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Phenazine–2,6-dihydroxybenzoic acid (1/1)

Maria Gdaniec[a]* and Tadeusz Połoński[b]

[a]Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland, and [b]Department of Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland

Correspondence e-mail: magdan@amu.edu.pl

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Key indicators

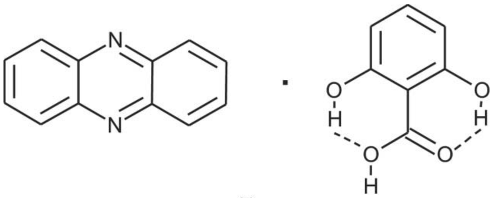
Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.048
wR factor = 0.112
Data-to-parameter ratio = 11.2

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

In the 1:1 cocrystal of phenazine with 2,6-dihydroxybenzoic acid, $C_{12}H_8N_2 \cdot C_7H_6O_4$, the two symmetry-independent molecules of phenazine are located on inversion centres. The carboxyl group of the acid assumes the *syn* conformation. One of the phenazine molecules is connected to two acid molecules *via* strong O—H⋯N interactions, forming a discrete hydrogen-bonded assembly. The phenazine molecules are arranged into infinite columns by π–π stacking interactions, and the carboxylic acid molecules, which are strongly tilted relative to the heterocyclic molecules, occupy channels formed between these columns.

Comment

Phenazine (Phz) has been used extensively as a reagent in supramolecular synthesis (Batchelor *et al.*, 2000; Gdaniec *et al.*, 2005; Kutasi *et al.*, 2002; Munakata *et al.*, 1994; Pedireddi *et al.*, 1996; Thalladi, Smolka, Boese & Sustmann, 2000; Thalladi, Smolka, Gehrke *et al.*, 2000; Tomura & Yamashita, 2000). Thalladi, Smolka, Boese & Sustmann (2000) have shown that Phz forms cocrystals with some biphenols where the Phz molecules, arranged into stacks, form a robust host framework with one-dimensional channels filled by the phenolic molecules. The molecules in the channels and the Phz molecules are nearly perpendicular. In turn, carboxylic acids generally bind to Phz *via* O—H⋯N and C—H⋯N hydrogen bonds, generating an $R_2^2(8)$ motif (Bernstein *et al.*, 1995) which leads to a nearly coplanar arrangement of the heterocyclic ring and the carboxylic acid group.



(I)

In the course of our studies of the cocrystals of aza-aromatic compounds (Gdaniec *et al.*, 2005; Kadzewski & Gdaniec, 2006), we have prepared cocrystals, (I), of Phz with 2,6-dihydroxybenzoic acid (DHB), with the aim of checking whether the molecular organization in these cocrystals resembles that of Phz molecular complexes with phenols or that observed in complexes with carboxylic acids. Depending on the system of intramolecular hydrogen bonds within the molecule of DHB, which is related to the *syn* or *anti* form adopted by the carboxylic acid group, it can bind to hydrogen-

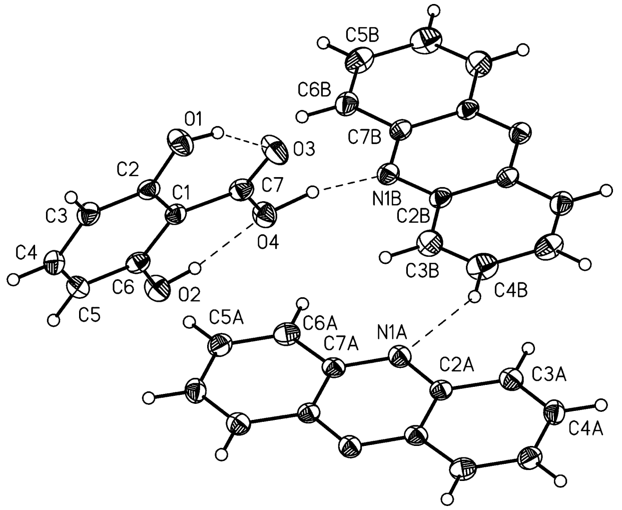


Figure 1
The molecular structure of (I), with displacement ellipsoids shown at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x+\frac{3}{2}, -y+\frac{3}{2}, -z+1)$ for Phz molecule A and by the symmetry operator $(-x+\frac{1}{2}, -y+\frac{3}{2}, -z+1)$ for Phz molecule B. Hydrogen bonds are shown as dashed lines.

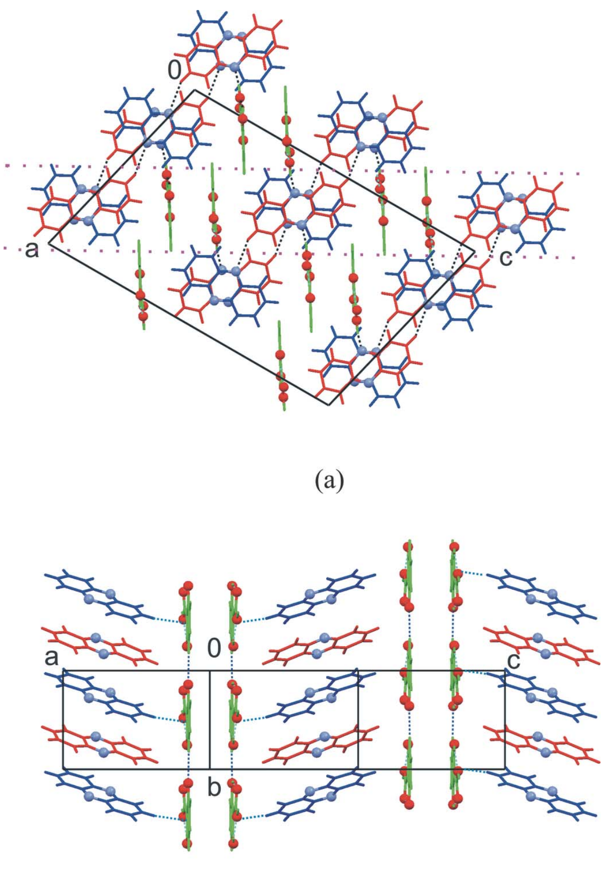
bond accepting molecules by either its phenolic or carboxylic H atom.

Phz and DHB cocrystallize in a 1:1 ratio, with two symmetry-independent heterocyclic molecules, *A* and *B*, located on inversion centres (Fig. 1). The DHB molecule, which is in the *syn* form, binds *via* an O—H···N interaction (Table 2) to heterobase *B*, forming discrete hydrogen-bonded assemblies composed of two DHB molecules and one Phz *B* molecule. The acid molecule forms a dihedral angle of 73.8 (1)° with the mean plane of the Phz *B* molecule, and therefore there is no C—H···O interaction between the carboxylic acid group and the heterocycle that would generate an $R_2^2(8)$ hydrogen-bond motif.

The Phz molecules *A* and *B*, which are nearly parallel, are arranged into irregular columns by π–π stacking interactions of the aromatic ring systems. There is a weak C4*B*—H4*B*···N1*A* interaction between Phz molecules in neighbouring stacks. The DHB molecules occupy channels formed between the Phz stacks (Fig. 2*a*). These channels, which are parallel to the *b* axis, are larger than in the complexes of Phz with biphenols (Thalladi, Smolka, Boese & Sustmann, 2000), since they accommodate two rows of translation-related acid molecules, with π–π stacking interactions formed between DHB molecules in neighbouring rows. A layer substructure parallel to $(10\overline{1})$, in which the interactions between the aromatic rings of the component molecules predominate, is shown in Fig. 2(*b*). Analogous substructures are a typical feature of many Phz cocrystals (Thalladi, Smolka, Boese & Sustmann, 2000; Gdaniec *et al.*, 2005).

Experimental

Compound (I) was obtained by slow evaporation of an ethanolic solution containing phenazine and 2,6-dihydroxybenzoic acid monohydrate in a 1:1 molar ratio.



(a)

(b)

Figure 2
The crystal structure of (I). (*a*) The packing of the molecules viewed down the *b* axis, with the shortest H···N and H···O contacts shown as dashed lines. (*b*) The arrangement of the molecules within the $(10\overline{1})$ layer [the layer indicated between dotted lines in part (*a*)].

Crystal data

$C_{12}H_8N_2\cdot C_7H_6O_4$
$M_r = 334.32$
Monoclinic, $C2/c$
$a = 16.5921$ (18) Å
$b = 7.4480$ (7) Å
$c = 25.297$ (2) Å
$\beta = 103.57$ (2)°
$V = 3038.9$ (6) Å^3
$Z = 8$
$D_x = 1.461$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 100$ (2) K
Block, yellow
0.15 × 0.12 × 0.09 mm

Data collection

Kuma KM4 κ-geometry CCD area-detector diffractometer
ω scans
Absorption correction: none
7257 measured reflections
2667 independent reflections
1876 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.113$
$S = 1.06$
2667 reflections
238 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0534P)^2 + 1.0575P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*O*···O4	0.89 (3)	1.86 (3)	2.616 (2)	141 (3)
O1—H1*O*···O3	0.91 (3)	1.73 (3)	2.568 (2)	152 (3)
O4—H4*O*···N1*B*	1.09 (3)	1.60 (3)	2.674 (2)	168 (3)
C4*B*—H4*B*···N1*A*	0.95	2.74	3.626 (3)	155
C3*A*—H3*A*···O3$^{\rm i}$	0.95	2.46	3.070 (3)	122
C3*A*—H3*A*···O2$^{\rm ii}$	0.95	2.64	3.206 (3)	119
C5—H5···O1$^{\rm iii}$	0.95	2.53	3.401 (3)	152
C5*B*—H5*B*···O2$^{\rm iv}$	0.95	2.68	3.300 (3)	124

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

All H atoms were located in electron-density difference maps. The H atoms of the OH groups were freely refined (bond lengths are in Table 1). H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.95 Å, and were refined as riding on their parent atoms, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *Mercury* (Version 1.4; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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