

Benzimidazolium 3,5-dihydroxybenzoate
benzimidazoleXuan Huang, Jia-Geng Liu and
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The crystal structure of the title compound, $C_7H_7N_2^{+} \cdot C_7H_5O_4^{-} \cdot C_7H_6N_2$, consists of discrete cations, anions and neutral molecules, with two of each species in the asymmetric unit. Through hydrogen bonding and π - π stacking the chemical components link to each other to form a sandwich-like supramolecular crystal structure.

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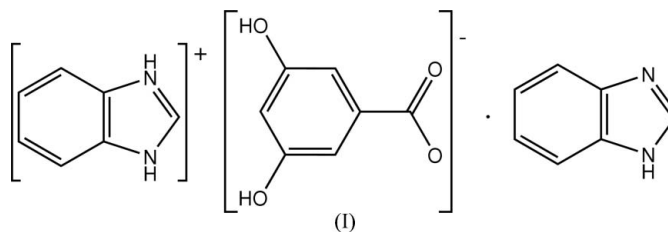
Key indicators

Single-crystal X-ray study
 $T = 295$ K
 Mean $\sigma(C-C) = 0.002$ Å
 Disorder in main residue
 R factor = 0.041
 wR factor = 0.112
 Data-to-parameter ratio = 17.0

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

Comment

During an investigation of the nature of aromatic stacking, we reported the crystal structure of benzimidazolium 3,5-dihydroxybenzoate (Huang *et al.*, 2006). In a similar experiment, we recently obtained the title compound, (I), which has a different but related composition.



The structure of the asymmetric unit is shown in Fig. 1; it contains two cations, two anions and two neutral molecules. The small differences between C—O bond distances for the carboxylate groups (Table 1) confirms their deprotonation. A

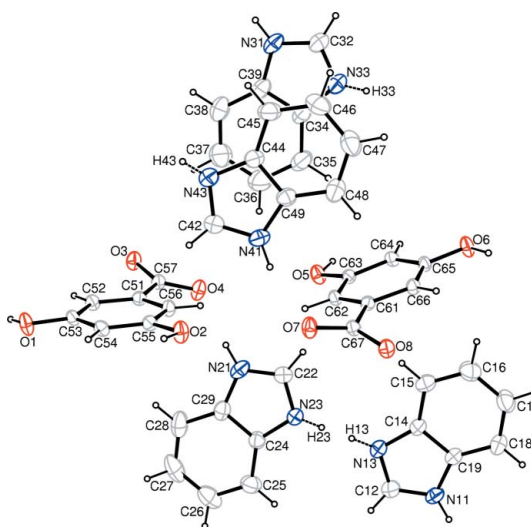


Figure 1

The asymmetric unit of (I), shown with 30% probability displacement ellipsoids (arbitrary spheres for H atoms). Dashed bonds indicate disordered H atoms.

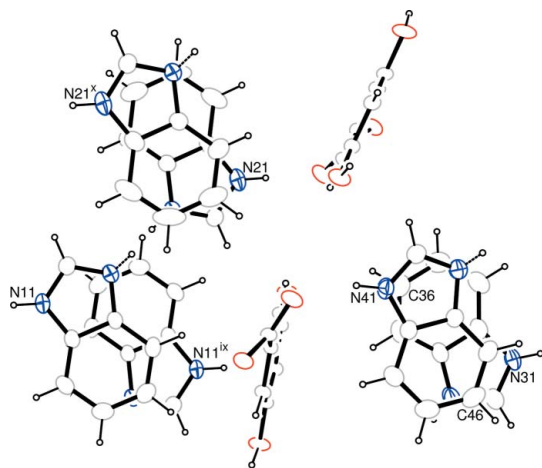


Figure 2
A diagram showing the partially overlapped arrangement of neighboring bzm rings [symmetry codes: (ix) $1 - x, -y, 1 - z$; (x) $1 - x, 1 - y, 1 - z$].

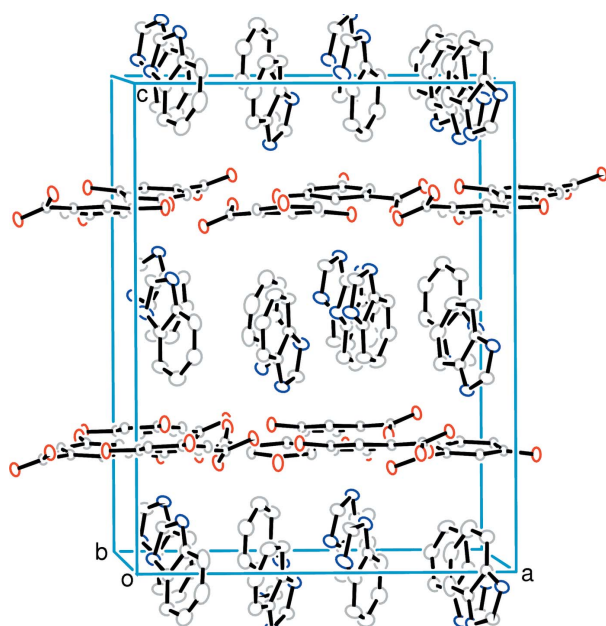


Figure 3
A packing diagram showing the sandwich-like supramolecular crystal structure.

difference Fourier map clearly shows half-protonation of all the benzimidazole units in the structure, with atoms H13, H23, H33 and H43 disordered, each with half-occupancy, generating alternative $N-H \cdots N$ and $N \cdots H-N$ arrangements of the cations and neutral molecules.

A partially overlapped arrangement is observed between bzm and Hbzm⁺ (benzimidazolium) units (Fig. 2). The face-to-face separations of 3.502 (10) Å between the N11-bzm and N11^{ix}-bzm units and 3.520 (12) Å between N21-bzm and N21^x-bzm suggest the existence of $\pi-\pi$ stacking between parallel aromatic rings (for symmetry codes, see Fig. 2). The centroid-to-centroid separation of 3.8743 (12) Å between the C36-ring and N41-ring also indicates $\pi-\pi$ stacking between nearly parallel bzm and Hbzm⁺ units [dihedral angle = 6.88 (7)°].

Extensive hydrogen bonding is observed in the crystal structure (Table 2), involving N and O atoms as both donors and acceptors. Through this hydrogen bonding and $\pi-\pi$ stacking, the chemical components link to each other, forming a sandwich-like supramolecular crystal structure (Fig. 3).

Experimental

Sr(NO₃)₂ (1 mmol), Na₂CO₃ (1 mmol), benzimidazole (2 mmol) and 3,5-dihydroxybenzoic acid (2 mmol) were dissolved in a water-ethanol solution (20 ml, 4:1). The mixture was refluxed for 2 h and then filtered. Single crystals of (I) were obtained from the filtrate after two weeks.

Crystal data

C₇H₇N₂⁺·C₇H₅O₄⁻·C₇H₆N₂
M_r = 390.39
 Monoclinic, *P*2₁/*n*
a = 15.070 (2) Å
b = 13.353 (2) Å
c = 19.358 (4) Å
 β = 90.262 (7)°
V = 3895.3 (11) Å³

Z = 8
D_x = 1.331 Mg m⁻³
 Mo *K*α radiation
 μ = 0.10 mm⁻¹
T = 295 (2) K
 Chunk, yellow
 0.41 × 0.32 × 0.20 mm

Data collection

Rigaku R-Axis RAPID
 diffractometer
 ω scans
 Absorption correction: none
 61723 measured reflections

8912 independent reflections
 5990 reflections with $I > 2\sigma(I)$
*R*_{int} = 0.048
 θ_{\max} = 27.5°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.041
wR (*F*²) = 0.112
S = 1.05
 8912 reflections
 524 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 0.0155P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0026 (3)

Table 1

Selected bond lengths (Å).

O3—C57	1.2495 (14)	O7—C67	1.2591 (14)
O4—C57	1.2620 (14)	O8—C67	1.2623 (14)

Table 2

Hydrogen-bond geometry (Å, °).

<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 O4 ⁱ	0.92	1.76	2.6730 (13)	170
O2—H2 \cdots O8 ⁱⁱ	0.90	1.80	2.6989 (13)	172
O5—H5 \cdots O3 ⁱⁱⁱ	0.96	1.70	2.6573 (12)	173
O6—H6 \cdots O7 ^{iv}	0.95	1.72	2.6610 (13)	168
N11—H11 \cdots O3 ^v	0.86	2.11	2.8490 (16)	144
N13—H13 \cdots N23	0.86	1.86	2.7038 (19)	168
N21—H21 \cdots O4	0.86	1.89	2.7374 (17)	167
N23—H23 \cdots N13	0.86	1.85	2.7038 (19)	174
N31—H31 \cdots O8 ^{vi}	0.86	1.91	2.7541 (17)	167
N33—H33 \cdots N33 ^{vii}	0.86	1.85	2.700 (2)	170
N41—H41 \cdots O7	0.86	2.07	2.8855 (16)	159
N43—H43 \cdots N43 ^{viii}	0.86	1.87	2.727 (2)	171

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

Hydroxyl H atoms were located in a difference Fourier map and refined as riding in their as-found relative positions, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. A difference Fourier map clearly shows peaks bonded to all N atoms of bzim. H atoms on N atoms of bzim were placed in calculated positions, with N—H = 0.86 Å, and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$; atoms H13, H23, H33 and H43 are disordered and their occupancies were fixed at 0.5. Other H atoms were placed in calculated positions, with C—H = 0.93 Å and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 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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