Supramolecular structures formed by 2-aminopyridine derivatives. Part I. Hydrogen-bonding networks *via* N–H···N interactions and the conformational polymorphism of *N*,*N*′-bis(2-pyridyl)aryldiamines

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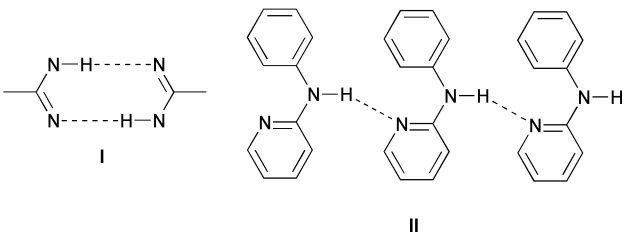
A family of *N*,*N*′-bis(2-pyridyl)aryldiamines were prepared and their solid state structures investigated by X-ray crystallography. Due to a low energy barrier to C–N rotation, the 2-arylaminopyridine system can adopt either *Z* or *E* conformations, which may lead to conformational polymorphism. The *E*,*E* conformers form designated hydrogen-bonded polymeric tapes with the dimeric $R_2^2(8)$ motif. In contrast, the *Z*,*Z* conformers assemble *via* N–H···N hydrogen bonds, generating the catemer motif that leads to complex 1D, 2D or 3D supramolecular structures. The two types of intermolecular hydrogen-bonding motifs observed in the crystal structures can be easily differentiated with the assistance of solid state IR spectroscopy.

Introduction

The rational design and synthesis of new solids with organized molecular frameworks and presenting desirable structural and functional features is a major goal of crystal engineering.[1] The macroscopic properties of a molecular solid depend upon the nature of the component molecules as well as their crystal packing. Unfortunately, in spite of many successful attempts in this area, at present, it is very difficult to predict the architecture of molecular crystals from the structure of their constituent molecules.[2] The possible appearance of unforeseen structures, which are more stable than the designed structures, or alternative packing patterns (known as polymorphism),[3] makes control of supramolecular organisation in the solid state a non-trivial task. However, systematic structural studies of various derivatives with finely tuned molecular structures and observation of their crystal packing modifications should lead to a better understanding of the factors governing molecular self-assembly. In particular, identification of the non-covalent substructural motifs, termed supramolecular synthons,[4] that lead to predictable structural patterns is extremely important for the successful design of new solids.

Organic crystal engineering relies solely on non-covalent intermolecular interactions which are weak and poorly directional in comparison with covalent bonds. Hydrogen bonds, because of their strength and directionality, play a decisive role in controlling the self-assembly of many molecular crystals and biopolymers. The majority of supramolecular synthons comprise complementary or self-complementary hydrogen-bonding units and, therefore, functional groups able to participate in H-bonds play a crucial role in the self-organization of molecular building blocks into various one-, two- or three-dimensional networks.[1,5]

The 2-aminopyridine functionality, closely related to biological systems, is able to form self-complementary intermolecular interaction **I**[6–8] and, therefore, it seems to be particularly promising for the construction of ordered supramolecular aggregates. Although the dimeric motif **I** [graph set notation: $R_2^2(8)$][9] has been frequently observed in crystal structures, including some centrosymmetric dimers of N-substituted 2-aminopyridines,[6] this functionality has been largely neglected in the generation of new solid materials. In contrast, *N*-acyl-2-aminopyridines,[7] as well as 2-aminopyrimidines,[8] usually in combination with carboxylic acids, are frequently used in the synthesis of two-component supramolecular frameworks. Since the formation of extended networks requires molecules having more than one bonding functional group, we prepared compounds **1**–**9** and studied their crystal structures. These compounds, bearing two 2-aminopyridyl moieties separated by linkers of different length, shape and rigidity, and devoid of any other functionalities that might compete for hydrogen-bond formation, could form polymeric non-covalent 1D networks *via* N–H···N hydrogen bonds using two equivalent synthons **I**. However, this requires the *N*-aryl-2-aminopyridine units to assume the *E* conformation. On the other hand, due to a low energy barrier to C–N rotation, this system can also adopt the *Z* conformation,[10] which may lead to catemer structure **II** analogous to that observed in the crystals of some carboxylic acids.[11] Thus, the topology of the hydrogen-bonding network in *N*,*N*′-bis(2-pyridyl)aryldiamines should determine which of the energetically similar conformations (*E*,*E*, *Z*,*Z* or *E*,*Z*) the molecules are going to assume. In such cases, conformational polymorphism[12] of the compounds studied should generally be expected. Therefore, we tried various crystallization conditions to isolate potential polymorphic forms of **1**–**9** with different



I **II**

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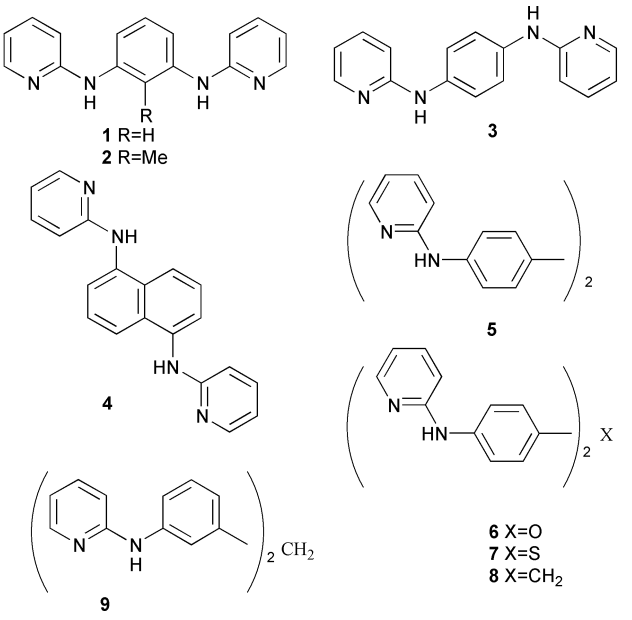
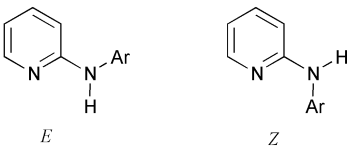




patterns of hydrogen bonds and packing modes. The analysis of their crystal structures should help in establishing the factors that can direct the formation of predictable and ordered H-bonding networks containing 2-aminopyridine derivatives.

Results and discussion

The compounds **1**–**9** were prepared by an autocatalyzed reaction of the corresponding aromatic diamines with an excess of boiling 2-chloropyridine. The hydrochlorides of the *N*,*N*′-bis(2-pyridyl)aryldiamines **1**–**9** were formed after 0.5–2 h in nearly quantitative yields. The products were liberated with aqueous ammonia and crystallized from various solvents, including methanol, ethanol, acetonitrile, ethyl acetate and toluene. Single crystals suitable for X-ray diffraction studies were grown by slow evaporation of the solvent under ambient conditions. The details of their X-ray analyses are summarized in Table 1.

During the crystallization of the 1,4-diaminobenzene derivative **3**, the simplest compound of the series reported here, we succeeded in isolating two polymorphic forms assigned as **3α** and **3β**. The form **3α**, obtained by evaporation from a saturated methanolic solution, crystallizes in the triclinic space group $P\bar{1}$, whereas the form **3β**, obtained from acetonitrile, crystallizes in the orthorhombic space group *Pbca*. The unit cell of the polymorph **3α** contains two symmetry-independent

Table 1 X-Ray structure determination summary

Crystal data	**1**	**2**	**3α**	**3β**	**4**	**5**
Empirical formula	$C_{16}H_{14}N_4$	$C_{17}H_{16}N_4$	$C_{16}H_{14}N_4$	$C_{16}H_{14}N_4$	$C_{20}H_{16}N_4$	$C_{22}H_{18}N_4$
Formula weight	262.31	276.34	262.31	262.31	312.37	338.40
T/K	293	293(2)	293(2)	293(2)	100(2)	293(2)
Crystal system	Orthorhombic	Monoclinic	Triclinic	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbcn*	$P2_1/n$	$P\bar{1}$	*Pbca*	$P\bar{1}$	$C2/c$
a/Å	19.917(4)	11.352(5)	7.778(2)	7.454(1)	8.118(2)	14.761(3)
b/Å	7.627(2)	7.702(2)	9.003(2)	8.991(2)	9.361(2)	13.162(3)
c/Å	8.677(2)	16.435(7)	10.240(2)	19.477(4)	11.803(2)	18.341(4)
α/°			101.77(3)		100.62(3)	
β/°		90.36(3)	97.54(3)		101.57(3)	104.70(3)
γ/°			105.52(3)		114.20(3)	
V/Å^3	1318.1(5)	1436.9(9)	663.1(3)	1305.3(4)	765.0(3)	3446.7(13)
Z	4	4	2	4	2	8
λ/Å	0.71073 (Mo-Kα)	1.54178 (Cu-Kα)	0.71073 (Mo-Kα)	0.71073 (Mo-Kα)	0.71073 (Mo-Kα)	0.71073 (Mo-Kα)
μ/mm^{-1}	0.082	0.621	0.082	0.083	0.083	0.080
Total reflections	1173	2286	2080	1027	5718	2810
Indep. reflect. (R_{int})	1173	2046 (0.020)	2080	1027	2499 (0.035)	2720 (0.059)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0378, 0.1001	0.0719, 0.1883	0.0429, 0.1109	0.0328, 0.0971	0.0631, 0.1689	0.0502, 0.1157
R_1, wR_2 (all data)	0.1054, 0.1103	0.1730, 0.2205	0.1126, 0.1220	0.1205, 0.1103	0.1108, 0.2022	0.1665, 0.1346

Crystal data	**6α**	**6β**	**7**	**8**	**9α**	**9β**
Empirical formula	$C_{22}H_{18}N_4O$	$C_{22}H_{18}N_4O$	$C_{22}H_{18}N_4S$	$C_{23}H_{20}N_4$	$C_{23}H_{20}N_4$	$C_{23}H_{20}N_4 \cdot 0.5EtOH$
Formula weight	354.40	354.40	370.46	352.43	352.43	375.46
T/K	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	$P2_1/c$	*Fdd*2	*Pbca*	$C2/c$	*P*4*nc*
a/Å	9.6437(5)	11.162(1)	34.619(7)	9.756(2)	11.4291(10)	15.039(2)
b/Å	11.8742(6)	18.893(1)	18.823(4)	17.048(3)	14.5351(13)	15.039(2)
c/Å	17.1611(8)	17.247(1)	5.6100(10)	22.116(4)	11.9115(11)	8.896(2)
α/°	79.732(4)					
β/°	89.713(4)	100.89(1)			107.555(8)	
γ/°	72.535(5)					
V/Å^3	1842.06(16)	3571.6(7)	3655.7(13)	3678.2(12)	1886.6(3)	2012.0(6)
Z	4	8	8	8	4	4
λ/Å	0.71073 (Mo-Kα)	0.71073 (Mo-Kα)	1.54178 (Cu-Kα)	1.54178 (Cu-Kα)	0.71073 (Mo-Kα)	1.54178 (Cu-Kα)
μ/mm^{-1}	0.081	0.084	1.674	0.603	0.075	0.600
Total reflections	15 254	17 631	1674	2746	4987	1550
Indep. reflect. (R_{int})	7401 (0.022)	6281 (0.025)	1503 (0.009)	2745	1839 (0.024)	882 (0.027)
R_1, wR_2 [$I > 2\sigma(I)$]	0.0506, 0.1343	0.0543, 0.1299	0.0347, 0.0898	0.0499, 0.1247	0.0409, 0.1089	0.0355, 0.0775
R_1, wR_2 (all data)	0.0741, 0.1500	0.0895, 0.1489	0.0352, 0.0904	0.1621, 0.1610	0.0653, 0.1192	0.0926, 0.0908

molecules with a crystallographically imposed inversion center. They have similar geometries and each of the two 2-aminopyridine units assumes the *E* conformation. The molecules are significantly distorted from planarity (the dihedral angle between the benzene and pyridine rings is 46.2 and 42.0° in molecules A and B, respectively), indicating strong steric interactions between the neighboring hydrogens in the pyridine and benzene rings. However, the molecules release the strain by different routes, as shown by differences in the values of the torsion angles involving two exocyclic C–N bonds (27.7, 27.6 and 42.7, 2.8° in molecules A and B, respectively). The molecules of **3** are joined by pairs of symmetrically independent and nearly linear N–H···N hydrogen bonds (Table 2), generating the asymmetric motif **I** that leads to infinite molecular tapes (Fig. 1). These tapes possess an undulating shape due to the non-planarity of the $R_2^2(8)$ rings **I**, as well as the constituent molecules.

At first glance, the orthorhombic polymorph **3β** has a completely unanticipated structure [Scheme 1, Fig. 2 and 4(a)]. Each molecule in the crystal resides on an inversion site, with half a molecule per asymmetric unit. Since both 2-aminopyridine moieties in **3β** adopt the *Z* conformation with a non-coplanar arrangement of the phenyl and pyridine rings (the interplanar angle is of 45.8°), only the catemer motif **II** is accessible for self-assembly of the molecules into a supramolecular structure *via* hydrogen bonds. This hydrogen-bonded pattern is generated by a glide plane with a translational component of *ca.* 4.5 Å along the catemer. Each molecule of **3** is involved in four hydrogen bonds belonging to two parallel **II** motifs running in opposite directions and further organizing the molecules into a 2D network. Further inspection of the 2D layer structure of **3β** reveals additional hydrogen bond motifs consisting of a large $R_4^4(26)$ ring and a C(9) chain propagating perpendicularly to the catemer **II** (Fig. 2). They are responsible for the formation of a helix with the 2_1 axis oriented parallel to the *x* direction. The existence of two conformational polymorphs of **3** is not surprising in view of the results of MNDO calculations[13] which show that the *E* conformer of *N*-phenyl-2-aminopyridine is more stable over the *Z* conformer by only 0.15 kcal mol^{-1}.

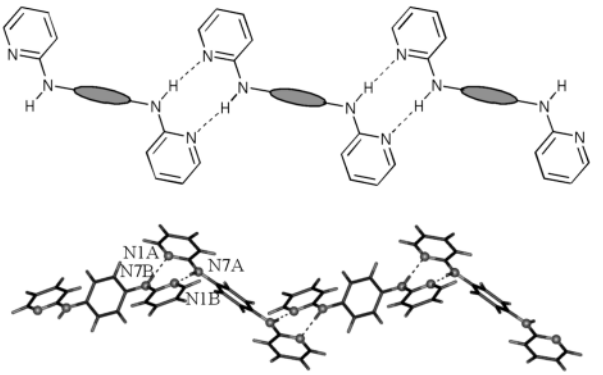
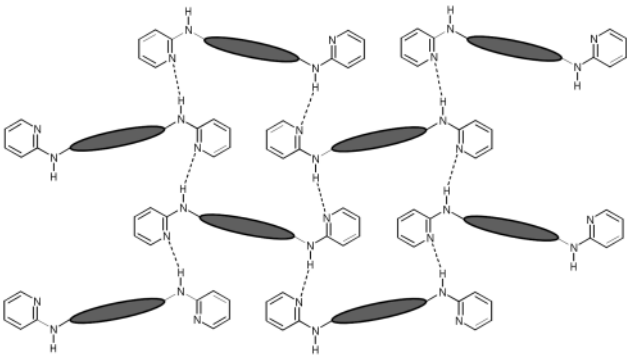


Fig. 1 Crystal structure and schematic representation of the hydrogen-bonded 1D network formed by the *E*,*E* conformers in **3α**. Nitrogen atoms are shown as spheres and hydrogen bonds are drawn with broken lines.

The structures described above represent the two principal hydrogen-bonding motifs observed in the title compounds and the intermolecular interaction patterns of the remaining *N*-aryl-2-aminopyridines can be related to them. In spite of many



Scheme 1

Table 2 Geometry of the N–H···N hydrogen bonds

Compound	Interaction[a]	D···A/Å	H···A/Å	∠D–H···A/°
1	N7–H···N1^{i}	3.082(3)	2.24(3)	171(2)
2	N7–H···N1^{ii}	3.006(7)	2.26	140
	N14–H14···N16^{iii}	2.990(7)	2.10	160
3α	N7A–H···N1B^{iv}	2.978(3)	2.09(3)	173(3)
	N7B–H···N1A^{iv}	3.037(3)	2.11(3)	174(2)
3β	N7–H···N1^{v}	3.098(3)	2.23(3)	173(2)
4	N7A–H···N1A^{vi}	3.037(4)	2.16	165
	N7B–H···N1B^{vii}	2.994(4)	2.11	168
5	N7A–H···N1A^{viii}	3.039(4)	2.14(4)	176(3)
	N7B–H···N1B^{ix}	3.019(4)	2.02(4)	179(3)
6α	N7A–H···N23A^{x}	2.965(2)	2.02(2)	179(2)
	N21A–H···N1A^{xi}	3.033(2)	2.12(2)	177(2)
	N7B–H···N1B^{xii}	3.175(2)	2.31(2)	173(2)
	N21B–H21B···N23B^{xiii}	3.029(2)	2.14(2)	172(2)
6β	N7A–H···N23A^{xiv}	3.210(3)	2.39	152
	N21A–H···N1A^{xv}	3.069(2)	2.18	172
	N7B–H···N23B^{xvi}	3.176(2)	2.43	140
	N21A–H···N1A^{xvii}	3.143(2)	2.25	172
7	N7–H···N1^{xviii}	3.373(2)	2.68(2)	163(2)
8	N7–H···N23^{xix}	3.083(4)	2.19	173
	N21–H···N1^{xx}	3.126(4)	2.29	173
9α	N7–H···N1^{xxi}	3.019(2)	2.12(2)	172(2)
9β	N7–H···N1^{xxii}	3.091(2)	2.12	172(2)

[a] Symmetry codes: (i) $x, -y, 0.5 + z$; (ii) $-x, -y, -z$; (iii) $-x, -y, -1 - z$; (iv) $-x, -y, 1 - z$; (v) $0.5 - x, 0.5 + y, z$; (vi) $1 - x, 1 - y, -z$; (vii) $2 - x, 2 - y, 1 - z$; (viii) $1.5 - x, 0.5 - y, 1 - z$; (ix) $1.5 - x, -0.5 - y, 1 - z$; (x) $1 + x, -1 + y, z$; (xi) $-1 + x, 1 + y, z$; (xii) $3 - x, 1 - y, 1 - z$; (xiii) $2 - x, -y, -z$; (xiv) $x, -0.5 - y, 0.5 + z$; (xv) $1 - x, -y, 1 - z$; (xvi) $x, 0.5 - y, -0.5 + z$; (xvii) $1 - x, -y, 1 - z$; (xviii) $0.25 - x, 0.25 + y, 0.25 + z$; (xix) $1 - x, -0.5 + y, 0.5 - z$; (xx) $1 - x, 0.5 + y, 0.5 - z$; (xxi) $1.5 - x, 0.5 - y, -z$; (xxii) $-0.5 + y, 0.5 + x, 0.5 + z$.

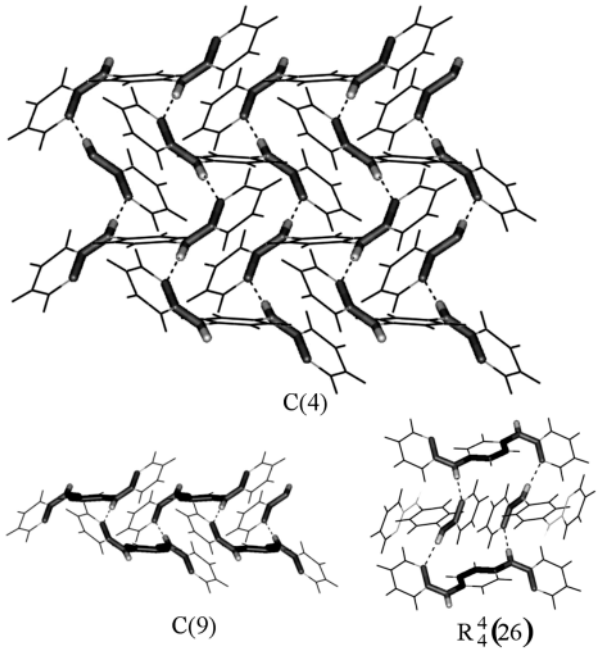


Fig. 2 The hydrogen-bonded 2D network formed by the *Z*,*Z* conformers of **3** in **3β** and the three main hydrogen-bonding motifs within this network.

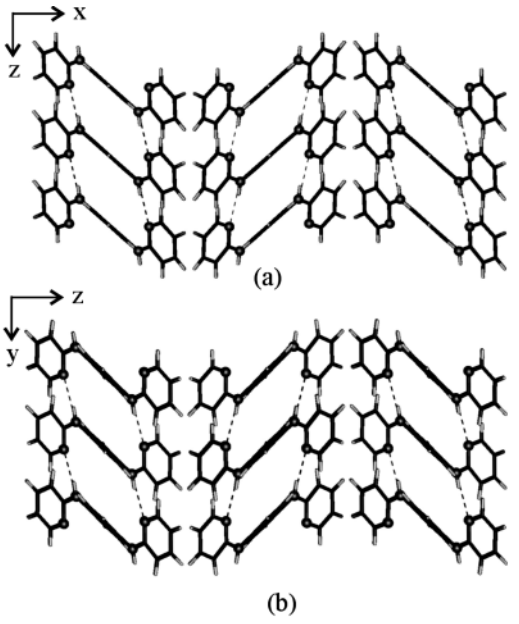


Fig. 4 Projections of the crystals structures: (a) **1** viewed along the direction [010]; (b) **3β** viewed along the direction [100].

efforts to obtain two polymorphs of **1**, we were able to isolate only one form crystallizing in the orthorhombic space group *Pbcn*. As in **3β**, the molecules of **1** are not planar and assume the *Z*,*Z* conformation. They are situated at a two-fold axis and assemble *via* the N–H···N hydrogen bonding motif **II** to form a 1D network composed of centrosymmetric $R_2^2(16)$ rings (Fig. 3). The catemer motif is generated by a glide plane with a translational component of *ca.* 4.3 Å along the catemer. Surprisingly, despite the considerable differences in the crystal packing of **1** and **3β**, these crystals have very similar unit cell parameters (Table 1) and the projections of their structures along the [010] and [100] directions, respectively, look nearly identical (Fig. 4).

The methyl derivative **2**, which is closely related to **1**, shows a very different packing motif. Its crystal structure (in the monoclinic space group $P2_1/n$) shows molecules of **2** self-assembled into a 1D network constructed of the *E*,*E* conformers, similar to that observed in **3α**, but formed through two crystallographically independent centrosymmetric $R_2^2(8)$ motifs [Fig. 5(a)]. The 1,5-diaminonaphthalene derivative **4**, crystallizing like **3α** in the $P\bar{1}$ space group with two half-molecules in the asymmetric unit, aggregates into two similar symmetry-independent non-parallel infinite tapes *via* the centrosymmetric motif **I** [Fig. 5(b)].

The crystal structure of the benzidine derivative **5** (the space group $C2/c$) is also characterized by two independent parallel 1D hydrogen-bonding networks generated by centrosymmetric $R_2^2(8)$ motifs [Fig. 5(c)]. The two symmetry-independent molecules of **5** belong to the C_2 point group and their central biphenyl moieties are considerably twisted (dihedral angles between the phenyl rings are 29.0 and 19.5° in molecules A and B, respectively). The infinite tapes are further arranged into a 2D layer structure by face-to-face π–π stacking interactions between the pyridine rings and edge-to-face interactions between the biphenyl moieties of neighboring networks (Fig. 6).

Two polymorphs were also isolated during the crystallization of **6**; colorless prisms of the form **6α** (m.p. 143–144 °C)

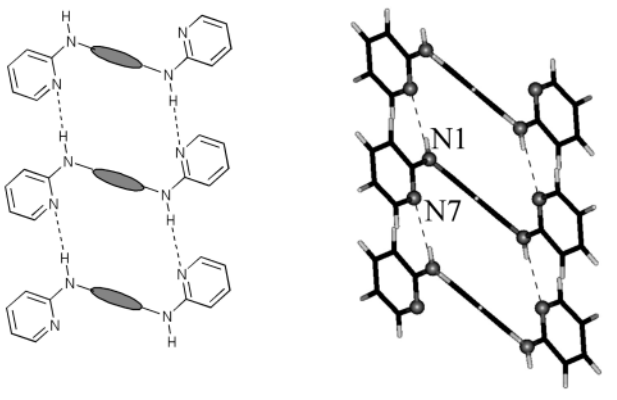


Fig. 3 The 1D network in the crystal structure of **1**. Nitrogen atoms are shown as spheres and hydrogen bonds are drawn with broken lines.

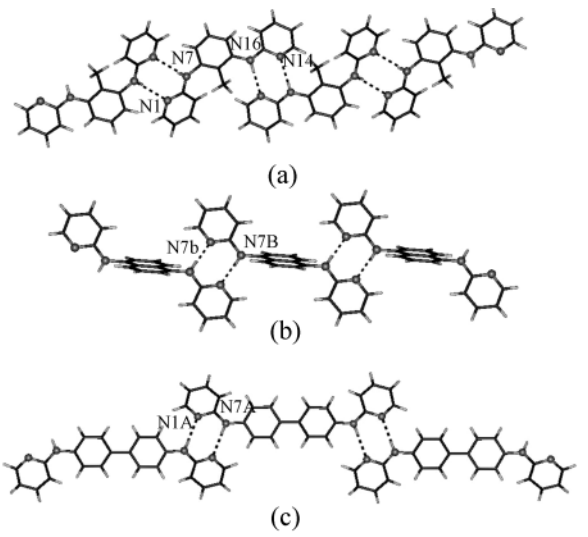


Fig. 5 Hydrogen-bonded 1D networks formed by the *E*,*E* conformers of **2** (a), **4** (b) and **5** (c). A second molecular position has been omitted for **2**. Only one of the two symmetry-independent networks is shown for **4** and **5**. Nitrogen atoms are shown as spheres and hydrogen bonds are drawn with broken lines.

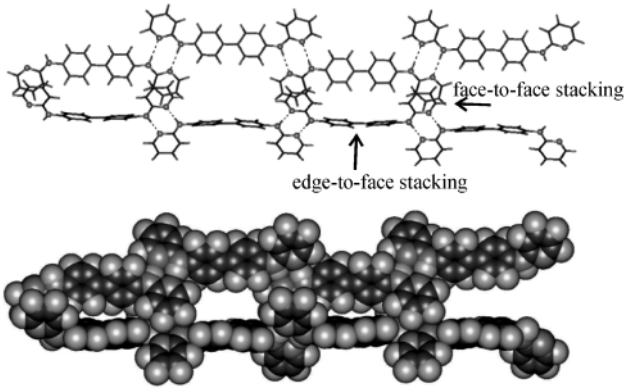


Fig. 6 The π–π stacking interactions between the pyridine rings and the edge-to-face interactions of the biphenyl moieties belonging to the two symmetry-independent networks in the crystals of the benzidine derivative **5**.

were grown from ethyl acetate, whereas block-like crystals of the form **6β** (m.p. 138–140 °C) were obtained from methanol. The form **6α**, like **3α**, crystallizes in the triclinic space group $P\bar{1}$, however there are two symmetry-independent molecules in the unit cell. Due to the *E*,*E* configuration adopted by both molecules, the hydrogen bonding $R_2^2(8)$ is again a principal motif of the two independent infinite and nearly perpendicularly oriented chains found in the crystal structure. As can be seen in Fig. 7, the two 1D networks generated by the motif **I** differ in their symmetry; that formed by the translationally related molecules A belongs to the rod symmetry group $P1$,[14] while that constructed from molecules B belongs to the symmetry group $P\bar{1}$ as a consequence of the asymmetric and centrosymmetric geometries of the corresponding $R_2^2(8)$ motifs, respectively.

In contrast, the two symmetry-independent molecules in the polymorph **6β** (monoclinic space group $P2_1/c$) form two separate similarly constructed and strongly puckered 2D networks of the layer symmetry $P12_1/c1$ stacking along the [100] direction (Scheme 2, Fig. 8). Due to the *Z* conformation assumed by the 2-aminopyridine units, the molecules are held together by the N–H···N hydrogen bonds, generating the motif **II**. A single catemer C(4) is created by a screw axis operation (with a translational component of 9.95 Å) relating pairs of the hydrogen-bonded and symmetry-independent 2-aminopyridine moieties. As a consequence, in **6β**, the

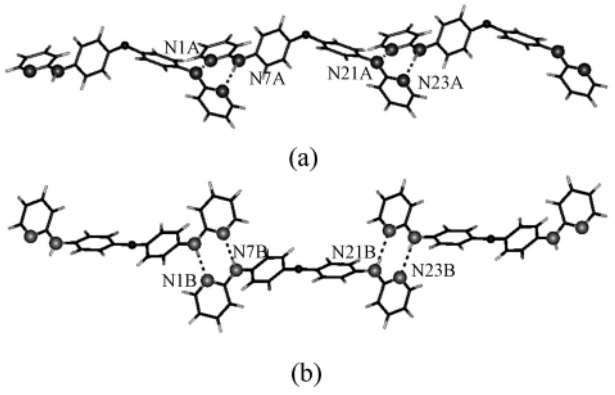
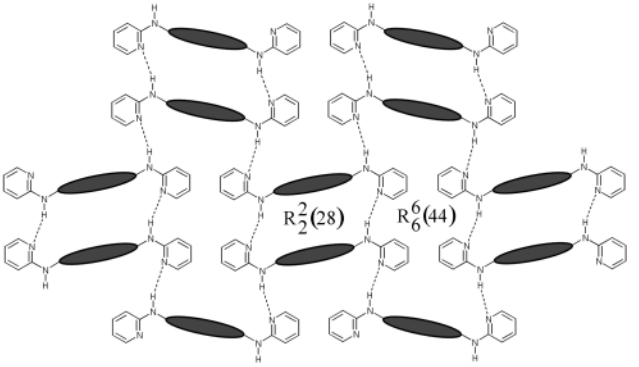


Fig. 7 Two symmetry-independent hydrogen-bonded 1D networks formed by the *E*,*E* conformers in **6α**: (a) tape with the rod symmetry $P1$ and strongly puckered pseudo-C_2 $R_2^2(8)$ motif; (b) tape with the rod symmetry $P\bar{1}$ and the centrosymmetric $R_2^2(8)$ motif. Nitrogen atoms are shown as large spheres and hydrogen bonds are drawn with broken lines.



Scheme 2

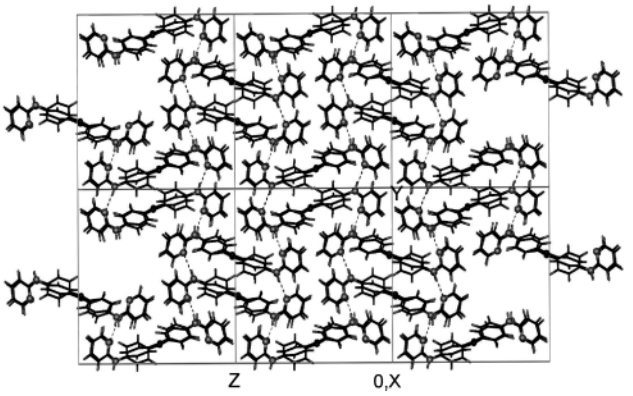


Fig. 8 Crystal structure of the polymorph **6β**. Projection of the crystal structure showing stacking of the 2D assemblies along the *x* axis.

topology of the 2D network based on motif **II** is quite different from that observed in **3β**. Instead of the single ring motif $R_4^4(26)$, two types of cycles, one 28- and the second 44-membered, with the graph symbols $R_2^2(28)$ and $R_6^6(44)$, respectively, can be easily distinguished within the 2D net (Scheme 2). There are several C–H···π interactions (T-shape geometry, the shortest C–H···ring centroid distance is 2.75 Å) between the aromatic rings accommodated inside smaller or larger cavities, formed within the 3D structure, that additionally stabilize the layer structure of **6β**.

Unexpectedly, the self-assembly *via* N–H···N hydrogen bonds of molecules of the thioanalogue **7**, which are closely related to **6**, generates a 3D supramolecular structure (Fig. 9). The crystals of **7** belong to the polar orthorhombic space group $Fdd2$, with the molecules residing on a two-fold axis and assuming the *Z*,*Z* conformation. Thus the hydrogen-bonding motif **II** is generated, where the translationally independent part of the catemer consists of the four N=C–N–H··· units related by a diamondoid glide plane d oriented perpendicularly to the *x* axis. These motifs run parallel to the lattice directions [011] and [01$\bar{1}$] with a unit translation vector of 19.64 Å. There is also an additional easily recognisable chain motif $C_2^2(18)$ generated by the screw axis operation, which creates a helix parallel to the *z* axis. It is noteworthy that the N–H···N hydrogen bond in **7** with a H···N contact of 2.68 Å is significantly longer than those in the other supramolecular structures presented in this account.

Obtaining diffraction quality crystals of **8** (orthorhombic space group *Pbca*) proved to be very difficult and after several trials they were grown from methanol. The crystal structure revealed that the *E*,*E* conformers are connected into a chiral 1D network by hydrogen bonds, generating the asymmetric (pseudo-C_2) $R_2^2(8)$ motifs with strongly puckered 8-membered

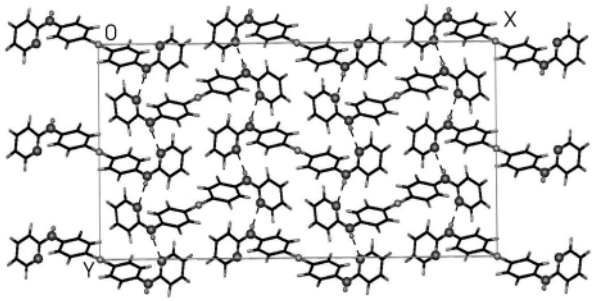


Fig. 9 Projection of the 3D network in the crystal structure of **7** along the *z* axis.

Fig. 12 Strongly corrugated hydrogen-bonded 1D network formed by the *E*,*E* conformers in **9α**. The molecules located at the 2-fold axis are joined through centrosymmetric $R_2^2(8)$ motifs.

rings (Fig. 10). The molecules forming H-bonded aggregates are related by the 2_1 axis and create a helix with deep grooves on its surface filled in a zipper-like mode by the molecules that belong to two parallel 1D networks of the opposite helicity (Fig. 11).

In the case of compound **9**, two pseudopolymorphs[12] were obtained: the form **9α**, crystallizing from methanol in the monoclinic space group $C2/c$, and the form **9β**, crystallizing from ethanol in the tetragonal space group $P4nc$ and containing disordered molecules of the solvent. In both crystals, the molecules are located at a two-fold axis. The molecules in **9α** assume a chiral conformation of C_2 symmetry with the 2-aminopyridine units adopting the *E* configuration. The packing of **9α** is built up from parallel undulating chains of the alternating conformational enantiomers of **9**, which are again connected by the centrosymmetric $R_2^2(8)$ hydrogen bond motif **I** (Fig. 12). In the acentric structure **9β**, the *Z*,*Z* conformers form, *via* a glide-generated catemer motif **II**, a new type of polar 1D network, with the two constituting C(4) chains propagating parallel to each other in the same direction (Fig. 13). This aggregate belongs to the orthogonal rod symmetry group $P2aa$, whereas the only 1D network with the C(4) motif observed in the structure of **1** was centrosymmetric (rod symmetry group $P12/a1$). The ethanol molecule enclosed in the crystal is disordered around the four-fold axis and is not involved in any intermolecular hydrogen bonds [Fig. 13(b)].

The **I** and **II** intermolecular hydrogen bonding patterns of **1**–**9** can be readily distinguished using IR spectroscopy. Comparison of the solid state spectra of **1** and **2** with those of the corresponding N-deuterated derivatives allowed unambiguous assignment of the N–H stretching (ν_{N-H}) and *in-plane*

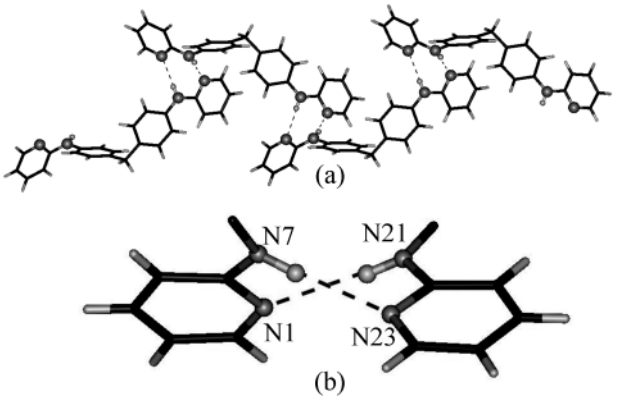


Fig. 10 Helical 1D network formed by the *E*,*E* conformers in **8** (a) and the pseudo-C_2 strongly non-planar $R_2^2(8)$ motif (b).

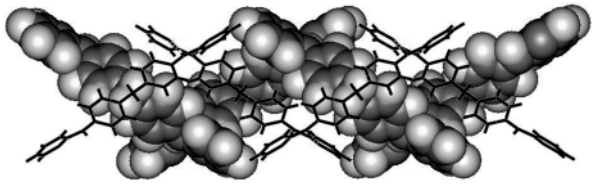


Fig. 11 Two parallel 1D networks of the opposite helicity arranged in a zipper-like mode in the crystals of **8**. There are only van der Waals interactions between the neighbouring chains.

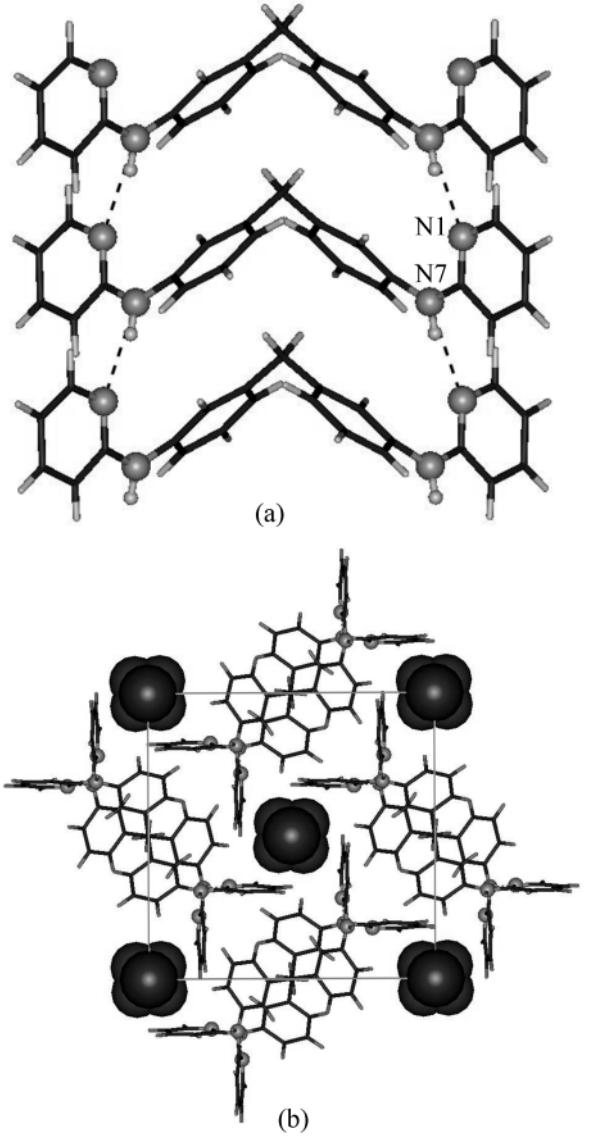


Fig. 13 Crystal structure of **9β**: (a) structure of the hydrogen-bonded 1D network generated by the motif **II**; (b) projection of the crystal packing along the *z* axis—the large black spots represent the disordered ethanol molecules.

Table 3 IR frequencies (cm^{-1}) of *N*,*N*′-bis(2-pyridyl)aryldiamines **1**–**9** in the solid state (KBr)

Compound	ν_{N-H}	δ_{N-H}
1	3256, 3175	1527
2	3212, 3173	1525
3α	3227, 3167	1539
3β	3256, 3172	1533
4	3192, 3181	1530
5	3228, 3165	1533
6α	3228, 3186	1529
6β	3280	1526
7	3318	1509
8	3232, 3175	1527
9α[a]	3229, 3173	1539

[a] Ethanol contained in the crystals of **9β** makes observation of the N–H vibrations impossible.

bending (δ_{N-H}) vibrations Table 3. The observed broad composite bands are consistent with the occurrence of strong and moderately strong hydrogen bonding. In the case of the structures **I** with the stronger dimeric hydrogen bonding $R_2^2(8)$, the stretching ν_{N-H} band is shifted by *ca.* 30 cm^{-1} to lower frequencies than in the case of those in the catemer **II** structures with the weaker N–H···N hydrogen bonds. The frequency of the bending δ_{N-H} vibrations is only slightly influenced by the hydrogen-bonding pattern.

To summarize, in the above reported crystal structures, the molecules of *N*,*N*′-bis(2-pyridyl)aryldiamines **1**–**9** adopted either the *E*,*E* or *Z*,*Z* conformation, whereas the potentially possible *E*,*Z* conformer was never observed. As predicted, the *E*,*E* conformers show a strong tendency to assemble into 1D networks through N–H···N self-complementary $R_2^2(8)$ hydrogen bonds. Irrespective of the symmetry of the constituent 1D networks, their crystal packing is persistently centrosymmetric. In five out of the twelve studied crystals, the 2-pyridylamine units adopted the *Z*,*Z* conformation, which generated molecular assemblies *via* the catemer motif C(4) that leads to the formation of 1D, 2D and 3D networks exhibiting various hydrogen-bonding patterns. Usually, these crystals belong to higher symmetry space groups than those built up from the *E*,*E* conformers, and in two cases, acentric crystal packing is produced. It is noteworthy that the molecular assemblies observed in **1**, **3β**, **6β**, **7** and **9β** resemble those reported for the crystals of some secondary arenedicarboxamides.[15] However, the catemer motif **II** can only be generated by a glide plane or a screw axis and not, as in numerous secondary dicarboxamides, by a translation operation. This might be due to steric reasons and/or the different H-bond acceptor properties of the carbonyl oxygen and the pyridine nitrogen. The conformational polymorphism of the title compounds, being a consequence of the low energy barrier to C–N rotation, decreases the level of control over their crystal structures and may cause serious problems in the rational design of hydrogen-bonded molecular assemblies.

Experimental

^1H and ^{13}C NMR spectra were obtained with Bruker DRX-500 and WP-200 spectrometers at 500 and 50 MHz, respectively. The deuteriated solvents were used as an internal lock for ^1H and ^{13}C NMR spectra. FT-IR absorptions were measured with a Bruker IFS66 spectrometer.

Syntheses

***N*,*N*′-Bis(2-pyridyl)-1,3-diaminobenzene (1).** 1,3-Diaminobenzene (2.16 g, 20 mmol) was dissolved in 2-chloropyridine (5.6 ml, 60 mmol) and refluxed for *ca.* 30 min. After cooling, the precipitated hydrochloride was filtered off and washed with diethyl ether. The crude hydrochloride (7.0 g) was dissolved in water (10 ml), 25% aqueous ammonia (20 ml) was added and the precipitated product was extracted with ethyl acetate. The organic layer was dried (Na_2SO_4), evaporated to dryness and the residue (5.0 g) was recrystallized from ethanol, yield: 4.5 g (86%); mp: 165–166 °C (lit.[16] mp: 160 °C); δ_H (DMSO-d_6): 8.88 (s, 2H, NH), 8.09 (m, 2H), 7.99 (s, 1H), 7.49 (t, $J = 7.2$ Hz, 2H), 7.19 (d, $J = 7.7$ Hz, 2H), 7.08 (t, $J = 7.9$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 2H), and 6.67 (m, 2H); δ_C (DMSO-d_6): 156.1, 147.4, 142.0, 137.2, 128.7, 114.2, 111.3, 110.6 and 108.3; ν_{max}(KBr)/cm^{-1}: 3256, 3176, 1613, 1595 and 1528.

***N*,*N*′-Bis(2-pyridyl)-1,3-diamino-2-methylbenzene (2).** Compound **2** was obtained from 2,6-diaminotoluene in a manner similar to that used to synthesise compound **1** in 61% yield; mp: 153–154 °C (toluene); δ_H (DMSO-d_6): 8.18 (s, 2H, NH), 7.99 (m, 2H), 7.45 (t, $J = 7.6$ Hz, 2H), 7.18 (d, $J = 7.9$ Hz, 2H), 7.06 (t, $J = 7.9$ Hz, 1H), 6.61 (s, 2H), 6.59 (d, $J = 7.6$ Hz, 2H) and 2.02 (s, 3H); δ_C (DMSO-d_6): 157.3, 147.6, 139.9, 137.2, 126.4, 125.5, 119.8, 113.6, 108.7 and 13.3; ν_{max}(KBr)/cm^{-1}: 32 123, 3173, 1603, 1573 and 1525. Anal. calcd for $C_{17}H_{16}N_4$: C, 73.89; H, 5.84; N, 20.28; found: C, 73.71; H, 5.92; N, 20.22%.

***N*,*N*′-Bis(2-pyridyl)-1,4-diaminobenzene (3).** Compound **3** was obtained from 1,4-diaminobenzene in a manner similar to that used to synthesise compound **1** in 78% yield; mp: 205–206 °C (acetonitrile) (lit.[16] mp: 200–201 °C); δ_H (DMSO-d_6) 8.90 (s, 2H, NH), 8.19 (m, 2H), 7.64 (s, 4H), 7.60 (m, 2H), 6.86 (d, $J = 8.4$ Hz, 2H) and 6.75 (m, 2H); δ_C (DMSO-d_6): 156.3, 147.3, 137.0, 135.2, 119.2, 113.5 and 109.8; ν_{max}(KBr)/cm^{-1}: 3260, 3172, 1601, 1532 and 1511.

***N*,*N*′-Bis(2-pyridyl)-1,5-diaminonaphthalene (4).** Compound **4** was obtained from 1,5-diaminonaphthalene in a manner similar to that used to synthesise compound **1** in 48% yield; mp: 258–260 °C (with dec.); δ_H (DMSO-d_6): 8.82 (s, 2H, NH), 8.03 (m, 2H), 7.84 (d, $J = 8.5$ Hz, 2H), 7.79 (d, $J = 7.5$ Hz, 2H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.41 (t, $J = 7.8$ Hz, 2H), 6.84 (d, $J = 8.3$ Hz, 2H) and 6.68 (m, 2H); δ_C (DMSO-d_6): 157.4, 147.4, 137.3, 136.9, 129.0, 125.1, 119.0, 118.1, 114.2 and 109.8; ν_{max}(KBr)/cm^{-1}: 3226, 3181, 1601, 1578 and 1530. Anal. calcd for $C_{20}H_{16}N_4$: C, 76.90; H, 5.16; N, 17.94; found: C, 76.66; H, 5.23; N, 18.18%.

***N*,*N*′-Bis(2-pyridyl)-4,4′-diaminobiphenyl (5).** Compound **5** was obtained from benzidine in a manner similar to that used to synthesise compound **1** in 92% yield; mp: 232–234 °C (dioxane–methanol); δ_H (DMSO-d_6): 9.10 (s, 2H, NH), 8.15 (m, 2H), 7.71 (d, $J = 8.8$ Hz, 4H), 7.56 (m, 2H), 7.53 (d, $J = 8.8$ Hz, 4H), 6.86 (d, $J = 8.4$ Hz, 2H) and 6.74 (m, 2H); δ_C (DMSO-d_6): 156.2, 151.4, 147.5, 137.5, 137.3, 120.2, 118.9, 114.4 and 110.5; ν_{max}(KBr)/cm^{-1}: 3228, 3165, 1596 and 1533; Anal. calcd for $C_{22}H_{18}N_4$: C, 78.08; H, 5.36; N, 16.56; found: C, 78.16; H, 5.50; N, 16.48%.

***N*,*N*′-Bis(2-pyridyl)-4,4′-oxybis(aminobenzene) (6).** Compound **6** was obtained from 4,4′-oxybisaniline in a manner similar to that used to synthesise compound **1** in 94% yield; mp: 143–144 °C (methanol); δ_H (DMSO-d_6): 8.71 (s, 2H, NH), 8.08 (m, 2H), 7.60 (d, $J = 9.0$ Hz, 4H), 7.52 (m, 2H), 6.91 (d, $J = 9.0$ Hz, 4H), 6.76 (d, $J = 8.4$ Hz, 2H) and 6.69 (m, 2H); δ_C (DMSO-d_6): 156.0, 147.4, 140.6, 137.7, 132.6, 126.4, 125.9, 118.9, 115.7, 114.6 and 111.1; ν_{max}(KBr)/cm^{-1}: 3279, 1608, 1597 and 1526. Anal. calcd for $C_{22}H_{18}N_4O$: C, 74.56; H, 5.12; N, 15.81; found: C, 74.56; H, 5.19; N, 15.75%.

***N*,*N*′-Bis(2-pyridyl)-4,4′-thiobis(aminobenzene) (7).** Compound **7** was obtained from 4,4′-thiobisaniline in a manner similar to that used to synthesise compound **1** in 72% yield; mp: 192–193 °C (ethyl acetate); δ_H (DMSO-d_6) 9.13 (s, 2H, NH), 8.12 (m, 2H), 7.65 (d, $J = 8.7$ Hz, 4H), 7.54 (m, 2H), 7.22 (d, $J = 8.7$ Hz, 4H), 6.81 (d, $J = 8.4$ Hz, 2H) and 6.74 (m, 2H); δ_C (DMSO-d_6): 155.6, 147.2, 141.2, 137.3, 131.6, 125.8, 118.6, 114.5 and 111.0; ν_{max}(KBr)/cm^{-1}: 3318, 1609, 1593 and 1509. Anal. calcd for $C_{22}H_{18}N_4S$: C, 71.33; H, 4.90; N, 15.12; S, 8.65; found: C, 71.50; H, 5.08; N, 14.93; S, 8.66.

***N*,*N*′-Bis(2-pyridyl)-4,4′-methylenebis(aminobenzene) (8).** Compound **8** was obtained from 4,4′-methylenebisaniline in a manner similar to that used to synthesise compound **1** in 82% yield; mp: 176–177 °C (ethanol); δ_H (DMSO-d_6): 8.88 (s, 2H, NH), 8.07 (m, 2H), 7.52 (d, $J = 8.4$ Hz, 4H), 7.47 (m, 2H), 7.06 (d, $J = 8.4$ Hz, 4H), 6.74 (d, $J = 8.4$ Hz, 2H), 6.65 (m, 2H) and 3.75 (s, 2H); δ_C (DMSO-d_6): 156.0, 147.3, 139.6, 137.1, 133.8, 128.7, 118.3, 113.9, 110.4 and 40.4; ν_{max}(KBr)/cm^{-1}: 3232, 3175, 1589, 1569 and 1527. Anal. calcd for $C_{23}H_{20}N_4$: C, 78.38; H, 5.72; N, 15.90; found: C, 78.13; H, 5.75; N, 15.88.

***N*,*N*′-Bis(2-pyridyl)-3,3′-methylenebis(aminobenzene) (9).** Compound **9** was obtained from 3,3′-methylenebisaniline in a manner similar to that used to synthesise compound **1** in 86% yield; mp: 156–157 °C (ethyl acetate); δ_H (DMSO-d_6): 8.94 (s, 2H, NH), 8.07 (m, 2H), 7.58 (d, $J = 7.8$ Hz, 2H), 7.48 (t, $J = 7.2$ Hz, 2H), 7.37 (s, 2H), 7.13 (t, $J = 7.8$ Hz, 2H), 6.75 (d, $J = 8.3$ Hz, 2H), 6.72 (d, $J = 7.5$ Hz, 2H), 6.66 (m, 2H) and 3.82 (s, 2H); δ_C (DMSO-d_6): 156.1, 147.4, 141.9, 137.6, 128.9, 121.4, 118.7, 116.1, 114.6, 110.9 and 41.9; ν_{max}(KBr)/cm^{-1}: 3229, 3173, 1579 and 1540. Anal. calcd for $C_{23}H_{20}N_4$: C, 78.38; H, 5.72; N, 15.90; found: C, 78.33; H, 5.85; N, 15.83.

X-Ray diffraction analysis

X-Ray diffraction studies were carried out using Kuma Diffraction KM-4 (**1**, **2**, **3α**, **3β**, **5**, **7**, **8**, **9β**) and CCD (**4**, **6α**, **6β**, **9α**) diffractometers. The data were collected at room temperature, except for **4** (100 K), and were corrected for Lorentz and polarization factors. Absorption correction (ψ-scan) was used in the case of **7**. The structures were solved by direct methods using SHELXS-97[17] and refined by the full-matrix least-squares method using the SHELXL-97 program.[18] The CH hydrogen atoms were placed geometrically, whereas the NH hydrogen atoms were located on the ΔF maps. In the analyses of **1**, **3α**, **3β**, **5**, **7** and **9α**, the positions and isotropic displacement parameters of the H-atoms were refined, whereas in the case of **4**, **6α**, **6β**, **8** and **9β**, they were allowed to ride on the pivot atom, with $U_H = 1.2U_{pivot}$. Compound **2** caused special problems due to crystal twinning. The crystals obtained from ethanol showed $a = 11.343(3)$, $b = 7.718(3)$, $c = 16.472(5)$ Å, $\beta = 91.25(3)°$, $V = 1441.7(7)$ Å^3, and many reflections had the double-peak profile indicative of twinning. The crystals obtained from acetonitrile solution showed wide peak profiles, but no double-peaks were observed for any of the reflections. The unit cell parameters are: $a = 11.352(5)$, $b = 7.702(2)$, $c = 16.435(7)$ Å, $\beta = 90.36(3)°$, $V = 1436.9(9)$ Å^3.

The diffraction data were collected from a crystal obtained from acetonitrile on a Kuma KM-4 diffractometer with Cu-Kα radiation. The structure was solved by direct methods, but refinement with the anisotropic model gave $R_1 = 0.22$, indicating the possibility of crystal twinning by a pseudo-merohedry. When the twin matrix [1 0 0 0 $\bar{1}$ 0 0 0 $\bar{1}$] was introduced into the refinement with SHELXL-97,[18] the R_1 value dropped to 0.12. However, the ΔF map calculated at this step showed relatively high electron density peaks which formed another molecule of **2**, indicating crystal disorder. This molecule was a mirror image of the refined molecule obtained by an operation of the non-crystallographic mirror plane perpendicular to x at $x = 0.25$. This second molecule was refined using a common isotropic displacement parameter for all the atoms and a rigid model derived by fitting the molecule to the peaks localized on the ΔF map. The occupancy factor for this molecule refined to 18%. The refined ratio of the two twin components was 72 : 28. The molecules in both positions are arranged in chains running parallel to the z axis. There is a considerable overlap of the molecular volumes for two such chains. However, no short intermolecular contacts have been found between these chains and surrounding 1D-networks, indicating the possible reason for the crystal disorder and twinning.

CCDC reference numbers 174152–174163. See http://www.rsc.org/suppdata/nj/b1/b108861k/ for crystallographic data in CIF or other electronic format.

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