Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

Isophthalic acid–3,6-bis(2-pyrazinyl)-1,4-dihydro-1,2,4,5-tetrazine (1/1)

Xiao-Juan Fu, Zhi-Hui Zhang and Miao Du*

College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300387, People's Republic of China
Correspondence e-mail: dumiao@public.tpt.tj.cn

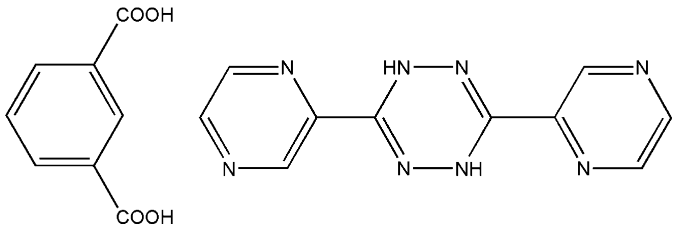
Received 29 April 2007; accepted 13 July 2007

Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.003 Å; R factor = 0.041; wR factor = 0.106; data-to-parameter ratio = 10.8.

The cocrystallization of isophthalic acid (H_2ip) with 3,6-bis(2-pyrazinyl)-1,4-dihydro-1,2,4,5-tetrazine (H_2bpztz) yields the title binary molecular cocrystal, $C_8H_6O_4 \cdot C_{10}H_8N_8$ or [(H_2ip)·(H_2bpztz)]. In the isophthalic acid molecule, a crystallographic twofold rotation axis passes between the carboxyl substituents. In the tricyclic molecule, a crystallographic twofold rotation axis is perpendicular to the central ring. Intermolecular O—H···N and C—H···O interactions between the carboxyl and pyrazinyl groups of the two components produces a one-dimensional zigzag tape. Further N—H···N hydrogen bonds between adjacent H_2bpztz molecules generate a three-dimensional supramolecular network. The resulting diamond networks are of fivefold parallel interpenetration and are consolidated by π–π stacking interactions (3.70 Å) between the aromatic rings.

Related literature

For related literature, see: Batten (2001); Desiraju (1989); Du *et al.* (2005, and references therein); Etter (1990); Sarkar *et al.* (2003); Steiner (2002); Wells (1977).



Experimental

Crystal data

$C_8H_6O_4 \cdot C_{10}H_8N_8$
M_r = 406.37
Orthorhombic, $Pnna$
a = 13.546 (4) Å
b = 33.654 (11) Å
c = 3.7035 (12) Å
V = 1688.3 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.12 mm^{-1}
T = 294 (2) K
0.32 × 0.10 × 0.06 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.764, T_{max} = 1.000
8125 measured reflections
1501 independent reflections
937 reflections with $I > 2\sigma(I)$
R_{int} = 0.080

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.106
S = 1.06
1501 reflections
139 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N2	0.82	1.94	2.752 (3)	172
N4—H4A···N1^{i}	0.90	2.53	3.166 (3)	128
C6—H6···O2	0.93	2.56	3.223 (3)	129

Symmetry code: (i) $x+\frac{1}{2}, y, -z+2$.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2* and *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (grant No. 20671071) and Tianjin Normal University.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GG3096).

References

Batten, S. R. (2001). *CrystEngComm*, **3**, 67–73.
Brandenburg, K. (2005). *DIAMOND*. Version 3.0d. Crystal Impact GbR, Bonn, Germany.
Bruker (2001). *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2003). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*. New York: Elsevier.
Du, M., Zhang, Z.-H. & Zhao, X.-J. (2005). *Cryst. Growth Des.* **5**, 1199–1208.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Sarkar, B., Kaim, W., Schleid, T., Hartenbach, I. & Fiedler, J. (2003). *Z. Anorg. Allg. Chem.* **629**, 1353–1357.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
Wells, A. F. (1977). *Three-Dimensional Nets and Polyhedra*. New York: Wiley.

doi:10.1107/S1600536807034423

supplementary materials

Acta Cryst. (2007). E**63**, o3530 [**doi:10.1107/S1600536807034423**]

Isophthalic acid-3,6-bis(2-pyrazinyl)-1,4-dihydro-1,2,4,5-tetrazine (1/1)

X.-J. Fu, Z.-H. Zhang and M. Du

Comment

Crystal engineering for the design and assembly of crystalline supramolecular solids is of current interest (Desiraju, 1989). In this regard, it is well known that weak interactions such as hydrogen bonding play an important role in regulating the final crystal packing (Etter, 1990; Steiner, 2002). Aromatic dicarboxylic acids, as robust hydrogen bonding participators, are widely used in the range of cocrystallization with complementary basic organic components to produce binary cocrystals with intriguing network structures (Du *et al.*, 2005, and references therein). As a result, the pyridyl ring prefers to create the familiar carboxyl-pyridyl heterosynthon [denoted as $R_2^2(7)$] with the carboxylic acid moiety. In this work, for the sake of further understanding the direction of hydrogen-bonding in such supramolecular frameworks, a multifunctional building block, namely 1,4-dihydro-3,6-bis(2-pyrazinyl)-1,2,4,5-tetrazine (H_2bpztz), is introduced to assemble with isophthalic acid (H_2ip). The resultant 1:1 binary cocrystal [(H_2ip)·(H_2bpztz)], (I), exhibits a novel 3-D hydrogen-bonding architecture of 5-fold interpenetrating (Batten, 2001) diamond networks.

X-ray structural analysis of (I) confirms the expected 1:1 stoichiometry, as depicted in Figure 1, and both H_2ip and H_2bpztz molecules are located at the 2-fold axes. As for isophthalic acid, two carboxyl groups are located in a *cis*-arrangement in order to self-adjust the generation of the favorite hydrogen-bonded patterns. Within each H_2bpztz molecule, two terminal pyrazinyl planes make the dihedral angle of 26.5 (1)° with the central 6-member distorted ring, and are inclined to each other by 53.0 (1)°. As anticipated, each pyrazinyl group of H_2bpztz is connected to the carboxyl of H_2ip *via* the O1—H1···N2 and C6—H6···O2 interactions [heterosynthon $R_2^2(7)$, see Table 1 for details], giving a 1-D zigzag hydrogen-bonded tape along [010]. Further, the adjacent H_2bpztz molecules are linked by a pair of N4—H4A···N1 bonds between the imido and pyrazinyl groups [$R_2^2(10)$, see Table 1 for details], featuring another 1-D ribbon array along the [100] direction. The detailed hydrogen-bonding surroundings are shown in Figure 2. Due to the nonplanar folded configuration of the H_2bpztz molecule, such hydrogen-bonding interactions interlink the two components to form a 3-D supramolecular structure. From the viewpoint of network topology, if each H_2bpztz building block is considered as a tetrahedral node, a familiar diamond network is realised (Wells, 1977). The scale of the molecular components suggests that the dimensions of the channels (along the [100] direction) in this network are as large as *ca* 19 × 19 Å. As a consequence, this hydrogen-bonding set in turn is entangled by other four parallel ones, which thus generates a novel 5-fold interpenetrating architecture (Figure 3). Further analysis of crystal packing reveals significant π···π stacking interactions between the pyrazinyl as well as phenyl rings and their counterparts at (x, y, $z - 1$), with the centroid-to-centroid distance of *ca* 3.70 Å.

Experimental

1,4-Dihydro-3,6-bis(2-pyrazinyl)-1,2,4,5-tetrazine (H_2bpztz) was synthesized according to the literature procedure (Sarkar *et al.*, 2003). A C_2H_5OH (5 ml) solution of isophthalic acid (16.6 mg, 0.1 mmol) was carefully layered onto a $CHCl_3$ (10 ml) solution of H_2bpztz (23.8 mg, 0.1 mmol) in a test tube. Orange prism crystals suitable for X-ray diffraction were observed on the tube wall over a period of 3 weeks. Yield: 28.4 mg (70%). Anal. Calcd for $C_{18}H_{14}N_8O_4$: C, 53.20; H, 3.47; N, 27.58%. Found: C, 53.17; H, 3.44; N, 27.69%. IR (KBr pellet, cm^{-1}): 3338(*m*), 1705(*s*).

Refinement

There was no evidence of crystal decay during data collection. The space group Pnna was uniquely assigned from the systematic absences. All H atoms were visible in difference maps. C– and N-bound H atoms were placed at the calculated positions, with C—H and N—H distances of 0.93 and 0.91 Å, and treated as riding. O-bound H atoms of carboxyl were refined as rigid groups, allowed to rotate but not tip with O—H = 0.82 Å. The U_{iso}(H) values were set to 1.2 (for C and N) or 1.5 (for O) U_{eq} with regard to their parent atoms.

Figures

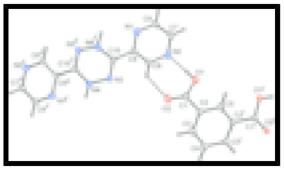


Fig. 1. Molecular structure of (I) with atom labeling, shown with 30% probability displacement ellipsoids. Symmetry codes: (i) *x*, 0.5 − *y*, −0.5 − *z*; (ii) 1.5 − *x*, −*y*, *z*.

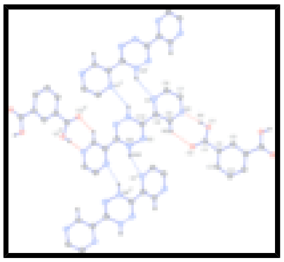


Fig. 2. Portion view of (I) showing the hydrogen bonding interactions (indicated as broken lines). Irrelevant hydrogen atoms were omitted for clarity. Symmetry codes: (i) −1/2 + *x*, *y*, 2 − *z*; (ii) 1 − *x*, −*y*, 2 − *z*; (iii) 1.5 − *x*, −*y*, *z*; (iv) 2 − *x*, −*y*, 2 − *z*; (v) 1/2 + *x*, *y*, 2 − *z*.

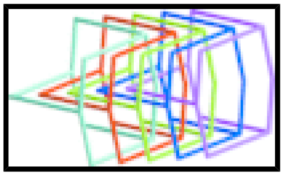


Fig. 3. Schematic illustration of the 5-fold interpenetrating hydrogen-bonding networks in (I).

Isophthalic acid–3,6-bis(2-pyrazinyl)-1,4-dihydro-1,2,4,5-tetrazine (1/1)

Crystal data

$C_8H_6O_4 \cdot C_{10}H_8N_8$	$F_{000} = 840$
$M_r = 406.37$	$D_x = 1.599$ Mg m^{-3}
Orthorhombic, *Pnna*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2a 2bc	Cell parameters from 650 reflections
a = 13.546 (4) Å	θ = 3.0–19.8°
b = 33.654 (11) Å	μ = 0.12 mm^{-1}
c = 3.7035 (12) Å	*T* = 294 (2) K
V = 1688.3 (9) Å^3	Prism, orange
Z = 4	0.32 × 0.10 × 0.06 mm

Data collection

Bruker APEX II CCD area-detector diffractometer	1501 independent reflections
Radiation source: fine-focus sealed tube	937 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.080$
$T = 294(2)$ K	$\theta_{\text{max}} = 25.0°$
φ and ω scans	$\theta_{\text{min}} = 2.4°$
Absorption correction: multi-Scan (SADABS; Sheldrick, 1996)	$h = -16 \rightarrow 16$
$T_{\text{min}} = 0.764$, $T_{\text{max}} = 1.000$	$k = -39 \rightarrow 33$
8125 measured reflections	$l = -4 \rightarrow 4$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.21$ e Å^{-3}
1501 reflections	$\Delta\rho_{\text{min}} = -0.22$ e Å^{-3}
139 parameters	Extinction correction: SHELXL97, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0076 (13)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	$U_{\text{iso}}*/U_{\text{eq}}$
O1	0.67031 (11)	0.18838 (5)	0.0948 (5)	0.0422 (5)
H1	0.6458	0.1681	0.1792	0.063*
O2	0.80749 (12)	0.15240 (5)	0.1263 (5)	0.0483 (6)

N1	0.52754 (13)	0.05363 (6)	0.7689 (5)	0.0301 (5)
N2	0.59035 (13)	0.12361 (5)	0.4414 (5)	0.0319 (5)
N3	0.78628 (13)	0.03824 (6)	0.8292 (5)	0.0303 (5)
N4	0.84163 (13)	0.00538 (5)	0.9555 (5)	0.0309 (5)
H4A	0.9065	0.0088	0.9066	0.037*
C1	0.76590 (17)	0.18285 (7)	0.0449 (7)	0.0308 (6)
C2	0.81727 (16)	0.21766 (6)	−0.1118 (6)	0.0264 (6)
C3	0.91976 (16)	0.21782 (7)	−0.1134 (6)	0.0323 (6)
H3	0.9542	0.1961	−0.0221	0.039*
C4	0.9707 (2)	0.2500	−0.2500	0.0356 (9)
H4	1.0394	0.2500	−0.2500	0.043*
C5	0.7662 (2)	0.2500	−0.2500	0.0284 (8)
H5	0.6975	0.2500	−0.2500	0.034*
C6	0.65414 (17)	0.09648 (6)	0.5560 (7)	0.0300 (6)
H6	0.7214	0.1011	0.5274	0.036*
C7	0.49510 (17)	0.11597 (7)	0.4964 (7)	0.0327 (6)
H7	0.4482	0.1345	0.4224	0.039*
C8	0.46425 (17)	0.08145 (7)	0.6598 (7)	0.0326 (6)
H8	0.3970	0.0774	0.6953	0.039*
C9	0.62340 (16)	0.06147 (7)	0.7171 (6)	0.0246 (6)
C10	0.69377 (15)	0.03110 (7)	0.8372 (6)	0.0245 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0314 (10)	0.0310 (11)	0.0641 (13)	0.0014 (8)	0.0053 (9)	0.0152 (10)
O2	0.0419 (11)	0.0300 (11)	0.0729 (15)	0.0081 (9)	0.0023 (9)	0.0182 (10)
N1	0.0262 (10)	0.0273 (12)	0.0368 (12)	0.0003 (10)	0.0014 (9)	0.0023 (9)
N2	0.0321 (11)	0.0228 (11)	0.0407 (13)	0.0029 (9)	0.0036 (9)	0.0036 (10)
N3	0.0246 (10)	0.0220 (11)	0.0445 (13)	0.0036 (9)	−0.0009 (9)	−0.0016 (10)
N4	0.0225 (10)	0.0234 (11)	0.0467 (13)	0.0019 (9)	−0.0062 (9)	−0.0062 (10)
C1	0.0319 (14)	0.0288 (14)	0.0316 (15)	0.0006 (12)	−0.0031 (11)	−0.0005 (11)
C2	0.0319 (13)	0.0226 (13)	0.0247 (14)	0.0009 (10)	−0.0011 (10)	−0.0002 (11)
C3	0.0333 (14)	0.0299 (15)	0.0336 (16)	0.0046 (11)	−0.0021 (11)	−0.0005 (12)
C4	0.0298 (18)	0.034 (2)	0.043 (2)	0.000	0.000	−0.0006 (18)
C5	0.0267 (17)	0.030 (2)	0.0282 (19)	0.000	0.000	−0.0026 (15)
C6	0.0271 (13)	0.0244 (13)	0.0385 (15)	−0.0001 (11)	0.0033 (11)	0.0014 (12)
C7	0.0309 (14)	0.0299 (14)	0.0374 (15)	0.0067 (12)	0.0015 (11)	0.0041 (12)
C8	0.0252 (12)	0.0315 (15)	0.0411 (16)	0.0037 (12)	0.0014 (11)	0.0054 (13)
C9	0.0255 (12)	0.0210 (13)	0.0273 (13)	0.0010 (10)	0.0014 (10)	−0.0023 (10)
C10	0.0254 (12)	0.0220 (13)	0.0260 (14)	−0.0008 (11)	0.0026 (10)	−0.0017 (11)

Geometric parameters (Å, °)

O1—C1	1.321 (3)	C3—C4	1.380 (3)
O1—H1	0.8200	C3—H3	0.9300
O2—C1	1.208 (3)	C4—C3^{ii}	1.380 (3)
N1—C8	1.332 (3)	C4—H4	0.9300

N1—C9	1.339 (3)	C5—C2^{ii}	1.388 (3)
N2—C6	1.327 (3)	C5—H5	0.9300
N2—C7	1.331 (3)	C6—C9	1.385 (3)
N3—C10	1.276 (3)	C6—H6	0.9300
N3—N4	1.416 (2)	C7—C8	1.375 (3)
N4—C10^{i}	1.389 (3)	C7—H7	0.9300
N4—H4A	0.9051	C8—H8	0.9300
C1—C2	1.481 (3)	C9—C10	1.467 (3)
C2—C5	1.388 (3)	C10—N4^{i}	1.389 (3)
C2—C3	1.388 (3)		
C1—O1—H1	109.5	C2^{ii}—C5—C2	120.2 (3)
C8—N1—C9	116.2 (2)	C2^{ii}—C5—H5	119.9
C6—N2—C7	116.7 (2)	C2—C5—H5	119.9
C10—N3—N4	111.42 (19)	N2—C6—C9	121.8 (2)
C10^{i}—N4—N3	113.79 (16)	N2—C6—H6	119.1
C10^{i}—N4—H4A	112.6	C9—C6—H6	119.1
N3—N4—H4A	110.4	N2—C7—C8	121.7 (2)
O2—C1—O1	122.8 (2)	N2—C7—H7	119.2
O2—C1—C2	123.4 (2)	C8—C7—H7	119.2
O1—C1—C2	113.8 (2)	N1—C8—C7	122.1 (2)
C5—C2—C3	119.6 (2)	N1—C8—H8	118.9
C5—C2—C1	122.1 (2)	C7—C8—H8	118.9
C3—C2—C1	118.3 (2)	N1—C9—C6	121.4 (2)
C4—C3—C2	120.3 (2)	N1—C9—C10	116.7 (2)
C4—C3—H3	119.8	C6—C9—C10	121.9 (2)
C2—C3—H3	119.8	N3—C10—N4^{i}	120.8 (2)
C3^{ii}—C4—C3	120.0 (3)	N3—C10—C9	120.0 (2)
C3^{ii}—C4—H4	120.0	N4^{i}—C10—C9	119.16 (18)
C3—C4—H4	120.0		
C10—N3—N4—C10^{i}	40.7 (2)	C9—N1—C8—C7	1.3 (3)
O2—C1—C2—C5	170.6 (2)	N2—C7—C8—N1	−0.6 (4)
O1—C1—C2—C5	−10.7 (3)	C8—N1—C9—C6	−0.5 (3)
O2—C1—C2—C3	−10.4 (4)	C8—N1—C9—C10	179.81 (19)
O1—C1—C2—C3	168.3 (2)	N2—C6—C9—N1	−0.9 (4)
C5—C2—C3—C4	0.3 (3)	N2—C6—C9—C10	178.7 (2)
C1—C2—C3—C4	−178.67 (17)	N4—N3—C10—N4^{i}	−0.7 (3)
C2—C3—C4—C3^{ii}	−0.16 (16)	N4—N3—C10—C9	179.97 (18)
C3—C2—C5—C2^{ii}	−0.16 (16)	N1—C9—C10—N3	−173.1 (2)
C1—C2—C5—C2^{ii}	178.8 (2)	C6—C9—C10—N3	7.3 (3)
C7—N2—C6—C9	1.5 (4)	N1—C9—C10—N4^{i}	7.6 (3)
C6—N2—C7—C8	−0.8 (4)	C6—C9—C10—N4^{i}	−172.1 (2)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N2	0.82	1.94	2.752 (3)	172
N4—H4A···N1^{iii}	0.90	2.53	3.166 (3)	128
C6—H6···O2	0.93	2.56	3.223 (3)	129

Symmetry codes: (iii) *x*+1/2, *y*, −*z*+2.

Fig. 1

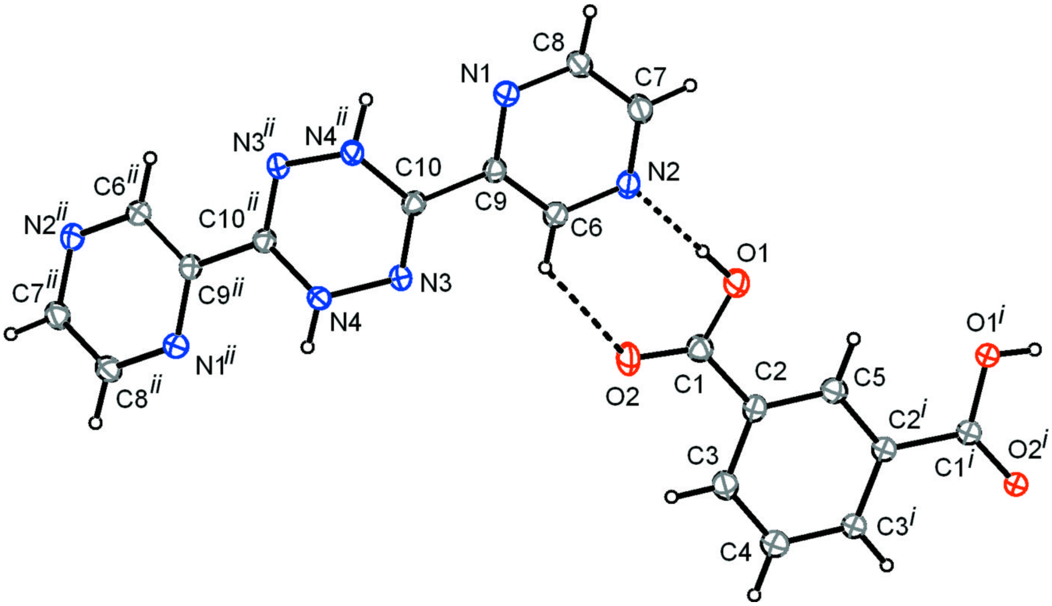

C8
N1
C7
N3^{ii}
N4^{ii}
C10
N2
C6^{ii}
C10^{ii}
C9
C6
N2^{ii}
O1
C7^{ii}
C9^{ii}
N3
N4
O1^{i}
N1^{ii}
O2
C1
C2
C5
C8^{ii}
C2^{i}
O2^{i}
C1^{i}
C3
C3^{i}
C4

Fig. 2

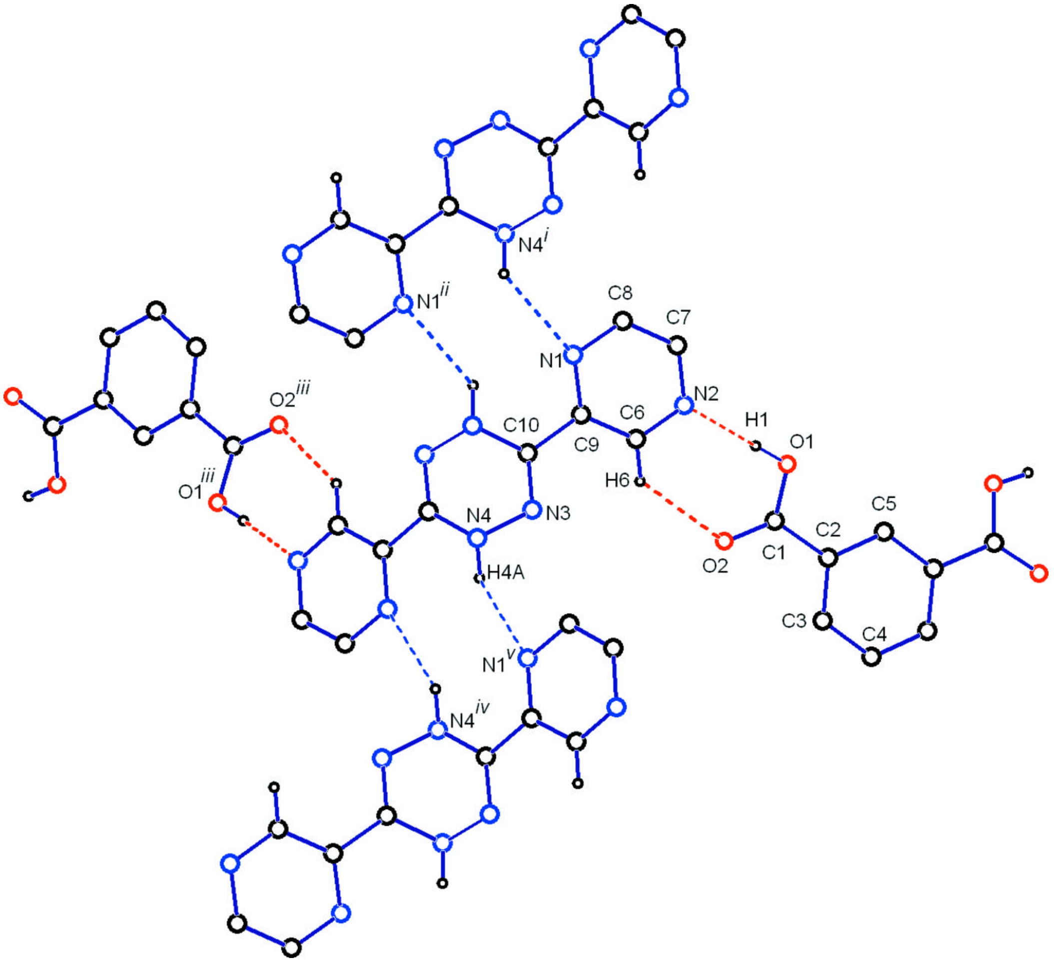

N4^{i}
N1^{ii}
C8
C7
N1
O2^{iii}
N2
H1
C10
C6
O1
C9
O1^{iii}
H6
C5
N4
N3
C2
O2
C1
H4A
C3
C4
N1^{v}
N4^{iv}

Fig. 3