Edge-to-edge aryl C−H···N dimer: a new supramolecular synthon

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Study of the lattice packing in the crystal structures of the diquinoline compounds 1 [$C_{23}H_{18}N_2$, $P\bar{1}$, $a = 6.1953(8)$, $b = 11.427(2)$, $c = 12.686(2)$ Å, $\alpha = 108.428(7)$, $\beta = 92.189(8)$, $\gamma = 103.437(7)^\circ$, $Z = 2$, $R = 0.038$] and 2·CHCl$_3$ [$C_{23}H_{16}Br_2N_2\cdot CHCl_3$, $P2_1/c$, $a = 9.865(3)$, $b = 15.307(3)$, $c = 17.946(5)$ Å, $\beta = 122.12(1)^\circ$, $Z = 4$, $R = 0.031$] reveals a previously unrecognised mode of intermolecular attraction which we term the edge-to-edge aryl C−H··· N dimer. Examination of the Cambridge Structural Database shows that this type of contact is present in a wide range of nitrogen-containing aromatic solids. In all 54 identified cases the two weak intermolecular hydrogen bonds are identical producing a symmetrical dimer and, in all cases but one, the arrangement created is centrosymmetric. Hence this new packing mode represents a predictable new synthon for supramolecular assembly.

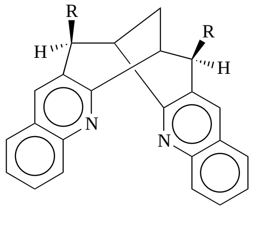
Introduction

Supramolecular chemistry has been described as ‘the designed chemistry of the intermolecular bond’.[1] Hence it is important for chemists to develop a close understanding of the weak forces operating between molecules and to learn how to use and even control them. Specific types of intermolecular attraction, for example, the cyclic hydrogen bonding arrangement present within a carboxylic acid dimer, are the supramolecular equivalents of conventional synthons in covalent bond-forming chemistry.[2,3] Therefore the identification of new classes of non-covalent attractions and the discovery of their roles in molecular assembly are central to progress in this field.[4–7]

The edge-to-edge aryl C−H···N dimer is a previously unrecognised mode of contact which is present in a wide range of aromatic heterocycles. We first observed this supramolecular synthon in the crystal structures of the diquinoline compounds[8] **1** and **2**·CHCl$_3$ and we report here on the general occurrence and implications of this intermolecular contact in the solid state.

Results and discussion

As part of a wider crystal engineering investigation into the design of new lattice inclusion hosts we required the V-shaped molecules **1** and **2**. The reaction of bicyclo[3.3.1]nonane-2,6-dione and *o*-aminobenzaldehyde by means of a Friedländer reaction[9] afforded the diquinoline derivative **1** easily and in 74% yield. Subsequent bromination using *N*-bromosuccinimide then produced specifically, in 71% yield, the *exo,exo*-dibromide **2**.



1 R = H
2 R = Br

The crystal structures of the racemic diquinoline derivatives **1** and **2**·CHCl$_3$ reveal that these V-shaped molecules fit together efficiently in the solid state. Numerical details of the solution and refinement of these structures are presented in Table 1.

Aryl face-to-face interactions, as observed in many aromatic compounds,[10,11] are the most immediately obvious packing mode present in solid **1**. Hence the *exo*-faces of two enantiomeric molecules contact each other by means of a parallel but offset π···π interaction. The resulting interplanar distance (3.84 Å) is significantly longer than usual (*ca.* 3.4–3.5 Å) due to the additional presence of two identical alkyl CH···π contacts. In these interactions the benzylic *exo*-hydrogen atoms are directed towards the benzo ring of the other quinoline partner with resulting H···C contacts of 3.05–3.12 Å. The net effect of these two complementary types of interactions, illustrated in Fig. 1, must be more favourable than just a shorter aryl π···π contact alone, since this could have been attained simply by mutually sliding the rings away from the benzylic hydrogens.

Molecules of the same chirality make another benzylic CH···π contact to the *endo*-face of a benzo ring of **1** with H···C distances of 2.83–3.30 Å (Fig. 2). Two molecules of **1** with the same chirality also form an aryl CH···π edge-to-face interaction as shown in Fig. 3.

In addition to the above contacts, an unexpected intermolecular motif was observed whereby two molecules of **1**, positioned edge-to-edge, form the centrosymmetric aryl C−H···N dimer illustrated in Fig. 4. This arrangement has aryl C−H···N and aryl C···N distances of 2.56 and 3.55 Å, respectively.

The relatively small changes in molecular structure caused by the bromine atoms in **2** result, as expected, in significant alterations to the lattice packing. The *exo*-bromo atoms rule out the *exo*-benzylic CH···π interactions present in solid **1**. Consequently racemic **2** packs less efficiently as a pure solid and prefers instead to form lattice inclusion compounds.[8] The host **2** selectively traps small polyhaloalkanes (in preference to alternative guests of comparable size and shape) because of the efficient network of halogen···halogen interactions[12] which can be created between the host and guest components.

The compound **2**·CHCl$_3$, in addition to the various intermolecular attractions described previously in our communication,[8] also contains the new edge-to-edge aryl C−H···N cyclodimer (with aryl−H···N and aryl C···N distances of 2.67 and 3.65 Å, respectively).

The observation of this previously unrecognised intermolecular contact in both structures led us to use the Cambridge Structural Database (CSD)[13] to search for further examples. We considered that the essential molecular features were likely to be fairly simple and general, namely a 1,3-*peri* arrangement of an aryl C−H and a nitrogen lone pair (see Fig. 4). However, initially we defined search parameters specify-

Table 1 Numerical details of the solution and refinement of the structures

Compound	**1**	**2**·$CHCl_3$
Formula	$C_{23}H_{18}N_2$	$C_{23}H_{16}Br_2N_2\cdot CHCl_3$
Formula mass	322.4	599.6
Crystal description	{001}{011}(−730) (7−30)	(100){010}{011} {01−1}(−101)(1−1−1) (11−1)(10−2)
Space group	$P\bar{1}$	$P2_1/c$
a/Å	6.1953(8)	9.865(3)
b/Å	11.427(2)	15.307(3)
c/Å	12.686(2)	17.946(5)
α/°	108.428(7)	(90)
β/°	92.189(8)	122.12(1)
γ/°	103.437(7)	(90)
V/Å^3	822.6(2)	2295(1)
T/°C	21(1)	21(1)
Z	2	4
D_{calc}/g cm^{-3}	1.30	1.73
Radiation, λ/Å	Cu-Kα, 1.5418	Mo-Kα, 0.7107
μ/cm^{-1}	5.54	38.6
Crystal dimensions/mm	0.40 × 0.35 × 0.08	~0.28 × 0.12 × 0.15
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max}$/°	140	50
ω scan angle	$0.60 + 0.15 \tan \theta$	$0.50 + 0.35 \tan \theta$
No. of intensity measurements	3083	4458
Criterion for observed reflection	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$
No. of indep. obsd. reflections	2567	2571
No. of reflections (m) and	2567	2571
variables (n) in final refinement	227	280
$R = \Sigma^m\lvert\Delta F\rvert/\Sigma^m\lvert F_o\rvert$	0.038	0.031
$R_w = [\Sigma^m{}_w\lvert\Delta F\rvert^2/\Sigma^m{}_w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.068	0.036
$s = [\Sigma^m{}_w\lvert\Delta F\rvert^2/(m-n)]^{\frac{1}{2}}$	2.64	1.13
Crystal decay	none	1–0.96
Max., min. transmission coefficients	0.96, 0.84	0.69, 0.60
R for (no.) multiple measurements	—	0.013 (338)
Largest peak in final diff. map/e Å^{-3}	0.22	0.55
Extinction correction	1.12×10^{-3}	—

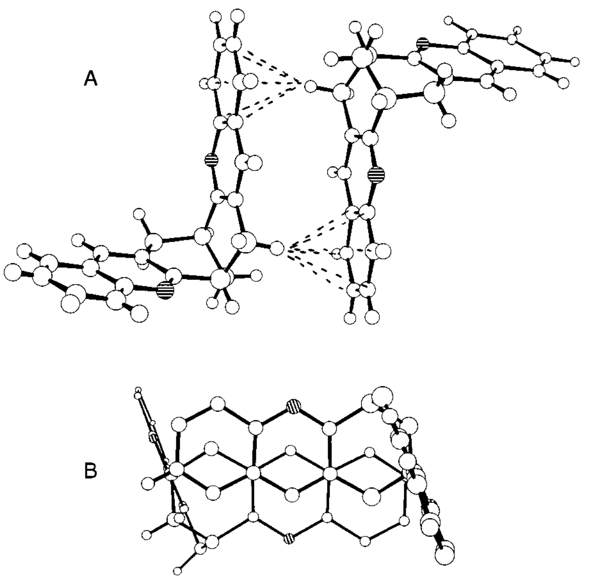


Fig. 1 Parallel offset π···π interaction (3.84 Å) and benzylic C–H···π interactions (dashed lines: 3.05–3.12 Å) present between the *exo*-faces of two molecules of **1** with opposite chirality. Diagram (A) shows a side view of these joint interactions, while (B) shows the overlap of the aromatic rings. Aromatic hydrogen atoms are omitted from the latter diagram for clarity. In these and subsequent figures the nitrogen atoms are designated by hatching.

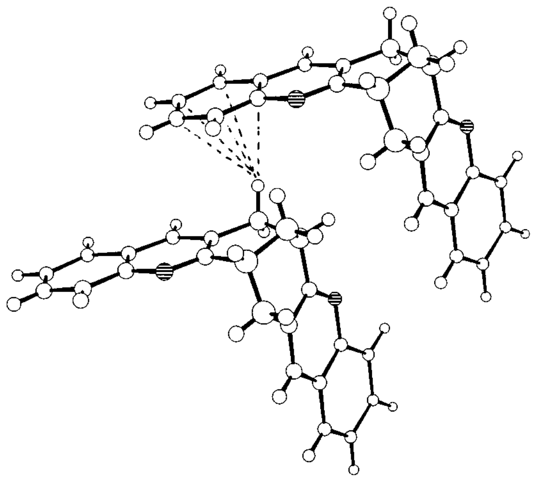


Fig. 2 Benzylic C–H···π contact present between molecules of **1** with the same chirality. Here the benzylic *exo*-hydrogen atom interacts (dashed lines: 2.83–3.30 Å) with the *endo*-face of a benzo ring of the neighbouring diquinoline **1** molecule.

ing just a quinoline sub-structure participating as a dimer with each C···N intermolecular separation being under 3.70 Å (though not necessarily of equal length). The aryl hydrogen atom was omitted at this stage in order to detect any structures where the hydrogen atom position had not been reported.

This search gave the histogram shown in Fig. 5 which indicated maxima for both low and high angles (simply called 'angle' in Tables 2–5) between the C···N vector of the intermolecular contact and the normal to the plane of the benzo group containing this C atom. The former (69 hits within 0–40°) represents face-to-face packing, whereas the latter (20 hits listed in Table 2, after including our data for **1** and CSD data for **2**·$CHCl_3$, within 60–90°) represents the new interaction. An exactly planar cyclodimer corresponds to the 90° case.

The structure **2**·$CHCl_3$ contains two different face-to-face π···π interactions as illustrated in Fig. 6(A). One of these [3.46 Å; Fig. 6(B)], the interaction between the *endo*-faces of two molecules, involves overlap of carbon atoms but not nitro-

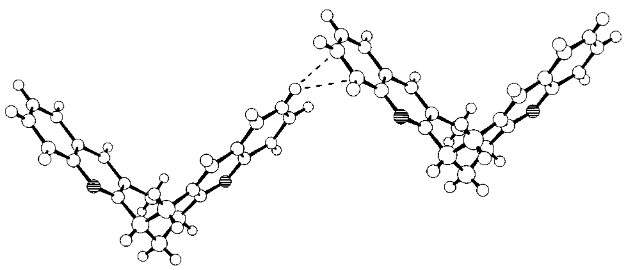


Fig. 3 Edge-to-face Ar–H · · · π interaction (dashed lines: 2.81–2.85 Å) present between two molecules of **1** with the same chirality

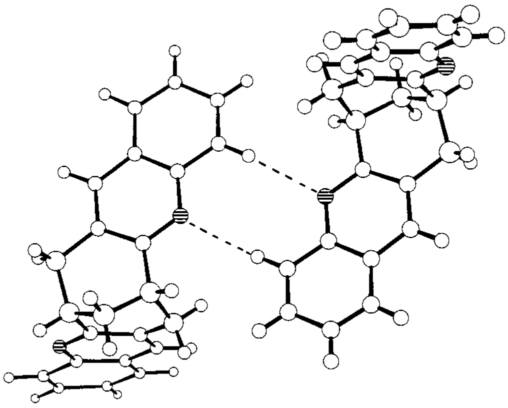


Fig. 4 Centrosymmetric edge-to-edge aryl C–H · · · N dimer present between molecules of **1**. The weak hydrogen bonds are indicated here by dashed lines.

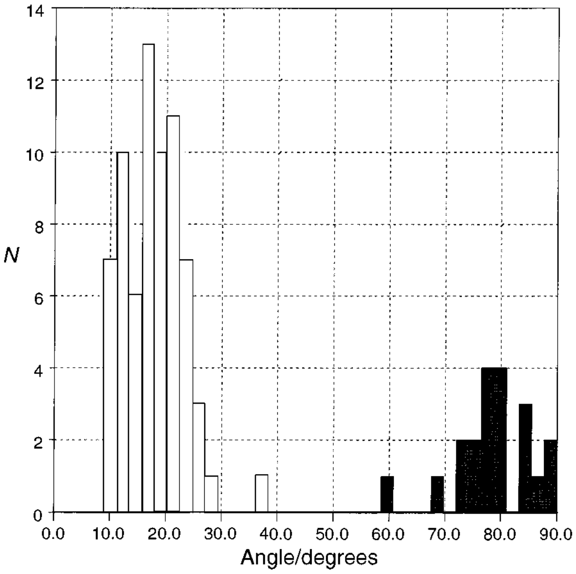


Fig. 5 Plot of the number of aryl C–H · · · N interactions present between quinoline sub-structures *vs.* the angle between the C · · · N vector of the intermolecular contact and the normal to the plane of the benzo group containing this C atom. The data for angles between 60–90° (black bars) correspond to the edge-to-edge cyclodimer structures detailed in Table 2.

gens. The second interaction [3.40 Å; Fig. 6(C)] operates between the *exo*-faces of two molecules and involves overlap of both carbon and nitrogen atoms. Hence this compound demonstrates both the modes of intermolecular C · · · N contact present in the histogram: the second π · · · π case just described, plus the edge-to-edge aryl C–H · · · N cyclodimer.

Quinoline derivatives are expected to favour face-to-face packing in the solid state but of the 260 structures reported in the CSD only the 69 'low angle' cases above (Fig. 5) showed overlap of carbon and nitrogen atoms under 3.70 Å, similar to Fig. 6(C). Some 70% of these low angle cases involved quinoline–metal complexes which clearly could not form the cyclodimer. Other significant groups of compounds had a protonated nitrogen, or did not have a *peri*-hydrogen atom, and these also were incompatible with the cyclodimer structural requirements. In fact, just three of these 69 hits could conceivably be successful. First, as just described, **2**·$CHCl_3$ (PORCOO[8]) actually exhibits both modes of C · · · N contact. Secondly, SIVZEC[14] apparently could work but the presence of an intramolecular O–H · · · N hydrogen bond rules out cyclodimer formation. Only in the third case, WACGEM,[15] does low angle face-to-face interaction occur as a genuine preference to potential cyclodimer formation. These observations suggested

Table 2 Compounds containing a quinoline part-structure which participates in the edge-to-edge aryl C–H · · · N dimer interaction

CSD refcode	Aryl C · · · N distance/Å	Aryl–H · · · N distance/Å	Angle/°
ACRDIN	3.60	*a*	73.9
BIWVUY	3.49	2.44	83.3
DAYDEM	3.68	*a*	86.1
DIGRUG	3.48	2.58	74.4
FUJSEI	3.59	2.59	78.2
GIGCEE	3.54	2.54	68.7
LICBII	3.61	2.90	60.7
MAPANA	3.61	2.80	75.9
PABPOX	3.67	2.73	85.0
PORCOO[8] (**2**·$CHCl_3$)	3.65	2.67	89.0
RABHIH	3.52	*a*	90.0
SAXKOR	3.55	2.65	80.8
SAXKUX	3.60	2.55	78.2
VUGZOM	3.53	2.57	79.1
WERXIA	3.69	2.69	76.6
WERXOG	3.66	2.66	78.8
WERXUM	3.64	2.80	77.8
ZENNOW	3.52	2.53	74.2
ZOKTEY	3.53	*a*	79.8
1	3.55	2.56	84.2

[a] Hydrogen position not reported.

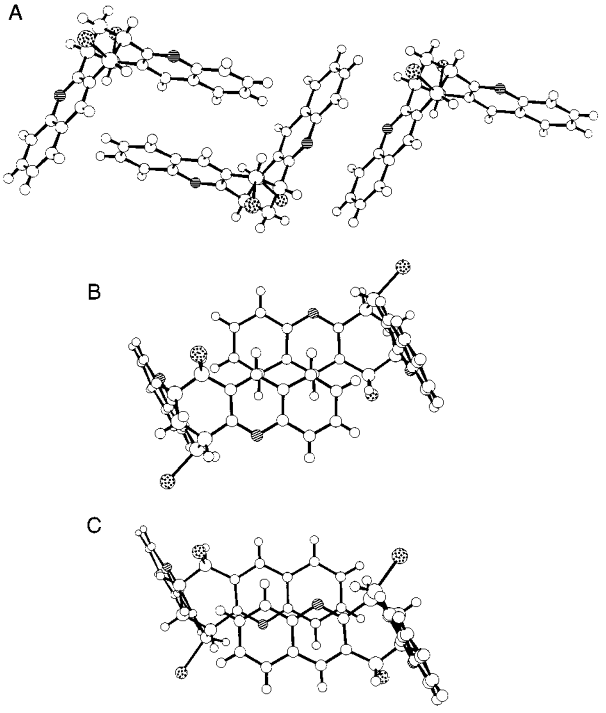


Fig. 6 (A) The two modes of parallel face-to-face π · · · π contact present between molecules of **2**; (B) overlap of ring carbon atoms between two *endo*-faces (3.46 Å); (C) overlap of ring nitrogen and carbon atoms between two *exo*-faces (3.40 Å). Bromine atoms are here indicated by heavy dots.

Table 3 Compounds containing a quinoline part-structure with an additional heteroatom in the heterocyclic ring, which also form the edge-to-edge aryl C−H · · · N dimer

CSD refcode	Aryl C · · · N distance/Å	Aryl–H · · · N distance/Å	Angle/°
BECNUS02	3.67	2.79	71.1
CANJUW	3.48	2.50	78.3
CORCOB	3.57	*a*	79.4
CRQZMC	3.52	*a*	86.6
DIBFEZ	3.59	2.78	73.3
FOCBUU	3.54	2.68	73.1
HAPKIS	3.59	2.52	84.6
JABDIZ	3.64	*a*	84.8
JUXWAA	3.70	2.73	73.2
KEYNOR	3.60	2.66	80.3
MISALX	3.57	2.66	85.9
PHENAZ01	3.67	2.83	71.2
QUAXDS	3.58	2.53	83.6
SACRET01	3.51	2.58	76.1
TRYTAN	3.62	2.61	78.3
VOWFIW	3.56	2.67	81.7
WEBFUE	3.66	2.62	89.7
WEFFAO	3.47	2.51	88.4
YOVVOU	3.52	*a*	88.4
ZEHHEZ	3.67	2.66	80.9
ZENBEZ	3.65	2.75	78.6
ZIVQOK	3.65	2.73	84.2

[a] Hydrogen position not reported.

Table 4 Heteroaromatic compounds containing fused benzo and 5-membered rings, which also exhibit the edge-to-edge aryl C−H · · · N dimer

CSD refcode	Aryl C · · · N distance/Å	Aryl–H · · · N distance/Å	Angle/°
BAZDOV	3.51	2.70	67.0
FAXVIJ	3.51	2.51	87.6
FOBCOO	3.62	2.73	71.4
HATYAC	3.56	2.65	78.8
JOSVOC	3.54	2.59	87.6
VAKMUP	3.65	*a*	89.3
YOSZOV	3.50	2.59	80.5

[a] Hydrogen position not reported.

Table 5 Compounds containing a phenyl ring conjugated to an imine substituent, which also exhibit the edge-to-edge aryl C−H · · · N dimer motif

CSD refcode	Aryl C · · · N distance/Å	Aryl–H · · · N distance/Å	Angle/°
CAZCAH	3.53	*a*	69.6
DIJXUP	3.63	2.62	77.1
GEXKUP	3.65	2.77	75.8
POHFUN	3.63	*a*	89.9
ZEPPAL01	3.59	2.70	72.7

[a] Hydrogen position not reported.

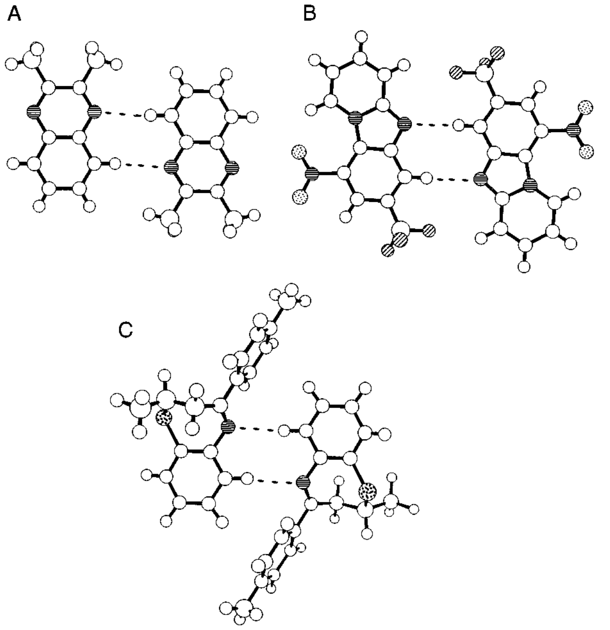


Fig. 7 Representative examples of the edge-to-edge aryl C−H · · · N dimer identified from the CSD and belonging to the structural classes presented in Tables 3–5. The following atom codes are used: nitrogen (horizontal hatching), fluorine (diagonal hatching), oxygen (light dots) and sulfur (heavy dots). (A) KEYNOR, 2,3-dimethylquinoxaline; (B) FAXJIV, 9-nitro-7-(trifluoromethyl)pyrido[1,2-*a*]benzimidazole; (C) DIXJUP, 2-methyl-4-(*p*-tolyl)-2,3-dihydro-1,5-benzothiazepine.

that the cyclodimer was likely to be both a favourable and predictable mode of intermolecular assembly.

The CSD search was then broadened to use two *N*-substituted benzene fragments, specifying a two-coordinate nitrogen atom but with its type of bonding undefined. These fragments were arranged as a dimer with the same C · · · N separation limit of 3.70 Å as before. An additional 34 hits were now recorded within the 60–90° angle window.

The 22 examples detailed in Table 3 describe molecules which involve a quinoline core incorporating an additional non-carbon atom in the heteroaromatic ring (such as quinazoline, quinoxaline or phenathiazine derivatives). Hence the 42 cases presented in Tables 2 and 3 all involve partial structures comprising fused benzo and six-membered aromatic rings.

Table 4 lists the seven examples found where the core unit involves fused benzo and five-membered rings (*e.g.* benzothiazole, benzimidazole, indole and benzoxazole derivatives), and Table 5 lists the five examples involving conjugated phenyl imine systems (with the imine C=N being either part of a further ring or acyclic). Fig. 7 illustrates one typical case of the dimeric interaction selected from each of Tables 3–5.

The majority of papers cited here only considered the molecular structure of the compounds reported and, even in those cases where intermolecular contacts were discussed, no comment was made on the existence of the dimeric aryl C−H · · · N synthon. The C−H · · · N interaction is regarded as a weak hydrogen bond[16,17] and it may simply have been overlooked in these cases, despite the aryl C−H · · · N≡C interaction having been recognised and employed as a construction unit by Desiraju and co-workers.[18] However, although the dimeric interaction is a relatively long-range intermolecular contact, it certainly is a favourable and significant contributor to the lattice packing of these molecules.

Conclusions

Note especially that all of the 54 identified examples above involve symmetrical structures with two identical aryl C−H · · · N and two identical aryl C · · · N distances. However, there does not appear to be any fundamental reason why this must be so. It is possible to imagine, for example, an effective unsymmetrical aryl C−H · · · N cyclodimer arising from hydrogen bonding between two quite different molecules or part-structures.

All of these dimeric structures are centrosymmetric, with the exception of DIGRUG which has a two-fold axis relating the two molecules. Hence there is a clearly preferred arrangement in the formation of these weakly hydrogen bonded cyclodimers. Furthermore, analysis of the histogram (Fig. 5) demonstrates that the cyclodimer will usually form in preference to aryl face-to-face interaction involving overlap of both carbon and nitrogen atoms. The molecular requirements of the cyclodimer are simple and, as revealed in Table 5, the nitrogen need not necessarily be either aromatic or within a ring. This newly recognised packing mode therefore represents a versatile new supramolecular synthon for use in intermolecular assembly. An unanswered question at this stage is whether chirally pure compounds (which inherently are incapable of centrosymmetric packing) would form aryl C−H···N cyclodimers or prefer to adopt an alternative type of intermolecular contact.

Experimental

^{1}H (300 MHz) and ^{13}C (75.3 MHz) NMR spectra were recorded using a Bruker ACF300 instrument and are reported as chemical shifts (δ) relative to $SiMe_4$. The substitution of carbon atoms was determined by the DEPT procedure and coupling constants (J) were measured in hertz (Hz). Melting points were measured using a Kofler instrument and are uncorrected. Electron impact mass spectra were recorded by Dr J. J. Brophy using a VG Quattro triple quadrupole instrument. Elemental analyses were carried out at the University of New South Wales by Dr H. P. Pham.

6,7,14,15-Tetrahydro-6,14-methanocycloocta[1,2-*b*:5,6-*b*′]-diquinoline, 1

Bicyclo[3.3.1]nonane-2,6-dione[19] (1.34 g, 8.84 mmol) and *o*-aminobenzaldehyde[20] (2.35 g, 19.4 mmol) were dissolved in methanol (15 cm^3) with stirring, cooled to 0 °C, then aqueous sodium hydroxide (2 mol dm^{-3}; 2.5 cm^3) was added dropwise. The solution was allowed to warm to room temperature and stirred overnight. The crude product was filtered and recrystallised from ethyl acetate (by leaving the final solution for 5 d at −15 °C before filtration) to give white needles of **1** (2.10 g, 74%) mp 248–249 °C (Found: C, 85.85; H, 5.8; N, 8.6. $C_{23}H_{18}N_2$ requires C, 85.7; H, 5.6; N, 8.7%); ν_{max}(paraffin mull)/cm^{-1} 1620w, 1595w, 1220w, 1155w, 1140w, 1020w, 1010w, 960w, 905w; δ_H(CDCl$_3$) 2.49 (2H, s), 3.30 and 3.35 (2H, H$_{AB}$, J 16.7), 3.45 and 3.51 (2H, two d, H$_{AB}$, J 16.7 and 5.2), 3.77 (2H, br s), 7.30–7.35 (2H, m), 7.51–7.61 (6H, m), 8.00 (2H, d, J 8.5); δ_C(CDCl$_3$) 28.9 (CH$_2$), 36.3 (CH), 38.1 (CH$_2$), 125.7 (CH), 126.9 (CH), 127.3 (C), 128.2 (CH), 128.7 (CH), 136.0 (CH), 147.6 (C), 162.8 (C), one Ar quaternary peak obscured; *m/z* 323 (22%), 322 (M, 100), 321 (52), 281 (16), 180 (95), 160 (47), 143 (52), 140 (18), 115 (26).

exo,*exo*-7,15-Dibromo-6,7,14,15-tetrahydro-6,14-methanocycloocta[1,2-*b*:5,6-*b*′]diquinoline, 2

A solution of *N*-bromosuccinimide (1.40 g, 7.8 mmol) and **1** (1.00 g, 3.12 mmol) in carbon tetrachloride (150 cm^3) were refluxed for 2.5 h. The reaction mixture was cooled, filtered and the succinimide residue washed with additional carbon tetrachloride. The filtrate was evaporated and the crude solid recrystallised from acetone–water. Scratching of the flask surface was often required to induce crystallisation. Dibromide **2** was obtained as fine light yellow needles (1.06 g, 71%) mp 230–232 °C (Found: C, 57.6; H, 3.65; N, 5.5. $C_{23}H_{16}N_2Br_2$ requires C, 57.5; H, 3.4; N, 5.8%); ν_{max}(paraffin mull)/cm^{-1} 1620w, 1595w, 1265w, 1200w, 1170w, 1080s, 1015w, 990w, 950w, 925w, 815w, 780w, 770s, 750s, 715s, 675w; δ_H(CDCl$_3$) 3.20 (2H, t, J 2.9), 4.08 (2H, m), 5.79 (2H, d, J 2.0), 7.42–7.47 (2H, m), 7.63–7.71 (4H, m), 7.97 (2H, s), 8.04 (2H, d, J 8.7); δ_C(CDCl$_3$) 20.4 (CH$_2$), 44.7 (CH), 52.7 (CH), 126.9 (CH), 127.6 (CH), 128.8 (CH), 129.2 (C), 130.5 (CH), 139.1 (CH), 148.2 (C), 155.5 (C), one aromatic quaternary peak obscured; *m/z* 482 (M + 2, 0.7%), 480 (M, ^{79}Br + ^{81}Br, 1.2), 478 (M − 2, 0.7), 401 (M − ^{79}Br, 45), 321 (17), 320 (58), 319 (100), 318 (38), 160 (95), 159 (71), 146 (25).

exo,*exo*-7,15-Dibromo-6,7,14,15-tetrahydro-6,14-methanocycloocta[1,2-*b*:5,6-*b*′]diquinoline·chloroform, 2·CHCl$_3$

Recrystallisation of the dibromide **2** from chloroform gave the 1:1 inclusion compound; loss of guest over 60–75 °C, then mp 230–232 °C (Found: C, 47.9; H, 3.2; N, 4.6. $C_{23}H_{16}N_2Br_2{\cdot}CHCl_3$ requires C, 48.1; H, 2.9; N, 4.7%).

Crystallography

Structure of 1. Reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using nickel filtered copper radiation (λ 1.5418 Å). Data were corrected for absorption.[21] Reflections with $I > 3\sigma(I)$ were considered to be observed. The positions of all atoms in the asymmetric unit were readily determined by direct phasing. All hydrogen atoms were included in calculated positions and were assigned thermal parameters equal to those of the atom to which they were bonded. Positional and anisotropic thermal parameters for the non-hydrogen atoms were refined using full matrix least squares. An extinction correction was included in the final stages. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{\frac{1}{2}}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^{\,2})^{\frac{1}{2}}$. Atomic scattering factors and anomalous dispersion parameters were obtained from *International Tables for X-Ray Crystallography.*[22] Structure solution was by MULTAN80[23] and refinement used BLOCKLS, a local version of ORFLS.[24] An IBM 3090 computer was used for calculations. Refinement converged with $R = 0.038$, and the largest peak in the final difference Fourier synthesis was 0.22 e Å^{-3}.

Structure of 2·CHCl$_3$. The procedures used were identical to those described above except for the following differences: graphite monochromatised molybdenum radiation (λ 0.7107 Å) was employed, the positions of the bromine atoms were readily determined by direct phasing, the remaining non-H atom positions were determined by Fourier methods and no extinction correction was included. Refinement converged with $R = 0.031$, and the largest peak in the final difference Fourier synthesis was 0.55 e Å^{-3}, in the vicinity of a bromine atom.

Supplementary structural data for **1** consisting of positional and thermal parameters, bond lengths and angles and torsion angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme see ‘Instructions for Authors’, *J. Chem. Soc., Perkin Trans. 2*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/92. Supplementary structural data for **2**·CHCl$_3$ is available through CSD refcode PORCOO.[8]

Full literature references and compound names relating to the CSD refcodes listed in Tables 2–5 are available as supplementary data from the British Library as Supplementary Publication No. 57271 (15 pp.). Details of the Supplementary Publications Scheme are as for CCDC material. Copies are also available on request from the authors.

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