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4-(Dimethylamino)benzohydrazide

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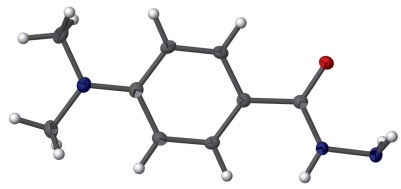
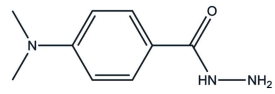
The title compound, $C_9H_{13}N_3O$, crystallizes in the monoclinic space group $C2/c$ and all non-hydrogen atoms are within 0.1 Å of the molecular mean plane. In the crystal, the hydrogen-bonding pattern results in [001] chains built up from fused $R_2^2(6)$ and $R_2^2(10)$ rings; the former consists of N—H···N bonds and the latter N—H···O bonds. Electrostatic and dispersion forces are major contributors to the lattice energy, which was estimated by DFT calculations to be −215.7 kJ mol^{-1}.

3D view



Chemical scheme



Structure description

For decades, there has been an interest in aroyl hydrazides because of their numerous applications, for instance, as synthetic precursors to a large number of potential antimicrobial (Popiołek, 2017) or anticancer (Kumar & Narasimhan, 2013) drugs, in addition to their own anti-tubercular activities (Sah & Peoples, 1954). In our search for inhibitors of bacterial virulence factors (Mossine *et al.*, 2016, 2020), we turned our attention to the title compound, which can be viewed as a structural analogue of isoniazid (Andrade *et al.*, 2008) and a potential precursor for pharmacologically active, iron-binding hydrazide-hydrazones. We now report its crystal structure.

The title compound crystallizes in the monoclinic space group $C2/c$, with eight molecules per unit cell. The asymmetric unit contains one molecule of the hydrazide (**I**), as shown in Fig. 1. All bond lengths and angles are within their expected ranges. The molecule is essentially flat, with the greatest deviation from the average molecular plane, among the non-hydrogen atoms, found for atom N1 at 0.074 (1) Å. The aromatic ring plane is at 1.08 (4)° to the molecular plane. The spatial arrangement of the hydrazido group, as defined by the torsion angle H2—N2—N3—H3B = 119.3 (15)°, corresponds to the lowest energy conformation that has been calculated for acyl hydrazides (Centore *et al.*, 2010).

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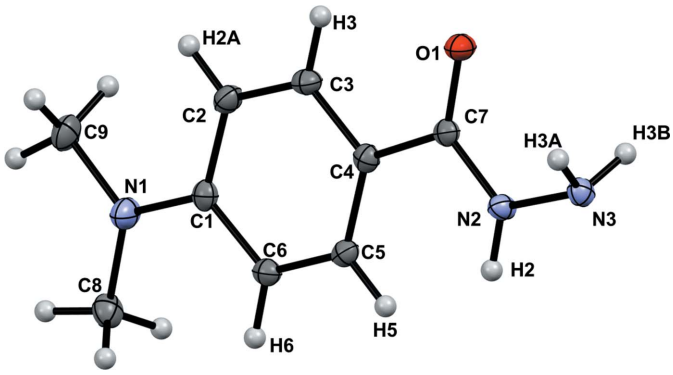


Figure 1
Atomic numbering and displacement ellipsoids at the 50% probability level for (**I**).

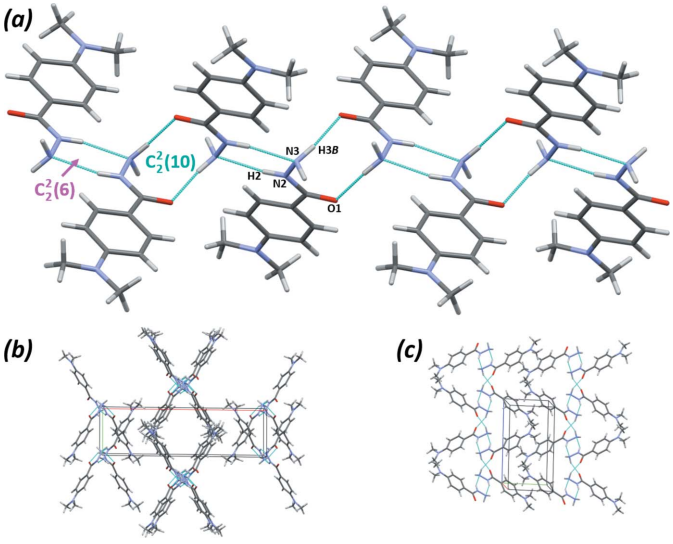


Figure 2
Molecular packing and hydrogen bonding in (**I**). (*a*) Hydrogen-bonding motifs; (*b*) and (*c*) molecular packing views down [001] and [100], respectively. Hydrogen bonds are shown as cyan dotted lines.

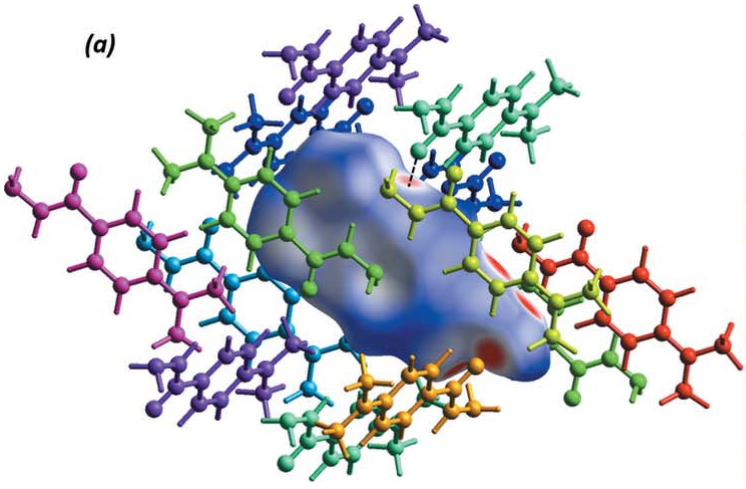
Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···N3^{i}	0.89 (2)	2.11 (2)	2.9203 (13)	151 (1)
N3—H3B···O1^{ii}	0.92 (2)	2.09 (1)	2.9516 (11)	157 (1)

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

The conventional hydrogen bonding in the extended structure of (**I**) is limited to two intermolecular heteroatom contacts (Table 1) involving the hydrazido groups only and is shown in Fig. 2. The hydrogen-bonding pattern includes infinite chains that propagate in the [001] direction and consist of fused $R_2^2(10)$ and $R_2^2(6)$ rings (Fig. 2*a*). The $R_2^2(10)$ motif is formed by pairs of molecules linked by the N3—H3B···O1 hydrogen bonds related by twofold rotation symmetry, while the $R_2^2(6)$ motif is formed by centrosymmetric dimers of (**I**) linked by the N2—H2···N3 hydrogen bonds. In addition, one short intermolecular contact, C6—H6···O1, which satisfies the distance and directionality conditions [C6···O1^{iii} = 3.4111 (13) Å, C6—H6···O1^{iii} = 172°; symmetry code: (iii) x, $1-y, \frac{1}{2}+z$], and which is shown in Fig. 3 as a dotted line, may also contribute to the stability of the molecular packing in the crystal. The intermolecular non-polar interactions are dominated by hydrogen–hydrogen contacts between the methyl groups; the shortest of these contacts, H8C···H9B, is about 0.1 Å less than the sum of the VdW radii. These interactions form a pattern of infinite chains, propagating in the [001] direction, in parallel to the hydrogen-bonded chains (Fig. 2*b* and 2*c*). The crystal structure lacks any strong π–π stacking interactions. However, a short N3—H3A···$Cg1$ [H3A···$Cg1^{iv}$ = 2.614 (15) Å; symmetry code: (iv) x, $y-1$, z] contact is present.

To account for all interactions involved in the build-up of the crystal structure of (**I**) we have performed DFT calculations, at the B3LYP/6–31 G(d,p) theory level (Mackenzie *et al.*, 2017; Thomas *et al.*, 2018), of the electrostatic, dispersion,



(b)

Pairwise interaction energies (kJ/mol)
B3LYP/6-31G(d,p) electron densities energy model

Color code	N	Symm operator	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-x, -y, -z	-76.5	-17.7	-20.3	87.8	-57.4
	1	x, y, 1/2-z	-45.3	-15.1	-21.8	61.4	-40.1
	1	-x, -y, -z	-9.6	-1.4	-26.9	13.9	-26.1
	2	x, y, z	-9.2	-2.8	-44.2	29.8	-31.9
	2	x, -y, z+1/2	-12.7	-5.1	-11.9	13.1	-19.5
	1	1/2-x, 1/2-y, -z	-7.7	-1.2	-14.7	8.6	-16.6
	2	1/2-x,1/2+y,1/2-z	-3.4	-1.8	-22.4	15.7	-14.7
	2	x, -y, 1/2+z	-1.1	-0.6	-8.5	3.5	-6.8
	1	1/2-x, 1/2-y, -z	0.2	-0.3	-3.2	0.3	-2.6

Figure 3
Interaction energies in crystal structure of (**I**). (*a*) A view of interactions between a central molecule, shown as its Hirshfeld surface, and 13 molecules that share the interaction surfaces with the central molecule. Red areas on the Hirshfeld surface encode the closest intermolecular contacts, which are hydrogen bonds involving the hydrazido groups, a short C—H···O type contact is shown as a dotted line; (*b*) Calculated energies (electrostatic, polarization, dispersion, repulsion, and total) of pairwise interactions between the central molecule and those indicated by respective colours.

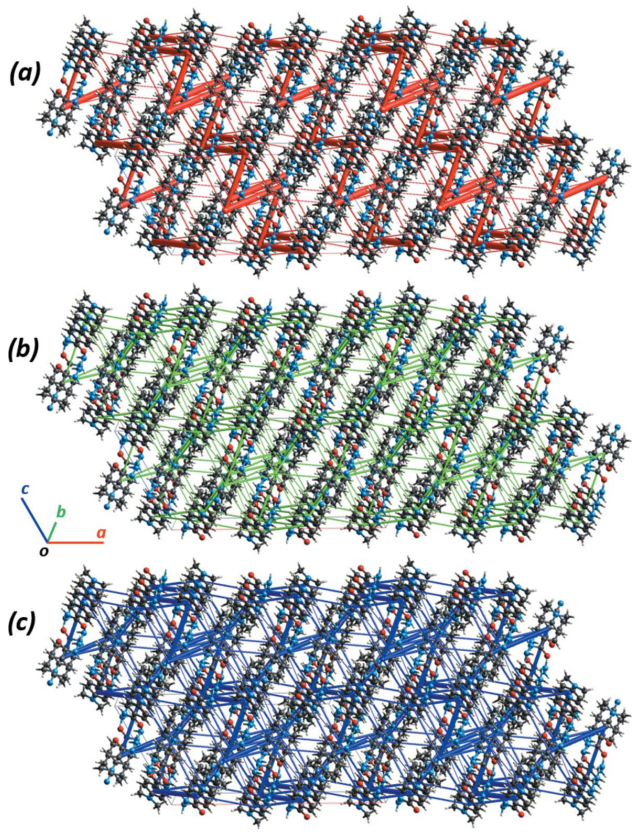


Figure 4
Energy frameworks for separate (*a*) electrostatic and (*b*) dispersion contributions to the (*c*) total pairwise interaction energies in (**I**). The cylinders link molecular centroids, and the cylinder thickness is proportional to the magnitude of the energies (see Fig. 3). For clarity, the cylinders corresponding to energies <5 kJ mol^{-1} are not shown. The directionality of the crystallographic axes is the same for all three diagrams.

polarization, and repulsion energies. According to these calculations, the interactions between hydrogen-bonded pairs of molecules contribute about 50% to the lattice energy, with the dispersion energy providing most of the attractive forces between non-hydrogen-bonded molecules of (**I**) (*i.e.* E_{ele} = −9.2 kJ mol^{-1}, E_{dis} = −44.2 kJ mol^{-1} for symmetry code = x, y, z). To estimate the lattice energy, all total energies of unique pairwise interactions between molecules were summed up, thus yielding E_l (l = lattice) = −216 kJ mol^{-1} for the crystal of (**I**). The calculated contributions to the overall lattice energy (kJ mol^{-1}) are as follows: E_{ele} = −165.3; E_{pol} = −46.0; E_{dis} = −173.9; E_{rep} = 234.1. The spatial distribution of the energetically most significant interactions is illustrated in Fig. 4, showing the interactions energy frameworks as cylinders penetrating the molecular packing of (**I**). As expected, the most extensive intermolecular interactions occur in the hydrogen-bonded chain direction parallel to [001].

Synthesis and crystallization

A sample of commercial 4-dimethylaminobenzhydrazide was recrystallized from hot 95% ethanol solution, affording colorless needles.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_9H_{13}N_3O$
M_r	179.22
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	100
a, *b*, *c* (Å)	24.7018 (6), 6.3093 (1), 13.2103 (3)
β (°)	118.0496 (8)
V (Å^3)	1817.01 (7)
Z	8
Radiation type	Cu *Kα*
μ (mm^{-1})	0.72
Crystal size (mm)	0.25 × 0.24 × 0.23
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*AXScale*; Bruker, 2016)
T_{min}, T_{max}	0.684, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15813, 1786, 1770
R_{int}	0.019
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.618
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.036, 0.098, 1.07
No. of reflections	1786
No. of parameters	130
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.22

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009), *CrystalExplorer17.5* (Mackenzie *et al.*, 2017), *Mercury* (Macrae *et al.*, 2020), and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

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full crystallographic data

IUCrData (2020). **5**, x201310 [https://doi.org/10.1107/S2414314620013103]

4-(Dimethylamino)benzohydrazide

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4-(Dimethylamino)benzohydrazide

Crystal data

$C_9H_{13}N_3O$
M_r = 179.22
Monoclinic, $C2/c$
a = 24.7018 (6) Å
b = 6.3093 (1) Å
c = 13.2103 (3) Å
β = 118.0496 (8)°
V = 1817.01 (7) Å^3
Z = 8
$F(000)$ = 768
D_x = 1.310 Mg m^{-3}
Cu $K\alpha$ radiation, λ = 1.54178 Å
Cell parameters from 9928 reflections
θ = 4.1–72.3°
μ = 0.72 mm^{-1}
T = 100 K
Irregular, colourless
0.25 × 0.24 × 0.23 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: Incoatec IMuS microfocus Cu tube
Multi-layer optics monochromator
φ and ω scans
Absorption correction: multi-scan (*AXScale*; Bruker, 2016)
T_{min} = 0.684, T_{max} = 0.754
15813 measured reflections
1786 independent reflections
1770 reflections with $I > 2\sigma(I)$
R_{int} = 0.019
θ_{max} = 72.4°, θ_{min} = 4.1°
$h = -29 \rightarrow 26$
$k = -7 \rightarrow 7$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.098
S = 1.07
1786 reflections
130 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 1.3587P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}
Extinction correction: SHELXL2017/1 (Sheldrick 2015), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0036 (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. The hydrazide H2, H3A, and H3B atoms were located in difference-Fourier maps while all other hydrogen atoms were initially placed in calculated positions with their coordinates constrained to ride on their carrier atoms [C—H(aromatic) = 0.95?Å, C—H(methyl) = 0.98?Å]. The constraint Uiso(H) = 1.2Ueq(carrier) or 1.5Ueq(methyl carrier) was applied in all cases.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.07812 (3)	0.16597 (12)	0.32634 (6)	0.0191 (2)
N2	0.03227 (4)	0.11655 (14)	0.43722 (7)	0.0155 (2)
H2	0.0261 (6)	0.151 (2)	0.4964 (12)	0.023*
N3	0.00327 (4)	−0.07477 (14)	0.38183 (7)	0.0155 (2)
H3A	0.0319 (7)	−0.162 (2)	0.3826 (12)	0.023*
H3B	−0.0235 (6)	−0.037 (2)	0.3076 (13)	0.023*
N1	0.18614 (4)	0.97723 (15)	0.64989 (8)	0.0218 (3)
C5	0.08706 (4)	0.50333 (16)	0.56022 (8)	0.0147 (2)
H5	0.060886	0.428200	0.582134	0.018*
C6	0.11601 (4)	0.68522 (16)	0.61942 (8)	0.0155 (2)
H6	0.109206	0.733294	0.680648	0.019*
C1	0.15565 (4)	0.80037 (16)	0.58975 (8)	0.0156 (2)
C2	0.16280 (5)	0.72556 (17)	0.49598 (9)	0.0174 (3)
H2A	0.188258	0.801208	0.472528	0.021*
C4	0.09528 (4)	0.42708 (16)	0.46894 (8)	0.0144 (2)
C3	0.13326 (5)	0.54379 (17)	0.43786 (9)	0.0166 (2)
H3	0.138925	0.496951	0.375132	0.020*
C7	0.06791 (4)	0.22760 (16)	0.40464 (8)	0.0141 (2)
C8	0.17404 (5)	1.06515 (18)	0.73873 (9)	0.0210 (3)
H8A	0.131656	1.116555	0.704356	0.032*
H8B	0.202237	1.183084	0.776385	0.032*
H8C	0.180052	0.955197	0.795469	0.032*
C9	0.22406 (5)	1.09916 (18)	0.61407 (10)	0.0222 (3)
H9A	0.258398	1.011548	0.620994	0.033*
H9B	0.239960	1.224711	0.662961	0.033*
H9C	0.199403	1.143461	0.534079	0.033*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0220 (4)	0.0209 (4)	0.0193 (4)	−0.0049 (3)	0.0137 (3)	−0.0052 (3)
N2	0.0196 (4)	0.0142 (4)	0.0150 (4)	−0.0038 (3)	0.0101 (4)	−0.0026 (3)
N3	0.0172 (4)	0.0139 (4)	0.0148 (4)	−0.0023 (3)	0.0071 (4)	−0.0015 (3)
N1	0.0232 (5)	0.0217 (5)	0.0240 (5)	−0.0086 (4)	0.0140 (4)	−0.0071 (4)
C5	0.0137 (5)	0.0157 (5)	0.0156 (5)	0.0009 (4)	0.0077 (4)	0.0024 (4)
C6	0.0157 (5)	0.0171 (5)	0.0143 (5)	0.0016 (4)	0.0075 (4)	0.0006 (4)

C1	0.0130 (5)	0.0153 (5)	0.0160 (5)	0.0007 (4)	0.0049 (4)	0.0007 (4)
C2	0.0167 (5)	0.0182 (5)	0.0194 (5)	−0.0023 (4)	0.0103 (4)	0.0012 (4)
C4	0.0135 (5)	0.0143 (5)	0.0145 (5)	0.0010 (4)	0.0058 (4)	0.0012 (4)
C3	0.0176 (5)	0.0188 (5)	0.0165 (5)	0.0006 (4)	0.0105 (4)	−0.0001 (4)
C7	0.0125 (5)	0.0159 (5)	0.0133 (5)	0.0018 (4)	0.0055 (4)	0.0016 (4)
C8	0.0214 (5)	0.0185 (5)	0.0225 (5)	−0.0020 (4)	0.0098 (4)	−0.0054 (4)
C9	0.0197 (5)	0.0199 (6)	0.0270 (6)	−0.0059 (4)	0.0109 (5)	−0.0024 (4)

Geometric parameters (Å, º)

O1—C7	1.2371 (12)	N2—H2	0.891 (15)
N2—N3	1.4187 (12)	N3—H3A	0.892 (17)
N2—C7	1.3444 (13)	N3—H3B	0.920 (15)
N1—C1	1.3715 (14)	C2—H2A	0.95
N1—C8	1.4506 (14)	C3—H3	0.95
N1—C9	1.4526 (14)	C5—H5	0.95
C5—C6	1.3835 (14)	C6—H6	0.95
C5—C4	1.3989 (14)	C8—H8A	0.98
C6—C1	1.4146 (14)	C8—H8B	0.98
C1—C2	1.4120 (14)	C8—H8C	0.98
C2—C3	1.3821 (15)	C9—H9A	0.98
C4—C3	1.3976 (14)	C9—H9B	0.98
C4—C7	1.4909 (14)	C9—H9C	0.98
C7—N2—N3	121.75 (8)	H3A—N3—H3B	109.9 (13)
C1—N1—C8	120.93 (9)	C1—C2—H2A	120
C1—N1—C9	120.31 (9)	C3—C2—H2A	120
C8—N1—C9	118.09 (9)	C2—C3—H3	119
C6—C5—C4	121.76 (9)	C4—C3—H3	119
C5—C6—C1	120.70 (9)	C4—C5—H5	119
N1—C1—C6	121.36 (9)	C6—C5—H5	119
N1—C1—C2	121.27 (9)	C1—C6—H6	120
C2—C1—C6	117.37 (9)	C5—C6—H6	120
C3—C2—C1	120.90 (9)	N1—C8—H8A	109
C5—C4—C7	124.79 (9)	N1—C8—H8B	109
C3—C4—C5	117.50 (9)	N1—C8—H8C	109
C3—C4—C7	117.69 (9)	H8A—C8—H8B	109
C2—C3—C4	121.73 (9)	H8A—C8—H8C	109
O1—C7—N2	121.71 (10)	H8B—C8—H8C	109
O1—C7—C4	121.71 (9)	N1—C9—H9A	109
N2—C7—C4	116.58 (9)	N1—C9—H9B	109
N3—N2—H2	114.0 (9)	N1—C9—H9C	109
C7—N2—H2	124.2 (9)	H9A—C9—H9B	109
N2—N3—H3A	108.3 (10)	H9A—C9—H9C	109
N2—N3—H3B	105.4 (8)	H9B—C9—H9C	109
C8—N1—C1—C2	173.90 (10)	C1—N1—C9—H9A	−64
C8—N1—C1—C6	−6.35 (15)	C1—N1—C9—H9B	176

C9—N1—C1—C2	3.50 (16)	C1—N1—C9—H9C	56
C9—N1—C1—C6	−176.75 (10)	C8—N1—C9—H9A	125
N3—N2—C7—O1	−1.50 (15)	C8—N1—C9—H9B	5
N3—N2—C7—C4	179.43 (9)	C8—N1—C9—H9C	−115
N1—C1—C2—C3	178.16 (11)	C7—N2—N3—H3A	54.0 (10)
C6—C1—C2—C3	−1.60 (16)	C7—N2—N3—H3B	−63.6 (11)
N1—C1—C6—C5	−177.96 (10)	H2—N2—N3—H3A	−123.2 (14)
C2—C1—C6—C5	1.79 (15)	H2—N2—N3—H3B	119.3 (15)
C1—C2—C3—C4	0.07 (18)	H2—N2—C7—O1	175.4 (11)
C2—C3—C4—C5	1.28 (16)	H2—N2—C7—C4	−3.7 (11)
C2—C3—C4—C7	−177.07 (10)	N1—C1—C2—H2A	−2
C3—C4—C5—C6	−1.08 (15)	C6—C1—C2—H2A	178
C7—C4—C5—C6	177.14 (10)	N1—C1—C6—H6	2
C3—C4—C7—O1	−0.02 (15)	C2—C1—C6—H6	−178
C3—C4—C7—N2	179.06 (10)	C1—C2—C3—H3	−180
C5—C4—C7—O1	−178.23 (10)	H2A—C2—C3—C4	−180
C5—C4—C7—N2	0.84 (15)	H2A—C2—C3—H3	0
C4—C5—C6—C1	−0.47 (16)	H3—C3—C4—C5	−179
C1—N1—C8—H8A	−65	H3—C3—C4—C7	3
C1—N1—C8—H8B	175	C3—C4—C5—H5	179
C1—N1—C8—H8C	55	C7—C4—C5—H5	−3
C9—N1—C8—H8A	106	C4—C5—C6—H6	180
C9—N1—C8—H8B	−14	H5—C5—C6—C1	180
C9—N1—C8—H8C	−134	H5—C5—C6—H6	0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N3^{i}	0.89 (2)	2.11 (2)	2.9203 (13)	151 (1)
N3—H3*B*···O1^{ii}	0.92 (2)	2.09 (1)	2.9516 (11)	157 (1)

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