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Hydrogen bonding in two benzene-1,2-diaminium pyridine-2-carboxylate salts and a cocrystal of benzene-1,2-diamine and benzoic acid

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The isostructural salts benzene-1,2-diaminium bis(pyridine-2-carboxylate), $0.5C_6H_{10}N_2^{2^+}\cdot C_6H_4NO_2^-$, (1), and 4,5-dimethylbenzene-1,2-diaminium bis(pyridine-2-carboxylate), $0.5C_8H_{14}N_2^{2^+}\cdot C_6H_4NO_2^-$, (2), and the 1:2 benzene-1,2-diamine-benzoic acid cocrystal, $0.5C_6H_8N_2\cdot C_7H_6O_2$, (3), are reported. All of the compounds exhibit extensive $N-H\cdots O$ hydrogen bonding that results in interconnected rings. $O-H\cdots N$ hydrogen bonding is observed in (3). Additional $\pi-\pi$ and $C-H\cdots\pi$ interactions are found in each compound. Hirshfeld and fingerprint plot analyses reveal the primary intermolecular interactions and density functional theory was used to calculate their strengths. Salt formation by (1) and (2), and cocrystallization by (3) are rationalized by examining pK_a differences. The $R_2^2(9)$ hydrogen-bonding motif is common to each of these structures.

1. Introduction

Hydrogen bonding plays an important role in the strategic design of solid-state structures with desirable architectures. Weaker intermolecular interactions (*e.g.* those involving π -stacking and/or C-H··· π interactions) can play a role in the self-assembly process, leading to nucleation and crystal growth, as well as cocrystal *versus* salt formation (Bora *et al.*, 2018). An understanding of the relative strengths of these interactions is of importance in the preparation of pharmaceuticals with consistent formulations (Anderson *et al.*, 2009; Thakuria *et al.*, 2007). When a formulation contains a weak acid and a weak base, the analytical characteristics of the components (*i.e.* relative acid/base strength) is a decisive determinant of salt *versus* cocrystal formation (Rajput *et al.*, 2017; Cruz-Cabeza, 2012).

The synthon benzene-1,2-diamine and its analogues provide multiple sites in close proximity for hydrogen bonding and an aromatic system with the potential to engage in π - π and C-H··· π interactions (Deng *et al.*, 2012). We have taken advantage of these attributes to prepare a variety of coordination polymers containing benzenediamine ligands (Geiger *et al.*, 2016; Geiger, Parsons & Zick, 2014; Geiger & Parsons, 2014).

We recently reported the preparation, structural characterization and calculated interaction energies of several protonated benzenediamines with inorganic anions (Zick & Geiger, 2018). Herein, we explore the structures of two isostructural salts, namely, benzene-1,2-diaminium bis(pyridine-2-carboxylate), (1), and 4,5-dimethylbenzene-1,2-diaminium bis(pyridine-2-carboxylate), (2). We also report the 1:2 benzene-1,2-diamine-benzoic acid cocrystal, (3). The results

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Table 1Experimental details.

	(1)	(2)	(3)
Crystal data			
Chemical formula	$0.5C_6H_{10}N_2^{2+}C_6H_4NO_2^{-}$	$0.5C_8H_{14}N_2^{2+}\cdot C_6H_4NO_2^{-1}$	$0.5C_6H_8N_2\cdot C_7H_6O_2$
Mr	177.18	191.21	176.19
Crystal system, space group	Monoclinic, C2/c	Monoclinic, $C2/c$	Orthorhombic, Pbcn
Temperature (K)	200	200	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	21.467 (5), 7.675 (2), 12.837 (3)	21.451 (4), 9.0100 (19), 12.585 (3)	20.061 (3), 7.8464 (10), 11.6895 (12)
α, β, γ (°)	90, 125.362 (7), 90	90, 123.447 (6), 90	90, 90, 90
$V(\dot{A}^3)$	1724.8 (7)	2029.5 (7)	1840.0 (4)
Z	8	8	8
Radiation type	Μο Κα	Μο Κα	Μο Κα
$\mu (\mathrm{mm}^{-1})$	0.10	0.09	0.09
Crystal size (mm)	$0.50 \times 0.30 \times 0.25$	$0.60 \times 0.50 \times 0.25$	$0.60 \times 0.48 \times 0.20$
Data collection			
Diffractometer	Bruker SMART X2S benchtop	Bruker SMART X2S benchtop diffractometer	Bruker SMART X2S benchtop
Absorption correction	Multi-scan (SADABS; Bruker, 2015)	Multi-scan (<i>SADABS</i> ; Bruker, 2015)	Multi-scan (SADABS; Bruker, 2015)
T_{\min}, T_{\max}	0.61, 0.98	0.61, 0.98	0.64, 0.98
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	8287, 1573, 1161	7764, 1794, 1201	30170, 1638, 1337
R _{int}	0.063	0.080	0.064
$(\sin \theta / \lambda)_{\rm max} ({\rm \AA}^{-1})$	0.602	0.603	0.598
Refinement			
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.047, 0.138, 1.04	0.044, 0.128, 1.01	0.030, 0.087, 1.05
No. of reflections	1573	1794	1638
No. of parameters	130	140	131
No. of restraints	3	3	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta \rho_{\rm max}, \Delta \rho_{\rm min} \ ({ m e} \ { m \AA}^{-3})$	0.20, -0.26	0.14, -0.19	0.12, -0.12

Computer programs: APEX2 (Bruker, 2015), SAINT (Bruker, 2015), SHELXS97 (Sheldrick, 2008), SHELXL2014 (Sheldrick, 2015), PLATON (Spek, 2009), Mercury (Macrae et al., 2008), and publcIF (Westrip, 2010).

of an exploration of the primary intermolecular interactions, including the calculation of hydrogen bond, π - π , and C-H··· π energies, are reported.



2. Experimental

2.1. Synthesis and crystallization

2.1.1. Preparation of benzene-1,2-diaminium bis(pyridine-2-carboxylate), (1). Benzene-1,2-diamine (1.00 g) was added to absolute ethanol (30 ml). The mixture was heated with stirring until the solid was dissolved. 2-Picolinic acid (2.30 g) was added to the reaction mixture with continued heating and stirring. The mixture was stirred at room temperature for a week. A white precipitate formed. The product (2.59 g) was collected by vacuum filtration (78.9% yield). ¹H NMR (400 MHz, DMSO, ppm): δ 8.67 (*d*, 2H), 8.02 (*d*, 2H), 7.96 (*t*, 2H), 7.58 (*t*, 2H), 6.55 (*s*, 2H), 6.43 (*s*, 2H). Single crystals were obtained *via* vapor diffusion of hexane into an ethyl acetate solution of the product at room temperature.

2.1.2. Preparation of 4,5-dimethylbenzene-1,2-diaminium bis(pyridine-2-carboxylate), (2). 4,5-Dimethylbenzene-1,2-diamine (1.10 g) was dissolved in absolute ethanol (20 ml) with stirring. A solution of 2-picolinic acid (2.00 g) in absolute ethanol (20 ml) was added with stirring. The resulting mixture was stirred for a week, during which time a pink-colored precipitate formed. The product (yield 2.52 g, 81.7%) was collected by vacuum filtration. ¹H NMR (400 MHz, DMSO, ppm): δ 8.66 (*d*, 2H), 8.02 (*d*, 2H), 7.95 (*t*, 2H), 7.59 (*t*, 2H), 6.35 (*s*, 2H), 1.96 (*s*, 6H). Single crystals were obtained *via* slow evaporation of a solution of the product in ethyl acetate at room temperature.

2.1.3. Preparation of benzene-1,2-diamine-benzoic acid (1/2), (3). Benzene-1,2-diamine (1.60 g) was dissolved in absolute ethanol (45 ml) with heating and stirring. Benzoic

acid (3.60 g) was added to the reaction mixture. Heating was stopped once the reagents dissolved, and the mixture was stirred at room temperature for a week. Ethanol (20 ml) was removed *via* rotary evaporation and hexane (15 ml) was added. After chilling, an orange precipitate formed. The product (yield 0.81 g, 15.7%) was collected by vacuum filtration. ¹H NMR (400 MHz, DMSO, ppm): δ 7.91 (*d*, 4H), 7.58 (*t*, 2H), 7.47 (*t*, 4H), 6.53 (*m*, 2H), 6.40 (*m*, 2H). Single crystals were obtained *via* vapor diffusion of hexane into a chloroform solution of the product at room temperature.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. For all compounds, H atoms bonded to C atoms were refined using a riding model, with C-H = 0.95 Å for aromatic C atoms and, for (2), C-H = 0.98 Å for methyl H atoms. For all structures, $U_{iso}(H) = kU_{eq}(C)$, where k = 1.2 for H atoms bonded to aromatic C atoms and 1.5 for H atoms bonded to methyl C atoms. For (1) and (2), the N-H bond lengths were restrained to 0.91 (2) Å; for (3), the N-H bond lengths were refined freely. For all compounds, the isotropic diplacement parameters of the H atoms bonded to N and O atoms were refined freely.

Large K values were noted in the analysis of variance for (1) and (2). However, the K value is large only for weak reflections $[F_c/F_c(\max)]$ is lower than 0.005 for (1) and 0.020 for (2)].

2.3. Hirshfeld surface, fingerprint plots, and interaction energy calculations

Hirshfeld surfaces, fingerprint plots, interaction energies, and energy frameworks (Turner *et al.*, 2015) were calculated using *CrystalExplorer17* (Turner *et al.*, 2017). Interaction energies for (3) were calculated employing the CE-B3LYP/6-31G(d,p) functional/basis set combination and are corrected for basis set superposition energy (BSSE) using the counterpoise (CP) method (Boys & Bernardi, 1970). The interaction energy is broken down as

$$E_{\text{tot}} = k_{\text{ele}} E'_{\text{ele}} + k_{\text{pol}} E'_{\text{pol}} + k_{\text{dis}} E'_{\text{dis}} + k_{\text{rep}} E'_{\text{rep}},$$

where the k values are scale factors, E'_{ele} represents the electrostatic component, E'_{pol} the polarization energy, E'_{dis} the dispersion energy, and E'_{rep} the exchange–repulsion energy (Turner *et al.*, 2014; Mackenzie *et al.*, 2017). The C–H bond lengths were converted to normalized values based on neutron diffraction results (Allen *et al.*, 2004).

Interaction energy calculations were also performed on molecules in the gas phase using *SPARTAN'16* (Wavefunction, 2016). Density functional theory (DFT) calculations using the M06-2X (Zhao & Truhlar, 2008) functional with a 6-31G(d,p) basis set were employed for the determination of interaction energies, which were corrected for BSSE employing the CP method (Boys & Bernardi, 1970). Atomic coordinates obtained from the crystallographic analysis were used for all non-H atoms. Because bond lengths obtained for H atoms from X-ray crystallographic analyses are inaccurate, the positions of the H atoms were adjusted based on normalized values determined by neutron diffraction results (Allen *et al.*, 2004) for (1) and (2). An additional pyridine-2carboxylate was included in interaction energy calculations for (1) and (2) in order to maintain charge neutrality. For (3), H-atom positions were optimized to their energy minima using the M06-2X/6-31G(d,p) functional/basis set combination.

3. Results and discussion

Compounds (1) and (2) are isostructural salts. Views of (1) and (2) displaying the atom-labeling schemes are shown in Figs. 1 and 2. The cation resides across a crystallographically imposed twofold rotation axis and the asymmetric unit contains the pyridine-2-carboxylate (pa^-) anion and one-half of the benzene-1,2-diaminium ($bdaH_2^{2+}$) dication for (1) and the 4,5-dimethylbenzene-1,2-diaminium ($Me_2bdaH_2^{2+}$) dication for (2). A search of the Cambridge Structural Database (CSD; Groom *et al.*, 2016) yielded only one organic structure containing a benzene-1,2-diaminium moiety (CSD refcode ZEXBEM; Amirthakumar *et al.*, 2018).

The hydrogen-bonding network for (1) is shown in Fig. 3. An extensive ring system involving protonated amine donors with a pyridine-ring N atom and carboxylate O atoms as acceptors is observed. The carboxylate and diaminium synthons result in $R_2^2(9)$ rings with each aminium group as donor to a different oxygen acceptor. An $R_1^2(5)$ ring is the product of a bifurcated aminium donor with a pyridine N atom and one of the carboxylate O atoms as acceptors. This hydrogen-bonding motif has been observed for other pyridine-2-carboxylate salts (Żesławska *et al.*, 2017). A third ring, $R_4^2(8)$, involves a single O atom from two different carboxylate acceptors and a single aminium group from two different cations, each behaving as a two-H-atom donor. The joined rings propagate along [001].

A weak $\pi - \pi$ interaction is observed in (1) with $Cg(pa^-) \cdots Cg(pa^-) = 3.9360$ (16) Å, where $Cg(pa^-)$ is the pyridine ring centroid. The corresponding distance in (2) is 4.6018 (15) Å. As seen in Fig. 3, rings involved in the π -stacking are related by the twofold screw axes. The large difference in stacking distance can be accounted for by the disparity in the *b*-axis lengths (Table 1 and Fig. 4). Both (1)



Figure 1

View of the molecular structure of (1), showing the atom-labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. [Symmetry code: (a) -x + 1, y, $-z + \frac{3}{2}$.]



Figure 2

View of the molecular structure of (2), showing the atom-labeling scheme. The atomic coordinates of the carboxylate anion have been transformed by $(-x + 1, y - 1, -z + \frac{1}{2})$ to show hydrogen bonding. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. [Symmetry code: (a) $-x + 1, y, -z + \frac{1}{2}$]

and (2) exhibit a weak $C-H\cdots\pi$ interaction involving a H atom belonging to the anion and the cation π -system (Tables 2 and 3). Together, the $C-H\cdots\pi$ and the $\pi-\pi$ contacts result in chains parallel to [110].

The Hirshfeld surface and fingerprint plots of (1) are shown in Fig. 5 and of (2) are in the supporting information. The surface coverage for $bdaH_2^{2^+}$ and ba^- are, respectively, $H \cdots H$ 39.0 and 29.0%, $C \cdots C$ 0.0 and 9.7%, $N \cdots H$ 9.7 and 7.2%, $O \cdots H$ 32.7 and 34.6%, $C \cdots H$ 18.4 and 16.9%, and $N \cdots C$ 0.0 and 3.4%. The primary intermolecular interactions are clearly observable in the fingerprint plot.

Compound (3) is a 1:2 cocrystal of benzene-1,2-diamine (bda) and benzoic acid (ba). The bda resides across a crystallographically imposed twofold rotation axis. As a result, the

Table 2				
Hydrogen-boi	nd geometry	(Å, °) f	or (1).	

 $Cg(bdaH_2^{2+})$ refers to the ring centroid of the benzene-1,2-diaminium cation.

$D - H \cdot \cdot \cdot A$	$D-{\rm H}$	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdot \cdot \cdot A$
$N1-H1A\cdotsO1^{i}$	0.93 (2)	2.24 (2)	2.958 (2)	135 (2)
$N1-H1A\cdots N2^{i}$	0.93(2)	2.08(2)	2.907 (2)	149 (2)
$N1 - H1B \cdots O2^{ii}$	0.96(2)	1.78 (2)	2.7137 (19)	164 (2)
$N1-H1C\cdots O1$	0.97(2)	1.70(2)	2.6533 (19)	168 (2)
$C8-H8\cdots Cg(bdaH_2^{2+})^{iii}$	0.95	2.65	3.592 (3)	170

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

Table 3Hydrogen-bond geometry (Å, $^{\circ}$) for (2).

 $Cg(Me_2bdaH_2^{2+})$ refers to the ring centroid of the 4,5-dimethylbenzene-1,2-diaminium cation.

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - H \cdot \cdot \cdot A$
$N2-H2A\cdots O2^{i}$	0.96 (2)	1.78 (2)	2.729 (2)	171 (2)
$N2-H2B\cdots O1^{ii}$	0.98(2)	1.67 (2)	2.639 (2)	169 (2)
$N2-H2C\cdots O1^{iii}$	0.91(1)	2.14 (2)	2.9032 (19)	141 (2)
$N2-H2C\cdots N1^{iii}$	0.91(1)	2.22 (2)	2.999 (2)	144 (2)
$C5-H5\cdots Cg(Me_2bdaH_2^{2+})^{iv}$	0.95	2.77	3.682 (3)	160

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

asymmetric unit contains one molecule of ba and one-half molecule of bda. A view of (3) showing the atom-labeling scheme is shown in Fig. 6. Searches of the CSD for related structures containing benzoic acid or benzene-1,2-diamine yielded a total of three results [CSD refcodes VOCZET02 (Meng *et al.*, 2009), URILAJ (Landenberger & Matzger, 2010), and ZEZHOD (Landenberger & Matzger, 2012)].



Figure 3

Partial packing diagram of (1), showing the hydrogen bonding resulting in strips along [001]. Only H atoms involved in the interactions are shown. For symmetry codes, see Table 2; additionally, (iv) -x + 1, y, $-z + \frac{3}{2}$.



Figure 4

Partial packing diagram of (1), showing the π - π and C-H··· π interactions leading to chains parallel to [110]. Only H atoms involved in these interations are shown. [Symmetry codes: (i) $-x + \frac{3}{2}$, $y + \frac{1}{2}$, $-z + \frac{3}{2}$; (ii) -x + 1, y, $-z + \frac{3}{2}$; (iii) $x - \frac{1}{2}$, $y + \frac{1}{2}$, z; (iv) $-x + \frac{3}{2}$, $y - \frac{1}{2}$, $-z + \frac{3}{2}$.]

An extensive hydrogen-bonding network composed of both $N-H\cdots O$ and $O-H\cdots N$ interactions exists. Alternating $R_2^2(9)$ and $R_4^2(8)$ rings result in chains parallel to [001], as seen in Table 4 and Fig. 7. In the $R_2^2(9)$ rings, both $N-H\cdots O$ and $O-H\cdots N$ hydrogen bonds are found, whereas the $R_4^2(8)$ rings are composed of only $N-H\cdots O$ hydrogen bonds.

In addition to N-H···O and O-H···N hydrogen bonding, the extended structure of (3) exhibits C-H··· π interactions (Table 4 and Fig. 8) in which the ba serves as the donor to the bda π -ring. Finally, the superstructure exhibits a weak π - π



d d, 2.4 2.4 2.2 2.2 2.0 2.0 C-H 1.8 1.8 1.6 1.6 N-H C-H 1.4 1.4 1.2 1.2 1.0 1.0 N-H---C 0.8 0.8 d, d, 0.6 1.6 1.8 2.2 2.0 2.4 0.8 1.8 2.0 2.2 2.4 1.0 1.2 1.2 0.6 1.0 1.2 1.2 1.6

Figure 5

(a) Hirshfeld surfaces and (b) fingerprint plots for (1). The diaminium cation is on the left and the carboxylate anion is on the right.

(b)

Table 4Hydrogen-bond geometry (Å, $^{\circ}$) for (3).

Cg(bda) refers to the ring centroid of the benzene-1,2-diamine ring.

$D - H \cdots A$	D-H	$H \cdot \cdot \cdot A$	$D \cdots A$	$D - \mathbf{H} \cdots A$
$01 - H1C \cdots N1 N1 - H1A \cdots O2^{i} N1 - H1B \cdots O2^{ii} C6 - H6 \cdots Cg(bda)^{iii}$	0.994 (19) 0.916 (15) 0.916 (16) 0.95	1.706 (19) 2.163 (16) 2.136 (16) 2.81	2.6852 (13) 3.0681 (14) 3.0160 (14) 3.7163 (16)	167.8 (16) 169.8 (12) 160.8 (12) 161

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

interaction between adjacent ba molecules, with a $Cg(ba)\cdots Cg(ba)^{iii}$ distance of 4.0487 (10) Å (see Table 4 for symmetry code).

The $\Delta p K_a$ rule can be used to rationalize observed salt formation *versus* cocrystallization of a weak acid and a weak base. Simply stated, if the difference in pK_a values of the acid and base is greater than 3, proton transfer from acid to base occurs resulting in salt formation. If the difference is less than 1, the acid remains protonated and cocrystallization results. For $\Delta p K_a$ values between 1 and 3, proton transfer is usually incomplete, resulting in greater ambiguity, referred to as the 'salt–cocrystal continuum' (Rajput *et al.*, 2017). In the present case, pyridine-2-carboxylic acid, benzoic acid, benzene-1,2diaminium, and 4,5-dimethylbenzene-1,2-diaminium have pK_a



View of the molecular structure of (3), showing the atom-labeling scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. [Symmetry code: (a) -x + 1, y, $-z + \frac{1}{2}$.]

Table 5

Interaction energies $(kJ mol^{-1})$ calculated for (3).

Interaction energies were calculated employing the CE-B3LYP/6-31G(d,p) functional/basis set combination and are corrected for BSSE using the CP method.

Interaction(s)	$E'_{\rm ele}$	$E'_{\rm pol}$	$E'_{\rm dis}$	$E'_{\rm rep}$	$E_{\rm tot}$
$O-H \cdot \cdot \cdot N/N - H \cdot \cdot \cdot O$	-98.5	-22.7	-17.0	119.5	-61.9
N-H···O	-20.5	-4.4	-9.2	20.2	-20.5
π – π	-2.7	-0.6	-24.8	11.7	-17.8
$C-H\cdots\pi$	-4.1	-1.0	-13.3	7.3	-12.1

Scale factors used to determine E_{tot} : $k_{\text{ele}} = 1.057$, $k_{\text{pol}} = 0.740$, $k_{\text{dis}} = 0.871$, and $k_{\text{rep}} = 0.618$ (Mackenzie *et al.*, 2017). See Section 2.3 for calculation details.

values of 1.01, 4.20, 4.47, and 5.12, respectively (Dean, 1985; Haynes, 2010). The resulting $\Delta p K_a$ values for (1), (2) and (3) are thus 3.46, 4.11 and 0.27, respectively. As predicted using the $\Delta p K_a$ rule, (1) and (2) are salts and (3) is a cocrystal.

Hirshfeld and fingerprint plots (Mackenzie *et al.*, 2017) for (3) are shown in Fig. 9. The principal interactions are clearly visible in the fingerprint plots. The surface coverage for bda and ba are, respectively, $H \cdots H$ 59.7 and 40.4%, $C \cdots C$ 0 and 9.8%, $N \cdots H$ 5.4 and 2.6%, $O \cdots H$ 17.0 and 23.8%, $C \cdots H$ 17.9 and 21.3%, and $C \cdots O$ 0.1 and 2.0%.

Interaction energies for (3) were calculated using two different methods, as described in Section 2.3. The results for the principal intermolecular interactions obtained using *CrystalExplorer* (Turner *et al.*, 2014; Mackenzie *et al.*, 2017) are shown in Table 5. The $O-H\cdots N$ and $N-H\cdots O$ hydrogenbonding interactions that result in the $R_2^2(9)$ rings $(-61.9 \text{ kJ mol}^{-1})$ are stronger than the two $N-H\cdots O$ interactions resulting in the $R_4^2(8)$ rings $(-20.5 \text{ kJ mol}^{-1} \text{ each})$. As expected for a traditional hydrogen bond, the primary contributor to the total energy is the electrostatic component.



Figure 7

Partial packing diagram of (3), showing the linked chains parallel to [001]. Only H atoms involved in these interactions are shown. [Symmetry codes: (i) -x + 1, y, $-z + \frac{1}{2}$; (ii) x, -y + 1, $z - \frac{1}{2}$.]



Figure 8

Partial packing diagram of (3), emphasizing the $\pi - \pi$ and $C - H \cdots \pi$ interactions. Only H atoms involved in these interations are shown. [Symmetry codes: (i) $x + \frac{1}{2}$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}$, $y - \frac{1}{2}$, z; (iii) $-x + \frac{1}{2}$, $y + \frac{1}{2}$, z.]

Using *SPARTAN'16* (Wavefunction, 2016) and the M06-2X functional, as described in Section 2.3, a value of $-56.0 \text{ kJ mol}^{-1}$ was obtained for the $R_2^2(9)$ ring interactions and a value of -20.6 kJ for the N-H···O interaction in the $R_4^2(8)$ ring. The M06 suite of density functionals are reported to outperform B3LYP for dispersion and ionic hydrogenbonding interactions (Walker *et al.*, 2013; Zhao & Truhlar, 2008; Zick & Geiger, 2018). For comparison, a value of



(a) Hirshfeld surfaces and (b) fingerprint plots for (3). The benzene-1,2diamine molecule is on the left and the benzoic acid molecule is on the right.

-70.3 kJ mol⁻¹ has been reported for the $R_2^2(8)$ ring composed of two fused pyridine rings as acceptors and two fused 4-pyridone rings as donors, *i.e.* two N-H···N interactions (Rozas, 2007). In the same study, an interaction energy of -47.2 kJ mol⁻¹ was calculated for an $R_2^1(6)$ ring composed of a pyridine acceptor and a fused 4-pyridone donor (*i.e.* two N-H donors and one N-atom acceptor) and -42.09 kJ mol⁻¹ for a four-membered ring with a bifurcated hydrogen bond (a 4-pyridone donor and two fused pyridine rings as acceptors). A value of -94.9 kJ mol⁻¹ obtained using the M06-2X functional has been reported for an N-H···N interaction between two benzene-1,3-diaminium cations (Zick & Geiger,

 $[H_2N\cdots H\cdots NH_3]^+$ (Steiner, 2002). The C-H··· π (-12.1 kJ mol⁻¹) and π - π (-17.8 kJ mol⁻¹) interactions are dominated by the dispersion energy. Although much weaker than the calculated traditional hydrogen-bond energies, these values compare favorably with the value of -7.7 kJ mol⁻¹ for a C-H··· π interaction between furan molecules (Geiger, Geiger & Deck, 2014) and the -9.4 kJ mol⁻¹ reported for a 'T-shaped' benzene dimer (Sherrill *et al.*, 2009). A value of -20.7 kJ mol⁻¹ was reported for a π - π interaction between benzene rings of a benzimidazole derivative (Geiger, Geiger & Deck, 2014) and -11 kJ mol⁻¹ for benzene rings in a coplanar orientation (Grimme, 2008).

2018) and a value of $-79.5 \text{ kJ mol}^{-1}$ was reported for

Calculations were also performed on (1) and (2) to estimate the charge-assisted hydrogen-bonding energy between the diaminium cation and the carboxylate counter-ion. For the $R_2^2(9)$ ring (two N-H···O), the BSSE-corrected interaction energies found were -546 and -543 kJ mol⁻¹ for (1) and (2), respectively. The values obtained for the $R_1^2(5)$ ring (bifurcated N-H···N,O) were -412 and -437 kJ mol⁻¹. The results suggest that the slight difference in basicities of the two diamines does not play a major role in determining the strengths of these hydrogen bonds. These values are less than that of -665 kJ mol⁻¹ found for the charge-assisted N-H···O hydrogen bonds in 3-aminoanilinium perchlorate (Zick & Geiger, 2018) and are close to the values found for the methylammonium···Cl⁻ and methylamine···Cl⁻ energies, *i.e.* -507 and -413 kJ mol⁻¹, respectively (Defazio *et al.*, 2005).

The results demonstrate that an aromatic-1,2-diamine and a carboxylic acid combine in an energetically favorable way to form a tecton with an $R_2^2(9)$ motif, regardless of the formation of a salt (*i.e.* deprotonation of the acid/protonation of the amine) or cocrystallization.

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Acta Cryst. (2019). C75 [https://doi.org/10.1107/S2053229619002262]

Hydrogen bonding in two benzene-1,2-diaminium pyridine-2-carboxylate salts and a cocrystal of benzene-1,2-diamine and benzoic acid

Kyle A. Powers and David K. Geiger

Computing details

For all structures, data collection: *APEX2* (Bruker, 2015); cell refinement: *APEX2* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Benzene-1,2-diaminium bis(pyridine-2-carboxylate) (1)

Crystal data 0.5 C II N^{2+}

0.5C₆H₁₀N₂²⁺·C₆H₄NO₂⁻⁷ $M_r = 177.18$ Monoclinic, C2/c a = 21.467 (5) Å b = 7.675 (2) Å c = 12.837 (3) Å $\beta = 125.362$ (7)° V = 1724.8 (7) Å³ Z = 8

Data collection

Bruker SMART X2S benchtop diffractometer
Radiation source: XOS X-beam microfocus source
Doubly curved silicon crystal monochromator
Detector resolution: 8.3330 pixels mm⁻¹
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2015)

Refinement

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.047$ $wR(F^2) = 0.138$ S = 1.041573 reflections 130 parameters 3 restraints F(000) = 744 $D_{x} = 1.365 \text{ Mg m}^{-3}$ Mo Ka radiation, $\lambda = 0.71073 \text{ Å}$ Cell parameters from 2197 reflections $\theta = 2.3-23.1^{\circ}$ $\mu = 0.10 \text{ mm}^{-1}$ T = 200 KPrism, clear brown $0.50 \times 0.30 \times 0.25 \text{ mm}$ $T_{\text{min}} = 0.61, T_{\text{max}} = 0.98$ 8287 measured reflections
1573 independent reflections
1161 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.063$

 $\begin{aligned} & \mathcal{H}_{\text{int}} = 0.003 \\ & \theta_{\text{max}} = 25.4^{\circ}, \ \theta_{\text{min}} = 2.3^{\circ} \\ & h = -25 \rightarrow 25 \\ & k = -9 \rightarrow 6 \\ & l = -15 \rightarrow 14 \end{aligned}$

Hydrogen site location: mixed H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0685P)^2 + 0.2917P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 0.20 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{min} = -0.26 \text{ e } \text{Å}^{-3}$

Special details

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

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$
N1	0.45266 (9)	0.5387 (2)	0.61312 (15)	0.0373 (4)
H1A	0.4185 (11)	0.559 (3)	0.5265 (15)	0.058 (6)*
H1B	0.4267 (11)	0.464 (2)	0.6356 (19)	0.058 (6)*
H1C	0.4938 (12)	0.470 (3)	0.624 (2)	0.082 (7)*
C1	0.47781 (9)	0.7015 (2)	0.68382 (16)	0.0348 (4)
C2	0.45715 (11)	0.8578 (2)	0.6183 (2)	0.0494 (5)
H2	0.4278	0.8585	0.5277	0.059*
C3	0.47923 (14)	1.0128 (3)	0.6850(2)	0.0671 (6)
Н3	0.4654	1.1202	0.6401	0.081*
O1	0.57010 (7)	0.38679 (19)	0.63284 (13)	0.0546 (4)
O2	0.64209 (8)	0.36981 (19)	0.84518 (13)	0.0583 (5)
C4	0.63292 (11)	0.3725 (2)	0.73992 (18)	0.0416 (5)
N2	0.69229 (9)	0.3856 (2)	0.62789 (14)	0.0456 (4)
C5	0.70385 (10)	0.3601 (2)	0.74123 (16)	0.0370 (4)
C6	0.77514 (11)	0.3280 (3)	0.85123 (18)	0.0501 (5)
H6	0.7817	0.31	0.9303	0.06*
C7	0.83688 (11)	0.3225 (3)	0.8442 (2)	0.0614 (6)
H7	0.8866	0.2985	0.9183	0.074*
C8	0.82608 (12)	0.3519 (3)	0.7301 (2)	0.0601 (6)
H8	0.8681	0.3509	0.7239	0.072*
C9	0.75375 (12)	0.3828 (3)	0.6250(2)	0.0560 (6)
Н9	0.7466	0.4034	0.5458	0.067*

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

Atomic displacement	parameters	$(Å^2)$
monte moptie entern	pen ennerers	(/

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0343 (8)	0.0485 (9)	0.0300 (9)	0.0001 (6)	0.0191 (7)	-0.0001 (7)
C1	0.0282 (8)	0.0462 (10)	0.0342 (9)	-0.0011 (7)	0.0204 (7)	-0.0006 (7)
C2	0.0485 (11)	0.0541 (12)	0.0388 (12)	0.0013 (9)	0.0212 (10)	0.0054 (9)
C3	0.0789 (15)	0.0464 (12)	0.0541 (13)	0.0022 (11)	0.0259 (12)	0.0083 (10)
01	0.0353 (7)	0.0875 (11)	0.0418 (9)	0.0081 (6)	0.0228 (7)	-0.0003 (7)
02	0.0554 (9)	0.0876 (11)	0.0445 (9)	0.0184 (7)	0.0362 (8)	0.0113 (7)
C4	0.0426 (11)	0.0479 (10)	0.0395 (12)	0.0071 (8)	0.0268 (10)	0.0030 (8)
N2	0.0367 (8)	0.0653 (11)	0.0371 (10)	0.0045 (7)	0.0227 (8)	0.0015 (7)
C5	0.0363 (10)	0.0433 (10)	0.0326 (11)	0.0045 (7)	0.0206 (9)	-0.0001 (7)
C6	0.0428 (11)	0.0667 (13)	0.0366 (11)	0.0098 (9)	0.0204 (9)	0.0009 (9)
C7	0.0350 (11)	0.0840 (16)	0.0522 (14)	0.0127 (10)	0.0178 (10)	-0.0041 (11)
C8	0.0404 (11)	0.0846 (16)	0.0636 (15)	0.0054 (10)	0.0349 (11)	-0.0058 (11)
C9	0.0497 (12)	0.0811 (15)	0.0500 (13)	0.0058 (10)	0.0361 (11)	0.0015 (11)

Geometric parameters (Å, °)

N1—C1	1.453 (2)	C4—C5	1.516 (2)
N1—H1A	0.925 (16)	N2—C9	1.341 (2)
N1—H1B	0.955 (15)	N2—C5	1.341 (2)
N1—H1C	0.969 (16)	C5—C6	1.377 (3)
C1—C2	1.382 (2)	C6—C7	1.381 (3)
C1—C1 ⁱ	1.386 (3)	С6—Н6	0.95
C2—C3	1.380 (3)	C7—C8	1.362 (3)
C2—H2	0.95	С7—Н7	0.95
C3—C3 ⁱ	1.362 (5)	C8—C9	1.365 (3)
С3—Н3	0.95	C8—H8	0.95
O1—C4	1.255 (2)	С9—Н9	0.95
O2—C4	1.248 (2)		
C1—N1—H1A	111.0 (14)	O1—C4—C5	116.96 (15)
C1—N1—H1B	113.7 (12)	C9—N2—C5	117.39 (17)
H1A—N1—H1B	105.6 (18)	N2—C5—C6	122.46 (16)
C1—N1—H1C	113.7 (15)	N2—C5—C4	115.13 (16)
H1A—N1—H1C	106.5 (18)	C6—C5—C4	122.40 (16)
H1B—N1—H1C	105.9 (19)	C5—C6—C7	118.53 (18)
C2-C1-C1 ⁱ	119.77 (11)	С5—С6—Н6	120.7
C2-C1-N1	119.62 (16)	С7—С6—Н6	120.7
C1 ⁱ —C1—N1	120.61 (9)	C8—C7—C6	119.54 (19)
C3—C2—C1	119.8 (2)	С8—С7—Н7	120.2
С3—С2—Н2	120.1	С6—С7—Н7	120.2
C1—C2—H2	120.1	C7—C8—C9	118.68 (18)
C3 ⁱ —C3—C2	120.42 (12)	C7—C8—H8	120.7
C3 ⁱ —C3—H3	119.8	С9—С8—Н8	120.7
С2—С3—Н3	119.8	N2—C9—C8	123.38 (19)
O2—C4—O1	125.73 (16)	N2—C9—H9	118.3
O2—C4—C5	117.31 (17)	С8—С9—Н9	118.3
C1 ⁱ C1C2C3	-1.6 (3)	O1—C4—C5—C6	-173.88 (18)
N1—C1—C2—C3	178.30 (17)	N2C5C6C7	0.2 (3)
C1-C2-C3-C3 ⁱ	-0.5 (4)	C4—C5—C6—C7	-178.61 (18)
C9—N2—C5—C6	-1.5 (3)	C5—C6—C7—C8	1.2 (3)
C9—N2—C5—C4	177.41 (16)	C6—C7—C8—C9	-1.2 (3)
O2—C4—C5—N2	-171.91 (16)	C5—N2—C9—C8	1.5 (3)
O1—C4—C5—N2	7.2 (2)	C7—C8—C9—N2	-0.1 (4)
O2—C4—C5—C6	7.0 (3)		

Symmetry code: (i) -x+1, y, -z+3/2.

Hydrogen-bond geometry (Å, °)

 $Cg(bdaH_2^{2+})$ refers to the ring centroid of the benzene-1,2-diaminium cation.

D—H···A	D—H	H···A	D····A	<i>D</i> —H··· <i>A</i>
N1—H1A····O1 ⁱⁱ	0.93 (2)	2.24 (2)	2.958 (2)	135 (2)

N1—H1A····N2 ⁱⁱ	0.93 (2)	2.08 (2)	2.907 (2)	149 (2)
N1—H1 <i>B</i> ···O2 ⁱ	0.96 (2)	1.78 (2)	2.7137 (19)	164 (2)
N1—H1C…O1	0.97 (2)	1.70 (2)	2.6533 (19)	168 (2)
C8—H8···· $Cg(bdaH_2^{2+})^{iii}$	0.95	2.65	3.592 (3)	170

F(000) = 808

 $\theta = 2.5 - 23.6^{\circ}$ $\mu = 0.09 \text{ mm}^{-1}$

T = 200 K

 $D_{\rm x} = 1.252 {\rm Mg} {\rm m}^{-3}$

Block, clear colourless

 $0.60 \times 0.50 \times 0.25 \text{ mm}$

Mo *K* α radiation, $\lambda = 0.71073$ Å

Cell parameters from 2093 reflections

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

4,5-Dimethylbenzene-1,2-diaminium bis(pyridine-2-carboxylate) (2)

Crystal data

0.5C₈H₁₄N₂²⁺·C₆H₄NO₂⁻⁻ $M_r = 191.21$ Monoclinic, C2/c a = 21.451 (4) Å b = 9.0100 (19) Å c = 12.585 (3) Å $\beta = 123.447$ (6)° V = 2029.5 (7) Å³ Z = 8

Data collection

Durlean SMADT V2S hanghtan	T = 0.61 T = 0.09
bruker SWART A25 benchiop	$I_{\rm min} = 0.01, \ I_{\rm max} = 0.98$
diffractometer	7764 measured reflections
Radiation source: XOS X-beam microfocus	1794 independent reflections
source	1201 reflections with $I > 2\sigma(I)$
Doubly curved silicon crystal monochromator	$R_{\rm int} = 0.080$
Detector resolution: 8.3330 pixels mm ⁻¹	$\theta_{\rm max} = 25.4^\circ, \ \theta_{\rm min} = 2.5^\circ$
ω scans	$h = -25 \rightarrow 25$
Absorption correction: multi-scan	$k = -10 \rightarrow 10$
(SADABS; Bruker, 2015)	$l = -15 \rightarrow 14$
Refinement	
Refinement on F^2	Secondary atom site location: difference For

Refinement on F^2	Secondary atom site location: difference Fourier
Least-squares matrix: full	map
$R[F^2 > 2\sigma(F^2)] = 0.044$	Hydrogen site location: mixed
$wR(F^2) = 0.128$	H atoms treated by a mixture of independent
S = 1.01	and constrained refinement
1794 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2]$
140 parameters	where $P = (F_0^2 + 2F_c^2)/3$
3 restraints	$(\Delta/\sigma)_{\rm max} < 0.001$
Primary atom site location: structure-invariant	$\Delta ho_{ m max} = 0.14 \ m e \ m \AA^{-3}$
direct methods	$\Delta \rho_{\rm min} = -0.19 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2$ 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.

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	
01	0.42726 (7)	0.91055 (15)	0.36543 (11)	0.0570 (4)	
O2	0.35918 (7)	0.87343 (16)	0.15592 (11)	0.0620 (4)	
N1	0.30655 (9)	0.89341 (16)	0.37525 (13)	0.0501 (4)	
N2	0.54686 (9)	0.02590 (15)	0.38711 (13)	0.0381 (4)	
H2A	0.5757 (10)	-0.034 (2)	0.3665 (19)	0.071 (6)*	
H2B	0.5048 (9)	-0.028 (2)	0.3788 (17)	0.066 (6)*	
H2C	0.5774 (9)	0.046 (2)	0.4716 (14)	0.058 (6)*	
C1	0.36696 (10)	0.87944 (17)	0.26126 (16)	0.0428 (5)	
C2	0.30035 (9)	0.84935 (18)	0.26854 (14)	0.0397 (4)	
C3	0.23710 (10)	0.7799 (2)	0.16953 (16)	0.0523 (5)	
H3	0.2342	0.7504	0.0945	0.063*	
C4	0.17839 (10)	0.7550 (2)	0.18321 (19)	0.0625 (6)	
H4	0.1348	0.7046	0.1186	0.075*	
C5	0.18355 (11)	0.8033 (2)	0.29038 (19)	0.0662 (6)	
H5	0.1431	0.7897	0.3003	0.079*	
C6	0.24789 (12)	0.8718 (2)	0.38375 (19)	0.0620 (6)	
H6	0.2509	0.9054	0.458	0.074*	
C7	0.52181 (8)	0.16447 (17)	0.31600 (14)	0.0351 (4)	
C8	0.54091 (9)	0.29813 (18)	0.38044 (15)	0.0438 (5)	
H8	0.5689	0.2977	0.4709	0.053*	
С9	0.52030 (10)	0.4332 (2)	0.31640 (17)	0.0520 (5)	
C10	0.54175 (15)	0.5765 (2)	0.3908 (2)	0.0838 (8)	
H10A	0.5755	0.6329	0.3764	0.126*	
H10B	0.567	0.5543	0.4817	0.126*	
H10C	0.4967	0.6351	0.3624	0.126*	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\hat{A}^2)

Atomic displacement parameters $(Å^2)$

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
01	0.0424 (8)	0.0826 (10)	0.0510 (8)	-0.0109 (6)	0.0289 (7)	0.0005 (6)
O2	0.0674 (9)	0.0805 (10)	0.0570 (8)	-0.0222 (7)	0.0462 (7)	-0.0156 (6)
N1	0.0465 (10)	0.0648 (10)	0.0475 (9)	-0.0058 (7)	0.0312 (7)	-0.0022 (7)
N2	0.0395 (9)	0.0422 (8)	0.0363 (8)	0.0010 (6)	0.0233 (7)	0.0011 (5)
C1	0.0464 (12)	0.0418 (9)	0.0466 (10)	-0.0046 (8)	0.0296 (9)	-0.0018 (7)
C2	0.0401 (11)	0.0426 (9)	0.0405 (9)	-0.0013 (7)	0.0247 (8)	0.0027 (6)
C3	0.0509 (12)	0.0557 (11)	0.0504 (11)	-0.0101 (9)	0.0279 (9)	-0.0037 (8)
C4	0.0429 (13)	0.0680 (13)	0.0675 (14)	-0.0153 (9)	0.0246 (10)	0.0040 (10)
C5	0.0474 (14)	0.0874 (17)	0.0781 (15)	-0.0065 (11)	0.0435 (12)	0.0096 (11)
C6	0.0559 (13)	0.0867 (15)	0.0595 (12)	-0.0032 (11)	0.0419 (11)	-0.0009 (10)
C7	0.0320 (10)	0.0399 (9)	0.0411 (8)	0.0003 (6)	0.0250 (7)	-0.0001 (6)
C8	0.0445 (11)	0.0479 (10)	0.0443 (10)	-0.0048 (8)	0.0278 (8)	-0.0043 (6)
С9	0.0557 (12)	0.0432 (10)	0.0662 (11)	-0.0033 (8)	0.0394 (10)	-0.0066 (7)
C10	0.117 (2)	0.0473 (12)	0.0915 (16)	-0.0099(12)	0.0600(15)	-0.0141(9)

Geometric parameters (Å, °)

O1—C1	1.265 (2)	C4—H4	0.95
O2—C1	1.243 (2)	C5—C6	1.371 (3)
N1—C6	1.334 (2)	С5—Н5	0.95
N1—C2	1.335 (2)	С6—Н6	0.95
N2—C7	1.455 (2)	C7—C8	1.382 (2)
N2—H2A	0.959 (16)	C7—C7 ⁱ	1.386 (3)
N2—H2B	0.979 (15)	C8—C9	1.390 (2)
N2—H2C	0.908 (14)	С8—Н8	0.95
C1—C2	1.506 (3)	C9—C9 ⁱ	1.395 (4)
C2—C3	1.386 (2)	C9—C10	1.510 (2)
C3—C4	1.380 (3)	C10—H10A	0.98
С3—Н3	0.95	C10—H10B	0.98
C4—C5	1.363 (3)	C10—H10C	0.98
	117.50 (1()	C4 C5 115	120.4
C_{0} NI C_{2}	117.50 (16)	C4—C5—H5	120.4
C/-N2-H2A	113.1 (13)	C6C5H5	120.4
C / - N Z - H Z B	110.8 (11)		123.00 (19)
$H_2A - N_2 - H_2B$	112.6(17)		118.5
C/-N2-H2C	109.7 (11)	C_{2} C_{2} C_{2} C_{2}	118.5
H2A—N2—H2C	105.7 (16)	$C_8 - C_7 - C_7$	119.29 (9)
$H_2B = N_2 = H_2C$	104.5 (17)	C8 - C / - N2	119.81 (14)
0201	125.06 (17)	C/-N2	120.89 (8)
02C1C2	118.88 (15)	C/C8C9	121.73 (16)
01	116.05 (15)	C/C8H8	119.1
N1—C2—C3	122.95 (17)	C9—C8—H8	119.1
N1—C2—C1	115.85 (14)	C8—C9—C9 ¹	118.90 (10)
C3—C2—C1	121.20 (16)	C8—C9—C10	119.88 (18)
C4—C3—C2	118.02 (18)	C9 ¹ —C9—C10	121.22 (12)
C4—C3—H3	121.0	С9—С10—Н10А	109.5
С2—С3—Н3	121.0	C9—C10—H10B	109.5
C5—C4—C3	119.31 (18)	H10A—C10—H10B	109.5
C5—C4—H4	120.3	C9—C10—H10C	109.5
C3—C4—H4	120.3	H10A—C10—H10C	109.5
C4—C5—C6	119.1 (2)	H10B—C10—H10C	109.5
C6—N1—C2—C3	-1.6(3)	C2—C3—C4—C5	2.2 (3)
C6-N1-C2-C1	178.42 (15)	C3-C4-C5-C6	-1.9(3)
02-C1-C2-N1	-163.60(16)	C_{2} N1 – C_{6} – C_{5}	2.0(3)
01-C1-C2-N1	15.8 (2)	C4—C5—C6—N1	-0.2(3)
02-C1-C2-C3	16.5 (3)	C7 ⁱ C7C8C9	-2.9(3)
01 - 01 - 02 - 03	-164.09(16)	N2-C7-C8-C9	177 82 (16)
N1 - C2 - C3 - C4	-0.4(3)	$C7 - C8 - C9 - C9^{i}$	-0.4(3)
1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -	179 53 (16)	C7 - C8 - C9 - C10	179 38 (18)
01 02 03 07	1, 7.55 (10)		1, 7.50 (10)

Symmetry code: (i) -x+1, y, -z+1/2.

Hydrogen-bond geometry (Å, °)

 $Cg(Me_2bdaH_2^{2+})$ refers to the ring centroid of the 4,5-dimethyl-benzene-1,2-diaminium cation.

<i>D</i> —Н	H···A	$D^{\dots}A$	D—H···A
0.96 (2)	1.78 (2)	2.729 (2)	171 (2)
0.98 (2)	1.67 (2)	2.639 (2)	169 (2)
0.91 (1)	2.14 (2)	2.9032 (19)	141 (2)
0.91 (1)	2.22 (2)	2.999 (2)	144 (2)
0.95	2.77	3.682 (3)	160
	<i>D</i> —H 0.96 (2) 0.98 (2) 0.91 (1) 0.91 (1) 0.95	D —H $H \cdots A$ 0.96 (2)1.78 (2)0.98 (2)1.67 (2)0.91 (1)2.14 (2)0.91 (1)2.22 (2)0.952.77	D—HH···AD···A0.96 (2)1.78 (2)2.729 (2)0.98 (2)1.67 (2)2.639 (2)0.91 (1)2.14 (2)2.9032 (19)0.91 (1)2.22 (2)2.999 (2)0.952.773.682 (3)

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

Benzene-1,2-diamine bis(benzoic acid) (3)

Crystal data

 $\begin{array}{l} 0.5 \mathrm{C}_{6}\mathrm{H}_{8}\mathrm{N}_{2} \cdot \mathrm{C}_{7}\mathrm{H}_{6}\mathrm{O}_{2} \\ M_{r} = 176.19 \\ \text{Orthorhombic, } Pbcn \\ a = 20.061 \ (3) \ \mathrm{\AA} \\ b = 7.8464 \ (10) \ \mathrm{\AA} \\ c = 11.6895 \ (12) \ \mathrm{\AA} \\ V = 1840.0 \ (4) \ \mathrm{\AA}^{3} \\ Z = 8 \\ F(000) = 744 \end{array}$

Data collection

Bruker SMART X2S benchtop diffractometer	$T_{\min} = 0.0$ 30170 m
Radiation source: XOS X-beam microfocus	1638 ind
source	1337 ref
Doubly curved silicon crystal monochromator	$R_{\rm int}=0.0$
Detector resolution: 8.3330 pixels mm ⁻¹	$\theta_{\rm max} = 25$
ω scans	h = -23 - 23 - 23 - 23 - 23 - 23 - 23 - 2
Absorption correction: multi-scan	$k = -9 \rightarrow$
(SADABS; Bruker, 2015)	l = -13 - 13 - 13 - 13 - 13 - 13 - 13 - 1
Refinement	
Refinement on F^2	H atoms

Refinement on F^2 Least-squares matrix: full $R[F^2 > 2\sigma(F^2)] = 0.030$ $wR(F^2) = 0.087$ S = 1.051638 reflections 131 parameters 0 restraints Hydrogen site location: mixed $D_x = 1.272 \text{ Mg m}^{-3}$ Mo K α radiation, $\lambda = 0.71073 \text{ Å}$ Cell parameters from 4994 reflections $\theta = 2.8-24.2^{\circ}$ $\mu = 0.09 \text{ mm}^{-1}$ T = 200 KPlate, clear colourless $0.60 \times 0.48 \times 0.20 \text{ mm}$

 $T_{\min} = 0.64, T_{\max} = 0.98$ 30170 measured reflections 1638 independent reflections 1337 reflections with $I > 2\sigma(I)$ $R_{int} = 0.064$ $\theta_{max} = 25.2^{\circ}, \theta_{min} = 2.8^{\circ}$ $h = -23 \rightarrow 23$ $k = -9 \rightarrow 9$ $I = -13 \rightarrow 13$

H atoms treated by a mixture of independent and constrained refinement $w = 1/[\sigma^2(F_o^2) + (0.0426P)^2 + 0.2144P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{max} < 0.001$ $\Delta\rho_{max} = 0.12$ e Å⁻³ $\Delta\rho_{min} = -0.12$ e Å⁻³ Extinction correction: SHELXL2014 (Sheldrick, 2015) Extinction coefficient: 0.036 (2)

Special details

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

	x	У	Ζ	$U_{ m iso}$ */ $U_{ m eq}$	
01	0.35377 (4)	0.51824 (13)	0.24544 (7)	0.0577 (3)	
H1C	0.3984 (9)	0.489 (2)	0.2143 (15)	0.094 (5)*	
O2	0.40648 (4)	0.59582 (12)	0.40443 (7)	0.0566 (3)	
N1	0.46617 (5)	0.40589 (14)	0.14608 (9)	0.0445 (3)	
H1A	0.4497 (7)	0.3912 (16)	0.0737 (13)	0.061 (4)*	
H1B	0.5014 (8)	0.4803 (19)	0.1440 (12)	0.060 (4)*	
C1	0.16309 (8)	0.6783 (2)	0.48889 (14)	0.0698 (4)	
H1	0.1204	0.7037	0.5196	0.084*	
C2	0.21951 (8)	0.71645 (18)	0.55063 (13)	0.0661 (4)	
H2	0.2156	0.7662	0.6244	0.079*	
C3	0.28164 (7)	0.68275 (16)	0.50592 (11)	0.0537 (4)	
Н3	0.3205	0.7097	0.5488	0.064*	
C4	0.28756 (6)	0.60956 (14)	0.39861 (10)	0.0421 (3)	
C5	0.35476 (6)	0.57469 (14)	0.35138 (10)	0.0425 (3)	
C6	0.16825 (7)	0.6037 (2)	0.38286 (14)	0.0668 (4)	
H6	0.1292	0.5757	0.341	0.08*	
C7	0.23038 (6)	0.56947 (16)	0.33734 (12)	0.0534 (3)	
H7	0.234	0.5184	0.2639	0.064*	
C8	0.48442 (7)	-0.05934 (19)	0.19776 (14)	0.0703 (4)	
H8	0.4736	-0.1642	0.1616	0.084*	
С9	0.46876 (6)	0.09306 (17)	0.14506 (11)	0.0544 (4)	
H9	0.4472	0.0922	0.0727	0.065*	
C10	0.48419 (5)	0.24690 (15)	0.19649 (10)	0.0403 (3)	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\hat{A}^2)

Atomic displacement parameters $(Å^2)$

U ²²	U^{33}	U^{12}	U^{13}	1/23
			÷	U
(5) 0.0887 (7)	0.0370 (5)	0.0157 (5)	-0.0043 (4)	-0.0083 (4)
(5) 0.0792 (6)	0.0470 (5)	0.0051 (4)	-0.0086 (4)	-0.0077 (4)
(6) 0.0623 (7)	0.0311 (6)	-0.0011 (5)	-0.0041 (4)	0.0016 (4)
(9) 0.0712 (9)	0.0815 (11)	0.0126 (7)	0.0262 (8)	0.0159 (8)
(10) 0.0680 (9)	0.0552 (9)	0.0142 (7)	0.0189 (7)	0.0008 (7)
(8) 0.0570 (7)	0.0452 (7)	0.0086 (6)	0.0016 (6)	-0.0003 (6)
(7) 0.0431 (6)	0.0387 (6)	0.0053 (5)	-0.0001 (5)	0.0060 (5)
(7) 0.0470 (6)	0.0350 (6)	0.0056 (5)	-0.0049 (5)	0.0033 (5)
(7) 0.0789 (10	0) 0.0793 (11)	-0.0010 (7)) 0.0007 (7)	0.0119 (8)
(7) 0.0624 (8)	0.0505 (8)	0.0002 (6)	-0.0025 (6)	0.0028 (6)
(9) 0.0578 (8)	0.0879 (11)	-0.0009 (7)	-0.0181 (8)	-0.0114 (7)
(7) 0.0673 (8)	0.0512 (8)	0.0002 (6)	-0.0078 (6)	-0.0111 (6)
(5) 0.0570 (7)	0.0352 (6)	0.0012 (5)	0.0019 (4)	-0.0005 (5)
	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	(5) $0.0887(7)$ $0.0370(5)$ (5) $0.0792(6)$ $0.0470(5)$ (6) $0.0623(7)$ $0.0311(6)$ (9) $0.0712(9)$ $0.0815(11)$ (10) $0.0680(9)$ $0.0552(9)$ (8) $0.0570(7)$ $0.0452(7)$ (7) $0.0431(6)$ $0.0387(6)$ (7) $0.0470(6)$ $0.0350(6)$ (7) $0.0789(10)$ $0.0793(11)$ (7) $0.0624(8)$ $0.0505(8)$ (9) $0.0578(8)$ $0.0879(11)$ (7) $0.0673(8)$ $0.0512(8)$ (5) $0.0570(7)$ $0.0352(6)$	(5) $0.0887(7)$ $0.0370(5)$ $0.0137(5)$ (5) $0.0792(6)$ $0.0470(5)$ $0.0051(4)$ (6) $0.0623(7)$ $0.0311(6)$ $-0.0011(5)$ (9) $0.0712(9)$ $0.0815(11)$ $0.0126(7)$ (10) $0.0680(9)$ $0.0552(9)$ $0.0142(7)$ (8) $0.0570(7)$ $0.0452(7)$ $0.0086(6)$ (7) $0.0431(6)$ $0.0387(6)$ $0.0053(5)$ (7) $0.0470(6)$ $0.0350(6)$ $0.0056(5)$ (7) $0.0789(10)$ $0.0793(11)$ $-0.0010(7)$ (7) $0.0624(8)$ $0.0879(11)$ $-0.0009(7)$ (7) $0.0673(8)$ $0.0512(8)$ $0.0002(6)$ (5) $0.0570(7)$ $0.0352(6)$ $0.0012(5)$	(5) $0.0887(7)$ $0.0370(5)$ $0.0157(5)$ $-0.0043(4)$ (5) $0.0792(6)$ $0.0470(5)$ $0.0051(4)$ $-0.0086(4)$ (6) $0.0623(7)$ $0.0311(6)$ $-0.0011(5)$ $-0.0041(4)$ (9) $0.0712(9)$ $0.0815(11)$ $0.0126(7)$ $0.0262(8)$ (10) $0.0680(9)$ $0.0552(9)$ $0.0142(7)$ $0.0189(7)$ (8) $0.0570(7)$ $0.0452(7)$ $0.0086(6)$ $0.0016(6)$ (7) $0.0431(6)$ $0.0387(6)$ $0.0053(5)$ $-0.0001(5)$ (7) $0.0470(6)$ $0.0350(6)$ $0.0056(5)$ $-0.0049(5)$ (7) $0.0624(8)$ $0.0505(8)$ $0.0002(6)$ $-0.0025(6)$ (9) $0.0578(8)$ $0.0879(11)$ $-0.0009(7)$ $-0.0181(8)$ (7) $0.0673(8)$ $0.0512(8)$ $0.0002(6)$ $-0.0078(6)$ (5) $0.0570(7)$ $0.0352(6)$ $0.0012(5)$ $0.0019(4)$

Geometric parameters (Å, °)

01	1.3153 (14)	С3—Н3	0.95
O1—H1C	0.994 (19)	C4—C7	1.3885 (17)

O2—C5	1.2201 (14)	C4—C5	1.4822 (16)
N1—C10	1.4262 (15)	C6—C7	1.3816 (19)
N1—H1A	0.916 (15)	С6—Н6	0.95
N1—H1B	0.916 (16)	С7—Н7	0.95
C1—C6	1.375 (2)	C8—C8 ⁱ	1.372 (3)
C1—C2	1.375 (2)	C8—C9	1.3814 (19)
C1—H1	0.95	С8—Н8	0.95
C2—C3	1.3771 (19)	C9—C10	1.3836 (17)
С2—Н2	0.95	С9—Н9	0.95
C3—C4	1.3848 (17)	C10-C10 ⁱ	1.403 (2)
C5—O1—H1C	114.1 (10)	O2—C5—C4	123.99 (11)
C10—N1—H1A	111.3 (8)	O1—C5—C4	113.52 (10)
C10—N1—H1B	111.9 (9)	C1—C6—C7	119.87 (14)
H1A—N1—H1B	109.5 (12)	С1—С6—Н6	120.1
C6—C1—C2	120.25 (13)	С7—С6—Н6	120.1
C6—C1—H1	119.9	C6—C7—C4	120.17 (13)
C2—C1—H1	119.9	С6—С7—Н7	119.9
C1—C2—C3	120.26 (13)	С4—С7—Н7	119.9
C1—C2—H2	119.9	C8 ⁱ —C8—C9	120.04 (8)
С3—С2—Н2	119.9	C8 ⁱ —C8—H8	120.0
C2—C3—C4	120.07 (13)	С9—С8—Н8	120.0
С2—С3—Н3	120.0	C8—C9—C10	120.69 (12)
С4—С3—Н3	120.0	С8—С9—Н9	119.7
C3—C4—C7	119.36 (11)	С10—С9—Н9	119.7
C3—C4—C5	119.48 (11)	C9-C10-C10 ⁱ	119.26 (7)
C7—C4—C5	121.16 (11)	C9—C10—N1	121.79 (11)
O2—C5—O1	122.49 (11)	C10 ⁱ —C10—N1	118.89 (6)
C6—C1—C2—C3	1.1 (2)	C2—C1—C6—C7	-1.1 (2)
C1—C2—C3—C4	-0.3 (2)	C1—C6—C7—C4	0.3 (2)
C2—C3—C4—C7	-0.53 (19)	C3—C4—C7—C6	0.52 (19)
C2—C3—C4—C5	179.74 (11)	C5—C4—C7—C6	-179.75 (11)
C3—C4—C5—O2	5.18 (18)	C8 ⁱ —C8—C9—C10	0.0 (3)
C7—C4—C5—O2	-174.54 (11)	C8-C9-C10-C10 ⁱ	-0.3 (2)
C3—C4—C5—O1	-174.73 (11)	C8—C9—C10—N1	-177.43 (12)
C7—C4—C5—O1	5.54 (16)		

Symmetry code: (i) -x+1, y, -z+1/2.

Hydrogen-bond geometry (Å, °)

Cg(bda) refers to the ring centroid of the benzene-1,2-diamine.

<i>D</i> —H··· <i>A</i>	D—H	Н…А	D····A	<i>D</i> —H··· <i>A</i>
01—H1C…N1	0.994 (19)	1.706 (19)	2.6852 (13)	167.8 (16)
N1—H1A····O2 ⁱⁱ	0.916 (15)	2.163 (16)	3.0681 (14)	169.8 (12)

N1—H1 <i>B</i> ···O2 ⁱ	0.916 (16)	2.136 (16)	3.0160 (14)	160.8 (12)
C6—H6··· $Cg(bda)^{iii}$	0.95	2.81	3.7163 (16)	161

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