

# (2Z)-3-Hydroxy-1-(pyridin-2-yl)-3-(pyridin-3-yl)-prop-2-en-1-one: crystal structure and Hirshfeld surface analysis

Sze-Ling Lee,<sup>a</sup> Ai Ling Tan,<sup>a</sup> David J. Young,<sup>b‡</sup> Mukesh M. Jotani<sup>c</sup> and Edward R. T. Tiekink<sup>d\*</sup>

Received 20 May 2016

Accepted 21 May 2016

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

‡ Additional correspondence author, e-mail: dyoung1@usc.edu.au.

**Keywords:** crystal structure; propane-1,3-dione; hydrogen bond; Hirshfeld surface.

**CCDC reference:** 1481225

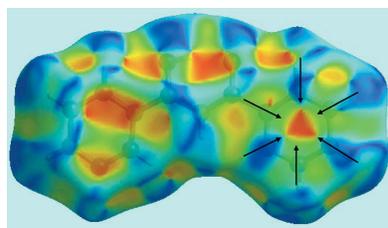
**Supporting information:** this article has supporting information at journals.iucr.org/e

<sup>a</sup>Faculty of Science, Universiti Brunei Darussalam, Jalan Tungku Link BE 1410, Negara Brunei Darussalam, <sup>b</sup>Faculty of Science, Health, Education and Engineering, University of the Sunshine Coast, Maroochydore DC, Queensland 4558, Australia, <sup>c</sup>Department of Physics, Bhavan's Sheth R. A. College of Science, Ahmedabad, Gujarat 380 001, India, and <sup>d</sup>Research Centre for Crystalline Materials, Faculty of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia. \*Correspondence e-mail: edwardt@sunway.edu.my

The title compound, C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> [also called 1-(pyridin-2-yl)-3-(pyridin-3-yl)propane-1,3-dione], features an almost planar (r.m.s. deviation = 0.0095 Å) central C<sub>3</sub>O<sub>2</sub> core consolidated by an intramolecular hydroxy-O—H···O(carbonyl) hydrogen bond. Twists are evident in the molecule, as seen in the dihedral angles between the central core and the 2- and pyridin-3-yl rings of 8.91 (7) and 15.88 (6)°, respectively. The conformation about the C=C bond [1.3931 (17) Å] is Z, and the N atoms lie to the same side of the molecule. In the molecular packing, supramolecular chains along the *a* axis are mediated by π(pyridin-2-yl)–π(pyridin-3-yl) interactions [inter-centroid distance = 3.7662 (9) Å]. The observation that chains pack with no directional interactions between them is consistent with the calculated electrostatic potential, which indicates that repulsive interactions dominate.

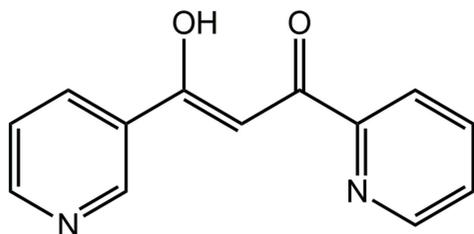
## 1. Chemical context

The β-diketonates of virtually all metals are known (Lamprey, 1960) because of the stability of the resulting six-membered metallocycle formed from bidentate coordination through the two oxygen atoms and the ability of the ligand to be accommodated within the common octahedral, tetrahedral and square-pyramidal coordination geometries. There has been an interest over the last few years to introduce extra donor functionality such as nitrile and pyridyl to this class of ligand to generate heterometallic complexes and novel coordination networks. Dipyridyl β-diketonates, for example, have been used to synthesize mixed-metal–organic frameworks. Burrows and co-workers employed di(pyridin-4-yl)propane-1,3-dione to prepare the corresponding Al<sup>III</sup> and Ga<sup>III</sup> octahedral building blocks for network structures linked by Ag<sup>I</sup> ions (Burrows *et al.*, 2010). Carlucci and co-workers used the same ligand to make Fe<sup>III</sup> metalloligands that were again joined by coordination to Ag<sup>I</sup> ions. The type of the resulting two- or three-dimensional coordination polymer depended on the nature of the counter-ion to silver (Carlucci *et al.*, 2011). By comparison, the di(pyridin-2-yl)propane-1,3-dione ligand, which also has extra donor functionality available for coordination, is sterically hindered to allow network formation. Tan and co-workers prepared the Cd<sup>II</sup> and Cu<sup>II</sup> complexes from this ligand and did indeed observe chelation through the 2,2'-nitrogen atoms (Tan *et al.*, 2012). However, they did not observe solid-state network formation from bridging oxygen-



OPEN ACCESS

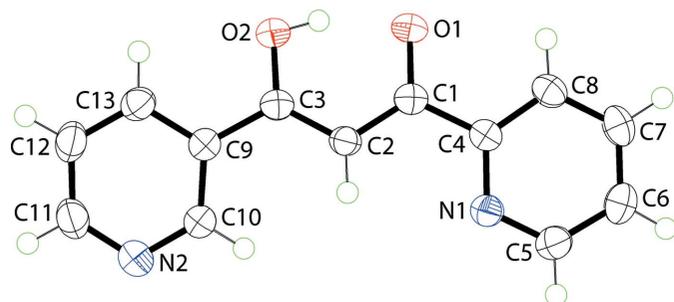
atom,  $\mu_2$ -Cl or  $\mu_3$ -Cl donors in the  $\text{Cd}^{\text{II}}$  complexes; the  $\text{Cu}^{\text{II}}$  complex was a tetranuclear oligomer linked *via* bridging water and acetate counter-ions (Tan *et al.*, 2012). Less work has been performed with the unsymmetrical pyridyl  $\beta$ -diketonates. Zhang and co-workers have made the  $\text{Fe}^{\text{III}}$  salt of 3-(pyridin-4-yl)-2,4-pentanedione as well as the mixed-MOF with  $\text{AgNO}_3$  in a two-dimensional honeycomb structure while at higher  $\text{Ag}^{\text{I}}$  concentrations, a one-dimensional ladder motif was formed (Zhang *et al.*, 2008). This ligand and the symmetrical 4,4'- and 3,3'- variants have been treated with hydrazine to give the corresponding pyrazoles that were used to prepare strongly photoluminescent  $\text{Cu}^{\text{I}}$  coordination polymers (Zhan *et al.*, 2011).



All of the mentioned dipyriddy ligands can be conveniently prepared by the Claisen condensation of an acetylpyridine with a pyridine carboxylic ester. The title compound, (I), has not previously been reported, but was prepared in this way from 2-acetylpyridine and ethyl nicotinate, and crystals suitable for X-ray crystallography were obtained by recrystallization from a mixture of dichloromethane and hexane. Herein, the crystal structure analysis of (I) is described along with a detailed investigation of the molecular packing by a Hirshfeld surface analysis.

## 2. Structural commentary

In (I), the assignment of carbonyl- *versus* hydroxy-O atoms is not readily confirmed by a great disparity in the C1–O1 [1.2871 (14) Å] and C3–O2 [1.3041 (14) Å] bond lengths. The assignment was based on an unrestrained refinement of the H1O atom which resulted in a O2–H1O bond length of 1.090 (18) Å. More certainty is associated with the assignment of the nitrogen atoms in the pyridyl rings. Thus, the short C5–N1 and C4–N1 [1.3325 (17) and 1.3484 (15) Å] and C10–N2 and C11–N2 [1.3371 (17) and 1.3397 (18) Å] bond lengths *cf.*



**Figure 1**  
The molecular structure of (I), showing the atom-labelling scheme and displacement ellipsoids at the 70% probability level.

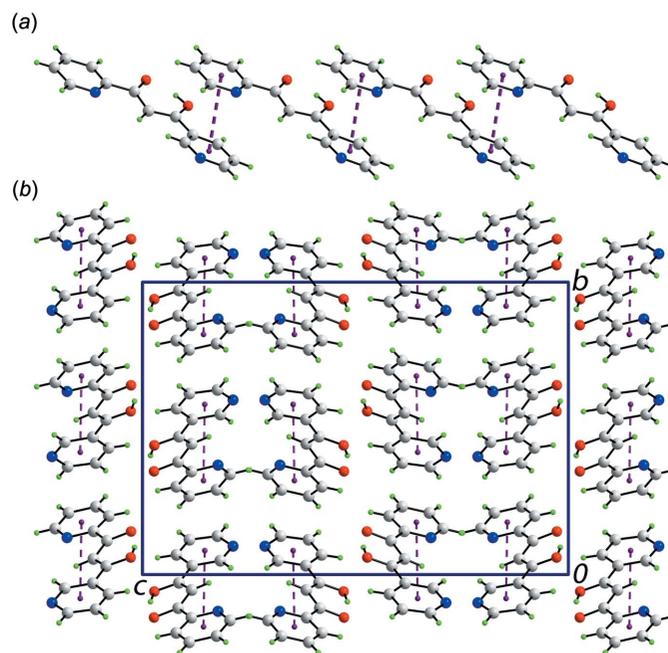
**Table 1**  
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2–H2O $\cdots$ O1	0.85 (2)	1.65 (1)	2.4673 (14)	160 (2)

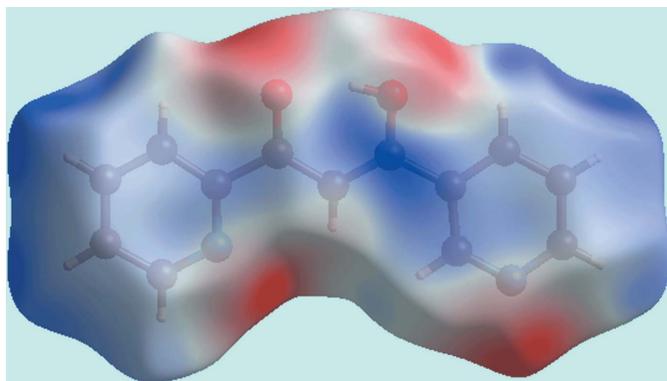
the C–C bonds in the rings confirm their assignment. The central  $\text{C}_3\text{O}_2$  residual in (I), Fig. 1, is essentially planar with the r.m.s. deviation of the five atoms being 0.0095 Å. The *syn* arrangement of the oxygen atoms enables the formation of an intramolecular hydroxy-O–H $\cdots$ O(carbonyl) hydrogen bond, Table 1. The dihedral angles formed between the central plane and the N1- and N2-pyridinyl rings are 8.91 (7) and 15.88 (6)°, respectively, indicating twists in the molecule. The dihedral angle between the pyridyl rings is 7.45 (7)°. The conformation about the C2=C3 [1.3931 (17) Å] is *Z*, and, to a first approximation, the N1 and N2 atoms lie to the same side of the molecule.

## 3. Supramolecular features

The molecular packing in the crystal is dominated by  $\pi$ – $\pi$  interactions formed between the N1- and N2-pyridinyl rings of translationally related molecules [ $C_g(\text{N1-pyridinyl})\cdots C_g(\text{N2-pyridinyl}) = 3.7662$  (9) Å, angle of inclination = 7.45 (6)° for symmetry operation  $1 + x, y, z$ ]. The result is the formation of a linear supramolecular chain, Fig. 2*a*. The chains pack with no directional interactions between them in accord with the distance criteria in *PLATON* (Spek, 2009), Fig. 2*b*.



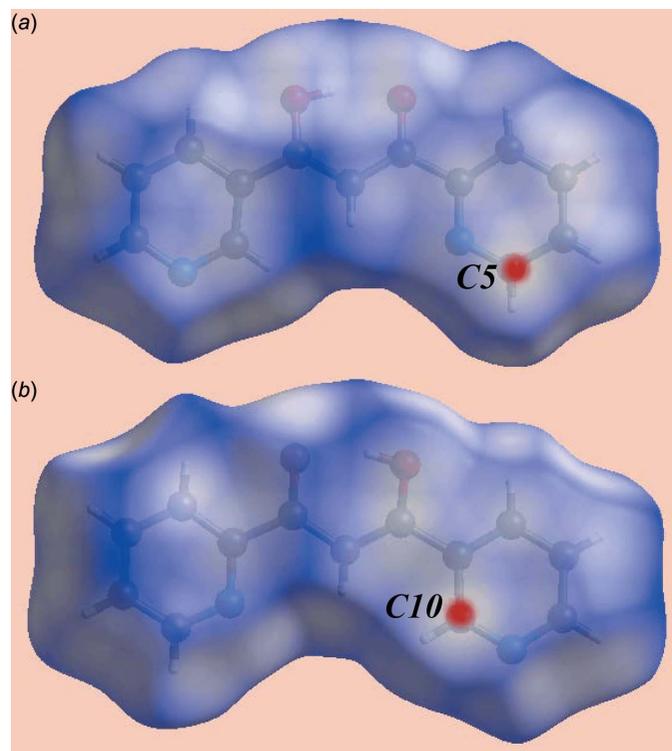
**Figure 2**  
Molecular packing in (I): (a) a view of the supramolecular chain along the *a* axis sustained by  $\pi$ – $\pi$  interactions and (b) unit-cell contents shown in projection down the *a* axis. The  $\pi$ – $\pi$  interactions are shown as purple dashed lines.



**Figure 3**  
A view of the Hirshfeld surface mapped over electrostatic potential for (I). The red and blue regions represent negative and positive electrostatic potentials, respectively.

#### 4. Hirshfeld surface analysis

The program *Crystal Explorer 3.1* (Wolff *et al.*, 2012) was used to generate Hirshfeld surfaces mapped over the electrostatic potential,  $d_{\text{norm}}$ , shape-index and curvedness. The electrostatic potential was calculated with *TONTO* (Spackman *et al.*, 2008; Jayatilaka *et al.*, 2005), integrated in *Crystal Explorer*, using the experimental geometry as the input. The electrostatic potentials were mapped on the Hirshfeld surface using the STO-3G basis set at the Hartree–Fock level of theory over a



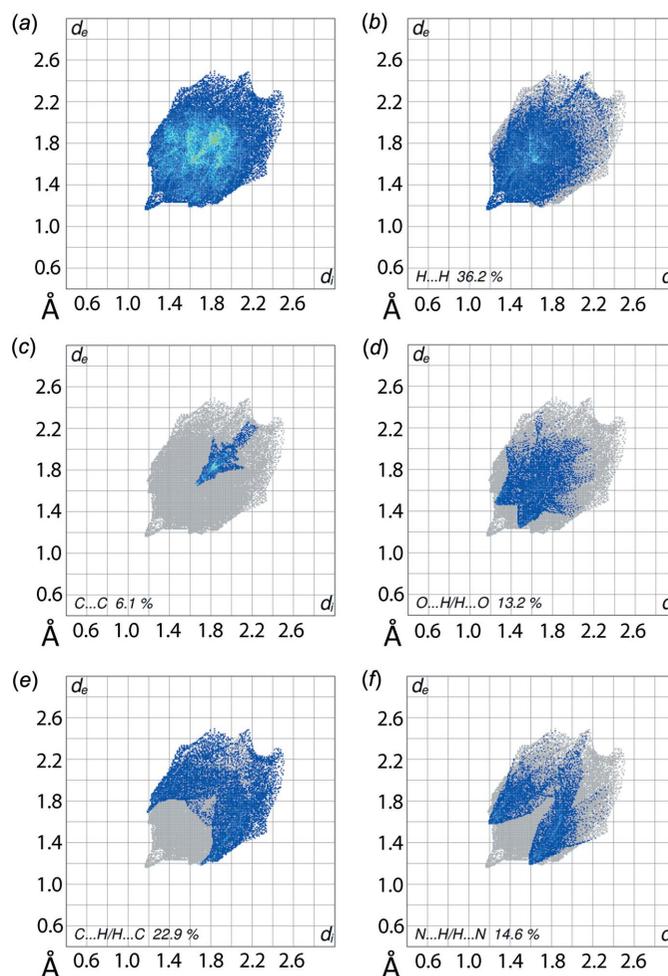
**Figure 4**  
Two views of the Hirshfeld surface mapped over  $d_{\text{norm}}$  for (I): the bright-red spots at (a) C5 and (b) C10 indicate their involvement in short intermolecular C...C contacts.

**Table 2**

Percentage contribution of the different intermolecular interactions to the Hirshfeld surface of (I).

Contact	%
H...H	36.2
O...H/H...O	13.2
C...H/H...C	22.9
N...H/H...N	14.6
C...C	6.1
C...O/O...C	2.9
C...N/N...C	2.8
O...O	0.9
N...N	0.4

range  $\pm 0.06$  au. The contact distances  $d_i$  and  $d_e$  from the Hirshfeld surface to the nearest atom inside and outside, respectively, enables the analysis of the intermolecular interactions through the mapping of  $d_{\text{norm}}$ . The combination of  $d_e$  and  $d_i$  in the form of a two-dimensional fingerprint plot (McKinnon *et al.*, 2004) provides a summary of the intermolecular contacts in the crystal.



**Figure 5**  
The two-dimensional fingerprint plots for (I): (a) all interactions, and delineated into (b) H...H, (c) C...C, (d) O...H/H...O, (e) C...H/H...C and (f) N...H/H...N interactions.

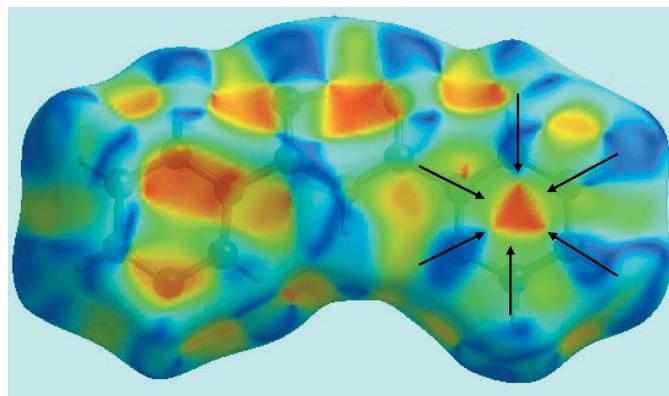
**Table 3**  
Dihedral angle ( $^{\circ}$ ) data for (I)–(III).

Structure	C <sub>3</sub> O <sub>2</sub> / <i>n</i> -pyridyl	C <sub>3</sub> O <sub>2</sub> /pyridin-2-yl or phenyl	ring/ring	CSD refcode <sup>a</sup>	Reference
(I)	$n = 3$ ; 15.88 (6)	8.91 (7)	7.45 (7)	–	This work
(II)	$n = 3$ ; 2.23 (9)	4.20 (8)	4.38 (9)	XIOXID	Dudek <i>et al.</i> (2011)
(III) <sup>b</sup>	$n = 4$ ; 8.10 (5)	11.41 (5)	3.88 (5)	BEDREJ	Dudek <i>et al.</i> (2011)

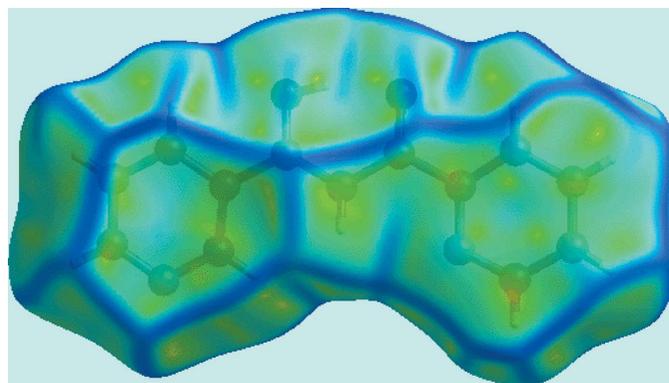
Notes: (a) Groom *et al.* (2016); (b) isolated as a 1:1 co-crystal with benzoic acid.

From the Hirshfeld surface mapped over electrostatic potential, Fig. 3, the negative potentials around the oxygen atoms of the hydroxy and carbonyl groups as well as about the nitrogen atoms of pyridyl rings prevent their participation in intermolecular interactions in the crystal of (I) due to the electrostatic repulsion that would eventuate. The presence of a short intermolecular C···C contact between the C5 and C10 atoms [C5···C10 = 3.313 (2) Å; symmetry code:  $-1 + x, y, z$ ], which fall within the  $\pi$ – $\pi$  contacts between pyridyl rings (Fig. 2a), is viewed as bright-red spots near these atoms on the Hirshfeld surface mapped over  $d_{\text{norm}}$ , Fig. 4.

The overall 2D fingerprint plot, Fig. 5a, and those delineated into H···H, C···C, O···H/H···O, C···H/H···C and N···H/H···N contacts are illustrated in Fig. 5b–f, respectively;



**Figure 6**  
A view of the Hirshfeld surface mapped with shape-index property for (I). The red and blue triangles identified with arrows indicate  $\pi$ – $\pi$  stacking interactions.



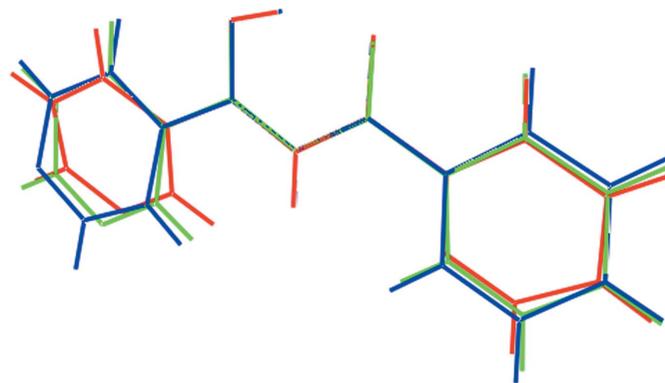
**Figure 7**  
A view of the Hirshfeld surface mapped over curvedness for (I). The flat regions highlight the involvement of rings in the  $\pi$ – $\pi$  stacking interactions.

their relative contributions to the surface are quantified in Table 2. The interatomic H···H contacts (McKinnon *et al.*, 2007) appear as the scattered points over the greater part of the plot shown in Fig. 5b, with a single peak at ( $d_e, d_i$ ) less than the van der Waals separation corresponding to a short H13···H13 contact of 2.33 Å (symmetry code:  $1 - x, -y, -z$ ). The short interatomic C5···C10 contact and  $\pi$ – $\pi$  stacking interactions appear as an arrow-like distribution of points with the tip at  $d_e + d_i \sim 3.3$  Å (Fig. 5c). The presence of  $\pi$ – $\pi$  stacking interactions between the pyridyl rings is also apparent from the appearance of red and blue triangle pairs on the Hirshfeld surface mapped with shape-index property identified with arrows in the image of Fig. 6, and in the flat region on the Hirshfeld surface mapped over curvedness in Fig. 7.

The two-dimensional fingerprint plots delineated into O···H/H···O, C···H/H···C and N···H/H···N interactions exhibit their usual characteristic features in their respective plots; Fig. 4d–f. However, the points are distributed at ( $d_e, d_i$ ) distances greater than their respective van der Waals separations. This is consistent with the repulsion between the atoms having electrostatic negative potential dominating the molecular packing, hence the lack of specific intermolecular interactions between supramolecular chains.

## 5. Database survey

A survey of the Cambridge Structural Database (Groom *et al.*, 2016) revealed that there are two closely related pyridyl-substituted propane-1,3-dione structures in the crystallographic literature. These are the mono-pyridyl derivatives



**Figure 8**  
Overlay diagram of molecules of (I) (red image), (II) (green) and (III) (blue). The molecules have been overlapped so that the central five-membered rings are coincident.

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	C <sub>13</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub>
<i>M<sub>r</sub></i>	226.23
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	273
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.2124 (9), 14.1782 (19), 20.794 (3)
<i>V</i> (Å <sup>3</sup> )	2126.4 (5)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
<i>μ</i> (mm <sup>-1</sup> )	0.10
Crystal size (mm)	0.20 × 0.20 × 0.19
Data collection	
Diffractometer	Bruker D8-Quest CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 1996)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.981, 0.982
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	46632, 2647, 2227
<i>R<sub>int</sub></i>	0.057
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.671
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.042, 0.121, 1.05
No. of reflections	2647
No. of parameters	157
No. of restraints	1
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	0.33, -0.24

Computer programs: *SMART* and *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001), *DIAMOND* (Brandenburg, 2006) and *pubCIF* (Westrip, 2010).

3-hydroxy-1-phenyl-3-(pyridin-3-yl)prop-2-en-1-one (II) and 3-hydroxy-1-phenyl-3-(pyridin-4-yl)prop-2-en-1-one (III), both published by Dudek *et al.* (2011). Each structure features a very similar central core with the intramolecular O—H...O hydrogen bond. In each of (II) and (III), the pyridyl ring is connected to the carbon atom bearing the hydroxy group. As seen from the overlay diagram (Fig. 8) and as quantified in Table 3, the three structures (I)–(III) have very similar conformations.

## 6. Synthesis and crystallization

2-Acetylpyridine (3.0562 g, 25.2 mmol) was added to a suspension of NaH (60% dispersion in mineral oil, 2.0058 g, 50.0 mmol) in anhydrous THF (10 ml) at room temperature with stirring. Ethyl nicotinate (7.5675 g, 50.1 mmol) in anhydrous THF (10 ml) was added dropwise to the mixture over 3 min. The yellow mixture was refluxed under a nitrogen atmosphere for 1.3 h and then quenched with ice-water (50 ml). Glacial acetic acid was added to adjust the pH to 6–7. The resulting yellow precipitate was collected by filtration, washed with cold water and dried under vacuum. Recrystallization from dichloromethane–hexane (1:1 *v/v*) solution afforded colourless crystals. Yield: 4.03 g (70.7%). M.p: 377–378 K. IR (KBr pellet) *ν*<sub>max</sub>/cm<sup>-1</sup>: 3121 (*m*), 3053 (*m*), 2922 (*m*), 2853 (*m*), 1611 (*s*), 1595 (*s*), 1539 (*m*), 1458 (*m*), 1418 (*m*), 1221 (*m*), 1188 (*m*), 1146 (*m*), 1115 (*m*), 1067 (*m*), 1018 (*m*), 989 (*m*), 926 (*m*), 775 (*s*), 739 (*m*), 679 (*s*), 611 (*m*). Analysis calculated for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>: C, 69.03; H, 4.42; N, 12.19. Found:

C, 68.73; H, 4.54; N, 12.16. MS: *m/z* 226. <sup>1</sup>H NMR (400 MHz, *d*<sub>6</sub>-DMSO) δ 9.22 (1H, *s*), 8.82 (2H, *m*), 8.44 (1H, *d*, *J* = 7.9 Hz), 8.17 (1H, *d*, *J* = 7.8 Hz), 8.09 (1H, *m*), 7.70 (1H, *m*), 7.63 (2H, *m*).

## 7. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 4. Carbon-bound H atoms were placed in their calculated positions (C—H = 0.95 Å) and were included in the refinement in the riding-model approximation, with *U*<sub>iso</sub>(H) set to 1.2*U*<sub>eq</sub>(C). The hydroxy-H atom was located in a difference map and refined with O—H = 0.82 ± 0.01 Å, and with *U*<sub>iso</sub>(H) set to 1.5*U*<sub>eq</sub>(O).

## Acknowledgements

We acknowledge the financial support from the Brunei Research Council (BRC) Science and Technology grant (S&T17).

## References

- Brandenburg, K. (2006). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruker (2007). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burrows, A. D., Frost, C. G., Mahon, M. F., Raithby, P. R., Renouf, C. L., Richardson, C. & Stevenson, A. J. (2010). *Chem. Commun.* **46**, 5067–5069.
- Carlucci, L., Ciani, G., Proserpio, D. M. & Visconti, M. (2011). *CrystEngComm*, **13**, 5891–5902.
- Dudek, M., Clegg, J. K., Glasson, C. R. K., Kelly, N., Gloe, K., Gloe, K., Kelling, A., Buschmann, H.-J., Jolliffe, K. A., Lindoy, L. F. & Meehan, G. V. (2011). *Cryst. Growth Des.* **11**, 1697–1704.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Gans, J. & Shalloway, D. (2001). *J. Mol. Graphics Modell.* **19**, 557–559.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Jayatilaka, D., Grimwood, D. J., Lee, A., Lemay, A., Russel, A. J., Taylo, C., Wolff, S. K., Chenai, C. & Whitton, A. (2005). *TONTO – A System for Computational Chemistry*. Available at: <http://hirshfeldsurface.net/>
- Lamprey, H. (1960). *Ann. NY Acad. Sci.* **88**, 519–525.
- McKinnon, J. J., Jayatilaka, D. & Spackman, M. A. (2007). *Chem. Commun.* pp. 3814–3816.
- McKinnon, J. J., Spackman, M. A. & Mitchell, A. S. (2004). *Acta Cryst.* **B60**, 627–668.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spackman, M. A., McKinnon, J. J. & Jayatilaka, D. (2008). *CrystEngComm*, **10**, 377–388.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tan, J.-T., Zhao, W.-J., Chen, S.-P., Li, X., Lu, Y.-L., Feng, X. & Yang, X.-W. (2012). *Chem. Pap.* **66**, 47–53.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wolff, S. K., Grimwood, D. J., McKinnon, J. J., Turner, M. J., Jayatilaka, D. & Spackman, M. A. (2012). *Crystal Explorer*. The University of Western Australia, Australia.
- Zhan, S.-Z., Li, M., Zhou, X.-P., Ni, J., Huang, X.-C. & Li, D. (2011). *Inorg. Chem.* **50**, 8879–8892.
- Zhang, Y., Chen, B., Fronczek, F. R. & Maverick, A. W. (2008). *Inorg. Chem.* **47**, 4433–4435.

## supporting information

*Acta Cryst.* (2016). E72, 849-853 [https://doi.org/10.1107/S205698901600832X]

## (2Z)-3-Hydroxy-1-(pyridin-2-yl)-3-(pyridin-3-yl)prop-2-en-1-one: crystal structure and Hirshfeld surface analysis

Sze-Ling Lee, Ai Ling Tan, David J. Young, Mukesh M. Jotani and Edward R. T. Tiekink

### Computing details

Data collection: *SMART* (Bruker, 2007); cell refinement: *SMART* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012), *QMol* (Gans & Shalloway, 2001) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### (2Z)-3-Hydroxy-1-(pyridin-2-yl)-3-(pyridin-3-yl)prop-2-en-1-one

#### Crystal data

$C_{13}H_{10}N_2O_2$

$M_r = 226.23$

Orthorhombic, *Pbca*

$a = 7.2124$  (9) Å

$b = 14.1782$  (19) Å

$c = 20.794$  (3) Å

$V = 2126.4$  (5) Å<sup>3</sup>

$Z = 8$

$F(000) = 944$

$D_x = 1.413$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 9904 reflections

$\theta = 3.0$ – $28.3^\circ$

$\mu = 0.10$  mm<sup>-1</sup>

$T = 273$  K

Block, colourless

$0.20 \times 0.20 \times 0.19$  mm

#### Data collection

Bruker D8-Quest CCD  
diffractometer

Radiation source: sealed tube

Graphite monochromator

Detector resolution: 8.366 pixels mm<sup>-1</sup>

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)

$T_{\min} = 0.981$ ,  $T_{\max} = 0.982$

46632 measured reflections

2647 independent reflections

2227 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\max} = 28.5^\circ$ ,  $\theta_{\min} = 3.0^\circ$

$h = -8 \rightarrow 9$

$k = -18 \rightarrow 18$

$l = -27 \rightarrow 27$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.121$

$S = 1.05$

2647 reflections

157 parameters

1 restraint

Hydrogen site location: mixed

$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.9349P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.33$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.24$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	−0.09862 (13)	0.14710 (7)	0.02692 (4)	0.0286 (2)
O2	0.19541 (13)	0.05816 (7)	0.02776 (4)	0.0276 (2)
H2O	0.1025 (19)	0.0929 (11)	0.0188 (8)	0.041*
N1	−0.33075 (15)	0.12603 (7)	0.17723 (5)	0.0246 (2)
N2	0.43366 (17)	−0.09680 (9)	0.21246 (6)	0.0335 (3)
C1	−0.13288 (17)	0.11505 (8)	0.08360 (6)	0.0217 (3)
C2	−0.01053 (16)	0.05315 (8)	0.11536 (5)	0.0214 (3)
H2	−0.0402	0.0290	0.1557	0.026*
C3	0.15550 (17)	0.02859 (8)	0.08551 (5)	0.0211 (2)
C4	−0.30743 (16)	0.14778 (8)	0.11462 (5)	0.0203 (2)
C5	−0.48525 (19)	0.15721 (9)	0.20520 (6)	0.0286 (3)
H5	−0.5044	0.1425	0.2483	0.034*
C6	−0.61954 (19)	0.21046 (9)	0.17384 (7)	0.0294 (3)
H6	−0.7244	0.2313	0.1957	0.035*
C7	−0.59415 (18)	0.23185 (9)	0.10951 (7)	0.0284 (3)
H7	−0.6819	0.2669	0.0871	0.034*
C8	−0.43511 (18)	0.19984 (8)	0.07917 (6)	0.0245 (3)
H8	−0.4141	0.2129	0.0360	0.029*
C9	0.29989 (16)	−0.03006 (8)	0.11646 (5)	0.0206 (2)
C10	0.30159 (18)	−0.04710 (9)	0.18265 (6)	0.0269 (3)
H10	0.2055	−0.0225	0.2073	0.032*
C11	0.57090 (19)	−0.13133 (10)	0.17598 (7)	0.0315 (3)
H11	0.6644	−0.1656	0.1960	0.038*
C12	0.58095 (19)	−0.11875 (9)	0.10999 (7)	0.0308 (3)
H12	0.6782	−0.1445	0.0865	0.037*
C13	0.44368 (18)	−0.06720 (9)	0.07980 (6)	0.0257 (3)
H13	0.4474	−0.0575	0.0356	0.031*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0318 (5)	0.0325 (5)	0.0214 (4)	0.0031 (4)	0.0021 (3)	0.0078 (3)
O2	0.0272 (5)	0.0349 (5)	0.0208 (4)	0.0036 (4)	0.0036 (3)	0.0050 (3)
N1	0.0235 (5)	0.0280 (5)	0.0224 (5)	−0.0003 (4)	−0.0005 (4)	0.0020 (4)
N2	0.0316 (6)	0.0394 (6)	0.0294 (6)	0.0077 (5)	−0.0005 (5)	0.0056 (5)
C1	0.0229 (6)	0.0215 (5)	0.0207 (5)	−0.0035 (4)	−0.0010 (4)	−0.0003 (4)
C2	0.0222 (6)	0.0232 (6)	0.0188 (5)	−0.0003 (4)	−0.0006 (4)	0.0020 (4)
C3	0.0226 (6)	0.0211 (5)	0.0195 (5)	−0.0033 (4)	−0.0009 (4)	−0.0010 (4)
C4	0.0225 (6)	0.0173 (5)	0.0211 (5)	−0.0022 (4)	−0.0023 (4)	−0.0002 (4)

C5	0.0282 (6)	0.0333 (7)	0.0243 (6)	0.0001 (5)	0.0023 (5)	0.0003 (5)
C6	0.0250 (6)	0.0277 (6)	0.0355 (7)	0.0030 (5)	0.0034 (5)	-0.0046 (5)
C7	0.0275 (6)	0.0220 (6)	0.0357 (7)	0.0049 (5)	-0.0053 (5)	0.0007 (5)
C8	0.0286 (6)	0.0209 (5)	0.0240 (6)	0.0006 (5)	-0.0034 (5)	0.0013 (4)
C9	0.0202 (5)	0.0191 (5)	0.0224 (5)	-0.0030 (4)	-0.0001 (4)	-0.0010 (4)
C10	0.0247 (6)	0.0320 (6)	0.0239 (6)	0.0044 (5)	0.0020 (5)	0.0022 (5)
C11	0.0263 (7)	0.0309 (7)	0.0373 (7)	0.0055 (5)	-0.0021 (5)	0.0043 (5)
C12	0.0276 (6)	0.0279 (6)	0.0369 (7)	0.0066 (5)	0.0059 (5)	-0.0008 (5)
C13	0.0284 (6)	0.0245 (6)	0.0243 (6)	0.0005 (5)	0.0036 (5)	-0.0012 (5)

*Geometric parameters (Å, °)*

O1—C1	1.2871 (14)	C5—H5	0.9300
O2—C3	1.3041 (14)	C6—C7	1.3839 (19)
O2—H2O	0.853 (9)	C6—H6	0.9300
N1—C5	1.3325 (17)	C7—C8	1.3855 (18)
N1—C4	1.3484 (15)	C7—H7	0.9300
N2—C10	1.3371 (17)	C8—H8	0.9300
N2—C11	1.3397 (18)	C9—C13	1.3907 (17)
C1—C2	1.4090 (16)	C9—C10	1.3975 (16)
C1—C4	1.4888 (17)	C10—H10	0.9300
C2—C3	1.3931 (17)	C11—C12	1.386 (2)
C2—H2	0.9300	C11—H11	0.9300
C3—C9	1.4800 (16)	C12—C13	1.3815 (18)
C4—C8	1.3915 (16)	C12—H12	0.9300
C5—C6	1.3905 (19)	C13—H13	0.9300
C3—O2—H2O	102.4 (12)	C6—C7—C8	118.55 (12)
C5—N1—C4	116.73 (11)	C6—C7—H7	120.7
C10—N2—C11	117.16 (12)	C8—C7—H7	120.7
O1—C1—C2	121.93 (11)	C7—C8—C4	118.71 (11)
O1—C1—C4	116.69 (10)	C7—C8—H8	120.6
C2—C1—C4	121.37 (10)	C4—C8—H8	120.6
C3—C2—C1	119.02 (11)	C13—C9—C10	117.90 (11)
C3—C2—H2	120.5	C13—C9—C3	119.94 (11)
C1—C2—H2	120.5	C10—C9—C3	122.12 (11)
O2—C3—C2	121.32 (11)	N2—C10—C9	123.63 (12)
O2—C3—C9	115.20 (10)	N2—C10—H10	118.2
C2—C3—C9	123.47 (10)	C9—C10—H10	118.2
N1—C4—C8	123.38 (11)	N2—C11—C12	123.53 (12)
N1—C4—C1	116.91 (10)	N2—C11—H11	118.2
C8—C4—C1	119.69 (11)	C12—C11—H11	118.2
N1—C5—C6	123.92 (12)	C13—C12—C11	118.73 (12)
N1—C5—H5	118.0	C13—C12—H12	120.6
C6—C5—H5	118.0	C11—C12—H12	120.6
C7—C6—C5	118.69 (12)	C12—C13—C9	119.05 (12)
C7—C6—H6	120.7	C12—C13—H13	120.5
C5—C6—H6	120.7	C9—C13—H13	120.5

O1—C1—C2—C3	2.34 (18)	N1—C4—C8—C7	0.49 (18)
C4—C1—C2—C3	-176.70 (10)	C1—C4—C8—C7	-178.19 (11)
C1—C2—C3—O2	-3.26 (17)	O2—C3—C9—C13	-14.19 (16)
C1—C2—C3—C9	175.33 (10)	C2—C3—C9—C13	167.14 (11)
C5—N1—C4—C8	-0.14 (17)	O2—C3—C9—C10	163.35 (11)
C5—N1—C4—C1	178.58 (11)	C2—C3—C9—C10	-15.33 (18)
O1—C1—C4—N1	-170.37 (10)	C11—N2—C10—C9	0.2 (2)
C2—C1—C4—N1	8.72 (17)	C13—C9—C10—N2	0.14 (19)
O1—C1—C4—C8	8.40 (16)	C3—C9—C10—N2	-177.44 (12)
C2—C1—C4—C8	-172.51 (10)	C10—N2—C11—C12	-0.6 (2)
C4—N1—C5—C6	-0.55 (19)	N2—C11—C12—C13	0.6 (2)
N1—C5—C6—C7	0.9 (2)	C11—C12—C13—C9	-0.27 (19)
C5—C6—C7—C8	-0.48 (19)	C10—C9—C13—C12	-0.09 (18)
C6—C7—C8—C4	-0.16 (18)	C3—C9—C13—C12	177.55 (11)

*Hydrogen-bond geometry (Å, °)*

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2O...O1	0.85 (2)	1.65 (1)	2.4673 (14)	160 (2)