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Pyrimidin-2-amine–1-phenylcyclopentane-1-carboxylic acid (1/1)

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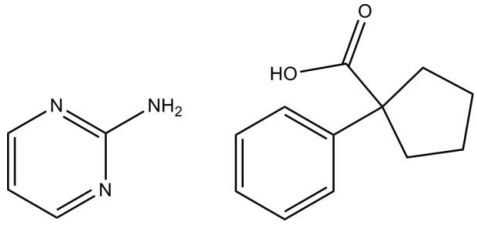
Key indicators: single-crystal X-ray study; T = 110 K; mean σ(C–C) = 0.003 Å; R factor = 0.068; wR factor = 0.178; data-to-parameter ratio = 18.0.

In the crystal structure of the title co-crystal, $C_4H_5N_3\cdot C_{12}H_{14}O_2$, the components are linked by N—H···O and O—H···N hydrogen bonds. Self-assembly of these dimeric units results in a four-component supramolecular unit featuring a homosynthon between two molecules of the pyrimidin-2-amine involving two N—H···O hydrogen bonds, and two heterosynthons between each one molecule of pyrimidin-2-amine and 1-phenylcyclopentane-1-carboxylic acid involving N—H···O and O—H···N hydrogen bonds.

Related literature

For the structure of pyrimidin-2-amine, see: Scheinbeim & Schempp (1976) and for the structure of 1-phenylcyclopentane-1-carboxylic acid, see: Margulis (1975). For molecular co-crystals of pyrimidin-2-amine, see: Serafin & Wheeler (2007); Shan *et al.* (2002); Goswami *et al.* (1999*a*,*b*, 2000); Chinnakali *et al.* (1999); Lynch *et al.* (1997). For a salt of 2-aminopyridine and 1-phenyl-1-cyclopropanecarboxylic acid, see: He *et al.* (2010). For a recent screening study for co-crystal and salt formation using pulse-gradient spin–echo nuclear magnetic resonance, see: He *et al.* (2009).



Experimental

Crystal data

$C_4H_5N_3\cdot C_{12}H_{14}O_2$
M_r = 285.34
Monoclinic, $P2_1/n$
a = 9.1461 (18) Å
b = 10.490 (2) Å
c = 15.474 (3) Å
β = 98.14 (3)°
V = 1469.7 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 110 K
0.44 × 0.44 × 0.22 mm

Data collection

Rigaku Saturn 70 CCD area-detector diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.963, T_{max} = 0.981
20335 measured reflections
3641 independent reflections
3516 reflections with $I > 2\sigma(I)$
R_{int} = 0.036

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.178
S = 1.21
3641 reflections
202 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H6···N1	0.87 (2)	1.79 (2)	2.653 (2)	173 (3)
N3—H5···O1	0.90 (3)	2.08 (3)	2.966 (2)	168 (2)
N3—H1···N2^{i}	0.88 (3)	2.13 (3)	3.006 (2)	173 (2)

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

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG5101).

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supporting information

Acta Cryst. (2011). E**67**, o552–o553 [doi:10.1107/S1600536811003667]

Pyrimidin-2-amine–1-phenylcyclopentane-1-carboxylic acid (1/1)

Guangwen He, Srinivasulu Aitipamula, Pui Shan Chow and Reginald B. H. Tan

S1. Comment

An analysis of the crystal structure of pyrimidin-2-amine reveals that it forms a homosynthon (I) involving two N–H···N hydrogen bonds (Scheinbeim and Schempp, 1976). However, when it is cocrystallized with the molecules possessing at least one carboxylic acid group in the structure, it forms a pyrimidin-2-amine–carboxylic acid supramolecular heterosynthon (II) (Fig. 1) involving two hydrogen bonds, namely N–H···O and O–H···N. These strong hydrogen bonds are preferred over potential alternative arrangements and play a significant role in structure-directing (Shan *et al.*, 2002). We have chosen pyrimidin-2-amine and 1-phenylcyclopentane-1-carboxylic acid for cocrystallization experiment as an extension work to our previous study on screening for molecular cocrystals and salts (He *et al.*, 2009).

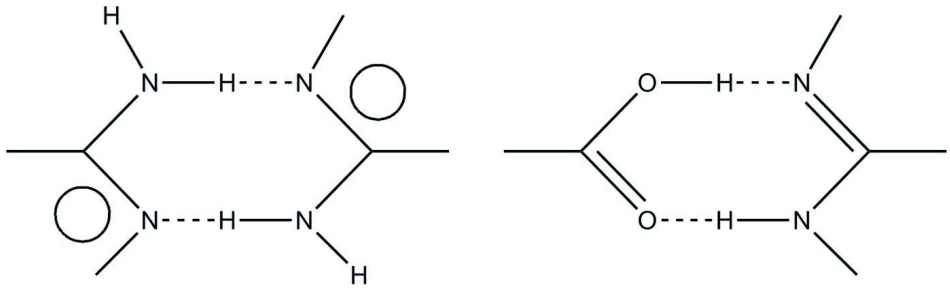
The crystal structure of the title cocrystal contains one molecule of pyrimidin-2-amine and one molecule of 1-phenylcyclopentane-1-carboxylic acid in the crystallographic asymmetric unit (Fig. 2). The identity of the cocrystal was confirmed by Fourier Transform Infrared (FT—IR) spectrum which showed carboxylic acid O—H stretching band at 3167 cm^{-1} and carbonyl stretching band at 1685 cm^{-1} (Fig. 3). Two pyrimidin-2-amine molecules that are related by an inversion center form the synthon I involving N–H···O (N···O = 3.006 (2) Å) hydrogen bonds. Two 1-phenylcyclopentane-1-carboxylic acid molecules hydrogen bond to either side of the dimeric motif involving synthon II which is sustained by N–H···O (N···O = 2.966 (2) Å) and O–H···O (O···O = 2.653 (2) Å) hydrogen bonds and forms a four-component supramolecular unit (Fig. 4). These four-component supramolecular units self assemble in the crystal structure *via* several weak C–H···O interactions (Fig. 5).

S2. Experimental

0.0957 g (1 mmol) of pyrimidin-2-amine (Alfa Aesar, 99%) and 0.1909 g (1 mmol) of 1-phenylcyclopentane-1-carboxylic acid (Alfa Aesar, 98%) and were dissolved into 7.6 ml of ethyl acetate (Fisher Scientific, HPLC). Solution was then filtered through a 0.22μm PTFE filter. Filtered solution was finally sealed with Parafilm and small holes were made to allow solvent to slowly evaporate. The block-shaped crystal (0.44 × 0.44 × 0.22 mm) suitable for single-crystal X-ray diffraction (Rigaku Saturn 70 CCD area detector with Mo K_α radiation = 0.71073 Å at 50 kV and 40 mA) was collected after one day. Fourier Transform Infrared (FT—IR) experiments were performed using Bio-Rad spectrometer (FTS3000MX) to confirm whether the resulting molecular complex is a cocrystal or a salt.

S3. Refinement

H atoms bonded to N and O atoms were located in a difference map and allowed to ride on their parent atoms in the refinement cycles.The O2—H6 bond distance which was found to be long in the normal refinement cycles was fixed using *DFIX* command in *SHELX*. Other H atoms were positioned geometrically and refined using a riding model.



I II

Figure 1

pyrimidin-2-amine–pyrimidin-2-amine supramolecular homosynthon (I) and pyrimidin-2-amine–carboxylic acid supramolecular heterosynthon (II).

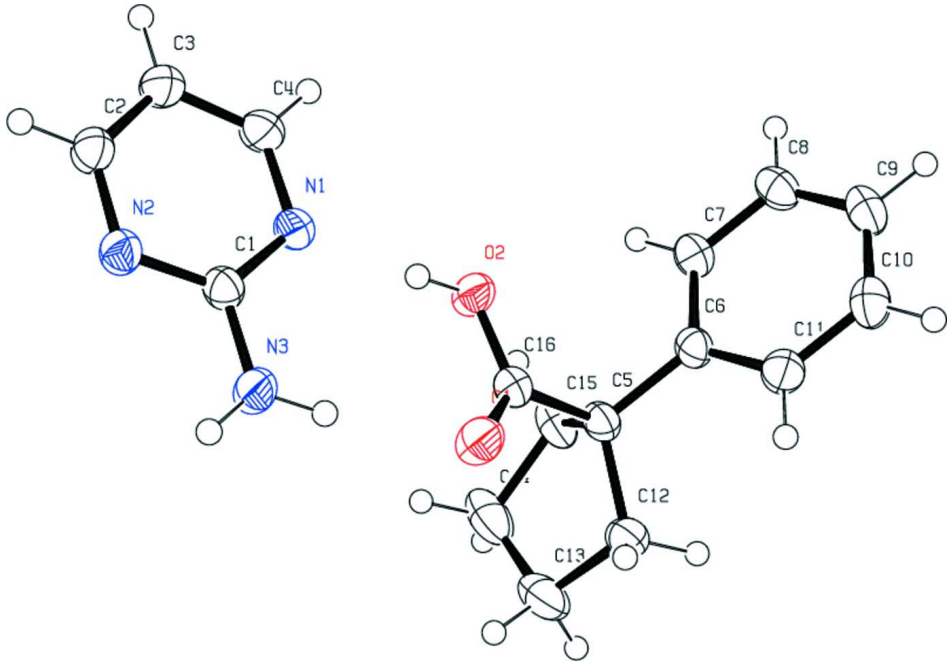


Figure 2

The molecular structures of pyrimidin-2-amine and 1-phenyl-1-cyclopropentanecarboxylic acid, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

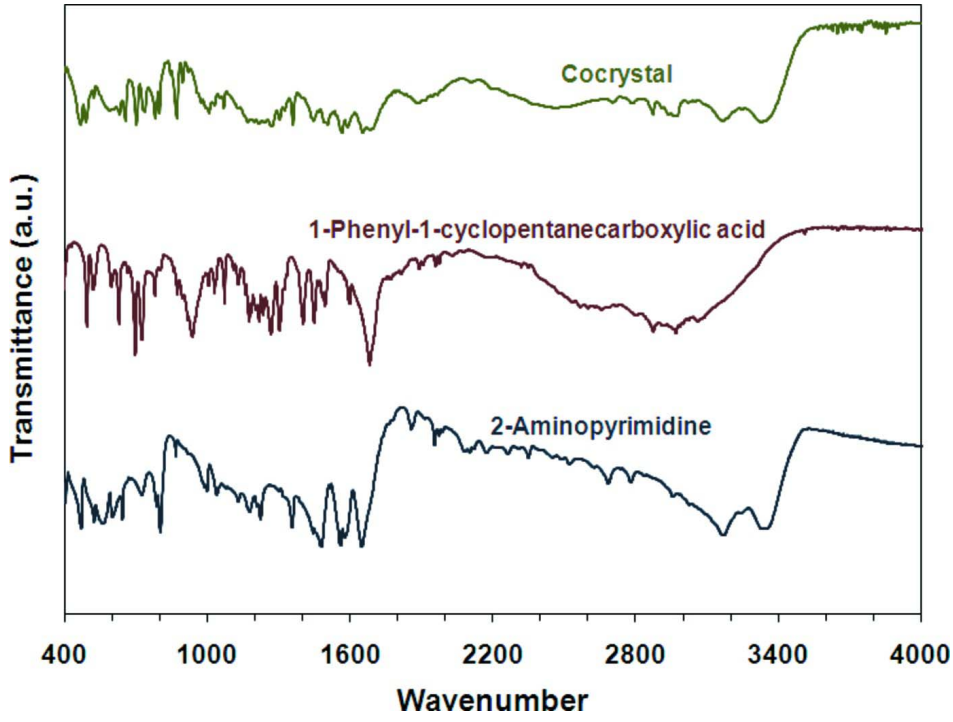


Figure 3

F T—IR spectra for pyrimidin-2-amine, 1-phenylcyclopentane-1-carboxylic acid and the 1/1 cocrystal of them, respectively.

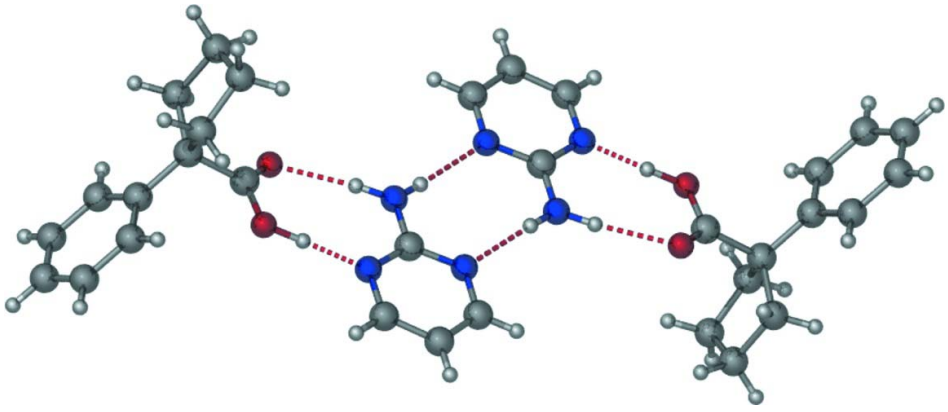


Figure 4

A four-component supramolecular unit that features N–H···O and O–H···N heterosynthon interactions, and O–H···O homosynthon interaction in the crystal structure of the title cocrystal.

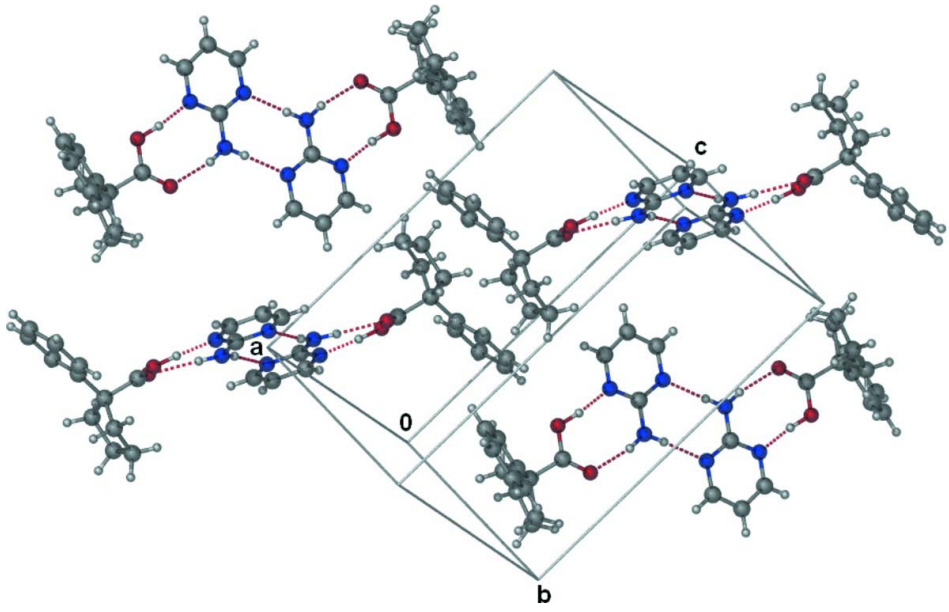


Figure 5

Part of the crystal structure of the title cocrystal, showing the arrangement of the four-component supramolecular units.

Pyrimidin-2-amine–1-phenylcyclopentane-1-carboxylic acid (1/1)

Crystal data

$C_4H_5N_3{\cdot}C_{12}H_{14}O_2$
$M_r = 285.34$
Monoclinic, $P2_1/n$
$a = 9.1461\ (18)$ Å
$b = 10.490\ (2)$ Å
$c = 15.474\ (3)$ Å
$\beta = 98.14\ (3)°$
$V = 1469.7\ (5)$ Å^3
$Z = 4$
$F(000) = 608$
$D_x = 1.290$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4896 reflections
$\theta = 1.9–31.1°$
$\mu = 0.09$ mm^{-1}
$T = 110$ K
Block, colorless
0.44 × 0.44 × 0.22 mm

Data collection

Rigaku Saturn 70 CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.963$, $T_{max} = 0.981$
20335 measured reflections
3641 independent reflections
3516 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 28.3°$, $\theta_{min} = 2.4°$
$h = -12\rightarrow12$
$k = -13\rightarrow13$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.178$
$S = 1.21$
3641 reflections
202 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
$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 0.5855P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-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 $F^2 > \sigma(F^2)$ 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}
O2	0.04632 (14)	0.55094 (13)	0.70052 (8)	0.0344 (3)
O1	0.22224 (15)	0.40633 (14)	0.73866 (9)	0.0397 (3)
C16	0.12059 (18)	0.47154 (16)	0.75641 (11)	0.0281 (3)
C6	−0.09084 (18)	0.42117 (16)	0.83708 (10)	0.0273 (3)
C5	0.06701 (18)	0.47220 (17)	0.84621 (11)	0.0289 (4)
C8	−0.35533 (19)	0.45531 (18)	0.80273 (12)	0.0337 (4)
H8	−0.4356	0.5110	0.7842	0.040*
C12	0.17880 (19)	0.3999 (2)	0.91211 (12)	0.0396 (4)
H12A	0.2180	0.3247	0.8843	0.047*
H12B	0.1319	0.3709	0.9625	0.047*
C7	−0.21065 (18)	0.50062 (17)	0.81043 (11)	0.0305 (4)
H7	−0.1936	0.5873	0.7972	0.037*
C10	−0.2643 (2)	0.24866 (18)	0.84809 (12)	0.0362 (4)
H10	−0.2821	0.1620	0.8610	0.043*
C11	−0.1195 (2)	0.29396 (17)	0.85543 (12)	0.0332 (4)
H11	−0.0395	0.2376	0.8731	0.040*
C15	0.0807 (2)	0.6105 (2)	0.88196 (13)	0.0380 (4)
H15A	0.0410	0.6727	0.8365	0.046*
H15B	0.0279	0.6204	0.9332	0.046*
C9	−0.3820 (2)	0.32934 (19)	0.82208 (12)	0.0354 (4)
H9	−0.4805	0.2985	0.8175	0.042*
C13	0.3039 (2)	0.4964 (3)	0.94177 (14)	0.0523 (6)
H13A	0.3269	0.4975	1.0062	0.063*
H13B	0.3945	0.4731	0.9172	0.063*
C14	0.2473 (2)	0.6273 (2)	0.90771 (16)	0.0517 (6)
H14A	0.2684	0.6930	0.9537	0.062*
H14B	0.2944	0.6530	0.8566	0.062*
H6	0.082 (3)	0.557 (3)	0.6516 (13)	0.066 (8)*
C2	0.24306 (19)	0.66091 (17)	0.39920 (12)	0.0318 (4)
H2	0.2760	0.6860	0.3462	0.038*
N3	0.36606 (18)	0.47957 (17)	0.58582 (11)	0.0391 (4)

N1	0.14713 (15)	0.58831 (14)	0.54997 (9)	0.0299 (3)
N2	0.33123 (16)	0.58740 (14)	0.45437 (10)	0.0314 (3)
C3	0.1056 (2)	0.70251 (18)	0.41554 (12)	0.0345 (4)
H3	0.0445	0.7554	0.3757	0.041*
C4	0.06304 (19)	0.66250 (18)	0.49318 (12)	0.0346 (4)
H4	−0.0304	0.6890	0.5068	0.041*
H5	0.331 (3)	0.447 (2)	0.6325 (17)	0.051 (7)*
C1	0.27973 (18)	0.55295 (16)	0.52886 (11)	0.0285 (3)
H1	0.451 (3)	0.454 (2)	0.5716 (16)	0.051 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O2	0.0317 (6)	0.0434 (7)	0.0300 (6)	0.0106 (5)	0.0113 (5)	0.0085 (5)
O1	0.0385 (7)	0.0472 (8)	0.0361 (7)	0.0150 (6)	0.0146 (6)	0.0093 (6)
C16	0.0247 (7)	0.0303 (8)	0.0297 (8)	−0.0005 (6)	0.0056 (6)	0.0009 (6)
C6	0.0259 (7)	0.0322 (8)	0.0249 (8)	−0.0013 (6)	0.0071 (6)	−0.0011 (6)
C5	0.0226 (7)	0.0380 (9)	0.0268 (8)	−0.0023 (6)	0.0055 (6)	−0.0003 (6)
C8	0.0249 (8)	0.0410 (9)	0.0361 (9)	0.0003 (7)	0.0070 (7)	−0.0050 (7)
C12	0.0264 (8)	0.0626 (13)	0.0297 (9)	0.0001 (8)	0.0039 (7)	0.0093 (8)
C7	0.0279 (8)	0.0307 (8)	0.0336 (9)	−0.0016 (6)	0.0074 (6)	−0.0031 (7)
C10	0.0408 (10)	0.0329 (9)	0.0364 (9)	−0.0097 (7)	0.0102 (7)	−0.0021 (7)
C11	0.0331 (9)	0.0333 (9)	0.0336 (9)	0.0005 (7)	0.0058 (7)	0.0018 (7)
C15	0.0305 (9)	0.0449 (10)	0.0402 (10)	−0.0110 (7)	0.0106 (7)	−0.0113 (8)
C9	0.0303 (8)	0.0436 (10)	0.0339 (9)	−0.0108 (7)	0.0104 (7)	−0.0084 (7)
C13	0.0274 (9)	0.0954 (18)	0.0335 (10)	−0.0092 (10)	0.0018 (8)	−0.0042 (11)
C14	0.0357 (10)	0.0700 (15)	0.0500 (12)	−0.0211 (10)	0.0082 (9)	−0.0156 (11)
C2	0.0328 (8)	0.0344 (9)	0.0292 (8)	0.0018 (7)	0.0077 (6)	0.0018 (7)
N3	0.0306 (8)	0.0513 (10)	0.0383 (9)	0.0149 (7)	0.0150 (7)	0.0168 (7)
N1	0.0238 (6)	0.0371 (8)	0.0294 (7)	0.0027 (5)	0.0065 (5)	0.0024 (6)
N2	0.0294 (7)	0.0340 (7)	0.0320 (8)	0.0035 (6)	0.0087 (6)	0.0040 (6)
C3	0.0304 (8)	0.0403 (10)	0.0326 (9)	0.0052 (7)	0.0045 (7)	0.0057 (7)
C4	0.0257 (8)	0.0437 (10)	0.0348 (9)	0.0070 (7)	0.0060 (6)	0.0041 (7)
C1	0.0256 (8)	0.0291 (8)	0.0316 (8)	0.0016 (6)	0.0066 (6)	0.0010 (6)

Geometric parameters (Å, º)

O2—C16	1.318 (2)	C15—H15A	0.9900
O2—H6	0.869 (17)	C15—H15B	0.9900
O1—C16	1.217 (2)	C9—H9	0.9500
C16—C5	1.537 (2)	C13—C14	1.535 (4)
C6—C7	1.392 (2)	C13—H13A	0.9900
C6—C11	1.397 (2)	C13—H13B	0.9900
C6—C5	1.527 (2)	C14—H14A	0.9900
C5—C12	1.538 (2)	C14—H14B	0.9900
C5—C15	1.551 (3)	C2—N2	1.334 (2)
C8—C9	1.384 (3)	C2—C3	1.387 (2)
C8—C7	1.395 (2)	C2—H2	0.9500

C8—H8	0.9500	N3—C1	1.340 (2)
C12—C13	1.548 (3)	N3—H5	0.90 (3)
C12—H12A	0.9900	N3—H1	0.88 (3)
C12—H12B	0.9900	N1—C4	1.334 (2)
C7—H7	0.9500	N1—C1	1.352 (2)
C10—C9	1.384 (3)	N2—C1	1.355 (2)
C10—C11	1.397 (2)	C3—C4	1.380 (3)
C10—H10	0.9500	C3—H3	0.9500
C11—H11	0.9500	C4—H4	0.9500
C15—C14	1.530 (3)		

C16—O2—H6	113.4 (19)	C5—C15—H15B	111.1
O1—C16—O2	123.13 (16)	H15A—C15—H15B	109.1
O1—C16—C5	123.93 (16)	C10—C9—C8	119.54 (16)
O2—C16—C5	112.93 (14)	C10—C9—H9	120.2
C7—C6—C11	118.03 (15)	C8—C9—H9	120.2
C7—C6—C5	120.77 (15)	C14—C13—C12	106.50 (16)
C11—C6—C5	121.20 (15)	C14—C13—H13A	110.4
C6—C5—C16	109.44 (13)	C12—C13—H13A	110.4
C6—C5—C12	114.81 (15)	C14—C13—H13B	110.4
C16—C5—C12	109.27 (14)	C12—C13—H13B	110.4
C6—C5—C15	112.84 (14)	H13A—C13—H13B	108.6
C16—C5—C15	107.86 (14)	C15—C14—C13	105.13 (18)
C12—C5—C15	102.24 (15)	C15—C14—H14A	110.7
C9—C8—C7	120.06 (17)	C13—C14—H14A	110.7
C9—C8—H8	120.0	C15—C14—H14B	110.7
C7—C8—H8	120.0	C13—C14—H14B	110.7
C5—C12—C13	105.58 (17)	H14A—C14—H14B	108.8
C5—C12—H12A	110.6	N2—C2—C3	123.13 (16)
C13—C12—H12A	110.6	N2—C2—H2	118.4
C5—C12—H12B	110.6	C3—C2—H2	118.4
C13—C12—H12B	110.6	C1—N3—H5	120.2 (16)
H12A—C12—H12B	108.8	C1—N3—H1	118.2 (16)
C6—C7—C8	121.24 (16)	H5—N3—H1	121 (2)
C6—C7—H7	119.4	C4—N1—C1	117.03 (15)
C8—C7—H7	119.4	C2—N2—C1	116.58 (15)
C9—C10—C11	120.36 (17)	C4—C3—C2	115.97 (16)
C9—C10—H10	119.8	C4—C3—H3	122.0
C11—C10—H10	119.8	C2—C3—H3	122.0
C10—C11—C6	120.76 (17)	N1—C4—C3	122.94 (16)
C10—C11—H11	119.6	N1—C4—H4	118.5
C6—C11—H11	119.6	C3—C4—H4	118.5
C14—C15—C5	103.19 (17)	N3—C1—N1	117.64 (16)
C14—C15—H15A	111.1	N3—C1—N2	118.00 (15)
C5—C15—H15A	111.1	N1—C1—N2	124.36 (16)
C14—C15—H15B	111.1		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H6···N1	0.87 (2)	1.79 (2)	2.653 (2)	173 (3)
N3—H5···O1	0.90 (3)	2.08 (3)	2.966 (2)	168 (2)
N3—H1···N2^{i}	0.88 (3)	2.13 (3)	3.006 (2)	173 (2)

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