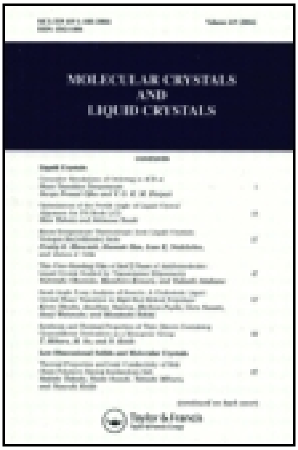

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Roger Bishop [a] , Donald C. Craig [a] , A. Noman [a] , M. M. Rahman [a] & Marcia L. Scudder [a]

[a] School of Chemistry, The University of New South Wales, Sydney, 2052, Australia

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GUEST INCLUSION WITHIN MOLECULAR PENS

Roger Bishop, Donald C. Craig, A. Noman M. M. Rahman,*
and Marcia L. Scudder
School of Chemistry, The University of New South Wales,
Sydney 2052, Australia

A convenient synthetic procedure has been developed for the preparation of a series of new C_2-symmetric clathrate hosts each containing three key structural components: two planar aromatic wings, two protruding sensor groups, and a central linker unit. The dibromo compound **4** *described here is built around the flexible bicyclo [3.3.0]octane ring system and has quinoline-based wings. Two molecules of the host wrap around a guest trapping it within a cyclophane-like molecular pen. The aromatic wings function like the fences enclosing an animal in a stockyard. With differing guests the wings slip relative to each other to give the best host-guest combination using a quadrilateral pen. The structures of the 2:1 inclusion compounds formed between* **4** *with 1,1,1-trichloroethane (methyl chloroform) and 1,1,2,2-tetrachloroethane are discussed.*

Keywords: crystal engineering; aryl-aryl interactions; inclusion compounds; C-H···N weak hydrogen bonds; supramolecular synthons; halogen-halogen interactions

INTRODUCTION

Lattice inclusion (clathrate) compounds arise from multiple interactions between two or more different types of molecules packed together in a crystal lattice [1]. These materials are therefore structurally distinct from the majority of inclusion compounds where a single guest species interacts with a preformed host receptor molecule [2]. Consequently, the design of new clathrand hosts presents an interesting crystal engineering challenge for the synthetic chemist [3,4].

In recent work we have adopted a modular synthetic approach whereby we quickly assemble a potential host molecule in a few simple steps from readily available precursors. The host is characterized by three key

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*Corresponding author

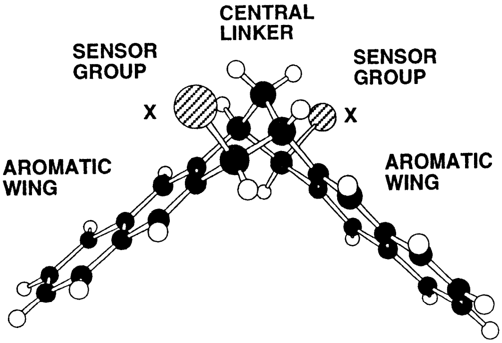

FIGURE 1 A schematic host molecule built up from three key structural elements: planar aromatic wings, sensor groups, and a flexible central linker group.

structural units: planar aromatic wings, a central linker group, and two protruding sensor groups(Fig. 1).

The central linker group conjoins the two aromatic wings and its flexibility also ensures that the molecule adopts C_2 symmetry. Hence the planes of the wings do not form a simple V-shape, but rather are twisted with respect to each other. Molecules containing inclined planes of this type frequently do not fit together efficiently and are prone to exhibiting inclusion properties [5,6].

Aryl face-face interactions are expected between the wings of neighbouring molecules but we have shown that protruding bromine sensor groups reduce the area of such interactions [7]. The sensor groups also encourage host-host and/or host-guest close contacts, for example through halogen-halogen interactions [8].

Earlier we have described the inclusion behaviour of new diquinoline [8] and diquinoxaline [9,10] lattice inclusion hosts which were assembled using a central bicyclo[3.3.1]nonane linker unit. Here we report the preparation and inclusion properties of a diquinoline derivative based around a bicyclo[3.3.0]octane linker. This new host **4** functions in a completely different manner to the earlier compounds [11].

RESULTS AND DISCUSSION

Friedländer condensation [12] of *o*-aminobenzaldehyde [13] **1** and bicyclo-[3.3.0]octane-2,6-dione [14] **2** affords a 75% yield of the diquinoline derivative **3**. This molecule is capable of efficient packing with itself and therefore shows no evidence of inclusion properties. The target compound **4** was obtained in 78% yield through benzylic bromination using *N*-bromosuccinimide (Fig. 2).

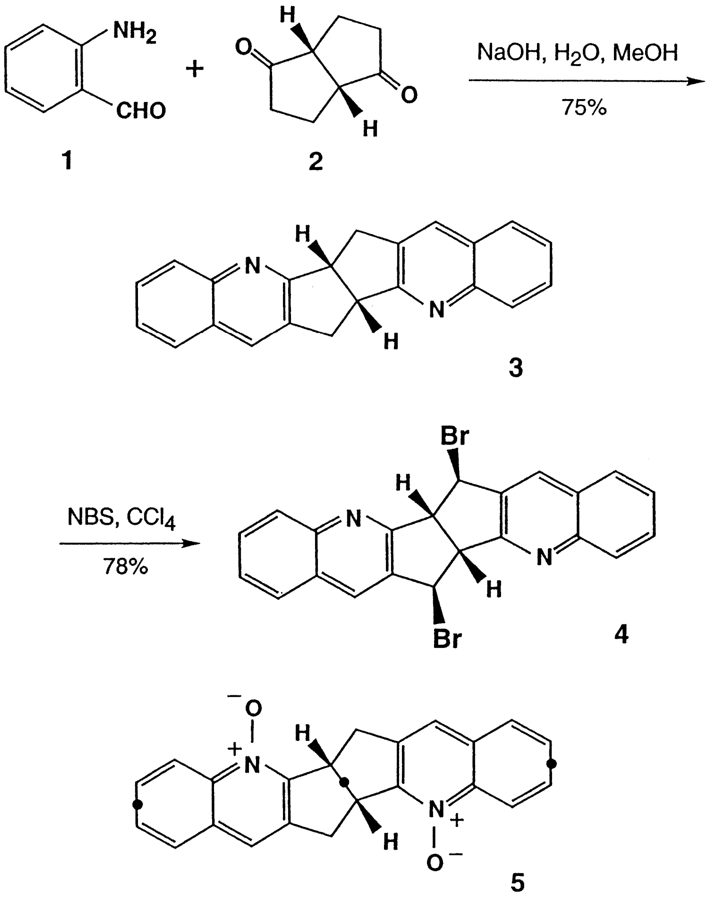

FIGURE 2 Synthesis of the dibromo diquinoline host **4** and related structures based on a central bicyclo[3.3.0]octane linker group.

Crystallisation of **4** from a range of organic solvents revealed that this compound was a potent inclusion host which combined with guests to give compounds of 2:1 stoichiometry. In all of these materials two molecules of **4** enclose a guest molecule by wrapping themselves around it. If these host molecules were linked covalently at their extremities then the result would be a cyclophane structure. To describe these materials we draw the colourful analogy with an animal fenced within a small enclosure. The guest molecule represents the captive animal and the four planar aromatic surfaces which surround it comprise the fences of its molecular pen.

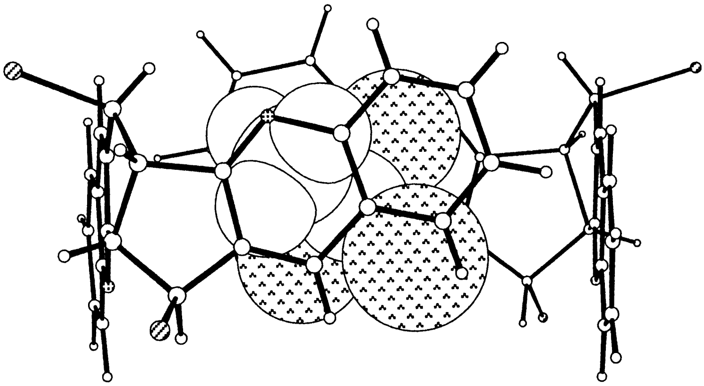

FIGURE 3 Side view of a square molecular pen in $(\mathbf{4})_2\cdot(CH_3\text{-}CCl_3)$. The guest is represented in space-filling form with the chlorine atoms stippled, and the host fences using framework representation.

The salient features of these inclusion compounds are illustrated by the structure of $(\mathbf{4})_2\cdot(CH_3\text{-}CCl_3)$ formed in space group *C*2/*c* when the host is crystallized from 1,1,1-trichloroethane. Molecular pens are produced as illustrated in Figure 3. These have a square cross-section and are arranged in regular rows to produce layers where the host molecules interact through bromine-bromine and aryl face-face interactions (Fig. 4). The layers, which pack on top of each other, are linked by means of centrosymmetric aryl C-H···N dimmers (Fig. 5) [7,16]. These contacts, generally regarded as weak hydrogen bonds [17], are reliable supramolecular synthons [18] in the intermolecular assembly of many quinoline derivatives. In this case the $\underline{C}$-H···$\underline{N}$ and $\underline{C}$-$\underline{H}$···$\underline{N}$ distances are 3.38 and 2.47Å respectively.

If host **4** is crystallized from other solvents then alternative inclusion compounds are produced with the same stoichiometry. Once again the guest molecules are enclosed in molecular pens, but the host molecules comprising the fences slip relative to each other to accommodate the guest most effectively. Several of these structures are in space group *P*2$_1$/*c* with two molecules of **4** in their symmetric unit. This leads to two pens of slightly different geometry being present. For example the structure $(4)_2\cdot(CHCl_2\text{-}CHCl_2)$ contains two rectangular-shaped pens in each layer as illustrated in Figure 6.

If we choose three appropriate points on the molecular skeleton, then a measure of the angle between the two wings can be obtained in each case and the various values compared. The points selected are the centers of the outermost aromatic carbon-carbon bonds of the wings and the center of the

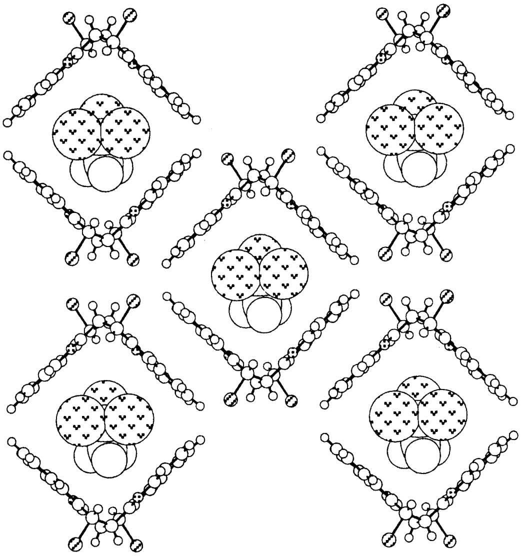

FIGURE 4 Part of a layer in the structure of $(\mathbf{4})_2\cdot(CH_3\text{-}CCl_3)$ showing the rows of square molecular pens. The host bromine atoms are diagonally hatched and the guest chlorines are stippled.

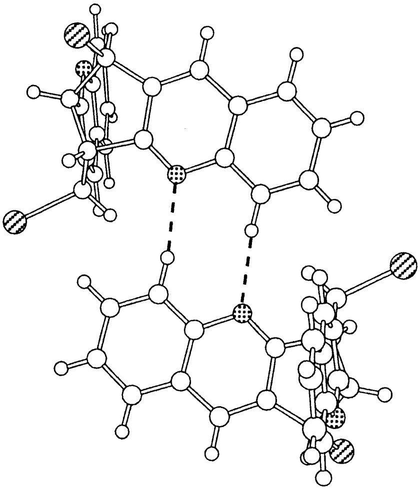

FIGURE 5 The centrosymmetric aryl C-H···N dimer linking molecules of **4** in different layers of the structure $(\mathbf{4})_2\cdot(CH_3\text{-}CCl_3)$.

aliphatic CH-CH bond through which the C_2 axis runs. These are marked by filled circles on structures **5** in Figure 2.

Angular values for the family of **4** molecular pens range between 95 and 101 degrees which results in approximately square, rhomboid, or rectangular shapes. Those illustrated in Figures 3 and 4 exhibit an angle of 97.7 degrees, while those in Figure 6 have values of 95.8 and 99.1 degrees.

The molecules are not compelled to behave in this manner, because the central bicyclo[3.3.0]octane ring is flexible and quite capable of adopting very different angles. The values in the solid state for the parent diquinoline **3** and its bis(*N*-oxide) derivative **5** [19] are 107.3 and 141.4 degrees respectively. In the latter case this very much flatter conformation is driven by the molecules packing as linear ribbons where both *N*-oxide groups interact with neighbouring molecules of **5** by means of bifurcated C-H ⋯ O(N) ⋯ H-C interactions (Fig. 7).

Despite this, it is noteworthy that throughout this new family of inclusion compounds pairs of host molecules prefer to wrap around the guests to produce quadrilateral molecular pens. These structures and their

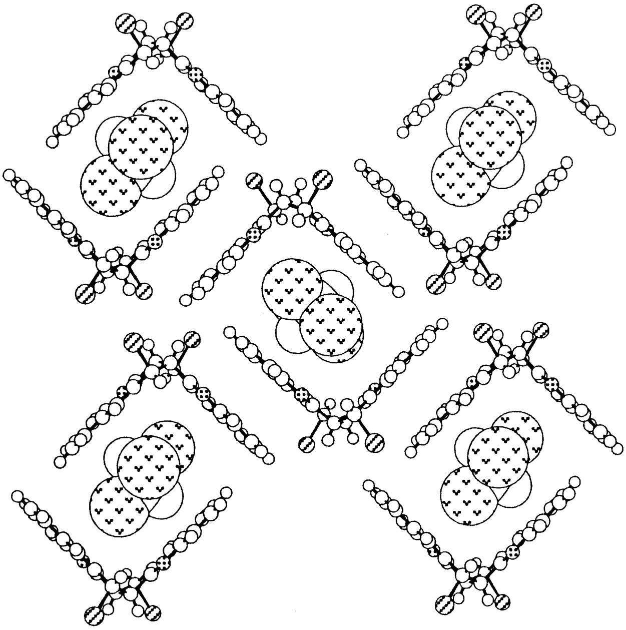

FIGURE 6 A partial layer of $(\mathbf{4})_2\cdot(CHCl_2\text{-}CHCl_2)$ showing the two different types of rectangular pens present. Each type contains one 1,1,2,2-tetrachloroethane molecule but with differing guest orientations.

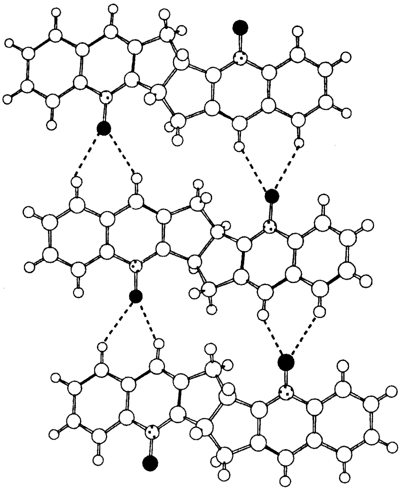

FIGURE 7 The pairs of bifurcated C-H···O(N)···H-C contacts linking **5** molecules as linear ribbons in the solid state. These double interactions are possible by means of the bis(*N*-oxide) molecules adopting a considerably flatter conformation than those adopted in the present investigation.

consistency are in marked contrast to the behaviour observed earlier when a bicyclo[3.3.1]nonane central linker was used [7,8].

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