organic compounds

tert-Butyl 4-(2-diazoacetyl)piperazine-1-carboxylate

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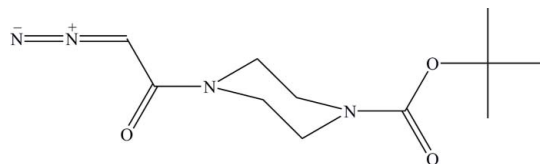
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The title crystal structure, $C_{11}H_{18}N_4O_3$, is the first diazo-acetamide in which the diazoacetyl group is attached to an N atom. The piperazine ring is in a chair form and hence the molecule has an extended conformation. Both ring N atoms are bonded in an essentially planar configuration with the sum of the C–N–C angles being 359.8 (2) and 357.7 (2)°. In the crystal structure, the O atom of the diazoacetyl group accepts two H atoms from C–H donors, thus generating chains of weak hydrogen-bonded $R_2^1(7)$ rings.

Related literature

For the only other reported synthesis of a diazoacetamide in the Chemical Abstracts Service (CAS, American Chemical Society, 2008) with a 1,4-diaza six-membered ring, see: Mickelson *et al.* (1996). For other diazoacetamides, see: Ouihia *et al.* (1993). For related structures, see: Fenlon *et al.* (2007); Wang *et al.* (2006); Miller *et al.* (1991). For synthetic details, see: Kaupang (2010); Toma *et al.* (2007). For hydrogen-bond graph-set notation, see: Bernstein *et al.* (1995). For a description of the Cambridge Structural Database, see: Allen (2002).

Experimental

Crystal data

$C_{11}H_{18}N_4O_3$	Monoclinic, $P2_1/c$
$M_r = 254.29$	$a = 14.654$ (10) Å

$b = 10.548$ (7) Å	Mo $K\alpha$ radiation
$c = 8.553$ (6) Å	$\mu = 0.10$ mm^{-1}
$\beta = 91.122$ (6)°	$T = 105$ K
$V = 1321.8$ (15) Å^3	$0.55 \times 0.42 \times 0.08$ mm
$Z = 4$	

Data collection

Bruker APEXII CCD diffractometer	7308 measured reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2007)	2692 independent reflections
$T_{min} = 0.870$, $T_{max} = 0.992$	2111 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.041$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.103$	
$S = 1.03$	
2692 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
169 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$\cdots$O1^i	0.946 (17)	2.313 (18)	3.250 (3)	170.6 (14)
C3—H32$\cdots$O1^i	0.99	2.36	3.327 (3)	164

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

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT-Plus* (Bruker, 2007); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5033).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
American Chemical Society (2008). Chemical Abstracts Service, American Chemical Society, Columbus, OH, USA; accessed Apr 27, 2010.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bruker (2007). *APEX2, SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Fenlon, T. W., Schwaebisch, D., Mayweg, A. V. W., Lee, V., Adlington, R. M. & Baldwin, J. E. (2007). *Synlett*, pp. 2679–2682.
Kaupang, Å. (2010). *Masters thesis, University of Oslo, Norway.* Available at http://www.duo.uio.no/.
Mickelson, J. W., Jacobsen, E. J., Carter, D. B., Im, H. K., Im, W. B., Schreur, P. J. K. D., Sethy, V. H., Tang, A. H., McGee, J. E. & Petke, J. D. (1996). *J. Med. Chem.* **39**, 4654–4666.
Miller, R. D., Theis, W., Heilig, G. & Kirchmeyer, S. (1991). *J. Org. Chem.* **56**, 1453–1463.
Ouihia, A., Rene, L., Guilhem, J., Pascard, C. & Badet, B. (1993). *J. Org. Chem.* **58**, 1641–1642.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Toma, T., Shimokawa, J. & Fukuyama, T. (2007). *Org. Lett.* **9**, 3195–3197.
Wang, J., Zeng, T., Li, M.-L., Duan, E.-H. & Li, J.-S. (2006). *Acta Cryst.* E**62**, o2912–o2913.

supporting information

tert-Butyl 4-(2-diazoacetyl)piperazine-1-carboxylate

Åsmund Kaupang, Carl Henrik Görbitz and Tore Hansen

S1. Comment

The tert-butyl 4-(2-diazoacetyl)piperazine-1-carboxylate (I) was prepared as part of a series of diazoacetamides, to be used in intramolecular C—H insertion reactions (Kaupang, 2010). It was synthesized from tert-butyl 4-(2-bromoacetyl)-piperazine-1-carboxylate by a slight modification of the procedure reported by Toma *et al.* (2007), employing 1,1,3,3-tetramethylguanidine as the base instead of 1,8-diazabicyclo[5.4.0]undec-7-ene.

Diffraction data were first collected at ambient temperature, yielding a structure with a massively disordered six-membered ring. At 105 K the ring is completely ordered in a well defined chair conformation, Fig. 1.

The diazoacetyl moiety is not an uncommon functional group in organic molecules, however only 15 occurrences were found in the Cambridge Structural Database (Version 5.31 of November 2009; Allen, 2002), and none where, as here, the group is attached to a N atom. In only two structures the group sits on a non-aromatic ring (Miller *et al.*, 1991; Fenlon *et al.*, 2007).

In a model molecule like trimethylamine the N atom is located about 0.45 Å above the plane defined by the three C atoms. In the structure of (I) N3 is 0.125 (2) Å above the plane defined by C2, C3 and C4, while N4 is only 0.039 (2) Å above the plane defined by C5, C6 and C7, which essentially shows a planar configuration (sum of C—N—C angles 359.8 (2) °). This is due to the double bond character of the amidic N3—C2 and N4—C7 bonds measuring 1.3515 (18) and 1.3483 (18) Å, respectively. An example of a related structure is 1,4-di(chloroacetyl)piperazine (Wang *et al.*, 2006).
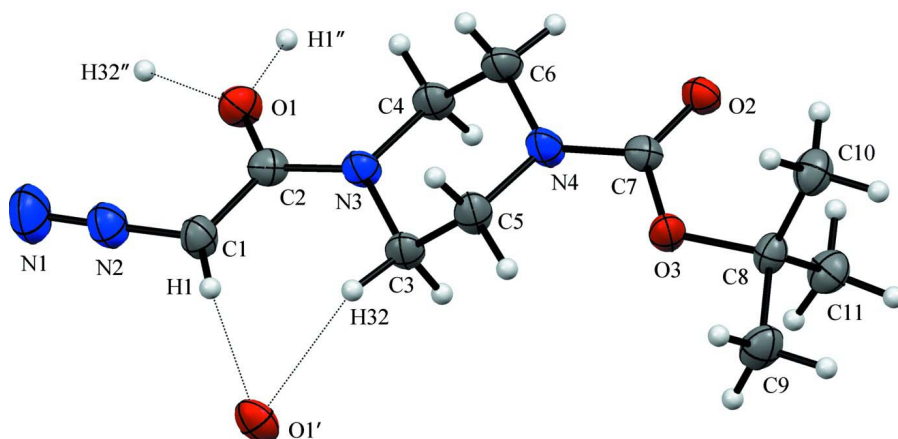
In the crystal structure, the O atom of the diazoacetyl group accepts two H atoms from C—H donors, thus generating chains of hydrogen-bonded $R^1_2(7)$ rings (Bernstein *et al.*, 1995).

S2. Experimental

A 2.5 ml vial containing tert-butyl 4-(2-diazoacetyl)piperazine-1-carboxylate (10.8 mg) and dichloromethane (1000 ml) was capped and a pinhole (0.5 mm) was made in the cap to allow for vapour diffusion of solvents. This vial was placed inside a 25 ml vial containing n-pentane (8 ml) that was subsequently capped and stored in the dark at ambient temperature for approximately 48 hours, affording bright yellow plate-shaped crystals.

S3. Refinement

Coordinates were refined for H1 (bonded to C1), which is involved in the shortest intermolcular interaction. Other H atoms were positioned with idealized geometry and fixed C–H distances set to 0.98 Å (methyl) or 0.99 Å (methylene). Free rotation was permitted for the methyl groups. U_{iso} values were $1.2U_{eq}$ of the carrier atom or $1.5U_{eq}$ for methyl groups.

Figure 1
The asymmetric unit of (I), with atomic numbering indicated, together with selected atoms of neighbouring molecules connected by weak hydrogen bonds shown as dotted lines (see Table 1, symmetry operations are -x,1/2+y,1/2-z for O′, -x,-1/2+y,1/2-z for H1" and H32"). Displacement ellipsoids are shown at the 50% probability level with H atoms as spheres of arbitrary size.

tert-**Butyl 4-(2-diazoacetyl)piperazine-1-carboxylate**

Crystal data

$C_{11}H_{18}N_4O_3$	$F(000) = 544$
$M_r = 254.29$	$D_x = 1.278$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 14.654$ (10) Å	Cell parameters from 2404 reflections
$b = 10.548$ (7) Å	$\theta = 2.4–26.4°$
$c = 8.553$ (6) Å	$\mu = 0.10$ mm^{-1}
$\beta = 91.122$ (6)°	$T = 105$ K
$V = 1321.8$ (15) Å^3	Plate, yellow
$Z = 4$	$0.55 \times 0.42 \times 0.08$ mm

Data collection

Bruker APEXII CCD diffractometer	Absorption correction: multi-scan (*SADABS*; Bruker, 2007)
Radiation source: fine-focus sealed tube	$T_{min} = 0.870$, $T_{max} = 0.992$
Graphite monochromator	7308 measured reflections
Detector resolution: 8.3 pixels mm^{-1}	2692 independent reflections
Three sets of frames each taken over 0.3° ω rotation with 20 s exposure time. Detector set at $2\theta = 26°$, crystal–to–detector distance 6.00 cm. scans	2111 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.041$
	$\theta_{max} = 26.4°$, $\theta_{min} = 2.4°$
	$h = -17 \rightarrow 18$
	$k = -10 \rightarrow 13$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.103$

$S = 1.03$

2692 reflections

169 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2 + 0.1671P]$ where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{max} = 0.17$ e Å^{-3}

$\Delta\rho_{min} = -0.23$ e Å^{-3}

Special details

Experimental. Crystallized from dichloromethane and n-pentane.

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

Refinement. Refinement of F^2 against ALL reflections.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.02567 (7)	0.20344 (9)	0.19361 (12)	0.0353 (3)
O2	0.38950 (6)	0.35633 (9)	0.62995 (11)	0.0296 (2)
O3	0.33388 (6)	0.55670 (8)	0.64091 (11)	0.0294 (2)
N1	−0.14125 (10)	0.34028 (15)	−0.00383 (19)	0.0562 (4)
N2	−0.08817 (8)	0.37402 (12)	0.08229 (16)	0.0377 (3)
N3	0.10933 (7)	0.34931 (10)	0.32642 (14)	0.0293 (3)
N4	0.27460 (8)	0.42179 (11)	0.46913 (15)	0.0350 (3)
C1	−0.02502 (10)	0.41229 (14)	0.18201 (17)	0.0324 (3)
H1	−0.0254 (10)	0.4999 (17)	0.2058 (19)	0.039*
C2	0.03721 (9)	0.31392 (13)	0.23569 (16)	0.0276 (3)
C3	0.11676 (9)	0.47080 (12)	0.40835 (18)	0.0301 (3)
H31	0.0971	0.4604	0.5177	0.036*
H32	0.0760	0.5337	0.3568	0.036*
C4	0.17261 (10)	0.25284 (13)	0.38538 (18)	0.0317 (3)
H41	0.1681	0.1763	0.3188	0.038*
H42	0.1561	0.2287	0.4931	0.038*
C5	0.21342 (9)	0.51824 (13)	0.40729 (18)	0.0322 (3)
H51	0.2304	0.5397	0.2990	0.039*
H52	0.2188	0.5960	0.4717	0.039*
C6	0.26896 (10)	0.30251 (13)	0.38538 (19)	0.0349 (4)
H61	0.3104	0.2399	0.4357	0.042*
H62	0.2886	0.3150	0.2763	0.042*
C7	0.33775 (9)	0.43825 (12)	0.58409 (16)	0.0259 (3)
C8	0.39795 (9)	0.59837 (13)	0.76528 (15)	0.0275 (3)
C9	0.36780 (11)	0.73381 (14)	0.79087 (18)	0.0387 (4)
H91	0.3721	0.7811	0.6927	0.058*

H92	0.4073	0.7734	0.8707	0.058*
H93	0.3045	0.7346	0.8258	0.058*
C10	0.49473 (10)	0.59327 (15)	0.70952 (17)	0.0354 (4)
H101	0.4989	0.6386	0.6099	0.053*
H102	0.5129	0.5047	0.6951	0.053*
H103	0.5354	0.6333	0.7873	0.053*
C11	0.38403 (10)	0.52052 (14)	0.91124 (17)	0.0351 (4)
H111	0.3190	0.5190	0.9358	0.053*
H112	0.4186	0.5583	0.9987	0.053*
H113	0.4055	0.4337	0.8939	0.053*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0331 (6)	0.0239 (5)	0.0487 (6)	−0.0044 (4)	−0.0025 (5)	−0.0072 (5)
O2	0.0298 (5)	0.0242 (5)	0.0348 (5)	0.0047 (4)	−0.0017 (4)	0.0004 (4)
O3	0.0326 (5)	0.0217 (5)	0.0336 (5)	0.0019 (4)	−0.0074 (4)	−0.0042 (4)
N1	0.0446 (8)	0.0565 (10)	0.0665 (10)	−0.0058 (7)	−0.0207 (8)	−0.0054 (8)
N2	0.0320 (7)	0.0341 (7)	0.0469 (8)	−0.0010 (5)	−0.0060 (6)	−0.0007 (6)
N3	0.0279 (6)	0.0200 (6)	0.0398 (7)	0.0018 (5)	−0.0042 (5)	−0.0041 (5)
N4	0.0304 (6)	0.0239 (6)	0.0503 (8)	0.0057 (5)	−0.0125 (6)	−0.0096 (5)
C1	0.0297 (8)	0.0281 (8)	0.0390 (8)	−0.0023 (6)	−0.0063 (6)	−0.0020 (6)
C2	0.0257 (7)	0.0241 (7)	0.0332 (7)	−0.0038 (5)	0.0042 (6)	−0.0018 (6)
C3	0.0324 (8)	0.0204 (7)	0.0373 (8)	0.0039 (6)	−0.0050 (6)	−0.0041 (6)
C4	0.0342 (8)	0.0202 (7)	0.0406 (8)	0.0031 (6)	−0.0035 (6)	−0.0040 (6)
C5	0.0341 (8)	0.0224 (7)	0.0396 (8)	−0.0002 (6)	−0.0089 (6)	−0.0014 (6)
C6	0.0325 (8)	0.0264 (7)	0.0455 (9)	0.0053 (6)	−0.0054 (7)	−0.0121 (6)
C7	0.0241 (7)	0.0237 (7)	0.0300 (7)	−0.0013 (5)	0.0030 (5)	−0.0008 (6)
C8	0.0314 (7)	0.0259 (7)	0.0249 (7)	−0.0041 (6)	−0.0037 (6)	−0.0013 (5)
C9	0.0523 (10)	0.0268 (8)	0.0367 (8)	−0.0006 (7)	−0.0048 (7)	−0.0049 (6)
C10	0.0346 (8)	0.0390 (8)	0.0325 (8)	−0.0078 (7)	−0.0006 (6)	0.0005 (6)
C11	0.0398 (8)	0.0354 (8)	0.0302 (8)	−0.0032 (7)	0.0025 (6)	0.0019 (6)

Geometric parameters (Å, º)

O1—C2	1.2303 (17)	C4—H41	0.9900
O2—C7	1.2099 (16)	C4—H42	0.9900
O3—C7	1.3422 (17)	C5—H51	0.9900
O3—C8	1.4722 (16)	C5—H52	0.9900
N1—N2	1.1189 (18)	C6—H61	0.9900
N2—C1	1.3099 (19)	C6—H62	0.9900
N3—C2	1.3515 (18)	C8—C10	1.506 (2)
N3—C4	1.4600 (18)	C8—C11	1.511 (2)
N3—C3	1.4635 (18)	C8—C9	1.513 (2)
N4—C7	1.3483 (18)	C9—H91	0.9800
N4—C5	1.4490 (18)	C9—H92	0.9800
N4—C6	1.4494 (19)	C9—H93	0.9800
C1—C2	1.450 (2)	C10—H101	0.9800

C1—H1	0.946 (17)	C10—H102	0.9800
C3—C5	1.503 (2)	C10—H103	0.9800
C3—H31	0.9900	C11—H111	0.9800
C3—H32	0.9900	C11—H112	0.9800
C4—C6	1.506 (2)	C11—H113	0.9800
C7—O3—C8	120.57 (10)	N4—C6—H61	109.6
N1—N2—C1	179.04 (18)	C4—C6—H61	109.6
C2—N3—C4	119.35 (12)	N4—C6—H62	109.6
C2—N3—C3	124.53 (11)	C4—C6—H62	109.6
C4—N3—C3	113.83 (11)	H61—C6—H62	108.1
C7—N4—C5	125.93 (12)	O2—C7—O3	125.31 (12)
C7—N4—C6	120.26 (11)	O2—C7—N4	124.15 (13)
C5—N4—C6	113.59 (12)	O3—C7—N4	110.52 (11)
N2—C1—C2	114.68 (13)	O3—C8—C10	110.59 (12)
N2—C1—H1	115.7 (9)	O3—C8—C11	109.89 (11)
C2—C1—H1	129.6 (9)	C10—C8—C11	112.67 (12)
O1—C2—N3	122.08 (12)	O3—C8—C9	101.68 (11)
O1—C2—C1	120.21 (13)	C10—C8—C9	111.04 (12)
N3—C2—C1	117.64 (12)	C11—C8—C9	110.43 (13)
N3—C3—C5	110.49 (12)	C8—C9—H91	109.5
N3—C3—H31	109.6	C8—C9—H92	109.5
C5—C3—H31	109.6	H91—C9—H92	109.5
N3—C3—H32	109.6	C8—C9—H93	109.5
C5—C3—H32	109.6	H91—C9—H93	109.5
H31—C3—H32	108.1	H92—C9—H93	109.5
N3—C4—C6	110.29 (12)	C8—C10—H101	109.5
N3—C4—H41	109.6	C8—C10—H102	109.5
C6—C4—H41	109.6	H101—C10—H102	109.5
N3—C4—H42	109.6	C8—C10—H103	109.5
C6—C4—H42	109.6	H101—C10—H103	109.5
H41—C4—H42	108.1	H102—C10—H103	109.5
N4—C5—C3	109.92 (12)	C8—C11—H111	109.5
N4—C5—H51	109.7	C8—C11—H112	109.5
C3—C5—H51	109.7	H111—C11—H112	109.5
N4—C5—H52	109.7	C8—C11—H113	109.5
C3—C5—H52	109.7	H111—C11—H113	109.5
H51—C5—H52	108.2	H112—C11—H113	109.5
N4—C6—C4	110.27 (12)		
C4—N3—C2—O1	−4.1 (2)	C7—N4—C6—C4	128.14 (15)
C3—N3—C2—O1	−165.84 (14)	C5—N4—C6—C4	−57.04 (17)
C4—N3—C2—C1	178.83 (13)	N3—C4—C6—N4	53.39 (17)
C3—N3—C2—C1	17.1 (2)	C8—O3—C7—O2	2.4 (2)
N2—C1—C2—O1	−3.6 (2)	C8—O3—C7—N4	−178.51 (11)
N2—C1—C2—N3	173.55 (13)	C5—N4—C7—O2	−177.86 (14)
C2—N3—C3—C5	−143.07 (14)	C6—N4—C7—O2	−3.7 (2)
C4—N3—C3—C5	54.32 (16)	C5—N4—C7—O3	3.0 (2)

C2—N3—C4—C6	142.52 (13)	C6—N4—C7—O3	177.17 (13)
C3—N3—C4—C6	−53.89 (17)	C7—O3—C8—C10	62.39 (16)
C7—N4—C5—C3	−128.35 (15)	C7—O3—C8—C11	−62.62 (16)
C6—N4—C5—C3	57.18 (17)	C7—O3—C8—C9	−179.61 (12)
N3—C3—C5—N4	−53.86 (17)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O1[i]	0.946 (17)	2.313 (18)	3.250 (3)	170.6 (14)
C3—H32···O1[i]	0.99	2.36	3.327 (3)	164

Symmetry code: (i) −*x*, *y*+1/2, −*z*+1/2.