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1,4-Diazoniabicyclo[2.2.2]octane bis(2,4,6-trinitrophenolate)

Weiwei SiMa

Ordered Matter Science Research Center, Southeast University, Nanjing 210096, People's Republic of China

Correspondence e-mail: nysima@126.com

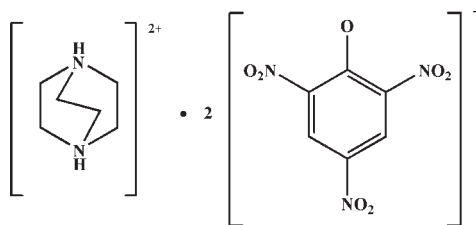
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Key indicators: single-crystal X-ray study; $T = 93$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.098; data-to-parameter ratio = 14.3.

In the title compound, $\text{C}_6\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$, the cation possesses crystallographically imposed twofold rotation symmetry. In the crystal structure, the cation and anions are linked into a trimeric aggregate by intermolecular $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds. The trimeric units are further connected by $\pi-\pi$ interactions [centroid-centroid distances = 3.507 (2)–3.660 (3) Å], forming layers parallel to the bc plane.

Related literature

For a discussion on hydrogen bonding in the title crystal, see: Kumai *et al.* (2007); Horiuchi *et al.* (2005). For related structures, see: Dabros *et al.* (2007); Jin *et al.* (2004); Glidewell *et al.* (1999); Chen *et al.* (2009).



Experimental

Crystal data

$\text{C}_6\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{C}_6\text{H}_2\text{N}_3\text{O}_7^-$
 $M_r = 570.40$
 Monoclinic, $C2/c$
 $a = 15.3808$ (11) Å

$b = 7.1520$ (5) Å
 $c = 25.3527$ (14) Å
 $\beta = 125.496$ (2)°
 $V = 2270.6$ (3) Å³

$Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 0.15$ mm⁻¹

$T = 93$ K
 $0.1 \times 0.1 \times 0.1$ mm

Data collection

Rigaku SCXmini diffractometer
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.857$, $T_{\max} = 1.000$

10700 measured reflections
 2590 independent reflections
 2218 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.098$
 $S = 1.07$
 2590 reflections

181 parameters
 H-atom parameters constrained
 $\Delta\rho_{\max} = 0.54$ e Å⁻³
 $\Delta\rho_{\min} = -0.59$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N4}-\text{H4A} \cdots \text{O1}$	0.93	1.69	2.589 (2)	161
$\text{N4}-\text{H4A} \cdots \text{O2}$	0.93	2.42	2.954 (2)	117

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalClear* (Rigaku, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PRPKAPPA* (Ferguson, 1999).

The author is grateful to the starter fund of Southeast University for financial support to buy the X-ray diffractometer.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RZ2442).

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supporting information

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1,4-Diazabicyclo[2.2.2]octane bis(2,4,6-trinitrophenolate)**Weiwei SiMa****S1. Comment**

The co-crystals of 1,4-diazabicyclo[2.2.2]octane (DABCO) and phenols are typically characterized by the presence of N—H \cdots O or O—H \cdots N hydrogen-bonded adducts (Kumai *et al.* (2007); Horiuchi *et al.*, 2005). Many of this type of co-crystals have been designed by employing crystal-engineering strategies, and their structures have been studied extensively (Dabros *et al.*, 2007; Jin *et al.*, 2004; Glidewell *et al.*, 1999). As a continuation of a study of phase transitions in hydrogen-bonded co-crystalline compounds between phenols and tertiary amines as N—H \cdots O-type systems (Chen *et al.*, 2009), the crystal structure of the 1:2 co-crystal of DABCO and 2,4,6-trinitrophenol obtained by a single-crystal X-ray analysis is reported herein. The compound shows no dielectric irregularity in the temperature range of 93–373K.

The title compound (Fig. 1) was obtained from the reaction of 1,4-diazabicyclo[2.2.2]octane and 2,4,6-trinitrophenol. The cation has crystallographically imposed twofold rotation symmetry. The two protonated N atoms in the cation are almost equivalent with very close C—N bond lengths [1.4930 (19) to 1.4952 (18) Å] and C—N—C angles [109.79 (11)° to 110.72 (11)°]. Within the benzene ring of the 2,4,6-trinitrophenol anion, the C—C—C bond angles of the three nitro-connected C atoms are in the range 121.92 (13)–126.76 (13)°, and are a little larger than the remaining three C—C—C bond angles. In the crystal structure (Fig. 2), cation and anions are linked into a trimeric aggregate by intermolecular N—H \cdots O hydrogen bonds (Table 1). The trimeric units are further connected by π – π interactions (centroid-to-centroid distance = 3.507 (2)–3.660 (3) Å) to form layers parallel to the *bc* plane.

S2. Experimental

1,4-Diazabicyclo[2.2.2]octane (DABCO) (2.5 mmol) was dissolved in ethanol (10 ml). The clear solution obtained was added to a solution of 2,4,6-trinitrophenol (5 mmol) in ethanol (20 ml). The formed precipitate was then filtered and the obtained yellow solid was redissolved in DMF (15 ml). Yellow co-crystals of the title compound suitable for X-ray diffraction analysis were obtained by slow evaporation of the mixture at room temperature after 7 days.

S3. Refinement

All the H atoms were calculated geometrically and were allowed to ride, with C—H = 0.95–0.99 Å, N—H = 0.93 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$.

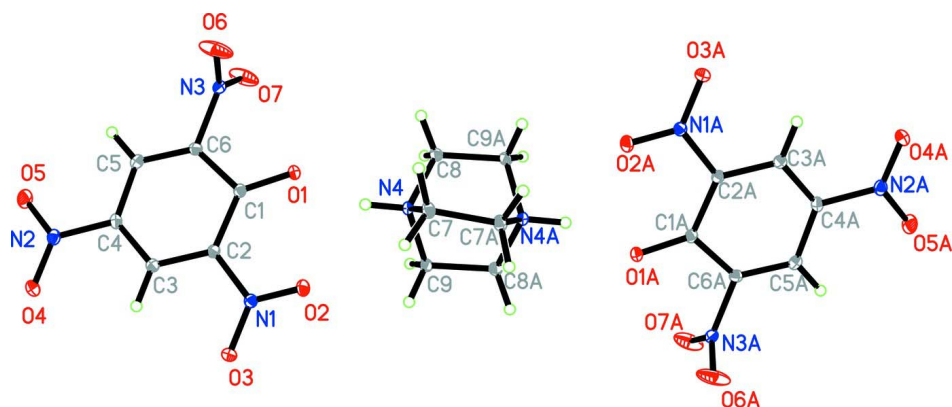


Figure 1

The molecular structure of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with suffix A are generated by the symmetry operation $(-x, y, 0.5-z)$.

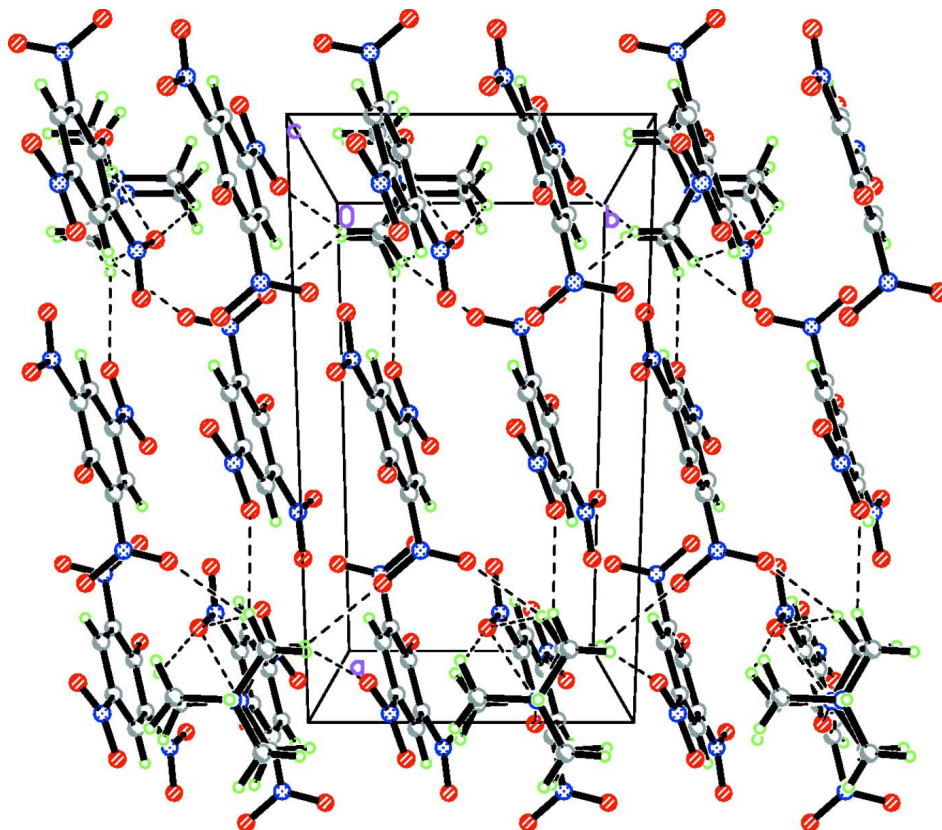


Figure 2

Crystal packing of the title compound viewed along the c axis. Dashed lines indicate hydrogen bonds.

1,4-Diazoniabicyclo[2.2.2]octane bis(2,4,6-trinitrophenolate)

Crystal data

$C_6H_{14}N_2^{2+} \cdot 2C_6H_2N_3O_7^-$

$M_r = 570.40$

Monoclinic, $C2/c$

Hall symbol: $-C 2yc$

$a = 15.3808(11) \text{ \AA}$

$b = 7.1520(5) \text{ \AA}$

$c = 25.3527 (14) \text{ \AA}$
 $\beta = 125.496 (2)^\circ$
 $V = 2270.6 (3) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 1176$
 $D_x = 1.669 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation, $\lambda = 0.71075 \text{ \AA}$

Cell parameters from 4042 reflections
 $\theta = 3.5\text{--}27.6^\circ$
 $\mu = 0.15 \text{ mm}^{-1}$
 $T = 93 \text{ K}$
 Prism, yellow
 $0.1 \times 0.1 \times 0.1 \text{ mm}$

Data collection

Rigaku SCXmini
 diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 Detector resolution: $13.6612 \text{ pixels mm}^{-1}$
 ω scans
 Absorption correction: multi-scan
 (*CrystalClear*; Rigaku, 2005)
 $T_{\min} = 0.857, T_{\max} = 1.000$

10700 measured reflections
 2590 independent reflections
 2218 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\max} = 27.5^\circ, \theta_{\min} = 3.1^\circ$
 $h = -19 \rightarrow 18$
 $k = -9 \rightarrow 9$
 $l = -32 \rightarrow 32$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.098$
 $S = 1.07$
 2590 reflections
 181 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-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0406P)^2 + 3.4753P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.54 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e \AA}^{-3}$

Special details

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. 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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.06908 (8)	0.27695 (17)	0.12769 (5)	0.0196 (2)
O2	-0.12313 (9)	0.44433 (16)	0.07242 (5)	0.0189 (2)
O3	-0.23908 (8)	0.41893 (16)	-0.03110 (5)	0.0192 (2)
O4	-0.13536 (9)	0.27577 (18)	-0.16941 (5)	0.0248 (3)
O5	0.01746 (9)	0.14572 (17)	-0.13108 (5)	0.0241 (3)
O6	0.28037 (11)	0.2978 (2)	0.13599 (8)	0.0563 (5)
O7	0.23717 (10)	0.01540 (18)	0.13396 (7)	0.0404 (4)
N1	-0.14821 (10)	0.39809 (17)	0.01833 (6)	0.0135 (3)
N2	-0.04785 (10)	0.21799 (18)	-0.12408 (6)	0.0167 (3)

N3	0.21729 (10)	0.17069 (18)	0.11151 (6)	0.0156 (3)
N4	0.00848 (9)	0.28214 (18)	0.20398 (6)	0.0136 (3)
H4A	0.0147	0.2825	0.1696	0.016*
C1	0.03700 (11)	0.2720 (2)	0.06954 (7)	0.0135 (3)
C2	-0.06664 (11)	0.3209 (2)	0.01256 (7)	0.0129 (3)
C3	-0.09268 (11)	0.30461 (19)	-0.04961 (7)	0.0133 (3)
H3A	-0.1616	0.3403	-0.0859	0.016*
C4	-0.01856 (12)	0.2367 (2)	-0.05864 (7)	0.0143 (3)
C5	0.08530 (12)	0.1875 (2)	-0.00629 (7)	0.0141 (3)
H5A	0.1364	0.1409	-0.0126	0.017*
C6	0.10876 (11)	0.2103 (2)	0.05401 (7)	0.0137 (3)
C7	0.01049 (12)	0.4793 (2)	0.22402 (7)	0.0163 (3)
H7A	-0.0450	0.5536	0.1862	0.020*
H7B	0.0809	0.5363	0.2414	0.020*
C8	0.10044 (12)	0.1762 (2)	0.25921 (7)	0.0182 (3)
H8A	0.1687	0.2302	0.2707	0.022*
H8B	0.0973	0.0438	0.2468	0.022*
C9	-0.09404 (11)	0.1889 (2)	0.18263 (7)	0.0149 (3)
H9A	-0.0970	0.0621	0.1660	0.018*
H9B	-0.1552	0.2620	0.1474	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0162 (5)	0.0311 (6)	0.0120 (5)	0.0027 (5)	0.0085 (4)	0.0029 (4)
O2	0.0207 (5)	0.0237 (6)	0.0143 (5)	0.0014 (4)	0.0113 (5)	-0.0021 (4)
O3	0.0138 (5)	0.0258 (6)	0.0153 (5)	0.0029 (4)	0.0069 (4)	0.0023 (4)
O4	0.0198 (6)	0.0389 (7)	0.0128 (5)	-0.0009 (5)	0.0078 (5)	0.0008 (5)
O5	0.0306 (6)	0.0267 (6)	0.0222 (6)	0.0043 (5)	0.0194 (5)	-0.0029 (5)
O6	0.0256 (7)	0.0389 (9)	0.0517 (9)	-0.0181 (6)	-0.0076 (7)	0.0214 (7)
O7	0.0271 (7)	0.0164 (6)	0.0401 (8)	0.0023 (5)	-0.0020 (6)	0.0064 (5)
N1	0.0144 (6)	0.0126 (6)	0.0138 (6)	-0.0010 (5)	0.0083 (5)	0.0008 (4)
N2	0.0201 (6)	0.0165 (6)	0.0153 (6)	-0.0040 (5)	0.0114 (5)	-0.0029 (5)
N3	0.0138 (6)	0.0181 (6)	0.0164 (6)	0.0000 (5)	0.0096 (5)	0.0013 (5)
N4	0.0142 (6)	0.0167 (6)	0.0113 (5)	0.0000 (5)	0.0082 (5)	0.0000 (4)
C1	0.0150 (7)	0.0125 (7)	0.0137 (6)	-0.0023 (5)	0.0087 (6)	0.0003 (5)
C2	0.0138 (7)	0.0118 (6)	0.0147 (6)	-0.0013 (5)	0.0092 (6)	-0.0003 (5)
C3	0.0140 (6)	0.0108 (6)	0.0137 (6)	-0.0028 (5)	0.0073 (6)	-0.0002 (5)
C4	0.0192 (7)	0.0118 (7)	0.0133 (6)	-0.0034 (5)	0.0103 (6)	-0.0018 (5)
C5	0.0168 (7)	0.0105 (7)	0.0182 (7)	-0.0008 (5)	0.0120 (6)	-0.0006 (5)
C6	0.0129 (6)	0.0118 (6)	0.0156 (7)	-0.0006 (5)	0.0078 (6)	0.0024 (5)
C7	0.0199 (7)	0.0155 (7)	0.0142 (7)	-0.0031 (6)	0.0102 (6)	-0.0015 (5)
C8	0.0142 (7)	0.0256 (8)	0.0141 (7)	0.0063 (6)	0.0077 (6)	0.0023 (6)
C9	0.0137 (6)	0.0167 (7)	0.0127 (6)	-0.0030 (5)	0.0067 (6)	-0.0027 (5)

Geometric parameters (Å, °)

O1—C1	1.2543 (17)	C2—C3	1.3876 (19)
O2—N1	1.2348 (16)	C3—C4	1.375 (2)
O3—N1	1.2297 (16)	C3—H3A	0.9500
O4—N2	1.2274 (17)	C4—C5	1.405 (2)
O5—N2	1.2307 (17)	C5—C6	1.361 (2)
O6—N3	1.2054 (19)	C5—H5A	0.9500
O7—N3	1.2037 (18)	C7—C7 ⁱ	1.528 (3)
N1—C2	1.4535 (18)	C7—H7A	0.9900
N2—C4	1.4510 (18)	C7—H7B	0.9900
N3—C6	1.4718 (18)	C8—C9 ⁱ	1.536 (2)
N4—C7	1.4930 (19)	C8—H8A	0.9900
N4—C9	1.4942 (18)	C8—H8B	0.9900
N4—C8	1.4952 (18)	C9—C8 ⁱ	1.536 (2)
N4—H4A	0.9300	C9—H9A	0.9900
C1—C6	1.440 (2)	C9—H9B	0.9900
C1—C2	1.4409 (19)		
O3—N1—O2	122.45 (12)	C5—C4—N2	119.00 (13)
O3—N1—C2	118.70 (12)	C6—C5—C4	116.45 (13)
O2—N1—C2	118.83 (12)	C6—C5—H5A	121.8
O4—N2—O5	123.34 (12)	C4—C5—H5A	121.8
O4—N2—C4	118.88 (12)	C5—C6—C1	126.76 (13)
O5—N2—C4	117.78 (12)	C5—C6—N3	119.86 (13)
O7—N3—O6	123.01 (14)	C1—C6—N3	113.38 (12)
O7—N3—C6	118.46 (12)	N4—C7—C7 ⁱ	108.68 (7)
O6—N3—C6	118.41 (13)	N4—C7—H7A	110.0
C7—N4—C9	110.72 (11)	C7 ⁱ —C7—H7A	110.0
C7—N4—C8	109.79 (11)	N4—C7—H7B	110.0
C9—N4—C8	109.80 (12)	C7 ⁱ —C7—H7B	110.0
C7—N4—H4A	108.8	H7A—C7—H7B	108.3
C9—N4—H4A	108.8	N4—C8—C9 ⁱ	108.41 (11)
C8—N4—H4A	108.8	N4—C8—H8A	110.0
O1—C1—C6	119.29 (13)	C9 ⁱ —C8—H8A	110.0
O1—C1—C2	128.51 (14)	N4—C8—H8B	110.0
C6—C1—C2	112.20 (12)	C9 ⁱ —C8—H8B	110.0
C3—C2—C1	122.68 (13)	H8A—C8—H8B	108.4
C3—C2—N1	116.72 (12)	N4—C9—C8 ⁱ	108.72 (11)
C1—C2—N1	120.56 (12)	N4—C9—H9A	109.9
C4—C3—C2	119.91 (13)	C8 ⁱ —C9—H9A	109.9
C4—C3—H3A	120.0	N4—C9—H9B	109.9
C2—C3—H3A	120.0	C8 ⁱ —C9—H9B	109.9
C3—C4—C5	121.92 (13)	H9A—C9—H9B	108.3
C3—C4—N2	119.08 (13)		
O1—C1—C2—C3	−178.37 (14)	N2—C4—C5—C6	179.14 (13)
C6—C1—C2—C3	1.4 (2)	C4—C5—C6—C1	2.8 (2)

O1—C1—C2—N1	4.2 (2)	C4—C5—C6—N3	-177.06 (12)
C6—C1—C2—N1	-175.98 (12)	O1—C1—C6—C5	176.35 (14)
O3—N1—C2—C3	10.33 (19)	C2—C1—C6—C5	-3.5 (2)
O2—N1—C2—C3	-167.99 (13)	O1—C1—C6—N3	-3.80 (19)
O3—N1—C2—C1	-172.10 (13)	C2—C1—C6—N3	176.37 (12)
O2—N1—C2—C1	9.59 (19)	O7—N3—C6—C5	-90.91 (18)
C1—C2—C3—C4	1.0 (2)	O6—N3—C6—C5	93.1 (2)
N1—C2—C3—C4	178.54 (12)	O7—N3—C6—C1	89.23 (18)
C2—C3—C4—C5	-1.9 (2)	O6—N3—C6—C1	-86.80 (19)
C2—C3—C4—N2	179.07 (13)	C9—N4—C7—C7 ⁱ	55.03 (18)
O4—N2—C4—C3	5.2 (2)	C8—N4—C7—C7 ⁱ	-66.36 (18)
O5—N2—C4—C3	-175.42 (13)	C7—N4—C8—C9 ⁱ	56.78 (15)
O4—N2—C4—C5	-173.87 (13)	C9—N4—C8—C9 ⁱ	-65.17 (13)
O5—N2—C4—C5	5.5 (2)	C7—N4—C9—C8 ⁱ	-64.33 (15)
C3—C4—C5—C6	0.1 (2)	C8—N4—C9—C8 ⁱ	57.06 (14)

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N4—H4A...O1	0.93	1.69	2.589 (2)	161
N4—H4A...O2	0.93	2.42	2.954 (2)	117