

Extensively Interlocked 2-D Supramolecular Architecture of Self-Adhesive Double-Tailed 1,3-Planar-2,4-upright-Calix[4]arene

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A novel interlocked 2-D supramolecular architecture is constructed through the synergistic intermolecular interactions of calix[4]arene 1,3-bis(4-nitrobenzoate) in the crystal, which are highly stabilized by the regular π - π and offset stacking, edge-to-face, and/or dipole-dipole interactions.

Molecular assembly and self-organization, which are central to the supramolecular chemistry, are currently investigated extensively in the fields of chemical, biological, and materials science and technology. It has been demonstrated that one of the most important features of such supramolecular architectures is the simultaneous operation of several cooperative weak forces working between receptor (host) and substrate (guest), such as hydrogen bonding, hydrophobic, π - π , and metal-ligand interactions.¹⁻³ Recently, Atwood et al.⁴ have prepared nanometer-scale spheres and tubules by controlling molecular self-organization through the non-covalent interactions. Reinhoudt et al.⁵ have reported self-assembling hydrogen-bonded rodlike nanostructures, which were characterized by tapping-mode scanning force microscopy and ¹H NMR spectroscopy. Reinhoudt et al.⁶ have also shown that β -cyclodextrin-calix[4]arene couples interconnect with each other to form aggregates such as vesicles or fibers through the accumulated hydrophobic interactions. Nolte et al.⁷ have found that disk-shaped molecules self-assemble to form coiled-coil aggregates with tunable helicity through the strong π - π stacking interactions. These supramolecular architectures are of significant academic and industrial importance, as the π - π interactions are known to play crucial roles in biology, chemistry, and materials science.⁸⁻¹⁰ Unfortunately, to the best of our knowledge, no direct evidence or structural detail has hitherto been found for the synergistic π - π interactions involved in the formation of self-assembled supramolecular architectures. In this paper, we have demonstrated that calix[4]arene derivative **1**,¹¹ shown in Chart 1, which possesses a calixarene head group in characteristic 1,3-planar-2,4-upright conformation and two extended nitrophenyl tails, self-assembles in the crystal to give an extensively interlocked 2-D supramolecular architecture. This unique architecture has a two-level structural hierarchy: i.e., the primary strand-like structure made up of mutually penetrating head groups and dual-stacking tails and the secondary inter-strand 2-D network, both of which are highly stabilized by the regular π - π and offset stacking, edge-to-face, and/or dipole-dipole interactions.

As shown in Figure 1, **1**, which obtained from chloroform-methanol mixture kept at 10 °C for a week, is in a pseudo C₂-symmetrical conformation in the crystal, where the unsub-

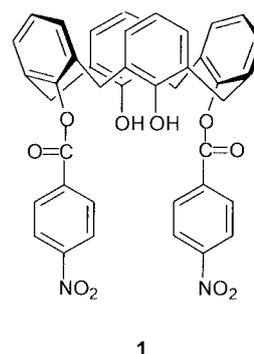


Chart 1. Molecular structure of calixarene derivative **1**

stituted phenol groups tilt down into the cavity, while the nitrobenzoate-substituted ones are in almost upright positions and the two nitrophenyl groups attached to the lower rim are almost parallel to each other. The steric hindrance between the two nitrophenyls and the transannular hydrogen bonding interactions of O1-H1...O7 ($d(\text{H1}\cdots\text{O7}) = 2.086 \text{ \AA}$; $\angle \text{O1-H1}\cdots\text{O7} = 168.25^\circ$) and O2-H2...O3 ($d(\text{H2}\cdots\text{O3}) = 2.094 \text{ \AA}$; $\angle \text{O2-H2}\cdots\text{O3} = 162.06^\circ$) are jointly responsible for such an open calixarene conformation of **1**. The resulting 1,3-planar-2,4-upright calixarene head group and the extended coplanar nitrophenyl tails are ready for the intermolecular head-to-head/tail-to-tail π - π interactions to form a consecutively penetrating/stacking strand-like supramolecular architecture in the solid state.

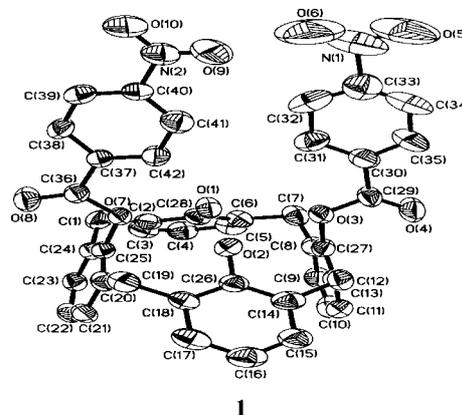


Figure 1. ORTEP representation of the molecular structure of **1** (hydrogen atoms are omitted for clarity).

As can be readily recognized from Figures 2A and 2B, each of the two extended nitrophenyl groups of **1** tightly overlaps with the respective nitrophenyls of another **1** at the identical distance of 3.53 Å. This cooperative double adhesion is highly stabilized not only by the conventional π - π stacking but also by the dipole-dipole interaction of the polarized nitrophenyl groups arranged in the antiparallel direction.

A more intriguing feature of this architecture is the interactions involved in the mutual penetration of calixarene moieties. As can be seen from Figures 2A and 2B, the upright phenyl is offset-stacked to one of the upright phenyls of a neighboring calixarene and is simultaneously interacting in the edge-to-face mode with both of the two "tilted-down" phenyls of the neighboring calixarene. The centroid separation of the offset stacking is 4.716 Å, while the centroid separations and dihedral angles of the edge-to-face interaction are 4.017 Å and 75.9°, 5.290 Å and 77.5°, respectively. These values are quite reasonable in view of the Hunter's rule⁹ and therefore such interactions contribute greatly to the stabilization of the neatly interlocked supramolecular strand-like structure.

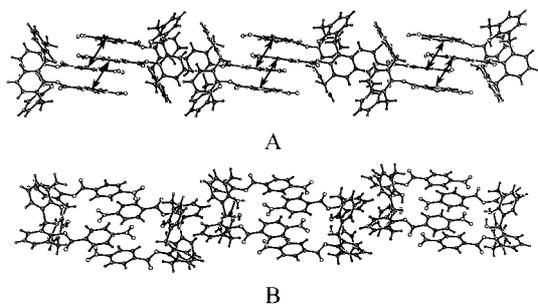


Figure 2. Side views (A and B) of the mutually penetrating/stacking structure of **1** from different angles (double-headed arrows represent the inter-plane centroid distance (3.54 Å) between the two nitrophenyls).

Interestingly, this linear assembly further forms a more sophisticated 2-D architecture through the interstrand interactions. Thus, the two adjacent strands are aligned along the *a* axis by the interstrand edge-to-face interactions. As can be seen from Figure 3, the 1,3-planar phenyls of each interlocked calixarene unit interact in the edge-to-face fashion with the relevant phenyls of adjacent strand, weaving a 2-D network spreaded on the *a*-*b* plane. The centroid separation of 5.14 Å with a dihedral angle of 75.4° is still effective for the edge-to-face interaction to weave across the aligned strands, producing the molecular "tartan-check" pattern.

We have presented the first direct evidence for the formation and structural details of a unique 2-D supramolecular architecture of crystalline 1,3-planar-2,4-upright-calix[4]arene 1,3-bis(nitrobenzoate). Both of the interlocked 1,3-planar-2,4-upright calixarene head and two self-adhesive extended nitrophenyl tails are essential for constructing the rigid linear strand structure, in which the synergetic regular π - π and offset stack-

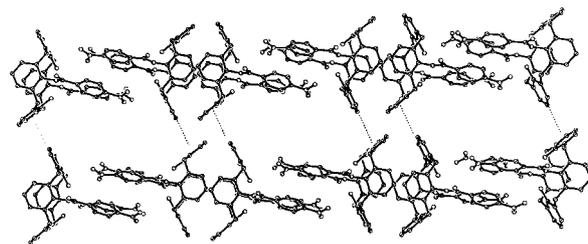


Figure 3. Higher-order 2-D supramolecular architecture of **1** extending over the *a*-*c* plane (the dotted lines indicate the interstrand edge-to-face interactions).

ing, edge-to-face, and/or dipole-dipole interactions play the major role. Further interstrand edge-to-face interaction network of the neighboring 1,3-planar phenyls ultimately weaves the higher-order 2-D architecture. The structural hierarchy and sophisticated modes of intermolecular/interstrand interactions revealed in the present study may be compared to the highly ordered biological supramolecular systems such as globular proteins⁸ and cysteine proteinases,¹² and applied to the design of relevant organic supramolecular assemblies based on the aromatic interactions.

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