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Molecular Tectonics I : The First Synthesis and X-ray Analysis of a Linear Koilate Obtained By Self-Assembly of Linear Koilands and Hexadiyne

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Abstract: The first synthesis and X-ray analysis of a koilate, *i. e.* a linear array in the solid state, resulting from an iterative assembling of a koiland (hollow molecule possessing two divergent cavities based on the double fusion of two *p-tert*-butylcalix[4]arenes by two silicon atoms), and hexadiyne as connector, as well as two binuclear complexes formed in the solid state between the above mentioned koiland and anisol and *para*-xylene is described.

The construction of large size molecules (10^{-6}-10^{-4} m scale) or hypermolecules with a predicted and programmed structure may hardly be envisaged through stepwise classical synthesis using covalent linkages. However, the preparation of such higher-order materials may be attained through iterative processes based on self-assembly[1] of individual tectons[2]. This particular area of research, called molecular tectonics [3], is currently under active investigation [4,5]. One of the most important aspects of molecular tectonics appears to be the fact that the assembling process is based on molecular recognition processes operating at the level of the complementary tectons. In other terms, the operational concepts in molecular tectonics are those defined for molecular recognition[6], plus topological features allowing iteration. These two requirements lead to molecular modules possessing connecting points or interaction sites located in a divergent fashion. Using both electrostatic interactions and H-bonding, the synthesis of solids based on iterative assembling of individual complementary tectons has been achieved[7].

The chemistry of inclusion complexes based on concave and convex molecules, *i.e.* the inclusion of a substrate within the cavity of a receptor molecule, is an established area. One may extend the concept of inclusion in solution to the construction of new networks in the solid state. For example, we have proposed[8,9] that *koilates* (one dimensional linear molecular arrays) may be assembled in the solid state using non-covalent van der Waals interactions between a rigid and compact direceptor possessing two divergent cavities with an angle of 180° between them (linear *koiland* , from Greek κοιλοσ : hollow), and a linear connector, possessing two extremities capable each to be included within the cavities of the direceptor (Figure 1).

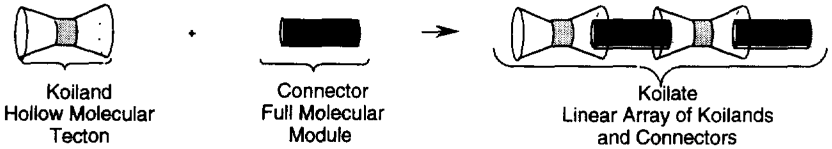

Figure 1: Schematic representation of a linear array (koilate) resulting from interpenetration of a convex molecule (connector) into the cavity of a concave receptor (koiland)

We report now the first example of a linear koilate obtained in the solid state between a linear koiland and hexadiyne as linear connector.

For the design of koilands, calix[4]arenes,[10] offering a genuine hydrophobic pocket surrounded by four aryl moieties as well as four hydroxy groups for further functionalisation, are candidate of choice (Figure 2). This basket-type cavity was shown to accommodate in the solid state a variety of neutral guests such as chloroform,[11] toluene,[12] anisol,[13] xylene[14] and benzene.[14] The fusion of two *p-tert*-butylcalix[4]arenes **1** in its cone conformation by two silicon atoms leads to a hollow brick (koiland) **2**[8,9] (Figure 2). Examples of fused *p-tert*-butylcalix[4]arenes using titanium,[15] niobium [16] and aluminium[17] have been also reported.

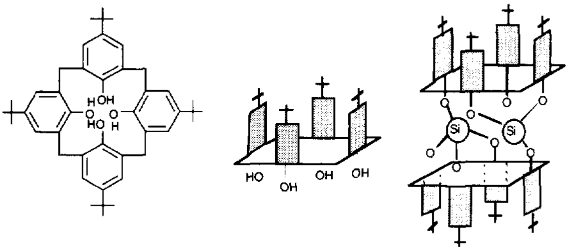

Figure 2: *p-tert*-butylcalix[4]arene **1** (left), schematic representation of its cone conformer (middle), schematic representation of the koiland **2** obtained by fusion of two **1** by two Si atoms (right)

In the solid state, the structure of **2** was analysed by X-ray crystallography.[9] Compound **2** was found to be a centro-symmetric silicon aryloxy dimer consisting of 2 Si and 2 calixarenes. Both calixarene units were in cone conformation, thus, presenting two divergent cavities. Although in the solid state a sandwich complex between two **1** and one anisol was reported,[13] in order to ascertain the possibility of double inclusion, a binuclear complex composed of **2** and anisol with a 1/2 ratio was prepared by crystallisation from anisol and its structure investigated by X-ray analysis (Figure 3).[18] The crystal study showed that amongst the four anisol molecules present, **2** accommodates, in a inclusive fashion, two anisol molecules within its two cavities. anisole penetrates deeply into the cavity by its CH_3 group. Anisol, due to its reduced dimensions and its bent shape, acts as a stopper and therefore is not a well suited connector for bridging the hollow modules **2**.

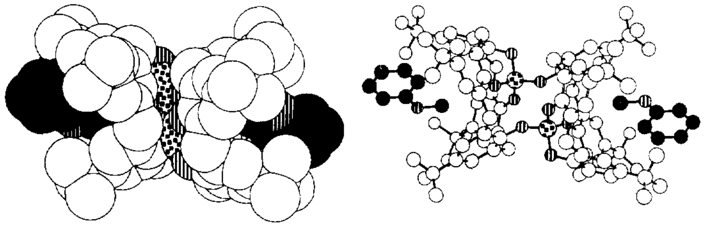

Figure 3: X-ray structure of the inclusion complex formed between **2** and anisol. O and Si are presented by dashed and speckled spheres, C are presented in white and grey, H atoms are omitted.

With *p*-xylene, a sandwich complex engaging two **1** and one *para*--xylene was reported[19]. With the koiland **2**, again a discrete binuclear inclusion complex in the solid state was obtained by crystallisation of **2** in *p*-xylene (Figure 4). The complex was again characterised by X-ray analysis[18] which revealed that amongst the three *p*-xylene molecules present, both cavities of **2** form inclusive complexes with two *p*-xylene. Each *p*-xylene, as in the case of anisol, penetrates deeply into the cavities of **2** through its CH_3 group acting as a stopper. Although the topology of *p*-xylene is well suited for connection of koilands, nevertheless, as it appears clearly on figure 4, the distance between the two CH_3 groups ($d_{C\text{-}C}$ = 5.83 Å) does not allow the formation of the koilate.

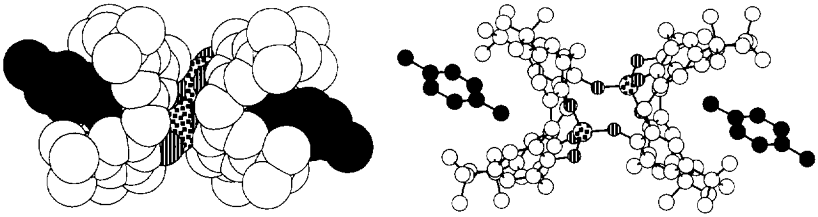

Figure 4: X-ray structure of the binuclear inclusion complex formed between compound **2** and *p*-xylene

Although, due to the discrete nature of the complex, *i.e.* the absence of interconnections between the binuclear complexes, *para*-xylene as connector does not lead to a linear koilate, nevertheless, the disposition, with respect to each other, of binuclear complexes in the solid state appeared to be rather interesting. Indeed, in the lattice, the different complexes are aligned indicating that with better suited connectors, one may succeed in preparing the linear koilates (Figure 5).

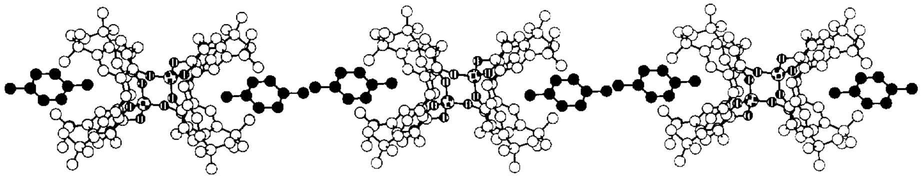

Figure 5: X-ray study of the binuclear *para*-xylene complex with **2** revealed that in the lattice the different modules are linearly arranged.

Hexadiyne, a rod type molecule, possessing both the requested linear geometry and a sufficient distance between its two terminal CH_3 groups (d_{C-C} = 6.65 Å) leads indeed to the formation of the desired koilate (Figure 5). The latter crystallises out from a $CHCl_3$/MeOH solution of koiland **2** and hexadiyne in large excess. The X-ray analysis revealed that in the crystal, in addition to **2** and hexadiyne present in 1/1 ratio, two $CHCl_3$ molecules were also present. Interestingly, the same structure was obtained from $CHCl_3$/hexane. The lattice is indeed composed of molecular linear arrays of koilates formed between koilands **2** and hexadiyne as connectors. Each connector bridges two consecutive hollow bricks by penetrating their cavities through its terminal CH_3 groups. The methyl groups of hexadiyne are deeply inserted into the cavity of the koiland. Indeed, the shortest distance between the CH_3 group of the connector and the aromatic carbon atom (CO) of the koiland is 3.64 Å. It is worth noting that the hexadiyne molecules are extremely well encapsulated by two consecutive koilands **2** forming a sandwich, the shortest distance between the CH_3 groups of the *tert*-butyl moieties of **2** being 3.51 Å. A detailed analysis (distances, angles and packing) of all three structures will be reported elsewhere.

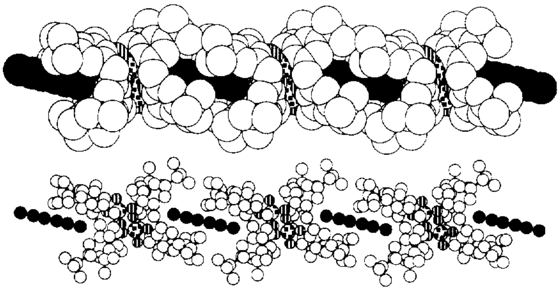

Figure 6: X-ray structure of the koilate formed between **2** and hexadiyne. space filling (top) and balls & sticks (bottom) representations.

As stated above, calix[4]arene derivatives are also interesting units since the preorganised cavity formed by their cone conformation may be tuned. Indeed, both the entrance and the depth of the cavity may be controlled by the nature of the substituant R at the *para* position, *i.e.* H, CH_3, $C(CH_3)_3$, Ph. In the next contribution, we report the synthesis of new koilands based on the fusion of two *p*-methyl- and *p*-phenyl-calix[4]arenes by two silicon atoms.

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18 *Crystal structure determination*: **2**-anisole: $C_{51}H_{52}O_4Si_2.2C_6H_5OCH_3$ (T=173 K), triclinic, P-1, a=13.732(3), b=16.978(3), c=12.375(3) Å, α=101.96(2)°, β=112.02(2)°, γ=71.97(2)°, V=2529.7 $Å^3$, Z=2, μ(CuKα)=7.692 cm^{-1} (graphite monochromator), total reflections 5206, R(F)=0.085. **2**-*p*-xylene: $C_{88}H_{104}O_8Si_2.3C_7H_{10}$ (T=173 K), triclinic, P-1, a=13.357(4), b=17.958(8), c=11.020(3) Å, α=100.75(2)°, β=104.21(2)°, γ=76.49(2)°, V=2468.0 $Å^3$, Z=1, μ(CuKα)=24.700 cm^{-1} (graphite monochromator), total reflections 5541, R(F)=0.047. **2**-hexadiyne: $C_{88}H_{104}O_8Si_2.C_6H_6.2CHCl_3$ (T=173 K), monoclinic, $P2_1/c$, a=15.903(4), b=20.513(6), c=13.727(3) Å, β=94.08(2)°, V=4466.6 $Å^3$, Z=2, μ(CuKα)=7.692 cm^{-1} (graphite monochromator), total reflections 5885, R(F)=0.083. Detailed analyses of all three structures will be published subsequently and the coordinates will then be available on request from Cambridge Crystallographic Data Centre.

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