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4-Amino-2,2,6,6-tetramethylpiperidin-1-oxyl radical (ATEMPO)

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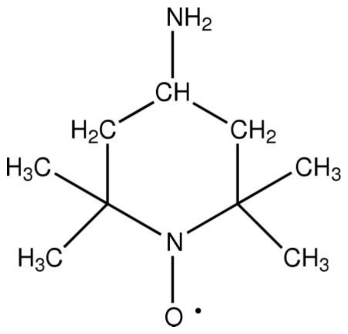
Key indicators: single-crystal X-ray study; T = 160 K; mean σ(C–C) = 0.002 Å; R factor = 0.040; wR factor = 0.101; data-to-parameter ratio = 11.9.

The title compound, $C_9H_{19}N_2O$, was studied in the context of nitroxide radicals bearing amino or hydroxy groups as candidates for obtaining thin films of molecular magnets by thermal evaporation in high vacuum on various substrates; the knowledge of its crystal structure is useful for checking the nature and quality of the films. In the crystal structure ATEMPO radicals are linked by weak intermolecular N—H⋯O hydrogen bonds to form infinite chains running along [010]. Structural features of the radical are similar to those reported for clathrates or adducts involving ATEMPO: the piperidine ring has a chair conformation and the N—O$^{\cdot}$ bond length is 1.2870 (13) Å.

Related literature

For the synthesis of ATEMPO, see Rosen (1974). For related structures, see Mazaki *et al.* (1992); Boubekeur *et al.* (2006). For literature on thin films of molecular magnets, see Miller & Epstein (1994); Caro *et al.* (1998).



Experimental

Crystal data

$C_9H_{19}N_2O$
M_r = 171.26
Monoclinic, $P2_1/n$
a = 5.721 (2) Å
b = 12.919 (3) Å
c = 13.955 (4) Å
β = 96.61 (4)°
V = 1024.6 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 160 (2) K
0.31 × 0.24 × 0.20 mm

Data collection

Stoe IPDS imaging plate diffractometer
Absorption correction: none
7824 measured reflections
1989 independent reflections
1618 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.101
S = 1.04
1989 reflections
167 parameters
All H-atom parameters refined
$\Delta\rho_{\rm max}$ = 0.18 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.14 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H2A⋯O1$^{\rm i}$	0.933 (19)	2.27 (2)	3.153 (2)	158 (3)

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

Data collection: *IPDS* (Stoe & Cie, 1996); cell refinement: *IPDS*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *CAMERON* (Pearce & Watkin, 1993) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank warmly Dr Lydie Valade for fruitful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2110).

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supplementary materials

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4-Amino-2,2,6,6-tetramethylpiperidin-1-oxyl radical (ATEMPO)

J.-P. Legros, **D. De Caro** and **H. Casellas**

Comment

The search for molecular magnets derived from nitroxides and composed exclusively of light elements is an active field (Miller & Epstein, 1994). When prepared as oriented thin films of good optical quality, applications are foreseen in magnetic-optics. Thin films of the nitrophenyl nitronyl nitroxide radical have been obtained by thermal evaporation in high vacuum on glass and cleaved NaCl (001) substrates (Caro *et al.*, 1998). Nitroxide radicals bearing amino or hydroxy groups seem good candidates for processing thin films in which molecule-molecule and molecule-substrate interactions would be favoured by hydrogen bonds. In this context we have prepared the 4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl radical (ATEMPO) according to a procedure described by Rosen (1974). The knowledge of the crystal structure is useful for checking the nature and the quality of the films. Single crystals of the material were obtained by evaporation of an ethanol solution. The molecular structure of ATEMPO is shown in Figure 1, in the solid state the piperidine ring displays a chair conformation. The N—O$^{\bullet}$ bond length is 1.2870 (13) Å. In the crystal structure ATEMPO radicals are linked by weak intermolecular N—H···O hydrogen bonds to form infinite chains running along [010] (Figure 2). The structural features of the isolated ATEMPO radical are similar to those reported for ATEMPO included in clathrates (Mazaki *et al.*, 1992) or adducts (Boubekeur *et al.*, 2006).

Experimental

The title compound was prepared according to a previously published procedure (Rosen, 1974). The resulting solid was dissolved in ethanol. Crystals suitable for X-ray structural study were obtained by evaporation of this ethanol solution.

Refinement

H atoms were clearly located in a difference map. Their positions were refined together with a common U_{iso}(H) which converged to a value of 0.0529 (11) Å^2. C—H distances are in the range 0.95 (2)–1.03 (2) Å, N—H distances are 0.85 (2) and 0.93 (2) Å, the longest being involved in a weak intermolecular N—H···O hydrogen bond.

Figures

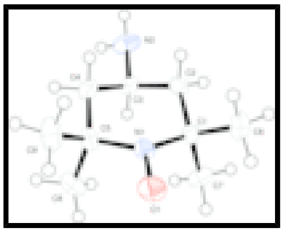

Fig. 1. The molecular structure of ATEMPO, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

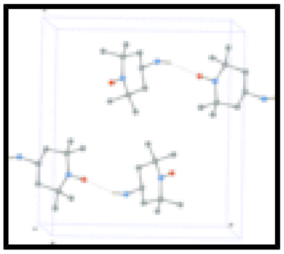

Fig. 2. The packing of ATEMPO. Hydrogen bonds drawn as dashed lines. H atoms not involved in hydrogen bonding have been omitted.

4-amino-2,2,6,6-tetramethylpiperidine 1-oxyl

Crystal data

$C_9H_{19}N_2O$

$M_r = 171.26$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 5.721$ (2) Å

$b = 12.919$ (3) Å

$c = 13.955$ (4) Å

$\beta = 96.61$ (4)°

$V = 1024.6$ (5) Å^3

$Z = 4$

$F_{000} = 380$

$D_x = 1.110$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 943 reflections

$\theta = 3.1$–26.1°

$\mu = 0.07$ mm^{-1}

$T = 160$ (2) K

Block, orange

0.31 × 0.24 × 0.20 mm

Data collection

Stoe IPDS imaging plate diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 160(2)$ K

φ scans with 1.5° steps

Absorption correction: none

7824 measured reflections

1989 independent reflections

1618 reflections with $I > 2\sigma(I)$

$R_{int} = 0.041$

$\theta_{max} = 26.1$°

$\theta_{min} = 1.7$°

$h = -7 \rightarrow 7$

$k = -15 \rightarrow 15$

$l = -16 \rightarrow 17$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.101$

$S = 1.04$

1989 reflections

167 parameters

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2 + 0.2605P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.18$ e Å^{-3}

$\Delta\rho_{min} = -0.14$ e Å^{-3}

Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. Cooling Device: Oxford Cryosystems Cryostream 600. Imaging plate detector. Frames collected: 133. Seconds exposure per frame: 180. Degrees rotation per frame: 1.5. Crystal-detector distance (mm): 70.0

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 $F^2 > 2\mathrm{sigma}(F^2)$ 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*	$U_{\mathrm{iso}}*/U_{\mathrm{eq}}$
O1	0.46460 (17)	0.20119 (8)	0.24316 (7)	0.0417 (3)
N1	0.31364 (17)	0.13055 (8)	0.25724 (7)	0.0274 (3)
N2	−0.2107 (3)	−0.09139 (10)	0.30952 (11)	0.0471 (3)
H2A	−0.114 (3)	−0.1495 (15)	0.3104 (12)	0.0529 (11)*
H2B	−0.317 (3)	−0.0991 (14)	0.2623 (13)	0.0529 (11)*
C1	0.2392 (2)	0.12590 (10)	0.35662 (8)	0.0282 (3)
C2	0.1046 (2)	0.02590 (10)	0.36838 (9)	0.0311 (3)
H21	0.032 (3)	0.0296 (13)	0.4281 (12)	0.0529 (11)*
H22	0.216 (3)	−0.0332 (14)	0.3748 (12)	0.0529 (11)*
C3	−0.0812 (2)	0.00122 (10)	0.28541 (9)	0.0300 (3)
H31	−0.197 (3)	0.0590 (14)	0.2763 (12)	0.0529 (11)*
C4	0.0425 (2)	−0.00881 (11)	0.19495 (9)	0.0329 (3)
H41	−0.073 (3)	−0.0298 (13)	0.1371 (12)	0.0529 (11)*
H42	0.159 (3)	−0.0678 (14)	0.2042 (12)	0.0529 (11)*
C5	0.1728 (2)	0.08874 (11)	0.16905 (8)	0.0308 (3)
C6	0.4609 (3)	0.12765 (14)	0.42811 (10)	0.0406 (4)
H61	0.545 (3)	0.1949 (14)	0.4229 (12)	0.0529 (11)*
H62	0.569 (3)	0.0673 (14)	0.4148 (12)	0.0529 (11)*
H63	0.415 (3)	0.1198 (13)	0.4950 (13)	0.0529 (11)*
C7	0.0874 (3)	0.22064 (11)	0.37282 (11)	0.0396 (3)
H71	0.054 (3)	0.2228 (13)	0.4410 (13)	0.0529 (11)*
H72	−0.070 (3)	0.2211 (13)	0.3335 (12)	0.0529 (11)*
H73	0.175 (3)	0.2829 (14)	0.3599 (12)	0.0529 (11)*
C8	0.0025 (3)	0.17256 (13)	0.12663 (11)	0.0439 (4)
H81	−0.128 (3)	0.1862 (13)	0.1671 (12)	0.0529 (11)*
H82	−0.068 (3)	0.1477 (13)	0.0618 (13)	0.0529 (11)*
H83	0.085 (3)	0.2351 (15)	0.1202 (12)	0.0529 (11)*
C9	0.3451 (3)	0.06182 (15)	0.09690 (10)	0.0466 (4)
H91	0.467 (3)	0.0109 (14)	0.1262 (12)	0.0529 (11)*

H92	0.255 (3)	0.0272 (13)	0.0418 (12)	0.0529 (11)*
H93	0.421 (3)	0.1224 (14)	0.0765 (12)	0.0529 (11)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0385 (5)	0.0427 (6)	0.0452 (6)	−0.0127 (4)	0.0104 (4)	0.0065 (4)
N1	0.0269 (5)	0.0293 (5)	0.0268 (5)	−0.0027 (4)	0.0059 (4)	0.0024 (4)
N2	0.0457 (8)	0.0297 (7)	0.0677 (9)	−0.0092 (6)	0.0139 (6)	−0.0015 (6)
C1	0.0314 (6)	0.0298 (6)	0.0241 (6)	−0.0011 (5)	0.0065 (4)	−0.0024 (5)
C2	0.0384 (7)	0.0285 (7)	0.0272 (6)	0.0001 (6)	0.0073 (5)	0.0045 (5)
C3	0.0311 (6)	0.0230 (6)	0.0369 (7)	−0.0012 (5)	0.0075 (5)	−0.0014 (5)
C4	0.0322 (7)	0.0333 (7)	0.0328 (7)	0.0012 (6)	0.0023 (5)	−0.0078 (5)
C5	0.0292 (6)	0.0398 (7)	0.0234 (6)	0.0023 (5)	0.0026 (5)	0.0012 (5)
C6	0.0383 (8)	0.0540 (9)	0.0287 (7)	−0.0040 (7)	0.0012 (5)	−0.0065 (6)
C7	0.0419 (8)	0.0294 (7)	0.0498 (8)	−0.0019 (6)	0.0148 (7)	−0.0082 (6)
C8	0.0404 (8)	0.0509 (9)	0.0396 (8)	0.0056 (7)	0.0006 (6)	0.0173 (7)
C9	0.0400 (8)	0.0727 (12)	0.0284 (7)	0.0003 (8)	0.0097 (6)	−0.0048 (7)

Geometric parameters (Å, °)

O1—N1	1.2870 (13)	C4—H42	1.009 (18)
N1—C5	1.4926 (16)	C5—C9	1.5283 (19)
N1—C1	1.4982 (15)	C5—C8	1.5295 (19)
N2—C3	1.4667 (17)	C6—H61	1.000 (18)
N2—H2A	0.933 (19)	C6—H62	1.025 (18)
N2—H2B	0.851 (19)	C6—H63	1.003 (17)
C1—C6	1.5209 (19)	C7—H71	0.993 (18)
C1—C2	1.5226 (17)	C7—H72	1.001 (18)
C1—C7	1.5326 (18)	C7—H73	0.977 (18)
C2—C3	1.5129 (19)	C8—H81	1.004 (18)
C2—H21	0.974 (17)	C8—H82	1.000 (18)
C2—H22	0.991 (18)	C8—H83	0.947 (19)
C3—C4	1.5222 (18)	C9—H91	1.011 (18)
C3—H31	0.995 (18)	C9—H92	0.984 (17)
C4—C5	1.5285 (19)	C9—H93	0.955 (18)
C4—H41	1.020 (17)		
O1—N1—C5	116.04 (10)	N1—C5—C9	107.31 (11)
O1—N1—C1	115.91 (10)	N1—C5—C4	109.58 (10)
C5—N1—C1	124.39 (9)	C9—C5—C4	109.71 (12)
C3—N2—H2A	110.1 (11)	N1—C5—C8	108.79 (12)
C3—N2—H2B	104.7 (12)	C9—C5—C8	109.67 (12)
H2A—N2—H2B	106.7 (16)	C4—C5—C8	111.67 (11)
N1—C1—C6	107.59 (10)	C1—C6—H61	109.7 (10)
N1—C1—C2	109.57 (10)	C1—C6—H62	110.1 (9)
C6—C1—C2	109.62 (11)	H61—C6—H62	110.1 (13)
N1—C1—C7	109.32 (11)	C1—C6—H63	108.7 (10)
C6—C1—C7	109.60 (11)	H61—C6—H63	109.5 (13)

C2—C1—C7	111.07 (11)	H62—C6—H63	108.6 (13)
C3—C2—C1	114.57 (10)	C1—C7—H71	109.9 (10)
C3—C2—H21	109.5 (10)	C1—C7—H72	114.5 (10)
C1—C2—H21	108.7 (10)	H71—C7—H72	105.2 (13)
C3—C2—H22	107.1 (10)	C1—C7—H73	108.5 (10)
C1—C2—H22	109.7 (10)	H71—C7—H73	108.4 (14)
H21—C2—H22	107.0 (14)	H72—C7—H73	110.2 (14)
N2—C3—C2	108.99 (11)	C5—C8—H81	112.9 (10)
N2—C3—C4	114.60 (11)	C5—C8—H82	107.1 (10)
C2—C3—C4	107.45 (11)	H81—C8—H82	108.5 (14)
N2—C3—H31	107.2 (10)	C5—C8—H83	109.7 (11)
C2—C3—H31	109.7 (10)	H81—C8—H83	108.6 (14)
C4—C3—H31	108.8 (10)	H82—C8—H83	110.1 (14)
C3—C4—C5	114.32 (10)	C5—C9—H91	110.4 (9)
C3—C4—H41	110.9 (9)	C5—C9—H92	107.3 (10)
C5—C4—H41	108.8 (9)	H91—C9—H92	107.3 (14)
C3—C4—H42	108.7 (9)	C5—C9—H93	111.2 (11)
C5—C4—H42	108.7 (10)	H91—C9—H93	109.6 (14)
H41—C4—H42	105.0 (13)	H92—C9—H93	110.9 (14)

O1—N1—C1—C6	−48.68 (14)	N2—C3—C4—C5	178.76 (12)
C5—N1—C1—C6	153.81 (12)	C2—C3—C4—C5	−59.98 (14)
O1—N1—C1—C2	−167.80 (10)	O1—N1—C5—C9	48.80 (15)
C5—N1—C1—C2	34.70 (15)	C1—N1—C5—C9	−153.72 (12)
O1—N1—C1—C7	70.27 (13)	O1—N1—C5—C4	167.87 (10)
C5—N1—C1—C7	−87.24 (14)	C1—N1—C5—C4	−34.65 (15)
N1—C1—C2—C3	−46.50 (14)	O1—N1—C5—C8	−69.79 (13)
C6—C1—C2—C3	−164.36 (11)	C1—N1—C5—C8	87.69 (14)
C7—C1—C2—C3	74.38 (14)	C3—C4—C5—N1	46.21 (14)
C1—C2—C3—N2	−175.07 (11)	C3—C4—C5—C9	163.78 (11)
C1—C2—C3—C4	60.21 (14)	C3—C4—C5—C8	−74.41 (15)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O1^{i}	0.933 (19)	2.27 (2)	3.153 (2)	158 (3)

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

Fig. 1

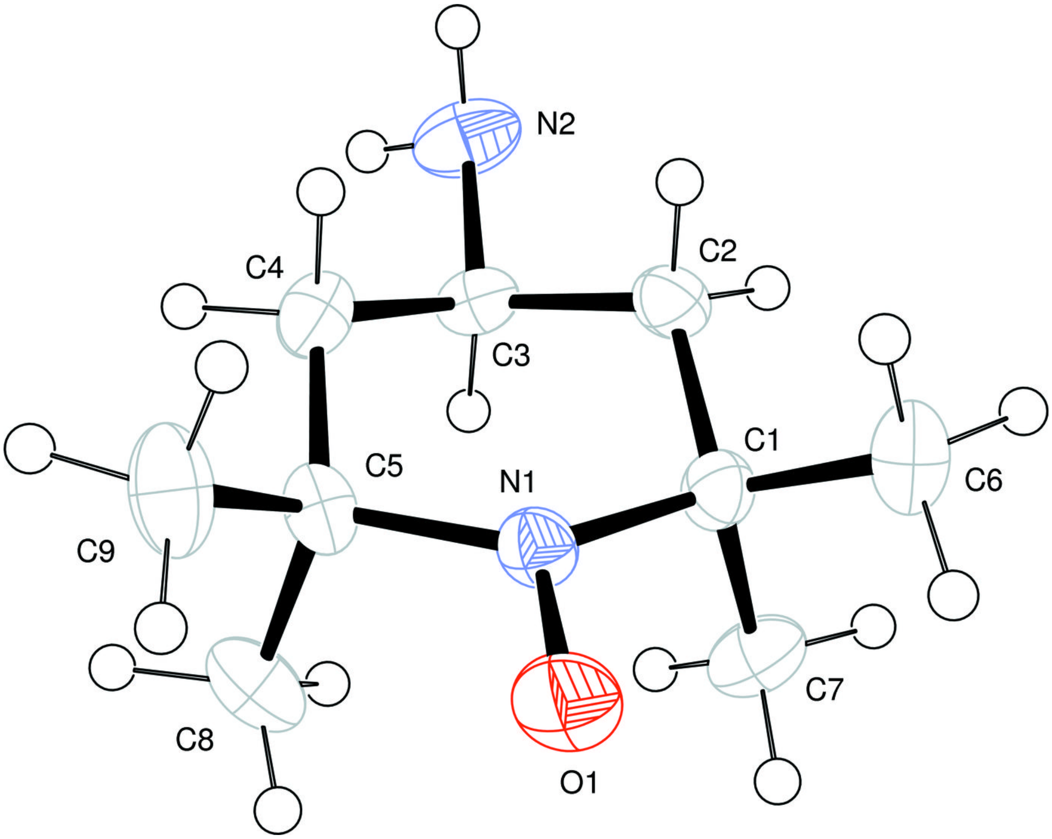

Fig. 2