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2-[(2*Z*)-Azepan-2-ylidene]-1-(4-nitrophenyl)ethanone

Siyanda T. Mthembu, Lee G. Madeley, Charles B. de Koning and Joseph P. Michael*

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, PO Wits 2050, South Africa
Correspondence e-mail: joseph.michael@wits.ac.za

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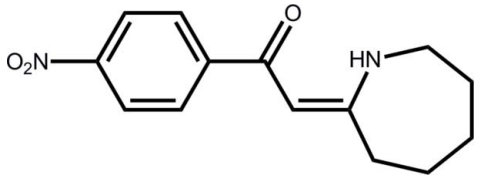
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.116; data-to-parameter ratio = 17.2.

The title compound, $C_{14}H_{16}N_2O_3$, is an NH-vinylogous amide (enaminone) produced by the reaction of 4-nitrophenacyl bromide with azepane-2-thione. The conformation about the C=C bond [1.3927 (14) Å] is *Z*, which allows for the formation of an intramolecular N—H···O hydrogen bond that leads to an *S*(6) loop. Inversion-related molecules associate *via* N—H···O hydrogen bonds to form a 12-membered $\{\cdots OC_3NH\}_2$ synthon.

Related literature

For uses and reactions of enaminones, see: Roth *et al.* (1971); Paulvannan & Stille (1994); Michael *et al.* (1999). For related structures, see: Balderson *et al.* (2007). For graph-set notation, see: Bernstein *et al.* (1995).



Experimental

Crystal data

$C_{14}H_{16}N_2O_3$
M_r = 260.29
Triclinic, $P\overline{1}$
a = 6.7963 (3) Å
b = 8.4054 (3) Å
c = 11.6649 (5) Å
α = 76.508 (2)°
β = 81.134 (2)°
γ = 80.596 (2)°
V = 634.58 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 173 K
0.56 × 0.5 × 0.42 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.905, T_{max} = 0.955
10354 measured reflections
3041 independent reflections
2732 reflections with $I > 2\sigma(I)$
R_{int} = 0.048

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.116
S = 1.06
3041 reflections
177 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.897 (16)	1.998 (15)	2.7041 (11)	134.6 (13)
N1—H1···O1^{i}	0.897 (16)	2.392 (15)	3.0303 (12)	128.2 (12)

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

This work was supported by the University of the Witwatersrand, which is thanked for providing the required infrastructure.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK5129).

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supporting information

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2-[(2*Z*)-Azepan-2-ylidene]-1-(4-nitrophenyl)ethanone

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S1. Comment

The title compound was prepared as part of an ongoing methodological investigation into the use of enaminones in the synthesis of azabicyclic alkaloids (Michael *et al.*, 1999). For example, its reaction with acryloyl chloride, according to the method of Paulvannan & Stille (1994), produced a 2,3,6,7-tetrahydro-5(1*H*)-indolizinone related to numerous natural products. The crystal structures of analogous 4-bromophenyl enaminones with 5-, 6- and 7-membered rings have been reported (Balderson *et al.*, 2007).

The asymmetric unit of (I) consists of one molecule of 2-[(2*Z*)-azepan-2-ylidene]-1-(4-nitrophenyl)ethan-1-one (Fig. 1). The hydrogen bonding consists of an intramolecular N—H···O═C hydrogen bond, and an intermolecular N—H···O═C hydrogen bond (Table 1). The combination of these two hydrogen bonds results in an $R^2_2(4)$ ring (Fig. 2) as described by graph set notation (Bernstein *et al.*, 1995).

S2. Experimental

The employed synthesis followed the Eschenmoser procedure (Roth *et al.*, 1971). *p*-Nitrophenacyl bromide (995 mg, 4.08 mmol) was added to a solution of azepane-2-thione (502 mg, 3.88 mmol) in dry acetonitrile (30 ml). The resulting solution was stirred at room temperature for 4 h, after which *S*-alkylation was complete as shown by the precipitation of the thioiminium salt. This was then followed by the addition of triphenylphosphine (1.069 g, 4.08 mmol) and triethylamine (413 mg, 4.08 mmol) to induce sulfur extrusion. The reaction mixture was poured into water and the organic components were extracted with diethyl ether (3 × 30 ml). The resulting organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*. The resulting residue was purified by column chromatography on silica gel with hexane:ethyl acetate (19:1 *v*/*v*) as eluent to yield 2-[(2*Z*)-azepan-2-ylidene]-1-(4-nitrophenyl)ethan-1-one (829 mg, 82%) as yellow crystals, m.p. 398–400 K.

S3. Refinement

The C-bound H atoms were geometrically placed [C—H = 0.95 Å (alkenyl- and aromatic-H) and 0.99 Å (methylene-H)] and refined as riding with U_{iso}(H) = 1.2U_{eq}(C). The N-bound H atom was located in a difference Fourier map and refined freely.

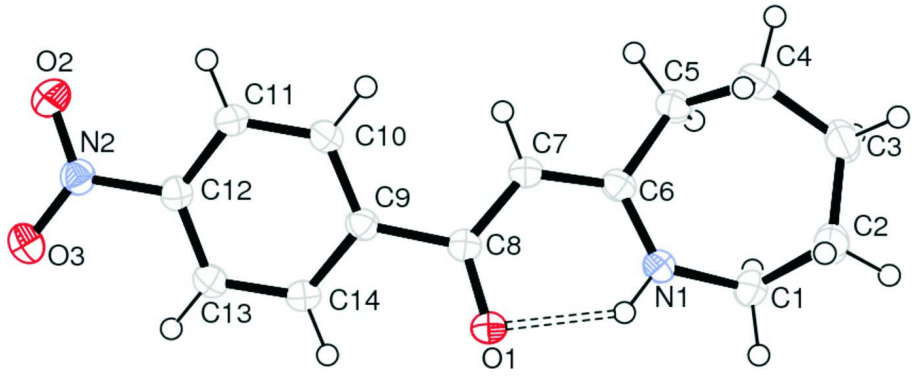

Figure 1

The molecular structure of (I) showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

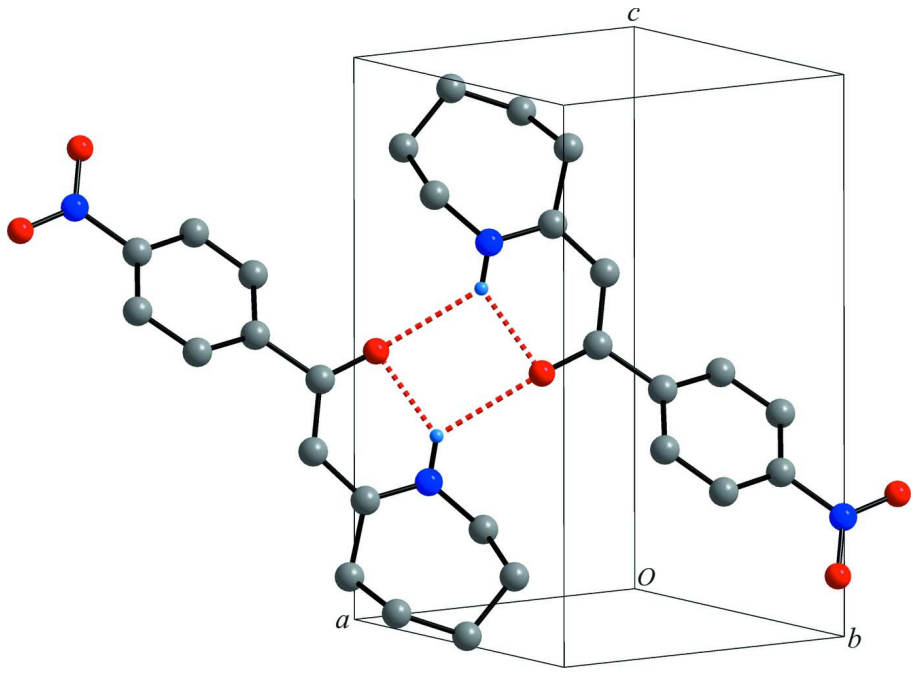

Figure 2

Hydrogen bonding diagram of the compound. Intermolecular and intramolecular N—H···O hydrogen bonds (shown as dashed red lines) form a four-membered ring. Non-participating H atoms have been omitted for clarity.

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Crystal data

$C_{14}H_{16}N_2O_3$
$M_r = 260.29$
Triclinic, $P\overline{1}$
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$\beta = 81.134\ (2)°$
$\gamma = 80.596\ (2)°$
$V = 634.58\ (5)$ Å^3
$Z = 2$
$F(000) = 276$
$D_x = 1.362$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6539 reflections
$\theta = 2.5–28.4°$
$\mu = 0.10$ mm^{-1}

T = 173 K
Block, red

0.56 × 0.5 × 0.42 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.905, T_{max} = 0.955
10354 measured reflections

3041 independent reflections
2732 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 28.0°, θ_{min} = 1.8°
h = −8→8
k = −11→11
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.116
S = 1.06
3041 reflections
177 parameters
0 restraints

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2 + 0.1127P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.170 (12)

Special details

Experimental. Absorption corrections were made using the program *SADABS* (Sheldrick, 1996)
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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
C1	1.01720 (16)	0.40728 (13)	0.79045 (9)	0.0296 (2)
H1A	1.0007	0.4794	0.8483	0.035*
H1B	1.155	0.4094	0.7482	0.035*
C2	0.99594 (18)	0.23125 (14)	0.85852 (10)	0.0342 (3)
H2A	1.1187	0.1856	0.8974	0.041*
H2B	0.9882	0.1633	0.8009	0.041*
C3	0.8137 (2)	0.21416 (15)	0.95278 (11)	0.0394 (3)
H3A	0.8141	0.096	0.9913	0.047*
H3B	0.8279	0.2735	1.0144	0.047*
C4	0.61162 (18)	0.27927 (13)	0.90694 (10)	0.0333 (3)
H4A	0.5034	0.2527	0.9728	0.04*
H4B	0.5976	0.2215	0.8443	0.04*
C5	0.58338 (16)	0.46611 (13)	0.85608 (9)	0.0281 (2)
H5A	0.4378	0.5065	0.8606	0.034*
H5B	0.6428	0.5213	0.9062	0.034*
C6	0.67677 (15)	0.51517 (12)	0.72942 (9)	0.0248 (2)
C7	0.55481 (15)	0.60086 (12)	0.64327 (9)	0.0256 (2)
H7	0.4135	0.6146	0.665	0.031*

C8	0.63077 (15)	0.66855 (12)	0.52480 (9)	0.0249 (2)
C9	0.48836 (15)	0.78776 (12)	0.44815 (8)	0.0236 (2)
C10	0.28080 (15)	0.78647 (13)	0.46714 (9)	0.0267 (2)
H10	0.2248	0.7046	0.5285	0.032*
C11	0.15532 (15)	0.90342 (13)	0.39730 (9)	0.0270 (2)
H11	0.0138	0.9038	0.411	0.032*
C12	0.24127 (15)	1.01984 (12)	0.30693 (9)	0.0244 (2)
C13	0.44670 (16)	1.02284 (12)	0.28387 (9)	0.0271 (2)
H13	0.5021	1.1028	0.2207	0.033*
C14	0.56934 (15)	0.90611 (13)	0.35534 (9)	0.0273 (2)
H14	0.7107	0.9064	0.3411	0.033*
N1	0.87397 (13)	0.47603 (11)	0.70420 (8)	0.0275 (2)
H1	0.923 (2)	0.5042 (18)	0.6274 (14)	0.042 (4)*
N2	0.10920 (13)	1.14105 (10)	0.23068 (8)	0.0275 (2)
O1	0.81102 (11)	0.64279 (10)	0.48208 (7)	0.0328 (2)
O2	−0.07169 (12)	1.15862 (11)	0.26345 (8)	0.0403 (2)
O3	0.18635 (12)	1.21881 (10)	0.13628 (7)	0.0373 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0269 (5)	0.0327 (5)	0.0286 (5)	−0.0022 (4)	−0.0067 (4)	−0.0047 (4)
C2	0.0361 (6)	0.0315 (5)	0.0320 (6)	0.0020 (4)	−0.0066 (5)	−0.0036 (4)
C3	0.0462 (7)	0.0339 (6)	0.0301 (6)	0.0000 (5)	−0.0018 (5)	0.0034 (4)
C4	0.0379 (6)	0.0319 (5)	0.0276 (5)	−0.0090 (4)	0.0047 (4)	−0.0041 (4)
C5	0.0294 (5)	0.0320 (5)	0.0213 (5)	−0.0027 (4)	0.0015 (4)	−0.0062 (4)
C6	0.0267 (5)	0.0249 (5)	0.0224 (5)	−0.0042 (4)	−0.0002 (4)	−0.0056 (4)
C7	0.0225 (5)	0.0283 (5)	0.0241 (5)	−0.0023 (4)	0.0005 (4)	−0.0045 (4)
C8	0.0238 (5)	0.0262 (5)	0.0241 (5)	−0.0030 (4)	−0.0017 (4)	−0.0050 (4)
C9	0.0241 (5)	0.0245 (5)	0.0218 (5)	−0.0030 (4)	−0.0008 (4)	−0.0057 (4)
C10	0.0265 (5)	0.0286 (5)	0.0233 (5)	−0.0064 (4)	−0.0012 (4)	−0.0017 (4)
C11	0.0213 (5)	0.0326 (5)	0.0262 (5)	−0.0048 (4)	−0.0016 (4)	−0.0047 (4)
C12	0.0265 (5)	0.0233 (5)	0.0235 (5)	−0.0016 (4)	−0.0040 (4)	−0.0055 (4)
C13	0.0283 (5)	0.0258 (5)	0.0257 (5)	−0.0063 (4)	−0.0014 (4)	−0.0020 (4)
C14	0.0217 (5)	0.0313 (5)	0.0272 (5)	−0.0050 (4)	−0.0006 (4)	−0.0036 (4)
N1	0.0253 (4)	0.0332 (5)	0.0211 (4)	−0.0019 (3)	−0.0017 (3)	−0.0023 (3)
N2	0.0282 (5)	0.0251 (4)	0.0286 (4)	−0.0026 (3)	−0.0040 (3)	−0.0047 (3)
O1	0.0236 (4)	0.0398 (4)	0.0278 (4)	0.0009 (3)	0.0021 (3)	0.0002 (3)
O2	0.0263 (4)	0.0435 (5)	0.0434 (5)	0.0029 (3)	−0.0038 (3)	0.0004 (4)
O3	0.0378 (5)	0.0363 (4)	0.0319 (4)	−0.0056 (3)	−0.0043 (3)	0.0049 (3)

Geometric parameters (Å, º)

C1—N1	1.4630 (13)	C7—C8	1.4174 (14)
C1—C2	1.5254 (15)	C7—H7	0.95
C1—H1A	0.99	C8—O1	1.2535 (12)
C1—H1B	0.99	C8—C9	1.5073 (14)
C2—C3	1.5259 (17)	C9—C10	1.3952 (14)

C2—H2A	0.99	C9—C14	1.3990 (14)
C2—H2B	0.99	C10—C11	1.3870 (14)
C3—C4	1.5219 (18)	C10—H10	0.95
C3—H3A	0.99	C11—C12	1.3877 (14)
C3—H3B	0.99	C11—H11	0.95
C4—C5	1.5353 (15)	C12—C13	1.3838 (14)
C4—H4A	0.99	C12—N2	1.4694 (13)
C4—H4B	0.99	C13—C14	1.3848 (15)
C5—C6	1.5060 (13)	C13—H13	0.95
C5—H5A	0.99	C14—H14	0.95
C5—H5B	0.99	N1—H1	0.897 (16)
C6—N1	1.3306 (13)	N2—O2	1.2253 (12)
C6—C7	1.3927 (14)	N2—O3	1.2300 (12)

N1—C1—C2	114.74 (9)	C7—C6—C5	119.10 (9)
N1—C1—H1A	108.6	C6—C7—C8	123.35 (9)
C2—C1—H1A	108.6	C6—C7—H7	118.3
N1—C1—H1B	108.6	C8—C7—H7	118.3
C2—C1—H1B	108.6	O1—C8—C7	124.12 (9)
H1A—C1—H1B	107.6	O1—C8—C9	118.04 (9)
C1—C2—C3	115.04 (9)	C7—C8—C9	117.72 (9)
C1—C2—H2A	108.5	C10—C9—C14	119.09 (9)
C3—C2—H2A	108.5	C10—C9—C8	122.91 (9)
C1—C2—H2B	108.5	C14—C9—C8	117.99 (9)
C3—C2—H2B	108.5	C11—C10—C9	120.69 (9)
H2A—C2—H2B	107.5	C11—C10—H10	119.7
C4—C3—C2	115.06 (10)	C9—C10—H10	119.7
C4—C3—H3A	108.5	C10—C11—C12	118.47 (9)
C2—C3—H3A	108.5	C10—C11—H11	120.8
C4—C3—H3B	108.5	C12—C11—H11	120.8
C2—C3—H3B	108.5	C13—C12—C11	122.46 (9)
H3A—C3—H3B	107.5	C13—C12—N2	118.91 (9)
C3—C4—C5	113.73 (9)	C11—C12—N2	118.60 (9)
C3—C4—H4A	108.8	C12—C13—C14	118.20 (9)
C5—C4—H4A	108.8	C12—C13—H13	120.9
C3—C4—H4B	108.8	C14—C13—H13	120.9
C5—C4—H4B	108.8	C13—C14—C9	121.06 (9)
H4A—C4—H4B	107.7	C13—C14—H14	119.5
C6—C5—C4	113.97 (9)	C9—C14—H14	119.5
C6—C5—H5A	108.8	C6—N1—C1	126.07 (9)
C4—C5—H5A	108.8	C6—N1—H1	115.6 (9)
C6—C5—H5B	108.8	C1—N1—H1	118.0 (9)
C4—C5—H5B	108.8	O2—N2—O3	123.31 (9)
H5A—C5—H5B	107.7	O2—N2—C12	118.66 (9)
N1—C6—C7	122.38 (9)	O3—N2—C12	118.02 (9)
N1—C6—C5	118.52 (9)		

N1—C1—C2—C3	−73.34 (13)	C9—C10—C11—C12	1.08 (16)

C1—C2—C3—C4	58.23 (14)	C10—C11—C12—C13	0.29 (16)
C2—C3—C4—C5	−64.07 (13)	C10—C11—C12—N2	178.33 (9)
C3—C4—C5—C6	82.62 (12)	C11—C12—C13—C14	−0.94 (16)
C4—C5—C6—N1	−60.10 (13)	N2—C12—C13—C14	−178.98 (9)
C4—C5—C6—C7	120.49 (11)	C12—C13—C14—C9	0.24 (16)
N1—C6—C7—C8	−6.73 (16)	C10—C9—C14—C13	1.07 (16)
C5—C6—C7—C8	172.66 (10)	C8—C9—C14—C13	−177.89 (9)
C6—C7—C8—O1	8.38 (17)	C7—C6—N1—C1	170.95 (10)
C6—C7—C8—C9	−167.41 (9)	C5—C6—N1—C1	−8.44 (15)
O1—C8—C9—C10	157.98 (10)	C2—C1—N1—C6	68.52 (14)
C7—C8—C9—C10	−25.96 (14)	C13—C12—N2—O2	−166.71 (9)
O1—C8—C9—C14	−23.10 (14)	C11—C12—N2—O2	15.17 (14)
C7—C8—C9—C14	152.95 (10)	C13—C12—N2—O3	13.97 (14)
C14—C9—C10—C11	−1.74 (16)	C11—C12—N2—O3	−164.14 (9)
C8—C9—C10—C11	177.16 (9)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.