Pergamon

Tetrahedron Letters 41 (2000) 10065–10069

TETRAHEDRON
LETTERS

Three-component supramolecular self-assembly based on a 5,5′-bicalix[4]arene exoditopic receptor

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Received 17 July 2000; revised 5 September 2000; accepted 14 September 2000

Abstract

5,5′-Bicalix[4]arene **1**, a ditopic host possessing two divergent cavities, crystallizes from CH_2Cl_2 and *p*-xylene to give an iterative assembly of a three-component zigzag array. This array is formed by CH-π inclusion of a linear CH_2Cl_2·*p*-xylene connector within the facing cavities of two molecules of **1**. Each zigzag array is perpendicularly interconnected to the lateral one through hydrophilic interactions of calixarene-OH groups. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: calixarenes; bicalixarenes; self-assembly; koilate; X-ray crystal structure; CH-π inclusion.

The design and construction of molecular networks or other arrangements in the solid state (crystal engineering)[1] is an actively investigated current research theme. The achievement of this goal has been rationalized through the introduction of new concepts, such as 'supramolecular synthon'[1] and 'molecular tecton',[2] which allow the prediction of iterative intermolecular interactions.[3] Among the large variety of possible interactions,[1–3] H-bonding has been largely favored on the basis of energetic and geometric grounds,[4] whereas other interactions, typical of host–guest inclusion compounds, for example CH-π interactions,[5] have been scarcely exploited. This has to be attributed partly to their lower energy but mainly to the difficulty encountered in controlling their directionality.

One promising approach is given by the use of a concave exoditopic receptor as molecular tecton in conjunction with a suitable convex counterpart. In this respect, bis-calix[4]arene derivatives may be considered particularly suitable because of their known propensity to include various guests inside their basket-shaped cavity.[6] Indeed, an effective demonstration of this

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PII: S0040-4039(00)01584-7

approach has been given by Hosseini and coworkers with the construction of a linear molecular array (a linear ‘koilate’) by assembling a silicon-bonded bis-calixarene units (‘koiland’) with a proper connector.[7]

On a similar grounds we envisioned that our recently introduced 5,5′-bicalix[4]arene **1**[8] could be used as a versatile module for the assembly of other molecular arrays by exploiting van der Waals type interactions. In fact, because of the free rotation around the biphenyl bond of **1** (or its simple derivatives) it can be anticipated that in the presence of a suitable ditopic guest a cooperative intramolecular inclusion or a polymeric intermolecular zigzag array can take place (Fig. 1). In order to test this hypothesis we have chosen *p*-xylene as convex ditopic guest since the propensity of $ArCH_3$ groups to establish CH-π interactions inside the calix[4]arene cavity is well documented.[6,7] Therefore, several unsuccessful attempts were made to crystallize **1** with *p*-xylene. However, when dichloromethane was added crystal formation was observed.

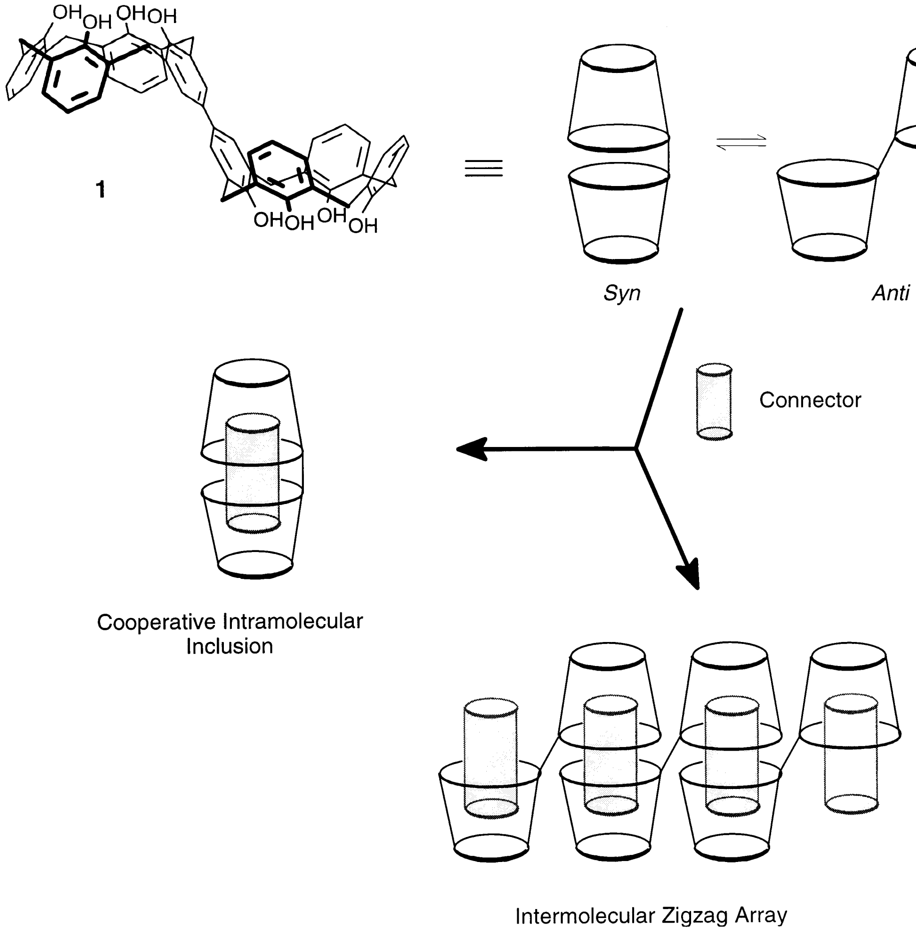

Figure 1. Structure of 5,5′-bicalix[4]arene exoditopic receptor (**1**) and schematic representation of its possible intra- or intermolecular inclusion complex with a proper convex connector

The X-ray diffraction analysis revealed a 1:1:1 ratio of **1**, *p*-$CH_3C_6H_4CH_3$ and CH_2Cl_2 (Fig. 2).[9] In analogy with a previously reported crystal structure, 5,5′-bicalix[4]arene **1** assumes an *anti*-oriented double-cone conformation with a small torsion angle (20.2°) between diphenyl aryl rings.[8]

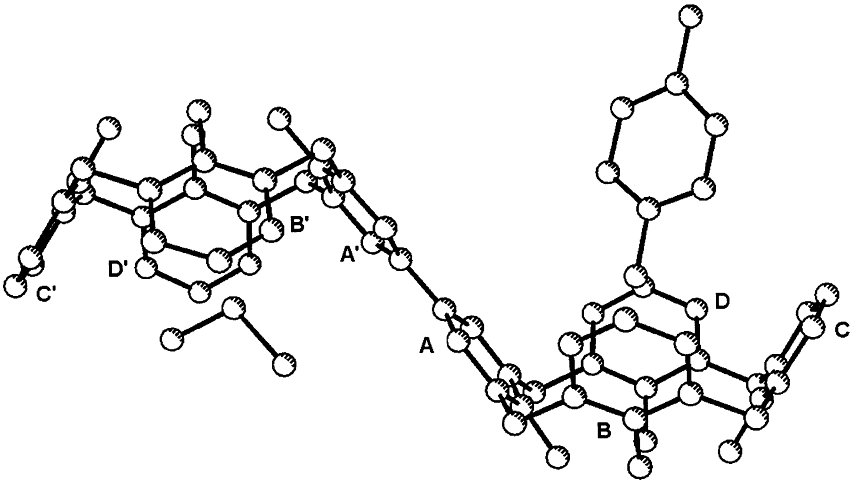

Figure 2. X-Ray crystal structure of the inclusion complex **1**·*p*-xylene·CH_2Cl_2. The labeling of aromatic rings is indicated while H atoms are omitted

As shown in Fig. 3, the expected zigzag molecular array of 5,5′-bicalix[4]arene and *p*-xylene is observed, but through the intermediacy of a CH_2Cl_2 molecule. In fact, one methyl group of *p*-xylene is included within one of the *anti*-oriented cavities of the 5,5′-bicalix[4]arene giving rise to probable CH-π interactions [C···centroid distance 3.73 (ring D), 3.83 (ring C), 3.85 Å (ring A)]. The opposite CH_3 of *p*-xylene points towards the central carbon of CH_2Cl_2 to give probable CH···Cl interactions (distance 3.83 and 3.91 Å). In turn, the CH_2Cl_2 protons point towards the

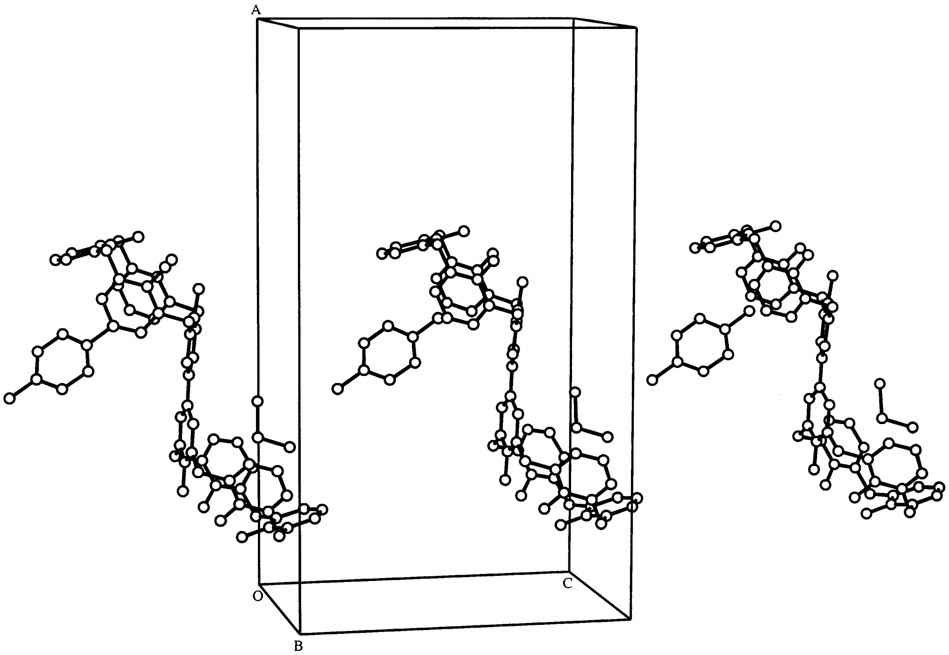

Figure 3. View of the zigzag molecular array held by CH-π and CH···Cl interactions

aromatic centroid of the cavity of a second 5,5′-bicalix[4]arene again with probable CH-π interactions [C···centroid distance 3.60 (ring A′) and 3.65 Å (ring B′)].[11] The role of CH_2Cl_2 seems to be essential to the build-up of the molecular array as indicated by its positional order and by the necessity of its presence to obtain crystals.

Each zigzag array is interconnected to the other through hydrophilic interactions of the OH groups between two different, symmetry related 5,5′-bicalix[4]arene molecules (the shortest distance between phenolic oxygens is 3.03 Å) (Fig. 4). In this way another zigzag arrangement held by the hydrophilic cores[11] is formed, perpendicular to that characterized by *endo*-calix inclusion. In conclusion, the crossing of both zigzag arrays gives rise to a corrugated planar network.

The *endo*-calix zigzag array can be compared to the linear koilate reported by Hosseini and consequently the term 'zigzag koilate' could be proposed. The main difference here is the presence of a CH_2Cl_2 molecule, which assumes a structural role in the three-component supramolecular assembling. It can be considered as a spacer that complements *p*-xylene to give the whole xylene·CH_2Cl_2 connector required for the right spanning imposed by the network.

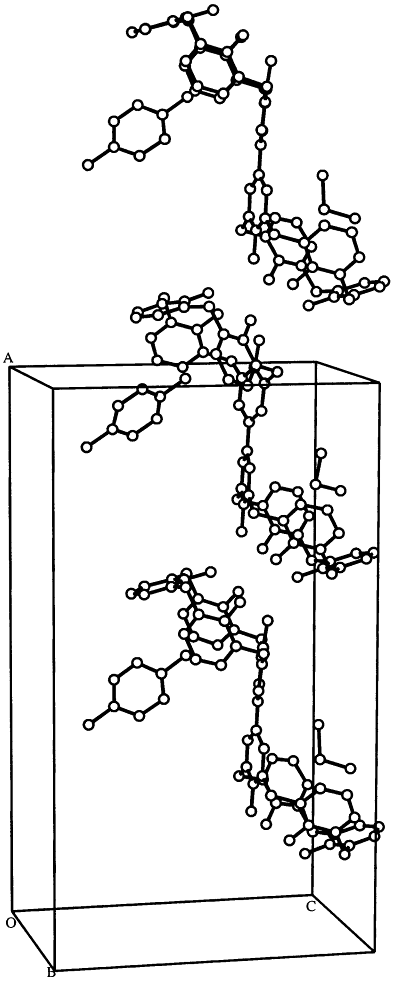

Figure 4. View of the perpendicular interconnection of the zigzag arrays through hydrophilic interactions of calixarene-OH groups

In conclusion, we have demonstrated that the 5,5′-bicalix[4]arene *exo*-receptor can give rise to a three-component zigzag assembly by exploiting also *endo*-calix CH-π interactions. The array is obtained by using a *p*-xylene·CH_2Cl_2 connector. It is to be expected that a single longer connector could give rise to a two-component zigzag 'koilate' mainly based on CH-π interactions. Undoubtedly, 5,5′-bicalix[4]arene derivatives can be considered useful and versatile molecular tectons for the design and construction of supramolecular assemblies in the solid state. Further work in this direction is currently underway in our laboratory.

Acknowledgements

Financial support from the Italian MURST (Supramolecular Devices Project) is gratefully acknowledged.

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9. *Crystal data* for **1**: $C_{56}H_{46}O_8 \cdot CH_2Cl_2 \cdot C_8H_{10}$, $M = 1038.1$, orthorhombic, space group *P*na21 (no. 33), $a = 28.181(2)$, $b = 11.769(2)$, $c = 15.838(2)$ Å, $U = 5253(2)$ Å^3, $Z = 4$, $D_c = 1.31$ g cm^{-3}, μ(Cu Kα) = 1.59 cm^{-1}, $F(000) = 2184$. Prismatic crystals were grown by slow evaporation from a *p*-xylene/dichloromethane solution. A crystal (0.55×0.25×0.20 mm) was sealed with its mother liquid in a Lindemann capillary and used for data collection on a Rigaku AFC5R diffractometer at room temperature. Data were collected until $2\theta_{max} = 124°$, LP-corrected, 4718 reflections measured, 4303 considered unique. The structure was solved and refined with the SIR97 program.[10] The final refinement was based on 3592 reflections with $F_o > 6.0\sigma(F_o)$ and 660 variable parameters (ratio 5.4): $R = 0.084$, $R_w = 0.092$, $\Delta\rho_{max} = 1.4$ and $\Delta\rho_{min} = -0.2$ e Å^{-3}.
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