

A new polymorph of benzene-1,2-diamine: isomorphism with 2-aminophenol and two-dimensional isostructurality of polymorphs

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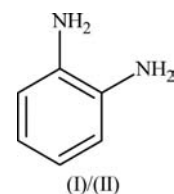
A new crystalline form of benzene-1,2-diamine, $C_6H_8N_2$, crystallizing in the space group $Pbca$, has been identified during screening for cocrystals. The crystals are constructed from molecular bilayers parallel to (001) that have the polar amino groups directed to the inside and the aromatic groups, showing a herringbone arrangement, directed to the outside. The known monoclinic form and the new orthorhombic polymorph exhibit two-dimensional isostructurality as the crystals consist of nearly identical bilayers. In the monoclinic form, neighbouring bilayers are generated by a unit translation along the a axis, whereas in the orthorhombic form they are generated by a c -glide. Moreover, the new form of benzene-1,2-diamine is essentially isomorphous with the only known form of 2-aminophenol.

Comment

Increased interest in cocrystals has resulted in several recent reports of the serendipitous formation of a new polymorph by one of the substrates during attempted cocrystallization experiments (Callear & Hursthouse, 2009; Dey *et al.*, 2006; Rafilovich & Bernstein, 2006; Wenger & Bernstein, 2007), with the most famous case represented by a new polymorph of aspirin (Vishweshwar *et al.*, 2005; Bond *et al.*, 2007). Our attempts to prepare new cocrystals have already resulted in obtaining the elusive β form of phenazine (Herbstein & Schmidt, 1955; Jankowski & Gdaniec, 2002) and the hydrated form of benzene-1,4-diamine (Czapiak *et al.*, 2010). Crystal structures of all three benzenediamine isomers are known (Betz *et al.*, 2008; Poveteva *et al.*, 1975; Stalhandske, 1981) and polymorphism has not been observed for any of these compounds so far. Recently, we have shown that unstable benzene-1,4-diamine dihydrate converts on dehydration to its known anhydrous form (Czapiak *et al.*, 2010). Polymorphism and hydrate formation are rather exceptional among aromatic amines, as shown by our survey of the Cambridge Structural

Database (CSD, Version 5.31; Allen, 2002), which gave 48 structures of aromatic amines of the general formula $[C_nH_m(NH_2)_x]$ with at least one primary amino group attached to the aromatic ring and with only C and H atoms in the remaining part of the molecule. Among these amines only benzidine has been shown to exhibit polymorphism, with four polymorphic forms characterized so far (Rafilovich & Bernstein, 2006). Another aspect that emerged from this CSD search was the unusually high percentage of structures with $Z' \neq 1$. Out of the 48 structures analysed, 15 had $Z' > 1$, 21 had $Z' = 1$ and 12 had $Z' < 1$.

In this paper, we report the crystal structure of a new polymorph, (II), of benzene-1,2-diamine with $Z' = 1$, produced unexpectedly during an attempt to synthesize cocrystals of phenazine with benzene-1,2-diamine. This new form was obtained from a 1:1 mixture of the above two components dissolved in methanol–diethyl ether (1:1 *v/v*). Slow evaporation of the solution resulted in the precipitation of two types of crystals, yellow needles (subsequently identified as the 2:1 phenazine–benzene-1,2-diamine complex) and a pale-pink tabloid crystal which has been shown to be a new orthorhombic form, (II), of benzene-1,2-diamine. The known form, (I), of benzene-1,2-diamine is monoclinic in the space group $P2_1/c$ and crystallizes with one molecule in the asymmetric unit (CSD refcode BAGFIY; Stalhandske, 1981).



The molecular structure of (II), together with the atom-numbering scheme, is shown in Fig. 1. In the two polymorphs, the molecules have very similar geometries and exhibit noncrystallographic C_2 symmetry, with both amino N atoms sp^3 hybridized and one of the N–H bonds of each NH_2 group virtually in the plane of the benzene ring, resulting in two short intramolecular $H \cdots N$ contacts between the *ortho* amino substituents, which in (II) are 2.507 (14) and 2.536 (14) Å. The C–N bond lengths of 1.4004 (16) and 1.4047 (15) Å are

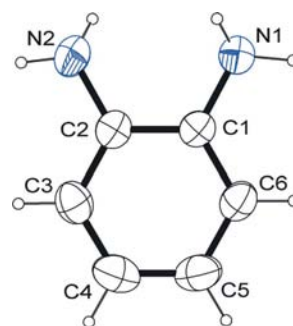
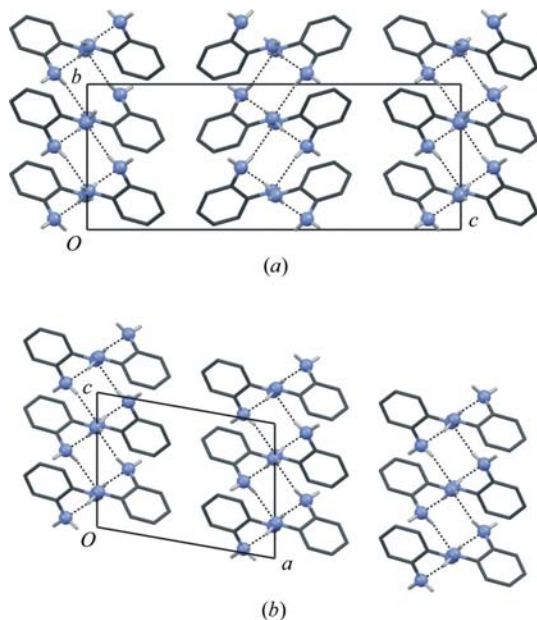


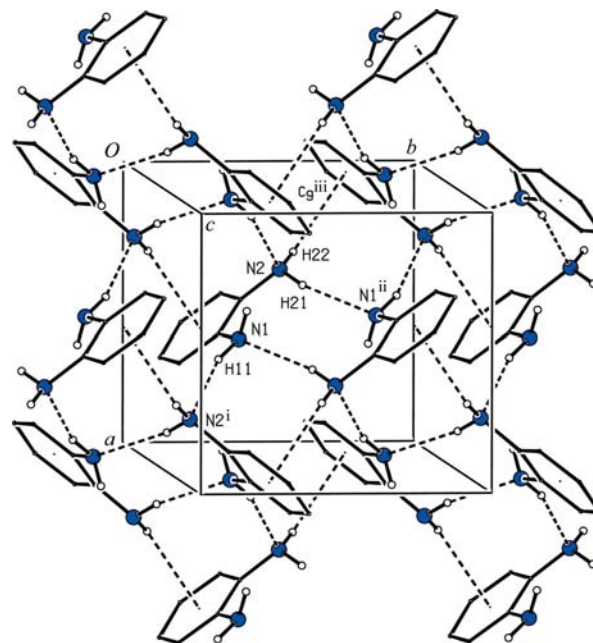
Figure 1
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 2**

Two-dimensional isostructurality among polymorphs of benzene-1,2-diamine, showing (a) the crystal packing in polymorph (II), viewed down the a axis, and (b) the crystal packing in polymorph (I), viewed down the b axis. Hydrogen bonds are shown as dotted lines.

consistent with the N-atom hybridization state, and the endocyclic bond angles at C1 and C2, both smaller than 120° , are consistent with the electron-donating character of the amine groups (Domenicano *et al.*, 1975).

A projection of the crystal structure of (II) along the a axis is shown in Fig. 2(a). This crystal structure can be seen as constructed from bilayers (centred at $z = 0, \frac{1}{2}, 1.0, \text{etc.}$) that are parallel to (001) and have the polar amino groups directed to the inside and the aromatic groups, which have a herringbone arrangement, directed to the outside. The amino groups, each acting as a single donor and a single acceptor, are involved in two weak intermolecular N—H...N hydrogen bonds (Table 1 and Fig. 3) operating between monolayers. Additionally, one of the amino groups forms an N2—H22... π interaction [$\text{H22}\cdots\text{Cg}^{\text{iii}} = 2.585(15) \text{ \AA}$ and $\text{N2—H22}\cdots\text{Cg}^{\text{iii}} = 140.7(12)^\circ$, where Cg is the centroid of the aromatic ring; symmetry code: (iii) $\frac{1}{2} - x, \frac{1}{2} + y, z$] with the aromatic ring of the b -glide-related molecule within the same monolayer (Fig. 3). A closer look at the structure of form (I) (Stalhandske, 1981; Fig. 2b) reveals that the two polymorphs of benzene-1,2-diamine exhibit two-dimensional isostructurality (Fábíán & Kálmán, 2004) because they are constructed from virtually identical bilayers with similar metric parameters [$b = 7.544(1) \text{ \AA}$, $c = 7.716(1) \text{ \AA}$ and $\alpha = 90^\circ$ in (I), and $a = 7.533(2) \text{ \AA}$, $b = 7.835(2) \text{ \AA}$ and $\gamma = 90^\circ$ in (II)] and the same layer group symmetry [$p12_1/c1$ in (I) and $p2_1/b11$ in (II)]. The two polymorphs differ in the stacking arrangement of the bilayers: in form (I), neighbouring bilayers are generated by a unit translation along the a axis, whereas in form (II) they are generated by a c -glide. In both crystalline forms, the interactions between the bilayer surface atoms are only of the van der Waals type, with all interlayer contacts

**Figure 3**

The structure of the (001) layer in (II), centred around $z = \frac{1}{2}$. Hydrogen bonds and N—H... π interactions are shown as dotted lines. For symmetry codes, see the *Comment* and Table 1.

being longer than the sum of the van der Waals radii of the appropriate atoms.

The melting temperatures measured for both polymorphs using a Boetius apparatus were 368–370 K for (I) (reference value 375.5 K; *CRC Handbook of Chemistry and Physics*, 1998) and 366–368 K for (II), and no phase changes were observed under a polarizing microscope when the crystals were heated from room temperature to the melting point. Interestingly, the two forms also have very similar volumes for a single diamine molecule [147.9 and 148.3 \AA^3 for (I) and (II), respectively] and thus also similar crystal densities, 1.214 and 1.211 Mg m^{-3} for forms (I) and (II), respectively. However, simulated powder diffractograms show that the two forms can be easily discerned from their diffraction patterns (Fig. 4)

Since one (N1—H12) of the N—H groups in (II) is not involved in any specific intermolecular interactions, we decided to check whether the monohydroxy congener of benzene-1,2-diamine, *viz.* 2-aminophenol, formed a similar structure. Aminophenols have been extensively studied (Allen *et al.*, 1997; Dey *et al.*, 2005, 2006) in the context of the saturated hydrogen-bond principle introduced by Ermer & Eling (1994) and in relation to crystal structure prediction using the supramolecular synthon approach. Indeed, the structure for form (II) reported here for benzene-1,2-diamine is essentially isomorphous with the only known orthorhombic form of 2-aminophenol (refcode AMPHOM10: Ashfaquzzaman & Pant, 1979; refcode AMPHOM02: Korp *et al.*, 1981; refcode AMPHOM03: Allen *et al.*, 1997) and very similar in structure to 2-amino-4-methylphenol (Kashino *et al.*, 1988; Dey *et al.*, 2005), which has its unit-cell c parameter elongated by *ca* 2.8 \AA compared with (II) due to the presence of methyl

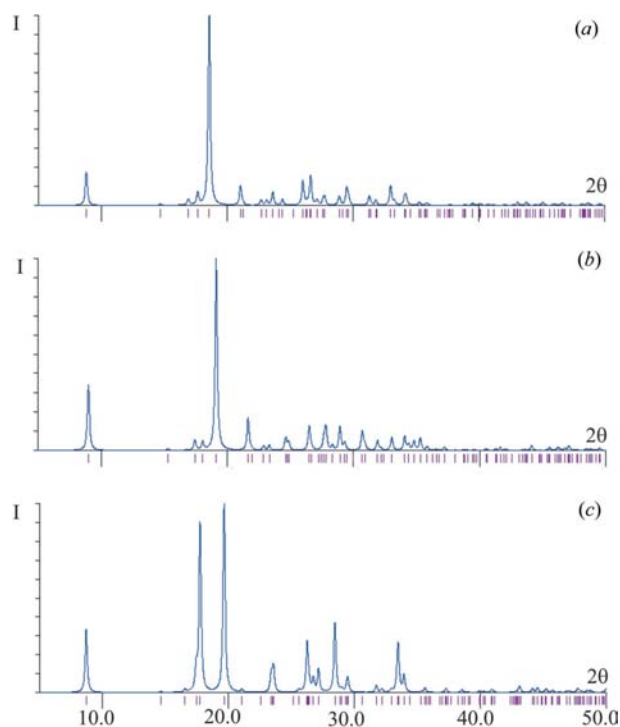


Figure 4
Simulated diffraction patterns for (a) (II), (b) aminophenol and (c) (I).

substituents on the bilayer surface. Moreover, the monoclinic polymorph, (I), closely resembles, in a similar manner, the structure of the monoclinic compounds 2-amino-4-chlorophenol (Ashfaquzzaman & Pant, 1979) and 2-amino-4-ethylphenol (Dey *et al.*, 2006). These examples show that *ortho*-aminophenols and aromatic *ortho*-diamines show extensive similarities in their crystal packing. However, these similarities do not extend to the *meta* and *para* isomers of these compounds.

Experimental

Polymorph (II) of benzene-1,2-diamine was formed during cocrystallization in a 1:1 molar ratio of benzene-1,2-diamine (6 mg) and phenazine (10 mg). The two components were dissolved in a methanol–diethyl ether (6 ml, 1:1 *v/v*) solvent mixture and the solution was evaporated slowly. As only one relatively large crystal of form (II) ($2 \times 1 \times 0.5$ mm) was found in the crystallization vial, it was cut into small pieces, one of which was used for structure determination. Unfortunately, our attempts to produce more crystals of form (II) by repeating the crystallization conditions were unsuccessful. Crystallization of benzene-1,2-diamine carried out under a wide range of different sets of conditions (different solvents, different co-solute molecules) led systematically to polymorph (I).

Crystal data

$C_6H_8N_2$	$V = 1186.2$ (4) \AA^3
$M_r = 108.14$	$Z = 8$
Orthorhombic, <i>Pbca</i>	Mo $K\alpha$ radiation
$a = 7.5330$ (17) \AA	$\mu = 0.08$ mm^{-1}
$b = 7.8350$ (15) \AA	$T = 293$ K
$c = 20.098$ (4) \AA	$0.5 \times 0.25 \times 0.1$ mm

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H11 \cdots N2^i$	0.944 (14)	2.207 (14)	3.1250 (16)	163.8 (11)
$N2-H21 \cdots N1^{ii}$	0.893 (15)	2.365 (15)	3.2404 (16)	166.6 (13)

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

Data collection

Oxford XcaliburE CCD area-detector diffractometer	6421 measured reflections
Absorption correction: multi-scan (<i>CrysAlis Pro</i> ; Oxford Diffraction, 2009)	1204 independent reflections
	817 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$
$T_{\text{min}} = 0.776, T_{\text{max}} = 1.000$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.088$	
$S = 0.94$	
1204 reflections	$\Delta\rho_{\text{max}} = 0.11$ e \AA^{-3}
89 parameters	$\Delta\rho_{\text{min}} = -0.20$ e \AA^{-3}

All H atoms were identified in difference Fourier maps, but for refinement all C-bound H atoms were placed in calculated positions, with $C-H = 0.93$ \AA , and refined as riding on their carrier atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. All N-bound H atoms were freely refined (coordinates and isotropic displacement parameters), giving N–H distances in the range 0.855 (14)–0.944 (14) \AA .

Data collection: *CrysAlis Pro* (Oxford Diffraction, 2009); cell refinement: *CrysAlis Pro*; data reduction: *CrysAlis Pro*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3158). Services for accessing these data are described at the back of the journal.

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