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A 1:2 co-crystal of isonicotinamide and propionic acid

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
R factor = 0.088
wR factor = 0.198
Data-to-parameter ratio = 17.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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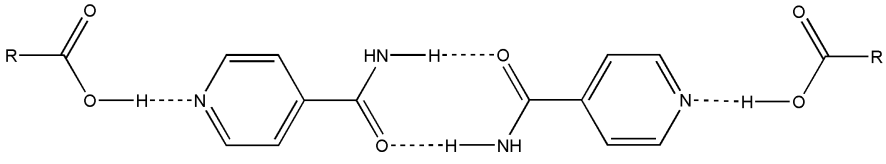
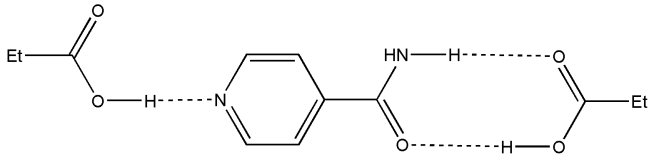
Isonicotinamide has been shown to form many 1:1 co-crystals with monofunctional carboxylic acids, but with propionic acid it forms a co-crystal containing two acid molecules and one isonicotinamide molecule per formula unit, $C_6H_6N_2O\cdot 2C_3H_6O_2$. The crystal structure consists of 'supermolecules' made up of of one isonicotinamide molecule and two acid molecules, and the asymmetric unit contains two of these supermolecules. One of the acid molecules is hydrogen bonded to the pyridine function, and the other to the amide function of the isonicotinamide. Further N—H···O hydrogen bonds connect these supermolecules into chains which run along the [100] direction. The chains are linked into layers perpendicular to (010) by C—H···O and π-stacking interactions. The layers are then linked together by further C—H···O interactions.

Comment

Isonicotinamide has been shown to crystallize with carboxylic acids in a 1:1 stoichiometry to form a robust building block or 'supermolecule' consisting of two amide and two acid molecules, (I) (Aakeröy *et al.*, 2002). When a saturated solution of isonicotinamide in warm propionic acid was allowed to cool, colourless crystalline laths were obtained. Single-crystal X-ray diffraction revealed these to be a co-crystal consisting of isonicotinamide and propionic acid in a 1:2 ratio, *viz*. (II).



(I)



(II)

Similar preparative routes with formic and acetic acids both yielded 1:1 co-crystals (Oswald, 2004). Attempts to prepare a 1:1 co-crystal with propionic acid failed. For example, a 1:1 mixture of propionic acid and isonicotinamide in ethanol yielded only crystals of (II); even in the presence of excess isonicotinamide, the only crystals obtained were isonicotinamide itself and (II).

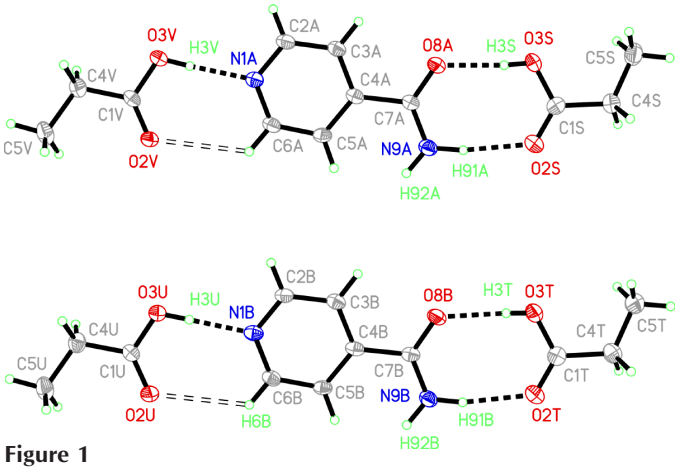


Figure 1
The two crystallographically independent supermolecules, with the atomic numbering. Displacement ellipsoids are drawn at the 30% probability level. Conventional hydrogen bonds are shown in heavy dashes and the H···O distances span 1.78 (4)–1.96 (4) Å (see Table 1). The C—H···O hydrogen bonds (shown as open dashes) are quite weak for this type of interaction (2.73 and 2.72 Å).

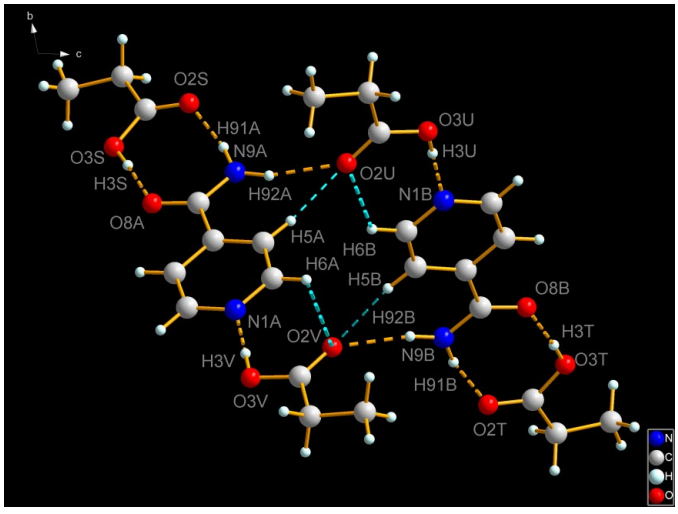


Figure 2
Hydrogen-bonded chains in the crystal structure of (II). Hydrogen bonds link supermolecules into chains. This view is approximately along the direct lattice direction [100]. Hydrogen bonds are shown as dashed lines, weak C—H···O hydrogen bonds are shown in turquoise.

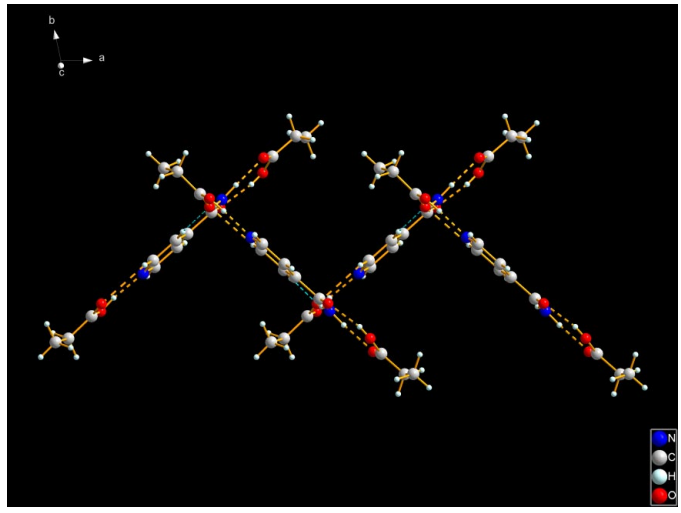


Figure 3
Hydrogen-bonded chains in the crystal structure of (II). Successive supermolecules are approximately perpendicular to each other; this view is perpendicular to (001).

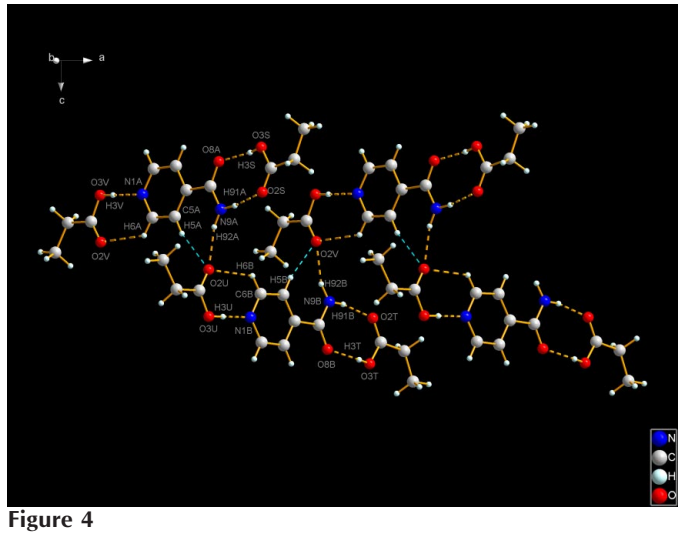


Figure 4
Hydrogen-bonded chains in the crystal structure of (II). View of the chain, showing the atom numbering; view approximately along [010].

The crystal structure of (II) consists of supermolecules comprising two acid and one isonicotinamide molecule. One acid forms an $R_2^2(8)$ motif with the amide moiety (Bernstein *et al.*, 1995). Another acid molecule forms a hydrogen bond to the pyridine N atom, supported by a weaker C—H···O hydrogen bond (Fig. 1 and Table 1). There are two supermolecules in the asymmetric unit and, in the terminology of Aakeröy *et al.* (2002), both are in the *trans–trans* conformation.

The independent supermolecules hydrogen-bond together using the second amide donor and the carbonyl group from the propionic acid molecules located at the pyridine end of the supermolecules. This builds up a helical chain in which successive supermolecules are aligned approximately perpendicular to one another (Figs. 2–4; hydrogen-bond dimensions are listed in Table 1). The chains run along the **a** direction, and they comprise all the conventional N—H···O and O—H···O hydrogen bonds in the crystal structure (see Table 1); additional C—H···O interactions (C5*A*—H5*A*···O2*U* and C5*B*—H5*B*···O2*V*) are also formed within the chains (Desiraju & Steiner, 1999).

Successive helical chains are distributed along the *c* direction at $z = \frac{1}{4}, \frac{3}{4}, \ldots$, *etc.* (Fig. 5). Though there are no direct hydrogen-bonding interactions between neighbouring chains, weak C—H···O interactions are formed between chains located one lattice-repeat away from each other (*e.g.* the red and blue chains in Fig. 5; see also Fig. 6). These interactions involve C2*A*—H2*A*···O3*T* and C2*B*—H2*B*···O3*S*. Supermolecules in neighbouring chains are interleaved to produce stacks of supermolecules along **a** (Fig. 5). Stacks containing only the supermolecules based on isonicotinamide molecule *A* occur at $z = \frac{1}{2}$, while stacks containing only those

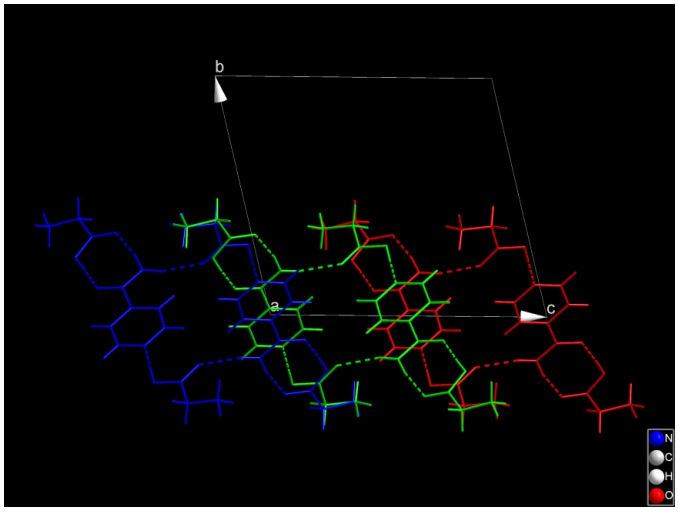


Figure 5
Packing of hydrogen-bonded chains in the crystal structure of (II), forming a layer perpendicular to **b***. Neighbouring chains are distributed along the *c* axis. Different chains (as shown in Figs. 2–4) are shown in different colours. This view is along **a**, *cf.* Fig. 2.

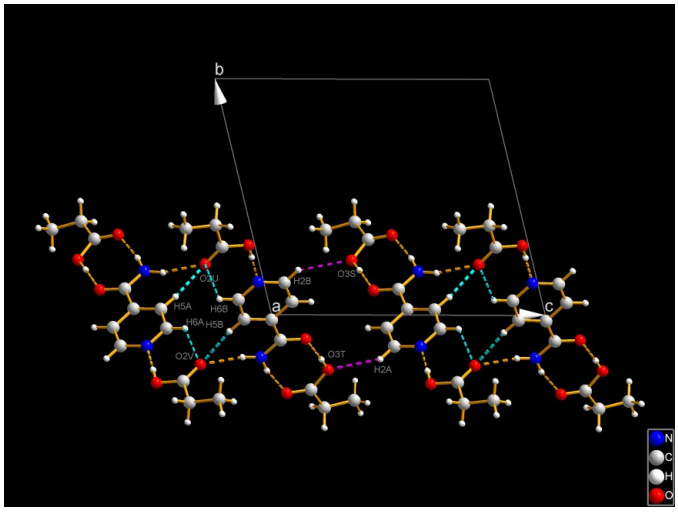


Figure 6
Packing of hydrogen-bonded chains in the crystal structure of (II), forming a layer perpendicular to **b***. As Fig. 5, but with the green molecule deleted to reveal C—H···O hydrogen bonds formed between the blue and red chains shown in Fig. 5. C—H···O hydrogen bonds within chains are shown in turquoise, those between chains are shown in magenta.

based on molecule *B* occur at z = 0, 1, ... *etc*. Within the stacks, pairs of pyridine moieties are π-stacked across inversion centres (Fig. 7). The stacking distances are 3.34 and 3.33 Å for the *A* and *B* pyridine rings, respectively.

Thus, layers are formed in the *ac*-plane by chains of hydrogen-bonded supermolecules linked by weak C—H···O and π-stacking interactions. The layers are connected *via* C—H···O hydrogen bonds involving pairs of C4*T*—H4*T*1···O2*T* and C4*V*—H4*V*1···O2*S* interactions disposed about inversion centres (Fig. 8).

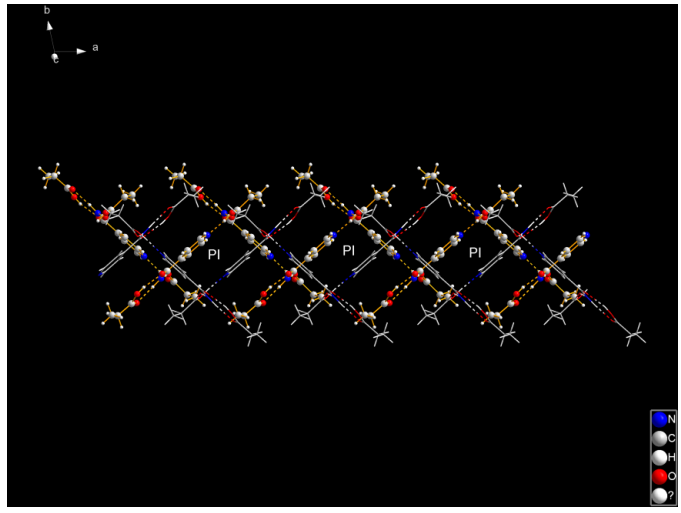


Figure 7
Packing of hydrogen-bonded chains in the crystal structure of (II), forming a layer perpendicular to [010]. Neighbouring chains are connected by π-stacking interactions. This figure shows two chains viewed along [001]. One chain is shown in ball-and-stick representation, the other as wireframe.

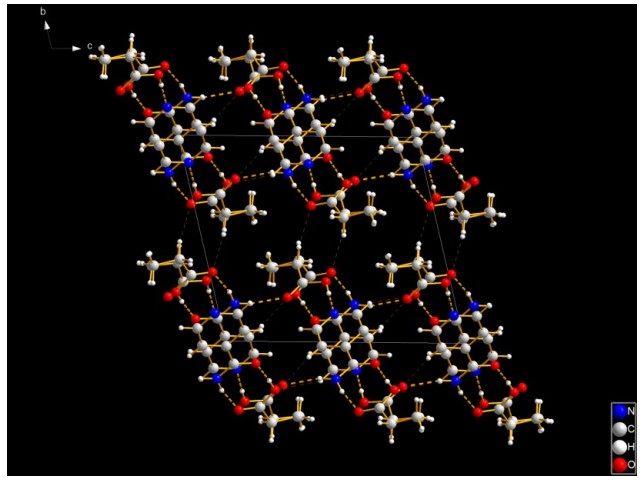


Figure 8
Full packing diagram of the crystal structure of (II), viewed along [100]. Different layers (as shown in Figs. 5–7) are shown in the top and bottom halves of the figure. C—H···O hydrogen bonds connect the layers.

Experimental

All materials were obtained from Aldrich and used as received. Isonicotinamide (0.50 g, 4.10 mmol) was dissolved in an excess of propionic acid (2.40 g, 32.43 mmol) and warmed until all the solid dissolved. The solution was cooled to room temperature, producing colourless laths.

Crystal data

$C_6H_6N_2O\cdot 2C_3H_6O_2$
M_r = 270.28
Triclinic, $P\overline{1}$
a = 10.038 (3) Å
b = 11.559 (4) Å
c = 12.740 (4) Å
α = 103.203 (6)°
β = 90.140 (6)°
γ = 102.247 (6)°
V = 1404.5 (8) Å^3
Z = 4
D_x = 1.278 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1107 reflections
θ = 2.6–22.2°
μ = 0.10 mm^{-1}
T = 150 (2) K
Lath, colourless
0.75 × 0.20 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)	12519 measured reflections 6498 independent reflections 3362 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.044$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2004)	$\theta_{max} = 28.9^\circ$ $h = -13 \rightarrow 13$
$T_{min} = 0.783$, $T_{max} = 1.000$	$k = -15 \rightarrow 15$ $l = -17 \rightarrow 17$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.3798P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.088$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.198$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.21$ e Å^{-3}
6498 reflections	
379 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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

D—H···A	D—H	H···A	D···A	D—H···A
O3*S*—H3*S*···O8*A*	0.79 (4)	1.86 (4)	2.639 (4)	170 (4)
O3*T*—H3*T*···O8*B*	0.76 (5)	1.89 (5)	2.639 (4)	169 (5)
O3*U*—H3*U*···N1*B*^{i}	0.87 (4)	1.78 (4)	2.649 (4)	177 (5)
O3*V*—H3*V*···N1*A*^{ii}	0.87 (5)	1.79 (5)	2.657 (4)	174 (5)
N9*A*—H91*A*···O2*S*	0.96 (5)	1.92 (4)	2.868 (4)	170 (5)
N9*B*—H91*B*···O2*T*	0.93 (4)	1.96 (4)	2.880 (4)	168 (3)
N9*A*—H92*A*···O2*U*^{iii}	0.92 (3)	2.02 (3)	2.901 (4)	161 (3)
N9*B*—H92*B*···O2*V*	0.93 (3)	2.01 (3)	2.900 (4)	160 (3)
C2*A*—H2*A*···O3*T*^{iv}	0.95	2.50	3.267 (5)	138
C2*B*—H2*B*···O3*S*^{v}	0.95	2.51	3.281 (5)	138
C5*A*—H5*A*···O2*U*^{iii}	0.95	2.40	3.328 (4)	167
C5*B*—H5*B*···O2*V*	0.95	2.39	3.322 (4)	168
C6*A*—H6*A*···O2*V*^{vi}	0.95	2.73	3.348 (4)	123
C6*B*—H6*B*···O2*U*^{i}	0.95	2.72	3.333 (4)	123
C4*T*—H4*T*1···O2*T*^{vii}	0.99	2.58	3.513 (5)	157
C4*V*—H4*V*1···O2*S*^{viii}	0.99	2.57	3.551 (4)	170

Symmetry codes: (i) $1-x, 2-y, -z$; (ii) $1+x, 1+y, z-1$; (iii) $1-x, 1-y, 1-z$; (iv) $x-1, y-1, z$; (v) $x, 1+y, z$; (vi) $x-1, y-1, 1+z$; (vii) $2-x, 1-y, -z$; (viii) $x, y, z-1$.

H atoms were placed on C atoms in calculated positions [U_{iso}(H) = 1.2U_{eq}(C)] and allowed to ride on their parent atoms [C(phenyl)—H = 0.95, C(methylene)—H = 0.99 and C(methyl)—H = 0.98 Å]. Amide and hydroxyl H atoms were located in difference maps and refined freely, the former subject to the restraint N—H = 0.95 (3) Å. The ranges of N—H and O—H bond lengths were 0.91 (2)–0.96 (1) and 0.75 (5)–0.87 (4) Å, respectively.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* ; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL, MERCURY* (Taylor & Macrae, 2001) and *DIAMOND* (Crystal Impact, 2004); software used to prepare material for publication: *SHELXTL*, *EnCIFer* (Allen *et al.*, 2004) and *PLATON* (Spek, 2003), as incorporated in *WinGX* (Farrugia, 1999)..

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supporting information

Acta Cryst. (2004). E**60**, o2380–o2383 [https://doi.org/10.1107/S1600536804028776]

A 1:2 co-crystal of isonicotinamide and propionic acid

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Isonicotinamide–propionic acid (1:2)

Crystal data

$C_6H_6N_2O{\cdot}2C_3H_6O_2$
$M_r = 270.28$
Triclinic, $P\overline{1}$
Hall symbol: -P1
$a = 10.038$ (3) Å
$b = 11.559$ (4) Å
$c = 12.740$ (4) Å
$\alpha = 103.203$ (6)°
$\beta = 90.140$ (6)°
$\gamma = 102.247$ (6)°
$V = 1404.5$ (8) Å^3
$Z = 4$
$F(000) = 576$
$D_x = 1.278$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1107 reflections
$\theta = 2.6$–22.2°
$\mu = 0.10$ mm^{-1}
$T = 150$ K
Lath, colourless
0.75 × 0.20 × 0.08 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2004)
$T_{min} = 0.783$, $T_{max} = 1.000$
12519 measured reflections
6498 independent reflections
3362 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 28.9°$, $\theta_{min} = 1.6°$
$h = -13 \rightarrow 13$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.088$
$wR(F^2) = 0.198$
$S = 1.04$
6498 reflections
379 parameters
4 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
$w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + 0.3798P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ 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. ABSTM02_ALERT_3_C The ratio of expected to reported Tmax/Tmin(*RR*′) is < 0.90
PLAT061_ALERT_3_C Tmax/Tmin Range Test *RR*′ too Large ·····. 0.84 T min and Tmax reported: 0.783 1.000 Tmin′ and Tmax expected: 0.927 0.992 Noted, but no action taken. *SADABS* attempts to correct for all systematic errors not just absorption. The large range could represent a small amount of crystal decay for example.
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low ·····. 0.98
==========

Resolution & Completeness Statistics (Cumulative)
==========

Theta sin(th)/Lambda Complete Expected Measured Missing ———————————————————————————————— —- —- 20.82 0.500 0.998 2939 2932 7 23.01 0.550 0.990 3900 3861 39 25.24 0.600 0.979 5085 4978 107 ———————————————————————————————— ACTA Min. Res. —- 27.51 0.650 0.961 6447 6198 249 29.84 0.700 0.875 7427 6498 929
PLAT063_ALERT_3_C Crystal Probably too Large for Beam Size ·····. 0.75 mm
Gorbitz has shown that use of a large crystal does not appear to matter. See C. H. Gorbitz Acta Cryst. (1999). B55, 1090–1098
PLAT414_ALERT_2_C Short Intra D—H.·H—*X* H5A.. H92A.. 1.98 A ng PLAT414_ALERT_2_C Short Intra D—H.·H—*X* H5B.. H92B.. 1.96 A ng PLAT480_ALERT_4_C Long H···A H-Bond Reported H6A.. O2V.. 2.73 A ng
PLAT480_ALERT_4_C Long H···A H-Bond Reported H6B.. O2U.. 2.72 A ng
See text.
PLAT222_ALERT_3_C Large Non-Solvent H U_{eq}(max)/U_{eq}(min) ··· 3.02 Ratio PLAT340_ALERT_3_C Low Bond Precision on C—C bonds (*x* 1000) Ang ··· 5 PLAT720_ALERT_4_C Number of Unusual/Non-Standard Label(*s*) ·····.. 20
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 4 C3 H6 O2
PLAT790_ALERT_4_C Centre of Gravity not Within Unit Cell: Resd. # 6 C3 H6 O2
No action taken.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1A	0.0374 (3)	−0.1364 (2)	0.5184 (2)	0.0340 (6)
C2A	0.0899 (3)	−0.1354 (3)	0.4224 (3)	0.0399 (9)
H2A	0.0424	−0.1899	0.3598	0.048*
C3A	0.2125 (3)	−0.0566 (3)	0.4114 (3)	0.0367 (8)
H3A	0.2482	−0.0576	0.3423	0.044*
C4A	0.2807 (3)	0.0225 (3)	0.5023 (2)	0.0307 (7)
C5A	0.2266 (3)	0.0211 (3)	0.6018 (3)	0.0358 (8)
H5A	0.2724	0.0739	0.6659	0.043*
C6A	0.1023 (3)	−0.0605 (3)	0.6056 (3)	0.0372 (8)
H6A	0.0635	−0.0610	0.6734	0.045*
C7A	0.4134 (3)	0.1076 (3)	0.4875 (3)	0.0300 (7)
O8A	0.4515 (2)	0.1028 (2)	0.39475 (18)	0.0422 (6)
N9A	0.4801 (3)	0.1821 (3)	0.5743 (2)	0.0400 (7)
H91A	0.559 (4)	0.239 (4)	0.561 (4)	0.13 (2)*
H92A	0.448 (4)	0.177 (4)	0.641 (2)	0.075 (14)*
N1B	0.6050 (2)	1.1345 (2)	−0.0179 (2)	0.0347 (7)
C2B	0.6559 (3)	1.1321 (3)	0.0769 (3)	0.0363 (8)

H2B	0.6352	1.1865	0.1396	0.044*
C3B	0.7394 (3)	1.0525 (3)	0.0886 (3)	0.0372 (8)
H3B	0.7738	1.0521	0.1580	0.045*
C4B	0.7705 (3)	0.9749 (3)	−0.0022 (2)	0.0318 (8)
C5B	0.7187 (3)	0.9781 (3)	−0.1016 (3)	0.0343 (8)
H5B	0.7395	0.9262	−0.1658	0.041*
C6B	0.6340 (3)	1.0601 (3)	−0.1058 (3)	0.0358 (8)
H6B	0.5967	1.0620	−0.1738	0.043*
C7B	0.8617 (3)	0.8898 (3)	0.0125 (3)	0.0315 (8)
O8B	0.9029 (2)	0.8942 (2)	0.10510 (18)	0.0435 (6)
N9B	0.8926 (3)	0.8168 (3)	−0.0743 (2)	0.0402 (7)
H91B	0.943 (4)	0.761 (3)	−0.064 (3)	0.079 (14)*
H92B	0.855 (3)	0.817 (3)	−0.141 (2)	0.059 (11)*
C1S	0.7475 (3)	0.3193 (3)	0.4192 (3)	0.0380 (8)
O2S	0.7115 (3)	0.3378 (2)	0.5096 (2)	0.0546 (7)
O3S	0.6802 (3)	0.2306 (2)	0.34051 (19)	0.0442 (7)
H3S	0.618 (4)	0.189 (3)	0.361 (3)	0.052 (13)*
C4S	0.8744 (4)	0.3943 (3)	0.3861 (3)	0.0473 (9)
H4S1	0.8645	0.4799	0.4013	0.057*
H4S2	0.9519	0.3916	0.4329	0.057*
C5S	0.9112 (4)	0.3599 (4)	0.2720 (3)	0.0597 (11)
H5S1	0.9249	0.2763	0.2558	0.090*
H5S2	0.9955	0.4155	0.2611	0.090*
H5S3	0.8374	0.3652	0.2241	0.090*
C1T	1.0981 (3)	0.6806 (3)	0.0803 (3)	0.0374 (8)
O2T	1.0571 (2)	0.6652 (2)	−0.0116 (2)	0.0521 (7)
O3T	1.0671 (3)	0.7648 (3)	0.1601 (2)	0.0468 (7)
H3T	1.029 (5)	0.809 (4)	0.145 (4)	0.10 (2)*
C4T	1.1877 (4)	0.6048 (3)	0.1135 (3)	0.0468 (9)
H4T1	1.1369	0.5189	0.0955	0.056*
H4T2	1.2686	0.6099	0.0691	0.056*
C5T	1.2363 (4)	0.6365 (4)	0.2284 (3)	0.0621 (12)
H5T1	1.2872	0.7214	0.2480	0.093*
H5T2	1.2960	0.5829	0.2395	0.093*
H5T3	1.1579	0.6263	0.2736	0.093*
C1U	0.5951 (3)	0.7137 (3)	0.1200 (3)	0.0331 (8)
O2U	0.5695 (2)	0.7875 (2)	0.19782 (18)	0.0417 (6)
O3U	0.5494 (3)	0.7069 (2)	0.02220 (19)	0.0440 (6)
H3U	0.496 (4)	0.757 (4)	0.021 (3)	0.086 (16)*
C4U	0.6782 (3)	0.6226 (3)	0.1251 (3)	0.0442 (9)
H4U1	0.7507	0.6291	0.0730	0.053*
H4U2	0.6191	0.5400	0.1026	0.053*
C5U	0.7439 (4)	0.6374 (4)	0.2361 (3)	0.0574 (11)
H5U1	0.8006	0.7198	0.2602	0.086*
H5U2	0.8010	0.5777	0.2326	0.086*
H5U3	0.6727	0.6243	0.2873	0.086*
C1V	0.7618 (3)	0.7141 (3)	−0.3789 (3)	0.0319 (8)
O2V	0.8246 (2)	0.7852 (2)	−0.30190 (18)	0.0417 (6)

O3V	0.8021 (3)	0.7075 (2)	−0.47843 (18)	0.0410 (6)
H3V	0.876 (5)	0.763 (4)	−0.479 (4)	0.11 (2)*
C4V	0.6318 (3)	0.6233 (3)	−0.3745 (3)	0.0419 (9)
H4V1	0.6485	0.5401	−0.3985	0.050*
H4V2	0.5621	0.6322	−0.4254	0.050*
C5V	0.5763 (4)	0.6378 (4)	−0.2626 (3)	0.0572 (11)
H5V1	0.6443	0.6283	−0.2118	0.086*
H5V2	0.4925	0.5756	−0.2645	0.086*
H5V3	0.5561	0.7189	−0.2393	0.086*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1A	0.0336 (15)	0.0404 (17)	0.0301 (16)	0.0147 (13)	0.0006 (12)	0.0068 (13)
C2A	0.044 (2)	0.048 (2)	0.0270 (19)	0.0148 (18)	0.0026 (15)	0.0027 (16)
C3A	0.039 (2)	0.043 (2)	0.0292 (19)	0.0145 (16)	0.0062 (15)	0.0059 (16)
C4A	0.0311 (18)	0.0397 (19)	0.0268 (18)	0.0192 (15)	0.0031 (14)	0.0082 (15)
C5A	0.040 (2)	0.041 (2)	0.0266 (18)	0.0118 (16)	−0.0037 (14)	0.0062 (15)
C6A	0.038 (2)	0.051 (2)	0.0258 (18)	0.0168 (17)	0.0034 (15)	0.0081 (16)
C7A	0.0331 (18)	0.0347 (19)	0.0273 (18)	0.0168 (15)	0.0033 (14)	0.0086 (15)
O8A	0.0419 (14)	0.0506 (15)	0.0308 (14)	0.0072 (11)	0.0074 (11)	0.0053 (11)
N9A	0.0385 (18)	0.053 (2)	0.0293 (17)	0.0112 (15)	0.0020 (14)	0.0098 (15)
N1B	0.0327 (15)	0.0389 (17)	0.0283 (16)	−0.0003 (12)	0.0036 (12)	0.0066 (13)
C2B	0.0356 (19)	0.042 (2)	0.0260 (18)	0.0049 (16)	0.0013 (14)	0.0008 (15)
C3B	0.0333 (19)	0.045 (2)	0.0300 (19)	0.0028 (16)	−0.0016 (14)	0.0074 (16)
C4B	0.0247 (17)	0.0384 (19)	0.0256 (18)	−0.0044 (14)	0.0012 (13)	0.0041 (15)
C5B	0.0316 (18)	0.041 (2)	0.0261 (18)	0.0027 (15)	0.0051 (14)	0.0039 (15)
C6B	0.0305 (18)	0.047 (2)	0.0277 (19)	0.0027 (16)	0.0031 (14)	0.0097 (16)
C7B	0.0240 (17)	0.040 (2)	0.0267 (18)	0.0002 (14)	0.0046 (14)	0.0058 (15)
O8B	0.0443 (14)	0.0561 (16)	0.0298 (14)	0.0148 (12)	−0.0054 (11)	0.0060 (12)
N9B	0.0369 (17)	0.057 (2)	0.0296 (17)	0.0164 (15)	0.0024 (13)	0.0105 (15)
C1S	0.037 (2)	0.036 (2)	0.041 (2)	0.0110 (16)	−0.0024 (17)	0.0075 (17)
O2S	0.0603 (17)	0.0601 (18)	0.0367 (16)	0.0011 (13)	0.0122 (13)	0.0086 (13)
O3S	0.0406 (15)	0.0520 (17)	0.0380 (16)	0.0037 (13)	0.0121 (12)	0.0123 (14)
C4S	0.048 (2)	0.046 (2)	0.048 (2)	0.0055 (18)	0.0052 (18)	0.0144 (19)
C5S	0.051 (2)	0.051 (3)	0.068 (3)	−0.001 (2)	0.015 (2)	0.007 (2)
C1T	0.0295 (18)	0.038 (2)	0.044 (2)	0.0010 (15)	0.0086 (16)	0.0140 (18)
O2T	0.0605 (17)	0.0616 (17)	0.0381 (16)	0.0204 (13)	−0.0049 (13)	0.0128 (13)
O3T	0.0473 (16)	0.0573 (18)	0.0402 (16)	0.0202 (14)	−0.0039 (12)	0.0122 (14)
C4T	0.041 (2)	0.053 (2)	0.048 (2)	0.0085 (18)	−0.0012 (17)	0.0167 (19)
C5T	0.071 (3)	0.062 (3)	0.055 (3)	0.027 (2)	−0.011 (2)	0.005 (2)
C1U	0.0280 (17)	0.038 (2)	0.032 (2)	0.0005 (15)	0.0009 (14)	0.0135 (16)
O2U	0.0442 (14)	0.0499 (15)	0.0316 (14)	0.0156 (12)	0.0041 (11)	0.0058 (12)
O3U	0.0492 (15)	0.0549 (17)	0.0311 (14)	0.0223 (14)	0.0019 (11)	0.0066 (12)
C4U	0.043 (2)	0.044 (2)	0.050 (2)	0.0134 (17)	0.0062 (17)	0.0182 (18)
C5U	0.055 (3)	0.055 (3)	0.069 (3)	0.018 (2)	−0.008 (2)	0.023 (2)
C1V	0.0361 (19)	0.038 (2)	0.0297 (19)	0.0199 (16)	0.0084 (15)	0.0135 (16)
O2V	0.0384 (13)	0.0551 (16)	0.0276 (14)	0.0075 (12)	0.0012 (11)	0.0042 (12)

O3V	0.0427 (15)	0.0500 (16)	0.0279 (13)	0.0070 (13)	0.0062 (11)	0.0070 (11)
C4V	0.041 (2)	0.039 (2)	0.048 (2)	0.0101 (17)	0.0103 (16)	0.0142 (17)
C5V	0.051 (2)	0.059 (3)	0.064 (3)	0.010 (2)	0.023 (2)	0.022 (2)

Geometric parameters (Å, º)

N1A—C6A	1.318 (4)	C4S—H4S1	0.9900
N1A—C2A	1.333 (4)	C4S—H4S2	0.9900
C2A—C3A	1.396 (5)	C5S—H5S1	0.9800
C2A—H2A	0.9500	C5S—H5S2	0.9800
C3A—C4A	1.375 (4)	C5S—H5S3	0.9800
C3A—H3A	0.9500	C1T—O2T	1.201 (4)
C4A—C5A	1.383 (4)	C1T—O3T	1.325 (4)
C4A—C7A	1.519 (4)	C1T—C4T	1.502 (5)
C5A—C6A	1.404 (4)	O3T—H3T	0.75 (5)
C5A—H5A	0.9500	C4T—C5T	1.479 (5)
C6A—H6A	0.9500	C4T—H4T1	0.9900
C7A—O8A	1.235 (4)	C4T—H4T2	0.9900
C7A—N9A	1.315 (4)	C5T—H5T1	0.9800
N9A—H91A	0.96 (3)	C5T—H5T2	0.9800
N9A—H92A	0.91 (2)	C5T—H5T3	0.9800
N1B—C2B	1.318 (4)	C1U—O2U	1.218 (4)
N1B—C6B	1.321 (4)	C1U—O3U	1.307 (4)
C2B—C3B	1.401 (4)	C1U—C4U	1.488 (5)
C2B—H2B	0.9500	O3U—H3U	0.87 (4)
C3B—C4B	1.375 (4)	C4U—C5U	1.517 (5)
C3B—H3B	0.9500	C4U—H4U1	0.9900
C4B—C5B	1.378 (4)	C4U—H4U2	0.9900
C4B—C7B	1.518 (4)	C5U—H5U1	0.9800
C5B—C6B	1.411 (4)	C5U—H5U2	0.9800
C5B—H5B	0.9500	C5U—H5U3	0.9800
C6B—H6B	0.9500	C1V—O2V	1.201 (4)
C7B—O8B	1.236 (4)	C1V—O3V	1.323 (4)
C7B—N9B	1.310 (4)	C1V—C4V	1.502 (4)
N9B—H91B	0.93 (2)	O3V—H3V	0.87 (5)
N9B—H92B	0.93 (2)	C4V—C5V	1.518 (5)
C1S—O2S	1.194 (4)	C4V—H4V1	0.9900
C1S—O3S	1.321 (4)	C4V—H4V2	0.9900
C1S—C4S	1.501 (5)	C5V—H5V1	0.9800
O3S—H3S	0.79 (4)	C5V—H5V2	0.9800
C4S—C5S	1.485 (5)	C5V—H5V3	0.9800
C6A—N1A—C2A	119.4 (3)	C4S—C5S—H5S1	109.5
N1A—C2A—C3A	121.9 (3)	C4S—C5S—H5S2	109.5
N1A—C2A—H2A	119.1	H5S1—C5S—H5S2	109.5
C3A—C2A—H2A	119.1	C4S—C5S—H5S3	109.5
C4A—C3A—C2A	118.9 (3)	H5S1—C5S—H5S3	109.5
C4A—C3A—H3A	120.5	H5S2—C5S—H5S3	109.5

C2A—C3A—H3A	120.5	O2T—C1T—O3T	122.7 (3)
C3A—C4A—C5A	119.2 (3)	O2T—C1T—C4T	122.4 (3)
C3A—C4A—C7A	117.6 (3)	O3T—C1T—C4T	114.9 (3)
C5A—C4A—C7A	123.2 (3)	C1T—O3T—H3T	117 (4)
C4A—C5A—C6A	118.2 (3)	C5T—C4T—C1T	117.1 (3)
C4A—C5A—H5A	120.9	C5T—C4T—H4T1	108.0
C6A—C5A—H5A	120.9	C1T—C4T—H4T1	108.0
N1A—C6A—C5A	122.4 (3)	C5T—C4T—H4T2	108.0
N1A—C6A—H6A	118.8	C1T—C4T—H4T2	108.0
C5A—C6A—H6A	118.8	H4T1—C4T—H4T2	107.3
O8A—C7A—N9A	124.2 (3)	C4T—C5T—H5T1	109.5
O8A—C7A—C4A	118.0 (3)	C4T—C5T—H5T2	109.5
N9A—C7A—C4A	117.8 (3)	H5T1—C5T—H5T2	109.5
C7A—N9A—H91A	115 (3)	C4T—C5T—H5T3	109.5
C7A—N9A—H92A	119 (3)	H5T1—C5T—H5T3	109.5
H91A—N9A—H92A	126 (4)	H5T2—C5T—H5T3	109.5
C2B—N1B—C6B	119.4 (3)	O2U—C1U—O3U	122.0 (3)
N1B—C2B—C3B	122.4 (3)	O2U—C1U—C4U	124.7 (3)
N1B—C2B—H2B	118.8	O3U—C1U—C4U	113.2 (3)
C3B—C2B—H2B	118.8	C1U—O3U—H3U	112 (3)
C4B—C3B—C2B	118.7 (3)	C1U—C4U—C5U	113.9 (3)
C4B—C3B—H3B	120.6	C1U—C4U—H4U1	108.8
C2B—C3B—H3B	120.6	C5U—C4U—H4U1	108.8
C3B—C4B—C5B	118.9 (3)	C1U—C4U—H4U2	108.8
C3B—C4B—C7B	117.8 (3)	C5U—C4U—H4U2	108.8
C5B—C4B—C7B	123.3 (3)	H4U1—C4U—H4U2	107.7
C4B—C5B—C6B	118.6 (3)	C4U—C5U—H5U1	109.5
C4B—C5B—H5B	120.7	C4U—C5U—H5U2	109.5
C6B—C5B—H5B	120.7	H5U1—C5U—H5U2	109.5
N1B—C6B—C5B	121.9 (3)	C4U—C5U—H5U3	109.5
N1B—C6B—H6B	119.0	H5U1—C5U—H5U3	109.5
C5B—C6B—H6B	119.0	H5U2—C5U—H5U3	109.5
O8B—C7B—N9B	124.1 (3)	O2V—C1V—O3V	122.6 (3)
O8B—C7B—C4B	118.2 (3)	O2V—C1V—C4V	125.0 (3)
N9B—C7B—C4B	117.7 (3)	O3V—C1V—C4V	112.5 (3)
C7B—N9B—H91B	117 (3)	C1V—O3V—H3V	110 (3)
C7B—N9B—H92B	119 (2)	C1V—C4V—C5V	113.2 (3)
H91B—N9B—H92B	123 (3)	C1V—C4V—H4V1	108.9
O2S—C1S—O3S	122.9 (3)	C5V—C4V—H4V1	108.9
O2S—C1S—C4S	122.5 (3)	C1V—C4V—H4V2	108.9
O3S—C1S—C4S	114.5 (3)	C5V—C4V—H4V2	108.9
C1S—O3S—H3S	112 (3)	H4V1—C4V—H4V2	107.7
C5S—C4S—C1S	117.6 (3)	C4V—C5V—H5V1	109.5
C5S—C4S—H4S1	107.9	C4V—C5V—H5V2	109.5
C1S—C4S—H4S1	107.9	H5V1—C5V—H5V2	109.5
C5S—C4S—H4S2	107.9	C4V—C5V—H5V3	109.5
C1S—C4S—H4S2	107.9	H5V1—C5V—H5V3	109.5
H4S1—C4S—H4S2	107.2	H5V2—C5V—H5V3	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*S*—H3*S*···O8*A*	0.79 (4)	1.86 (4)	2.639 (4)	170 (4)
O3*T*—H3*T*···O8*B*	0.76 (5)	1.89 (5)	2.639 (4)	169 (5)
O3*U*—H3*U*···N1*B*^{i}	0.87 (4)	1.78 (4)	2.649 (4)	177 (5)
O3*V*—H3*V*···N1*A*^{ii}	0.87 (5)	1.79 (5)	2.657 (4)	174 (5)
N9*A*—H91*A*···O2*S*	0.96 (5)	1.92 (4)	2.868 (4)	170 (5)
N9*B*—H91*B*···O2*T*	0.93 (4)	1.96 (4)	2.880 (4)	168 (3)
N9*A*—H92*A*···O2*U*^{iii}	0.92 (3)	2.02 (3)	2.901 (4)	161 (3)
N9*B*—H92*B*···O2*V*	0.93 (3)	2.01 (3)	2.900 (4)	160 (3)
C2*A*—H2*A*···O3*T*^{iv}	0.95	2.50	3.267 (5)	138
C2*B*—H2*B*···O3*S*^{v}	0.95	2.51	3.281 (5)	138
C5*A*—H5*A*···O2*U*^{iii}	0.95	2.40	3.328 (4)	167
C5*B*—H5*B*···O2*V*	0.95	2.39	3.322 (4)	168
C6*A*—H6*A*···O2*V*^{vi}	0.95	2.73	3.348 (4)	123
C6*B*—H6*B*···O2*U*^{i}	0.95	2.72	3.333 (4)	123
C4*T*—H4*T*1···O2*T*^{vii}	0.99	2.58	3.513 (5)	157
C4*V*—H4*V*1···O2*S*^{viii}	0.99	2.57	3.551 (4)	170

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*; (ii) *x*+1, *y*+1, *z*−1; (iii) −*x*+1, −*y*+1, −*z*+1; (iv) *x*−1, *y*−1, *z*; (v) *x*, *y*+1, *z*; (vi) *x*−1, *y*−1, *z*+1; (vii) −*x*+2, −*y*+1, −*z*; (viii) *x*, *y*, *z*−1.