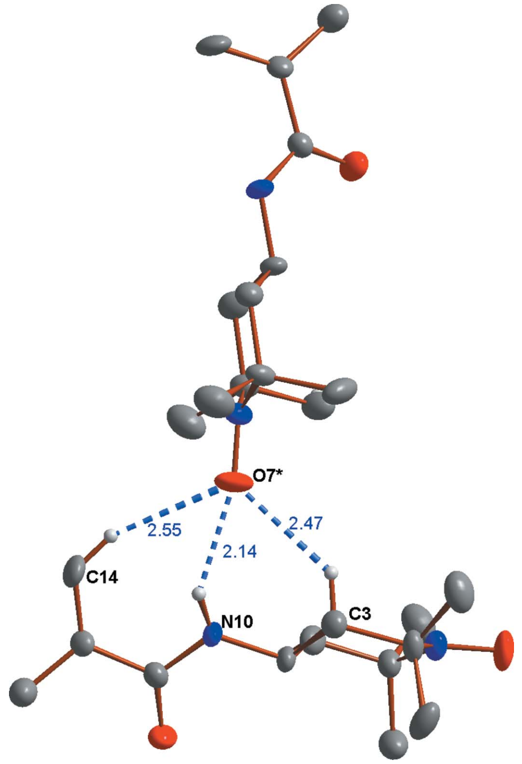


Figure 3
Two neighbouring molecules related by symmetry code ($x, \frac{1}{2} - y, z - \frac{1}{2}$), with a detailed view of the three hydrogen bonds (dashed lines) responsible for chain formation. Distances are given in Å.

The mixture was held at laboratory temperature for 4 d. The methanol was removed by evaporation and the product was recrystallized from dichloromethane–hexane (1:1).

Crystal data

$C_{13}H_7D_{16}N_2O_2$
$M_r = 255.44$
Monoclinic, $P2_1/c$
$a = 12.0838$ (5) Å
$b = 11.6346$ (6) Å
$c = 11.5420$ (6) Å
$\beta = 116.522$ (4)°
$V = 1451.92$ (13) Å^3
$Z = 4$
$D_x = 1.169$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16217 reflections
$\theta = 1.0$–29.5°
$\mu = 0.07$ mm^{-1}
$T = 150$ K
Irregular fragment, yellow
0.27 × 0.18 × 0.09 mm

Data collection

Oxford Sapphire 2 CCD area-detector diffractometer
ω scans
Absorption correction: none
16217 measured reflections
2632 independent reflections
2147 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\rm max} = 25.4$°
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.109$
$S = 1.12$
2632 reflections
226 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···O7^{i}	0.99 (1)	2.47 (2)	3.256 (2)	136 (1)
N10—H10···O7^{i}	0.83 (2)	2.14 (2)	2.921 (1)	157 (1)
C14—H14B···O7^{i}	0.93	2.55	3.455 (1)	165
C17—H17A···O12^{ii}	0.97 (2)	2.46 (1)	3.373 (2)	156 (1)
C15—H15A···O12^{iii}	0.96	2.54	3.464 (2)	161
C14—H14A···O12^{iii}	0.93	2.59	3.438 (2)	151

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y, -z+1$; (iii) $x, -y-\frac{1}{2}, z-\frac{1}{2}$.

All H atoms were found in a difference Fourier map. The H atoms of the more flexible methacryloyl part were refined as riding, with C—H = 0.96 Å for –CH$_3$ or 0.93 Å for =CH$_2$ groups, and with $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(C). The deuterium atoms of the methyl groups of the piperidine ring were considered as H atoms and were stable during the refinement procedure, as well as the remaining H atoms attached to C3 and N2; accordingly, they were refined freely and isotropically.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Brandenburg, K. & Putz, H. (2005). *DIAMOND*. Release 3.0c. Crystal Impact GbR, Bonn, Germany.

Hawker, C. J. (1997). *Acc. Chem. Res.* **30**, 373–382.

Naik, N. & Braslau, R. (1998). *Tetrahedron*, **54**, 667–696.

Oxford Diffraction (2004). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd., Abingdon, Oxford, England.

Pilar, J., Labsky, J., Marek, A., Konak, C. & Schlick, S. (1999). *Macromolecules*, **32**, 8230–8233.

Sheldrick G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

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