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2,6-Diamino-4-chloropyrimidine–benzoic acid (1/1)

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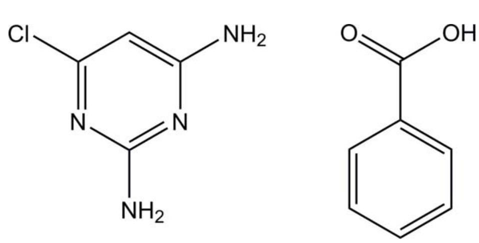
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.101; data-to-parameter ratio = 11.5.

The benzoic acid molecule of the title compound, $C_4H_5ClN_4 \cdot C_7H_6O_2$, is approximately planar, with a dihedral angle of 1.28 (9)° between the carboxy group and the benzene ring. In the crystal, two acid and two base molecules are linked through N—H···O and O—H···N hydrogen bonds, forming a centrosymmetric 2 + 2 unit with $R_2^2(8)$ and $R_4^2(8)$ motifs. These units are further linked through a pair of N—H···N hydrogen bonds into a tape structure along [1$\bar{2}$0]. The crystal structure also features weak π–π [centroid–centroid distance = 3.5984 (11) Å] and C—H···π interactions.

Related literature

For the biological activity of pyrimidine and aminopyrimidine derivatives, see: Hunt *et al.* (1980); Baker & Santi (1965). For related structures, see: Schwalbe & Williams (1982); Hu *et al.* (2002); Chinnakali *et al.* (1999); Skovsgaard & Bond (2009). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For bond-length data, see: Allen *et al.* (1987). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_4H_5ClN_4 \cdot C_7H_6O_2$
M_r = 266.69
Monoclinic, $P2_1/c$
a = 8.7817 (17) Å
b = 5.7032 (12) Å
c = 24.026 (4) Å
β = 95.493 (4)°
V = 1197.8 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 100 K
0.36 × 0.30 × 0.16 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.895, T_{max} = 0.951
7539 measured reflections
2097 independent reflections
1891 reflections with $I > 2\sigma(I)$
R_{int} = 0.052

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.101
S = 1.09
2097 reflections
183 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

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

*Cg*1 is the centroid of the C5–C10 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*1···N2	0.87 (2)	1.74 (2)	2.5976 (18)	168 (3)
N4—H2*N*4···O2	0.88 (2)	2.03 (2)	2.894 (2)	171.2 (18)
N4—H1*N*4···O2^{i}	0.88 (2)	2.07 (2)	2.902 (2)	158.2 (19)
N3—H1*N*3···N1^{ii}	0.85 (2)	2.18 (2)	3.020 (2)	171 (2)
C9—H9*A*···*Cg*1^{iii}	0.95	2.99	3.6557 (19)	128

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y+2, -z+1$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; 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* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS5218).

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‡ Thomson Reuters ResearcherID: A-5599-2009.

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2,6-Diamino-4-chloropyrimidine–benzoic acid (1/1)

Kaliyaperumal Thanigaimani, Nuridayanti Che Khalib, Suhana Arshad and Ibrahim Abdul Razak

S1. Comment

Pyrimidine and aminopyrimidine derivatives are biologically important compounds as they occur in nature as components of nucleic acids. Some aminopyrimidine derivatives are used as antifolate drugs (Hunt *et al.*, 1980; Baker & Santi, 1965). The crystal structures of aminopyrimidine derivatives (Schwalbe & Williams, 1982), aminopyrimidine carboxylates (Hu *et al.*, 2002) and co-crystal structures (Chinnakali *et al.*, 1999; Skovsgaard & Bond, 2009) have ben reported. In the present study, hydrogen-bonding patterns in the 2,6-diamino-4-chloropyrimidine–benzoic acid (1/1) co-crystal are investigated.

The asymmetric unit (Fig. 1) contains one 2,6-diamino-4-chloropyrimidine molecule and one benzoic acid molecule. The 2,6-diamino-4-chloropyrimidine molecule is essentially planar, with a maximum deviation of 0.009 (2) Å for atom C4. The carboxyl group of the benzoic acid molecule is twisted slightly from the ring with a dihedral angle between C5–C10 ring and O1/O2/C10/C11 plane being 1.28 (9)°. The bond lengths (Allen *et al.*, 1987) and angles are normal.

In the crystal packing (Fig. 2), the 2,6-diamino-4-chloropyrimidine molecules interact with the carboxylic group of the respective benzoic acid molecules through N4—H2N4···O2 and O1—H1O1···N2 hydrogen bonds, forming a cyclic hydrogen-bonded motif of $R_2^2(8)$ (Bernstein *et al.*, 1995). These motifs are centrosymmetrically paired *via* N4—H1N4···O2^{i} hydrogen bonds, resulting in a DADA array (Where D is a hydrogen-bond donor and A is a hydrogen-bond acceptor) of quadruple hydrogen bonds (symmetry code in Table 1); this can be represented by the graph-set notations of $R_2^2(8)$ and $R_4^2(8)$. The quadruple hydrogen-bonding motifs are further extended through a couple of N3—H1N3···N1^{ii} hydrogen bonds (symmetry code in Table 1), leading to the formation of hydrogen-bonded supramolecular tape. The crystal structure is further stabilized by π–π interactions between the pyrimidine (*Cg*2; N1/N2/C1–C4) rings [*Cg*2···*Cg*2 = 3.5984 (11) Å; $-x$, $1 - y$, $1 - z$] and C—H···π interactions (Table 1) involving the centroid of the C5–C10 (centroid *Cg*1) ring.

S2. Experimental

A hot methanol solutions (20 ml) of 2,6-diamino-4-chloropyrimidine (36 mg, Aldrich) and benzoic acid (30 mg, Merck) were mixed and warmed over a heating magnetic stirrer hotplate for a few minutes. The resulting solution was allowed to cool slowly at room temperature and crystals of the title compound (I) appeared after a few days.

S3. Refinement

O- and N-bound H Atoms were located in a difference Fourier maps and refined freely [O—H = 0.866 (10) Å and N—H = 0.79 (2)–0.88 (2) Å]. The remaining hydrogen atoms were positioned geometrically (C—H = 0.95 Å) and were refined using a riding model, with U_{iso}(H) = 1.2 U_{eq}(C).

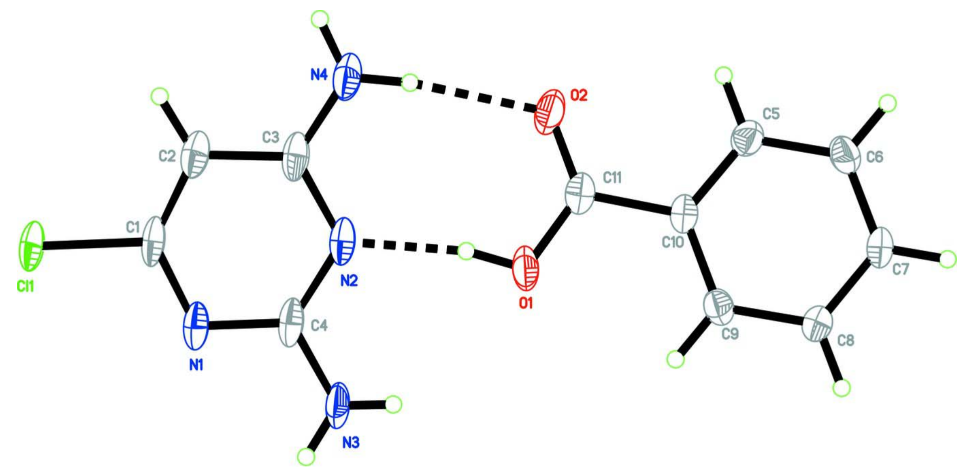

Figure 1

The molecular structure of the title compound with atom labels with 50% probability displacement ellipsoids. Dashed lines indicate the hydrogen bonds.

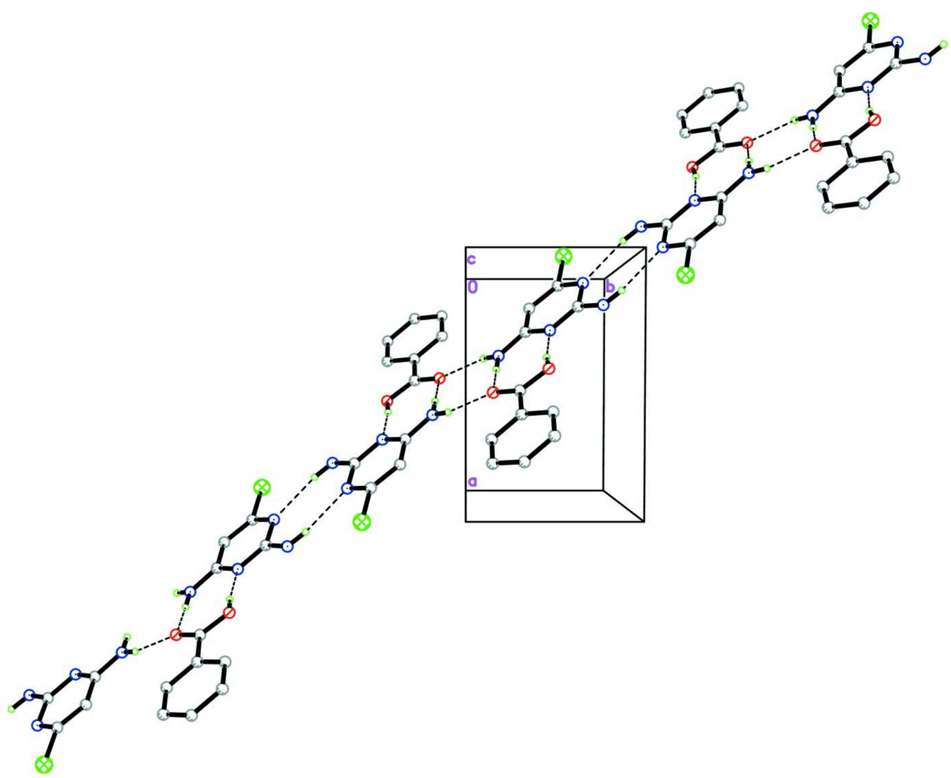

Figure 2

The crystal packing of the title compound. H atoms not involved in the intermolecular interactions (dashed lines) have been omitted for clarity.

2,6-Diamino-4-chloropyrimidine–benzoic acid (1/1)

Crystal data

$C_4H_5ClN_4\cdot C_7H_6O_2$
$M_r = 266.69$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.7817$ (17) Å
$b = 5.7032$ (12) Å
$c = 24.026$ (4) Å
$\beta = 95.493$ (4)°
$V = 1197.8$ (4) Å^3
$Z = 4$
$F(000) = 552$
$D_x = 1.479$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 5646 reflections
$\theta = 3.0$–30.0°
$\mu = 0.32$ mm^{-1}
$T = 100$ K
Block, colourless
0.36 × 0.30 × 0.16 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
$T_{min} = 0.895$, $T_{max} = 0.951$
7539 measured reflections
2097 independent reflections
1891 reflections with $I > 2\sigma(I)$
$R_{int} = 0.052$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.3°$
$h = -10 \rightarrow 10$
$k = -6 \rightarrow 6$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.101$
$S = 1.09$
2097 reflections
183 parameters
1 restraint
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
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.4196P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.25$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Experimental. The crystal was placed in the cold stream of an Oxford Cryosystems Cobra open-flow nitrogen cryostat (Cosier & Glazer, 1986) operating at 100.0 (1) K.

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 $F^2 > \sigma(F^2)$ 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cl1	−0.05557 (4)	0.64565 (9)	0.367228 (16)	0.03348 (18)
O1	0.43197 (13)	0.5175 (2)	0.61239 (5)	0.0312 (3)

O2	0.52962 (16)	0.1720 (2)	0.59015 (5)	0.0372 (3)
N1	0.07033 (15)	0.7543 (3)	0.46563 (5)	0.0274 (4)
N2	0.27154 (14)	0.5362 (3)	0.51588 (5)	0.0266 (4)
N3	0.16941 (19)	0.8669 (3)	0.55310 (6)	0.0313 (4)
N4	0.37676 (16)	0.2112 (3)	0.47835 (7)	0.0325 (4)
C1	0.07703 (17)	0.5991 (3)	0.42471 (7)	0.0272 (4)
C2	0.17389 (17)	0.4136 (4)	0.42399 (7)	0.0287 (4)
H2A	0.1734	0.3108	0.3929	0.034*
C3	0.27541 (17)	0.3846 (3)	0.47284 (7)	0.0272 (4)
C4	0.17144 (17)	0.7163 (3)	0.51057 (6)	0.0265 (4)
C5	0.71603 (19)	0.1587 (3)	0.69200 (7)	0.0264 (4)
H5A	0.7220	0.0302	0.6672	0.032*
C6	0.80722 (19)	0.1626 (3)	0.74236 (7)	0.0276 (4)
H6A	0.8760	0.0372	0.7519	0.033*
C7	0.79790 (17)	0.3497 (3)	0.77877 (7)	0.0251 (4)
H7A	0.8608	0.3526	0.8132	0.030*
C8	0.69723 (17)	0.5321 (3)	0.76507 (7)	0.0258 (4)
H8A	0.6908	0.6594	0.7902	0.031*
C9	0.60544 (17)	0.5293 (3)	0.71455 (7)	0.0241 (4)
H9A	0.5361	0.6542	0.7052	0.029*
C10	0.61545 (17)	0.3430 (3)	0.67768 (6)	0.0214 (4)
C11	0.52134 (18)	0.3366 (3)	0.62273 (7)	0.0249 (4)
H2N3	0.233 (3)	0.851 (4)	0.5785 (10)	0.039 (6)*
H2N4	0.432 (2)	0.196 (4)	0.5105 (10)	0.045 (6)*
H1N4	0.388 (2)	0.113 (4)	0.4508 (9)	0.033 (5)*
H1N3	0.109 (2)	0.983 (4)	0.5499 (9)	0.037 (6)*
H1O1	0.386 (3)	0.508 (7)	0.5789 (7)	0.113 (13)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0286 (3)	0.0508 (4)	0.0183 (2)	−0.00328 (18)	−0.01233 (16)	0.00310 (18)
O1	0.0260 (6)	0.0437 (8)	0.0220 (6)	0.0042 (6)	−0.0080 (5)	0.0035 (6)
O2	0.0521 (8)	0.0321 (8)	0.0240 (6)	−0.0019 (6)	−0.0147 (6)	−0.0010 (6)
N1	0.0230 (6)	0.0382 (9)	0.0190 (7)	−0.0093 (6)	−0.0076 (5)	0.0077 (7)
N2	0.0203 (6)	0.0395 (9)	0.0183 (7)	−0.0085 (6)	−0.0059 (5)	0.0068 (6)
N3	0.0318 (8)	0.0370 (10)	0.0217 (8)	−0.0044 (7)	−0.0144 (6)	0.0040 (7)
N4	0.0262 (7)	0.0503 (11)	0.0195 (7)	−0.0020 (7)	−0.0058 (6)	0.0009 (7)
C1	0.0202 (7)	0.0439 (11)	0.0159 (8)	−0.0113 (7)	−0.0071 (6)	0.0080 (7)
C2	0.0218 (8)	0.0457 (12)	0.0177 (8)	−0.0074 (8)	−0.0032 (6)	0.0029 (8)
C3	0.0178 (7)	0.0447 (12)	0.0181 (8)	−0.0098 (7)	−0.0029 (6)	0.0071 (7)
C4	0.0214 (7)	0.0387 (11)	0.0178 (8)	−0.0124 (7)	−0.0062 (6)	0.0083 (7)
C5	0.0325 (9)	0.0257 (10)	0.0201 (8)	0.0009 (7)	−0.0015 (7)	−0.0003 (7)
C6	0.0283 (8)	0.0292 (10)	0.0244 (8)	0.0070 (7)	−0.0030 (7)	0.0050 (7)
C7	0.0220 (8)	0.0322 (10)	0.0196 (8)	−0.0019 (7)	−0.0053 (6)	0.0024 (7)
C8	0.0249 (8)	0.0268 (10)	0.0244 (8)	−0.0006 (7)	−0.0038 (6)	−0.0034 (7)
C9	0.0199 (7)	0.0248 (10)	0.0267 (8)	0.0005 (7)	−0.0027 (6)	0.0028 (7)
C10	0.0192 (7)	0.0263 (9)	0.0181 (8)	−0.0046 (6)	−0.0014 (6)	0.0039 (6)

C11	0.0243 (8)	0.0291 (10)	0.0205 (8)	−0.0063 (7)	−0.0023 (6)	0.0043 (7)

Geometric parameters (Å, º)

Cl1—C1	1.7395 (15)	C2—C3	1.414 (2)
O1—C11	1.306 (2)	C2—H2A	0.9500
O1—H1O1	0.866 (10)	C5—C6	1.386 (2)
O2—C11	1.229 (2)	C5—C10	1.395 (2)
N1—C1	1.328 (2)	C5—H5A	0.9500
N1—C4	1.348 (2)	C6—C7	1.387 (3)
N2—C4	1.350 (2)	C6—H6A	0.9500
N2—C3	1.351 (2)	C7—C8	1.384 (2)
N3—C4	1.336 (2)	C7—H7A	0.9500
N3—H2N3	0.79 (2)	C8—C9	1.392 (2)
N3—H1N3	0.85 (2)	C8—H8A	0.9500
N4—C3	1.328 (3)	C9—C10	1.391 (2)
N4—H2N4	0.88 (2)	C9—H9A	0.9500
N4—H1N4	0.88 (2)	C10—C11	1.490 (2)
C1—C2	1.358 (3)		
C11—O1—H1O1	110 (2)	C6—C5—C10	120.18 (16)
C1—N1—C4	114.40 (16)	C6—C5—H5A	119.9
C4—N2—C3	118.60 (14)	C10—C5—H5A	119.9
C4—N3—H2N3	117.1 (16)	C5—C6—C7	119.92 (16)
C4—N3—H1N3	119.2 (15)	C5—C6—H6A	120.0
H2N3—N3—H1N3	123 (2)	C7—C6—H6A	120.0
C3—N4—H2N4	118.1 (15)	C8—C7—C6	120.20 (15)
C3—N4—H1N4	121.4 (13)	C8—C7—H7A	119.9
H2N4—N4—H1N4	121 (2)	C6—C7—H7A	119.9
N1—C1—C2	126.90 (15)	C7—C8—C9	120.15 (16)
N1—C1—Cl1	114.35 (13)	C7—C8—H8A	119.9
C2—C1—Cl1	118.76 (14)	C9—C8—H8A	119.9
C1—C2—C3	115.25 (17)	C10—C9—C8	119.83 (15)
C1—C2—H2A	122.4	C10—C9—H9A	120.1
C3—C2—H2A	122.4	C8—C9—H9A	120.1
N4—C3—N2	117.76 (15)	C9—C10—C5	119.71 (15)
N4—C3—C2	122.23 (17)	C9—C10—C11	121.29 (15)
N2—C3—C2	120.01 (17)	C5—C10—C11	118.99 (15)
N3—C4—N1	116.94 (17)	O2—C11—O1	123.62 (15)
N3—C4—N2	118.24 (15)	O2—C11—C10	121.44 (16)
N1—C4—N2	124.81 (16)	O1—C11—C10	114.94 (15)
C4—N1—C1—C2	−0.5 (2)	C10—C5—C6—C7	0.3 (3)
C4—N1—C1—Cl1	179.02 (11)	C5—C6—C7—C8	0.3 (3)
N1—C1—C2—C3	1.1 (3)	C6—C7—C8—C9	−0.4 (2)
Cl1—C1—C2—C3	−178.45 (11)	C7—C8—C9—C10	−0.2 (2)
C4—N2—C3—N4	178.65 (15)	C8—C9—C10—C5	0.9 (2)
C4—N2—C3—C2	−1.2 (2)	C8—C9—C10—C11	−178.71 (14)

C1—C2—C3—N4	179.98 (15)	C6—C5—C10—C9	−0.9 (2)
C1—C2—C3—N2	−0.1 (2)	C6—C5—C10—C11	178.67 (15)
C1—N1—C4—N3	−179.82 (14)	C9—C10—C11—O2	−179.79 (15)
C1—N1—C4—N2	−1.0 (2)	C5—C10—C11—O2	0.6 (2)
C3—N2—C4—N3	−179.31 (15)	C9—C10—C11—O1	0.5 (2)
C3—N2—C4—N1	1.9 (2)	C5—C10—C11—O1	−179.08 (14)

Hydrogen-bond geometry (Å, º)

*Cg*1 is the centroid of the C5–C10 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*O*1···N2	0.87 (2)	1.74 (2)	2.5976 (18)	168 (3)
N4—H2*N*4···O2	0.88 (2)	2.03 (2)	2.894 (2)	171.2 (18)
N4—H1*N*4···O2^{i}	0.88 (2)	2.07 (2)	2.902 (2)	158.2 (19)
N3—H1*N*3···N1^{ii}	0.85 (2)	2.18 (2)	3.020 (2)	171 (2)
C9—H9*A*···*Cg*1^{iii}	0.95	2.99	3.6557 (19)	128

Symmetry codes: (i) −*x*+1, −*y*, −*z*+1; (ii) −*x*, −*y*+2, −*z*+1; (iii) −*x*+1, *y*+1/2, −*z*+3/2.