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The synthesis and characterization of a series of cocrystals of an isoniazid derivative with butan-2-one and propan-2-one

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Four cocrystals containing *N*′-(butan-2-ylidene)pyridine-4-carbohydrazide (**izbt**) and one cocrystal containing *N*′-isopropylideneisonicotinohydrazide (**izact**) were synthesized by reacting isoniazid with either butan-2-one (for the former) or acetone (for the latter). The coformers used to synthesize the **izbt** cocrystals were 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2-chloro-4-nitrobenzoic acid and 1-naphthoic acid. 1-Naphthoic acid was also used with **izact** to form a cocrystal. The 1:1 cocrystals are: *N*′-(butan-2-ylidene)pyridine-4-carbohydrazide–1-naphthoic acid (**izbt–1nta**), $C_{10}H_{13}N_3O{\cdot}C_{11}H_8O_2$, *N*′-(butan-2-ylidene)pyridine-4-carbohydrazide–2,4-dihydroxybenzoic acid (**izbt–2,4-dhba**), $C_{10}H_{13}N_3O{\cdot}C_7H_6O_4$, *N*′-(propan-2-ylidene)pyridine-4-carbohydrazide–1-naphthoic acid (**izact–1nta**), $C_9H_{11}N_3O{\cdot}C_{11}H_8O_2$, *N*′-(butan-2-ylidene)pyridine-4-carbohydrazide–2-chloro-4-nitrobenzoic acid (**izbt–2c4n**), $C_{10}H_{13}N_3O{\cdot}C_7H_4ClNO_4$, and *N*′-(butan-2-ylidene)pyridine-4-carbohydrazide–2,5-dihydroxybenzoic acid (**izbt–2,5-dhba**), $C_{10}H_{13}N_3O{\cdot}C_7H_6O_4$. The cocrystals containing **izbt** were compared to those containing the same (or similar) coformers with **izact** that have been reported either here or in the Cambridge Structural Database (CSD). Most of the cocrystals showed different packing despite having the same hydrogen-bonding motifs. The cocrystals were characterized by single-crystal X-ray diffraction (SC-XRD), powder X-ray diffraction (PXRD) and differential scanning calorimetry (DSC).

1. Introduction

In the pharmaceutical industry, it is often typical for new and existing drugs to have poor physicochemical properties. The poor performance from these drugs can hamper their success on the market. The modification of an existing drug can yield a new product with possibly improved properties compared to the original drug molecule. Although this would require new clinical trials, it could prove to be advantageous for long-term success. From a crystal engineering perspective, this could prove to be an opportunity to explore new solid-state structural landscapes.

One approach of crystal engineering with repsect to changing the solid-state form of active pharmaceutical ingredients (APIs) is to use cocrystals. Although no universal definition of a cocrystal exists, several different definitions have been proposed by different authors. The definition proposed by Aitipamula *et al.* (2012) is as follows: 'cocrystals are solids that are crystalline single phase materials composed of two or more different molecular and/or ionic compounds generally in a stoichiometric ratio.' Grothe defines a cocrystal as 'a crystal with a coformer molecule plus either another coformer or at least two ions,' with further classifications depending on whether the crystal also contains ions, solvate molecules or

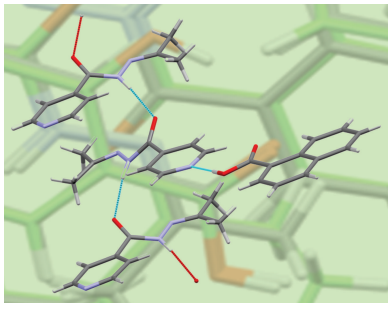


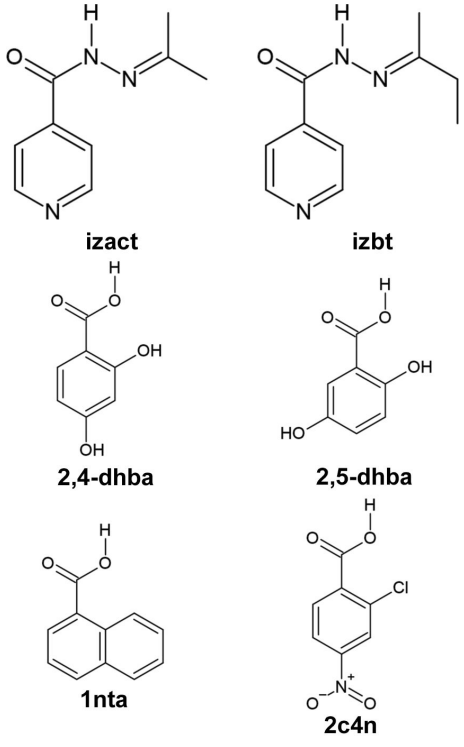
Table 1
Cocrystals of **izact** and **izbt** that share the same coformer.

The Crystal Structure Similarity tool of *Mercury* (Macrae *et al.*, 2020) was used to help determine if related structures were isostructural.

Coformer	**izact** refcode	**izbt** refcode	Isostructural
4-*tert*-Butylbenzoic acid	GIYMAF	GIYMEJ	Yes
2-Hydroxybenzoic acid (salicylic acid)*	LATLAV	UBILAW	No
3-Hydroxybenzoic acid (anhydrous)	FADHUP	FADHOJ	No
3-Hydroxybenzoic acid hydrate	SAYPIT	SAYPOZ	Yes
4-Nitrobenzoic acid	XOPYEJ	XOPYUZ	Yes

Note: (*) it should be noted that the unit-cell parameters of both structures are similar but the orientations of the molecules with respect to the unit cells differ significantly.

water (Grothe *et al.*, 2016). Cocrystals have been proven to have new properties, such as having a different solubility or bioavailability over the starting material (Karimi-Jafari *et al.*, 2018). It can even lead to the possibility of having multiple drugs in one crystal form (Wang *et al.*, 2021). Unfortunately, cocrystal design and synthesis is not straightforward; it is possible to fail creating a cocrystal despite using a reasonable cocrystal design methodology (Bučar *et al.*, 2013).



Scheme 1

Isoniazid (**inh**) is an antibacterial drug used to treat *Mycobacterium tuberculosis* bacteria (TB). It is often combined with several different drugs in a fixed-dose combination (FDC) as part of the treatment for this disease (Murray *et al.*, 2015). However, **inh** has been known to undergo degradation in the presence of other drugs (Bhutani *et al.*, 2005). **Inh** is a fairly simple drug molecule, consisting of a pyridine ring, an amide group and a hydrazine group. One way to modify **inh** is to employ a Schiff base reaction using **inh** and either an aldehyde or a ketone. In previous work, we modified isoniazid with acetone, butan-2-one, 4-hydroxy-4-methylpentan-2-one and benzophenone, and explored a different number of cocrystal and molecular salt crystal structures (Lemmerer *et al.*, 2010; Madeley *et al.*, 2019; Scheepers & Lemmerer, 2022; Lemmerer, 2012). In particular, a decent number of cocrystals and molecular salts with isoniazid derived from acetone and butan-2-one have been reported, with seven crystal structures containing *N*′-(butan-2-ylidene) pyridine-4-carbohydrazide (butan-2-one-based derivative, **izbt**) and 15 containing *N*′-isopropylideneisonicotinohydrazide (acetone-based derivative, **izact**). Out of these, only five pairs share the same coformer, of which, three pairs are isostructural (Table 1). It should not be too surprising to find crystal structures becoming isostructural when certain functional groups are exchanged with a similar one, for example, changing a chlorine to a bromine or methyl to an amino group (Clarke *et al.*, 2012). However, it is still possible that exchanging one functional group for another can yield a completely different structure. In the case of **izact** and **izbt**, the difference is the presence or absence of the methylene group in the alkyl group. In three of the cases, this had no effect, but in the case of the anyhydrous forms of **izact**– and **izbt**–3-hydroxybenzoic acid, and **izact**– and **izbt**–2-hydrobenzoic acid, there was a significant difference in the packing. Based on the structures listed in Table 1, we would expect that the methylene group would very likely have a small or even insignificant effect on the overall packing of the molecules in the crystal structure; however, with a small sample size it is difficult to assess if this is a reasonable assertion. Therefore, the aim of this work is to expand the number of multicomponent crystal structure pairs and compare them, in order to confirm whether the addition of the methylene group can have a significant impact of the packing of these structures. The simplest way to achieve this is to expand the number of **izbt** cocrystals using coformers that worked for **izact**; the coformers used include: 2,4-dihydroxybenzoic acid (**2,4-dhba**), 2,5-dihydroxybenzoic acid (**2,5-dhba**) and 2-chloro-4-nitrobenzoic acid (**2c4n**). In addition, cocrystals containing 1-naphthoic acid (**1nta**) with **izact** and **izbt**, respectively, were synthesized and characterized. **1nta** was used to observe the effect of using a bulky double ring as opposed to using coformers consisting of a single ring. The structures of these compounds are represented in Scheme 1.

2. Experimental

2.1. Materials

All materials were purchased from Sigma–Aldrich and were used without further purification.

2.2. General procedure for the synthesis of izbt and izact cocrystals

The general procedure for synthesizing cocrystals featuring either **izbt** or **izact** is as follows: stoichiometric ratios of **inh** and the respective coformer (1:1 ratio) were dissolved in absolute ethanol (5 ml) in a small vial. The deriving ketone (acetone or butan-2-one) (1 ml) was added. This vial was

Table 2
Experimental details.

For all structures: $Z = 4$. Experiments were carried out with Mo $K\alpha$ radiation using a Bruker D8 VENTURE PHOTON CMOS 100 area-detector diffractometer.

	izbt–1nta	**izbt–2,4-dhba**	**izact–1nta**
Crystal data			
Chemical formula	$C_{10}H_{13}N_3O{\cdot}C_{11}H_8O_2$	$C_{10}H_{13}N_3O{\cdot}C_7H_6O_4$	$C_9H_{11}N_3O{\cdot}C_{11}H_8O_2$
M_r	363.41	345.35	349.38
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, Cc
Temperature (K)	173	173	173
a, b, c (Å)	7.4355 (13), 34.195 (6), 7.7242 (14)	11.0834 (6), 13.8364 (8), 12.0014 (7)	7.6312 (3), 33.5293 (12), 7.3493 (3)
α, β, γ (°)	90, 112.512 (4), 90	90, 115.710 (3), 90	90, 114.298 (1), 90
V (Å^3)	1814.3 (6)	1658.26 (17)	1713.88 (12)
μ (mm^{-1})	0.09	0.10	0.09
Crystal size (mm)	0.34 × 0.28 × 0.12	0.32 × 0.25 × 0.21	0.72 × 0.33 × 0.08
Data collection			
Absorption correction	–	–	Multi-scan (*SADABS*; Sheldrick, 2001; Krause *et al.*, 2015)
T_{min}, T_{max}	–	–	0.684, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35501, 4511, 3552	25708, 4008, 1946	39441, 6819, 6145
R_{int}	0.033	0.092	0.056
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.668	0.660	0.782
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.054, 0.142, 1.03	0.061, 0.219, 1.02	0.043, 0.122, 1.08
No. of reflections	4511	4008	6819
No. of parameters	254	248	238
No. of restraints	0	39	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.34	0.70, −0.27	0.33, −0.17
Absolute structure	–	–	Flack x determined using 2626 quotients $[(I^+) - (I^-)]/[(I^+) + (I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	–	–	0.0 (3)

	izbt–2c4n	**izbt–2,5-dhba**
Crystal data		
Chemical formula	$C_7H_4ClNO_4{\cdot}C_{10}H_{13}N_3O$	$C_{10}H_{13}N_3O{\cdot}C_7H_6O_4$
M_r	392.79	345.35
Crystal system, space group	Monoclinic, $P2_1/n$	Triclinic, $P\overline{1}$
Temperature (K)	173	123
a, b, c (Å)	7.2682 (3), 34.0775 (15), 7.6124 (3)	9.2054 (3), 11.5589 (4), 15.6268 (6)
α, β, γ (°)	90, 111.081 (2), 90	92.383 (2), 93.092 (2), 90.666 (2)
V (Å^3)	1759.27 (13)	1658.74 (10)
μ (mm^{-1})	0.26	0.10
Crystal size (mm)	0.46 × 0.26 × 0.11	0.45 × 0.38 × 0.13
Data collection		
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	111394, 5624, 5056	73254, 8026, 5972
R_{int}	0.081	0.079
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.726	0.661
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.047, 0.129, 1.07	0.068, 0.191, 1.04
No. of reflections	5624	8026
No. of parameters	250	506
No. of restraints	0	21
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.41, −0.28	1.33, −0.68

Computer programs: *APEX2* (Bruker, 2012), *SAINT-Plus* (Bruker, 2012), *SHELXT2018* (Sheldrick, 2015*a*), *SHELXL2018* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020), *ORTEP-3 for Windows* (Farrugia, 2012), *XPREP* (Bruker, 2012) and *WinGX* (Farrugia, 2012).

closed and the mixture stirred for 4 h. Afterwards, the lid on the vial was replaced with a lid with a hole in it and the vial kept in a dark cupboard. After several days, crystals remained after the solvent evaporated.

2.3. Powder X-ray diffraction (PXRD)

PXRD was used to determine the bulk phase purity of each sample. PXRD data for all forms were measured at 293 K on a Bruker D2 Phaser diffractometer which employs a sealed tube Co X-ray source (λ = 1.78896 Å), operating at 30 kV and 10 mA, and a LynxEye PSD detector in Bragg–Brentano geometry. The powder patterns for the cocrystals are presented in the supporting information, where the experimentally measured pattern is compared to the calculated patterns obtained from the single-crystal X-ray diffraction (SC-XRD) data, as well as the calculated patterns of its components using data from the Cambridge Structural Database (CSD, Version 2022.1.0; Groom *et al.*, 2016).

2.4. Single-crystal X-ray diffraction (SC-XRD) and refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All carbon-bound H atoms were placed in idealized positions and refined as riding atoms, with U_{iso}(H) parameters 1.2 or 1.5 times those of the parent atoms. Most nitrogen- and oxygen-bound H atoms were located in difference Fourier maps, and their coordinates and isotropic displacement parameters were refined freely.

2.5. The Cambridge Structural Database (CSD)

The CSD (Version 2022.1.0; Groom *et al.*, 2016) was used to compare the cocrystals presented in this work with the cocrystals of **izact**. The only restriction was that entries must be classified as being organic. *Mercury* (Macrae *et al.*, 2020) was used to inspect the crystal structures. The Crystal Structure Similarity tool was used to compare the structural similarity of selected structures.

2.6. Differential scanning calorimetry (DSC)

DSC data were collected using a Mettler Toledo DSC 3 with aluminium pans under nitrogen gas (flow rate = 10 ml min^{-1}). Exothermic events were shown as peaks. Samples were heated and cooled to determine the melting points, as well as any additional phase transitions. The temperature and energy calibrations were performed using pure indium (purity 99.99%, m.p. 156.6 °C, heat of fusion: 28.45 J g^{-1}) and pure zinc (purity 99.99%, m.p. 479.5 °C, heat of fusion: 107.5 J g^{-1}). Samples were heated to 250 °C from 25 °C before being cooled back down to 25 °C at a heating or cooling rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Synthesis of cocrystals

In this work, six cocrystals were synthesized and characterized. Five of these cocrystals contained **izbt** and one contained **izact**. The four coformers chosen were: 2,4-dihydroxybenzoic acid (**2,4-dhba**), 2,5-dihydroxybenzoic acid

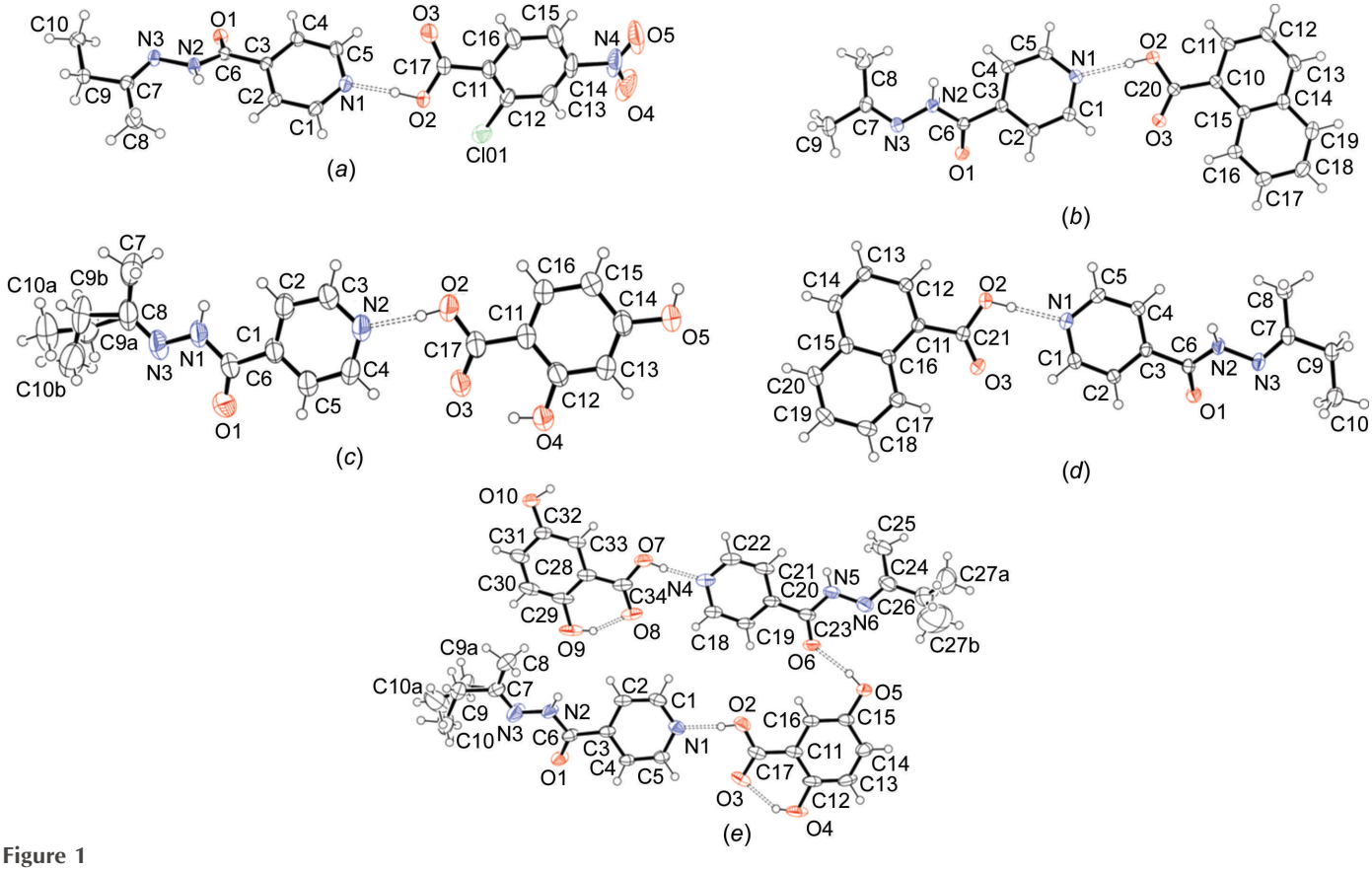


Figure 1
The molecular structures of (*a*) **izbt–2c4n**, (*b*) **izact–1nta**, (*c*) **izbt–2,4-dhba**, (*d*) **izbt–1nta** and (*e*) **izbt–2,5-dhba**. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

(gentisic acid, abbreviated as **2,5-dhba**), 2-chloro-4-nitrobenzoic acid (**2c4n**) and 1-naphthoic acid (**1nta**). The first three coformers were chosen because previous cocrystals containing said coformers with **izact** had been synthesized and characterized previously, and it would be a good reference to compare the respective corystals. **1nta** was chosen due to its naphthalene ring, as it would be interesting to see if its bulky nature had an effect on the overall packing. These cocrystals are described below, together with that of **izbt** compared to its **izact** counterpart, as well as any other notable cocrystal of **izact**. The crystal structure data are given in Table 2, while the displacement ellipsoid plots are shown in Fig. 1. Hydrogen-bond tables can be found in the supporting information.

Powder patterns were collected for each sample and were compared to the powder patterns calculated from the single-crystal structural data. These powder patterns are also compared to the powder patterns of each of the components, including the polymorphic forms of the components which are polymorphic. It should be noted that we are comparing the hydrated form of **izbt** to the powder patterns of the cocrystals presented here. This was done because it was the closest form to a 'pure' component we can get, and in our own investigations, we have obtained the hydrated form of **izbt** exclusively when using the same crystallizing conditions we used to obtain the cocrystals presented here, which indicates that **izbt** is most likely highly hygroscopic, obtaining the water from either the waters of reaction or atmospheric moisture, or both. This comparison between the experimental and calculated patterns was made to confirm the bulk phase purity. These patterns are presented in the supporting information.

3.2. Crystal structure of izbt–2,4-dhba

Izbt formed a cocrystal with **2,4-dhba** which crystallized as colourless blocks in the space group $P2_1/n$, with the asymmetric unit consisting of one molecule each of **izbt** and **2,4-dhba**. A disorder model is present, where two C atoms (C9 and C10) of the alkyl portion of **izbt** were split over two different positions, respectively. The pyridine ring of **izbt** forms a hydrogen bond with the carboxylic acid group of **2,4-dhba**, while the hydroxy group at the 4-position of the **2,4-dhba** molecule (O5—H5) forms two different hydrogen bonds with the amide group of **izbt**, one where the hydroxy group is the hydrogen-bond donor, forming a hydrogen bond with the O atom of the amide group [O5—H5$\cdots$O1^{i}; symmetry code: (i) $x+\frac{3}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$], and one where the hydroxy group is the hydrogen-bond acceptor, forming a hydrogen bond with the amine portion of the amide group [N1—H1$\cdots$O5^{ii}; symmetry code: (ii) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$] [Fig. 2(*a*)]. This hydrogen-bond arrangement ultimately forms a tetramer with an $R_4^4(12)$ ring hydrogen-bond motif. The hydroxy group at the 2-position of **2,4-dhba** does not form any strong hydrogen bonds other than the typical intramolecular hydrogen bond with the carboxylic

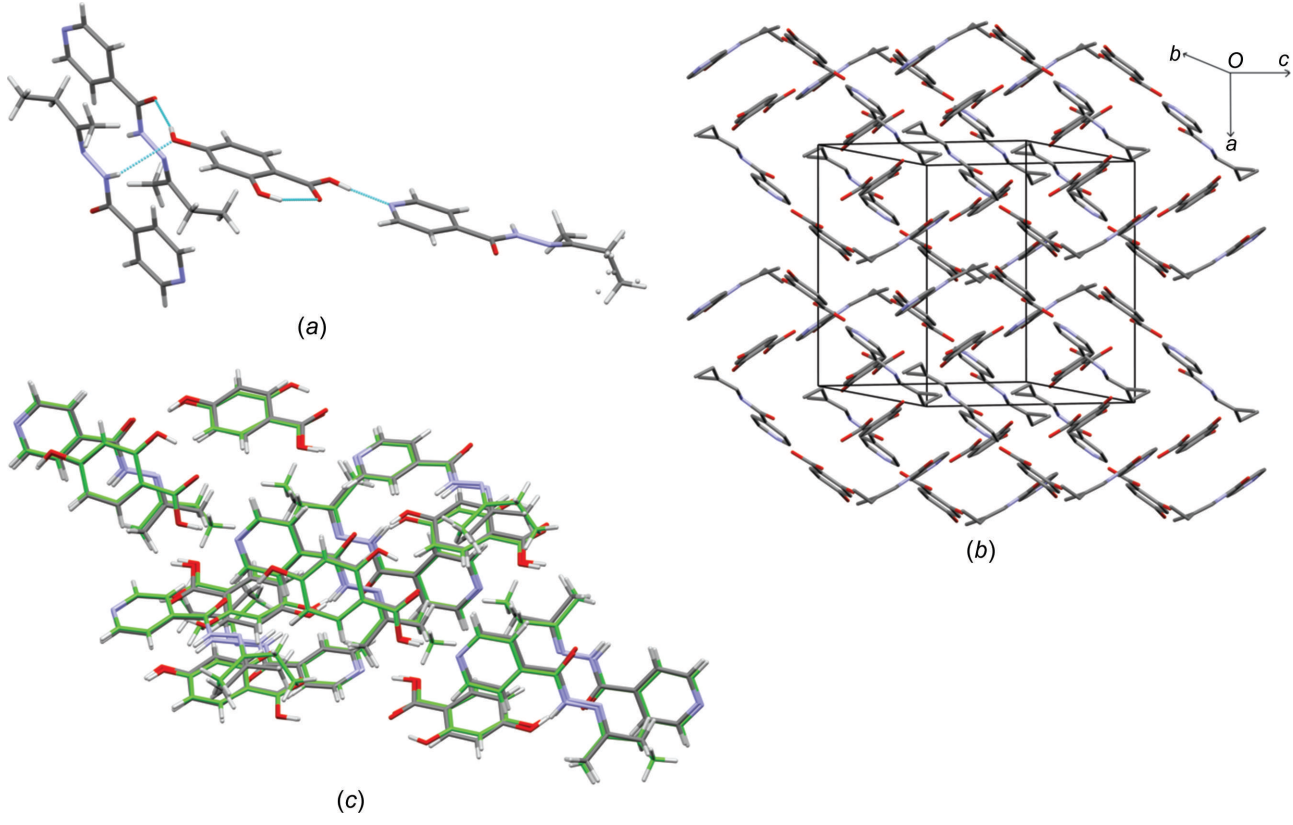


Figure 2
The crystal structure of **izbt–2,4-dhba**, showing (*a*) the hydrogen bonding present in the structure, (*b*) the packing of the structure (with H atoms omitted) and (*c*) an overlay of **izbt–2,4-dhba** with **izact–4hba**, showing their isostructurality.

acid group. The overall packing of the structure resembles a herringbone-type structure [Fig. 2(*b*)].

Although there is no equivalent cocrystal featuring **2,4-dhba** and **izact**, the crystal structure of **izbt–2,4-dhba** may be compared to that of **izact–4hba** (CSD refcode LATKOI). Fig. 2(*c*) shows the overlay of these two structures using the Crystal Structure Similarity tool of *Mercury* (Macrae *et al.*, 2020). The crystal structure parameters of **izact–4hba** match closely with those of **izbt–2,4-dhba**, and when the Crystal Structure Similarity tool of *Mercury* was used, it showed that the respective molecules matched up well, indicating that they were isostructural. This implies that, in this case, the hydroxy group at the 2-position and the extra methyl group on the alkyl chain did not have any significant effect on the overall packing on the structure.

3.3. Crystal structure of izbt–2,5-dhba

Izbt formed a cocrystal with **2,5-dhba** which crystallized as colourless blocks in the space group $P\overline{1}$, with the asymmetric unit consisting of two molecules each of **izbt** and **2,5-dhba**. A disorder model exists where the methylene group of one of the **izbt** molecules has been split into two different sites (C26*A* and C26*B*). Like **izbt–2,4-dhba**, the corystals of **izbt–2,5-dhba** exhibit a similar hydrogen-bonding trend: a hydrogen bond is formed between the pyridine ring of **izbt** and the carboxylic acid group of **2,5-dhba**, while the hydroxy group at the 5-position of **2,5-dhba** forms a $C_2^2(11)$ chain–ring hydrogen-bond motif with the O and H atom of the amide group of adjacent **izbt** molecules [Fig. 3(*a*)]. The overall packing is a layered-type structure, with the alkyl group separating the ring layers [Fig. 3(*b*)]. In comparison, the structure of **izact–2,5-dhba** (refcode NAKYOQ; Oruganti *et al.*, 2016) is very similar to its **izbt** counterpart. Both exhibit the same hydrogen-bond pattern, as well as the overall packing pattern, and the reduced unit-cell lengths of NAKYOQ are comparable (a = 9.119, b = 11.581 and c = 15.273 Å) [Fig. 3(*c*)].

3.4. Crystal structure of izbt–2c4n

Izbt and **2c4n** formed a cocrystal, crystallizing as yellow plates. The asymmetric unit consists of one molecule each of **izbt** and **2c4n**, crystallizing in the space group $P2_1/n$. The hydrogen bonding observed in **izact–2c4n** consists of the typical scheme observed for these types of structures: the carboxylic acid group of **2c4n** forms a hydrogen bond with the pyridine ring of **izbt**, while the amide group of **izbt** forms a $C(4)$ chain hydrogen-bond motif between the H atom of the amide group and the O atom of the amide group of another **izbt** molecule [Fig. 4(*a*)]. This chain hydrogen-bond motif causes the molecules of **izbt** to lie almost perpendicular with respect to each other in an alternating pattern, and extends along the a and c axes. This ultimately forms a series of ribbons which pack together to form the crystal structure observed in Fig. 4(*c*).

The **izact–2c4n** cocrystal (refcode LATLID) is much different in comparison. According to Grothe *et al.* (2016), this crystal system can be defined as a 'cocrystal salt', since its

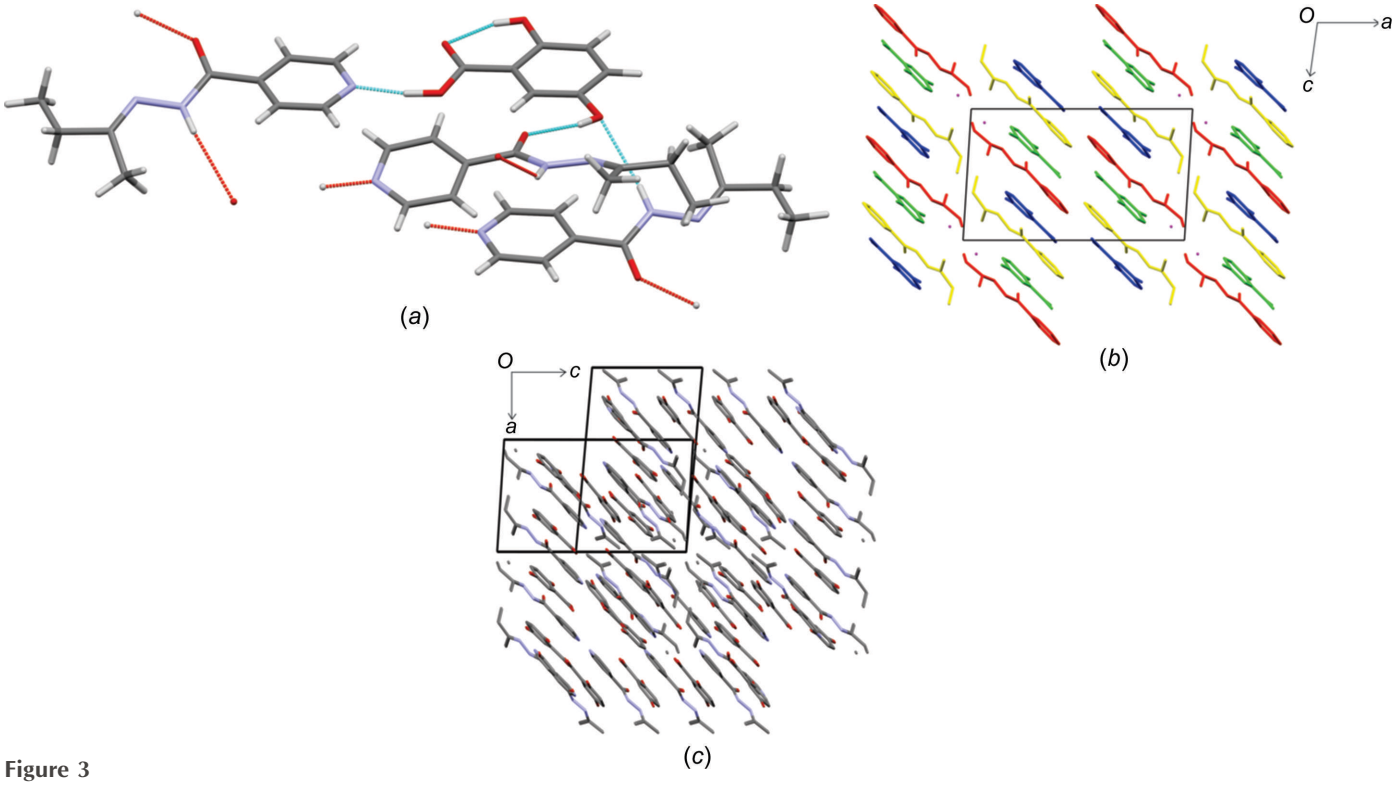


Figure 3
The crystal structure of **izbt–2,5-dhba**, showing (*a*) the hydrogen bonding present, (*b*) the packing (with H atoms omitted, **izbt** in blue and green, and **2,5-dhba** in red and yellow) and (*c*) the overlay of **izact–2,5-dhba** and **izbt–2,5-dhba**.

Table 3
Onset temperatures and associated enthalpies for the DSC curves of the cocrystals presented in this work, as well as the melting points and enthalpies of some of the comparison cocrystals.

Thermal event	Onset (°C)	Enthalpy (J g^{-1})	Enthalpy (kJ mol^{-1})
Izact–1nta melting/decomposition	106.1 ± 0.5	170.9 ± 5.2	59.7 ± 2
Izbt–1nta melting/decomposition	89.5± 0.1	167.8 ± 2.5	61.0 ± 1
Izbt–2c4n melting/decomposition	102.1 ± 0.2	100.6 ± 2.3	39.5 ± 1
Izbt–2,4-dhba melting/decomposition	174.8± 0.2	226.3 ± 4.3	78.2 ± 1
Izbt–2,5-dhba melting/decomposition	151.2 ± 0.2	132.5 ± 3.2	45.8 ± 1
Izact m.p. (Lemmerer, 2012)	160.0	–	29.7
Izact–2c4n m.p. (Lemmerer, 2012)	93.4	–	33.4

asymmetric unit consists of three neutral molecules of **2c4n** and one ion of **2c4n**, with three neutral molecules of **izact** and one protonated ion of **izact** [Fig. 4(*b*)]. This crystal structure crystallizes in the chiral space group $P2_1$. Like the structure of **izbt–2c4n**, molecules and ions of **izact** are connected to each other *via* a series of $C_4^4(16)$ chain hydrogen-bond motifs involving the H atom of the amide group forming a hydrogen bond with the O atom of the amide group from another **izact** molecule. The carboxylic acid group of **2c4n** also forms a hydrogen bond with the pyridine ring of **izact** (charge-assisted

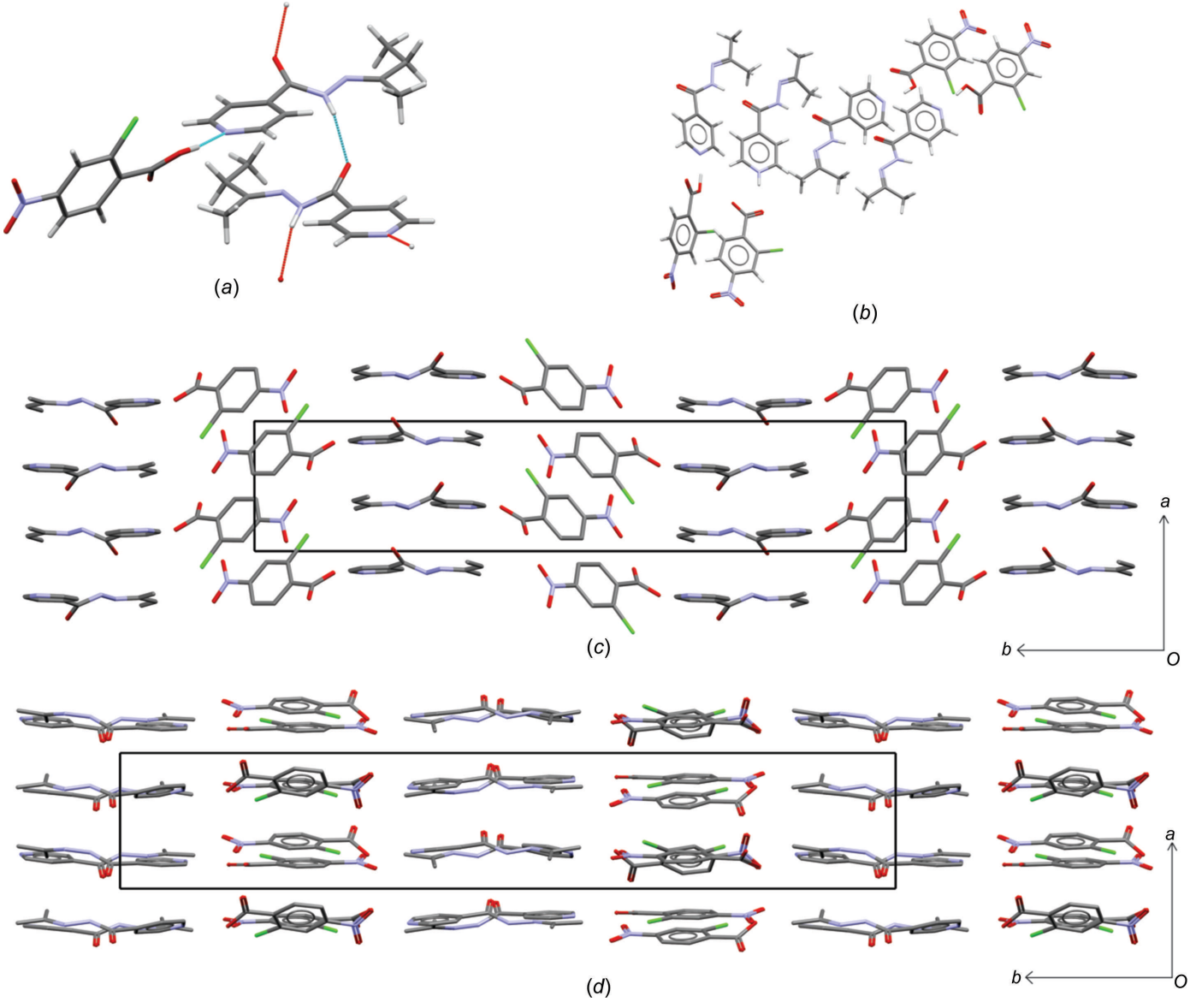


Figure 4
The crystal structure of **izbt–2c4n** and **izact–2c4n** (CSD refcode LATLID), showing (*a*) the hydrogen bonding present in **izbt–2c4n**, (*b*) the asymmetric unit of **izact–2c4n**, (*c*) the packing of **izbt–2c4n** (with H atoms omitted for clarity) and (*d*) the packing of **izact–2c4n** (with H atoms omitted for clarity).

for the cation–anion pair). The overall packing of **izact–2c4n** also consists of ribbons, but these differ from the structure of **izbt–2c4n** [Fig. 4(*d*)]. Unlike in the crystal structure of **izbt–2c4n**, the arrangement of the **izbt–2c4n** bonded pairs lie almost parallel to each other, instead of the rotation of almost 90° seen in **izbt–2c4n**.

3.5. Crystal structures of izact–1nta and izbt–1nta

Izact and **izbt** each formed a cocrystal with **1nta**, both crystallizing as colourless plates. Despite sharing similar unit-cell parameters, the structures are not isostructural, as the crystal structure of **izact–1nta** crystallizes in the space group *Cc*, while the crystal structure of **izbt–1nta** crystallizes in the space group $P2_1/n$. These structures are also not isostructural with **izbt–2c4n**, despite sharing similar unit-cell parameters, as can be seen in Fig. 5(*d*). Both crystal structures share the same hydrogen-bonding patterns. **1nta** forms a hydrogen bond with the isoniazid derivative, while the isoniazid derivative forms a *C*(4) chain hydrogen-bond motif involving the H atom of the amide group and the O atom of the amide group from a neighbouring molecule of the isoniazid derivative [Fig. 5(*a*)], which expands generally in the direction of the *a* axis as ribbons. The key difference between the two structures lies in the packing, where the difference between the $P2_1/n$ and *Cc* space groups is that the inversion centres in $P2_1/n$ [Fig. 5(*b*)] are replaced by glide planes in *Cc* [Fig. 5(*c*)]. This changes the orientation of the molecules existing in both structures with respect to the unit cell. Overall, the packing of both structures may be described as herringbone.

3.6. Thermal analysis

DSC curves were collected for all ten cocrystals. The DSC curve of **izbt–1nta** is presented in Fig. 6 as a representative curve, while the remaining DSC curves can be found in the supporting information. The onset and enthalpy values are presented in Table 3. The melting points and enthalpies of some of the cocrystals related to the cocrystals presented in this work are also included. In each of the curves, only one large distinct peak was observed on the heating stage, which correlates to the melting/decomposition of the sample. No peaks were observed on the cooling stage of the DSC curves, indicating that no recrystallization occurred. A common feature between the cocrystals is that their melting points are much lower than the melting points of the acid coformers. This makes sense since the $R_2^2(8)$ hydrogen-bond ring motif formed between the carboxylic acid pairs is expected to be stronger than that formed by carboxylic acid–pyridine. From a pharmaceutical point of view, a lower melting point is usually indicative of a product that has a better drug solubility, which indicates the possibility of having better pharmaceutical properties compared to their individual components (Chu & Yalkowsky, 2009). A comparison of the melting/decomposition points and enthalpies of the **izact** cocrystals with those of their **izbt** counterparts indicates that the values tend

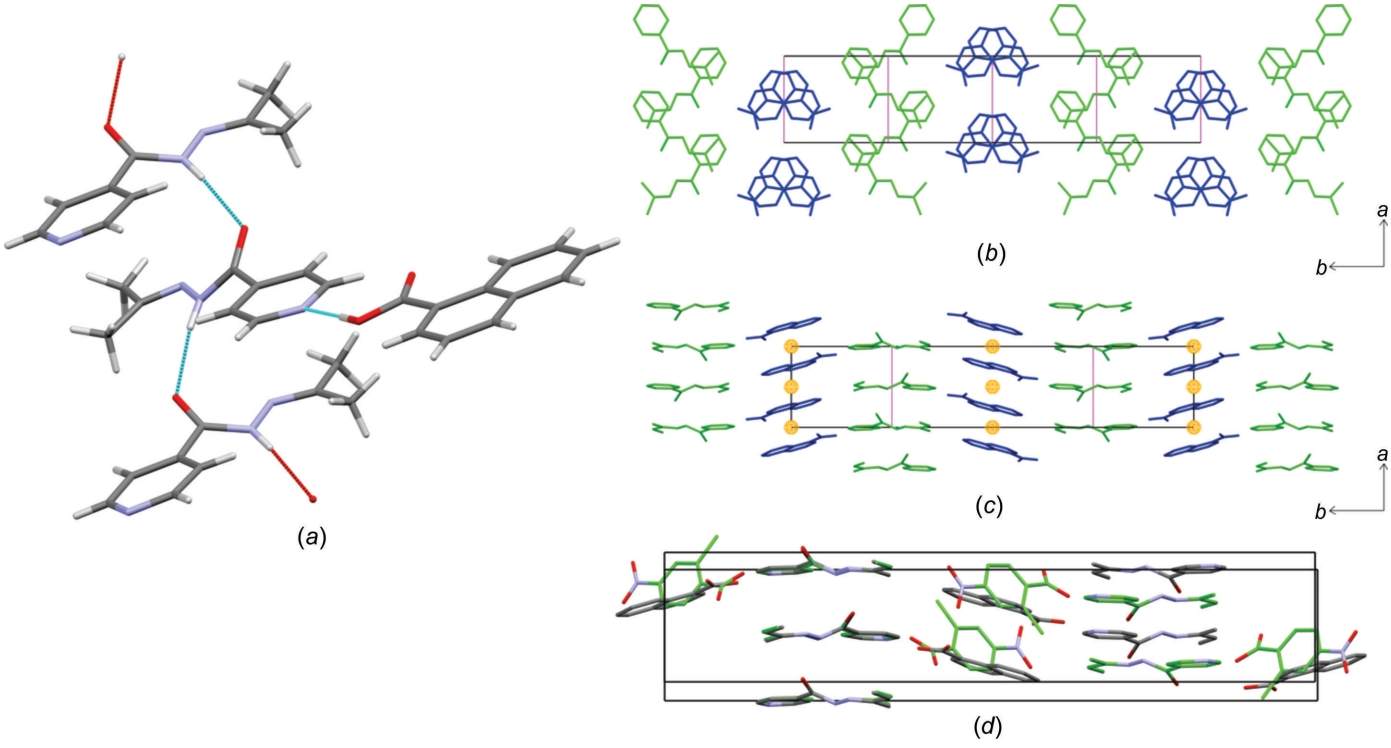


Figure 5
(*a*) The hydrogen bonding present in **izact–1nta**, showing the typical hydrogen bonding in the structures of **izact–1nta** and **izbt–1nta**. The packing present in the crystal structure of (*b*) **izact–1nta** and (*c*) **izbt–1nta**, with the H atoms omitted for clarity. In parts (*b*) and (*c*), the respective isoniazid derivative is presented in green, **1nta** in blue, glide planes as magenta lines and inversion centres as orange spheres. (*d*) The overlap of **izbt–1nta** and **izbt–2c4n** (molecules in green), showing that the structures are not isostructural.

to be similar to each other, which would make sense considering their overall similar hydrogen-bond schemes.

4. Conclusions

Four cocrystals containing **izbt** and one cocrystal containing **izact** were synthesized and characterized. The structures of the cocrystals containing **izbt** were compared to their **izact** counterparts, except for **izbt–2,4-dhba**, which was instead compared to **izact–4hba**. Most of the structures of the cocrystals of **izbt** were different compared to their **izact** counterparts in terms of packing, despite sharing similar hydrogen-bond patterns. This would imply that the presence or absence of a methylene group can have a significant impact on the overall crystal structure packing, contrary to our initial assumption that the methylene group has a small or even insignificant effect on the packing of molecules in the crystal structure. The melting/decomposition points were found to be much lower than those of the coformers. The overall result shows that many crystal systems are temperamental: small differences between molecules can lead to big changes in the overall packing.

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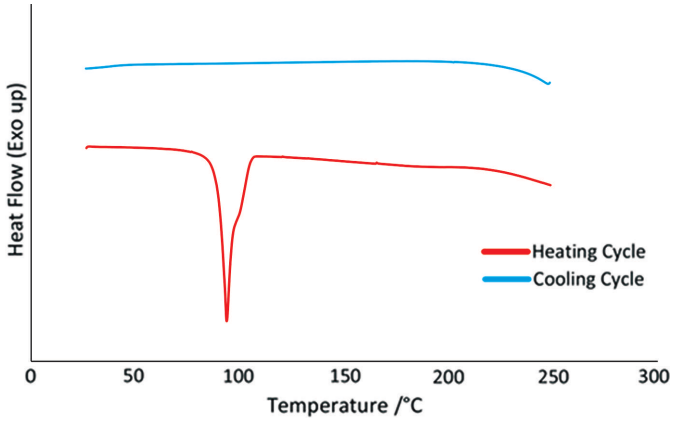

Figure 6
DSC curve for **izbt–1nta**, representing the typical DSC curve observed for each of the cocrystals.

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supporting information

Acta Cryst. (2023). C**79**, 365-373 [https://doi.org/10.1107/S2053229623007179]

The synthesis and characterization of a series of cocrystals of an isoniazid derivative with butan-2-one and propan-2-one

Matthew Clarke Scheepers and Andreas Lemmerer

Computing details

Data collection: *APEX2* (Bruker, 2012) for izbt1nta, izbt24dhba, izact1nta, izbt2c4n. Cell refinement: *SAINT-Plus* (Bruker, 2012) for izbt1nta, izbt24dhba, izact1nta, izbt2c4n. Data reduction: *SAINT-Plus* (Bruker, 2012) for izbt1nta, izbt24dhba, izact1nta, izbt2c4n. For all structures, program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015*b*). Molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2020) for izbt1nta, izbt24dhba, izact1nta, izbt2c4n; *ORTEP-3 for Windows* (Farrugia, 2012) for izbt25dhba. Software used to prepare material for publication: *WinGX* (Farrugia, 2012) and *XPREP* (Bruker, 2012) for izbt1nta, izbt24dhba, izact1nta, izbt2c4n; *WinGX* (Farrugia, 2012) for izbt25dhba.

N′-(Butan-2-ylidene)pyridine-4-carbohydrazide; 1-naphthoic acid (izbt1nta)

Crystal data

$C_{10}H_{13}N_3O{\cdot}C_{11}H_8O_2$
M_r = 363.41
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 7.4355 (13) Å
b = 34.195 (6) Å
c = 7.7242 (14) Å
β = 112.512 (4)°
V = 1814.3 (6) Å^3
Z = 4
$F(000)$ = 768
D_x = 1.33 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9890 reflections
θ = 2.9–28.3°
μ = 0.09 mm^{-1}
T = 173 K
Block, colourless
0.34 × 0.28 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
35501 measured reflections
4511 independent reflections
3552 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 28.3°, θ_{min} = 3.4°
h = −9→9
k = −45→45
l = −10→10

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.142
S = 1.03
4511 reflections
254 parameters
0 restraints
0 constraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0637P)^2 + 1.0375P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.54 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4865 (3)	0.64234 (5)	0.5961 (2)	0.0289 (4)
H1	0.479346	0.614625	0.599541	0.035*
C2	0.5137 (2)	0.66303 (4)	0.7582 (2)	0.0244 (3)
H2A	0.528577	0.649764	0.870961	0.029*
C3	0.5189 (2)	0.70353 (4)	0.7527 (2)	0.0208 (3)
C4	0.5009 (2)	0.72157 (5)	0.5857 (2)	0.0264 (3)
H4	0.504198	0.749257	0.577421	0.032*
C5	0.4780 (3)	0.69843 (5)	0.4313 (2)	0.0300 (4)
H5	0.467633	0.710899	0.317944	0.036*
C6	0.5592 (2)	0.72591 (4)	0.9309 (2)	0.0219 (3)
C7	0.4945 (2)	0.82004 (5)	1.0579 (2)	0.0269 (3)
C8	0.4585 (3)	0.84331 (5)	0.8828 (2)	0.0367 (4)
H8A	0.514858	0.829582	0.804171	0.055*
H8B	0.519033	0.86913	0.916433	0.055*
H8C	0.317967	0.846392	0.813647	0.055*
C9	0.5210 (3)	0.84343 (5)	1.2308 (2)	0.0312 (4)
H9A	0.630337	0.861863	1.253523	0.037*
H9B	0.402059	0.859191	1.20623	0.037*
C10	0.5606 (3)	0.82005 (6)	1.4061 (2)	0.0376 (4)
H10A	0.448383	0.803278	1.389922	0.056*
H10B	0.582875	0.837824	1.511822	0.056*
H10C	0.676282	0.80377	1.430932	0.056*
C11	0.3204 (2)	0.54602 (4)	0.0208 (2)	0.0218 (3)
C12	0.3179 (2)	0.55966 (4)	−0.1480 (2)	0.0241 (3)
H12	0.354523	0.585992	−0.156468	0.029*
C13	0.2629 (2)	0.53579 (5)	−0.3079 (2)	0.0281 (3)
H13	0.26264	0.545884	−0.42259	0.034*
C14	0.2099 (2)	0.49802 (5)	−0.2971 (2)	0.0289 (4)
H14	0.172404	0.481852	−0.405159	0.035*
C15	0.2097 (2)	0.48253 (5)	−0.1277 (2)	0.0253 (3)
C16	0.2665 (2)	0.50632 (4)	0.0363 (2)	0.0221 (3)
C17	0.2661 (2)	0.48883 (5)	0.2031 (2)	0.0282 (3)
H17	0.304248	0.503862	0.314877	0.034*
C18	0.2117 (3)	0.45067 (5)	0.2051 (3)	0.0346 (4)
H18	0.212744	0.439598	0.318294	0.042*
C19	0.1544 (3)	0.42767 (5)	0.0429 (3)	0.0374 (4)
H19	0.116051	0.401269	0.046069	0.045*

C20	0.1539 (3)	0.44330 (5)	−0.1191 (3)	0.0334 (4)
H20	0.115288	0.427542	−0.22866	0.04*
C21	0.3808 (2)	0.57384 (5)	0.1818 (2)	0.0273 (3)
N1	0.4697 (2)	0.65943 (4)	0.43437 (19)	0.0295 (3)
N2	0.4799 (2)	0.76157 (4)	0.91231 (18)	0.0261 (3)
N3	0.5099 (2)	0.78278 (4)	1.07692 (18)	0.0273 (3)
O1	0.66638 (17)	0.71153 (3)	1.08121 (15)	0.0301 (3)
O2	0.3999 (2)	0.61035 (4)	0.13403 (18)	0.0412 (3)
O3	0.4134 (3)	0.56528 (4)	0.34138 (18)	0.0645 (5)
H2	0.385 (3)	0.7684 (6)	0.805 (3)	0.039 (5)*
H2B	0.432 (4)	0.6256 (8)	0.232 (4)	0.063 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0369 (9)	0.0208 (8)	0.0284 (8)	−0.0006 (6)	0.0117 (7)	−0.0033 (6)
C2	0.0285 (8)	0.0207 (7)	0.0221 (7)	−0.0009 (6)	0.0077 (6)	−0.0003 (6)
C3	0.0202 (7)	0.0208 (7)	0.0193 (7)	0.0001 (5)	0.0051 (5)	−0.0027 (5)
C4	0.0349 (9)	0.0202 (7)	0.0246 (7)	0.0004 (6)	0.0119 (6)	0.0001 (6)
C5	0.0404 (9)	0.0287 (8)	0.0232 (7)	−0.0007 (7)	0.0148 (7)	−0.0006 (6)
C6	0.0232 (7)	0.0210 (7)	0.0199 (7)	−0.0030 (6)	0.0064 (6)	−0.0028 (5)
C7	0.0236 (8)	0.0261 (8)	0.0295 (8)	−0.0014 (6)	0.0085 (6)	−0.0070 (6)
C8	0.0486 (11)	0.0262 (9)	0.0314 (9)	−0.0017 (7)	0.0113 (8)	−0.0017 (7)
C9	0.0349 (9)	0.0269 (8)	0.0332 (9)	−0.0017 (7)	0.0145 (7)	−0.0080 (7)
C10	0.0428 (10)	0.0366 (10)	0.0337 (9)	−0.0006 (8)	0.0150 (8)	−0.0074 (7)
C11	0.0234 (7)	0.0218 (7)	0.0201 (7)	0.0016 (6)	0.0083 (6)	−0.0012 (5)
C12	0.0283 (8)	0.0216 (7)	0.0230 (7)	0.0012 (6)	0.0103 (6)	0.0006 (6)
C13	0.0335 (9)	0.0307 (8)	0.0205 (7)	0.0028 (7)	0.0106 (6)	0.0001 (6)
C14	0.0295 (8)	0.0321 (8)	0.0224 (7)	0.0021 (7)	0.0069 (6)	−0.0077 (6)
C15	0.0219 (7)	0.0239 (7)	0.0285 (8)	0.0016 (6)	0.0081 (6)	−0.0028 (6)
C16	0.0209 (7)	0.0216 (7)	0.0241 (7)	0.0033 (6)	0.0090 (6)	0.0007 (6)
C17	0.0320 (9)	0.0267 (8)	0.0294 (8)	0.0029 (6)	0.0156 (7)	0.0021 (6)
C18	0.0378 (10)	0.0298 (9)	0.0424 (10)	0.0037 (7)	0.0224 (8)	0.0095 (7)
C19	0.0381 (10)	0.0232 (8)	0.0527 (11)	−0.0032 (7)	0.0195 (9)	0.0022 (8)
C20	0.0318 (9)	0.0254 (8)	0.0408 (10)	−0.0019 (7)	0.0114 (7)	−0.0065 (7)
C21	0.0344 (9)	0.0241 (8)	0.0229 (7)	−0.0005 (6)	0.0105 (6)	−0.0019 (6)
N1	0.0368 (8)	0.0279 (7)	0.0250 (7)	−0.0007 (6)	0.0130 (6)	−0.0058 (5)
N2	0.0306 (7)	0.0231 (7)	0.0194 (6)	0.0020 (5)	0.0037 (5)	−0.0051 (5)
N3	0.0294 (7)	0.0270 (7)	0.0231 (6)	−0.0010 (5)	0.0075 (5)	−0.0077 (5)
O1	0.0364 (6)	0.0266 (6)	0.0193 (5)	0.0020 (5)	0.0017 (5)	−0.0001 (4)
O2	0.0758 (10)	0.0223 (6)	0.0276 (6)	−0.0044 (6)	0.0222 (7)	−0.0052 (5)
O3	0.1335 (16)	0.0346 (8)	0.0231 (7)	−0.0192 (9)	0.0272 (8)	−0.0066 (5)

Geometric parameters (Å, º)

C1—N1	1.341 (2)	C11—C12	1.378 (2)
C1—C2	1.384 (2)	C11—C16	1.433 (2)
C1—H1	0.95	C11—C21	1.492 (2)

C2—C3	1.387 (2)	C12—C13	1.404 (2)
C2—H2A	0.95	C12—H12	0.95
C3—C4	1.389 (2)	C13—C14	1.362 (2)
C3—C6	1.5016 (19)	C13—H13	0.95
C4—C5	1.386 (2)	C14—C15	1.412 (2)
C4—H4	0.95	C14—H14	0.95
C5—N1	1.335 (2)	C15—C20	1.413 (2)
C5—H5	0.95	C15—C16	1.427 (2)
C6—O1	1.2311 (18)	C16—C17	1.422 (2)
C6—N2	1.338 (2)	C17—C18	1.368 (2)
C7—N3	1.283 (2)	C17—H17	0.95
C7—C8	1.502 (2)	C18—C19	1.400 (3)
C7—C9	1.504 (2)	C18—H18	0.95
C8—H8A	0.98	C19—C20	1.359 (3)
C8—H8B	0.98	C19—H19	0.95
C8—H8C	0.98	C20—H20	0.95
C9—C10	1.501 (2)	C21—O3	1.198 (2)
C9—H9A	0.99	C21—O2	1.325 (2)
C9—H9B	0.99	N2—N3	1.4054 (17)
C10—H10A	0.98	N2—H2	0.89 (2)
C10—H10B	0.98	O2—H2B	0.87 (3)
C10—H10C	0.98		

N1—C1—C2	123.30 (15)	C12—C11—C16	119.79 (13)
N1—C1—H1	118.3	C12—C11—C21	117.61 (14)
C2—C1—H1	118.3	C16—C11—C21	122.60 (13)
C1—C2—C3	118.61 (14)	C11—C12—C13	121.94 (14)
C1—C2—H2A	120.7	C11—C12—H12	119
C3—C2—H2A	120.7	C13—C12—H12	119
C2—C3—C4	118.55 (13)	C14—C13—C12	119.39 (14)
C2—C3—C6	118.61 (13)	C14—C13—H13	120.3
C4—C3—C6	122.66 (13)	C12—C13—H13	120.3
C5—C4—C3	118.82 (14)	C13—C14—C15	121.05 (14)
C5—C4—H4	120.6	C13—C14—H14	119.5
C3—C4—H4	120.6	C15—C14—H14	119.5
N1—C5—C4	123.08 (15)	C14—C15—C20	120.28 (15)
N1—C5—H5	118.5	C14—C15—C16	120.26 (14)
C4—C5—H5	118.5	C20—C15—C16	119.46 (15)
O1—C6—N2	124.39 (14)	C17—C16—C15	117.54 (14)
O1—C6—C3	119.40 (13)	C17—C16—C11	124.88 (14)
N2—C6—C3	116.15 (12)	C15—C16—C11	117.57 (13)
N3—C7—C8	127.34 (14)	C18—C17—C16	120.98 (15)
N3—C7—C9	116.82 (15)	C18—C17—H17	119.5
C8—C7—C9	115.82 (14)	C16—C17—H17	119.5
C7—C8—H8A	109.5	C17—C18—C19	121.03 (16)
C7—C8—H8B	109.5	C17—C18—H18	119.5
H8A—C8—H8B	109.5	C19—C18—H18	119.5
C7—C8—H8C	109.5	C20—C19—C18	119.72 (16)

H8A—C8—H8C	109.5	C20—C19—H19	120.1
H8B—C8—H8C	109.5	C18—C19—H19	120.1
C10—C9—C7	115.56 (14)	C19—C20—C15	121.26 (16)
C10—C9—H9A	108.4	C19—C20—H20	119.4
C7—C9—H9A	108.4	C15—C20—H20	119.4
C10—C9—H9B	108.4	O3—C21—O2	121.05 (15)
C7—C9—H9B	108.4	O3—C21—C11	125.43 (15)
H9A—C9—H9B	107.5	O2—C21—C11	113.50 (13)
C9—C10—H10A	109.5	C5—N1—C1	117.61 (14)
C9—C10—H10B	109.5	C6—N2—N3	117.53 (12)
H10A—C10—H10B	109.5	C6—N2—H2	119.9 (13)
C9—C10—H10C	109.5	N3—N2—H2	120.1 (14)
H10A—C10—H10C	109.5	C7—N3—N2	115.64 (13)
H10B—C10—H10C	109.5	C21—O2—H2B	110.2 (17)

N1—C1—C2—C3	1.8 (3)	C12—C11—C16—C17	179.06 (15)
C1—C2—C3—C4	−1.4 (2)	C21—C11—C16—C17	−0.8 (2)
C1—C2—C3—C6	−176.73 (14)	C12—C11—C16—C15	−0.7 (2)
C2—C3—C4—C5	0.2 (2)	C21—C11—C16—C15	179.46 (14)
C6—C3—C4—C5	175.28 (15)	C15—C16—C17—C18	−0.5 (2)
C3—C4—C5—N1	0.9 (3)	C11—C16—C17—C18	179.73 (16)
C2—C3—C6—O1	32.2 (2)	C16—C17—C18—C19	−0.1 (3)
C4—C3—C6—O1	−142.93 (16)	C17—C18—C19—C20	0.4 (3)
C2—C3—C6—N2	−150.56 (15)	C18—C19—C20—C15	−0.2 (3)
C4—C3—C6—N2	34.3 (2)	C14—C15—C20—C19	179.39 (16)
N3—C7—C9—C10	−0.6 (2)	C16—C15—C20—C19	−0.4 (2)
C8—C7—C9—C10	−178.93 (16)	C12—C11—C21—O3	−170.22 (19)
C16—C11—C12—C13	0.3 (2)	C16—C11—C21—O3	9.6 (3)
C21—C11—C12—C13	−179.86 (14)	C12—C11—C21—O2	8.6 (2)
C11—C12—C13—C14	0.1 (2)	C16—C11—C21—O2	−171.56 (15)
C12—C13—C14—C15	−0.1 (2)	C4—C5—N1—C1	−0.7 (3)
C13—C14—C15—C20	179.88 (16)	C2—C1—N1—C5	−0.7 (3)
C13—C14—C15—C16	−0.3 (2)	O1—C6—N2—N3	−4.8 (2)
C14—C15—C16—C17	−179.06 (14)	C3—C6—N2—N3	178.06 (13)
C20—C15—C16—C17	0.7 (2)	C8—C7—N3—N2	−3.4 (2)
C14—C15—C16—C11	0.7 (2)	C9—C7—N3—N2	178.55 (14)
C20—C15—C16—C11	−179.47 (14)	C6—N2—N3—C7	156.63 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O3	0.95	2.51	3.208 (2)	130
C8—H8*C*···O1^{i}	0.98	2.62	3.128 (2)	112
N2—H2···O1^{i}	0.89 (2)	1.98 (2)	2.8732 (17)	174 (2)
O2—H2*B*···N1	0.87 (3)	1.88 (3)	2.7472 (18)	173 (2)

Symmetry code: (i) *x*−1/2, −*y*+3/2, *z*−1/2.

N′-(Butan-2-ylidene)pyridine-4-carbohydrazide; 2,4-dihydroxybenzoic acid (izbt24dhba)

Crystal data

$C_{10}H_{13}N_3O·C_7H_6O_4$
M_r = 345.35
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 11.0834 (6) Å
b = 13.8364 (8) Å
c = 12.0014 (7) Å
β = 115.710 (3)°
V = 1658.26 (17) Å^3
Z = 4
$F(000)$ = 728
D_x = 1.383 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2614 reflections
θ = 2.4–21.7°
μ = 0.10 mm^{-1}
T = 173 K
Block, colourless
0.32 × 0.25 × 0.21 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
25708 measured reflections
4008 independent reflections
1946 reflections with $I > 2\sigma(I)$
R_{int} = 0.092
θ_{max} = 28.0°, θ_{min} = 2.1°
h = −14→14
k = −14→18
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.061
$wR(F^2)$ = 0.219
S = 1.02
4008 reflections
248 parameters
39 restraints
0 constraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1075P)^2 + 0.2167P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ < 0.001
$\Delta\rho_{max}$ = 0.70 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.2256 (3)	0.3307 (2)	0.1115 (2)	0.0462 (7)	
C2	0.3201 (3)	0.3638 (2)	0.2233 (3)	0.0517 (7)	
H2A	0.294648	0.40267	0.274882	0.062*	
C3	0.4529 (3)	0.3395 (2)	0.2596 (3)	0.0565 (8)	
H3	0.517455	0.363307	0.336671	0.068*	
C4	0.4034 (3)	0.2515 (3)	0.0874 (3)	0.0656 (9)	
H4A	0.431538	0.211008	0.039242	0.079*	
C5	0.2688 (3)	0.2722 (2)	0.0432 (3)	0.0611 (8)	
H5A	0.20651	0.246347	−0.033661	0.073*	
C6	0.0790 (3)	0.3539 (2)	0.0579 (3)	0.0486 (7)	
C7	−0.0363 (4)	0.4971 (3)	0.2909 (4)	0.0926 (13)	

H7A	−0.085959	0.531016	0.329609	0.139*	
H7B	−0.00322	0.435334	0.333219	0.139*	
H7C	0.03954	0.536836	0.297237	0.139*	
C8	−0.1270 (3)	0.4788 (2)	0.1576 (4)	0.0669 (9)	
C9A	−0.2718 (8)	0.5139 (7)	0.0969 (7)	0.068 (2)	0.681 (9)
H9A1	−0.273761	0.584595	0.109021	0.082*	0.681 (9)
H9A2	−0.310308	0.501278	0.006909	0.082*	0.681 (9)
C10A	−0.3526 (6)	0.4664 (5)	0.1481 (7)	0.093 (2)	0.681 (9)
H10A	−0.444645	0.490666	0.107151	0.14*	0.681 (9)
H10B	−0.352183	0.396541	0.134913	0.14*	0.681 (9)
H10C	−0.315658	0.479809	0.236963	0.14*	0.681 (9)
C9B	−0.2550 (16)	0.5059 (17)	0.1534 (14)	0.086 (5)	0.319 (9)
H9B1	−0.266817	0.476516	0.223158	0.104*	0.319 (9)
H9B2	−0.261527	0.577059	0.158046	0.104*	0.319 (9)
C10B	−0.3542 (15)	0.4705 (11)	0.0377 (13)	0.095 (4)	0.319 (9)
H10D	−0.443548	0.486929	0.029738	0.143*	0.319 (9)
H10E	−0.340753	0.500108	−0.030243	0.143*	0.319 (9)
H10F	−0.346015	0.400111	0.034516	0.143*	0.319 (9)
N1	0.0399 (2)	0.40980 (18)	0.1262 (2)	0.0549 (7)	
H1	0.098313	0.429903	0.199395	0.066*	
N2	0.4951 (2)	0.28521 (19)	0.1933 (2)	0.0582 (7)	
N3	−0.0929 (2)	0.43602 (19)	0.0816 (3)	0.0626 (7)	
O1	0.00257 (19)	0.32187 (16)	−0.0423 (2)	0.0651 (6)	
C11	0.9062 (2)	0.17767 (19)	0.1967 (2)	0.0437 (6)	
C12	0.9337 (3)	0.1210 (2)	0.1135 (3)	0.0462 (7)	
C13	1.0644 (3)	0.0963 (2)	0.1403 (3)	0.0483 (7)	
H13	1.082847	0.058264	0.083628	0.058*	
C14	1.1674 (2)	0.1266 (2)	0.2486 (3)	0.0461 (7)	
C15	1.1424 (3)	0.1830 (2)	0.3328 (3)	0.0518 (7)	
H15	1.213819	0.20393	0.407784	0.062*	
C16	1.0126 (3)	0.2074 (2)	0.3052 (3)	0.0497 (7)	
H16	0.994989	0.245932	0.362002	0.06*	
C17	0.7666 (3)	0.2014 (2)	0.1685 (3)	0.0473 (7)	
O2	0.74959 (18)	0.25109 (16)	0.25335 (18)	0.0598 (6)	
H2	0.667349	0.259116	0.231809	0.09*	
O3	0.67159 (18)	0.17496 (15)	0.07253 (18)	0.0559 (6)	
O4	0.83565 (18)	0.08837 (17)	0.00710 (18)	0.0614 (6)	
H4	0.760984	0.105658	0.002523	0.092*	
O5	1.29304 (18)	0.09825 (15)	0.27164 (19)	0.0567 (6)	
H5	1.348308	0.124958	0.336623	0.085*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0322 (13)	0.0605 (18)	0.0483 (17)	0.0021 (12)	0.0197 (13)	0.0023 (13)
C2	0.0377 (15)	0.069 (2)	0.0518 (18)	0.0077 (13)	0.0226 (14)	0.0001 (15)
C3	0.0337 (14)	0.078 (2)	0.0557 (18)	0.0036 (14)	0.0172 (14)	−0.0056 (16)
C4	0.0418 (16)	0.097 (3)	0.066 (2)	0.0071 (16)	0.0309 (17)	−0.0140 (18)

C5	0.0379 (15)	0.088 (2)	0.0595 (19)	0.0001 (15)	0.0230 (15)	−0.0129 (17)
C6	0.0323 (14)	0.0587 (18)	0.0574 (19)	0.0000 (12)	0.0218 (15)	0.0013 (14)
C7	0.080 (3)	0.106 (3)	0.125 (4)	−0.013 (2)	0.076 (3)	−0.028 (3)
C8	0.0505 (18)	0.064 (2)	0.105 (3)	0.0021 (15)	0.050 (2)	0.0004 (19)
C9A	0.056 (4)	0.088 (4)	0.071 (5)	0.016 (3)	0.037 (4)	0.006 (4)
C10A	0.064 (4)	0.103 (5)	0.135 (6)	0.010 (3)	0.064 (4)	0.018 (4)
C9B	0.063 (8)	0.110 (10)	0.113 (11)	0.027 (7)	0.063 (8)	0.018 (10)
C10B	0.098 (9)	0.086 (9)	0.132 (10)	0.009 (7)	0.079 (8)	−0.007 (8)
N1	0.0325 (12)	0.0766 (17)	0.0606 (16)	0.0031 (11)	0.0250 (12)	−0.0011 (13)
N2	0.0351 (12)	0.0826 (19)	0.0602 (16)	0.0074 (12)	0.0237 (13)	−0.0070 (14)
N3	0.0336 (12)	0.0738 (18)	0.0819 (19)	0.0088 (11)	0.0265 (13)	0.0040 (14)
O1	0.0379 (11)	0.0789 (15)	0.0678 (15)	0.0051 (10)	0.0129 (11)	−0.0127 (12)
C11	0.0340 (13)	0.0511 (17)	0.0505 (16)	0.0028 (11)	0.0226 (13)	0.0028 (13)
C12	0.0325 (13)	0.0589 (18)	0.0467 (17)	−0.0021 (12)	0.0168 (13)	−0.0012 (13)
C13	0.0383 (14)	0.0592 (18)	0.0535 (17)	0.0019 (12)	0.0257 (14)	−0.0057 (14)
C14	0.0311 (13)	0.0525 (17)	0.0561 (18)	0.0036 (11)	0.0201 (14)	−0.0002 (13)
C15	0.0346 (14)	0.0643 (19)	0.0531 (18)	−0.0004 (12)	0.0158 (13)	−0.0096 (14)
C16	0.0364 (14)	0.0598 (18)	0.0549 (18)	0.0042 (12)	0.0216 (14)	−0.0067 (14)
C17	0.0352 (14)	0.0590 (18)	0.0507 (17)	0.0041 (12)	0.0215 (14)	0.0058 (14)
O2	0.0373 (10)	0.0837 (15)	0.0614 (13)	0.0108 (10)	0.0242 (10)	−0.0097 (11)
O3	0.0325 (10)	0.0817 (15)	0.0535 (13)	0.0023 (9)	0.0187 (10)	−0.0035 (10)
O4	0.0361 (10)	0.0921 (16)	0.0542 (13)	0.0026 (10)	0.0179 (10)	−0.0153 (11)
O5	0.0316 (10)	0.0738 (14)	0.0651 (14)	0.0044 (9)	0.0212 (10)	−0.0110 (10)

Geometric parameters (Å, º)

C1—C2	1.374 (4)	C9B—C10B	1.432 (10)
C1—C5	1.378 (4)	C9B—H9B1	0.99
C1—C6	1.500 (4)	C9B—H9B2	0.99
C2—C3	1.383 (4)	C10B—H10D	0.98
C2—H2A	0.95	C10B—H10E	0.98
C3—N2	1.319 (4)	C10B—H10F	0.98
C3—H3	0.95	N1—N3	1.379 (3)
C4—N2	1.321 (4)	N1—H1	0.88
C4—C5	1.379 (4)	C11—C16	1.386 (4)
C4—H4A	0.95	C11—C12	1.403 (4)
C5—H5A	0.95	C11—C17	1.471 (3)
C6—O1	1.215 (3)	C12—O4	1.346 (3)
C6—N1	1.329 (4)	C12—C13	1.384 (3)
C7—C8	1.496 (5)	C13—C14	1.371 (4)
C7—H7A	0.98	C13—H13	0.95
C7—H7B	0.98	C14—O5	1.355 (3)
C7—H7C	0.98	C14—C15	1.397 (4)
C8—N3	1.273 (4)	C15—C16	1.371 (3)
C8—C9B	1.447 (18)	C15—H15	0.95
C8—C9A	1.526 (9)	C16—H16	0.95
C9A—C10A	1.445 (7)	C17—O3	1.232 (3)
C9A—H9A1	0.99	C17—O2	1.308 (3)

C9A—H9A2	0.99	O2—H2	0.84
C10A—H10A	0.98	O4—H4	0.84
C10A—H10B	0.98	O5—H5	0.84
C10A—H10C	0.98		

C2—C1—C5	117.6 (2)	C10B—C9B—C8	105.9 (13)
C2—C1—C6	124.9 (2)	C10B—C9B—H9B1	110.6
C5—C1—C6	117.5 (3)	C8—C9B—H9B1	110.6
C1—C2—C3	118.8 (3)	C10B—C9B—H9B2	110.6
C1—C2—H2A	120.6	C8—C9B—H9B2	110.6
C3—C2—H2A	120.6	H9B1—C9B—H9B2	108.7
N2—C3—C2	123.8 (3)	C9B—C10B—H10D	109.5
N2—C3—H3	118.1	C9B—C10B—H10E	109.5
C2—C3—H3	118.1	H10D—C10B—H10E	109.5
N2—C4—C5	123.4 (3)	C9B—C10B—H10F	109.5
N2—C4—H4A	118.3	H10D—C10B—H10F	109.5
C5—C4—H4A	118.3	H10E—C10B—H10F	109.5
C1—C5—C4	119.4 (3)	C6—N1—N3	119.5 (3)
C1—C5—H5A	120.3	C6—N1—H1	120.2
C4—C5—H5A	120.3	N3—N1—H1	120.2
O1—C6—N1	123.3 (2)	C3—N2—C4	117.0 (2)
O1—C6—C1	120.5 (2)	C8—N3—N1	116.2 (3)
N1—C6—C1	116.3 (3)	C16—C11—C12	118.4 (2)
C8—C7—H7A	109.5	C16—C11—C17	122.1 (2)
C8—C7—H7B	109.5	C12—C11—C17	119.5 (2)
H7A—C7—H7B	109.5	O4—C12—C13	118.1 (2)
C8—C7—H7C	109.5	O4—C12—C11	121.9 (2)
H7A—C7—H7C	109.5	C13—C12—C11	120.1 (3)
H7B—C7—H7C	109.5	C14—C13—C12	120.1 (2)
N3—C8—C9B	133.3 (7)	C14—C13—H13	119.9
N3—C8—C7	125.0 (3)	C12—C13—H13	119.9
C9B—C8—C7	100.8 (6)	O5—C14—C13	117.7 (2)
N3—C8—C9A	112.6 (4)	O5—C14—C15	121.5 (2)
C7—C8—C9A	122.4 (4)	C13—C14—C15	120.8 (2)
C10A—C9A—C8	111.7 (6)	C16—C15—C14	118.7 (3)
C10A—C9A—H9A1	109.3	C16—C15—H15	120.7
C8—C9A—H9A1	109.3	C14—C15—H15	120.7
C10A—C9A—H9A2	109.3	C15—C16—C11	122.0 (3)
C8—C9A—H9A2	109.3	C15—C16—H16	119
H9A1—C9A—H9A2	107.9	C11—C16—H16	119
C9A—C10A—H10A	109.5	O3—C17—O2	122.1 (2)
C9A—C10A—H10B	109.5	O3—C17—C11	122.4 (3)
H10A—C10A—H10B	109.5	O2—C17—C11	115.5 (3)
C9A—C10A—H10C	109.5	C17—O2—H2	109.5
H10A—C10A—H10C	109.5	C12—O4—H4	109.5
H10B—C10A—H10C	109.5	C14—O5—H5	109.5

C5—C1—C2—C3	2.0 (4)	C9A—C8—N3—N1	174.3 (4)

C6—C1—C2—C3	−177.7 (3)	C6—N1—N3—C8	171.1 (3)
C1—C2—C3—N2	−0.6 (5)	C16—C11—C12—O4	179.1 (3)
C2—C1—C5—C4	−1.7 (5)	C17—C11—C12—O4	0.8 (4)
C6—C1—C5—C4	178.1 (3)	C16—C11—C12—C13	−0.1 (4)
N2—C4—C5—C1	−0.1 (5)	C17—C11—C12—C13	−178.5 (2)
C2—C1—C6—O1	179.6 (3)	O4—C12—C13—C14	−178.9 (3)
C5—C1—C6—O1	−0.2 (4)	C11—C12—C13—C14	0.4 (4)
C2—C1—C6—N1	−0.9 (4)	C12—C13—C14—O5	178.4 (3)
C5—C1—C6—N1	179.4 (3)	C12—C13—C14—C15	−0.3 (4)
N3—C8—C9A—C10A	116.4 (6)	O5—C14—C15—C16	−178.6 (3)
C7—C8—C9A—C10A	−65.7 (8)	C13—C14—C15—C16	0.1 (4)
N3—C8—C9B—C10B	2 (2)	C14—C15—C16—C11	0.2 (5)
C7—C8—C9B—C10B	−166.8 (13)	C12—C11—C16—C15	−0.1 (4)
O1—C6—N1—N3	−2.0 (4)	C17—C11—C16—C15	178.2 (3)
C1—C6—N1—N3	178.5 (2)	C16—C11—C17—O3	−179.7 (3)
C2—C3—N2—C4	−1.1 (5)	C12—C11—C17—O3	−1.4 (4)
C5—C4—N2—C3	1.5 (5)	C16—C11—C17—O2	−1.0 (4)
C9B—C8—N3—N1	−170.6 (12)	C12—C11—C17—O2	177.3 (2)
C7—C8—N3—N1	−3.6 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O5^{i}	0.88	2.58	3.124 (3)	121
O2—H2···N2	0.84	1.8	2.633 (3)	175
C4—H4*A*···O3	0.95	2.56	3.233 (3)	128
O4—H4···O3	0.84	1.82	2.568 (3)	147
O5—H5···O1^{ii}	0.84	1.85	2.665 (3)	163

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

N′-(Propan-2-ylidene)pyridine-4-carbohydrazide; 1-naphthoic acid (izact1nta)

Crystal data

$C_9H_{11}N_3O·C_{11}H_8O_2$
M_r = 349.38
Monoclinic, *Cc*
Hall symbol: C -2yc
a = 7.6312 (3) Å
b = 33.5293 (12) Å
c = 7.3493 (3) Å
β = 114.298 (1)°
V = 1713.88 (12) Å^3
Z = 4
F(000) = 736
D_x = 1.354 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 9944 reflections
θ = 2.4–32.0°
μ = 0.09 mm^{-1}
T = 173 K
Plate, colourless
0.72 × 0.33 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Sheldrick, 2001; Krause *et al.*, 2015)
T_{min} = 0.684, T_{max} = 0.747
39441 measured reflections
6819 independent reflections
6145 reflections with $I > 2\sigma(I)$
R_{int} = 0.056
θ_{max} = 33.7°, θ_{min} = 2.4°

$h = -11 \rightarrow 11$
$k = -52 \rightarrow 52$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.122$
$S = 1.08$
6819 reflections
238 parameters
2 restraints
0 constraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0746P)^2 + 0.0558P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Absolute structure: Flack *x* determined using 2626 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013)
Absolute structure parameter: 0.0 (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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4245 (2)	0.64077 (4)	0.5306 (3)	0.0271 (3)
H1	0.427394	0.612495	0.5399	0.033*
C2	0.2532 (2)	0.66022 (4)	0.4942 (2)	0.0245 (3)
H2	0.140806	0.645537	0.476333	0.029*
C3	0.2488 (2)	0.70167 (4)	0.4844 (2)	0.0213 (2)
C4	0.4160 (2)	0.72176 (4)	0.5094 (2)	0.0268 (3)
H4	0.417923	0.750066	0.504539	0.032*
C5	0.5808 (2)	0.69982 (5)	0.5418 (3)	0.0294 (3)
H5	0.694221	0.713739	0.556449	0.035*
C6	0.0586 (2)	0.72170 (4)	0.4316 (2)	0.0231 (2)
C7	−0.1291 (2)	0.81130 (4)	0.4976 (2)	0.0270 (3)
C8	0.0322 (3)	0.84017 (5)	0.5454 (3)	0.0378 (4)
H8A	0.099418	0.843103	0.690592	0.057*
H8B	−0.018815	0.866102	0.485523	0.057*
H8C	0.122164	0.830294	0.491653	0.057*
C9	−0.3242 (3)	0.82752 (6)	0.4609 (3)	0.0387 (4)
H9A	−0.325317	0.836275	0.587683	0.058*
H9B	−0.421165	0.806654	0.402073	0.058*
H9C	−0.353539	0.850212	0.369082	0.058*
C10	0.98959 (19)	0.54175 (4)	0.6266 (2)	0.0229 (3)
C11	1.1694 (2)	0.55617 (5)	0.6594 (2)	0.0275 (3)
H11	1.18928	0.584175	0.662443	0.033*
C12	1.3245 (2)	0.53034 (5)	0.6887 (3)	0.0330 (3)
H12	1.44702	0.54094	0.710834	0.04*
C13	1.2980 (2)	0.49021 (5)	0.6851 (3)	0.0321 (3)

H13	1.402665	0.472883	0.704124	0.039*
C14	1.1176 (2)	0.47396 (5)	0.6536 (2)	0.0263 (3)
C15	0.9586 (2)	0.49954 (4)	0.6251 (2)	0.0228 (2)
C16	0.7820 (2)	0.48134 (5)	0.5987 (3)	0.0307 (3)
H16	0.674184	0.497554	0.581332	0.037*
C17	0.7649 (3)	0.44058 (5)	0.5979 (3)	0.0362 (4)
H17	0.645341	0.429103	0.580891	0.043*
C18	0.9200 (3)	0.41547 (5)	0.6216 (3)	0.0375 (4)
H18	0.905031	0.38732	0.618488	0.045*
C19	1.0922 (3)	0.43199 (5)	0.6491 (3)	0.0340 (3)
H19	1.197449	0.415057	0.665593	0.041*
C20	0.8321 (2)	0.57131 (4)	0.5883 (2)	0.0249 (3)
N1	0.58678 (19)	0.65991 (4)	0.5534 (2)	0.0284 (3)
N2	0.06057 (18)	0.75731 (4)	0.5167 (2)	0.0249 (2)
H2A	0.168276	0.76959	0.591197	0.03*
N3	−0.12045 (19)	0.77355 (4)	0.4788 (2)	0.0270 (3)
O1	−0.08842 (17)	0.70564 (3)	0.3110 (2)	0.0312 (3)
O2	0.89085 (18)	0.60918 (3)	0.6040 (2)	0.0338 (3)
H2B	0.797958	0.62443	0.58666	0.051*
O3	0.66461 (19)	0.56323 (4)	0.5423 (3)	0.0446 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0247 (6)	0.0208 (5)	0.0370 (7)	0.0017 (5)	0.0138 (6)	0.0004 (5)
C2	0.0205 (6)	0.0196 (5)	0.0317 (7)	−0.0001 (4)	0.0090 (5)	0.0007 (5)
C3	0.0190 (5)	0.0195 (5)	0.0236 (6)	0.0011 (4)	0.0069 (5)	0.0001 (5)
C4	0.0251 (6)	0.0204 (5)	0.0359 (8)	−0.0021 (5)	0.0137 (6)	−0.0015 (5)
C5	0.0240 (7)	0.0260 (6)	0.0415 (8)	−0.0031 (5)	0.0169 (6)	−0.0027 (6)
C6	0.0199 (6)	0.0187 (5)	0.0274 (6)	0.0004 (4)	0.0064 (5)	0.0021 (5)
C7	0.0292 (7)	0.0231 (6)	0.0262 (6)	0.0057 (5)	0.0088 (6)	0.0027 (5)
C8	0.0355 (9)	0.0235 (7)	0.0441 (10)	−0.0003 (6)	0.0062 (7)	0.0027 (6)
C9	0.0390 (9)	0.0343 (8)	0.0450 (10)	0.0149 (7)	0.0195 (8)	0.0070 (7)
C10	0.0184 (6)	0.0237 (6)	0.0272 (6)	0.0007 (4)	0.0100 (5)	−0.0006 (5)
C11	0.0196 (6)	0.0282 (7)	0.0352 (7)	−0.0008 (5)	0.0117 (6)	0.0042 (6)
C12	0.0199 (6)	0.0389 (8)	0.0415 (9)	0.0038 (6)	0.0138 (6)	0.0094 (7)
C13	0.0246 (7)	0.0364 (8)	0.0373 (8)	0.0094 (6)	0.0147 (6)	0.0083 (6)
C14	0.0266 (7)	0.0263 (6)	0.0263 (6)	0.0056 (5)	0.0113 (6)	0.0037 (5)
C15	0.0211 (6)	0.0223 (6)	0.0247 (6)	0.0008 (5)	0.0091 (5)	−0.0005 (5)
C16	0.0252 (7)	0.0242 (6)	0.0422 (9)	−0.0023 (5)	0.0133 (6)	−0.0025 (6)
C17	0.0316 (8)	0.0253 (7)	0.0475 (10)	−0.0054 (6)	0.0121 (7)	−0.0022 (6)
C18	0.0416 (9)	0.0223 (7)	0.0428 (9)	0.0002 (6)	0.0115 (8)	−0.0022 (6)
C19	0.0377 (9)	0.0255 (7)	0.0368 (8)	0.0089 (6)	0.0134 (7)	0.0025 (6)
C20	0.0212 (6)	0.0213 (6)	0.0338 (7)	−0.0011 (5)	0.0129 (5)	−0.0033 (5)
N1	0.0233 (6)	0.0260 (6)	0.0386 (7)	0.0013 (5)	0.0155 (5)	−0.0018 (5)
N2	0.0189 (5)	0.0204 (5)	0.0307 (6)	0.0019 (4)	0.0054 (5)	−0.0012 (4)
N3	0.0214 (5)	0.0241 (6)	0.0337 (7)	0.0038 (4)	0.0095 (5)	0.0017 (4)
O1	0.0211 (5)	0.0240 (5)	0.0382 (6)	0.0005 (4)	0.0017 (4)	−0.0036 (4)

O2	0.0219 (5)	0.0207 (5)	0.0578 (8)	−0.0017 (4)	0.0152 (5)	−0.0047 (5)
O3	0.0235 (6)	0.0256 (5)	0.0863 (12)	−0.0018 (4)	0.0242 (6)	−0.0063 (6)

Geometric parameters (Å, º)

C1—N1	1.342 (2)	C10—C15	1.4344 (19)
C1—C2	1.385 (2)	C10—C20	1.4923 (19)
C1—H1	0.95	C11—C12	1.409 (2)
C2—C3	1.3914 (18)	C11—H11	0.95
C2—H2	0.95	C12—C13	1.359 (2)
C3—C4	1.386 (2)	C12—H12	0.95
C3—C6	1.4987 (19)	C13—C14	1.409 (2)
C4—C5	1.390 (2)	C13—H13	0.95
C4—H4	0.95	C14—C19	1.419 (2)
C5—N1	1.340 (2)	C14—C15	1.4293 (19)
C5—H5	0.95	C15—C16	1.418 (2)
C6—O1	1.2311 (18)	C16—C17	1.372 (2)
C6—N2	1.3450 (18)	C16—H16	0.95
C7—N3	1.2778 (19)	C17—C18	1.403 (3)
C7—C8	1.490 (2)	C17—H17	0.95
C7—C9	1.501 (2)	C18—C19	1.362 (3)
C8—H8A	0.98	C18—H18	0.95
C8—H8B	0.98	C19—H19	0.95
C8—H8C	0.98	C20—O3	1.2109 (18)
C9—H9A	0.98	C20—O2	1.3357 (17)
C9—H9B	0.98	N2—N3	1.4021 (17)
C9—H9C	0.98	N2—H2A	0.88
C10—C11	1.3794 (19)	O2—H2B	0.84
N1—C1—C2	123.21 (13)	C10—C11—C12	121.57 (14)
N1—C1—H1	118.4	C10—C11—H11	119.2
C2—C1—H1	118.4	C12—C11—H11	119.2
C1—C2—C3	118.74 (13)	C13—C12—C11	119.80 (15)
C1—C2—H2	120.6	C13—C12—H12	120.1
C3—C2—H2	120.6	C11—C12—H12	120.1
C4—C3—C2	118.52 (12)	C12—C13—C14	120.87 (14)
C4—C3—C6	123.86 (12)	C12—C13—H13	119.6
C2—C3—C6	117.45 (12)	C14—C13—H13	119.6
C3—C4—C5	118.92 (12)	C13—C14—C19	120.15 (14)
C3—C4—H4	120.5	C13—C14—C15	120.38 (14)
C5—C4—H4	120.5	C19—C14—C15	119.47 (14)
N1—C5—C4	122.97 (13)	C16—C15—C14	117.61 (13)
N1—C5—H5	118.5	C16—C15—C10	124.78 (13)
C4—C5—H5	118.5	C14—C15—C10	117.61 (13)
O1—C6—N2	123.76 (14)	C17—C16—C15	120.83 (15)
O1—C6—C3	119.27 (13)	C17—C16—H16	119.6
N2—C6—C3	116.95 (12)	C15—C16—H16	119.6
N3—C7—C8	126.46 (15)	C16—C17—C18	121.53 (16)

N3—C7—C9	115.53 (15)	C16—C17—H17	119.2
C8—C7—C9	117.98 (14)	C18—C17—H17	119.2
C7—C8—H8A	109.5	C19—C18—C17	119.15 (15)
C7—C8—H8B	109.5	C19—C18—H18	120.4
H8A—C8—H8B	109.5	C17—C18—H18	120.4
C7—C8—H8C	109.5	C18—C19—C14	121.39 (15)
H8A—C8—H8C	109.5	C18—C19—H19	119.3
H8B—C8—H8C	109.5	C14—C19—H19	119.3
C7—C9—H9A	109.5	O3—C20—O2	120.99 (13)
C7—C9—H9B	109.5	O3—C20—C10	125.43 (13)
H9A—C9—H9B	109.5	O2—C20—C10	113.56 (12)
C7—C9—H9C	109.5	C5—N1—C1	117.63 (13)
H9A—C9—H9C	109.5	C6—N2—N3	115.52 (12)
H9B—C9—H9C	109.5	C6—N2—H2A	122.2
C11—C10—C15	119.76 (12)	N3—N2—H2A	122.2
C11—C10—C20	117.79 (13)	C7—N3—N2	117.00 (13)
C15—C10—C20	122.43 (12)	C20—O2—H2B	109.5

N1—C1—C2—C3	−1.3 (3)	C20—C10—C15—C16	−3.5 (2)
C1—C2—C3—C4	0.6 (2)	C11—C10—C15—C14	−1.5 (2)
C1—C2—C3—C6	176.11 (14)	C20—C10—C15—C14	176.86 (13)
C2—C3—C4—C5	0.5 (2)	C14—C15—C16—C17	−0.9 (2)
C6—C3—C4—C5	−174.67 (14)	C10—C15—C16—C17	179.51 (16)
C3—C4—C5—N1	−1.1 (3)	C15—C16—C17—C18	−0.5 (3)
C4—C3—C6—O1	139.64 (16)	C16—C17—C18—C19	1.0 (3)
C2—C3—C6—O1	−35.6 (2)	C17—C18—C19—C14	−0.2 (3)
C4—C3—C6—N2	−38.5 (2)	C13—C14—C19—C18	179.09 (18)
C2—C3—C6—N2	146.30 (14)	C15—C14—C19—C18	−1.1 (3)
C15—C10—C11—C12	1.1 (2)	C11—C10—C20—O3	174.12 (18)
C20—C10—C11—C12	−177.37 (15)	C15—C10—C20—O3	−4.3 (2)
C10—C11—C12—C13	−0.1 (3)	C11—C10—C20—O2	−4.2 (2)
C11—C12—C13—C14	−0.4 (3)	C15—C10—C20—O2	177.43 (14)
C12—C13—C14—C19	179.62 (17)	C4—C5—N1—C1	0.6 (3)
C12—C13—C14—C15	−0.1 (2)	C2—C1—N1—C5	0.6 (3)
C13—C14—C15—C16	−178.58 (15)	O1—C6—N2—N3	7.5 (2)
C19—C14—C15—C16	1.7 (2)	C3—C6—N2—N3	−174.42 (12)
C13—C14—C15—C10	1.1 (2)	C8—C7—N3—N2	3.5 (2)
C19—C14—C15—C10	−178.71 (15)	C9—C7—N3—N2	−178.53 (14)
C11—C10—C15—C16	178.10 (15)	C6—N2—N3—C7	−157.47 (14)

_N′_-(Butan-2-ylidene)pyridine-4-carbohydrazide; 2-chloro-4-nitrobenzoic acid (izbt2c4n)

Crystal data

$C_7H_4ClNO_4·C_{10}H_{13}N_3O$	c = 7.6124 (3) Å
M_r = 392.79	β = 111.081 (2)°
Monoclinic, $P2_1/n$	V = 1759.27 (13) Å^3
Hall symbol: -P 2yn	Z = 4
a = 7.2682 (3) Å	$F(000)$ = 816
b = 34.0775 (15) Å	D_x = 1.483 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9966 reflections
θ = 2.4–30.8°
μ = 0.26 mm^{-1}

T = 173 K
Plate, colourless
0.46 × 0.26 × 0.11 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
111394 measured reflections
5624 independent reflections
5056 reflections with $I > 2\sigma(I)$

R_{int} = 0.081
θ_{max} = 31.1°, θ_{min} = 2.4°
h = −10→10
k = −49→49
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.129
S = 1.07
5624 reflections
250 parameters
0 restraints
0 constraints
Primary atom site location: dual

Secondary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0581P)^2 + 0.7134P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.41 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.34552 (19)	0.70488 (4)	0.34294 (16)	0.0265 (2)
H1	0.338196	0.718339	0.231343	0.032*
C2	0.36445 (17)	0.72661 (3)	0.50281 (16)	0.0236 (2)
H2A	0.368392	0.754461	0.500126	0.028*
C3	0.37753 (15)	0.70697 (3)	0.66653 (14)	0.01940 (19)
C4	0.37152 (18)	0.66621 (3)	0.66495 (16)	0.0239 (2)
H4	0.382589	0.651968	0.77559	0.029*
C5	0.34909 (19)	0.64679 (4)	0.49885 (18)	0.0281 (2)
H5	0.341789	0.61895	0.496836	0.034*
C6	0.41408 (16)	0.72790 (3)	0.84962 (14)	0.01968 (19)
C7	0.35850 (16)	0.82289 (3)	0.97889 (16)	0.0224 (2)
C8	0.3268 (2)	0.84432 (4)	0.79821 (18)	0.0308 (3)
H8A	0.398513	0.830927	0.728525	0.046*
H8B	0.375439	0.871288	0.826095	0.046*
H8C	0.185714	0.844755	0.721955	0.046*
C9	0.38785 (18)	0.84802 (3)	1.14869 (17)	0.0252 (2)
H9A	0.270812	0.865116	1.122133	0.03*
H9B	0.502954	0.865278	1.167495	0.03*

C10	0.4201 (2)	0.82623 (4)	1.33066 (18)	0.0306 (3)
H10A	0.303647	0.81027	1.317269	0.046*
H10B	0.441788	0.84514	1.43314	0.046*
H10C	0.535749	0.809159	1.35937	0.046*
C11	0.2577 (2)	0.55646 (4)	−0.06804 (19)	0.0329 (3)
C12	0.4153 (2)	0.55063 (4)	−0.12851 (19)	0.0359 (3)
C13	0.4172 (3)	0.51828 (4)	−0.2402 (2)	0.0497 (5)
H13	0.524522	0.513935	−0.281211	0.06*
C14	0.2596 (4)	0.49280 (4)	−0.2897 (2)	0.0552 (5)
C15	0.1001 (3)	0.49746 (5)	−0.2356 (2)	0.0532 (5)
H15	−0.006369	0.479348	−0.272787	0.064*
C16	0.1008 (3)	0.52969 (4)	−0.1245 (2)	0.0429 (4)
H16	−0.008083	0.533764	−0.085449	0.051*
C17	0.2412 (2)	0.58813 (4)	0.0638 (2)	0.0339 (3)
Cl01	0.62203 (6)	0.58034 (2)	−0.06254 (6)	0.04457 (12)
N1	0.33722 (16)	0.66570 (3)	0.34045 (15)	0.0273 (2)
N2	0.33516 (15)	0.76384 (3)	0.83540 (13)	0.02305 (19)
H2	0.264867	0.773703	0.724711	0.028*
N3	0.36705 (15)	0.78542 (3)	1.00102 (13)	0.02341 (19)
N4	0.2662 (4)	0.45802 (4)	−0.4029 (2)	0.0803 (8)
O1	0.51772 (13)	0.71240 (2)	0.99850 (11)	0.02553 (18)
O2	0.33658 (16)	0.62034 (3)	0.06437 (13)	0.0320 (2)
O3	0.1408 (3)	0.58288 (4)	0.1583 (3)	0.0712 (5)
O4	0.4196 (5)	0.45158 (5)	−0.4308 (3)	0.1193 (10)
O5	0.1146 (4)	0.43750 (4)	−0.4613 (2)	0.0987 (8)
H2B	0.326 (4)	0.6369 (7)	0.163 (4)	0.075 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0313 (6)	0.0300 (6)	0.0208 (5)	0.0006 (4)	0.0124 (4)	−0.0006 (4)
C2	0.0288 (5)	0.0221 (5)	0.0216 (5)	0.0003 (4)	0.0111 (4)	0.0005 (4)
C3	0.0186 (4)	0.0216 (5)	0.0174 (4)	0.0007 (3)	0.0058 (4)	−0.0007 (3)
C4	0.0277 (5)	0.0213 (5)	0.0217 (5)	0.0014 (4)	0.0077 (4)	0.0004 (4)
C5	0.0338 (6)	0.0226 (5)	0.0280 (6)	0.0006 (4)	0.0111 (5)	−0.0040 (4)
C6	0.0202 (4)	0.0208 (5)	0.0171 (4)	−0.0010 (4)	0.0055 (4)	−0.0004 (3)
C7	0.0212 (5)	0.0239 (5)	0.0210 (5)	−0.0006 (4)	0.0063 (4)	−0.0018 (4)
C8	0.0407 (7)	0.0259 (5)	0.0234 (5)	−0.0039 (5)	0.0085 (5)	0.0009 (4)
C9	0.0292 (5)	0.0228 (5)	0.0243 (5)	−0.0011 (4)	0.0107 (4)	−0.0033 (4)
C10	0.0371 (6)	0.0318 (6)	0.0242 (5)	−0.0035 (5)	0.0127 (5)	−0.0014 (4)
C11	0.0482 (8)	0.0233 (5)	0.0264 (6)	0.0043 (5)	0.0123 (5)	−0.0024 (4)
C12	0.0565 (9)	0.0266 (6)	0.0269 (6)	0.0121 (6)	0.0178 (6)	0.0037 (5)
C13	0.0922 (14)	0.0308 (7)	0.0333 (7)	0.0233 (8)	0.0313 (8)	0.0064 (6)
C14	0.1142 (17)	0.0216 (6)	0.0247 (6)	0.0129 (8)	0.0189 (8)	−0.0011 (5)
C15	0.0877 (14)	0.0268 (7)	0.0341 (8)	−0.0060 (8)	0.0087 (8)	−0.0048 (6)
C16	0.0588 (10)	0.0281 (6)	0.0367 (7)	−0.0036 (6)	0.0111 (7)	−0.0052 (5)
C17	0.0411 (7)	0.0288 (6)	0.0351 (7)	−0.0022 (5)	0.0176 (6)	−0.0086 (5)
Cl01	0.0506 (2)	0.0406 (2)	0.0516 (2)	0.01217 (15)	0.02936 (18)	0.00589 (15)

N1	0.0296 (5)	0.0295 (5)	0.0239 (5)	0.0001 (4)	0.0109 (4)	−0.0059 (4)
N2	0.0280 (5)	0.0215 (4)	0.0159 (4)	0.0033 (3)	0.0035 (3)	−0.0019 (3)
N3	0.0259 (5)	0.0242 (4)	0.0180 (4)	0.0014 (3)	0.0053 (3)	−0.0039 (3)
N4	0.180 (2)	0.0260 (7)	0.0347 (7)	0.0174 (10)	0.0383 (11)	−0.0012 (6)
O1	0.0293 (4)	0.0247 (4)	0.0179 (4)	0.0024 (3)	0.0028 (3)	0.0015 (3)
O2	0.0455 (5)	0.0255 (4)	0.0291 (4)	−0.0021 (4)	0.0184 (4)	−0.0069 (3)
O3	0.0978 (12)	0.0514 (8)	0.0994 (12)	−0.0357 (8)	0.0777 (11)	−0.0389 (8)
O4	0.243 (3)	0.0530 (10)	0.0986 (15)	0.0310 (14)	0.1064 (19)	−0.0144 (9)
O5	0.199 (2)	0.0292 (6)	0.0447 (8)	0.0000 (10)	0.0163 (11)	−0.0110 (6)

Geometric parameters (Å, º)

C1—N1	1.3361 (16)	C10—H10A	0.98
C1—C2	1.3885 (16)	C10—H10B	0.98
C1—H1	0.95	C10—H10C	0.98
C2—C3	1.3874 (15)	C11—C12	1.394 (2)
C2—H2A	0.95	C11—C16	1.402 (2)
C3—C4	1.3897 (15)	C11—C17	1.5076 (18)
C3—C6	1.5019 (14)	C12—C13	1.396 (2)
C4—C5	1.3838 (16)	C12—Cl01	1.7297 (17)
C4—H4	0.95	C13—C14	1.377 (3)
C5—N1	1.3423 (16)	C13—H13	0.95
C5—H5	0.95	C14—C15	1.372 (3)
C6—O1	1.2316 (13)	C14—N4	1.476 (2)
C6—N2	1.3400 (14)	C15—C16	1.385 (2)
C7—N3	1.2865 (15)	C15—H15	0.95
C7—C8	1.5001 (16)	C16—H16	0.95
C7—C9	1.5004 (16)	C17—O3	1.2077 (19)
C8—H8A	0.98	C17—O2	1.2974 (17)
C8—H8B	0.98	N2—N3	1.4051 (13)
C8—H8C	0.98	N2—H2	0.88
C9—C10	1.5139 (17)	N4—O4	1.228 (4)
C9—H9A	0.99	N4—O5	1.244 (3)
C9—H9B	0.99	O2—H2B	0.96 (3)
N1—C1—C2	122.35 (11)	H10A—C10—H10B	109.5
N1—C1—H1	118.8	C9—C10—H10C	109.5
C2—C1—H1	118.8	H10A—C10—H10C	109.5
C3—C2—C1	118.89 (11)	H10B—C10—H10C	109.5
C3—C2—H2A	120.6	C12—C11—C16	118.74 (13)
C1—C2—H2A	120.6	C12—C11—C17	126.39 (13)
C2—C3—C4	118.86 (10)	C16—C11—C17	114.78 (14)
C2—C3—C6	122.45 (10)	C11—C12—C13	120.22 (16)
C4—C3—C6	118.51 (9)	C11—C12—Cl01	123.50 (11)
C5—C4—C3	118.61 (11)	C13—C12—Cl01	116.19 (14)
C5—C4—H4	120.7	C14—C13—C12	118.36 (18)
C3—C4—H4	120.7	C14—C13—H13	120.8
N1—C5—C4	122.66 (11)	C12—C13—H13	120.8

N1—C5—H5	118.7	C15—C14—C13	123.66 (14)
C4—C5—H5	118.7	C15—C14—N4	118.4 (2)
O1—C6—N2	124.65 (10)	C13—C14—N4	117.9 (2)
O1—C6—C3	119.72 (10)	C14—C15—C16	117.22 (18)
N2—C6—C3	115.56 (9)	C14—C15—H15	121.4
N3—C7—C8	125.98 (10)	C16—C15—H15	121.4
N3—C7—C9	117.93 (10)	C15—C16—C11	121.79 (18)
C8—C7—C9	116.07 (10)	C15—C16—H16	119.1
C7—C8—H8A	109.5	C11—C16—H16	119.1
C7—C8—H8B	109.5	O3—C17—O2	124.04 (13)
H8A—C8—H8B	109.5	O3—C17—C11	120.00 (13)
C7—C8—H8C	109.5	O2—C17—C11	115.95 (12)
H8A—C8—H8C	109.5	C1—N1—C5	118.62 (10)
H8B—C8—H8C	109.5	C6—N2—N3	118.58 (9)
C7—C9—C10	115.82 (10)	C6—N2—H2	120.7
C7—C9—H9A	108.3	N3—N2—H2	120.7
C10—C9—H9A	108.3	C7—N3—N2	114.68 (10)
C7—C9—H9B	108.3	O4—N4—O5	125.48 (19)
C10—C9—H9B	108.3	O4—N4—C14	117.8 (2)
H9A—C9—H9B	107.4	O5—N4—C14	116.7 (2)
C9—C10—H10A	109.5	C17—O2—H2B	107.9 (15)
C9—C10—H10B	109.5		

N1—C1—C2—C3	0.76 (18)	C13—C14—C15—C16	−0.3 (3)
C1—C2—C3—C4	0.10 (17)	N4—C14—C15—C16	178.00 (15)
C1—C2—C3—C6	175.11 (10)	C14—C15—C16—C11	−0.4 (2)
C2—C3—C4—C5	−1.16 (17)	C12—C11—C16—C15	1.1 (2)
C6—C3—C4—C5	−176.37 (11)	C17—C11—C16—C15	−175.78 (14)
C3—C4—C5—N1	1.49 (19)	C12—C11—C17—O3	−153.35 (18)
C2—C3—C6—O1	−143.50 (12)	C16—C11—C17—O3	23.2 (2)
C4—C3—C6—O1	31.53 (15)	C12—C11—C17—O2	27.9 (2)
C2—C3—C6—N2	33.63 (15)	C16—C11—C17—O2	−155.51 (13)
C4—C3—C6—N2	−151.34 (11)	C2—C1—N1—C5	−0.49 (19)
N3—C7—C9—C10	−1.45 (16)	C4—C5—N1—C1	−0.66 (19)
C8—C7—C9—C10	−179.90 (11)	O1—C6—N2—N3	−1.73 (17)
C16—C11—C12—C13	−1.1 (2)	C3—C6—N2—N3	−178.70 (9)
C17—C11—C12—C13	175.29 (14)	C8—C7—N3—N2	−2.66 (17)
C16—C11—C12—Cl01	−177.59 (11)	C9—C7—N3—N2	179.06 (10)
C17—C11—C12—Cl01	−1.2 (2)	C6—N2—N3—C7	153.96 (11)
C11—C12—C13—C14	0.6 (2)	C15—C14—N4—O4	−171.23 (19)
Cl01—C12—C13—C14	177.25 (11)	C13—C14—N4—O4	7.1 (3)
C12—C13—C14—C15	0.2 (2)	C15—C14—N4—O5	8.4 (2)
C12—C13—C14—N4	−178.11 (13)	C13—C14—N4—O5	−173.23 (15)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.88	2.05	2.8809 (13)	158

C4—H4···O2^{ii}	0.95	2.58	3.5082 (15)	167
C1—H1···O1^{iii}	0.95	2.56	3.2966 (15)	135
C8—H8*B*···O5^{iv}	0.98	2.47	3.380 (2)	154
C8—H8*C*···O1^{i}	0.98	2.59	3.2095 (15)	122
C13—H13···O4^{v}	0.95	2.64	3.297 (3)	126
C15—H15···O3^{vi}	0.95	2.61	3.413 (2)	142
O2—H2*B*···N1	0.96 (3)	1.65 (3)	2.6076 (13)	173 (2)
N2—H2···O1^{i}	0.88	2.05	2.8809 (13)	158
C4—H4···O2^{ii}	0.95	2.58	3.5082 (15)	167
C1—H1···O1^{iii}	0.95	2.56	3.2966 (15)	135
C8—H8*B*···O5^{iv}	0.98	2.47	3.380 (2)	154
C8—H8*C*···O1^{i}	0.98	2.59	3.2095 (15)	122
C13—H13···O4^{v}	0.95	2.64	3.297 (3)	126
C15—H15···O3^{vi}	0.95	2.61	3.413 (2)	142
O2—H2*B*···N1	0.96 (3)	1.65 (3)	2.6076 (13)	173 (2)

Symmetry codes: (i) $x-1/2, -y+3/2, z-1/2$; (ii) $x, y, z+1$; (iii) $x, y, z-1$; (iv) $-x+1/2, y+1/2, -z+1/2$; (v) $-x+1, -y+1, -z-1$; (vi) $-x, -y+1, -z$.

N′-(Butan-2-ylidene)pyridine-4-carbohydrazide; 2,5-dihydroxybenzoic acid (izbt25dhba)

Crystal data

$C_{10}H_{13}N_3O{\cdot}C_7H_6O_4$
$M_r = 345.35$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 9.2054$ (3) Å
$b = 11.5589$ (4) Å
$c = 15.6268$ (6) Å
$\alpha = 92.383$ (2)°
$\beta = 93.092$ (2)°
$\gamma = 90.666$ (2)°
$V = 1658.74$ (10) Å^3
$Z = 4$
$F(000) = 728$
$D_x = 1.383$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9903 reflections
$\theta = 2.2$–$27.3°$
$\mu = 0.10$ mm^{-1}
$T = 123$ K
Plate, colourless
0.45 × 0.38 × 0.13 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
73254 measured reflections
8026 independent reflections
5972 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 28°$, $\theta_{min} = 1.8°$
$h = -12\rightarrow12$
$k = -15\rightarrow15$
$l = -20\rightarrow20$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.191$
$S = 1.04$
8026 reflections
506 parameters
21 restraints
0 constraints
Primary atom site location: dual
Secondary atom site location: dual
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0779P)^2 + 1.3095P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.33$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
C1	0.2112 (3)	0.59980 (18)	0.42485 (14)	0.0394 (5)	
H1	0.228948	0.524065	0.444016	0.047*	
C2	0.1065 (2)	0.61362 (17)	0.36000 (14)	0.0350 (4)	
H2	0.05337	0.548625	0.335013	0.042*	
C3	0.0796 (2)	0.72412 (16)	0.33160 (13)	0.0302 (4)	
C4	0.1587 (2)	0.81679 (16)	0.37099 (13)	0.0315 (4)	
H4	0.141596	0.893651	0.354046	0.038*	
C5	0.2624 (2)	0.79498 (17)	0.43507 (14)	0.0332 (4)	
H5	0.317352	0.858236	0.461266	0.04*	
C6	−0.0350 (2)	0.75020 (17)	0.26420 (15)	0.0349 (4)	
C7	−0.2250 (4)	0.5985 (2)	0.0953 (2)	0.0687 (9)	
C8	−0.1519 (4)	0.4878 (2)	0.0876 (2)	0.0647 (8)	
H8A	−0.04954	0.501106	0.076189	0.097*	
H8B	−0.199055	0.440653	0.04015	0.097*	
H8C	−0.158024	0.447199	0.141079	0.097*	
C9	−0.3335 (6)	0.6135 (4)	0.0212 (3)	0.0541 (16)	0.625 (10)
H9A	−0.288822	0.587217	−0.032332	0.065*	0.625 (10)
H9B	−0.418717	0.562531	0.028434	0.065*	0.625 (10)
C10	−0.3857 (7)	0.7345 (6)	0.0110 (4)	0.074 (2)	0.625 (10)
H10A	−0.461649	0.734997	−0.035398	0.111*	0.625 (10)
H10B	−0.304234	0.784378	−0.002877	0.111*	0.625 (10)
H10C	−0.425497	0.763312	0.064652	0.111*	0.625 (10)
C11	0.6568 (2)	0.73609 (16)	0.68602 (14)	0.0332 (4)	
C12	0.7330 (2)	0.83240 (17)	0.72385 (17)	0.0407 (5)	
C13	0.8377 (3)	0.81677 (18)	0.78881 (18)	0.0451 (6)	
H13	0.89199	0.881548	0.813175	0.054*	
C14	0.8644 (3)	0.70739 (19)	0.81880 (17)	0.0423 (5)	
H14	0.936431	0.697752	0.863681	0.051*	
C15	0.7863 (2)	0.61188 (16)	0.78356 (14)	0.0337 (4)	
C16	0.6847 (2)	0.62589 (16)	0.71685 (13)	0.0318 (4)	
H16	0.633109	0.560325	0.69155	0.038*	
C17	0.5472 (3)	0.75068 (18)	0.61543 (14)	0.0375 (5)	
C18	0.2402 (2)	0.30223 (17)	0.56766 (15)	0.0378 (5)	
H18	0.184874	0.361575	0.541748	0.045*	
C19	0.3424 (2)	0.33290 (17)	0.63206 (15)	0.0373 (5)	
H19	0.358276	0.411827	0.649888	0.045*	
C20	0.4225 (2)	0.24569 (17)	0.67075 (16)	0.0365 (5)	
C21	0.3967 (2)	0.13173 (17)	0.64134 (17)	0.0411 (5)	
H21	0.450213	0.070407	0.665901	0.049*	

C22	0.2930 (3)	0.10924 (18)	0.57636 (16)	0.0430 (5)	
H22	0.275925	0.031203	0.556543	0.052*	
C23	0.5371 (2)	0.28117 (18)	0.73810 (17)	0.0405 (5)	
C24	0.7335 (3)	0.1562 (2)	0.9060 (2)	0.0587 (7)	
C25	0.6514 (4)	0.0440 (2)	0.9189 (2)	0.0685 (9)	
H25A	0.698797	0.00369	0.966535	0.103*	
H25B	0.550861	0.061286	0.931974	0.103*	
H25C	0.651695	−0.005447	0.866372	0.103*	
C26	0.8651 (4)	0.1869 (3)	0.9665 (3)	0.0792 (10)	
H26A	0.896188	0.267519	0.957394	0.095*	
H26B	0.836178	0.183245	1.026426	0.095*	
C27A	0.9875 (6)	0.1110 (6)	0.9547 (4)	0.108 (2)	0.773 (9)
H27A	1.068248	0.135148	0.995175	0.161*	0.773 (9)
H27B	0.958489	0.031188	0.964948	0.161*	0.773 (9)
H27C	1.018548	0.11553	0.895861	0.161*	0.773 (9)
C27B	0.988 (2)	0.239 (3)	0.932 (2)	0.164 (10)	0.227 (9)
H27D	1.063797	0.254299	0.977489	0.246*	0.227 (9)
H27E	1.025203	0.187517	0.887217	0.246*	0.227 (9)
H27F	0.959234	0.312707	0.906915	0.246*	0.227 (9)
C28	−0.1528 (2)	0.21103 (17)	0.31637 (15)	0.0359 (5)	
C29	−0.2306 (3)	0.30216 (18)	0.28099 (18)	0.0444 (6)	
C30	−0.3371 (3)	0.2784 (2)	0.2164 (2)	0.0506 (6)	
H30	−0.393105	0.339704	0.193844	0.061*	
C31	−0.3626 (3)	0.1658 (2)	0.18448 (19)	0.0472 (6)	
H31	−0.435107	0.150553	0.139709	0.057*	
C32	−0.2823 (2)	0.07531 (17)	0.21785 (15)	0.0374 (5)	
C33	−0.1794 (2)	0.09764 (17)	0.28375 (14)	0.0342 (4)	
H33	−0.125851	0.035639	0.307325	0.041*	
C34	−0.0415 (3)	0.23411 (18)	0.38673 (15)	0.0394 (5)	
N1	0.2889 (2)	0.68817 (15)	0.46199 (11)	0.0370 (4)	
N2	−0.0756 (2)	0.66280 (16)	0.20764 (14)	0.0439 (5)	
N3	−0.1888 (3)	0.6817 (2)	0.1479 (2)	0.0776 (9)	
N4	0.2149 (2)	0.19217 (15)	0.53972 (13)	0.0401 (4)	
N5	0.5822 (2)	0.20013 (16)	0.79252 (15)	0.0432 (5)	
N6	0.7001 (2)	0.22903 (18)	0.84909 (16)	0.0526 (6)	
O1	−0.08959 (17)	0.84598 (13)	0.26287 (12)	0.0440 (4)	
O2	0.49050 (19)	0.65507 (13)	0.58071 (10)	0.0423 (4)	
H2B	0.423495	0.670814	0.544597	0.063*	
O3	0.51263 (19)	0.84794 (13)	0.59033 (11)	0.0456 (4)	
O4	0.7059 (2)	0.94157 (13)	0.69790 (14)	0.0548 (5)	
H4A	0.644075	0.938517	0.656275	0.082*	
O5	0.81552 (18)	0.50542 (12)	0.81722 (10)	0.0380 (4)	
O6	0.58774 (19)	0.37970 (14)	0.74097 (14)	0.0543 (5)	
O7	0.0166 (2)	0.14267 (13)	0.41965 (10)	0.0448 (4)	
H7	0.080114	0.163181	0.458094	0.067*	
O8	−0.0078 (2)	0.33425 (13)	0.41276 (11)	0.0479 (4)	
O9	−0.2047 (2)	0.41438 (14)	0.30888 (16)	0.0575 (5)	
O10	−0.31118 (18)	−0.03452 (13)	0.18240 (12)	0.0434 (4)	

C9A	−0.4007 (9)	0.6164 (8)	0.0684 (6)	0.061 (3)	0.375 (10)
H9AA	−0.456209	0.542674	0.069361	0.074*	0.375 (10)
H9AB	−0.444497	0.674963	0.106875	0.074*	0.375 (10)
C10A	−0.3944 (13)	0.6563 (13)	−0.0178 (11)	0.099 (5)	0.375 (10)
H10D	−0.355335	0.595055	−0.054862	0.149*	0.375 (10)
H10E	−0.331215	0.725178	−0.017286	0.149*	0.375 (10)
H10F	−0.492491	0.67574	−0.039729	0.149*	0.375 (10)
H2A	−0.020 (3)	0.600 (2)	0.2030 (16)	0.044 (7)*	
H5B	0.742 (3)	0.460 (3)	0.7997 (19)	0.061 (9)*	
H5A	0.526 (4)	0.137 (3)	0.798 (2)	0.075 (10)*	
H9	−0.134 (5)	0.409 (4)	0.349 (3)	0.127 (19)*	
H10	−0.239 (4)	−0.082 (3)	0.207 (2)	0.088 (12)*	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0562 (14)	0.0226 (9)	0.0405 (11)	0.0040 (9)	0.0094 (10)	0.0040 (8)
C2	0.0423 (11)	0.0194 (9)	0.0440 (11)	−0.0030 (8)	0.0112 (9)	−0.0006 (8)
C3	0.0279 (9)	0.0205 (8)	0.0426 (11)	0.0002 (7)	0.0084 (8)	−0.0016 (7)
C4	0.0312 (10)	0.0189 (8)	0.0445 (11)	−0.0001 (7)	0.0042 (8)	0.0002 (7)
C5	0.0351 (10)	0.0232 (9)	0.0413 (11)	0.0015 (7)	0.0046 (8)	−0.0025 (8)
C6	0.0260 (9)	0.0240 (9)	0.0542 (12)	0.0000 (7)	0.0027 (8)	−0.0049 (8)
C7	0.079 (2)	0.0343 (13)	0.088 (2)	−0.0137 (13)	−0.0413 (17)	0.0059 (13)
C8	0.082 (2)	0.0470 (15)	0.0618 (17)	−0.0132 (14)	−0.0140 (15)	−0.0107 (13)
C9	0.061 (3)	0.050 (3)	0.049 (3)	−0.003 (2)	−0.015 (2)	−0.002 (2)
C10	0.084 (4)	0.072 (4)	0.061 (3)	0.034 (3)	−0.028 (3)	−0.019 (3)
C11	0.0362 (10)	0.0217 (9)	0.0433 (11)	0.0021 (7)	0.0127 (9)	0.0043 (8)
C12	0.0391 (11)	0.0177 (9)	0.0670 (15)	0.0003 (8)	0.0160 (10)	0.0042 (9)
C13	0.0375 (12)	0.0206 (9)	0.0765 (17)	−0.0053 (8)	0.0063 (11)	−0.0077 (10)
C14	0.0366 (11)	0.0285 (10)	0.0609 (14)	0.0004 (8)	0.0001 (10)	−0.0061 (9)
C15	0.0353 (10)	0.0207 (9)	0.0454 (11)	0.0022 (7)	0.0065 (9)	0.0010 (8)
C16	0.0363 (10)	0.0188 (8)	0.0409 (10)	−0.0005 (7)	0.0085 (8)	0.0002 (7)
C17	0.0461 (12)	0.0264 (10)	0.0420 (11)	0.0065 (8)	0.0156 (9)	0.0077 (8)
C18	0.0384 (11)	0.0240 (9)	0.0521 (13)	−0.0012 (8)	0.0112 (9)	0.0034 (8)
C19	0.0325 (10)	0.0203 (9)	0.0599 (13)	−0.0018 (7)	0.0092 (9)	0.0025 (8)
C20	0.0283 (10)	0.0203 (9)	0.0622 (14)	−0.0010 (7)	0.0111 (9)	0.0056 (8)
C21	0.0371 (11)	0.0210 (9)	0.0670 (15)	0.0033 (8)	0.0162 (10)	0.0031 (9)
C22	0.0515 (14)	0.0219 (9)	0.0568 (14)	−0.0028 (9)	0.0186 (11)	−0.0025 (9)
C23	0.0272 (10)	0.0242 (10)	0.0710 (15)	0.0001 (8)	0.0059 (10)	0.0094 (9)
C24	0.0481 (15)	0.0388 (13)	0.090 (2)	0.0071 (11)	−0.0034 (14)	0.0163 (13)
C25	0.070 (2)	0.0406 (14)	0.095 (2)	−0.0018 (13)	−0.0085 (17)	0.0245 (15)
C26	0.0548 (18)	0.0601 (19)	0.121 (3)	−0.0008 (14)	−0.0222 (18)	0.0203 (19)
C27A	0.073 (3)	0.102 (5)	0.141 (5)	0.020 (3)	−0.035 (3)	−0.012 (4)
C27B	0.123 (16)	0.15 (2)	0.23 (2)	−0.035 (14)	0.033 (15)	0.029 (18)
C28	0.0381 (11)	0.0217 (9)	0.0493 (12)	−0.0007 (8)	0.0181 (9)	−0.0002 (8)
C29	0.0423 (12)	0.0195 (9)	0.0737 (16)	0.0003 (8)	0.0236 (11)	0.0043 (9)
C30	0.0376 (12)	0.0274 (11)	0.0890 (19)	0.0049 (9)	0.0128 (12)	0.0173 (11)
C31	0.0340 (11)	0.0331 (11)	0.0755 (17)	−0.0022 (9)	0.0033 (11)	0.0152 (11)

C32	0.0324 (10)	0.0243 (9)	0.0562 (13)	−0.0017 (8)	0.0072 (9)	0.0035 (9)
C33	0.0339 (10)	0.0210 (9)	0.0488 (12)	0.0001 (7)	0.0114 (9)	0.0022 (8)
C34	0.0510 (13)	0.0240 (9)	0.0446 (12)	−0.0058 (9)	0.0204 (10)	−0.0036 (8)
N1	0.0463 (10)	0.0283 (9)	0.0368 (9)	0.0069 (7)	0.0054 (8)	0.0010 (7)
N2	0.0381 (10)	0.0248 (9)	0.0662 (13)	0.0025 (7)	−0.0114 (9)	−0.0091 (8)
N3	0.0660 (16)	0.0400 (12)	0.119 (2)	0.0099 (11)	−0.0517 (16)	−0.0155 (13)
N4	0.0460 (11)	0.0268 (9)	0.0483 (10)	−0.0054 (7)	0.0136 (8)	−0.0004 (7)
N5	0.0358 (10)	0.0251 (9)	0.0693 (13)	−0.0005 (7)	0.0021 (9)	0.0120 (8)
N6	0.0353 (10)	0.0390 (11)	0.0839 (16)	−0.0011 (8)	−0.0041 (10)	0.0178 (10)
O1	0.0360 (8)	0.0258 (7)	0.0684 (11)	0.0074 (6)	−0.0066 (7)	−0.0091 (7)
O2	0.0569 (10)	0.0297 (8)	0.0402 (8)	0.0081 (7)	−0.0009 (7)	0.0035 (6)
O3	0.0568 (10)	0.0285 (8)	0.0539 (10)	0.0121 (7)	0.0133 (8)	0.0144 (7)
O4	0.0524 (11)	0.0180 (7)	0.0956 (15)	−0.0001 (7)	0.0130 (10)	0.0095 (8)
O5	0.0407 (8)	0.0225 (7)	0.0498 (9)	−0.0005 (6)	−0.0052 (7)	0.0021 (6)
O6	0.0416 (9)	0.0256 (8)	0.0951 (14)	−0.0106 (7)	−0.0117 (9)	0.0181 (8)
O7	0.0642 (11)	0.0259 (7)	0.0438 (9)	−0.0065 (7)	0.0033 (8)	−0.0013 (6)
O8	0.0626 (11)	0.0245 (7)	0.0569 (10)	−0.0098 (7)	0.0181 (8)	−0.0092 (7)
O9	0.0582 (12)	0.0171 (7)	0.0991 (16)	0.0008 (7)	0.0220 (11)	0.0012 (8)
O10	0.0389 (9)	0.0258 (7)	0.0644 (11)	−0.0019 (6)	−0.0071 (8)	0.0010 (7)
C9A	0.052 (5)	0.080 (6)	0.050 (5)	0.005 (4)	−0.005 (4)	−0.025 (4)
C10A	0.073 (7)	0.097 (10)	0.131 (12)	−0.001 (6)	−0.001 (7)	0.059 (9)

Geometric parameters (Å, º)

C1—N1	1.334 (3)	C22—H22	0.95
C1—C2	1.376 (3)	C23—O6	1.224 (3)
C1—H1	0.95	C23—N5	1.345 (3)
C2—C3	1.390 (3)	C24—N6	1.278 (3)
C2—H2	0.95	C24—C25	1.519 (4)
C3—C4	1.391 (3)	C24—C26	1.526 (4)
C3—C6	1.492 (3)	C25—H25A	0.98
C4—C5	1.379 (3)	C25—H25B	0.98
C4—H4	0.95	C25—H25C	0.98
C5—N1	1.342 (3)	C26—C27B	1.419 (11)
C5—H5	0.95	C26—C27A	1.450 (6)
C6—O1	1.222 (2)	C26—H26A	0.99
C6—N2	1.350 (3)	C26—H26B	0.99
C7—N3	1.268 (4)	C27A—H27A	0.98
C7—C8	1.456 (4)	C27A—H27B	0.98
C7—C9	1.506 (5)	C27A—H27C	0.98
C7—C9A	1.667 (9)	C27B—H27D	0.98
C8—H8A	0.98	C27B—H27E	0.98
C8—H8B	0.98	C27B—H27F	0.98
C8—H8C	0.98	C28—C29	1.397 (3)
C9—C10	1.496 (8)	C28—C33	1.400 (3)
C9—H9A	0.99	C28—C34	1.475 (3)
C9—H9B	0.99	C29—O9	1.365 (3)
C10—H10A	0.98	C29—C30	1.385 (4)

C10—H10B	0.98	C30—C31	1.387 (3)
C10—H10C	0.98	C30—H30	0.95
C11—C12	1.401 (3)	C31—C32	1.391 (3)
C11—C16	1.402 (3)	C31—H31	0.95
C11—C17	1.471 (3)	C32—C33	1.376 (3)
C12—O4	1.363 (2)	C32—O10	1.381 (3)
C12—C13	1.381 (4)	C33—H33	0.95
C13—C14	1.387 (3)	C34—O8	1.241 (2)
C13—H13	0.95	C34—O7	1.303 (3)
C14—C15	1.388 (3)	N2—N3	1.386 (3)
C14—H14	0.95	N2—H2A	0.89 (3)
C15—C16	1.378 (3)	N5—N6	1.391 (3)
C15—O5	1.382 (2)	N5—H5A	0.90 (4)
C16—H16	0.95	O2—H2B	0.84
C17—O3	1.245 (2)	O4—H4A	0.84
C17—O2	1.302 (3)	O5—H5B	0.88 (3)
C18—N4	1.341 (3)	O7—H7	0.84
C18—C19	1.373 (3)	O9—H9	0.88 (5)
C18—H18	0.95	O10—H10	0.95 (4)
C19—C20	1.395 (3)	C9A—C10A	1.446 (18)
C19—H19	0.95	C9A—H9AA	0.99
C20—C21	1.390 (3)	C9A—H9AB	0.99
C20—C23	1.491 (3)	C10A—H10D	0.98
C21—C22	1.371 (4)	C10A—H10E	0.98
C21—H21	0.95	C10A—H10F	0.98
C22—N4	1.334 (3)		

N1—C1—C2	122.84 (19)	N5—C23—C20	117.07 (19)
N1—C1—H1	118.6	N6—C24—C25	125.4 (3)
C2—C1—H1	118.6	N6—C24—C26	116.5 (3)
C1—C2—C3	119.01 (19)	C25—C24—C26	118.1 (3)
C1—C2—H2	120.5	C24—C25—H25A	109.5
C3—C2—H2	120.5	C24—C25—H25B	109.5
C2—C3—C4	118.4 (2)	H25A—C25—H25B	109.5
C2—C3—C6	123.74 (18)	C24—C25—H25C	109.5
C4—C3—C6	117.78 (17)	H25A—C25—H25C	109.5
C5—C4—C3	118.75 (18)	H25B—C25—H25C	109.5
C5—C4—H4	120.6	C27B—C26—C24	118.2 (14)
C3—C4—H4	120.6	C27A—C26—C24	113.4 (4)
N1—C5—C4	122.76 (19)	C27A—C26—H26A	108.9
N1—C5—H5	118.6	C24—C26—H26A	108.9
C4—C5—H5	118.6	C27A—C26—H26B	108.9
O1—C6—N2	123.0 (2)	C24—C26—H26B	108.9
O1—C6—C3	120.31 (19)	H26A—C26—H26B	107.7
N2—C6—C3	116.69 (18)	C26—C27A—H27A	109.5
N3—C7—C8	126.1 (3)	C26—C27A—H27B	109.5
N3—C7—C9	121.6 (3)	H27A—C27A—H27B	109.5
C8—C7—C9	111.3 (3)	C26—C27A—H27C	109.5

N3—C7—C9A	105.9 (4)	H27A—C27A—H27C	109.5
C8—C7—C9A	123.6 (4)	H27B—C27A—H27C	109.5
C7—C8—H8A	109.5	C26—C27B—H27D	109.5
C7—C8—H8B	109.5	C26—C27B—H27E	109.5
H8A—C8—H8B	109.5	H27D—C27B—H27E	109.5
C7—C8—H8C	109.5	C26—C27B—H27F	109.5
H8A—C8—H8C	109.5	H27D—C27B—H27F	109.5
H8B—C8—H8C	109.5	H27E—C27B—H27F	109.5
C10—C9—C7	115.1 (4)	C29—C28—C33	119.6 (2)
C10—C9—H9A	108.5	C29—C28—C34	120.31 (19)
C7—C9—H9A	108.5	C33—C28—C34	120.1 (2)
C10—C9—H9B	108.5	O9—C29—C30	119.1 (2)
C7—C9—H9B	108.5	O9—C29—C28	121.5 (2)
H9A—C9—H9B	107.5	C30—C29—C28	119.4 (2)
C9—C10—H10A	109.5	C29—C30—C31	120.6 (2)
C9—C10—H10B	109.5	C29—C30—H30	119.7
H10A—C10—H10B	109.5	C31—C30—H30	119.7
C9—C10—H10C	109.5	C30—C31—C32	120.1 (2)
H10A—C10—H10C	109.5	C30—C31—H31	119.9
H10B—C10—H10C	109.5	C32—C31—H31	119.9
C12—C11—C16	119.4 (2)	C33—C32—O10	122.89 (19)
C12—C11—C17	120.30 (18)	C33—C32—C31	119.7 (2)
C16—C11—C17	120.32 (19)	O10—C32—C31	117.4 (2)
O4—C12—C13	119.1 (2)	C32—C33—C28	120.5 (2)
O4—C12—C11	121.4 (2)	C32—C33—H33	119.7
C13—C12—C11	119.49 (19)	C28—C33—H33	119.7
C12—C13—C14	120.6 (2)	O8—C34—O7	122.9 (2)
C12—C13—H13	119.7	O8—C34—C28	121.6 (2)
C14—C13—H13	119.7	O7—C34—C28	115.43 (18)
C13—C14—C15	120.3 (2)	C1—N1—C5	118.24 (19)
C13—C14—H14	119.8	C6—N2—N3	118.15 (19)
C15—C14—H14	119.8	C6—N2—H2A	119.9 (17)
C16—C15—O5	122.69 (18)	N3—N2—H2A	121.0 (17)
C16—C15—C14	119.58 (19)	C7—N3—N2	117.1 (2)
O5—C15—C14	117.7 (2)	C22—N4—C18	118.3 (2)
C15—C16—C11	120.56 (19)	C23—N5—N6	117.11 (19)
C15—C16—H16	119.7	C23—N5—H5A	120 (2)
C11—C16—H16	119.7	N6—N5—H5A	122 (2)
O3—C17—O2	122.6 (2)	C24—N6—N5	116.7 (2)
O3—C17—C11	122.0 (2)	C17—O2—H2B	109.5
O2—C17—C11	115.34 (17)	C12—O4—H4A	109.5
N4—C18—C19	122.9 (2)	C15—O5—H5B	106 (2)
N4—C18—H18	118.6	C34—O7—H7	109.5
C19—C18—H18	118.6	C29—O9—H9	103 (3)
C18—C19—C20	118.57 (19)	C32—O10—H10	106 (2)
C18—C19—H19	120.7	C10A—C9A—C7	101.5 (8)
C20—C19—H19	120.7	C10A—C9A—H9AA	111.5
C21—C20—C19	118.4 (2)	C7—C9A—H9AA	111.5

C21—C20—C23	123.8 (2)	C10A—C9A—H9AB	111.5
C19—C20—C23	117.71 (18)	C7—C9A—H9AB	111.5
C22—C21—C20	119.0 (2)	H9AA—C9A—H9AB	109.3
C22—C21—H21	120.5	C9A—C10A—H10D	109.5
C20—C21—H21	120.5	C9A—C10A—H10E	109.5
N4—C22—C21	122.9 (2)	H10D—C10A—H10E	109.5
N4—C22—H22	118.6	C9A—C10A—H10F	109.5
C21—C22—H22	118.6	H10D—C10A—H10F	109.5
O6—C23—N5	123.0 (2)	H10E—C10A—H10F	109.5
O6—C23—C20	119.9 (2)		

N1—C1—C2—C3	−0.1 (3)	N6—C24—C26—C27B	−39.4 (16)
C1—C2—C3—C4	−0.9 (3)	C25—C24—C26—C27B	141.7 (16)
C1—C2—C3—C6	−177.54 (19)	N6—C24—C26—C27A	−112.4 (5)
C2—C3—C4—C5	1.4 (3)	C25—C24—C26—C27A	68.7 (5)
C6—C3—C4—C5	178.25 (18)	C33—C28—C29—O9	−177.8 (2)
C3—C4—C5—N1	−1.0 (3)	C34—C28—C29—O9	1.3 (3)
C2—C3—C6—O1	153.6 (2)	C33—C28—C29—C30	2.5 (3)
C4—C3—C6—O1	−23.1 (3)	C34—C28—C29—C30	−178.4 (2)
C2—C3—C6—N2	−25.0 (3)	O9—C29—C30—C31	177.7 (2)
C4—C3—C6—N2	158.3 (2)	C28—C29—C30—C31	−2.6 (4)
N3—C7—C9—C10	4.3 (7)	C29—C30—C31—C32	0.8 (4)
C8—C7—C9—C10	−164.9 (5)	C30—C31—C32—C33	1.2 (4)
C16—C11—C12—O4	−177.7 (2)	C30—C31—C32—O10	−179.0 (2)
C17—C11—C12—O4	1.4 (3)	O10—C32—C33—C28	178.92 (19)
C16—C11—C12—C13	2.2 (3)	C31—C32—C33—C28	−1.2 (3)
C17—C11—C12—C13	−178.6 (2)	C29—C28—C33—C32	−0.6 (3)
O4—C12—C13—C14	177.7 (2)	C34—C28—C33—C32	−179.67 (19)
C11—C12—C13—C14	−2.3 (4)	C29—C28—C34—O8	−4.4 (3)
C12—C13—C14—C15	0.2 (4)	C33—C28—C34—O8	174.6 (2)
C13—C14—C15—C16	1.8 (3)	C29—C28—C34—O7	174.84 (19)
C13—C14—C15—O5	−178.7 (2)	C33—C28—C34—O7	−6.1 (3)
O5—C15—C16—C11	178.74 (18)	C2—C1—N1—C5	0.5 (3)
C14—C15—C16—C11	−1.8 (3)	C4—C5—N1—C1	0.0 (3)
C12—C11—C16—C15	−0.2 (3)	O1—C6—N2—N3	−2.9 (4)
C17—C11—C16—C15	−179.35 (19)	C3—C6—N2—N3	175.6 (2)
C12—C11—C17—O3	−4.1 (3)	C8—C7—N3—N2	−4.9 (6)
C16—C11—C17—O3	175.05 (19)	C9—C7—N3—N2	−172.5 (4)
C12—C11—C17—O2	175.17 (19)	C9A—C7—N3—N2	152.1 (5)
C16—C11—C17—O2	−5.7 (3)	C6—N2—N3—C7	179.9 (3)
N4—C18—C19—C20	−0.7 (3)	C21—C22—N4—C18	0.4 (3)
C18—C19—C20—C21	1.0 (3)	C19—C18—N4—C22	0.0 (3)
C18—C19—C20—C23	177.6 (2)	O6—C23—N5—N6	−5.6 (4)
C19—C20—C21—C22	−0.7 (3)	C20—C23—N5—N6	173.0 (2)
C23—C20—C21—C22	−177.1 (2)	C25—C24—N6—N5	−2.7 (5)
C20—C21—C22—N4	0.0 (3)	C26—C24—N6—N5	178.5 (3)
C21—C20—C23—O6	155.2 (2)	C23—N5—N6—C24	173.4 (3)
C19—C20—C23—O6	−21.2 (3)	N3—C7—C9A—C10A	106.4 (9)

C21—C20—C23—N5	−23.4 (3)	C8—C7—C9A—C10A	−95.9 (9)
C19—C20—C23—N5	160.2 (2)		