

Hydrogen-bonded one-dimensional networks in 1:1 complexes of *N,N'*-bis(2-pyridyl)aryldiamines with anilic acid

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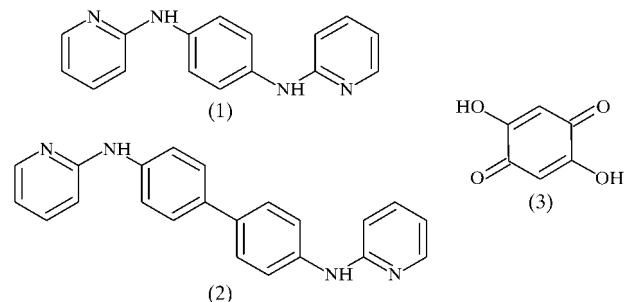
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The 1:1 complexes *N,N'*-bis(2-pyridyl)benzene-1,4-diamine–anilic acid (2,5-dihydroxy-1,4-benzoquinone) (1/1), C₁₆H₁₄N₄·C₆H₄O₄, (I), and *N,N'*-bis(2-pyridyl)biphenyl-4,4'-diamine–anilic acid (1/1), C₂₂H₁₈N₄·C₆H₄O₄, (II), have been prepared and their solid-state structures investigated. The component molecules of these complexes are connected *via* conventional N–H···O and O–H···N hydrogen bonds, leading to the formation of an infinite one-dimensional network generated by the cyclic motif $R_2^2(9)$. The anilic acid molecules in both crystal structures lie around inversion centres and the observed bond lengths are typical for the neutral molecule. Nevertheless, the pyridine C–N–C angles [120.9 (2) and 120.13 (17)° for complexes (I) and (II), respectively] point to a partial H-atom transfer from anilic acid to the bispyridylamine, and hence to H-atom disorder in the OHN bridge. The bispyridylamine molecules of (I) and (II) also lie around inversion centres and exhibit disorder of their central phenyl rings over two positions.

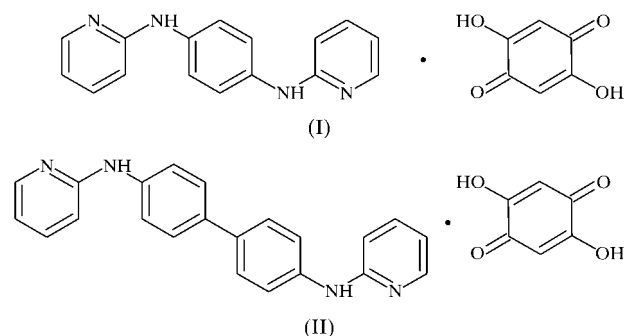
Comment

N,N'-Bis(2-pyridyl)aryldiamines (Bensemann *et al.*, 2002), bearing two H-atom-donor and two H-atom-acceptor sites, can be used as versatile substrates in the synthesis of extended supramolecular arrays, as we have shown recently (Bensemann *et al.*, 2003). For example, cocrystallization of these compounds with dicarboxylic acids or with squaric acid yields 1:1 complexes of predictable structures, involving infinite chains of alternating components joined by the cyclic hydrogen-bond motifs $R_2^2(8)$ and $R_2^2(9)$, respectively [for graph-set notation, see Etter (1990) and Bernstein *et al.* (1995)]. In addition, further assembly of these one-dimensional networks into two-dimensional structures *via* weaker C–H···O and C–H··· π interactions occurs in a predictable way, since the infinite acid–base chains are always related by a characteristic unit translation of *ca* 9 Å, forming densely packed layers (Bensemann *et al.*, 2003).

Anilic acid, (3), being a weak dibasic acid structurally related to squaric acid (Karle *et al.*, 1996), has frequently been used in the preparation of transition metal coordination polymers [for a review, see Kitagawa & Kawata (2002)], and only recently has found broader application as a potential structural element in the construction of organic supramolecular networks (Zaman *et al.*, 2001, and references therein; Cowan, Howard & Leech, 2001; Cowan, Howard *et al.* 2001).



We expected that the 2-aminopyridine moiety should be capable of forming cyclic $R_2^2(9)$ hydrogen-bond motifs with the α -hydroxycarbonyl functions of (3), which may generate well defined extended one-dimensional supramolecular frameworks. Indeed, cocrystallization of equimolar amounts of either *N,N'*-bis(2-pyridyl)benzene-1,4-diamine, (1), or *N,N'*-bis(2-pyridyl)biphenyl-4,4'-diamine, (2), with (3) from acetonitrile gave the 1:1 complexes (I) and (II), respectively, the crystals of which were suitable for X-ray analysis. The structures of these two 1:1 complexes are presented here.



As expected, the bispyridylamines and (3) in complexes (I) and (II) are assembled into infinite one-dimensional networks analogous to those observed earlier in the squaric acid complex of (1) (Bensemann *et al.*, 2003). The component molecules alternating along the chain are connected *via* hydrogen bonds to form heterodimeric $R_2^2(9)$ motifs. The hydrogen-bonded 2-aminopyridine moieties and the molecules of (3) are nearly coplanar, as shown by the corresponding dihedral angles of 7.0 (2) and 6.5 (1)° for (I) and (II), respectively. Diagrams of the one-dimensional networks and the atom-labelling schemes in (I) and (II) are shown in Figs. 1 and 2, respectively. The asymmetric units of (I) and (II) contain one half-molecule of bispyridylamine and one half-molecule of (3). All molecules are situated around inversion centres.

The molecule of (3) in both complexes exhibits a pronounced quinoid character, with a bond-length pattern (Tables 1 and 3) similar to that observed for the neutral molecule (Cowan, Howard & Leech, 2001; Jene *et al.*, 2001; Semmingsen, 1977). Nevertheless, we observe a systematic shortening of the C—O bonds to the hydroxyl groups [1.292 (2) and 1.307 (2) Å in (I) and (II), respectively] and partial C2A—C3A double bonds [1.410 (3) and 1.422 (3) Å in (I) and (II), respectively] compared with the neutral molecule of (3), with C—O and C—C bond lengths falling in the ranges 1.328–1.333 and 1.438–1.450 Å, respectively (Cowan, Howard & Leech, 2001; Jene *et al.*, 2001; Semmingsen, 1977).

The above geometric parameters point either to a strong polarization of the O—H bond of (3) or to a partial deprotonation of (3), with the H atom transferred from the hydroxy group to the pyridine N atom (Tables 2 and 4). This is supported by the values of the pyridine C—N—C angles [120.9 (2) and 120.13 (17)° in (I) and (II), respectively], which indicate that the pyridine moiety is in a state intermediate between neutral and fully protonated (Cowan, Howard & Leech, 2001; Dega-Szafran *et al.*, 1992).

Because the electron-density difference map showed a broad peak with an unequal intensity double maximum close to the middle of the O—N vector, H-atom disorder in the

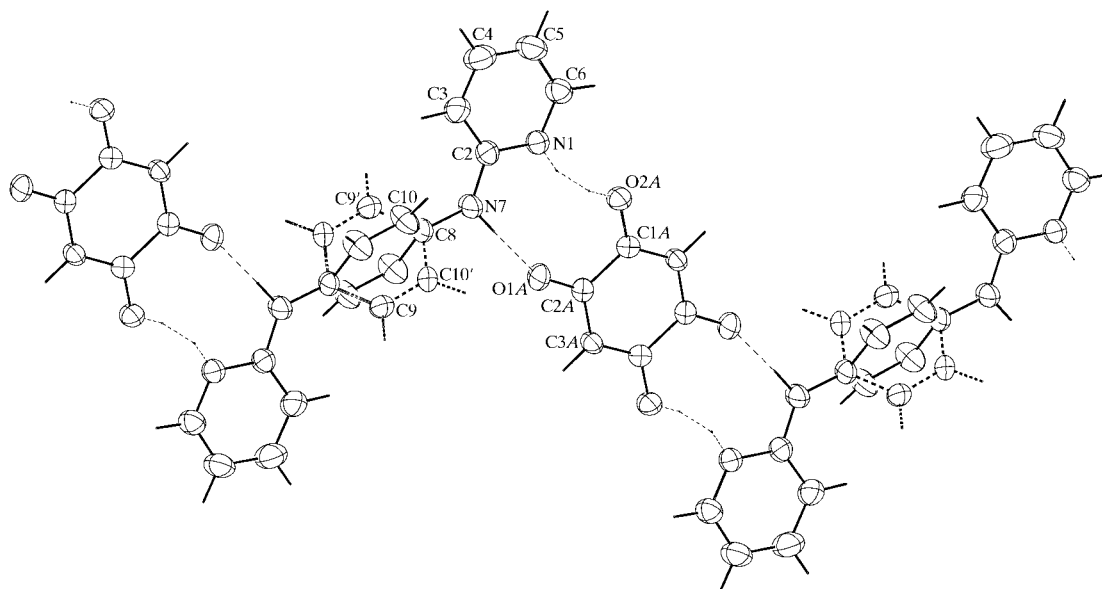


Figure 1
A view of the hydrogen-bonded one-dimensional network in (I), shown with 50% probability displacement ellipsoids.

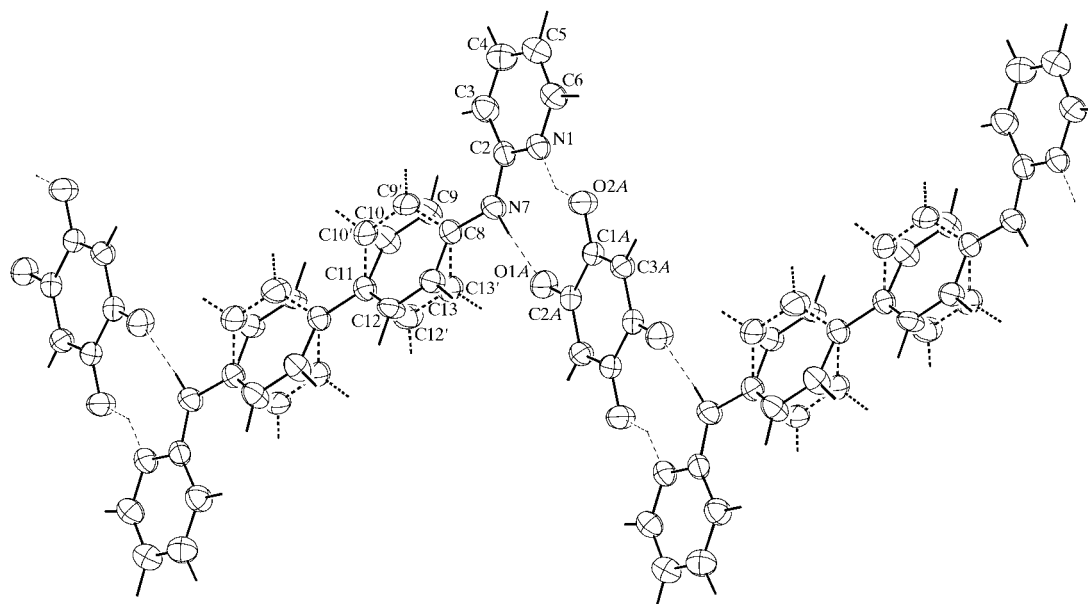


Figure 2
A view of the hydrogen-bonded one-dimensional network in (II), shown with 50% probability displacement ellipsoids.

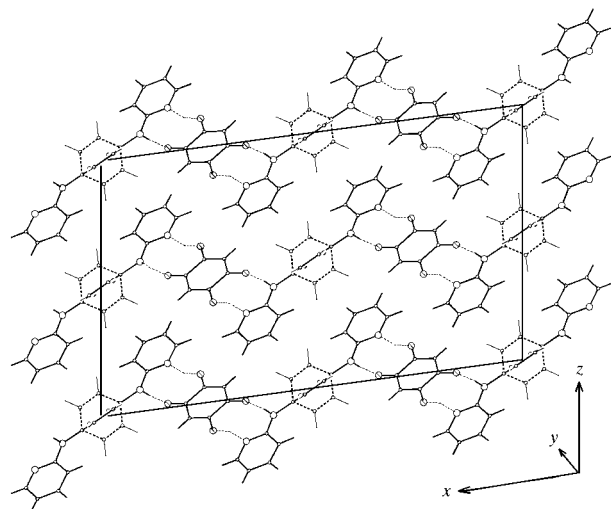


Figure 3
A projection of the crystal packing of (I) along the y axis.

NHO bridge was assumed. However, subsequent refinement of the occupancy factors for the two H-atom positions in the NHO bridge gave equal occupancies for the two positions, indicating that, in complexes (I) and (II), the molecule of (3) exists as a monoanion.

The hydrogen-bonded one-dimensional networks in (I) run in two directions, *viz.* $[120]$ and $[\bar{1}20]$. They are arranged into layers parallel to (001) by forming stacks along the y axis (translation parameter 5.03 Å). No close-packed chains of (1), analogous to those observed in the 1:1 complexes of (1) with dicarboxylic acids, were found here.

The central phenyl ring of the bispyridylamine molecule in (I) is disordered over two perpendicular orientations related by rotation around the $C8 \cdots C8'$ vector. The phenyl ring is twisted relative to the aminopyridine unit about the $C-N$ bond, by -43.2 (4)° for the primed orientation and 50.0 (4)° for the unprimed one. As can be seen from Fig. 3, the phenyl ring is parallel to the y axis in one orientation and nearly

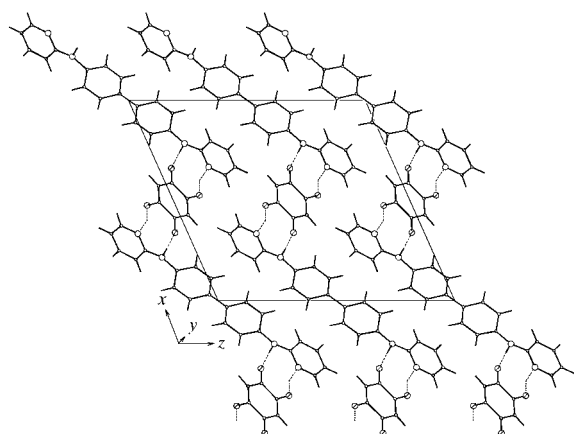


Figure 4
A projection of the crystal packing of (II) along the y axis.

perpendicular to it in the other. The observed disorder can be explained if we assume that adjacent phenyl rings packed along the y axis are mutually perpendicular, which actually means that a single stack is ordered. However, there are two types of stacks, one with a primed ring located around the inversion centre at $y = 0$ and the other with the primed ring at $y = \frac{1}{2}$. We observe superposition of these two stacks due to their random distribution in the crystal.

The one-dimensional networks in complex (II) run in the $[210]$ and $[2\bar{1}0]$ directions and, as in (I), they stack along the y axis (translation parameter 5.08 Å) and form layers parallel to (001) (Fig. 4).

The biphenyl unit of (II), with the phenyl rings found in two positions and forming a dihedral angle of 36.5 (7)°, is disordered. Because a centrosymmetric biphenyl fragment has to be planar, the observed disorder reflects one of two possible situations: superposition of two flat but differently oriented biphenyl units or, more probably, superposition of two oppositely twisted biphenyl fragments. The hydrogen-bonded one-dimensional networks adjacent to the $[001]$ direction show edge-to-face aromatic–aromatic interactions between the phenyl and pyridine rings.

Experimental

N,N'-Bis(2-pyridyl)aryldiamines (1) and (2) were prepared according to Bensemann *et al.* (2002). Complex (I) was prepared by dissolving (1) and anilic acid, (3), in an equimolar ratio in boiling acetonitrile and allowing the solution to crystallize slowly at room temperature. In the case of (II), a hot solution of (3) in acetonitrile was added to (2) dissolved in a small amount of *N,N*-dimethylformamide and the resulting mixture allowed to stand at room temperature.

Compound (I)

Crystal data

$C_{16}H_{14}N_4 \cdot C_6H_4O_4$
 $M_r = 402.40$
Monoclinic, $C2/c$
 $a = 25.166$ (3) Å
 $b = 5.0290$ (5) Å
 $c = 15.1590$ (16) Å
 $\beta = 97.648$ (9)°
 $V = 1901.5$ (4) Å³
 $Z = 4$

$D_x = 1.406$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 2140 reflections
 $\theta = 4-25^\circ$
 $\mu = 0.10$ mm⁻¹
 $T = 296$ (2) K
Plate, colourless
 $0.20 \times 0.10 \times 0.02$ mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
 ω scans
4700 measured reflections
1665 independent reflections
909 reflections with $I > 2\sigma(I)$

$R_{int} = 0.043$
 $\theta_{max} = 25.0^\circ$
 $h = -29 \rightarrow 29$
 $k = -5 \rightarrow 5$
 $l = -15 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.088$
 $S = 0.94$
1665 reflections
160 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0338P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.13$ e Å⁻³
 $\Delta\rho_{min} = -0.13$ e Å⁻³
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0034 (5)

Table 1
Selected geometric parameters (Å, °) for (I).

O1A—C2A	1.247 (2)	C1A—C2A	1.521 (3)
O2A—C1A	1.292 (2)	C2A—C3A	1.410 (3)
C1A—C3A ¹	1.359 (3)		
C6—N1—C2	120.9 (2)		
C3—C2—N7—C8	−6.0 (4)	C2—N7—C8—C9 ¹	50.0 (4)
C2—N7—C8—C10	−43.2 (4)		

Symmetry code: (i) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H...A	D—H	H...A	D...A	D—H...A
O2A—H2O...N1	0.85	1.86	2.650 (3)	154
N1—H1...O2A	0.90	1.83	2.650 (3)	151
N7—H7...O1A	0.90	1.86	2.756 (3)	172

Compound (II)

Crystal data

C ₂₂ H ₁₈ N ₄ ·C ₆ H ₄ O ₄	$D_x = 1.442 \text{ Mg m}^{-3}$
$M_r = 478.50$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 2223 reflections
$a = 14.8368 (18) \text{ \AA}$	$\theta = 4-25^\circ$
$b = 5.0801 (6) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 16.0207 (16) \text{ \AA}$	$T = 294 (2) \text{ K}$
$\beta = 114.106 (11)^\circ$	Plate, colourless
$V = 1102.2 (2) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.02 \text{ mm}$
$Z = 2$	

Data collection

Kuma KM-4 CCD area-detector diffractometer	$R_{\text{int}} = 0.024$
ω scans	$\theta_{\text{max}} = 25^\circ$
5270 measured reflections	$h = -17 \rightarrow 17$
1919 independent reflections	$k = -4 \rightarrow 6$
1195 reflections with $I > 2\sigma(I)$	$l = -18 \rightarrow 19$

Table 3
Selected geometric parameters (Å, °) for (II).

C1A—O2A	1.307 (2)	C2A—O1A	1.240 (2)
C1A—C3A ¹	1.355 (2)	C2A—C3A	1.422 (2)
C1A—C2A	1.507 (2)		
C6—N1—C2	120.13 (17)		
C3—C2—N7—C8	−21.3 (3)	C2—N7—C8—C9 ¹	−2.4 (8)
C2—N7—C8—C9	40.7 (5)		

Symmetry code: (i) $1 - x, -y, 1 - z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H...A	D—H	H...A	D...A	D—H...A
O2A—H2O...N1	0.85	1.91	2.687 (2)	150
N1—H1...O2A	0.90	1.88	2.687 (2)	148
N7—H7...O1A	0.90	1.99	2.891 (2)	176

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0597P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.93$	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
1919 reflections	$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$
204 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.007 (2)

In both complexes, the central aryl moieties of the bispyridylamine molecules are disordered over two positions. During refinement, the sum of the occupancy factors for the two orientations was kept fixed at 1.0, and the occupancy factors for the primed orientations refined to 0.493 (4) and 0.453 (11) for (I) and (II), respectively. No restraints were imposed on the geometry of the phenyl rings during refinement. All H atoms were located in electron-density difference maps. The H atom in the N1...H...O2A bridge appeared as a broad peak and disorder over two positions was assumed. Atoms H1 and H2O were placed in calculated positions (N—H = 0.90 Å and O—H = 0.85 Å) and were refined as riding, with a common isotropic displacement parameter. The sum of their occupancy factors was kept fixed at 1.0 and the occupancy factors for H2O refined to 0.51 (4) [$U_{\text{iso}} = 0.044 (6) \text{ \AA}^2$] and 0.49 (3) [$U_{\text{iso}} = 0.076 (11) \text{ \AA}^2$] for (I) and (II), respectively. The H atoms of C—H groups were placed in calculated positions (C—H = 0.96 Å) and were allowed to refine as riding models, with displacement parameters fixed at 120% of those of their attached C atoms.

For both compounds, data collection: *CrysAlis* (Oxford Diffraction, 2000); cell refinement: *CrysAlis*; data reduction: *CrysAlis*; 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).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1587). Services for accessing these data are described at the back of the journal.

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