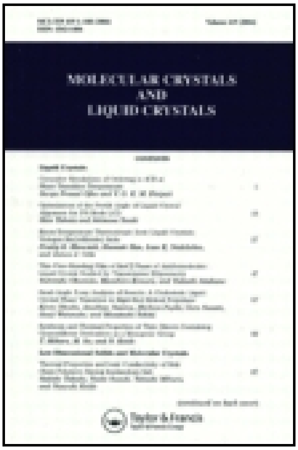

Molecular Crystals and Liquid Crystals

The Pi - Halogen Dimer (PHD) Interaction: A Versatile New Construction Unit for Crystal Engineering

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The Pi – Halogen Dimer (PHD) Interaction: A Versatile New Construction Unit for Crystal Engineering

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The pi – halogen dimer (PHD) interaction is a new type of intermolecular packing motif discovered in certain crystalline diquinoline compounds. It consists of a combination of one aromatic offset face-face (OFF) interaction, and four aromatic pi – halogen interactions, and provides a compact building block for the self-assembly of lattice inclusion compounds. This article reviews the current state of knowledge about this new solid-state construction motif.

Keywords: crystal engineering; inclusion compounds; layer structures; pi – halogen interactions; staircase structures; X-ray crystal structures

INTRODUCTION

In recent work, we have been investigating the design of new lattice inclusion hosts [1,2], based on V-shaped diquinoline molecular structures that are unable to use strong hydrogen bonding interactions [3] in their molecular assembly processes. Processes involving only weak intermolecular forces [4,5] then become dominant. This has led us to the recognition of important new types of crystal packing motifs such as the ether-1,3-*peri* hydrogen interaction [6], and the aromatic edge-edge C−H···N dimer [7,8].

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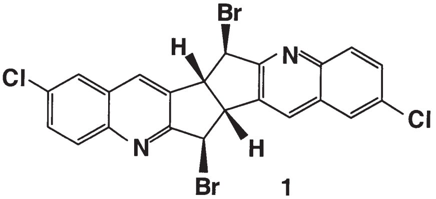
In the crystal structures of many of these diquinoline compounds, only the standard aromatic interactions are observed. These allow the molecules to associate by offset face-face (OFF) and/or edge-face (EF) associations [9,10].

The new pi – halogen dimer (PHD) interaction occurs, however, in the crystal structures of many of the diquinolines that are halogenated on their aryl rings. It is an efficient combination of one aromatic (OFF) and four aromatic pi – halogen interactions [11,12]. One electron rich aryl halogen atom from each molecule positions itself within the V-shaped cleft, and over the electron deficient π-systems of the pyridine rings, of its partner. Typical ring centroid–halogen distances, indicated by vertical and horizontal arrows in Figure 1, are around 3.5–3.7 Å and 3.7–4.2 Å respectively. The OFF ring separation is around 3.5–3.6 Å. The PHD motif operates between opposite molecular enantiomers, is normally centrosymmetric, and provides a compact building block for molecular assembly.



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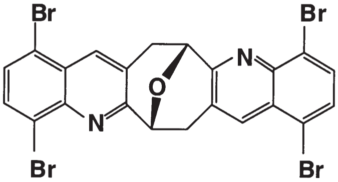

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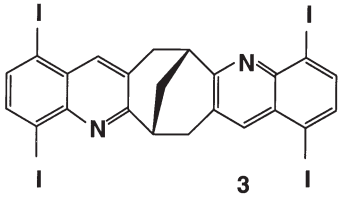

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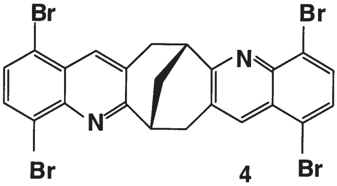

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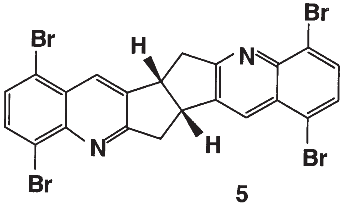

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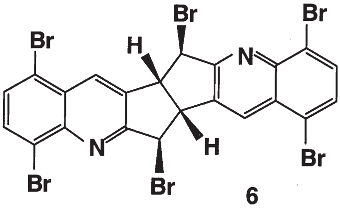

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Thus far, six host molecules **1–6** have been synthesised that employ the PHD interaction as a key building block in their inclusion lattices. The pi – halogen dimer units pack along with the trapped guest

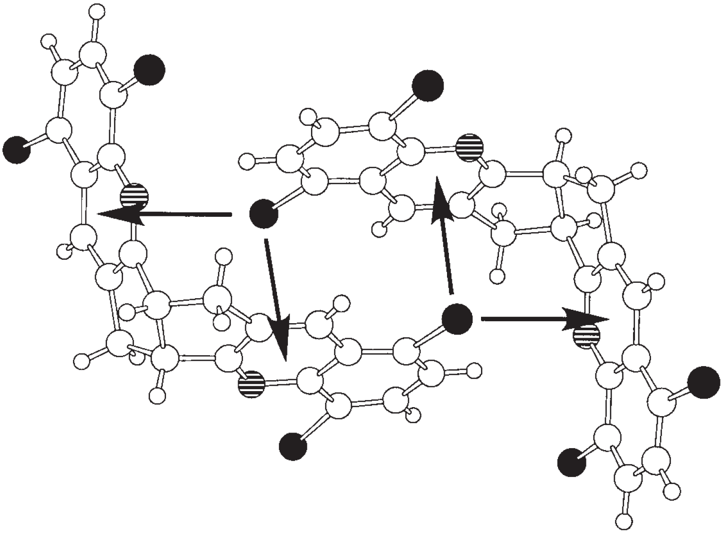


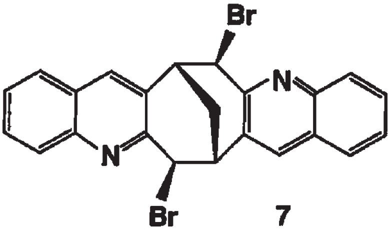
FIGURE 1 A typical centrosymmetric PHD interaction showing the OFF interaction between two *endo*-faces of the diquinoline **5**, and with the four pi – halogen associations indicated by arrows. Atom code: N horizontal hatching, Br black sphere.

molecules to produce either staircase or layer inclusion structures. It is the intention of this article to review the current situation relating to their PHD interactions.

RESULTS AND DISCUSSION

Comparison of the PHD Motif with the more Familiar OFF and EF Interactions

When V-shaped diquinoline molecules pack in the solid state, they often interact by means of aromatic offset face-face (OFF) and/or edge-face (EF) interactions. A pleasing example, that illustrates both these modes, is present in the crystal structure of compound **7** [13].



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In solid **7**, pairs of molecules associate as shown in Figure 2. Each molecule contributes the *endo*-face of one of its aromatic wings to form an OFF interaction with its partner. Excellent facial overlap occurs between the two pi-systems. Concomitantly, the hydrogen atoms at the ends of each of these wings interact in EF mode with the second aromatic wing of its partner molecule. The outcome is a compact centrosymmetric dimeric unit for crystal packing.

The PHD interaction is rather similar to the situation in Figure 2, except that the two molecules comprising the dimer are mutually rotated so that an aryl halogen atom of each molecule now is positioned over the pyridine rings of its partner. Effectively, the two EF interactions are replaced by four pi – halogen contacts. The OFF interaction is retained in the PHD motif, but the extent of aromatic overlap is markedly reduced. These effects are illustrated in Figure 3 for compound **5** [14].

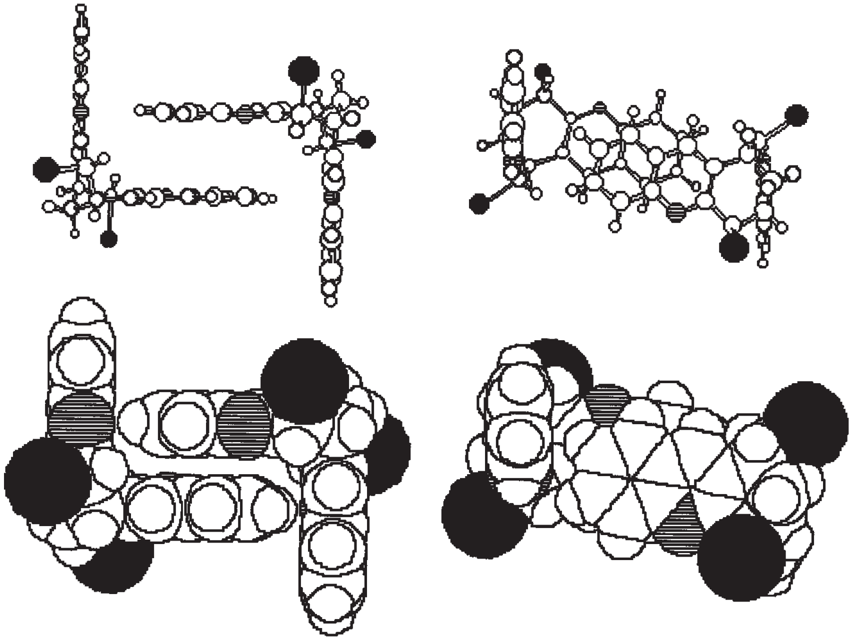

FIGURE 2 The association of two molecules of **7** into a solid-state centrosymmetric dimer by means of one OFF and two EF interactions. Upper diagrams: ball and stick form. Lower diagrams: space filling representation.

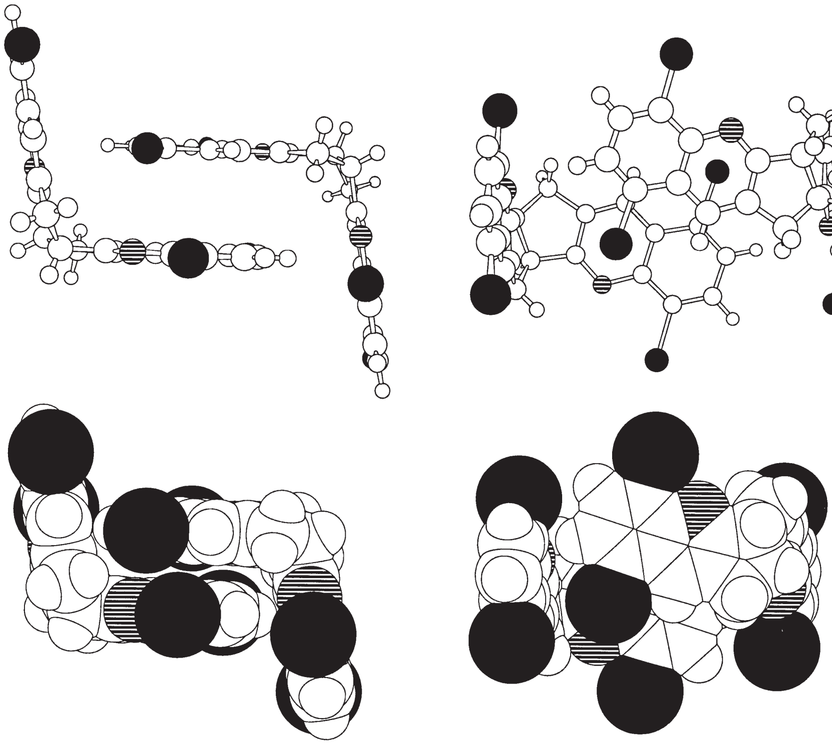

FIGURE 3 One of the two crystallographically independent PHD motifs present in the compound $(\mathbf{5})_2 \cdot$(allyl cyanide). Upper: shown in ball and stick form. Lower: space filling representation. (These diagrams should be compared to those shown in Figure 2 for the OFF and EF interactions in solid **7**).

Some PHD Statistics

At present, we have synthesised a total of six new molecules **1–6** that have been shown to form PHD interactions. All of these hosts form lattice inclusion compounds on crystallisation from appropriate solvents.

Eighteen crystal structures have been determined for inclusion compounds formed by **1-6** that feature PHD motifs. Of these, twelve contain staircase structures, and the remaining six contain layer structures.

A total of twenty-six individual PHD motifs are present in these crystal structures. (Several of these crystals contain more than one independent host molecule within their structures). All of the PHD motifs are constructed from molecules of opposite handedness, and twenty-three of these are centrosymmetric.

A number of different construction modes for the PHD unit have been observed at the crystallographic level, and these will be discussed later.

Types of Halogen Atom Involved in the PHD Motif

Chlorine, bromine, and iodine atoms have all been shown to participate in PHD interactions, and representative examples of these are illustrated. We have not yet attempted to obtain a fluorine-containing analogue.

The dichloro compound **1** is not a versatile host molecule and, as the solvent-free apohost, it forms a fascinating interlocking grid lattice [15]. However, it does crystallise from benzene in space group $C2/c$ as the inclusion compound $(\mathbf{1})_2\cdot$(benzene) [16]. This is a typical example of a staircase lattice inclusion compound.

In such substances, the PHD units stack on top of each other by means of aromatic OFF interactions and form parallel infinite staircases. The steps of each staircase are built up by using one aromatic wing of each host, with the second wing becoming a staircase surround. These surrounds are directed upward on one side of the staircase, and downward on the other. Adjacent staircases associate by further OFF interactions and the guest molecules occupy interstitial spaces [17].

In the case of $(\mathbf{1})_2\cdot$(benzene) it is one aryl chlorine atom from each host molecule that participates in the PHD interaction. There is only one crystallographically independent host present, and adjacent PHD units are related by a twofold axis as illustrated in Figure 4.

The oxa-bridged tetrabromo diquinoline **2** crystallises in space group $C2/c$ from dichloromethane as $(\mathbf{2})_2\cdot$(dichloromethane) [18]. The construction of the PHD unit and the molecular staircase of this compound contain the same symmetry elements as the previous example. This time, however, it is one of the four aryl bromine atoms in each host that participates in the PHD interaction. Figure 5 shows a projection of five parallel staircases and their spatial relationship to the dichloromethane guest molecules.

The tetraiodo diquinoline **3** crystallises from toluene in space group $P\bar{1}$ as the $(\mathbf{3})_4\cdot$(toluene) staircase compound [19,20]. Here, it is one aryl iodine atom from each of two hosts that participates in the PHD unit. However, two crystallographically independent molecules **3** (A, B) are present, and both A-A* and B-B* PHD units are formed (where A* and B* indicate the opposite enantiomers). Once again, these PHD units are centrosymmetric. They stack along the staircase

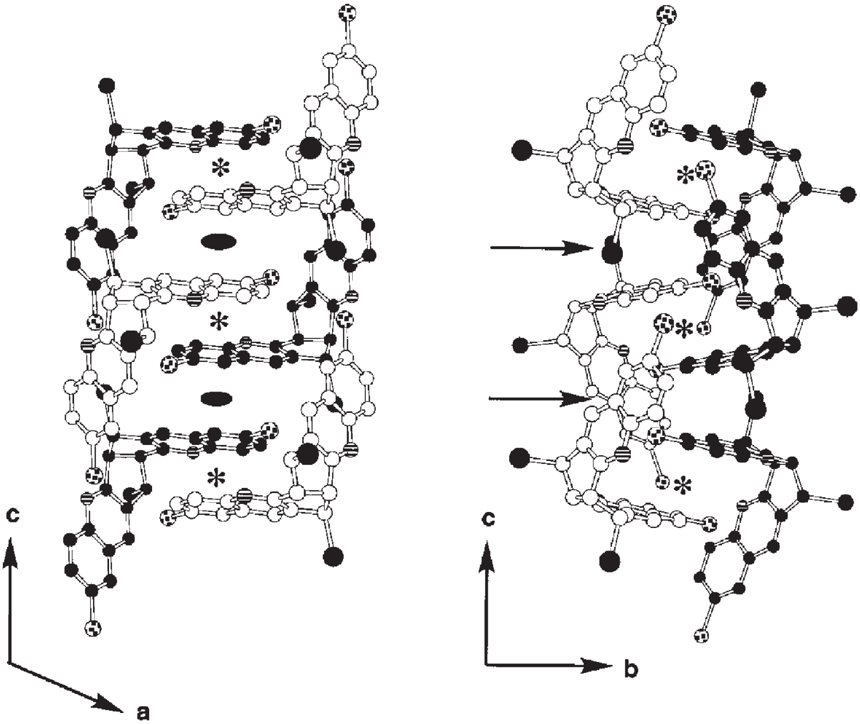

FIGURE 4 Two orthogonal views of one molecular staircase along *c* in solid $(\mathbf{1})_2\cdot$(benzene). Opposite enantiomers of **1** are indicated by black or white C atoms. There are centres of symmetry (*) in the middle of each PHD unit, and twofold axes (solid ellipse or arrow) normal to the plane of this diagram between adjacent PHD units. Atom code: N horizontal hatching, Br black sphere, Cl stippling.

as a B*-B A-A* repeat, but with no symmetry present between adjacent PHD units, as shown in Figure 6.

PHD Staircase Structures

Of the 18 crystal structures determined for **1–6** inclusion compounds containing PHD units, twelve have staircase structures. With one exception, the host:guest ratio in these compounds is $\geq$2:1. In the two instances (**1**,**6**) where crystalline apohosts could also be obtained, the PHD motif was not present in these solvent-free crystal structures. There is no reason why PHD motifs should not occur in mono-component crystal structures, but the evidence available so far suggests that their presence is preferred in lattice inclusion

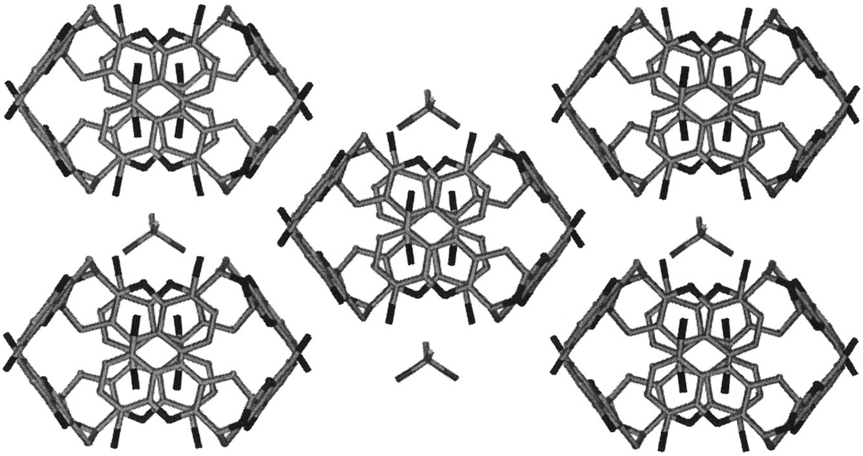

FIGURE 5 Five molecular staircases in structure $(\mathbf{2})_2 \cdot$(dichloromethane) projected onto the *ab* plane, showing their hexagonal cross-sections and how the guest molecules occupy channels between them.

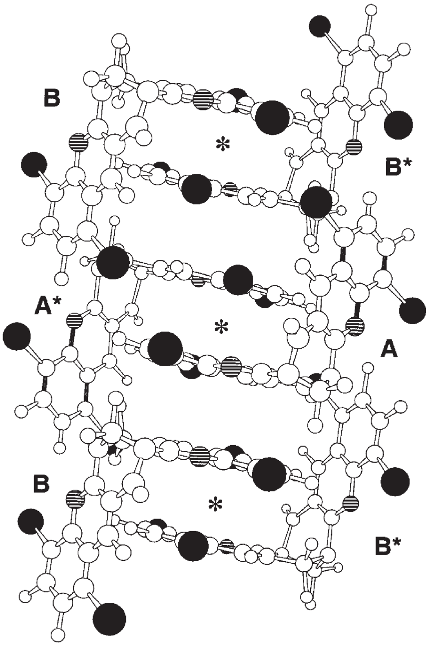

FIGURE 6 Part of one staircase running along *b* in the $(\mathbf{3})_4 \cdot$(toluene) inclusion compound structure. Molecules A and B are crystallographically independent; A* and B* are their enantiomers. Atom code: I black sphere.

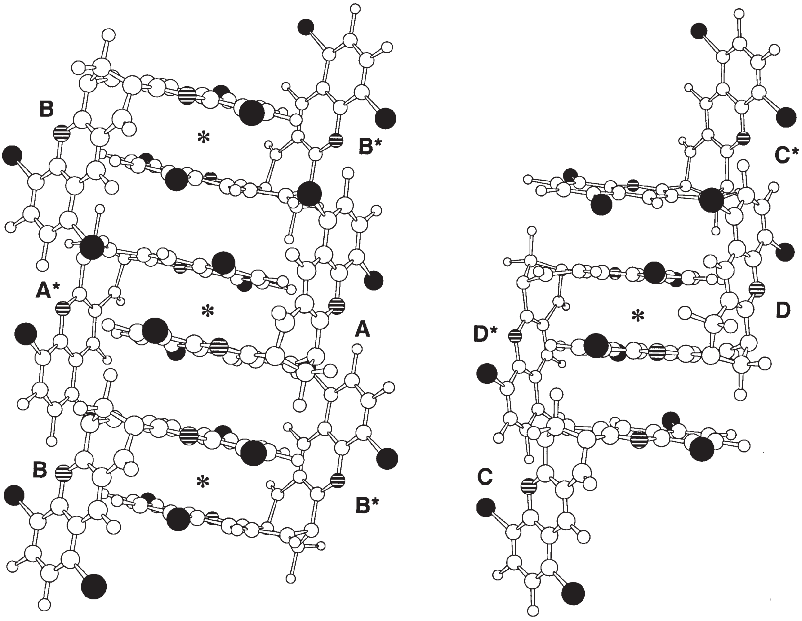

FIGURE 7 The two types of staircase assembly present in $(\mathbf{4})_4 \cdot$(ethyl acetate). Left: part of the infinite staircase containing A-A* and B-B* PHD units. Right: the truncated staircase containing a D-D* PHD motif.

compounds, perhaps due to their involvement as part of the structural fine-tuning while accommodating the guest component.

Three different PHD construction arrangements have been observed in these compounds.

1. One crystallographically independent molecule (A), and its enantiomer (A*), is present in the crystalline solid. The PHD units stack A*-A A-A* A*-A etc. along the staircase axis, and a twofold axis is present between adjacent PHD units. Five crystal structures and five PHD units recorded: $(\mathbf{1})_2 \cdot$(benzene) [16], $(\mathbf{2})_2 \cdot$(dichloromethane) [18], $(\mathbf{2})_2 \cdot$(chloroform) [18], $(\mathbf{4})_2 \cdot$(dichloromethane) [19,20], $(\mathbf{4})_2 \cdot$(allyl cyanide)$\cdot$(water) [19,20].
2. Two independent molecules (A, B), and their enantiomers (A*, B*), are present. Now the PHD units assemble A*-A B-B* A*-A etc. to form the staircase structure. There is no symmetry present between adjacent PHD units. Six crystal structures and twelve PHD units recorded: $(\mathbf{3})_4 \cdot$(toluene) [19,20], $(\mathbf{4})_4 \cdot$(trifluoro-(trifluoromethylbenzene) [19,20], $(\mathbf{4})_4 \cdot$(benzene) [19,20,21],

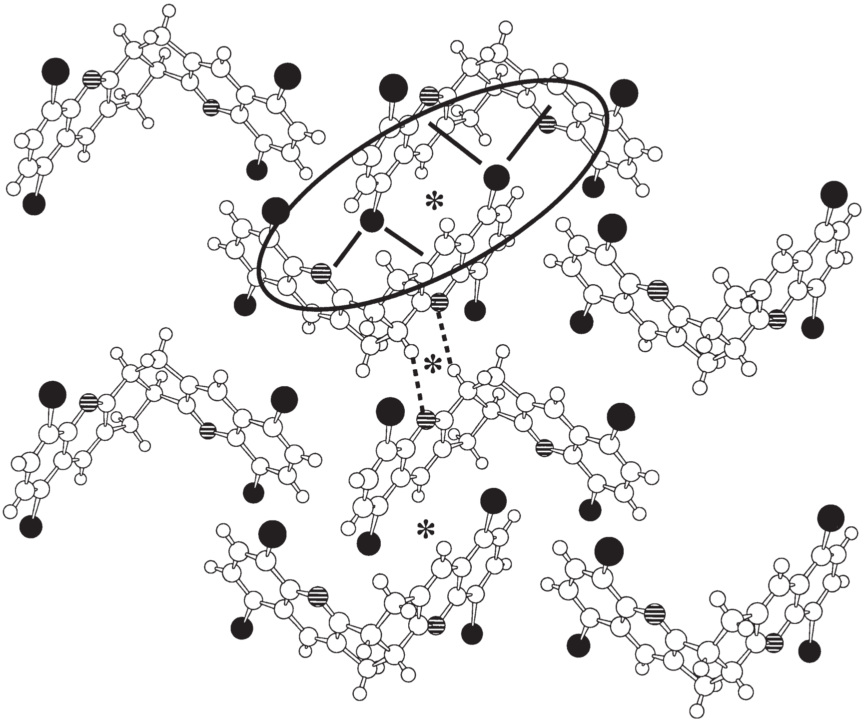

FIGURE 8 The host molecule arrangement within a layer of the solid inclusion compound (**5**) · (methyl chloroform). One of the PHD units, with the pi – halogen interactions indicated by black lines, is highlighted by enclosure within an ellipse. Asterisks indicate the centres of symmetry within the PHD and edge-edge C-H···N dimer motifs that link the molecules of **5**.

$(\mathbf{4})_4$ · (toluene) [19,20], $(\mathbf{5})_2$ · (allyl cyanide) [14,22], $(\mathbf{5})_2$ · (1,2,3-trichloropropane) [14].

3. Four crystallographically independent host molecules (A-D), and their enantiomers (A*-D*), are present. One crystal structure and three PHD units recorded. In the unique case of $(\mathbf{4})_4$ · (ethyl acetate), the A-A* and B-B* PHD units form infinite staircase assemblies identical to those described under (2). These are accompanied, however, by truncated staircases of structure C D-D* C*. Only the D and D* molecules form a PHD unit in this four-molecule truncated arrangement [19,20]. All three PHD motifs are shown in Figure 7.

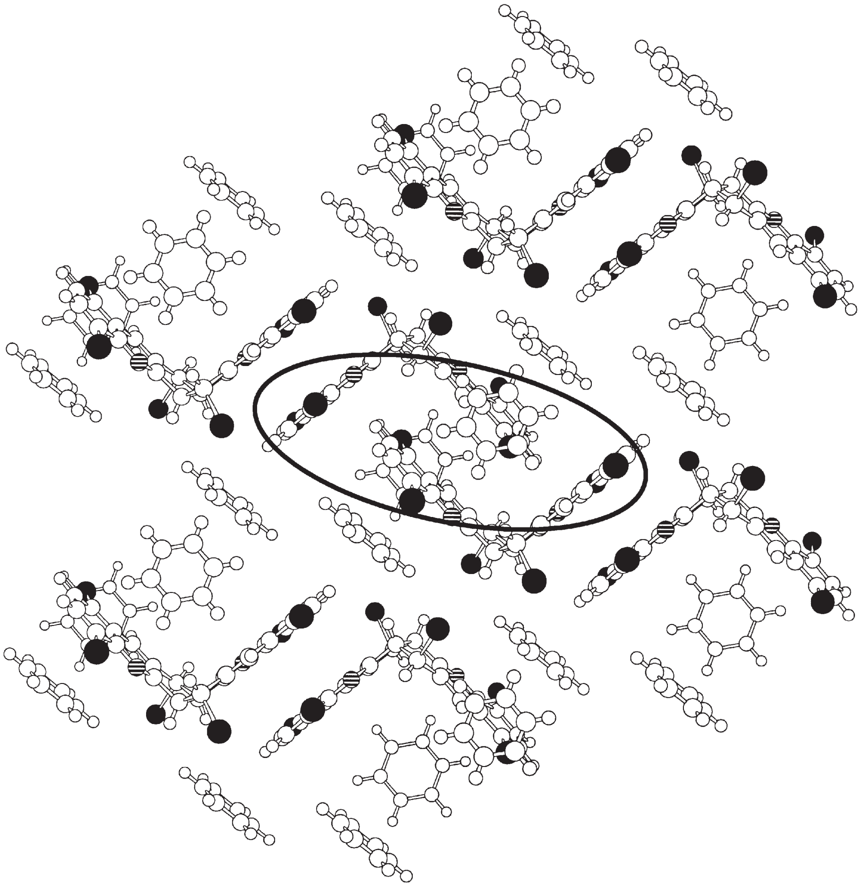

FIGURE 9 Part of one layer in the structure $(\mathbf{6})_2 \cdot (\text{benzene})_3$, with one PHD unit highlighted by the ellipse. The PHD units associate with each other by means of OFF interactions, and with the two independent benzene guest molecules through aromatic OFF and EF interactions.

PHD Layer Structures

Of the 18 crystal structures determined so far that contain PHD units, six have layer inclusion structures. In contrast to the staircase structures, all of these have a host:guest ratio of $<2{:}1$. Two different PHD construction arrangements have been observed in these compounds.

1. One crystallographically independent molecule (A), and its enantiomer (A^*), is present in the crystalline solid. Individual PHD units

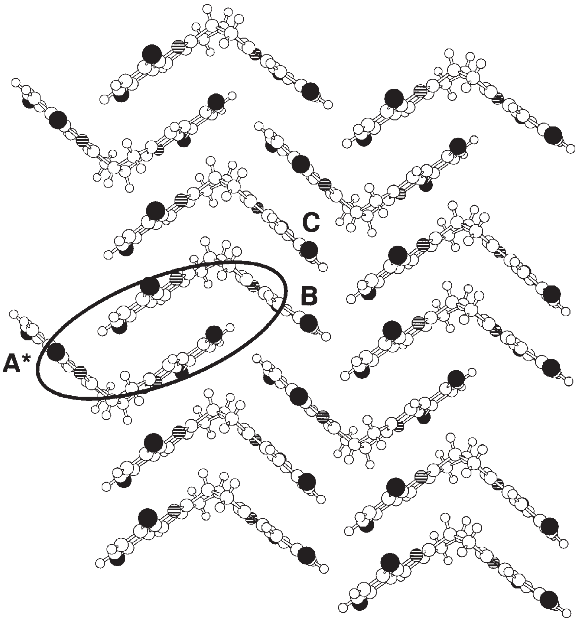

FIGURE 10 Projection view in the *ab* plane of a layer in the $(\mathbf{5})_3 \cdot$(chloro-(chlorobenzene)$_2$ structure, with one PHD unit highlighted by an ellipse. Here, the host molecules form A*-B PHD units that are linked through C molecules by means of OFF interactions. (The adjacent layers contain the A, B* and C* host molecules). The chlorobenzene guests are omitted from this figure for clarity.

A*-A are formed. Three crystal structures and three PHD units recorded: $(\mathbf{5}) \cdot$(methyl chloroform) [14], $(\mathbf{5}) \cdot$(carbon tetrachloride) [14,22], $(\mathbf{6})_2 \cdot (\text{benzene})_3$ [23]. The methyl chloroform and carbon tetrachloride compounds are isostructural. Structures of the methyl chloroform and benzene compounds are illustrated in Figures 8 and 9, respectively.

2. Three independent molecules (A-C), and their enantiomers (A*-C*), are present. PHD units A*-B (and their enantiomers A-B*) are formed, and these are the only non-centrosymmetric PHD motifs so far recorded in our studies. The molecules C and C* do not contribute to PHD units. Three crystal structures and three PHD units recorded: $(\mathbf{5})_3 \cdot (\text{chlorobenzene})_2$ [14], $(\mathbf{5})_3 \cdot (\text{toluene})_2$ [14,24], $(\mathbf{5})_3 \cdot (\text{benzene})_{2.5} \cdot (\text{water})_{0.5}$ [14]. The structure of the first of these is shown in Figure 10, and the host arrangement in the other two cases is similar.

CONCLUSIONS

The pi – halogen dimer (PHD) motif is shown to be a compact and efficient building block in the solid-state construction of several new diquinoline lattice inclusion hosts. A total of 18 crystal structures, containing 26 individual PHD motifs, has been studied so far. All of these PHD units are formed between opposite host enantiomers, and 23 of these are centrosymmetric.

Aryl chlorine, bromine and iodine substituents have all been shown to participate in PHD motifs, and these halogens may be situated on different ring positions. So far, all cases of PHD units observed have comprised part of a lattice inclusion structure. The host:guest stoichiometry differs for the staircase (usually $\geq$ 2:1) and layer ($<$ 2:1) inclusion structures.

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