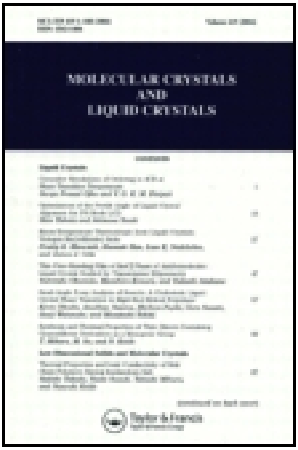

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A Robust New Motif for Supramolecular Construction: The Edge to Edge Aryl C—H···N Dimer

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The edge to edge aryl C—H···N dimer is a previously unrecognised intermolecular hydrogen bonded lattice packing motif; a search of the Cambridge Structural Database revealing that it is widespread amongst many classes of aromatic nitrogen-containing solids. This weak attractive interaction can be retained throughout crystal engineering studies as typified by the systematic modification of the diquinoline **1** into host-guest compounds formed by its dibromo derivative **2**. The latter is a molecule designed to form multimolecular inclusion compounds specifically with small polyhalocarbon guests.

Keywords: hydrogen bonding; C—H···N interactions; inclusion compounds; host-guest compounds; polyhalocarbons; aromatic heterocycles

INTRODUCTION

Lehn has succinctly described supramolecular chemistry as being 'the designed chemistry of the intermolecular bond'.[1] Furthermore, as argued convincingly by Desiraju, specific types of intermolecular attraction must be regarded as the supramolecular equivalents of the synthons employed by synthetic chemists in conventional covalent bond forming and breaking reactions.[2] Consequently, advance and progress in this exciting field is closely related to our level of understanding of the roles weak forces play between individual molecules. Familiar examples of such supramolecular synthons include the edge to face and offset face to face interactions commonly encountered amongst aromatic compounds, and the hydrogen bonded cyclodimer formed between two carboxylic acid groups.[3] Attractive arrangements such as these are therefore the building blocks available for supramolecular construction. Not only must we learn to recognise new examples of these supramolecular synthons but also how to employ them reliably in assembly processes.

During work on the deliberate design of new multimolecular[4] inclusion hosts we became aware of a new cyclic supramolecular synthon which is often present in the solid state structures of certain nitrogen-containing aromatic systems. The structure and scope of this previously unrecognised intermolecular arrangement, the aryl C—H···N dimer, is presented here together with preliminary results describing its involvement in the lattice construction of three compounds including the first two members of this new host-guest family.

RESULTS AND DISCUSSION

Scope of Aryl C—H···N Dimer Formation

The Cambridge Structural Database (CSD)[5] was initially searched for molecules containing a quinoline sub-structure which associated as intermolecular dimers in the solid state. Each C···N distance was specified as being under 3.70 Å but the two such separations present were allowed to be different. In order to target cases where the hydrogen atom position had not been reported in the structure, the aryl hydrogen was omitted at this stage but was checked later against the molecular structure of the hits obtained. An angular value of 90° between the C···N vector of the intermolecular contact and the normal to the plane of the benzo ring containing this C atom would correspond to an exactly planar cyclodimer. A total of 19 hits was found between 60 and 90° with the maximum frequency present between 78-80°. In all cases the two C···N distances were identical and, with one exception, the cyclodimer was centrosymmetric. Figure 1 illustrates a representative example of the centrosymmetric aryl C—H···N dimer.

Extension of the CSD search to include molecules containing a quinoline sub-structure with a further non-carbon atom in the heteroaromatic ring, but retaining the same distance and angular constraints, produced a further 22 examples of the weak hydrogen bonding interaction. Ring systems such as quinoxaline, quinazoline, and phenathiazine were now present, and all of these

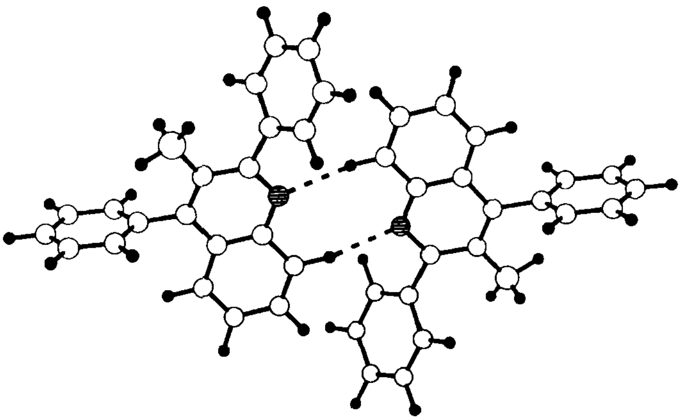


FIGURE 1 The aryl C—H···N dimer present in the crystal structure of 2,4-diphenyl-3-methylquinoline (refcode ZENNOW).[6] Here the —H···N and C···N distances are 2.53 and 3.52 Å respectively, and the angular value is 74.2°. In this and subsequent figures hydrogen bonds are represented by dashed lines, carbon atoms are white, nitrogen atoms are indicated by horizontal hatching, and hydrogen atoms are shown as small black spheres.

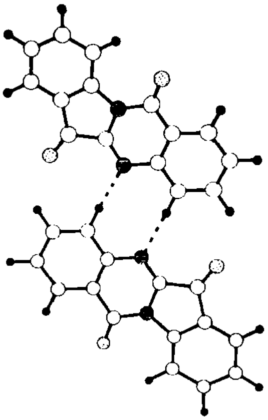


FIGURE 2 Crystal structure of indolo[2,1-*b*]quinazoline-6,12-dione (refcode TRYTAN)[7] showing the aryl C—H···N dimer present between two neighbouring molecules. The —H···N and C···N distances are 2.61 and 3.62 Å respectively, and the angular value is 78.3°. Oxygen atoms are indicated by stippling.

new examples involved centrosymmetric intermolecular arrangements. Figure 2 shows a representative example.

A further 7 centrosymmetric examples were found where the sub-structure involved a benzo group fused to a five-membered heterocyclic ring; e.g. benzothiazole, indole, benzimidazole, and benzoxazole derivatives (Figure 3).

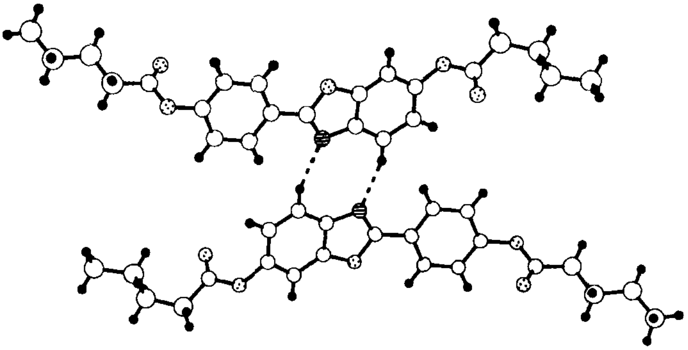


FIGURE 3 The intermolecular aryl C—H···N dimer present in the crystal structure of 2-[4-(pentanoyloxy)phenyl]benzoxazol-6-yl pentanoate (refcode HATYAC).[8] In this case the —H···N and C···N distances are 2.65 and 3.56 Å respectively, and the angular value is 78.8°.

Finally, using the previous distance and angular parameters but specifying only two *N*-substituted benzene units where the nitrogen atoms were two-coordinate but of undefined bonding type, a further 5 centrosymmetric hits were obtained. These were all conjugated phenyl imine structures but the imine group could either be acyclic or included as part of a further ring (see Figure 4).

For some time the C—H···N attraction has been recognised as being due to a weak hydrogen bond,[10,11] and Desiraju has investigated the aryl C—H···N≡C interaction in crystal engineering work.[12] Despite this background the aryl C—H···N cyclodimer has escaped previous attention. Our CSD survey identified 53 examples of this motif but it was not discussed in any of these papers, not even in those attempting analysis of the intermolecular attractions present. Although it is a relatively long range contact its regular appearance in crystal structures, across a wide range of compound types, indicates that it plays a significant role in the lattice packing of suitable molecules.

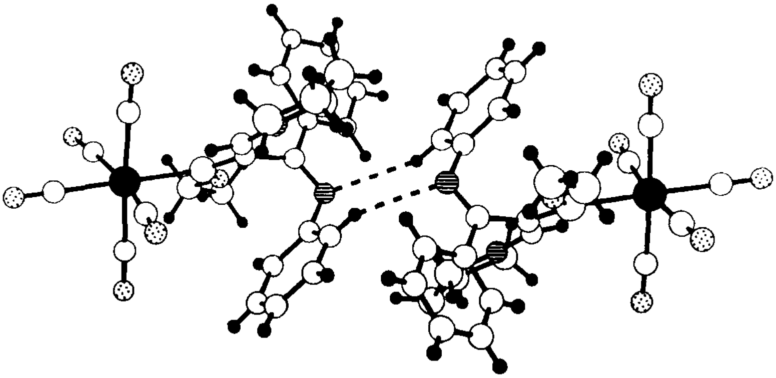
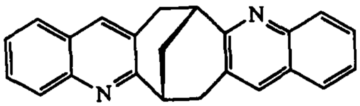


FIGURE 4 Crystal structure of *s-cis*-pentacarbonyl-{1-ethoxy-3-phenyl-3-phenylimino-2[(*E*)-pyrrolidinomethylene]propan-1-ylidene}tungsten showing the aryl C—H···N dimer linking two adjacent molecules (refcode ZEPPAL01).[9] The —H···N and C···N distances are 2.70 and 3.59 Å respectively, and the angular value is 72.7°. In addition to the previous atom designators tungsten atoms are shown here as large black circles.

All 53 identified cases of the cyclodimer revealed symmetrical structures with both sets of interbond distances being indentical, and 52 of the total were centrosymmetric. (The one exception, DIGRUG,[13] has a twofold axis relating the two molecules). This indicated clear structural preferences which could be expected reasonably to be carried over to new structures and suggested that the cyclodimer has considerable potential as a supramolecular synthon for crystal engineering.[14]

Diquinolines and the New Supramolecular Synthon

As part of a crystal engineering project aimed at the deliberate design of new multimolecular[4] inclusion hosts we synthesised the V-shaped diquinoline derivative **1**. This also contains the aryl C—H···N dimer as part of its solid state intermolecular packing. In this instance the —H···N and C···N distances are 2.56 and 3.55 Å respectively, and the angular value is 84.2°. Molecules of **1** pack efficiently within their crystals and therefore, as anticipated, this diquinoline compound does not act as a host molecule.



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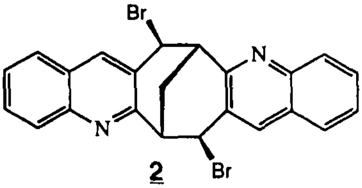

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This situation immediately changes for the dibromo derivative **2** where the *exo*-bromine atoms cause the molecules to pack less efficiently as the pure solid by partially disrupting the aromatic face to face packing modes.[15] As a consequence compound **2** prefers to form lattice inclusion compounds such as **2**•$CHCl_3$. Here adjacent molecules of the diquinoline interact through the aryl C—H•••N dimer and chloroform guest molecules hydrogen bond to the remaining nitrogen atoms as shown in Figure 5.

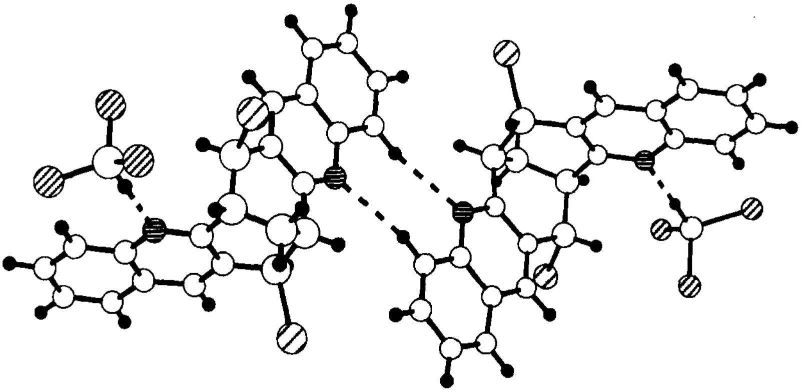

FIGURE 5 Part of the crystal structure of **2**•$CHCl_3$ showing the two types of C—H•••N hydrogen bonding present. For the cyclodimer the —H•••N and C•••N distances are 2.67 and 3.65 Å respectively, and the angular value is 89.0°. The C•••N distance is 3.37 Å between the host and guest. Bromine and chlorine atoms are indicated by wide- and close-spaced diagonal hatching respectively.

Small polyhalocarbons are trapped by **2** in preference to other guests of comparable size and shape because of the efficient network of halogen•••halogen interactions[16] which is generated between host and guest molecules. For **2**·$CHCl_3$ this results in alternating layers of hydrocarbon and halogen moieties as shown in Figure 6.

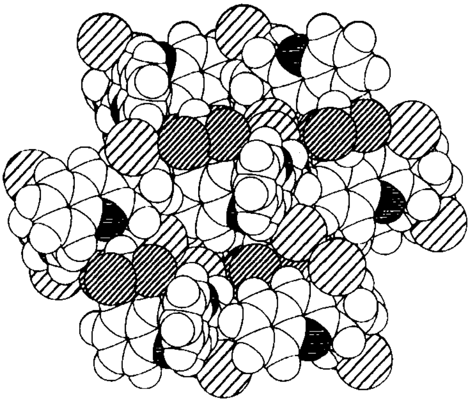

FIGURE 6 View of the crystal structure of **2**·$CHCl_3$ showing the alternating layers of host hydrocarbon and host-guest halogen functionalities. The resulting inclusion compound is stabilised by multiple host-guest and guest-guest halogen···halogen interactions.

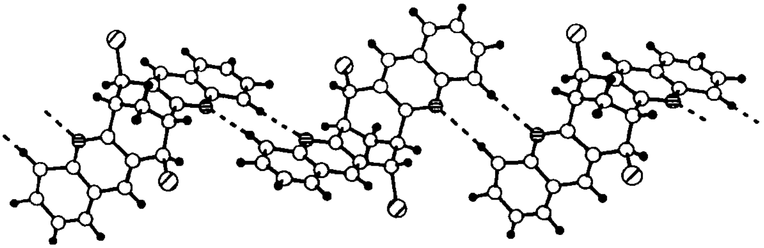

FIGURE 7 Part of the crystal structure of **2**·$(CH_3CCl_3)_2$ showing the hydrogen bonded chains of host molecules. The cyclodimer —H···N and C···N distances are 2.60 and 3.59 Å respectively, and the angular value is 89.2°.

Methylchloroform is incapable of hydrogen bonding to the nitrogen atom of diquinoline **2**, but molecules of **2** can still form the hydrogen bonded cyclodimer. Consequently, in **2**·$(CH_3CCl_3)_2$, chains of host molecules are produced through each diquinoline forming two centrosymmetric aryl C—H···N dimers with its neighbours (Figure 7).

Layers of these chains cross each other orthogonally to produce a low density host lattice where the gaps between the chains are filled with methylchloroform molecules. Hence these guests occupy cage-like sites where they are partly stabilised by a surrounding network of multiple host-guest Br···Cl and guest-guest Cl···Cl attractive forces (see Figure 8).

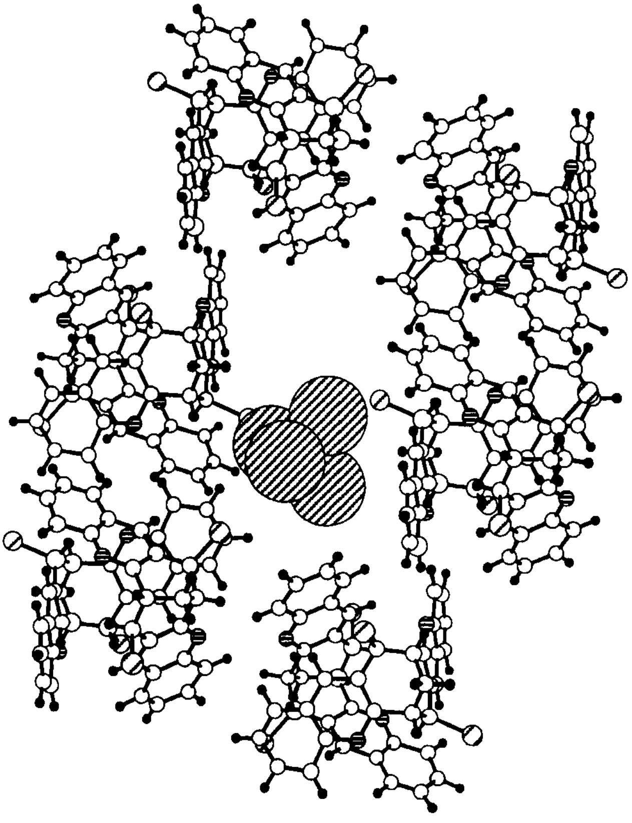

FIGURE 8 The crystal structure of 2·$(CH_3CCl_3)_2$ showing one of the four methylchloroform guests occupying a cage-like site within the host lattice. Due to the similar size of methyl and chloro substituents some guest disorder is present in this structure which therefore is symbolised here using a simplified tetrahedral CCl_4 model for the guest occupancy.

CONCLUSIONS

The aryl C—H···N dimer is a widespread and predictable packing motif for aromatic nitrogen compounds and provides edge to edge packing (not usually encountered amongst aromatic hydrocarbon structures). It is a robust structure which can survive crystal engineering modifications and therefore it is a valuable new synthon for supramolecular construction.

Acknowledgement

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