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## Structure Reports

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# 1,4-Bis(2-diazoacetyl)piperazine

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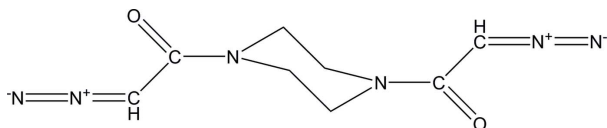
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 Key indicators: single-crystal X-ray study;  $T = 105$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.034;  $wR$  factor = 0.090; data-to-parameter ratio = 14.5.

The asymmetric unit of the title compound,  $\text{C}_8\text{H}_{10}\text{N}_6\text{O}_2$ , contains one-half molecule, which is completed by a crystallographic center of symmetry. The piperazine ring adopts a chair conformation. In the crystal, weak  $\text{C}-\text{H}\cdots\text{O}$  interactions link the molecules into layers parallel to the  $bc$  plane. The crystal packing also exhibits short  $\text{N}\cdots\text{N}$  contacts of 3.0467 (16) Å between the terminal diazo N atoms from neighbouring molecules.

## Related literature

For related structures in the Cambridge Structural Database (Version 5.34 of November 2012; Allen, 2002), see: Kaupang (2010); Kaupang *et al.* (2010, 2011); Aliev *et al.* (1980); Fitzgerald & Jensen (1978); Hope & Black (1972). For normal bond lengths in organic compounds, see: Allen *et al.* (1987). For synthetic details, see: Kaupang & Bonge-Hansen (2013); Kaupang (2010); Toma *et al.* (2007). For the synthesis of other diazoacetamides with a 1,4-diaza six-membered ring, see: Kaupang (2010); Mickelson *et al.* (1996). For the synthesis of other diazoacetamides, see: Ouhia *et al.* (1993). For the Chemical Abstracts Service, see: American Chemical Society (2008). For graph-set notation for hydrogen-bonding patterns, see: Etter *et al.* (1990).



## Experimental

### Crystal data

 $\text{C}_8\text{H}_{10}\text{N}_6\text{O}_2$ 
 $M_r = 222.22$ 

 Monoclinic,  $P2_1/c$ 
 $a = 4.0630$  (7) Å

 $b = 9.0941$  (15) Å

 $c = 13.230$  (2) Å

 $\beta = 94.453$  (2)°

 $V = 487.38$  (14) Å<sup>3</sup>
 $Z = 2$ 

 Mo  $K\alpha$  radiation

 $\mu = 0.12$  mm<sup>-1</sup>
 $T = 105$  K

 $1.4 \times 0.2 \times 0.2$  mm

### Data collection

Bruker APEXII CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Bruker, 2007)

 $T_{\min} = 0.859$ ,  $T_{\max} = 0.977$ 

4255 measured reflections

1190 independent reflections

 1013 reflections with  $I > 2\sigma(I)$ 
 $R_{\text{int}} = 0.021$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.034$ 
 $wR(F^2) = 0.090$ 
 $S = 1.04$ 

1190 reflections

82 parameters

3 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.30$  e Å<sup>-3</sup>
 $\Delta\rho_{\text{min}} = -0.22$  e Å<sup>-3</sup>
**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H21}\cdots\text{O1}^i$	0.92 (1)	2.39 (1)	3.2219 (15)	151 (1)

 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: CV5412).

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## supplementary materials

*Acta Cryst.* (2013). E69, o1241 [doi:10.1107/S1600536813018801]

## 1,4-Bis(2-diazoacetyl)piperazine

Åsmund Kaupang, Carl Henrik Görbitz and Tore Bonge-Hansen

### Comment

The *N,N'*-bis(2-diazoacetyl)piperazine (I) was prepared as part of a series of diazoacetamides (Kaupang *et al.*, 2010; 2011) used in the intramolecular C—H insertion reactions taking place upon thermolysis of their corresponding  $\alpha$ -bromo-diazoacetamides (Kaupang, 2010). The title compound was synthesized from *N,N'*-bis(2-bromoacetyl)piperazine following a procedure reported by Toma *et al.* (2007), modified to employ 1,1,3,3-tetramethylguanidine as the base instead of 1,8-diazabicyclo[5.4.0]undec-7-ene. No previous reports of this compound were found in the Chemical Abstracts Service (CAS; American Chemical Society, 2008).

In (I) (Fig. 1), the piperazine ring is in a normal chair conformation, with one half of the molecule constituting the asymmetric unit. In the Scheme the diazoacetyl group is illustrated in the normal way with C=N<sup>+</sup> and N<sup>+</sup>=N<sup>-</sup> double bonds, but sometimes a C—N single bond and a N≡N triple bond is used. N2—N3 = 1.1239 (14) Å is actually close in length to the triple bond in N<sub>2</sub>(g) = 1.0976 Å, but N2—C2 = 1.3099 (14) Å is clearly shorter than a normal N=N—C(sp<sup>3</sup>) single bond = 1.493 Å (Allen *et al.*, 1987), illustrating clearly the double bond nature.

As pointed out previously (Kaupang *et al.*, 2010), the ring N atoms have an amide rather than amine character and display an almost planar configuration [sum of C—N1—C angles 358.86 (15)°] due to the double bond character of N1—C1 = 1.3621 (13) Å. There are two interesting intermolecular interactions in the crystal packing (Fig. 2) - a C2—H21...O1 contact (Table 1) giving rise to chains and rings, and a 3.047 (14) Å N3...N3(1 - x, -y, -z) contact between the diazo groups with an associated N2—N3...N3 angle of 115.56 (10)° and N2—N3...N3—N2 torsion angle 180.0°. The diazoacetyl moiety is a relatively rare functional group occurring in 20 different organic molecules in the Cambridge Structural Database (CSD, Version 5.34 of November 2012; Allen 2002), and only three (Aliev *et al.*, 1980; Fitzgerald & Jensen, 1978; Hope & Black, 1972) participate in this type of interaction. Among more general compounds with a diazo group, 40 structures with 53 N...N distance < 3.5 Å were found in the CSD. Most contacts are within the 3.0 to 3.4 Å range. N—N...N angles have a wide distribution, but 45 are in the range 75 - 140° with average value 107°. A *trans* orientation for the N—N...N—N torsion angle is preferred; 36 out of 53 contacts have values in the range 180 ± 20°. Almost all structures with N...N contacts < 3.2 Å fall into this group.

### Experimental

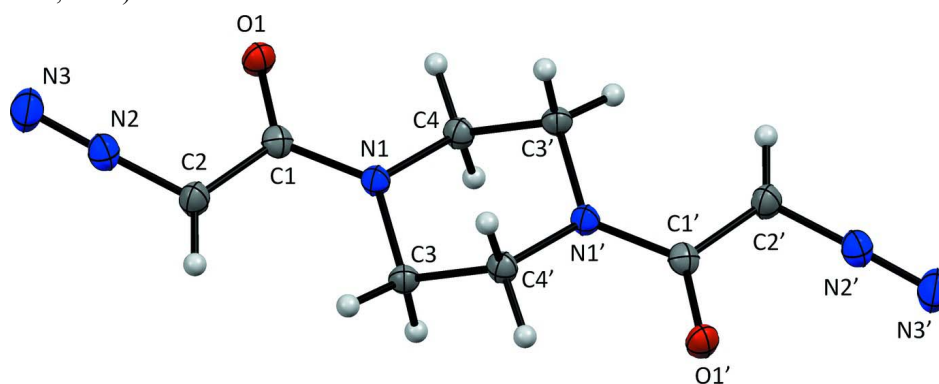
A solution of 4.0 mg of the title compound in 500  $\mu$ L of MeCN was placed in a vial measuring 30 × 6 mm and the open vial stored in the dark, exposed to air and at ambient temperature. Slow evaporation afforded yellow needles after 48 h. Crystals are rather fragile and easily fracture if cut with a scalpel. A rather long needle, 1.4 × 0.2 × 0.2 mm, was thus used for data collection.

## Refinement

H atoms bonded to C4 were positioned with idealized geometry and with fixed C—H distances at 0.99 Å, while positional coordinates were refined for H atoms bonded to C2 and C3, as too short intramolecular H···H distances resulted from putting these H atoms in theoretical positions. Distance restraints were imposed on the C2—H21 and C3—H31/H32 bonds utilizing *SHELX DFIX* 0.95 0.02 and *DFIX* 0.99 0.02 commands, respectively.

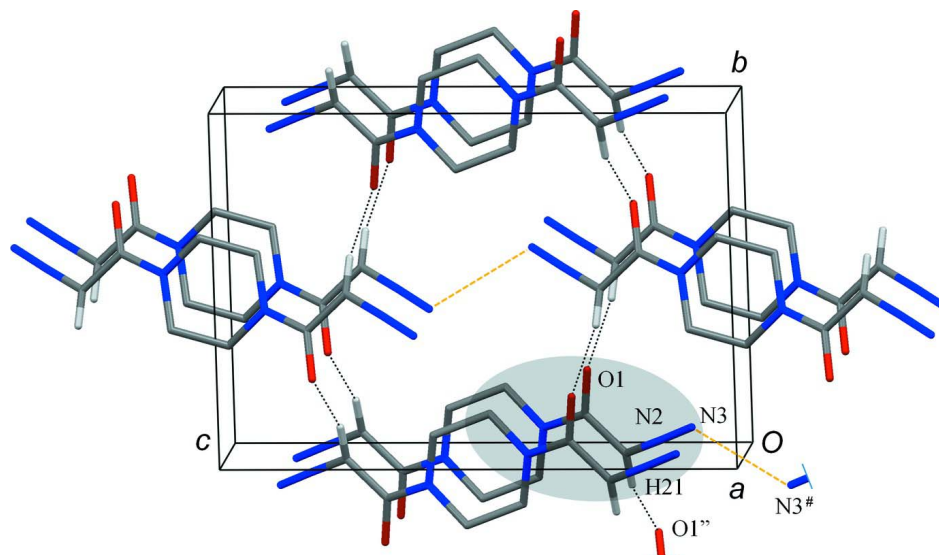
## Computing details

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



**Figure 1**

The molecular structure of (I) showing the atomic numbering and 50% probability displacement ellipsoids [symmetry code: (')  $-x, -y, 1 - z$ ].

**Figure 2**

The unit cell and crystal packing of (I) viewed approximately along the *a* axis with the asymmetric unit covered by a grey ellipse. H atoms not involved in short intermolecular contacts (indicated by dotted lines) have been omitted for clarity. The molecules are connected by C21—H21···O1''(-*x*, *y*-1/2-*y*, 1/2-*z*) hydrogen bonds into two-dimensional sheets with *C*(4) chain and *R*<sub>4</sub><sup>4</sup>(26) ring motifs (for graph set notation, see Etter *et al.*, 1990). An intermolecular N3···N3#(1-*x*, -*y*, -*z*) contact has been highlighted in orange.

### 1,4-Bis(2-diazoacetyl)piperazine

#### Crystal data

$C_8H_{10}N_6O_2$

$M_r = 222.22$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc

$a = 4.0630$  (7) Å

$b = 9.0941$  (15) Å

$c = 13.230$  (2) Å

$\beta = 94.453$  (2)°

$V = 487.38$  (14) Å<sup>3</sup>

$Z = 2$

$F(000) = 232$

$D_x = 1.514$  Mg m<sup>-3</sup>

Melting point: 382 K

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

Cell parameters from 1727 reflections

$\theta = 2.7$ – $28.7$ °

$\mu = 0.12$  mm<sup>-1</sup>

$T = 105$  K

Needle, yellow

$1.4 \times 0.2 \times 0.2$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3 pixels mm<sup>-1</sup>

Sets of exposures each taken over 0.5°  $\omega$

rotation scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2007)

$T_{\min} = 0.859$ ,  $T_{\max} = 0.977$

4255 measured reflections

1190 independent reflections

1013 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$

$\theta_{\max} = 28.7$ °,  $\theta_{\min} = 2.7$ °

$h = -5 \rightarrow 5$

$k = -11 \rightarrow 11$

$l = -17 \rightarrow 17$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.090$   
 $S = 1.04$   
 1190 reflections  
 82 parameters  
 3 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.1317P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.30 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.22 \text{ e } \text{\AA}^{-3}$

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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1936 (3)	0.09488 (12)	0.31650 (8)	0.0164 (2)
C2	0.2433 (3)	-0.01250 (13)	0.23807 (8)	0.0206 (3)
H21	0.165 (3)	-0.1064 (14)	0.2306 (11)	0.025*
C3	-0.0658 (3)	-0.10152 (12)	0.41721 (8)	0.0168 (2)
H31	0.016 (3)	-0.1708 (14)	0.3686 (10)	0.020*
H32	-0.308 (3)	-0.1005 (15)	0.4067 (10)	0.020*
C4	-0.0370 (3)	0.15403 (11)	0.47597 (8)	0.0169 (2)
H41	-0.2791	0.1688	0.4685	0.020*
H42	0.0701	0.2495	0.4638	0.020*
N1	0.0575 (2)	0.04673 (10)	0.40139 (7)	0.0165 (2)
N2	0.4038 (2)	0.03769 (10)	0.16317 (7)	0.0208 (2)
N3	0.5432 (3)	0.08327 (13)	0.10006 (8)	0.0295 (3)
O1	0.2787 (2)	0.22436 (9)	0.30680 (6)	0.0208 (2)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.0158 (5)	0.0172 (5)	0.0158 (5)	0.0018 (4)	-0.0009 (4)	0.0016 (4)
C2	0.0285 (6)	0.0176 (5)	0.0162 (5)	-0.0020 (4)	0.0047 (4)	0.0010 (4)
C3	0.0204 (5)	0.0141 (5)	0.0162 (5)	-0.0021 (4)	0.0026 (4)	-0.0006 (4)
C4	0.0202 (5)	0.0142 (5)	0.0167 (5)	0.0009 (4)	0.0030 (4)	-0.0012 (4)
N1	0.0221 (4)	0.0131 (4)	0.0145 (4)	-0.0008 (3)	0.0035 (3)	-0.0006 (3)
N2	0.0264 (5)	0.0189 (5)	0.0171 (5)	0.0024 (4)	0.0021 (4)	-0.0006 (4)
N3	0.0395 (6)	0.0282 (6)	0.0222 (5)	-0.0010 (5)	0.0110 (5)	0.0007 (4)
O1	0.0282 (4)	0.0154 (4)	0.0193 (4)	-0.0016 (3)	0.0047 (3)	0.0017 (3)

Geometric parameters (Å, °)

C1—O1	1.2367 (14)	C3—H31	0.978 (12)
C1—N1	1.3621 (13)	C3—H32	0.985 (12)
C1—C2	1.4504 (16)	C4—N1	1.4602 (13)
C2—N2	1.3099 (14)	C4—H41	0.9900
C2—H21	0.915 (12)	C4—H42	0.9900
C3—N1	1.4589 (13)	N2—N3	1.1239 (14)
C3—C4 <sup>i</sup>	1.5193 (15)		
O1—C1—N1	121.76 (10)	H31—C3—H32	107.6 (11)
O1—C1—C2	120.75 (10)	N1—C4—C3 <sup>i</sup>	110.54 (9)
N1—C1—C2	117.48 (10)	N1—C4—H41	109.5
N2—C2—C1	114.31 (10)	C3 <sup>i</sup> —C4—H41	109.5
N2—C2—H21	115.7 (9)	N1—C4—H42	109.5
C1—C2—H21	129.7 (9)	C3 <sup>i</sup> —C4—H42	109.5
N1—C3—C4 <sup>i</sup>	110.57 (9)	H41—C4—H42	108.1
N1—C3—H31	111.3 (8)	C1—N1—C3	125.53 (9)
C4 <sup>i</sup> —C3—H31	109.1 (8)	C1—N1—C4	119.16 (9)
N1—C3—H32	108.8 (8)	C3—N1—C4	114.17 (8)
C4 <sup>i</sup> —C3—H32	109.5 (8)	N3—N2—C2	178.58 (12)
O1—C1—C2—N2	4.86 (16)	C2—C1—N1—C4	-171.95 (9)
N1—C1—C2—N2	-173.69 (9)	C4 <sup>i</sup> —C3—N1—C1	137.76 (10)
O1—C1—N1—C3	176.58 (10)	C4 <sup>i</sup> —C3—N1—C4	-54.61 (12)
C2—C1—N1—C3	-4.88 (15)	C3 <sup>i</sup> —C4—N1—C1	-136.92 (9)
O1—C1—N1—C4	9.51 (15)	C3 <sup>i</sup> —C4—N1—C3	54.59 (12)

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

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H21 <sup>ii</sup> ⋯O1 <sup>ii</sup>	0.92 (1)	2.39 (1)	3.2219 (15)	151 (1)

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