

1,4-Bis(imidazol-1-yl)benzene–terephthalic acid (1/1)

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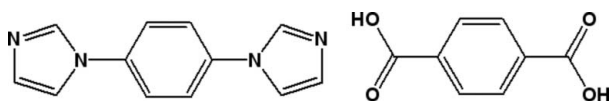
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.045; wR factor = 0.132; data-to-parameter ratio = 12.0.

In the title compound, $\text{C}_{12}\text{H}_{10}\text{N}_4 \cdot \text{C}_8\text{H}_6\text{O}_4$, 1,4-bis(imidazol-1-yl)benzene and terephthalic acid molecules are joined *via* strong $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds to form infinite zigzag chains. Both molecules are located on crystallographic inversion centers. The $\text{O}-\text{H} \cdots \text{N}$ hydrogen-bonded chains are assembled into two-dimensional layers through weak $\text{C}-\text{H} \cdots \text{O}$ and strong $\pi-\pi$ stacking interactions [centroid-centroid distance = $3.818(2)$ Å], leading to the formation of a three-dimensional supramolecular structure.

Related literature

For general background, see: Aakeröy *et al.* (2006); Aakeröy & Seddon (1993); Desiraju, 2007; Corna *et al.* (2004); Dobrzanska *et al.* (2006); Van Roey *et al.* (1991). For similar structures, see: Wang *et al.* (2007); Su *et al.* (2007).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{10}\text{N}_4 \cdot \text{C}_8\text{H}_6\text{O}_4$
 $M_r = 376.37$
 Monoclinic, $P2_1/n$
 $a = 5.2780(17)$ Å
 $b = 10.599(5)$ Å
 $c = 15.449(5)$ Å
 $\beta = 91.17(3)^\circ$

$V = 864.1(6)$ Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 293(2)$ K
 $0.25 \times 0.22 \times 0.15$ mm

Data collection

Enraf–Nonius CAD-4
 diffractometer

Absorption correction: none
 1895 measured reflections

1538 independent reflections
 904 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.008$

3 standard reflections
 every 200 reflections
 intensity decay: 2.5%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.132$
 $S = 0.95$
 1538 reflections

128 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.18$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
$\text{O1}-\text{H1} \cdots \text{N2}^{\text{i}}$	0.82	1.79	2.60885	178
$\text{C2}-\text{H2} \cdots \text{O2}^{\text{ii}}$	0.93	2.54	3.376 (3)	150
$\text{C4}-\text{H4} \cdots \text{O2}^{\text{iii}}$	0.93	2.56	3.463 (3)	162

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

Data collection: *DIFRAC* (Gabe & White, 1993); cell refinement: *DIFRAC*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

This work was supported by grants from the National Natural Science Foundation of China (grant No. 20702035) and Sichuan University experimental technical project (grant No. 07-57, 07-61).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2155).

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supplementary materials

Acta Cryst. (2009). E65, o26 [doi:10.1107/S1600536808040324]

1,4-Bis(imidazol-1-yl)benzene-terephthalic acid (1/1)

S. Zhang, Y. Tang, Z. Mao, M. Li, J. Lan and X. Su

Comment

Supramolecular architectures assembled via various delicate noncovalent interactions such as hydrogen bonds, π – π stacking and electrostatic interactions, *etc.*, have attracted intense interest in recent years because of their fascinating structural diversity and potential applications for functional materials (Desiraju, 2007; Corna *et al.*, 2004). Especially, the application of intermolecular hydrogen bonds is a well known and efficient tool in the field of organic crystal design owing to its strength and directional properties (Aakeröy & Seddon, 1993). Imidazoles, as excellent N-donor compounds, have attracted special attention in the construction of organic cocrystals in recent years (Aakeröy *et al.*, 2006; Van Roey *et al.*, 1991). We recently presented organic crystals composed of flexible diimidazole compounds and dicarboxylic acids (Wang *et al.*, 2007; Su *et al.*, 2007). In further development of such interesting hydrogen-bonded supramolecular systems and as a continuation of our research in this area, we report herein the crystal structure of the title compound formed from rigid diimidazole and dicarboxylic acids molecules.

As shown in Figure 1, the asymmetric unit of the title compound contains each half a molecule of 1,4-bis(1-imidazolyl)benzene and terephthalic acid which are both located on crystallographic inversion centers. The carboxyl groups of the terephthalic acid interact with the imidazol-1-yl nitrogen atoms of 1,4-bis(1-imidazolyl)benzene *via* O1—H1 \cdots N2 hydrogen bonds (O1 \cdots N2 = 2.608 (8) Å and O1—H1 \cdots N2 = 178°), and thus the hydrogen bonds further propagate the acid-base subunits into an infinite one-dimensional zig-zag chain. Meanwhile, these chains are assembled into two-dimensional layers through weak C2—H2 \cdots O2 and C4—H4 \cdots O2 hydrogen bonds, with C2 \cdots O2 = 3.376 (3) Å, C2—H2 \cdots O2 = 150° and C4 \cdots O2 = 3.463 (3) Å, C4—H4 \cdots O2 = 162° (Figure 2). Moreover, the supramolecular layers are further stabilized by intermolecular π – π interactions to form a three-dimensional structure as depicted in Figure 3. A relative strong π – π interaction between one imidazole ring (*Cg*1: N1—C4—N2—C5—C6) and contiguous phenyl ring (*Cg*2: C1—C3—C2—C1b—C3b—C2b) of 1,4-bis(1-imidazolyl)benzene from another chain (centroid-centroid distance = 3.818 (2) Å, dihedral angle = 27.12) plays an important part in the connection of adjacent layers, where *Cg*1 is the centroid of the imidazole ring of the molecule at (1 - *x*, 1 - *y*, -*z*) and (-1 + *x*, *y*, *z*), and *Cg*2 is the centroid of the phenyl ring of the molecule at (1 - *x*, 1 - *y*, -*z*) and (1 + *x*, *y*, *z*).

Experimental

A methanol solution (5 ml) of 1,4-bis(1-imidazolyl)benzene (0.05 mmol, 10.5 mg) was added slowly with constant stirring to a solution of terephthalic acid (0.05 mmol, 8.3 mg) in methanol (2 ml) and water (0.5 ml) to give a clear solution. Then the reaction mixture was filtered and left to stand at room temperature. Colorless block crystals suitable for X-ray analysis were obtained after one week by slow evaporation of the solvent. Yield, 85%; ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.34 (s, 2H), 8.04 (s, 4H), 7.83 (t, 6H), 7.13 (s, 2H).

Refinement

All non-hydrogen atoms were located using direct methods and successive difference Fourier syntheses, and refined with anisotropic thermal parameters. All hydrogen atoms were positioned theoretically and refined with the riding model approximation with C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, and O—H = 0.82 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$

Figures

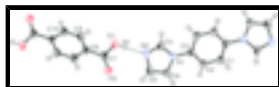


Fig. 1. The molecular structure of the title compound, showing 50% probability displacement ellipsoids; hydrogen bonds are illustrated by dashed lines.

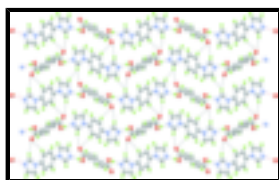


Fig. 2. A two-dimensional network layer of the title compound viewed along the *c* axis. Dashed lines indicate O—H···N and C—H···O hydrogen bonds. C, gray; H, green; O, red; N, cyan.

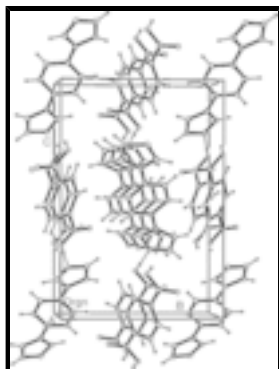


Fig. 3. A three-dimensional view of the supramolecular layers of the title compound.

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Crystal data

$\text{C}_{12}\text{H}_{10}\text{N}_4\text{C}_8\text{H}_6\text{O}_4$

$M_r = 376.37$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 5.2780\ (17)\ \text{\AA}$

$b = 10.599\ (5)\ \text{\AA}$

$c = 15.449\ (5)\ \text{\AA}$

$\beta = 91.17\ (3)^\circ$

$V = 864.1\ (6)\ \text{\AA}^3$

$Z = 2$

$F_{000} = 392$

$D_x = 1.447\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 18 reflections

$\theta = 4.5\text{--}7.6^\circ$

$\mu = 0.10\ \text{mm}^{-1}$

$T = 293\ (2)\ \text{K}$

Block, colourless

$0.25 \times 0.22 \times 0.15\ \text{mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.008$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 25.5^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 2.3^\circ$
$T = 293(2)$ K	$h = -6 \rightarrow 6$
$\omega/2\theta$ scans	$k = 0 \rightarrow 12$
Absorption correction: none	$l = -9 \rightarrow 18$
1895 measured reflections	3 standard reflections
1538 independent reflections	every 200 reflections
904 reflections with $I > 2\sigma(I)$	intensity decay: 2.5%

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.132$	$w = 1/[\sigma^2(F_o^2) + (0.0842P)^2]$
$S = 0.95$	where $P = (F_o^2 + 2F_c^2)/3$
1538 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
128 parameters	$\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$
	Extinction correction: none

Special details

Experimental. 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 $F^2 > 2\sigma(F^2)$ 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.

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
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supplementary materials

N1	0.3750 (4)	0.57026 (17)	0.12218 (11)	0.0403 (5)
N2	0.7031 (4)	0.5588 (2)	0.21140 (12)	0.0489 (6)
C1	0.0819 (5)	0.6228 (2)	0.00451 (16)	0.0467 (6)
H1A	0.1382	0.7059	0.0073	0.056*
C2	-0.1041 (5)	0.5891 (2)	-0.05539 (15)	0.0467 (6)
H2	-0.1745	0.6495	-0.0923	0.056*
C3	0.1844 (4)	0.5339 (2)	0.06017 (13)	0.0375 (5)
C4	0.5583 (4)	0.4962 (2)	0.15707 (14)	0.0445 (6)
H4	0.5788	0.4112	0.1440	0.053*
C5	0.6087 (5)	0.6786 (2)	0.21254 (16)	0.0531 (7)
H5	0.6740	0.7444	0.2460	0.064*
C6	0.4073 (3)	0.68757 (13)	0.15820 (8)	0.0504 (7)
H6	0.3095	0.7590	0.1472	0.061*
O1	0.0950 (3)	0.49725 (13)	0.30802 (8)	0.0499 (5)
H1	-0.0288	0.5179	0.2784	0.075*
O2	0.0072 (4)	0.67524 (16)	0.37876 (12)	0.0601 (6)
C7	0.1260 (5)	0.5775 (2)	0.37186 (15)	0.0428 (6)
C8	0.3231 (4)	0.5370 (2)	0.43721 (14)	0.0387 (6)
C9	0.5136 (4)	0.4536 (2)	0.41709 (14)	0.0415 (6)
H9	0.5236	0.4221	0.3611	0.050*
C10	0.6897 (4)	0.4164 (2)	0.47922 (14)	0.0435 (6)
H10	0.8171	0.3600	0.4650	0.052*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0420 (11)	0.0393 (11)	0.0391 (10)	0.0033 (9)	-0.0132 (9)	0.0005 (8)
N2	0.0476 (12)	0.0568 (13)	0.0415 (11)	-0.0001 (11)	-0.0184 (9)	-0.0007 (9)
C1	0.0516 (15)	0.0374 (12)	0.0504 (13)	0.0036 (11)	-0.0187 (12)	0.0008 (10)
C2	0.0542 (15)	0.0390 (13)	0.0460 (12)	0.0053 (12)	-0.0196 (11)	0.0056 (10)
C3	0.0369 (12)	0.0418 (13)	0.0334 (11)	0.0059 (10)	-0.0102 (9)	-0.0028 (9)
C4	0.0446 (13)	0.0476 (14)	0.0405 (12)	0.0064 (12)	-0.0176 (10)	-0.0021 (10)
C5	0.0619 (16)	0.0460 (14)	0.0506 (14)	-0.0053 (13)	-0.0198 (12)	-0.0023 (12)
C6	0.0588 (16)	0.0377 (14)	0.0539 (15)	0.0035 (12)	-0.0198 (13)	-0.0039 (11)
O1	0.0495 (10)	0.0531 (10)	0.0462 (9)	0.0021 (8)	-0.0205 (7)	-0.0019 (8)
O2	0.0645 (12)	0.0425 (10)	0.0720 (13)	0.0053 (9)	-0.0335 (10)	-0.0041 (9)
C7	0.0400 (13)	0.0422 (14)	0.0457 (13)	-0.0084 (12)	-0.0128 (11)	0.0030 (11)
C8	0.0412 (13)	0.0335 (12)	0.0409 (12)	-0.0106 (10)	-0.0133 (10)	0.0058 (9)
C9	0.0427 (13)	0.0441 (13)	0.0372 (11)	-0.0040 (11)	-0.0087 (10)	-0.0003 (10)
C10	0.0363 (13)	0.0440 (14)	0.0498 (13)	-0.0044 (11)	-0.0083 (11)	0.0019 (11)

Geometric parameters (\AA , $^\circ$)

N1—C4	1.349 (3)	C5—H5	0.9300
N1—C6	1.371 (2)	C6—H6	0.9300
N1—C3	1.428 (3)	O1—C7	1.31010
N2—C4	1.305 (3)	O1—H1	0.8200
N2—C5	1.364 (3)	O2—C7	1.217 (3)
C1—C3	1.379 (3)	C7—C8	1.498 (3)

C1—C2	1.383 (3)	C8—C9	1.379 (3)
C1—H1A	0.9300	C8—C10 ⁱⁱ	1.385 (3)
C2—C3 ⁱ	1.372 (3)	C9—C10	1.380 (3)
C2—H2	0.9300	C9—H9	0.9300
C3—C2 ⁱ	1.372 (3)	C10—C8 ⁱⁱ	1.385 (3)
C4—H4	0.9300	C10—H10	0.9300
C5—C6	1.344 (3)		
C4—N1—C6	106.45 (17)	N2—C5—H5	125.0
C4—N1—C3	126.9 (2)	C5—C6—N1	106.22 (16)
C6—N1—C3	126.66 (17)	C5—C6—H6	126.9
C4—N2—C5	105.8 (2)	N1—C6—H6	126.9
C3—C1—C2	120.3 (2)	C7—O1—H1	109.5
C3—C1—H1A	119.8	O2—C7—O1	124.20
C2—C1—H1A	119.8	O2—C7—C8	122.5 (2)
C3 ⁱ —C2—C1	119.7 (2)	O1—C7—C8	113.31
C3 ⁱ —C2—H2	120.1	C9—C8—C10 ⁱⁱ	119.2 (2)
C1—C2—H2	120.1	C9—C8—C7	122.1 (2)
C2 ⁱ —C3—C1	119.9 (2)	C10 ⁱⁱ —C8—C7	118.7 (2)
C2 ⁱ —C3—N1	120.35 (19)	C8—C9—C10	120.7 (2)
C1—C3—N1	119.7 (2)	C8—C9—H9	119.7
N2—C4—N1	111.5 (2)	C10—C9—H9	119.7
N2—C4—H4	124.2	C9—C10—C8 ⁱⁱ	120.1 (2)
N1—C4—H4	124.2	C9—C10—H10	119.9
C6—C5—N2	110.01 (19)	C8 ⁱⁱ —C10—H10	119.9
C6—C5—H5	125.0		
C3—C1—C2—C3 ⁱ	-0.9 (4)	N2—C5—C6—N1	0.0 (3)
C2—C1—C3—C2 ⁱ	0.9 (4)	C4—N1—C6—C5	0.3 (2)
C2—C1—C3—N1	-179.5 (2)	C3—N1—C6—C5	-179.9 (2)
C4—N1—C3—C2 ⁱ	26.8 (4)	O2—C7—C8—C9	-157.3 (2)
C6—N1—C3—C2 ⁱ	-153.0 (2)	O1—C7—C8—C9	23.07
C4—N1—C3—C1	-152.9 (2)	O2—C7—C8—C10 ⁱⁱ	23.6 (4)
C6—N1—C3—C1	27.3 (3)	O1—C7—C8—C10 ⁱⁱ	-155.90
C5—N2—C4—N1	0.5 (3)	C10 ⁱⁱ —C8—C9—C10	0.2 (4)
C6—N1—C4—N2	-0.5 (3)	C7—C8—C9—C10	-178.8 (2)
C3—N1—C4—N2	179.6 (2)	C8—C9—C10—C8 ⁱⁱ	-0.2 (4)
C4—N2—C5—C6	-0.3 (3)		

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots N2 ⁱⁱⁱ	0.82	1.79	2.60885	178
C2—H2 \cdots O2 ^{iv}	0.93	2.54	3.376 (3)	150
C4—H4 \cdots O2 ^v	0.93	2.56	3.463 (3)	162

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

Fig. 1

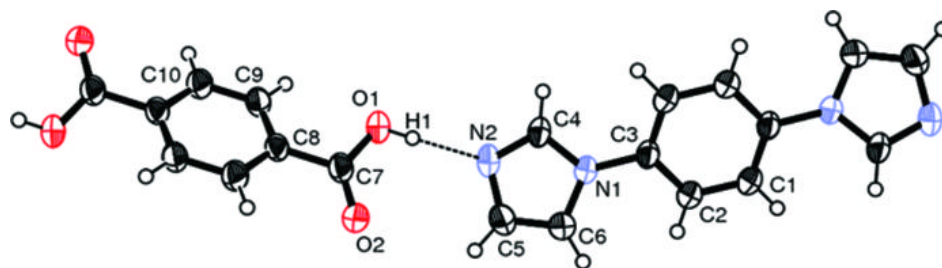


Fig. 2

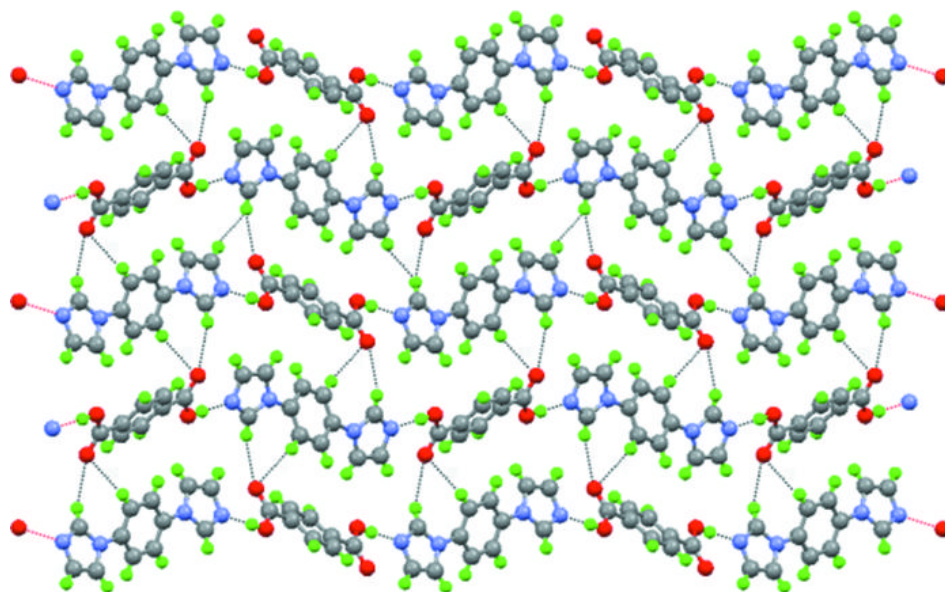


Fig. 3

