The crystal structures and Hirshfeld surface analysis of *N′,N″′*-((1*E*,1′*E*)-{[methylenebis(oxy)]bis(6-bromo-3,1-phenylene)}bis(methanylylidene))-bis(isonicotinohydrazide) dihydrate and *N′,N″′*-((1*E*,1′*E*)-{[butane-1,4-diylbis(oxy)]bis(2,1-phenyl-ene)}bis(methanylylidene))bis(isonicotino-hydrazide) [+ solvent]

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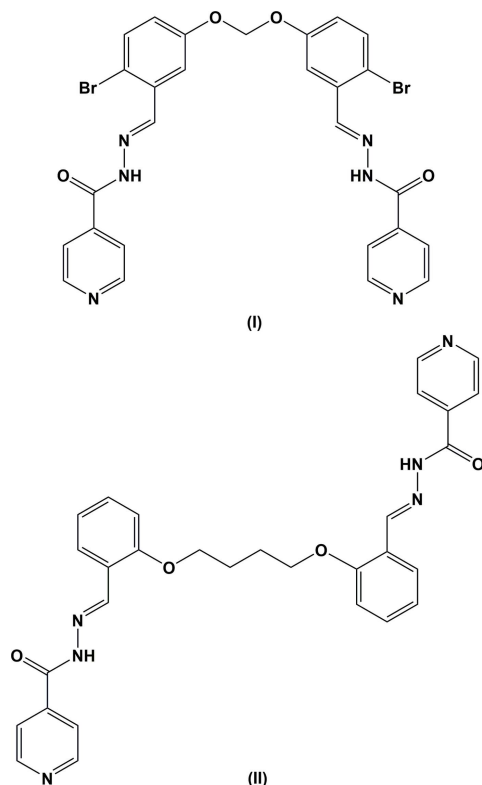
The title compounds, $C_{27}H_{20}Br_2N_6O_4 \cdot 2H_2O$, (I), and $C_{30}H_{28}N_6O_4 \cdot$[+ solvent], (II), both crystallize with one half-molecule in the asymmetric unit. The whole molecule of (I) is generated by twofold rotation symmetry, with the twofold rotation axis bisecting the C atom of the –O—CH_2—O– bridge. This results in a folded or U-shaped conformation of the molecule. The whole molecule of (II) is generated by inversion symmetry, with the central CH_2—CH_2 bond of the –O—$(CH_2)_4$—O– bridge being located about a center of inversion. This results in a step-like conformation of the molecule. The central C(=O)N—N=C regions of the isonicotinohydrazide moieties in both compounds are planar and the configuration about the imine C=N bonds is *E*. In compound (I), the benzene and pyridine rings are inclined to each other by 37.60 (6)°. The two symmetry-related pyridine rings are inclined to each other by 74.24 (6)°, and the two symmetry-related benzene rings by 7.69 (6)°. In compound (II), the benzene and pyridine rings are inclined to each other by 25.56 (11)°. The symmetry-related pyridine rings are parallel, as are the two symmetry-related benzene rings. In the crystal of (I), a pair of water molecules link the organic molecules *via* O_{water}—H···O and O_{water}—H···N hydrogen bonds, forming chains along [001], and enclosing an $R_4^2(8)$ and two $R_1^2(5)$ ring motifs. The chains are linked by N—H···$N_{pyridine}$ hydrogen bonds, forming a supramolecular framework. There are also a number of C—H···O hydrogen bonds, and C—H···π and offset π–π interactions [interplanar distance = 3.294 (1) Å] present reinforcing the framework. In the crystal of (II), molecules are linked by N—H···$N_{pyridine}$ hydrogen bonds, forming a supramolecular framework. Here too there are also a number of C—H···O hydrogen bonds present, and a C—H···π interaction, reinforcing the framework. For compound (II), a region of disordered electron density was corrected for using the SQUEEZE [Spek (2015). Acta Cryst. C71, 9–18] routine in *PLATON*. Their formula mass and unit-cell characteristics were not taken into account during refinement.
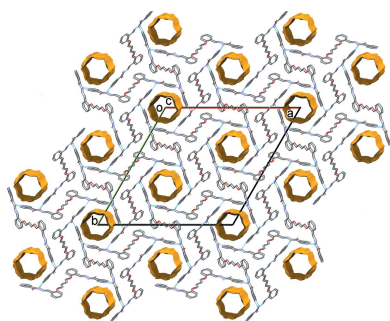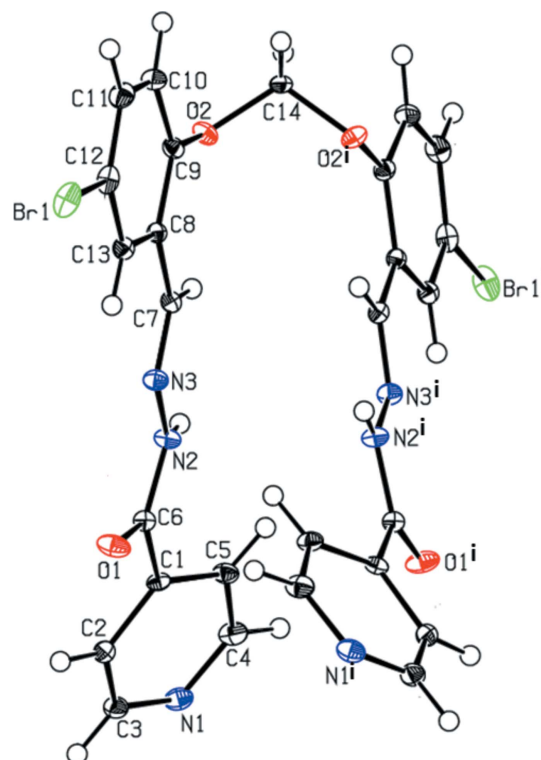
1. Chemical context

Hydrazide-hydrazone compounds are found to be associated with a wide spectrum of biological and medicinal applications. such as antimicrobial, anticonvulsant, analgesic, anti-inflammatory (Kaplancikli *et al.*, 2012), anti-platelet, antibacterial,

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antifungal, anti-tubercular and anti-tumor properties (Babahan *et al.*, 2013; Bedia *et al.*, 2006). Schiff bases of the general type *p*-*R*'-C$_6$H$_4$—CH—N—C$_6$H$_4$—*R*"-*p* are well-known reagents that find practical application in various areas, *e.g.* photography and medicinal and pharmaceutical chemistry (Sethuram *et al.*, 2013). Hydrazide Schiff base ligands arise owing to the presence of electron-donating nitrogen and oxygen atoms, allowing these to act as multidentate ligands, and their transition-metal complexes have been used in the treatment of tuberculosis, in colorimetric or fluorimetric analytic determinations, as well as in applications involving catalytic processes (Torje *et al.*, 2012) and, in some cases, function as supramolecular building blocks in their molecular assemblies (Wei *et al.*, 2015). Hydrazone derivatives containing an azomethine (–CONHN=CH–) group act as cytotoxic agents with the capability to prevent cell series in cancerous cells through different mechanisms (Patil *et al.*, 2011). Pyridine heterocycles and their derivatives are present in many large molecules having photo-chemical, electro-chemical and catalytic applications (Thirunavukkarsu *et al.*, 2017; Venda *et al.*, 2017; Jauhar *et al.*, 2016; Babu *et al.*, 2014*a*,*b*, 2015; Rajkumar *et al.*, 2014, 2015; Huq *et al.*, 2010). As a part of our research study, we report herein the synthesis and the crystal structures of the title compounds, (I) and (II), which contain several donor functions of a different nature: hydrazide and pyridine.

Figure 1
View of the molecular structure of compound (I), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by a twofold rotation axis [symmetry code (i): $-x + 1$, y, $-z + \frac{3}{2}$]. For clarity, the two water molecules of crystallization have been omitted.

(I)

(II)

2. Structural commentary

The molecular structures of the title compounds (I) and (II) are illustrated in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Tables 1 and 2 for compounds
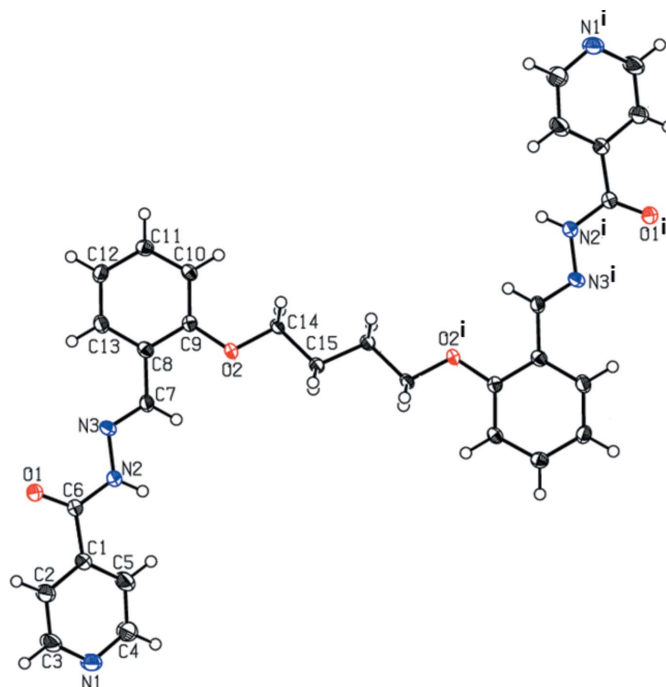
Figure 2
View of the molecular structure of compound (II), with the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by inversion symmetry [symmetry code (i): $-x$, $-y + 1$, $-z$].

Table 1
Selected geometric parameters (Å, °) for (I).

O1—C6	1.2300 (16)	N3—C7	1.2820 (16)
N2—C6	1.3512 (16)	C1—C6	1.4976 (17)
N2—N3	1.3857 (15)	C7—C8	1.4677 (17)
C6—N2—N3	117.46 (11)	O1—C6—C1	120.81 (11)
C7—N3—N2	114.86 (11)	N2—C6—C1	115.38 (11)
O1—C6—N2	123.81 (12)		
C6—N2—N3—C7	−173.82 (11)	N3—N2—C6—C1	−179.82 (10)
N3—N2—C6—O1	0.24 (19)	N2—N3—C7—C8	176.82 (11)

Table 2
Selected geometric parameters (Å, °) for (II).

O1—C6	1.223 (2)	N3—C7	1.278 (2)
N2—C6	1.355 (2)	C1—C6	1.501 (3)
N2—N3	1.388 (2)	C7—C8	1.463 (3)
C6—N2—N3	118.93 (15)	O1—C6—C1	120.65 (16)
C7—N3—N2	115.07 (15)	N2—C6—C1	115.29 (15)
O1—C6—N2	124.00 (17)		
C6—N2—N3—C7	179.08 (17)	N3—N2—C6—C1	171.51 (15)
N3—N2—C6—O1	−5.6 (3)	N2—N3—C7—C8	179.54 (15)

(I) and (II), respectively. The conformations of the two molecules differ considerably. Compound (I) has a folded or U-shaped conformation, while compound (II) has an open step-like conformation. In compound (I), the benzene (C8–C13) and pyridine (N1/C1–C5) rings are inclined to each other by 37.60 (6)°. The two symmetry-related pyridine rings are inclined to each other by 74.24 (6)°, and the two symmetry-related benzene rings by 7.69 (6)°. In compound (II), the benzene and pyridine rings are inclined to each other by 25.56 (11)°. The symmetry-related pyridine rings are parallel, as are the two symmetry-related benzene rings. In both compounds, the hydrazone molecule adopts an E configuration with respect to the hydrazone bridge N3=C7, with torsion angle N2—N3—C7—C8 = 176.82 (11) ° in (I) and 179.5 (2)° in (II). On the other hand, torsion angles N3—N2—C6—C1 [−179.8 (1) ° for (I) and 171.5 (2)° for (II)] and C6—N2—N3—C7 [−173.8 (1) ° for (I) and 179.1 (2)° for (II)], are consistent with an *all-trans* relationship in the central chain.

The bond lengths and angles in the carbohydrazide group of the title compounds can be compared with the values reported for related structures (Prabhu *et al.*, 2011; Bikas *et al.*, 2010). The N3—N2—C6—O1 torsion angle of 0.2 (2) and −5.6 (3)° for (I) and (II), respectively, indicates the *cis* configuration of the O1 atom with respect to the hydrazine nitrogen atom N3. The C6—N2 and C7=N3 bond lengths differ by 0.068 (2) Å in (I) and by 0.077 (2) Å in (II), hence these two bonds are properly assigned as single and double bonds, respectively. Bond lengths in the amide unit of aroyl hydrazones are in the ranges 1.218–1.292 Å for C=O bonds and 1.313–1.365 Å for C—N bonds in the keto tautomeric form, and 1.284−1.314 Å for C=O bonds and 1.291–1.331 Å for C—N bonds in the enol tautomeric form (Hosseini-Monfared *et al.*, 2013). Hence, compounds (I) and (II) are in the keto tautomeric form, which can be verified from the C=O and C—NH bond lengths of the amide unit: O1=C6 [1.230 (2) Å for (I) and 1.223 (2) Å for

Table 3
Hydrogen-bond geometry (Å, °) for (I).

$Cg1$ is the centroid of N1/C1–C5 pyridine ring.

D—H···A	D—H	H···A	D···A	D—H···A
N2—H$N2$···N1[i]	0.85 (2)	2.179 (19)	3.0261 (16)	174 (2)
O1W—H1W···O1	0.86 (2)	2.06 (2)	2.8756 (15)	158 (2)
O1W—H1W···N3	0.86 (2)	2.61 (2)	3.2476 (16)	131.3 (19)
O1W—H2W···O1[ii]	0.83 (3)	2.19 (3)	3.0244 (16)	174 (2)
C3—H3···O1W[iii]	0.93	2.56	3.4450 (17)	159
C4—H4···Br1[iv]	0.93	2.94	3.8554 (13)	169
C10—H10···O1[v]	0.93	2.56	3.4123 (17)	152
C13—H13···O1W	0.93	2.59	3.5148 (18)	171
C14—H14A···$Cg1$[v]	0.97	2.74	3.594 (1)	144
C14—H14B···$Cg1$[vi]	0.97	2.74	3.594 (1)	144

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

(II)] and N2—C6 [1.351 (2) Å for (I) and 1.355 (2) Å for (II)]. The bond distances C7=N3 [1.282 (2) Å for (I) and 1.278 (2) Å for (II)] and C6=O1 [1.229 (2) Å for (I) and 1.220 (2) Å for (II)], are very close to the recognized double C=N and C=O bond lengths (Prasanna *et al.*, 2013; Wang *et al.*, 2010), confirming that the carbohydrazide exists as an amido tautomer in the solid state. In the two compounds, the three bond angles around atom C6 (see Tables 1 and 2) differ from 120°, probably in order to decrease the repulsion between the lone pairs present on atoms N2 and O1.

3. Supramolecular features

In the crystal of (I), a pair of water molecules link the organic molecules *via* O_{water}—H···O and O_{water}—H···N hydrogen bonds, forming chains along [001] and enclosing an $R_4^2(8)$ and
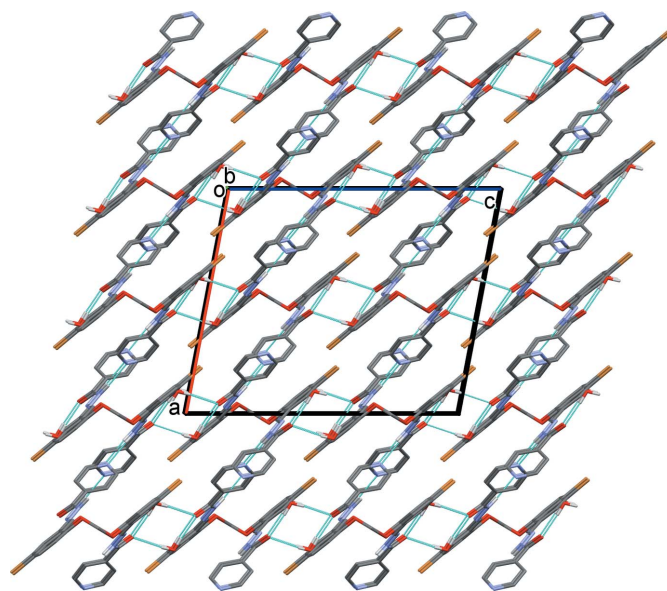
Figure 3
The crystal packing of compound (I), viewed along the *b* axis. The hydrogen bonds are shown as dashed lines (see Table 3 for details). For clarity, the C-bound H atoms have been omitted.

Table 4
Hydrogen-bond geometry (Å, °) for (II).
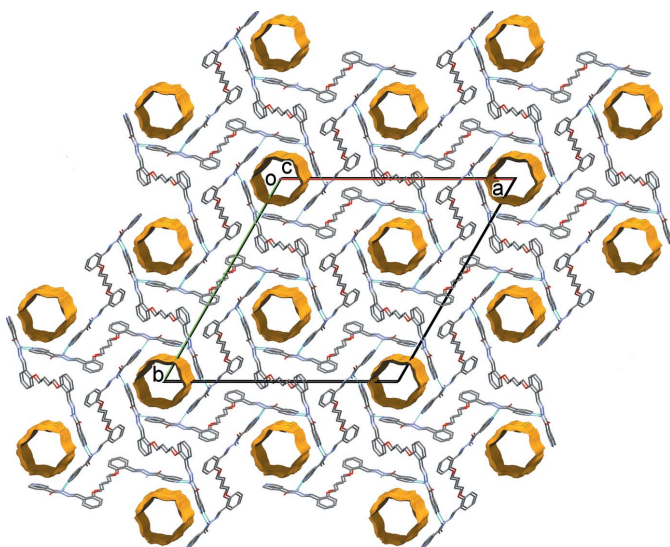
$Cg2$ is the centroid of the C8–C13 benzene ring.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
N2—H2$N\cdots$N1^i	0.91 (2)	2.04 (2)	2.907 (2)	159 (2)
C3—H3$\cdots$O1^{ii}	0.93	2.60	3.449 (3)	153
C3—H3$\cdots$N3^{ii}	0.93	2.55	3.223 (3)	129
C7—H7$\cdots$N1^i	0.93	2.63	3.372 (3)	137
C12—H12$\cdots$O1^{iii}	0.93	2.43	3.331 (2)	163
C15—H15$A\cdots$Cg2^{iv}	0.97	2.91	3.748 (2)	145

Symmetry codes: (i) $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{1}{3}$; (ii) $x - y + \frac{2}{3}, x + \frac{1}{3}, -z + \frac{4}{3}$; (iii) $-y + \frac{1}{3}, x - y + \frac{2}{3}, z - \frac{1}{3}$; (iv) $x, y, z - 1$.
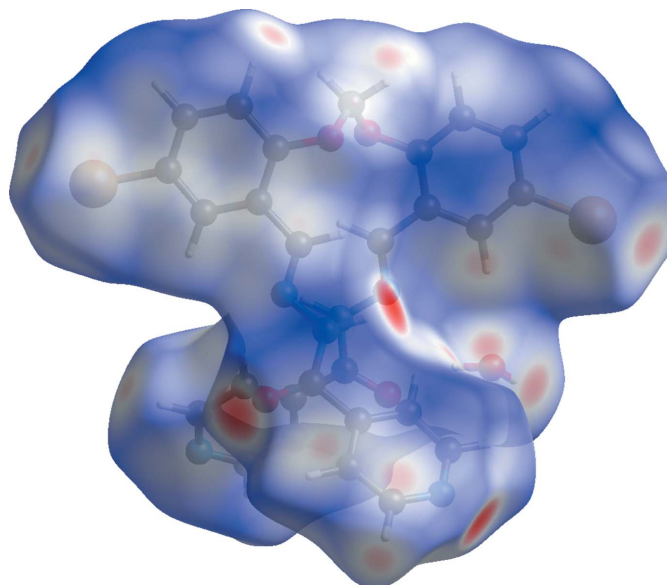
two $R_1^2(5)$ ring motifs (Table 3 and Fig. 3). The chains are linked by N—H$\cdots$N$_{pyridine}$ hydrogen bonds, forming a supramolecular framework. There are also a number of C—H$\cdots$O hydrogen bonds, and C—H$\cdots\pi$ and offset π–π interactions [interplanar distance = 3.294 (1) Å] present, reinforcing the framework (Table 3). The offset π-π- interactions involve inversion-related C8–C13 benzene rings, centroid $Cg2$. The intercentroid distance $Cg2\cdots Cg2(-x + 1, -y + 1, -z + 1)$ is 3.766 (1) Å, α = 0.00 (6)°, β = 29°, interplanar distance = 3.294 (1) Å, offset of 1.824 Å.

In the crystal of (II), molecules are linked by N—H$\cdots$N$_{pyridine}$ hydrogen bonds, forming a supramolecular framework (Table 4 and Fig. 4). Here too there are also a number of C—H$\cdots$O hydrogen bonds present, and a C—H$\cdots\pi$ interaction (Table 4), reinforcing the framework, but no π–π interactions are observed.

For compound (II) a region of disordered electron density with a potential solvent-accessible void of volume 1220 Å^3 with an electron count of 357 per unit cell was corrected for

Figure 5
The Hirshfeld surfaces of compound (I), mapped over d_{norm}; fixed colour scale of −0.512 (red) to 1.285 (blue) arbitrary units.

using the SQUEEZE routine in *PLATON* (Spek, 2015). The voids in the crystal structure of (II) are illustrated in Fig. 4.

4. Hirshfeld surface analysis

The Hirshfeld surface analysis (Spackman & Jayatilaka, 2009), and the associated two-dimensional fingerprint plots (McKinnon *et al.*, 2007), were calculated to analyse the intermolecular contacts in the crystals. The various calculations were performed with *CrystalExplorer17* (Turner *et al.*, 2017). The use of such calculations to analyse intermolecular contacts in crystals has been reported on recently by Tiekink and collaborators (Tan *et al.*, 2019).

The Hirshfeld surfaces of compounds (I) and (II) mapped over d_{norm} are given in Figs. 5 and 6, respectively. For (I) the intermolecular contacts are illustrated in Fig. 7, and for (II) in

Figure 4
The crystal packing of compound (II), viewed along the c axis. The hydrogen bonds are shown as dashed lines (see Table 4 for details). For clarity, the C-bound H atoms have been omitted. The cylindrical cavities are shown in yellow and brown (*Mercury*; Macrae *et al.*, 2008).
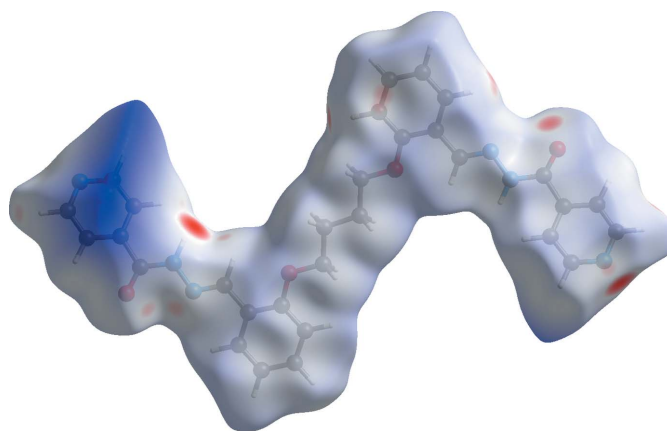

Figure 6
The Hirshfeld surfaces of compound (II), mapped over d_{norm}; fixed colour scale of −0.490 (red) to 4.945 (blue) arbitrary units.
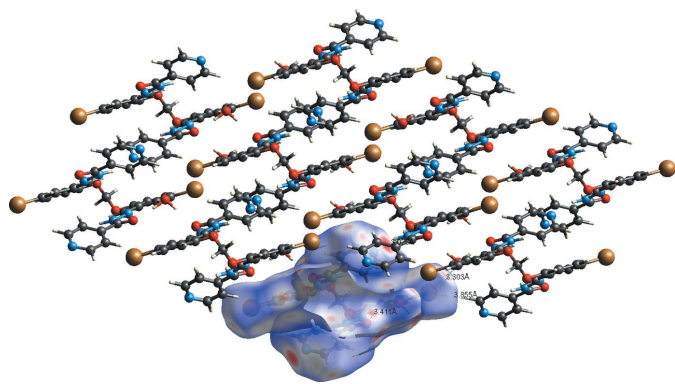
Figure 7
A view of the Hirshfeld surface mapped over d_{norm} of compound (I), showing the various intermolecular contacts in the crystal.

Fig. 8. They are colour-mapped with the normalized contact distance, d_{norm}, from red (distances shorter than the sum of the van der Waals radii) through white to blue (distances longer than the sum of the van der Waals radii). The d_{norm} surface was mapped over a fixed colour scale of −0.512 (red) to 1.285 (blue) for compound (I) and −0.490 (red) to 4.945 (blue) for compound (II), where the red spots indicate the inter-molecular contacts involved in hydrogen bonding (remembering that the disordered solvent in the channels of (II) have been *SQUEEZED* out).

The fingerprint plots are given in Figs. 9 and 10, for compounds (I) and (II), respectively. For compound (I), the principal intermolecular contacts are H···H at 28.9% (Fig. 9b), O···H/H···O at 13.8% (Fig. 9c), N···H/H···N at 11.3% (Fig. 9d), Br···H/H···Br at 14.3% (Fig. 9e) and C···H/H···C contacts at 13.6% (Fig. 9f). C···C contacts account for 8.4%, while C···Br are 3.0%, C···N are 3.0%, and finally C···O contacts amount to 1.4%.

For compound (II), the fingerprint plots reveal that the principal intermolecular contacts are H···H at 35.0% (Fig. 10b), O···H/H···O at 13.3% (Fig. 10c), N···H/H···N at

Figure 9
The full two-dimensional fingerprint plot for compound (I), and fingerprint plots delineated into (b) H···H, (c) O···H/H···O, (d) N···H/H···N, (e) Br···H/H···Br and (f) C···H/H···C contacts.

16.2% (Fig. 10d), and C···H/H···C at 33.6% (Fig. 10e). The remaining contacts are extremely weak, *ca* 1% each.

5. Database survey

A search of the Cambridge Structural Database (CSD, Version 5.40, February 2019; Groom *et al.*, 2016) for compounds with an O atom in position 3 of the benzylidene ring, *i.e.* (3-*OR*-benzylidene)isonicotinohydrazide (*R* = C) skeleton gave 51 hits (supporting information file S1). The majority of these compounds were with an OMe or an OEt substituent.

A search for compounds with an O atom in position 2 of the benzylidene ring, *i.e.* (2-*OR*-benzylidene)isonicotinohydrazide (*R* = C) skeleton gave 23 hits (supporting information file S2). Again, the majority of these compounds have an OMe or an OEt substituent. However, here the most interesting and relevant compound concerns the ligand *N'*,*N''*-[ethane-1,2-di-ylbis(oxy-2,1-phenylenemethylylidene)]bis(pyridine-4-carbo-
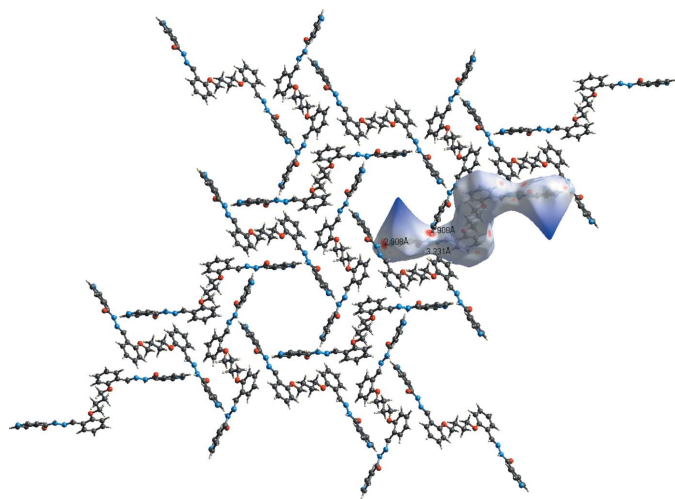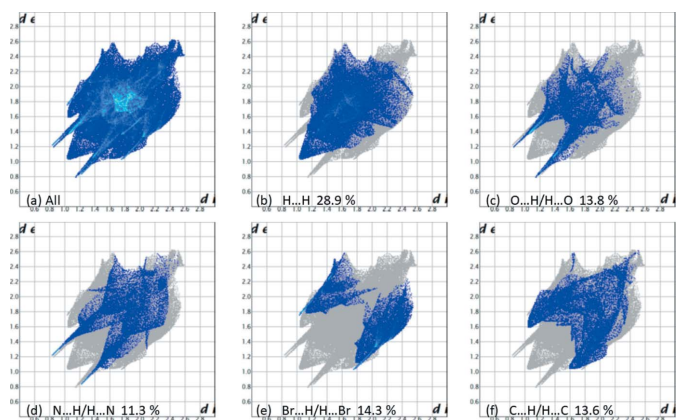

Figure 8
A view of the Hirshfeld surface mapped over d_{norm} of compound (II), showing the various intermolecular contacts in the crystal.
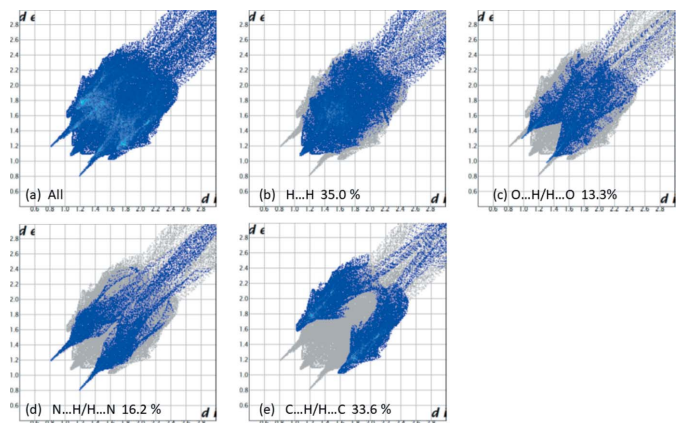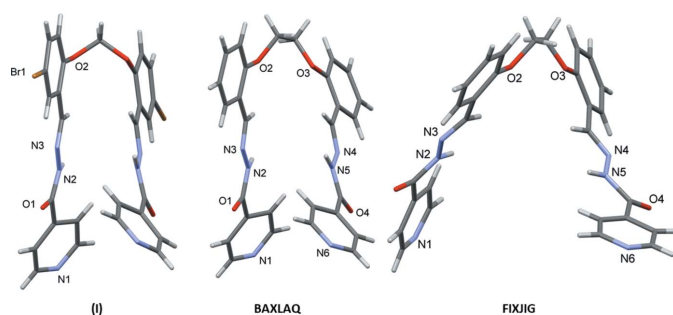

Figure 10
The full two-dimensional fingerprint plot for compound (II), and fingerprint plots delineated into (b) H···H, (c) O···H/H···O, (d) N···H/H···N, (e) C···H/H···C contacts.

Table 5
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_{27}H_{20}Br_2N_6O_4 \cdot 2H_2O$	$C_{30}H_{28}N_6O_4$[+solvent]
M_r	688.34	536.58
Crystal system, space group	Monoclinic, $C2/c$	Trigonal, $R\overline{3}{:}H$
Temperature (K)	293	293
a, b, c (Å)	15.1206 (2), 10.1497 (2), 18.0253 (3)	34.3186 (2), 34.3186 (2), 6.7855 (3)
α, β, γ (°)	90, 100.7960 (4), 90	90, 90, 120
V (Å^3)	2717.37 (8)	6921.0 (3)
Z	4	9
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	3.04	0.08
Crystal size (mm)	$0.38 \times 0.28 \times 0.21$	$0.30 \times 0.25 \times 0.20$
Data collection		
Diffractometer	Bruker Kappa APEXII CCD	Bruker Kappa APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.499, 0.746	0.630, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	29418, 3387, 3202	22262, 3805, 2619
R_{int}	0.033	0.076
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668	0.667
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.054, 1.05	0.057, 0.142, 1.05
No. of reflections	3387	3805
No. of parameters	199	185
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})	0.49, −0.32	0.47, −0.34

Computer programs: *APEX2* and *SAINT* (Bruker, 2008), *SHELXS2018* (Sheldrick, 2008), *SHELXL2018* (Sheldrick, 2015), *ORTEP-3 for Windows* and *WinGX* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

hydrazide), in which a 1,2-dioxyethane bridge links two N'-benzylideneisonicotinohydrazide units. The crystal structures of two polymorphs have been described: a monoclinic $P2_1$ polymorph that crystallizes as a methanol disolvate (BAXLAQ; Mahmoudi *et al.*, 2017) and a triclinic $P\overline{1}$ polymorph (FIXJIG; Tai *et al.*, 2004). The conformation of both compounds is U-shaped, similar to that of compound (I). The molecular structures of compounds (I), BAXLAQ and FIXJIG are compared in Fig. 11. The principal difference in the conformation of the three molecules is reflected in the dihedral angle involving the benzene rings, which are inclined to each other by 7.69 (6)° in (I), by 25.0 (2)° in BAXLAQ and by 55.27 (7)° in FIXJIG.

Figure 11
The molecular structures of compounds (I), BAXLAQ (Mahmoudi *et al.*, 2017) and FIXJIG (Tai *et al.*, 2004).

An interesting HgI$_2$ complex of this ligand, bis(μ-{N',N''-[ethane-1,2-diylbis(oxy-2,1-phenylenemethylylidene)] bis-(pyridine-4-carbohydrazide)})tetrakis(iodo)dimercury methanol disolvate (BAXKUJ; Mahmoudi *et al.*, 2017), has a metallamacrocyclic architecture.

6. Synthesis and crystallization

Compound I: To 2-hydroxybenzaldehyde (5 mmol), in a 250 ml round-bottom (RB) flask was added DMF (30 ml) and potassium carbonate (12.5 mmol). The mixture was stirred at room temperature and then 1,1-diiodobutane (2.5 mmol) was added dropwise and the reaction mixture was stirred for 12 h. It was then partitioned between water and ethyl acetate. The ethyl acetate layer was collected and concentrated under reduced pressure. To 1,4-bis(2-carboxyaldehydephen-oxy)butane (2 mmol) and isonicotinic acid hydrazide (4 mmol) in a 250 ml RB flask was added 100 ml of methanol and two drops of glacial acetic acid. The reaction mixture was stirred at room temperature and within 5 min a white-coloured product had formed. The reaction was continued for a further 30 min. The title compound was isolated by filtration and washed with methanol, then chloroform and followed by acetone. The final product was recrystallized using DMSO and yielded colourless block-like crystals of compound (I).

Compound I: To 5-bromo-2-hydroxybenzaldehyde (5 mmol), in a 250 ml RB flask, was added 50 ml of DMF and

potassium carbonate (12.5 mmol). The mixture was stirred at room temperature and then 1,1-diiodomethane (2.5 mmol) was added dropwise. Then, the reaction mixture was stirred for 12 h. The product obtained was extracted in ethyl acetate medium. Methanol (100 ml) and two drops of glacial acetic acid were added to a mixture of 6,6′-[methylenebis(oxy)] bis(3-bromobenzaldehyde) (2 mmol) and isoniazid (4 mmol) in a 250 ml RB flask. The reaction mixture was stirred at room temperature and within 5 min a white-coloured product had formed and the reaction was continued for a further 30 min. The solid obtained was washed with methanol, then chloroform and followed by acetone. The final product was recrystallized using DMSO and yielded colourless block-like crystals of compound (II).

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. The NH H atoms for both compounds, and the water molecule H atoms for compound (I), were located in difference-Fourier maps and refined freely. For both compounds the C-bound H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms: C—H = 0.93-0.97 Å with $U_{iso}(H)$ = $1.2U_{eq}(C)$.

For compound (II), a region of disordered electron density with a potential solvent accessible void of volume 1220 Å^3 with an electron count of 357 per unit cell was corrected for using the SQUEEZE routine in *PLATON* (Spek, 2015). Their formula mass and unit-cell characteristics were not taken into account during refinement.

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supporting information

The crystal structures and Hirshfeld surface analysis of N′,N′′′-((1E,1′E)-{[methylenebis(oxy)]bis(6-bromo-3,1-phenylene)}bis-(methanylylidene))bis(isonicotinohydrazide) dihydrate and N′,N′′′-((1E,1′E)-{[butane-1,4-diylbis(oxy)]bis(2,1-phenylene)}bis(methanylyl-idene))bis(isonicotinohydrazide) [+ solvent]

S. Syed Abuthahir, M. NizamMohideen, V. Viswanathan, Tamilselvan Abiraman and Sengottuvelan Balasubramanian

Computing details

For both structures, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT* (Bruker, 2008); program(s) used to solve structure: *SHELXS2018* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *WinGX* (Farrugia, 2012), *publCIF* (Westrip, 2010) and *PLATON* (Spek, 2009).

N′,N′′′-((1E,1′E)-{[Methylenebis(oxy)]bis(6-bromo-3,1-phenylene)}bis(methanylylidene))bis(isonicotinohydrazide) dihydrate (I)

Crystal data

$C_{27}H_{20}Br_2N_6O_4 \cdot 2H_2O$	$F(000) = 1384$
$M_r = 688.34$	$D_x = 1.683$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.1206$ (2) Å	Cell parameters from 3387 reflections
$b = 10.1497$ (2) Å	$\theta = 1.8$–$26.9°$
$c = 18.0253$ (3) Å	$\mu = 3.04$ mm^{-1}
$\beta = 100.7960$ (4)°	$T = 293$ K
$V = 2717.37$ (8) Å^3	Block, colourless
$Z = 4$	$0.38 \times 0.28 \times 0.21$ mm

Data collection

Bruker Kappa APEXII CCD diffractometer	3387 independent reflections
	3202 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.033$
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)	$\theta_{max} = 28.4°$, $\theta_{min} = 2.8°$
	$h = -20 \rightarrow 20$
$T_{min} = 0.499$, $T_{max} = 0.746$	$k = -13 \rightarrow 13$
29418 measured reflections	$l = -24 \rightarrow 24$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.021$	and constrained refinement
$wR(F^2) = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 3.4271P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
3387 reflections	$(\Delta/\sigma)_{max} = 0.002$
199 parameters	$\Delta\rho_{max} = 0.49$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.32$ e Å^{-3}
Primary atom site location: structure-invariant	Extinction correction: (SHELXL2018;
direct methods	Sheldrick, 2015),
Secondary atom site location: difference Fourier	$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
map	Extinction coefficient: 0.00152 (17)

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)
Br1	0.70412 (2)	0.52186 (2)	0.47663 (2)	0.01933 (6)	
O1	0.45281 (7)	1.00457 (9)	0.61053 (6)	0.0176 (2)	
O2	0.45956 (6)	0.35751 (9)	0.68829 (5)	0.01363 (18)	
N1	0.22417 (8)	1.19161 (11)	0.75048 (7)	0.0152 (2)	
N2	0.41385 (7)	0.82530 (10)	0.67331 (6)	0.0115 (2)	
HN2	0.3760 (12)	0.7919 (18)	0.6974 (10)	0.019 (4)*	
N3	0.47208 (7)	0.74664 (10)	0.64190 (6)	0.0120 (2)	
C1	0.34534 (8)	1.03494 (11)	0.68973 (7)	0.0105 (2)	
C2	0.30431 (9)	1.14287 (12)	0.65037 (7)	0.0125 (2)	
H2	0.317244	1.165550	0.603561	0.015*	
C3	0.24360 (9)	1.21635 (13)	0.68217 (7)	0.0144 (2)	
H3	0.214768	1.286668	0.654615	0.017*	
C4	0.26812 (9)	1.09117 (13)	0.78941 (8)	0.0160 (3)	
H4	0.257654	1.074883	0.837801	0.019*	
C5	0.32847 (9)	1.00994 (12)	0.76160 (8)	0.0135 (2)	
H5	0.356824	0.940616	0.790387	0.016*	
C6	0.40899 (9)	0.95414 (12)	0.65410 (7)	0.0111 (2)	
C7	0.46797 (8)	0.62336 (12)	0.65637 (7)	0.0105 (2)	
H7	0.430077	0.593995	0.688011	0.013*	
C8	0.52265 (8)	0.52824 (12)	0.62335 (7)	0.0101 (2)	
C9	0.51576 (8)	0.39410 (12)	0.63961 (7)	0.0114 (2)	
C10	0.55993 (9)	0.29921 (13)	0.60449 (8)	0.0154 (3)	
H10	0.552015	0.210250	0.613749	0.018*	
C11	0.61571 (9)	0.33760 (14)	0.55570 (8)	0.0164 (3)	
H11	0.646693	0.275109	0.532790	0.020*	
C12	0.62469 (9)	0.47104 (13)	0.54149 (7)	0.0136 (2)	
C13	0.57828 (8)	0.56652 (13)	0.57324 (7)	0.0118 (2)	

H13	0.583938	0.654965	0.561477	0.014*	
C14	0.500000	0.27859 (17)	0.750000	0.0157 (4)	
H14A	0.454724	0.222442	0.765344	0.019*	0.5
H14B	0.545278	0.222447	0.734654	0.019*	0.5
O1W	0.60456 (7)	0.90764 (12)	0.55169 (7)	0.0256 (2)	
H1W	0.5551 (16)	0.914 (2)	0.5685 (12)	0.037 (6)*	
H2W	0.5926 (16)	0.934 (2)	0.5072 (14)	0.041 (6)*	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.01383 (9)	0.03079 (10)	0.01546 (8)	−0.00484 (5)	0.00808 (5)	−0.00590 (5)
O1	0.0203 (5)	0.0125 (4)	0.0235 (5)	0.0021 (4)	0.0133 (4)	0.0048 (4)
O2	0.0142 (4)	0.0126 (4)	0.0148 (4)	0.0007 (3)	0.0046 (3)	0.0048 (3)
N1	0.0150 (5)	0.0127 (5)	0.0192 (6)	−0.0003 (4)	0.0067 (4)	−0.0031 (4)
N2	0.0114 (5)	0.0095 (5)	0.0158 (5)	0.0010 (4)	0.0080 (4)	0.0013 (4)
N3	0.0116 (5)	0.0108 (5)	0.0147 (5)	0.0021 (4)	0.0052 (4)	−0.0003 (4)
C1	0.0095 (6)	0.0082 (5)	0.0143 (6)	−0.0016 (4)	0.0035 (4)	−0.0019 (4)
C2	0.0138 (6)	0.0123 (5)	0.0115 (5)	0.0001 (4)	0.0024 (4)	−0.0008 (4)
C3	0.0144 (6)	0.0122 (5)	0.0163 (6)	0.0023 (5)	0.0020 (5)	−0.0008 (5)
C4	0.0204 (7)	0.0135 (6)	0.0167 (6)	−0.0017 (5)	0.0099 (5)	−0.0003 (5)
C5	0.0164 (6)	0.0097 (5)	0.0154 (6)	−0.0013 (4)	0.0055 (5)	0.0015 (4)
C6	0.0104 (6)	0.0106 (5)	0.0125 (6)	0.0000 (4)	0.0027 (4)	0.0000 (4)
C7	0.0091 (5)	0.0116 (5)	0.0108 (5)	0.0003 (4)	0.0023 (4)	0.0008 (4)
C8	0.0080 (6)	0.0104 (5)	0.0112 (6)	0.0006 (4)	0.0003 (4)	0.0000 (4)
C9	0.0098 (6)	0.0117 (5)	0.0124 (5)	0.0006 (4)	0.0012 (4)	0.0012 (4)
C10	0.0176 (6)	0.0112 (6)	0.0169 (6)	0.0028 (5)	0.0020 (5)	−0.0006 (5)
C11	0.0144 (6)	0.0178 (6)	0.0170 (6)	0.0044 (5)	0.0030 (5)	−0.0044 (5)
C12	0.0087 (6)	0.0211 (6)	0.0118 (6)	−0.0007 (5)	0.0036 (5)	−0.0018 (5)
C13	0.0095 (6)	0.0128 (5)	0.0128 (6)	−0.0004 (4)	0.0014 (4)	0.0000 (4)
C14	0.0271 (10)	0.0076 (7)	0.0118 (8)	0.000	0.0019 (7)	0.000
O1W	0.0151 (5)	0.0396 (7)	0.0241 (6)	0.0057 (5)	0.0085 (4)	0.0119 (5)

Geometric parameters (Å, º)

Br1—C12	1.8978 (13)	C4—H4	0.9300
O1—C6	1.2300 (16)	C5—H5	0.9300
O2—C9	1.3818 (16)	C7—C8	1.4677 (17)
O2—C14	1.4134 (13)	C7—H7	0.9300
N1—C4	1.3412 (18)	C8—C13	1.3997 (18)
N1—C3	1.3421 (18)	C8—C9	1.4007 (17)
N2—C6	1.3512 (16)	C9—C10	1.3904 (18)
N2—N3	1.3857 (15)	C10—C11	1.384 (2)
N2—HN2	0.851 (18)	C10—H10	0.9300
N3—C7	1.2820 (16)	C11—C12	1.3897 (19)
C1—C2	1.3869 (17)	C11—H11	0.9300
C1—C5	1.3898 (18)	C12—C13	1.3818 (18)
C1—C6	1.4976 (17)	C13—H13	0.9300

C2—C3	1.3873 (18)	C14—H14A	0.9700
C2—H2	0.9300	C14—H14B	0.9700
C3—H3	0.9300	O1W—H1W	0.86 (2)
C4—C5	1.3910 (19)	O1W—H2W	0.83 (3)
C9—O2—C14	115.16 (8)	C8—C7—H7	119.8
C4—N1—C3	116.75 (11)	C13—C8—C9	118.83 (12)
C6—N2—N3	117.46 (11)	C13—C8—C7	122.10 (11)
C6—N2—HN2	120.5 (12)	C9—C8—C7	119.00 (11)
N3—N2—HN2	121.2 (12)	O2—C9—C10	120.53 (11)
C7—N3—N2	114.86 (11)	O2—C9—C8	118.22 (11)
C2—C1—C5	118.58 (12)	C10—C9—C8	121.14 (12)
C2—C1—C6	118.36 (11)	C11—C10—C9	119.76 (12)
C5—C1—C6	123.00 (11)	C11—C10—H10	120.1
C1—C2—C3	118.72 (12)	C9—C10—H10	120.1
C1—C2—H2	120.6	C10—C11—C12	118.94 (12)
C3—C2—H2	120.6	C10—C11—H11	120.5
N1—C3—C2	123.64 (12)	C12—C11—H11	120.5
N1—C3—H3	118.2	C13—C12—C11	122.17 (12)
C2—C3—H3	118.2	C13—C12—Br1	119.57 (10)
N1—C4—C5	123.79 (13)	C11—C12—Br1	118.26 (10)
N1—C4—H4	118.1	C12—C13—C8	119.06 (12)
C5—C4—H4	118.1	C12—C13—H13	120.5
C1—C5—C4	118.37 (12)	C8—C13—H13	120.5
C1—C5—H5	120.8	O2ⁱ—C14—O2	110.96 (14)
C4—C5—H5	120.8	O2ⁱ—C14—H14A	109.4
O1—C6—N2	123.81 (12)	O2—C14—H14A	109.4
O1—C6—C1	120.81 (11)	O2ⁱ—C14—H14B	109.4
N2—C6—C1	115.38 (11)	O2—C14—H14B	109.4
N3—C7—C8	120.47 (11)	H14A—C14—H14B	108.0
N3—C7—H7	119.8	H1W—O1W—H2W	106 (2)
C6—N2—N3—C7	−173.82 (11)	N3—C7—C8—C9	−179.26 (12)
C5—C1—C2—C3	−4.17 (18)	C14—O2—C9—C10	57.04 (16)
C6—C1—C2—C3	178.46 (11)	C14—O2—C9—C8	−126.67 (12)
C4—N1—C3—C2	1.2 (2)	C13—C8—C9—O2	−179.05 (11)
C1—C2—C3—N1	2.3 (2)	C7—C8—C9—O2	−2.05 (17)
C3—N1—C4—C5	−2.8 (2)	C13—C8—C9—C10	−2.79 (18)
C2—C1—C5—C4	2.71 (19)	C7—C8—C9—C10	174.21 (12)
C6—C1—C5—C4	179.95 (12)	O2—C9—C10—C11	179.78 (11)
N1—C4—C5—C1	0.9 (2)	C8—C9—C10—C11	3.60 (19)
N3—N2—C6—O1	0.24 (19)	C9—C10—C11—C12	−1.5 (2)
N3—N2—C6—C1	−179.82 (10)	C10—C11—C12—C13	−1.4 (2)
C2—C1—C6—O1	29.80 (18)	C10—C11—C12—Br1	178.26 (10)
C5—C1—C6—O1	−147.44 (13)	C11—C12—C13—C8	2.17 (19)
C2—C1—C6—N2	−150.15 (12)	Br1—C12—C13—C8	−177.48 (9)
C5—C1—C6—N2	32.61 (18)	C9—C8—C13—C12	−0.08 (18)

N2—N3—C7—C8	176.82 (11)	C7—C8—C13—C12	−176.98 (11)
N3—C7—C8—C13	−2.37 (19)	C9—O2—C14—O2ⁱ	87.86 (9)

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

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of N1/C1–C5 pyridine ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H*N*2···N1ⁱⁱ	0.85 (2)	2.179 (19)	3.0261 (16)	174 (2)
O1*W*—H1*W*···O1	0.86 (2)	2.06 (2)	2.8756 (15)	158 (2)
O1*W*—H1*W*···N3	0.86 (2)	2.61 (2)	3.2476 (16)	131.3 (19)
O1*W*—H2*W*···O1ⁱⁱⁱ	0.83 (3)	2.19 (3)	3.0244 (16)	174 (2)
C3—H3···O1*W*^{iv}	0.93	2.56	3.4450 (17)	159
C4—H4···Br1^v	0.93	2.94	3.8554 (13)	169
C10—H10···O1^{vi}	0.93	2.56	3.4123 (17)	152
C13—H13···O1*W*	0.93	2.59	3.5148 (18)	171
C14—H14*A*···Cg1^{vi}	0.97	2.74	3.594 (1)	144
C14—H14*B*···Cg1^{vii}	0.97	2.74	3.594 (1)	144

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

N′,N′′′-((1*E*,1′*E*)-{[Butane-1,4-diylbis(oxy)]\ bis(2,1-phenylene)}bis(methanylylidene))bis(isonicotinohydrazide) (II)

Crystal data

C₃₀H₂₈N₆O₄[+solvent]
*M*ᵣ = 536.58
Trigonal, *R*3̄:*H*
a = 34.3186 (2) Å
c = 6.7855 (3) Å
V = 6921.0 (3) Å³
Z = 9
F(000) = 2538

*D*ₓ = 1.159 Mg m⁻³
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 3792 reflections
θ = 1.8–26.9°
μ = 0.08 mm⁻¹
T = 293 K
Block, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Bruker Kappa APEXII CCD diffractometer
ω and *φ* scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2008)
*T*ₘᵢₙ = 0.630, *T*ₘₐₓ = 0.746
22262 measured reflections

3805 independent reflections
2619 reflections with *I* > 2*σ*(*I*)
*R*ᵢₙₜ = 0.076
*θ*ₘₐₓ = 28.3°, *θ*ₘᵢₙ = 2.1°
h = −45→36
k = −29→45
l = −9→9

Refinement

Refinement on *F*²
Least-squares matrix: full
R[*F*² > 2*σ*(*F*²)] = 0.057
wR(*F*²) = 0.142
S = 1.05
3805 reflections
185 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 11.1328P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.47$ 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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.20009 (4)	0.45231 (5)	0.72823 (18)	0.0262 (3)
O2	0.02621 (4)	0.46026 (4)	0.34035 (18)	0.0214 (3)
N1	0.31092 (6)	0.49292 (7)	0.1812 (2)	0.0346 (4)
N2	0.16142 (5)	0.46016 (5)	0.4732 (2)	0.0218 (3)
H2N	0.1653 (8)	0.4749 (8)	0.358 (3)	0.033 (6)*
N3	0.12211 (5)	0.44325 (5)	0.5828 (2)	0.0210 (3)
C1	0.23686 (6)	0.47415 (6)	0.4186 (3)	0.0223 (4)
C2	0.27559 (8)	0.47786 (10)	0.4947 (3)	0.0471 (7)
H2	0.277753	0.474161	0.629269	0.056*
C3	0.31139 (8)	0.48705 (10)	0.3729 (3)	0.0480 (7)
H3	0.337126	0.489203	0.428924	0.058*
C4	0.27280 (9)	0.48779 (11)	0.1061 (3)	0.0538 (8)
H4	0.271346	0.490922	−0.029363	0.065*
C5	0.23528 (8)	0.47810 (10)	0.2170 (3)	0.0457 (7)
H5	0.209289	0.474298	0.156458	0.055*
C6	0.19813 (6)	0.46179 (6)	0.5561 (3)	0.0201 (4)
C7	0.08925 (6)	0.44343 (6)	0.4950 (3)	0.0207 (4)
H7	0.093119	0.454627	0.367374	0.025*
C8	0.04564 (6)	0.42628 (6)	0.5923 (3)	0.0197 (4)
C9	0.03514 (7)	0.40109 (6)	0.7662 (3)	0.0240 (4)
H9	0.056366	0.395193	0.822447	0.029*
C10	−0.00624 (7)	0.38487 (7)	0.8553 (3)	0.0243 (4)
H10	−0.012915	0.368208	0.970983	0.029*
C11	−0.03787 (6)	0.39371 (6)	0.7700 (3)	0.0216 (4)
H11	−0.065758	0.382899	0.830143	0.026*
C12	−0.02860 (6)	0.41838 (6)	0.5968 (3)	0.0188 (4)
H12	−0.050141	0.423846	0.540846	0.023*
C13	0.01323 (6)	0.43478 (6)	0.5082 (2)	0.0177 (4)
C14	−0.00685 (6)	0.46611 (6)	0.2364 (2)	0.0178 (4)
H14A	−0.018719	0.480568	0.320625	0.021*
H14B	−0.031546	0.437179	0.195219	0.021*
C15	0.01615 (6)	0.49521 (6)	0.0585 (3)	0.0186 (4)
H15A	0.027315	0.480095	−0.025658	0.022*
H15B	0.041679	0.523411	0.101427	0.022*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0225 (7)	0.0348 (8)	0.0211 (6)	0.0142 (6)	−0.0014 (5)	0.0027 (6)
O2	0.0183 (6)	0.0283 (7)	0.0212 (6)	0.0143 (6)	−0.0004 (5)	0.0057 (5)
N1	0.0244 (9)	0.0535 (12)	0.0251 (9)	0.0188 (9)	0.0017 (7)	−0.0010 (8)
N2	0.0211 (8)	0.0262 (9)	0.0211 (8)	0.0142 (7)	0.0002 (6)	0.0028 (7)
N3	0.0177 (8)	0.0254 (8)	0.0232 (8)	0.0132 (7)	0.0008 (6)	0.0005 (6)
C1	0.0206 (9)	0.0237 (9)	0.0228 (9)	0.0113 (8)	−0.0012 (7)	−0.0003 (7)
C2	0.0322 (12)	0.094 (2)	0.0212 (10)	0.0365 (14)	0.0023 (9)	0.0105 (12)
C3	0.0279 (12)	0.092 (2)	0.0276 (11)	0.0325 (13)	−0.0028 (9)	0.0021 (12)
C4	0.0447 (15)	0.110 (2)	0.0207 (10)	0.0492 (17)	0.0037 (10)	0.0085 (13)
C5	0.0340 (13)	0.087 (2)	0.0291 (11)	0.0399 (14)	−0.0010 (10)	0.0054 (12)
C6	0.0206 (9)	0.0199 (9)	0.0205 (9)	0.0108 (8)	−0.0020 (7)	−0.0010 (7)
C7	0.0232 (9)	0.0244 (10)	0.0186 (8)	0.0149 (8)	−0.0006 (7)	0.0017 (7)
C8	0.0202 (9)	0.0204 (9)	0.0206 (8)	0.0118 (8)	−0.0023 (7)	−0.0034 (7)
C9	0.0255 (10)	0.0283 (10)	0.0233 (9)	0.0174 (9)	−0.0037 (8)	0.0000 (8)
C10	0.0298 (10)	0.0259 (10)	0.0203 (9)	0.0162 (9)	0.0024 (8)	0.0045 (8)
C11	0.0204 (9)	0.0228 (9)	0.0223 (9)	0.0113 (8)	0.0009 (7)	−0.0027 (7)
C12	0.0178 (9)	0.0194 (9)	0.0206 (8)	0.0103 (7)	−0.0043 (7)	−0.0043 (7)
C13	0.0204 (9)	0.0169 (8)	0.0172 (8)	0.0103 (7)	−0.0024 (7)	−0.0027 (7)
C14	0.0157 (8)	0.0215 (9)	0.0193 (8)	0.0116 (7)	−0.0022 (7)	−0.0004 (7)
C15	0.0173 (9)	0.0198 (9)	0.0199 (8)	0.0102 (8)	−0.0011 (7)	−0.0003 (7)

Geometric parameters (Å, º)

O1—C6	1.223 (2)	C7—C8	1.463 (3)
O2—C13	1.368 (2)	C7—H7	0.9300
O2—C14	1.433 (2)	C8—C9	1.399 (3)
N1—C3	1.318 (3)	C8—C13	1.405 (2)
N1—C4	1.331 (3)	C9—C10	1.379 (3)
N2—C6	1.355 (2)	C9—H9	0.9300
N2—N3	1.388 (2)	C10—C11	1.391 (3)
N2—H2N	0.91 (2)	C10—H10	0.9300
N3—C7	1.278 (2)	C11—C12	1.389 (3)
C1—C2	1.371 (3)	C11—H11	0.9300
C1—C5	1.379 (3)	C12—C13	1.390 (2)
C1—C6	1.501 (3)	C12—H12	0.9300
C2—C3	1.380 (3)	C14—C15	1.513 (2)
C2—H2	0.9300	C14—H14A	0.9700
C3—H3	0.9300	C14—H14B	0.9700
C4—C5	1.381 (3)	C15—C15^i	1.527 (3)
C4—H4	0.9300	C15—H15A	0.9700
C5—H5	0.9300	C15—H15B	0.9700
C13—O2—C14	118.16 (13)	C13—C8—C7	119.36 (16)
C3—N1—C4	116.33 (19)	C10—C9—C8	120.95 (17)
C6—N2—N3	118.93 (15)	C10—C9—H9	119.5

C6—N2—H2N	117.6 (15)	C8—C9—H9	119.5
N3—N2—H2N	122.5 (15)	C9—C10—C11	119.22 (17)
C7—N3—N2	115.07 (15)	C9—C10—H10	120.4
C2—C1—C5	116.64 (18)	C11—C10—H10	120.4
C2—C1—C6	118.21 (17)	C12—C11—C10	121.25 (17)
C5—C1—C6	124.87 (17)	C12—C11—H11	119.4
C1—C2—C3	120.44 (19)	C10—C11—H11	119.4
C1—C2—H2	119.8	C11—C12—C13	119.25 (17)
C3—C2—H2	119.8	C11—C12—H12	120.4
N1—C3—C2	123.3 (2)	C13—C12—H12	120.4
N1—C3—H3	118.4	O2—C13—C12	124.04 (16)
C2—C3—H3	118.4	O2—C13—C8	115.63 (15)
N1—C4—C5	124.1 (2)	C12—C13—C8	120.32 (16)
N1—C4—H4	118.0	O2—C14—C15	107.28 (13)
C5—C4—H4	118.0	O2—C14—H14A	110.3
C1—C5—C4	119.1 (2)	C15—C14—H14A	110.3
C1—C5—H5	120.4	O2—C14—H14B	110.3
C4—C5—H5	120.4	C15—C14—H14B	110.3
O1—C6—N2	124.00 (17)	H14A—C14—H14B	108.5
O1—C6—C1	120.65 (16)	C14—C15—C15^i	111.20 (18)
N2—C6—C1	115.29 (15)	C14—C15—H15A	109.4
N3—C7—C8	121.04 (16)	C15^i—C15—H15A	109.4
N3—C7—H7	119.5	C14—C15—H15B	109.4
C8—C7—H7	119.5	C15^i—C15—H15B	109.4
C9—C8—C13	119.01 (17)	H15A—C15—H15B	108.0
C9—C8—C7	121.63 (16)		
C6—N2—N3—C7	179.08 (17)	N3—C7—C8—C13	167.81 (17)
C5—C1—C2—C3	2.7 (4)	C13—C8—C9—C10	−0.3 (3)
C6—C1—C2—C3	176.9 (2)	C7—C8—C9—C10	−179.49 (17)
C4—N1—C3—C2	−2.6 (4)	C8—C9—C10—C11	0.2 (3)
C1—C2—C3—N1	0.3 (5)	C9—C10—C11—C12	0.2 (3)
C3—N1—C4—C5	1.8 (4)	C10—C11—C12—C13	−0.5 (3)
C2—C1—C5—C4	−3.4 (4)	C14—O2—C13—C12	−7.6 (2)
C6—C1—C5—C4	−177.2 (2)	C14—O2—C13—C8	173.57 (15)
N1—C4—C5—C1	1.2 (5)	C11—C12—C13—O2	−178.45 (16)
N3—N2—C6—O1	−5.6 (3)	C11—C12—C13—C8	0.4 (3)
N3—N2—C6—C1	171.51 (15)	C9—C8—C13—O2	178.94 (16)
C2—C1—C6—O1	−4.9 (3)	C7—C8—C13—O2	−1.8 (2)
C5—C1—C6—O1	168.8 (2)	C9—C8—C13—C12	0.0 (3)
C2—C1—C6—N2	177.9 (2)	C7—C8—C13—C12	179.25 (16)
C5—C1—C6—N2	−8.4 (3)	C13—O2—C14—C15	−179.86 (14)
N2—N3—C7—C8	179.54 (15)	O2—C14—C15—C15^i	−178.00 (17)
N3—C7—C8—C9	−13.0 (3)		

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

Hydrogen-bond geometry (Å, º)

Cg2 is the centroid of the C8–C13 benzene ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*N*···N1ⁱⁱ	0.91 (2)	2.04 (2)	2.907 (2)	159 (2)
C3—H3···O1ⁱⁱⁱ	0.93	2.60	3.449 (3)	153
C3—H3···N3ⁱⁱⁱ	0.93	2.55	3.223 (3)	129
C7—H7···N1ⁱⁱ	0.93	2.63	3.372 (3)	137
C12—H12···O1ⁱᵛ	0.93	2.43	3.331 (2)	163
C15—H15*A*···*Cg*2ᵛ	0.97	2.91	3.748 (2)	145

Symmetry codes: (ii) *y*−1/3, −*x*+*y*+1/3, −*z*+1/3; (iii) *x*−*y*+2/3, *x*+1/3, −*z*+4/3; (iv) −*y*+1/3, *x*−*y*+2/3, *z*−1/3; (v) *x*, *y*, *z*−1.