

Solid state conformations of symmetrical aromatic biheterocycles: an X-ray crystallographic investigation

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Accurate, low temperature X-ray crystal structure determinations show that 3,3'-biquinoline (**6**), 2,2'-biquinazoline (**7**), 2,2'-biquinoxaline (**8**), 2,2'-bibenzoxazole (**10**) and 2,2'-bibenzothiazole (**11**) all exist in the solid state in centrosymmetric, planar conformations that minimise their dipole moments and maximise both conjugation between the rings and various types of attractive intermolecular associations. In contrast, 4,4'-biquinazoline (**9**) and 1,1'-bibenzotriazole (**12**) display non-planar conformations due to repulsive intramolecular interactions.

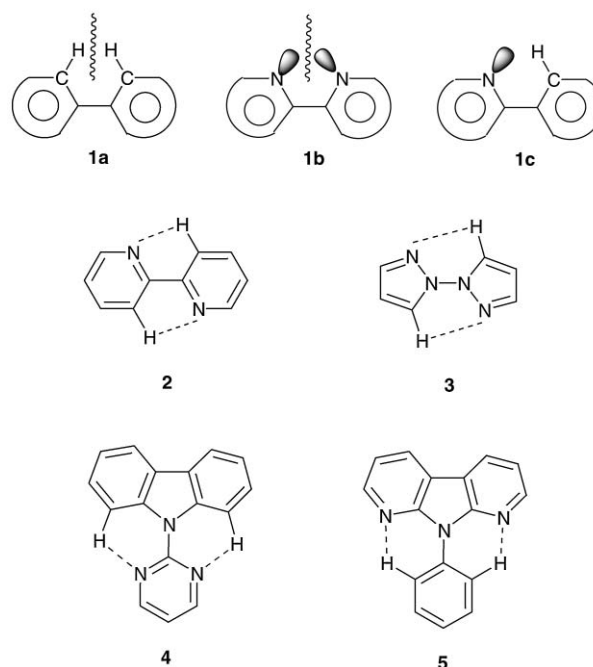
Introduction

Aromatic biheterocycles represent an important class of compounds with relevance in many areas of chemistry.¹ For example, they exist as subunits in many naturally occurring compounds and act as models for higher oligo- and poly-heterocycles.² By far their most common use, however, is as chelating (e.g. 2,2'-bipyridine) or bridging (e.g. 4,4'-bipyridine) ligands for metal coordination.³ Such metal complexes have numerous applications in inorganic, organometallic and analytical chemistry.⁴ The syntheses, structures and properties of all the parent aromatic biheterocycles have been comprehensively reviewed.¹

The conformations of biheterocycles have been the focus of much experimental and computational study.¹ From such investigations it has been proposed that the conformation about the inter-ring bond in biheterocycles is determined by the nature of the adjacent atom groupings.⁵ Specifically, two types of interactions have been identified as destabilising [*viz.* C–H...H–C (**1a**) and N...N (**1b**)] and one as stabilising [C–H...N (**1c**)]. Such arguments have been used to rationalise the *s-trans* conformations of molecules such as 2,2'-bipyridine (**2**) and 1,1'-bipyrazole (**3**).⁵ Considerable computational and experimental evidence supports the importance of these factors in the gas phase and in solution. However, we believe that these factors are likely to be much less important in the solid state. Whilst both intermolecular and intramolecular C–H...N interactions are well known to influence solid state crystal structures, these are energetically rather weak interactions.⁶ We contend that factors such as molecular packing, conjugation issues and dipole minimisation effects are much more influential in controlling the solid state conformations of such molecules.⁷ For example, biphenyl is well known to be non-planar in both the gas phase and in solution, but is strictly planar in the crystalline state,⁸ despite the presence of two repulsive interactions of type **1a**. Similarly, 2,2'-bipyrimidine is planar,⁹ but possesses only interactions of type **1b**.

Nevertheless, the conformations of biheterocycles and higher oligomers in the solid state are regularly rationalised on the basis of the above arguments. In an elegant study some years ago,¹⁰ Avendano *et al.* reported the syntheses and X-ray crystal structures of a family of aza-substituted 9-phenylcarbazoles as a test for the validity of these proposals. They interpreted the observation that the pyrimidyl derivative **4** was close to planar (torsional angle 7.4°) as strong support for the existence of intramolecular C(Ar)–H...N hydrogen bonds, despite the fact that the isomeric compound **5** was far from planar.

In the case of symmetrical biheterocycles the situation can become more complex, since by adopting an *s-trans* coplanar



conformation about the inter-ring bond, and only by doing so, the dipole moment of the molecule reduces to zero. We believe that this is a very important factor in determining the solid state conformations of such molecules. Indeed, by adopting an *s-trans* coplanar conformation the molecule not only minimises its dipole moment but also facilitates crystallisation about a crystallographic centre of inversion. This in turn allows crystallisation in a non-polar, centrosymmetric space group. Furthermore, a planar conformation allows for more efficient π - π stacking interactions between molecules, such as one of the various herringbone packing motifs common for planar aromatic molecules which crystallise in $P2_1/c$, the most common of all space groups.¹¹

In order to test the hypothesis that this factor is indeed the most important in determining solid state conformations, we herein describe the accurate, low temperature X-ray crystal structures of seven symmetrical aromatic biheterocycles. Since each of these compounds is also capable of acting as a chelating and/or bridging ligand, this study is also likely to be of interest to chemists studying the coordination and supramolecular chemistry of such ligands.

Results and discussion

The seven biheterocycles studied (**6–12**) were prepared by literature procedures and chosen for their ability to test the factors discussed above. Each could potentially exist in two planar conformations of different symmetry. Accurate X-ray crystal structure determinations of all seven compounds were performed at low temperature. 3,3'-Biquinoline (**6**), 2,2'-biquinazoline (**7**) and 2,2'-biquinoxaline (**8**) are all aza-2,2'-binaphthyls and were all found to exist in a planar conformation in the solid state (Fig. 1–3). Furthermore, each exists with an *s-trans* conformation about the inter-ring bond and crystallises about a crystallographic centre of inversion with only half a molecule in the asymmetric unit. Thus, the dihedral angles between the rings are crystallographically restricted to being 180°.

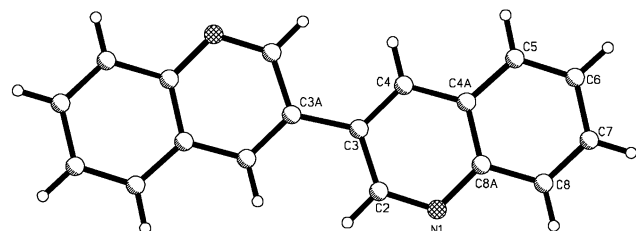
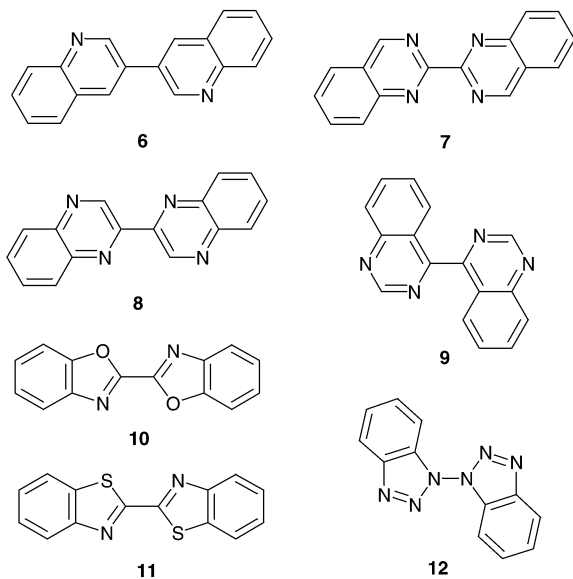


Fig. 1 Perspective view of **6**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1–C2 1.303(3), N1–C8A 1.356(3), C2–C3 1.404(3), C3–C4 1.351(3), C3–C3A 1.473(4), C4–C4A 1.391(3), C2–N1–C8A 117.1(2), N1–C2–C3 125.3(2), C4–C3–C2 116.6(2), C4–C3–C3A 123.5(3), C2–C3–C3A 119.9(3), C3–C4–C4A 120.3(2), N1–C8A–C4A 122.0(2), N1–C8A–C8 118.1(2).

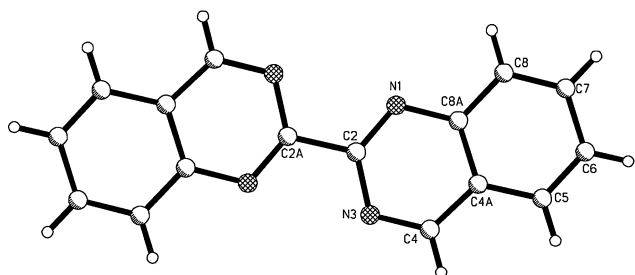


Fig. 2 Perspective view of **7**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1–C2 1.318(3), N1–C8A 1.371(3), C2–N3 1.379(2), C2–C2A 1.507(4), N3–C4 1.312(3), C2–N1–C8A 116.29(2), N1–C2–N3 127.2(2), N1–C2–C2A 117.4(2), N3–C2–C2A 115.4(2), C4–N3–C2 116.4(2), N3–C4–C4A 122.8(2), N1–C8A–C4A 121.3(2).

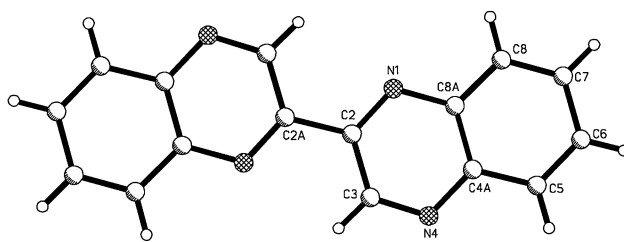


Fig. 3 Perspective view of **8**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1–C2 1.318(1), N1–C8A 1.370(1), C2–C3 1.421(2), C2–C2A 1.478(2), C3–N4 1.313(1), N4–C4A 1.368(1), C2–N1–C8A 116.6(1), N1–C2–C3 121.6(1), N1–C2–C2A 118.2(1), C3–C2–C2A 120.3(1), N4–C3–C2 123.5(1), C3–N4–C4A 115.96(9), N4–C4A–C5 119.5(1), N4–C4A–C8A 121.1(1), N1–C8A–C8 119.7(1), N1–C8A–C4A 121.20(9).

Both possible planar conformations of the biquinoline (**6**) have two interactions of type **1a** and this compound would therefore be expected to be non-planar. Similarly, the biquinoxaline (**7**) can only have interactions of type **1b** in a planar form and again would be expected to be non-planar. In contrast the biquinoxaline (**8**) could have two very different planar conformations, one with only interactions of type **1c** (as is found to be the case) and another with one type **1a** and one type **1b** interaction. The fact that all three compounds are found to exist in planar centrosymmetric conformations in the solid state supports our contention these types of interactions are not the most important in determining the solid state conformation. We believe that these structures are favoured as they represent the only conformations with no dipole moments and that the resulting planar conformations maximise energetically favourable intermolecular forces.

This is supported by inspection of the molecular packing, which is very similar for all three compounds. Fig. 4 shows a packing diagram for compound **6**. The molecules pack in a γ -herringbone manner¹¹ with the molecules packed along the *b*-axis of the unit cell. The molecules are arranged with each quinoline ring stacked on top of another, but offset so that the linking carbon atom lies over the centre of an adjacent benzo-fused ring. It has been proposed that such offset stacking maximises the electrostatic attraction between coplanar aromatic systems.¹² The distances between the mean-planes in the structures of **6**, **7** and **8** are 3.398(5), 3.410(4) and 3.428(3) Å, respectively, which are similar to the distance between the planes of carbon atoms in graphite (3.35 Å). The γ -herringbone pattern also allows edge-to-face interactions to occur between molecules of adjacent stacks. These C–H \cdots π interactions lie in the range 2.7–2.9(5) Å, which are typical values for these types of interactions.¹³ The angles between the molecules of adjacent stacks varies from 64°, in the structures of **6** and **7**, to 80° for **8**.

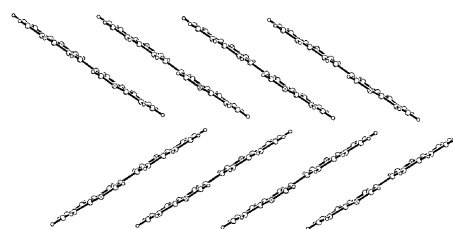


Fig. 4 View of the packing of **6**, showing π - π stacking and edge-to-face interactions.

In contrast to the planar structures found for compounds **6–8**, 4,4'-biquinazoline (**9**) is non-planar in the solid state (Fig. 5). This is in direct conflict with the predictions discussed in the Introduction, since a centrosymmetric planar conformation would facilitate two C–H \cdots N interactions, similar to those depicted in the structure of **4**. This aza-1,1-binaphthyl again crystallises with only half a molecule in the asymmetric unit, but

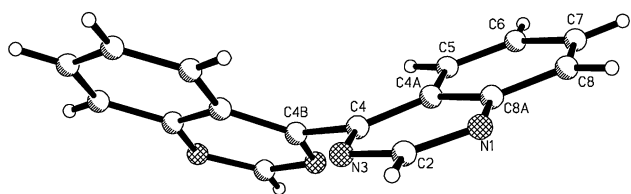


Fig. 5 Perspective view of **9**, with atomic labelling shown. Selected bond lengths (Å) and angles (°): N1–C2 1.318(4), N1–C8A 1.377(4), C2–N3 1.362(4), N3–C4 1.322(4), C4–C4A 1.436(4), C4–C4B 1.503(6), C2–N1–C8A 116.1(3), N1–C2–N3 127.7(3), C4–N3–C2 117.2(3), N3–C4–C4A 121.7(3), N3–C4–C4B 116.1(3), C4A–C4–C4B 122.2(3), N1–C8A–C4A 121.3(3).

this time about a two-fold rotation axis. The angle between the mean-planes of the quinazoline rings is $50.9(1)^\circ$.¹⁴

Once again, there is π – π stacking between adjacent molecules (Fig. 6) with the mean-planes of the quinazoline rings separated by 3.531(5) Å, indicating a slightly weaker interaction than for the planar molecules described above. Also, there are no edge-to-face C–H... π intermolecular interactions between adjacent chains of molecules in this case. We believe that the centrosymmetric planar structure **9a** is actually destabilised by the C–H...N interaction shown, as this arrangement of an aza-1,1'-binaphthyl brings these atoms closer than the energy minimum for such an interaction. Support for this proposal comes from the observation that an analogous, complementary interaction exists in 8,8'-biquinoline (**13**), which is also non-planar in the solid state (angle between planes = 98.6°).¹⁵

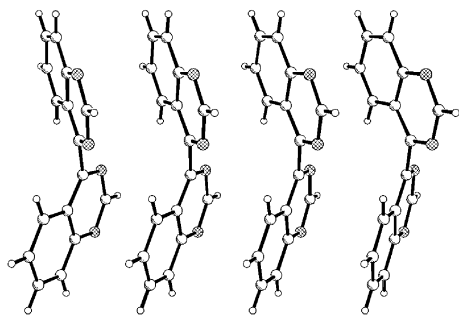
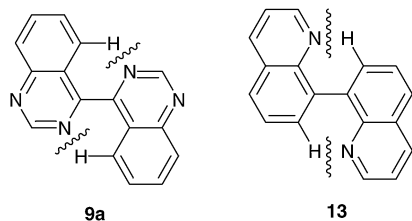


Fig. 6 View of the packing of **9**.

We next turned our attention to the bibenzazoles (**10–12**). 2,2'-Bibenzoxazole (**10**) and 2,2'-bibenzothiazole (**11**) both crystallise in a planar conformation about a crystallographic centre of inversion (Fig. 7, 8), with a crystallographically imposed dihedral angle between the rings of 180° . During the course of this study the room temperature X-ray structure of **10** was reported by other workers,¹⁶ but is included here for strict comparison under identical conditions to the other compounds. Once again, these centrosymmetric planar conformations maximise conjugation between the ring systems, minimise the dipole moments and facilitate the strongest intermolecular stacking interactions. Both compounds pack in a γ -herringbone manner with π – π stacking of adjacent molecules separated by 3.386(4) and 3.620(5) Å for **10** and **11**, respectively. There are also edge-to-face C–H... π interactions (<3.0 Å) between adjacent stacks of molecules.

1,1'-Bibenzotriazole (**12**) crystallises in the chiral orthorhombic space group $P2_12_12_1$, with the asymmetric unit containing

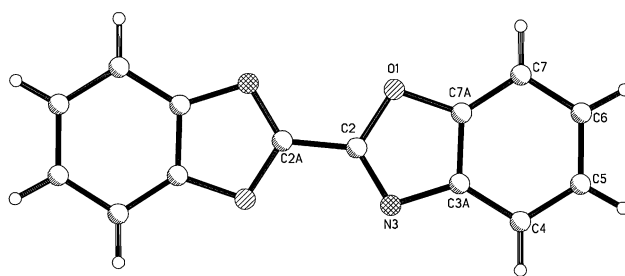


Fig. 7 Perspective view, with atom labelling, of **10**. Selected bond lengths (Å) and angles (°): O1–C7A 1.388(2), C2–N3 1.301(2), N3–C3A 1.396(3), C3A–C7A 1.378(3), C5–C6 1.391(3), C7A–C7 1.373(3), O1–C2 1.352(3), C2–C2' 1.449(4), C3A–C4 1.399(3), C4–C5 1.378(3), C6–C7 1.391(3), C7A–O1–C2 103.4(2), N3–C2–O1 116.7(2), C2–N3–C3A 103.0(2), C3A–C7A–O1 107.3(2).

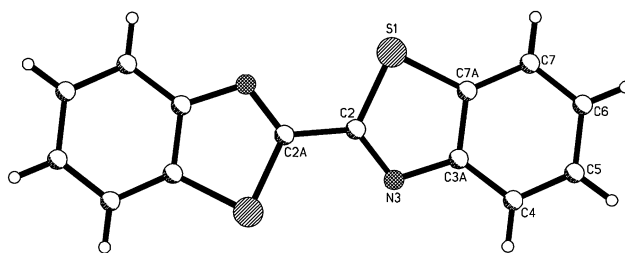


Fig. 8 Perspective view, with atom labelling, of **11**. Selected bond lengths (Å) and angles (°): S1–C2 1.741(2), S1–C7A 1.730(2), C2–N3 1.300(3), C2–C2' 1.459(4), N3–C3A 1.390(2), C3A–C7A 1.408(3), C5–C6 1.401(3), C7–C7A 1.400(3), C3A–C4 1.397(3), C4–C5 1.375(3), C6–C7 1.378(3), C7A–S1–C2 88.12(9), N3–C2–S1 117.6(2), C2–N3–C3A 109.2(2), C3A–C7A–S1 110.0(1).

one full molecule. Both rings of the ligand are planar [mean deviation from the plane = 0.005(1) Å for both rings], and are very nearly orthogonal to each other [$84.5(1)^\circ$] (Fig. 9). This non-planar conformation is not expected on the basis of the types of interaction discussed in the Introduction, as a centrosymmetric planar conformation would have two C–H...N interactions similar to those found in compound **4**. As before, we believe that fusion of the benzo-rings adjacent to the inter-ring bond disfavors a planar conformation.

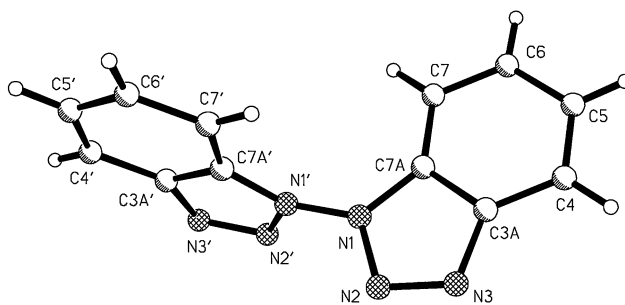


Fig. 9 Perspective view, with atom labelling of the contents of the asymmetric unit, of **12**. Selected bond lengths (Å) and angles (°): N1–N2 1.366(5), N2–N3 1.304(5), C3A–C7A 1.398(6), C7A–N1 1.377(5), N1–N1' 1.366(5), N1'–N2' 1.391(5), N2'–N3' 1.294(5), C3A'–C7A' 1.387(6), C7A'–N1' 1.379(5), N1–N2–N3 106.9(3), N2–N1–C7A 128.0(4), N1'–N2'–N3' 107.6(3).

The molecular packing of **12** is intriguing and involves a complex system of intermolecular interactions. As shown in Fig. 10, significant interactions connect adjacent molecules related by all three orthogonal screw axes. Molecules related by the two-fold screw axis in the a -direction exhibit head-to-tail π – π stacking with a separation of $ca.$ 3.41 Å. Two sets of interactions connect molecules along the b -axis; the first is a face-to-face stacking interaction between molecules related by a screw axis and the second is a C–H...N (2.56 Å) interaction between molecules in adjacent units cells. Finally, the above chains of

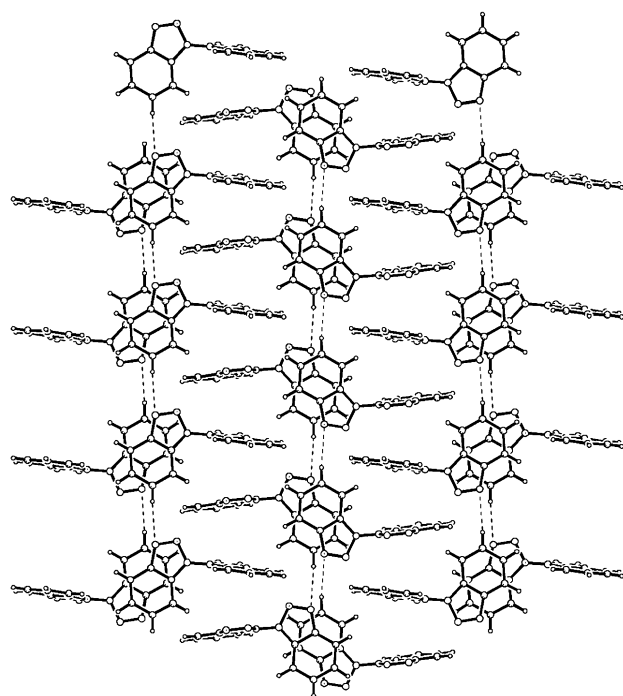


Fig. 10 View of the molecular packing down the *a*-axis in the crystal structure of **12**.

molecules are connected along the *c*-axis by interdigitation of the π - π stacking. The combined effects of these numerous intermolecular interactions are almost certainly sufficient to override the weaker intramolecular interactions discussed above.

Conclusions

The X-ray crystal structures of the seven symmetrical bi-heterocycles **6–12** support our contention that the solid state conformations of such compounds are dominated by a proclivity to adopt a planar centrosymmetric structure. This serves to maximise conjugation between the rings, minimise the dipole moment and maximise favourable intermolecular interactions and is sufficient to override other (weaker) intramolecular interactions. However, for molecules containing benzo-fused rings adjacent to the inter-ring bond, repulsive interactions exist that lead to non-planar conformations.

Experimental

Sample preparations

3,3'-Biquinoline (**6**) was synthesised by the homocoupling of 3-bromoquinoline, following the procedure of Hassan *et al.*,¹⁷ and recrystallised from methanol. 2,2'-Biquinazoline (**7**) was prepared by the ring closing reaction of ammonia with *N,N'*-(*di-*o**-formylphenyl)oxanilide, following the method of Armarego and Willette,¹⁸ which directly furnished crystals suitable for structure determination. 2,2'-Biquinoxaline (**8**) was synthesised using the method of Chupakhin *et al.*,¹⁹ and was crystallised by diffusion of methanol into a dichloromethane solution of the compound. 4,4'-Biquinazoline (**9**) was synthesised using the method of Armarego and Willette,¹⁸ by reaction of quinazoline with sodium cyanide, followed by oxidation of the intermediate with manganese dioxide. Crystals suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of the compound. 2,2'-Bibenzoxazole (**10**) and 2,2-bibenzothiazole (**11**) were prepared by polyphosphoric acid-induced cyclocondensation reactions of diethyl oxalate with 2-aminophenol and 2-aminothiophenol, respectively, according to literature procedures.^{20,21} X-Ray quality crystals were obtained by recrystallisation from chloroform and dioxane,

Table 1 Crystal data and X-ray experimental data for compounds **6–12**

Compound	6	7	8	9	10	11	12
Collection device	CCD	CCD	CCD	CCD	P4s	P4s	CCD
Empirical formula	C ₁₈ H ₁₂ N ₂	C ₁₆ H ₁₀ N ₄	C ₁₆ H ₁₀ N ₄	C ₁₆ H ₁₀ N ₄	C ₁₄ H ₈ N ₂ O ₂	C ₁₄ H ₈ N ₂ S ₂	C ₁₂ H ₈ N ₆
Formula weight	256.30	258.28	258.28	258.28	236.22	268.346	236.224
Temperature/K	163(2)	170(2)	163(2)	163(2)	163(2)	163(2)	168(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> /Å	8.964(6)	8.557(4)	5.779(3)	22.523(17)	4.627(1)	8.993(1)	7.277(3)
<i>b</i> /Å	6.265(4)	6.330(3)	5.350(3)	3.912(3)	16.480(2)	5.998(1)	7.639(3)
<i>c</i> /Å	11.241(8)	11.841(5)	18.906(10)	6.979(5)	7.004(1)	11.445(2)	19.940(8)
β /°	107.109(18)	106.689(6)	91.466(7)	106.140(10)	94.34(1)	110.87(1)	90
Volume/Å ³	603.3(7)	614.4(5)	584.3(5)	590.6(7)	535.5(2)	575.9(2)	1108.5(7)
<i>Z</i>	2	2	2	2	2	2	4
Density (calc.)/Mg m ⁻³	1.411	1.396	1.468	1.452	1.473	1.548	1.416
Abs. coefficient/mm ⁻¹	0.084	0.087	0.092	0.091	0.101	0.441	0.094
<i>F</i> (000)	268	268	268	268	244	276	488
Crystal size/ μ m	350 × 250 × 10	750 × 250 × 120	300 × 300 × 150	590 × 200 × 50	340 × 220 × 180	770 × 210 × 130	510 × 250 × 160
θ range/°	2.57–25.05	2.61–26.46	2.16–26.36	3.04–25.20	2.47–26.00	2.42–26.99	2.86–25.05
Reflections collected	6814	7439	6979	3477	1733	1618	13016
Independent data [<i>R</i> (int)]	1070 [0.068]	1253 [0.030]	1190 [0.013]	619 [0.082]	1044 [0.035]	1261 [0.027]	1170 [0.098]
Observed data [<i>I</i> > 2 σ (<i>I</i>)]	532	891	954	466	741	964	929
Data/parameters	1070/92	1253/91	1190/91	619/92	1044/82	1261/82	1170/163
Goodness-of-fit on <i>F</i> ²	0.843	1.026	1.064	0.965	0.920	0.928	1.146
<i>wR</i> ₂ (all data)	0.1043	0.1328	0.1112	0.1082	0.1126	0.0876	0.1331
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0433	0.0547	0.0359	0.0457	0.0441	0.0342	0.0558

respectively. 1,1'-Bibenzotriazole (**12**) was obtained from 2,2'-diaminoazobenzene by diazotisation followed by reductive cyclisation, as described by Harder *et al.*,²² and was recrystallised from ethyl acetate.

X-Ray crystallography

The crystal data, data collection and refinement parameters are given in Table 1. Measurements were made with a Bruker CCD area detector or a Siemens P4s four-circle diffractometer using graphite monochromatised Mo K α ($\lambda = 0.71073$ Å) radiation. The intensities were corrected for Lorentz and polarisation effects and for absorption. The structures were solved by direct methods using SHELXS,²³ and refined on F^2 using all data by full-matrix least-squares procedures using SHELXL-97.²⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in calculated positions with isotropic displacement parameters 1.2 times the isotropic equivalent of their carrier carbon atoms. The functions minimised were $\Sigma w(F_o^2 - F_c^2)$, with $w = [\sigma^2(F_o^2) + aP^2 + bP]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]/3$. The bonding geometries within the individual rings of the various compounds were all found to be similar to those observed in structurally related compounds containing the same ring systems.²⁵

Crystallographic data, as CIF files, have been deposited with the Cambridge Crystallographic Data Centre; CCDC reference numbers 253922–253928. See <http://www.rsc.org/suppdata/ob/b4/b416553e/> for crystallographic data in .cif format.

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