

Benzoic acid–2,2′-biimidazole (2/1)

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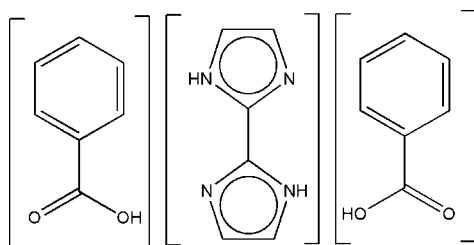
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.098; wR factor = 0.188; data-to-parameter ratio = 11.8.

In the title compound, $\text{C}_6\text{H}_6\text{N}_4\cdot 2\text{C}_7\text{H}_6\text{O}_2$, the asymmetric unit contains a half-molecule of biimidazole and one benzoic acid molecule. The unit cell contains two biimidazole molecules and four benzoic acid molecules, giving the reported 2:1 ratio of benzoic acid to biimidazole. The biimidazole molecule is located on an inversion center (passing through the central C–C bond). Strong $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds link the benzoic acid molecules with the neutral biimidazole molecules, which lie in planar sheets. In the crystal packing, the parallel sheets are related by a twofold rotation axis and an inversion centre, respectively, forming an interwoven three-dimensional network *via* weak $\text{C}=\text{O}\cdots\pi$ intermolecular interactions between neighboring molecules.

Related literature

For background to the use of 2,2′-biimidazoles in crystal engineering, see: Matthews *et al.* (1990); Tadokoro & Nakasuji (2000). For similar structures, see: Gao *et al.* (2009); Li & Yang (2006); Mori & Miyoshi (2004).



Experimental

Crystal data

 $\text{C}_6\text{H}_6\text{N}_4\cdot 2\text{C}_7\text{H}_6\text{O}_2$
 $M_r = 378.38$

Monoclinic, $P2_1/n$
 $a = 11.232$ (5) Å
 $b = 5.082$ (2) Å
 $c = 16.342$ (7) Å
 $\beta = 99.832$ (6)°
 $V = 919.2$ (7) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.10$ mm⁻¹
 $T = 298$ K
 $0.40 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
 $T_{\min} = 0.962$, $T_{\max} = 0.990$

3367 measured reflections
 1550 independent reflections
 1243 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.098$
 $wR(F^2) = 0.188$
 $S = 1.25$
 1550 reflections
 131 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

 $Cg1$ is the centroid of the $\text{N}1/\text{C}1/\text{N}2/\text{C}3/\text{C}2$ ring.

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O}1-\text{H}1A\cdots\text{N}2^i$	0.86	1.77	2.613 (5)	170
$\text{N}1-\text{H}1\cdots\text{O}2^{ii}$	0.88 (5)	1.89 (5)	2.767 (5)	173 (5)
$\text{C}4-\text{O}2\cdots\text{C}g1$	1.22 (1)	3.67 (1)	4.388 (2)	118 (1)

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

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1997) and SHELXTL/PC (Sheldrick, 2008); software used to prepare material for publication: SHELXTL/PC.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2323).

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supplementary materials

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Benzoic acid-2,2'-biimidazole (2/1)

X. Gao and M. Zhu

Comment

Compounds containing the 2,2'-biimidazole moiety have been the focus of several investigations not only due to their biological activity, but also due to their contribution to the field of crystal engineering (Matthews, *et al.* 1990; Tadokoro & Nakasuji, 2000). In these compounds weak interactions, such as C—H \cdots O and C=O \cdots π , play crucial roles in building the overall three-dimensional structure (Mori & Miyoshi, 2004; Li & Yang, 2006; Gao *et al.*, 2009).

The asymmetric unit of compound (I) contains one benzoic acid and 1/2 neutral biimidazole molecule, in which the imidazole rings are coplanar (Fig. 1). Each biimidazole molecule is linked to two benzoic acids *via* strong N—H \cdots O and O—H \cdots N hydrogen bonds (Table 1) twithin planar sheets (Figure 2). These sheets further assemble to layers *via* weak C=O \cdots π (see Table 1, Cg1 for centre of N1/C1/N2/C3/C2) interactions between neighboring molecules and arrange alternatively and across along *b* and *c* axis in two-dimensional structure, and the dihedral angle of the planes are 92.7°. In contrast, two groups of these parallel layers on a twofold rotation axis and inversion centre forming a zigzag conformation along *c* axis in whole three-dimensional network as shown in Fig. 3.

Experimental

Benzoic acid (0.25 g, 2 mmol) and biimidazole (1 mmol) were dissolved in water(10 ml) by adding 1.4 ml of 2 M HCl while stirring. The solutions were stirred for 1 h, then filtered. Filtrate was left to stand at room temperature. Crystals suitable for data collection appeared after a few weeks by slow evaporation of the aqueous solvent.

Refinement

H atoms attached to C atoms were placed in geometrically idealized positions, with $C_{sp^2} = 0.93 \text{ \AA}$, and constrained to ride on their carrier atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms attached to N1 and O1 atoms were located in difference Fourier maps and refined with $U_{iso}(H \text{ for N}) = 0.06 \text{ \AA}^2$ and $U_{iso}(H) = 1.5U_{eq}(O)$; N—H distance is 0.88 (5) \AA and the O—H distance is 0.856 \AA .

Figures

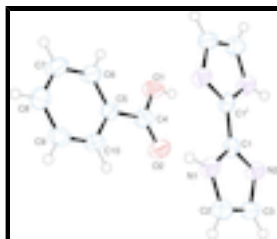


Fig. 1. A view of the structure of compound (I) with displacement ellipsoids drawn at the 50% probability level, the biimidazole sits on a center of symmetry passing through the C1—C1 bond. Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*.

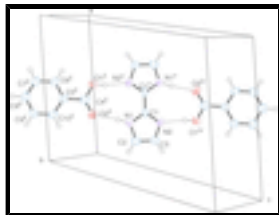


Fig. 2. H-bonds (dotted line) in (I). Symmetry codes: (ii) $x, 1 + y, z$; (iv) $1 - x, -y, 1 - z$; (v) $1 - x, 1 - y, 1 - z$.

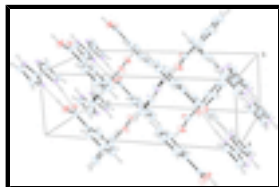


Fig. 3. The packing view in the title compound (I), dotted line for H-bonds.

Benzoic acid-2,2'-biimidazole (2/1)

Crystal data

$C_6H_6N_4 \cdot 2C_7H_6O_2$

$M_r = 378.38$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 11.232 (5) \text{ \AA}$

$b = 5.082 (2) \text{ \AA}$

$c = 16.342 (7) \text{ \AA}$

$\beta = 99.832 (6)^\circ$

$V = 919.2 (7) \text{ \AA}^3$

$Z = 2$

$F(000) = 396$

$D_x = 1.367 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 698 reflections

$\theta = 2.5\text{--}20.8^\circ$

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

$T = 298 \text{ K}$

Block, colorless

$0.40 \times 0.20 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1K CCD area-detector diffractometer

Radiation source: fine-focus sealed tube graphite

ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2000)

$T_{\min} = 0.962, T_{\max} = 0.990$

3367 measured reflections

1550 independent reflections

1243 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\max} = 25.0^\circ, \theta_{\min} = 2.1^\circ$

$h = -13 \rightarrow 12$

$k = -6 \rightarrow 2$

$l = -19 \rightarrow 19$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.098$

$wR(F^2) = 0.188$

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$S = 1.25$

1550 reflections

131 parameters

0 restraints

$$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 1.0781P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$$

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 $F^2 > \sigma(F^2)$ 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	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.3655 (3)	0.6966 (8)	0.4607 (2)	0.0406 (10)
H1	0.383 (4)	0.809 (10)	0.423 (3)	0.064 (17)*
N2	0.3784 (3)	0.3740 (7)	0.5510 (2)	0.0389 (9)
C1	0.4360 (4)	0.5176 (8)	0.5031 (2)	0.0307 (10)
C2	0.2533 (4)	0.6694 (10)	0.4821 (3)	0.0436 (12)
H2	0.1846	0.7679	0.4624	0.052*
C3	0.2630 (4)	0.4717 (10)	0.5372 (3)	0.0453 (12)
H3	0.2003	0.4097	0.5625	0.054*
C4	0.4969 (4)	0.1219 (9)	0.3172 (3)	0.0376 (11)
C5	0.4964 (4)	0.3271 (9)	0.2521 (2)	0.0347 (10)
C6	0.5982 (4)	0.3745 (10)	0.2158 (3)	0.0451 (12)
H6	0.6687	0.2790	0.2329	0.054*
C7	0.5946 (4)	0.5616 (10)	0.1549 (3)	0.0516 (13)
H7	0.6625	0.5916	0.1308	0.062*
C8	0.4913 (4)	0.7050 (10)	0.1294 (3)	0.0491 (13)
H8	0.4897	0.8321	0.0883	0.059*
C9	0.3913 (4)	0.6618 (10)	0.1641 (3)	0.0458 (12)
H9	0.3216	0.7595	0.1468	0.055*
C10	0.3934 (4)	0.4739 (10)	0.2247 (3)	0.0441 (12)
H10	0.3244	0.4447	0.2478	0.053*
O1	0.5977 (3)	-0.0029 (7)	0.3367 (2)	0.0532 (10)
H1A	0.5971	-0.1186	0.3747	0.080*
O2	0.4086 (3)	0.0801 (7)	0.3491 (2)	0.0517 (9)

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.043 (2)	0.037 (2)	0.042 (2)	-0.0004 (19)	0.0097 (18)	0.009 (2)
N2	0.041 (2)	0.035 (2)	0.043 (2)	-0.0011 (18)	0.0116 (17)	0.0088 (19)
C1	0.044 (2)	0.022 (2)	0.027 (2)	0.003 (2)	0.0077 (19)	0.0055 (19)
C2	0.037 (3)	0.048 (3)	0.046 (3)	0.004 (2)	0.007 (2)	0.000 (3)
C3	0.032 (2)	0.057 (3)	0.048 (3)	0.000 (2)	0.009 (2)	0.011 (3)
C4	0.041 (3)	0.029 (2)	0.043 (3)	-0.004 (2)	0.009 (2)	-0.002 (2)
C5	0.038 (2)	0.032 (3)	0.034 (2)	-0.004 (2)	0.0064 (19)	-0.005 (2)
C6	0.037 (3)	0.046 (3)	0.053 (3)	0.002 (2)	0.012 (2)	0.008 (3)
C7	0.048 (3)	0.052 (3)	0.060 (3)	-0.001 (3)	0.024 (2)	0.013 (3)
C8	0.051 (3)	0.048 (3)	0.049 (3)	-0.003 (3)	0.008 (2)	0.013 (3)
C9	0.036 (3)	0.046 (3)	0.054 (3)	0.006 (2)	0.004 (2)	0.009 (3)
C10	0.033 (2)	0.055 (3)	0.046 (3)	-0.005 (2)	0.013 (2)	0.002 (3)
O1	0.0371 (17)	0.058 (2)	0.065 (2)	0.0067 (18)	0.0089 (15)	0.0244 (19)
O2	0.0465 (19)	0.051 (2)	0.063 (2)	0.0094 (17)	0.0220 (16)	0.0155 (18)

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

N1—C1	1.322 (5)	C5—C10	1.385 (6)
N1—C2	1.371 (5)	C5—C6	1.397 (6)
N1—H1	0.88 (5)	C6—C7	1.371 (6)
N2—C1	1.319 (5)	C6—H6	0.9300
N2—C3	1.370 (5)	C7—C8	1.374 (6)
C1—C1 ⁱ	1.469 (8)	C7—H7	0.9300
C2—C3	1.342 (6)	C8—C9	1.359 (6)
C2—H2	0.9300	C8—H8	0.9300
C3—H3	0.9300	C9—C10	1.373 (6)
C4—O2	1.216 (5)	C9—H9	0.9300
C4—O1	1.289 (5)	C10—H10	0.9300
C4—C5	1.489 (6)	O1—H1A	0.8564
C1—N1—C2	106.9 (4)	C6—C5—C4	121.4 (4)
C1—N1—H1	129 (3)	C7—C6—C5	120.1 (4)
C2—N1—H1	124 (3)	C7—C6—H6	119.9
C1—N2—C3	104.4 (4)	C5—C6—H6	119.9
N2—C1—N1	112.4 (4)	C6—C7—C8	120.5 (4)
N2—C1—C1 ⁱ	124.0 (5)	C6—C7—H7	119.8
N1—C1—C1 ⁱ	123.6 (5)	C8—C7—H7	119.8
C3—C2—N1	105.9 (4)	C9—C8—C7	120.2 (5)
C3—C2—H2	127.0	C9—C8—H8	119.9
N1—C2—H2	127.0	C7—C8—H8	119.9
C2—C3—N2	110.4 (4)	C8—C9—C10	120.0 (4)
C2—C3—H3	124.8	C8—C9—H9	120.0
N2—C3—H3	124.8	C10—C9—H9	120.0
O2—C4—O1	123.6 (4)	C9—C10—C5	121.2 (4)
O2—C4—C5	121.7 (4)	C9—C10—H10	119.4

O1—C4—C5	114.7 (4)	C5—C10—H10	119.4
C10—C5—C6	118.0 (4)	C4—O1—H1A	113.7
C10—C5—C4	120.6 (4)		
C3—N2—C1—N1	0.0 (5)	O1—C4—C5—C6	0.5 (6)
C3—N2—C1—C1 ⁱ	-179.6 (5)	C10—C5—C6—C7	0.0 (7)
C2—N1—C1—N2	0.0 (5)	C4—C5—C6—C7	178.9 (4)
C2—N1—C1—C1 ⁱ	179.6 (5)	C5—C6—C7—C8	0.4 (7)
C1—N1—C2—C3	0.0 (5)	C6—C7—C8—C9	-0.3 (8)
N1—C2—C3—N2	0.0 (5)	C7—C8—C9—C10	-0.1 (7)
C1—N2—C3—C2	0.0 (5)	C8—C9—C10—C5	0.5 (7)
O2—C4—C5—C10	-1.3 (6)	C6—C5—C10—C9	-0.4 (7)
O1—C4—C5—C10	179.3 (4)	C4—C5—C10—C9	-179.3 (4)
O2—C4—C5—C6	179.8 (4)		

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

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

Cg1 is the centroid of the [please define] ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1A \cdots N2 ⁱⁱ	0.86	1.77	2.613 (5)	170
N1—H1 \cdots O2 ⁱⁱⁱ	0.88 (5)	1.89 (5)	2.767 (5)	173 (5)
C4—O2 \cdots Cg1	1.216 (5)	3.674 (2)	4.388 (2)	118.37 (6)

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

Fig. 1

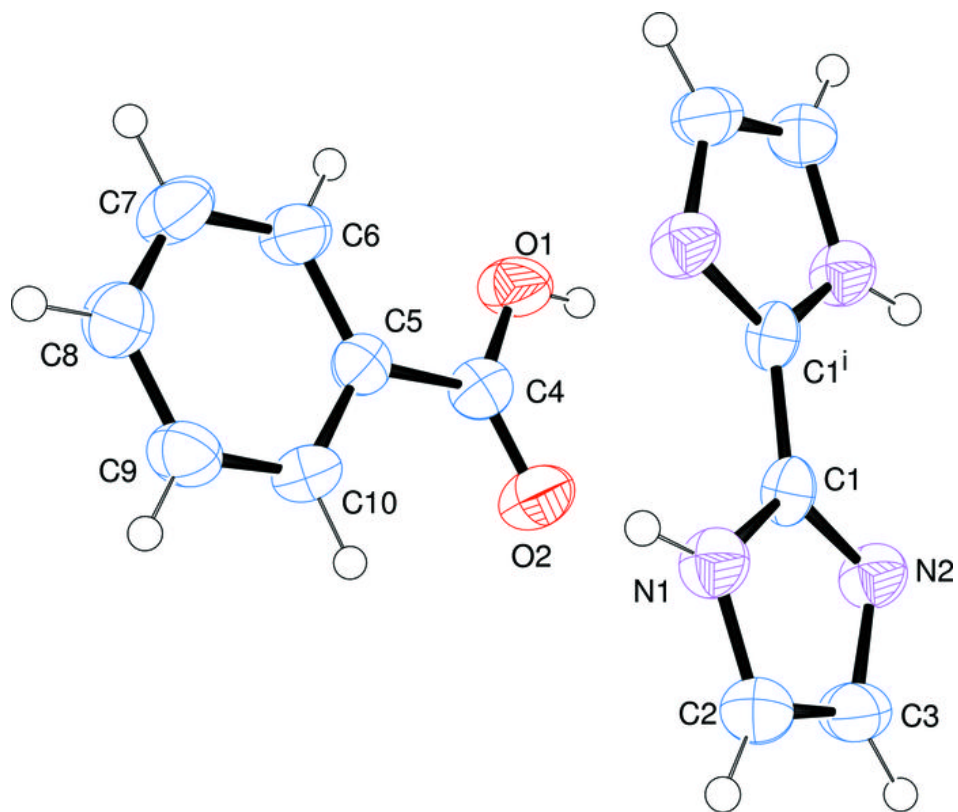


Fig. 2

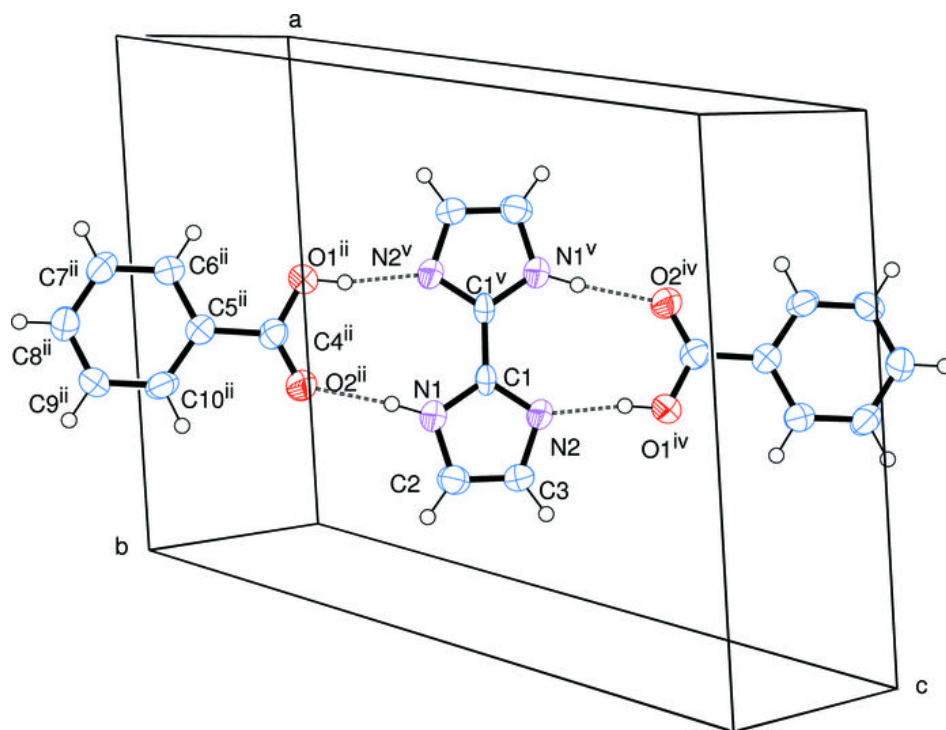


Fig. 3

