

Benzimidazolium 3,5-dihydroxybenzoate

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.041

wR factor = 0.115

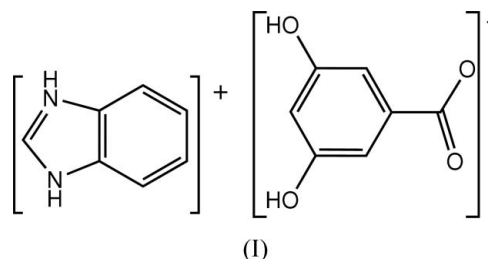
Data-to-parameter ratio = 15.9

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

In the crystal structure of the title compound, $\text{C}_7\text{H}_7\text{N}_2^+\cdot\text{C}_7\text{H}_5\text{O}_4^-$, the partially overlapped arrangement and the face-to-face separation of $3.557(7) \text{ \AA}$ suggest π - π stacking between parallel benzimidazolium cations, and the $\text{C}-\text{H}\cdots\text{Cg}$ angle of 173° and $\text{H}\cdots\text{Cg}$ separation of 2.64 \AA (where Cg is the centroid of the benzene ring) suggest $\text{C}-\text{H}\cdots\pi$ stacking between the benzimidazolium cation and dihydroxybenzoate anion. Classical $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ and weak $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds consolidate the crystal structure.

Comment

We have been interested in the nature of aromatic stacking in complexes for several years (Chen *et al.*, 2003; Pan & Xu, 2004; Li *et al.*, 2005) because aromatic stacking is an important intermolecular non-covalent interaction which correlates with electron transfer in some biological systems (Deisenhofer & Michel, 1989). We present here the structure of the title compound, (I), which contains both benzene and benzimidazole aromatic ring systems.



The asymmetric unit of (I) consists of a benzimidazolium (bzim) cation and a dihydroxybenzoate (dhba) anion (Fig. 1). The carboxylate group of dhba is coplanar with the benzene ring [dihedral angle $1.05(9)^\circ$]. The small difference of $0.025(2) \text{ \AA}$ between the $\text{C1}-\text{O1}$ and $\text{C1}-\text{O2}$ bond distances (Table 1) is consistent with the value of $0.022(4) \text{ \AA}$ found in piperazinium bis(3,5-dihydroxybenzoate) (Burchell *et al.*, 2001) and indicates the deprotonation of the carboxyl group.

Approximately symmetric $\text{N}-\text{C}$ bonds are observed in the protonated bzim cation; the differences between the $\text{N1}-\text{C8}$ and $\text{N2}-\text{C8}$ bond distances and between the $\text{N1}-\text{C13}$ and $\text{N2}-\text{C14}$ bond distances are smaller than twice the standard uncertainties (Table 1).

A partially overlapped arrangement is observed between parallel N1-bzim and $\text{N1}^{\text{vi}}\text{-bzim}$ cations [symmetry code: (vi) $-x + 1, -y + 1, -z + 1$] (Fig. 2). The face-to-face distance of $3.557(7) \text{ \AA}$ suggests the existence of π - π stacking. $\text{C}-\text{H}\cdots\pi$ stacking is observed between bzim and dhba (Fig. 1), the

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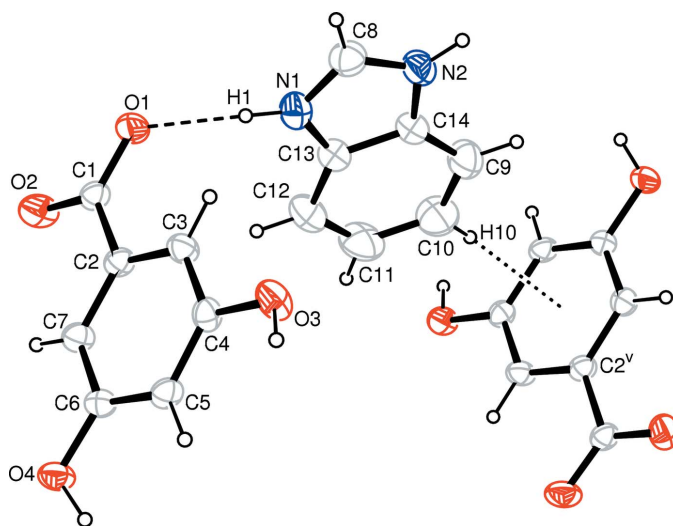


Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids (arbitrary spheres for H atoms). The dashed line indicates a hydrogen bond and the dotted line indicates C–H... π stacking. [Symmetry code: (v) $x - \frac{1}{2}, y - \frac{1}{2}, z + \frac{1}{2}$]

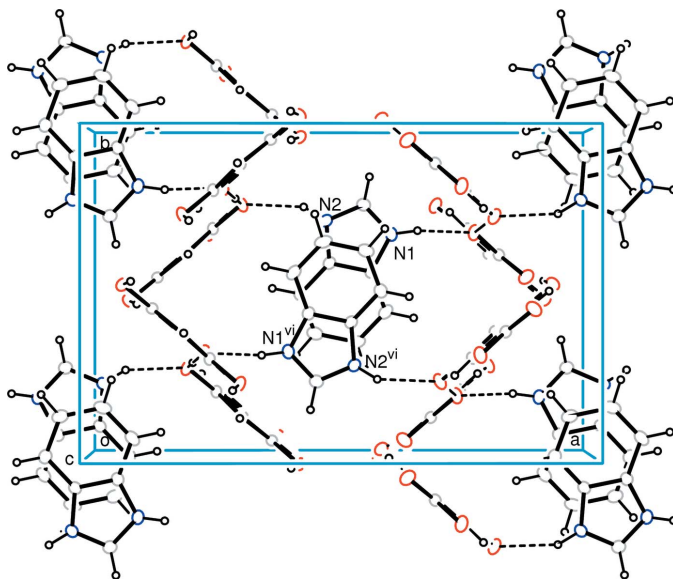


Figure 2
A packing diagram, showing classical hydrogen bonding (dashed lines) and π - π stacking between parallel bzim cations. [Symmetry code: (vi) $-x + 1, -y + 1, -z + 1$]

C10–H10...C_g angle and H...C_g separation being 173° and 2.64 Å, respectively, where C_g is the centroid of the C₂-containing benzene ring [symmetry code: (v) $x - \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$].

Classical N–H...O and O–H...O and weak C–H...O hydrogen bonds occur (Table 2), consolidating the crystal structure of (I).

Experimental

CdCl₂ (1 mmol), 3,5-dihydroxybenzoic acid (2 mmol), benzimidazole (2 mmol) and Na₂CO₃ (1 mmol) were dissolved in a water/ethanol

solution (20 ml, 1:1). The mixture was refluxed for 2 h and filtered after cooling to room temperature. Single crystals of (I) were obtained from the filtrate after 10 d.

Crystal data

C₇H₇N₂⁺·C₇H₅O₄[−]
M_r = 272.26
 Orthorhombic, *Pbcn*
a = 16.297 (4) Å
b = 10.600 (3) Å
c = 14.649 (5) Å
V = 2530.6 (13) Å³
Z = 8
D_x = 1.429 Mg m^{−3}

Mo K α radiation
 Cell parameters from 19663 reflections
 θ = 3.1–27.0°
 μ = 0.11 mm^{−1}
T = 295 (2) K
 Chunk, brown
 0.40 × 0.38 × 0.36 mm

Data collection

Rigaku R-Axis RAPID diffractometer
 ω scans
 Absorption correction: none
 23272 measured reflections
 2901 independent reflections

2435 reflections with $I > 2\sigma(I)$
*R*_{int} = 0.037
 θ_{\max} = 27.5°
h = −21 → 20
k = −13 → 13
l = −19 → 19

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.041
wR(*F*²) = 0.115
S = 1.09
 2901 reflections
 182 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0603P)^2 + 0.6188P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.35 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.29 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0108 (10)

Table 1

Selected bond distances (Å).

N1–C8	1.3160 (19)	O1–C1	1.2690 (15)
N1–C13	1.3862 (19)	O2–C1	1.2445 (15)
N2–C8	1.3200 (18)	O3–C4	1.3607 (14)
N2–C14	1.3875 (19)	O4–C6	1.3573 (14)

Table 2

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>
N1–H1...O1	0.86	1.87	2.7128 (18)	168
N2–H2...O3 ⁱ	0.86	2.08	2.8510 (18)	149
O3–H3A...O1 ⁱⁱ	0.93	1.72	2.6499 (16)	179
O4–H4A...O2 ⁱⁱⁱ	0.91	1.72	2.6289 (15)	178
C8–H8...O2 ^{iv}	0.93	2.34	3.235 (2)	162

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

Hydroxy H atoms were located in a difference Fourier map and refined as riding in their as-found relative positions (Table 2) with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. Other H atoms were placed in calculated positions, with C–H = 0.93 Å and N–H = 0.86 Å, and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia,

1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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