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Multicavitands V : Synthesis and X-ray Analysis of Unsymmetrical Linear Koilands Based on Double Fusion of Two Different Calix[4]arenes by Two Silicon Atoms.

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Abstract: Unsymmetrical hollow molecular modules possessing two cavities oriented divergently were prepared by fusing two different calix[4]arene derivatives with two silicon atoms. Several of the compounds obtained were characterised by X-ray analysis. © 1997 Elsevier Science Ltd.

Linear koilates[1] are defined as α-networks in the solid state (Figure 1).[2] These networks or unidimensional solids are formed between linear koilands (hollow molecular modules) possessing two receptor cavities oriented at 180° angle, and convex molecular connectors capable of penetrating the cavities. Our initial design of koilands was based on the double fusion of two calix[4]arenes derivatives in cone conformation offering thus a preorganised cavity as well as four hydroxy groups allowing their interconnection by two silicon atoms.[3] Calix[4]arene derivatives have been also fused using other elements[4a] or interconnected by organic[4b] or organometallic bridges.[4c] The preparation and characterisation of the first koilate using the centrosymmetric compound **12** and hexadiyne as the connector have been previously reported.[5] More recently, a second koilate based on a doubly fused *p*-allylcalix[4]arenes and *p*-xylene as the connector was also prepared.[6] These two cases clearly demonstrate the viability of our approach. In dealing with α-networks, a further step *i.e.* the control of the directionality of the assembly still remains an important and challenging issue. In the present communication, we present our approach to the design and synthesis of non-centrosymmetric koilands.

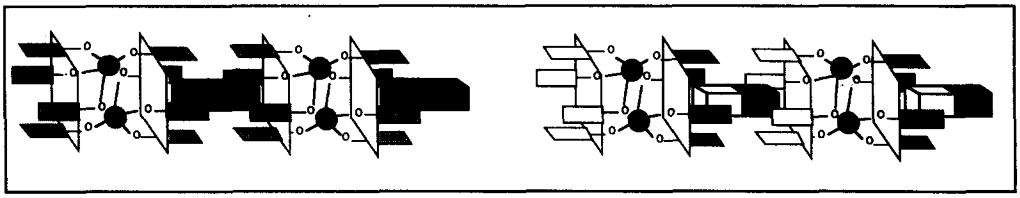

Figure 1. Schematic representation of non-directional (left) and directional (right) koilates based on interconnection of centrosymmetric and non-centrosymmetric koilands (hollow molecular modules) and connectors.

As stated above, although the formation of dimensionally controlled molecular assemblies, *i.e.* the formation of an α-network, could be achieved by the proper design of both the koilands and connector

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molecules, however, in both cases previously reported, due to the centrosymmetric nature of the molecular modules composing the solid, the molecular arrays obtained were centrosymmetric.[5,6] The formation of both dimensionally and directionally controlled α-networks, *i.e.* non-centrosymmetric linear molecular arrays, may, in principle, be envisaged using non-centrosymmetric molecular modules. Thus, one might control the directionality of the linear koilates by using non-centrosymmetric koilands and/or connectors.

The design of non-centrosymmetric koilands may be based either on electronic or on geometric differentiation. Due to the employed fusing strategy, *i.e.* each fusing atom is triply coordinated to one of the calix units and singly coordinated to the other one, the electronic differentiation may be achieved either by using two different fusing atoms possessing the same oxidation state IV such as Si and Ti,[7] or by using two different atoms possessing different oxidation states III and IV such as B and Si. On the other hand, the geometric differentiation may be accomplished, by using the same fusing element such as Si along with two different calix units.

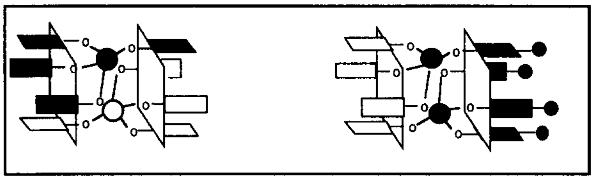
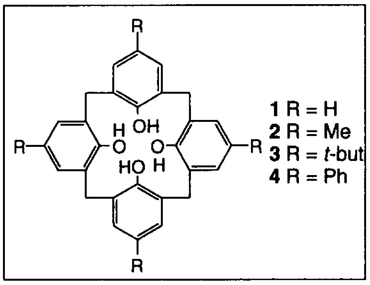


Figure 2. Schematic representation of electronically differentiated koiland based on double fusion of two identical calix[4]arenes by two different elements (left) and of geometrically differentiated koiland based on the double fusion of two different calix [4]arenes by two identical fusing elements (right).



The calix[4]arene backbone, in addition to the above mentioned properties, offers also the possibility of controlling the shape and the size of the cavity by using different substituants at the *para* positions.[3] This aspect has been previously used to prepare other centrosymmetric koilands such as **9** and **14** possessing both two identical cavities but differing in their shape and size.[8] Our general strategy for the preparation of non-symmetric koilands **6-8**, **10**, **11**, and **13** was based on a combinatorial approach.

Upon treatment of a combination of two different calix[4]arenes [X,Y, X = Y = **1**[9a], **2**[9b], **3**[9c], **4**[9d]] with base, followed by reaction with $SiCl_4$, one would expect to form three different koilands [X-X], [Y-Y] of the homo type (centrosymmetric) and [X-Y] of the hetero type (non-centrosymmetric). Indeed, by treating equimolar mixtures of two different calix derivatives with NaH at r. t. and in dry THF for 20 h., followed by addition of $SiCl_4$, and further stirring at r. t. for 3 h. all desired heterodimers could be isolated by chromatography (SiO_2, CH_2Cl_2/Hexane 2 : 8). Whereas in the case of **1**, no trace of the homodimer **5** [1-1] was observed; for all other [X,Y] combinations, in addition to the desired non-centrosymmetric heterodimers [1-2] **6**, [1-3] **7**, [1-4] **8**, [2-4] **10**, [2-3] **11** and [3-4] **13**, three centrosymmetric homodimers [2-2] **9**[8], [3-3] **12**[1] and [4-4] **14**[8] were obtained. The synthesis of compound [1-1] **5** has been previously attempted[8] without success and the present result confirms our previous observation. The yield for the formation of the heterodimers (**6** : 6 %, **7** : 10 %, **8** : 4 %, **10** : 4 %, **11** : 3 %, **13** : 10 %) could not be enhanced by varying the ratio of the two parent calix derivatives. The yield for the formation of homodimers was dependent upon the combination of calix derivatives used. The highest yield of *ca* 50 % was obtained for the formation of **12**, whereas for all other cases the yield was rather poor (5-10 %).

All new compounds reported were characterised by high resolution mass spectrometry as well as by both ^{1}H and ^{13}C NMR spectroscopy which revealed the non-centrosymmetric nature of the heterodimers **6-8**, **10-11** and **13**.[10] In addition to the above mentioned classical characterisation techniques, the heterodimers were also characterised by ^{29}Si NMR. For the non-centrosymmetric heterodimers two signals (δ in ppm, $CDCl_3$: -113.35, -113.45 for **6**; -112.41, -113.29 for **7**; -112.46, -112.66 for **10**; -111.65, -112.28 for **11**; -112.30, -113.07 for **13**) were observed as expected. Further more, the solid state structures of compounds **6**, **7** and **9** were confirmed by X-ray analysis (Figure 4).[11] For all three compounds, the coordination geometry around the silicon atoms was tetrahedral with an average Si-O distance of ca 1.60 Å and average OSiO angle of *ca* 109.4°. For all three cases, both tetrahedrons around the silicon atoms were composed of 3 oxygen atoms belonging to one of the two calixarenes and the fourth one to the other calix unit. The Si-Si distance varied only slightly from 3.84 Å for **6** to 3.77 Å for **7** and to 3.78 Å for **9**. These values are similar to those previously observed for compound **12**.[1]

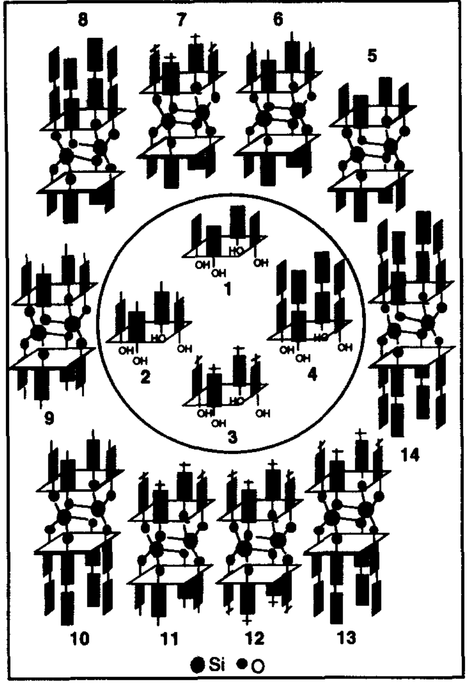


Figure 3. Schematic representation of parent calix[4]arenes **1-4** in cone conformation, and of doubly fused homo- and hetero-dimers **5-14**.

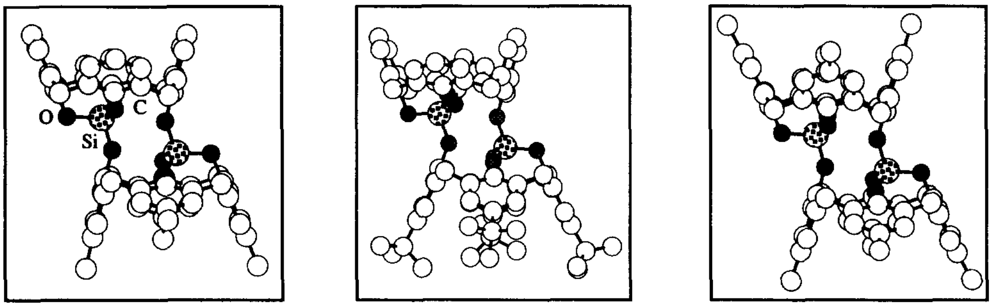


Figure 4. X-ray structures of the heterodimers **6** (left) and **7** (middle) and of the homodimer **9** (right). For the sake of clarity, hydrogen atoms as well as solvent molecules are not presented.

In conclusion, we have shown that non-centrosymmetric koilands based on the double fusion of two different calix[4]arenes by two silicon atoms could be prepared using a combonatorial approach. The self-assembly of the heterodimers into directional koilates using different connectors is under current investigation.

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10 All new compounds gave satisfactory elemental analysis and were also characterised by high resolution mass spectrometry . Selected NMR (δ(ppm)) data: **6**: ^{1}H (CDCl$_3$, 200 MHz, 25 °C): δ(ppm): 2.06 (s, CH$_3$, 3H); 2.13 (s, CH$_3$, 3H); 2.25 (s, CH$_3$, 6H); 3.30 (d, J=13.3 Hz, CH$_2$, 2H); 3.35 (d, J=13.6 Hz, CH$_2$, 2H); 3.90 (d, J=13.4 Hz, CH$_2$, 2H); 3.45 (d, J=13.7 Hz, CH$_2$, 2H); 4.46 (d, J=13.5 Hz, CH$_2$, 2H); 4.51 (d, J=13.6 Hz, CH$_2$, 2H); 4.56 (d, J=13.4 Hz, CH$_2$,2H); 4.64 (d, J=13.5 Hz, CH$_2$, 2H); 6.74 (s, arom., 2H); 6.85 (s, arom., 2H); 6.87 (s, arom., 2H); 6.91 (s, arom., 2H); 6.77-7.12 (m, arom., 12H); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): δ(ppm): 20.5, 20.7, 20.9 (CH$_3$); 33.2, 34.1 (CH$_2$); 122.9, 123.2, 124.6, 128.4, 128.5, 129.1, 129.7, 130.2, 131.6 (CH, arom.); 129.8, 130.3, 132.2, 132.6, 132.9, 133.7 (C arom.); 144.8, 147.1, 148.2, 148.4; 150.6 (C arom., C-O); **7**: ^{1}H (CDCl$_3$, 200 MHz, 25 °C): δ(ppm): 1.13 (s, CH$_3$, 9H); 1.21 (s, CH$_3$, 9H); 1.28 (s, CH$_3$, 18H); 3.37 (d, J=12.4 Hz, CH$_2$, 4H); 3.43 (d, J=13.4 Hz, CH$_2$, 2H); 3.45 (d, J=13.9 Hz, CH$_2$, 2H); 4.52 (d, J=15.6 Hz, CH$_2$, 2H); 4.59 (d, J=13.2 Hz, CH$_2$, 2H); 4.66 (d, J=12.5 Hz, CH$_2$, 2H); 6.73-7.13 (m, arom., 12H); 6.96 (s, arom., 2H); 7.04 (br. s, arom., 2H); 7.06 (br. s, arom., 2H); 7.09 (s, arom., 2H); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): δ(ppm): 31.41, 31.48, 31.59 (CH$_3$); 33.27, 33.99, 34.13, 34.97 (CH$_2$); 122.44, 123.11,125.13, 125.28, 126.27, 126.63, 128.34, 128.54, 129.80 (CH arom.); 127.79, 128.92, 129.70, 130.28, 130.50, 132.37, 133.07 (C arom.); 145.03, 148.25, 150.64 (C arom., CO); **8**: ^{1}H (CDCl$_3$, 200 MHz, 25 °C): δ(ppm): 3.55 (d, J= 13.5 Hz, CH$_2$, 2H); 3.57 (d, J=14.2 Hz, CH$_2$, 2H); 3.64 (d, J=14.6 Hz, CH$_2$, 2H); 3.71 (d, J=13.5 Hz, CH$_2$, 2H); 4.59 (d, J= 13.5 Hz, CH$_2$, 2H); 4.68 (d, J= 4.9 Hz, CH$_2$, 2H); 4.71 (d, J=13.5 Hz, CH$_2$, 2H); 4.76 (d, J=13.5 Hz, CH$_2$, 2H); 6.81- 7.42 (m, arom., 40H); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): δ(ppm): 35.2, 35.5; 35.8, 36.2 (CH$_2$); 124.9, 128.9, 129.1, 129.3, 129.7, 130.4, 130.5, 130.7, 130.8, 131.8, 131.9, 132.0 (CH, C arom.); 132.4, 132.6, 132.8, 134.6, 136.3, 137.9, 139.4, 140.3, 142.4 (C arom.); 148.5, 148.9, 149.9, 152.4 (C arom., C-O); **10**: ^{1}H (CDCl$_3$, 200 MHz, 25 °C): δ(ppm): 2.09 (s, CH$_3$, 3H); 2.16 (s, CH$_3$, 3H); 2.27 (s, CH$_3$, 6H); 3.37 (d, J=13.5 Hz, CH$_2$, 4H); 3.39 (d, J=13.8 Hz, CH$_2$, 2H); 3.57 (d, J=13.4 Hz, CH$_2$, 2H); 3.62 (d, J=13.7 Hz, CH$_2$, 2H); 4.52 (d, J=13.6 Hz, CH$_2$, 2H); 4.52 (d, J=13.3 Hz, CH$_2$, 2H); 4.64 (d, J=13.7 Hz, CH$_2$, 2H); 4.77 (d, J=13.4 Hz, CH$_2$, 4H); 6.78 (s, arom., 2H); 6.88 (s, arom., 2H); 6.92 (s, arom., 2H); 6.94 (br. s, arom., 2H); 7.15-7.59 (m, arom. 28H); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): δ(ppm): 20.5, 20.7 (CH$_3$); 33.3, 33.7, 34.1, 34.5 (CH$_2$); 127.0, 128.5, 128.8, 129.1 (CH arom.); 126.8, 127.3, 127.5, 129.3, 129.9, 130.3, 130.5, 130.6, 131.7, 132.5, 133.1, 135.6, 135.7, 140.5, 140.6 (C arom.); 144.8, 148.4, 150.2 (C arom., C-O); **11**: ^{1}H (CDCl$_3$, 200 MHz, 25 °C): δ(ppm): 1.13 (s, CH$_3$, 9H); 1.21 (s, CH$_3$, 9H); 1.29 (s, CH$_3$, 18H); 2.06 (s, CH$_3$, 3H); 2.13 (s, CH$_3$, 3H); 2.26 (s, CH$_3$, 6H); 3.26 (d, J=13.6 Hz, CH$_2$, 2H); 3.35 (d, J=13.8 Hz, CH$_2$, 4H); 3.42 (d, J=14.1 Hz, CH$_2$, 2H); 4.46 (d, J=13.6 Hz, CH$_2$, 2H); 4.51 (d, J=13.6 Hz, CH$_2$, 2H); 4.58 (d, J=13.5 Hz, CH$_2$, 2H); 4.59 (d, J=13.3 Hz, CH$_2$, 2H); 6.72 (s, arom., 2H); 6.84 (s, arom., 2H); 6.86 (br. s, arom., 2H); 6.90 (br. s, arom., 2H); 6.95 (s, arom., 2H); 7.03 (d, J=2.5 Hz, arom., 2H); 7.06 (d, J=2.5 Hz, arom., 2H); 7.09 (s, arom., 2H); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): δ(ppm): 20.39, 20.65, 20.83, 31.34, 31.42, 31.53 (CH$_3$); 33.22, 33.99, 34.28, 34.84 (CH$_2$); 125.18, 126.13, 126.54 (CH arom.); 128.89, 129.88, 130.21, 132.38 (C arom.); 128.99, 129.99, 130.36 (CH arom.); 129.37, 130.21, 131.28, 132.75, 133.48 (C arom.); 144.80, 145.13, 148.22, 144.80, 145.13, 146.42 (C-O); **13**: ^{1}H (CDCl$_3$, 200 MHz, 25 °C): δ(ppm): 1.16 (s, CH$_3$, 9H); 1.23 (s, CH$_3$, 9H); 1.29 (s, CH$_3$, 18H); 3.43 (d, J=13.3 Hz, CH$_2$, 2H); 3.48 (d, J=14.1 Hz, CH$_2$, 2H); 3.55 (d, J=15.7 Hz, CH$_2$, 2H); 3.63 (d, J=14.2 Hz, CH$_2$, 2H); 4.58 (d, J=13;7 Hz, CH$_2$, 2H); 4.67 (d, J=13.5 Hz, CH$_2$, 2H); 4.73 (d, J=13.4 Hz, CH$_2$, 2H); 4.80 (d, J=13.5 Hz, CH$_2$, 2H); 7.01 (s, arom., 2H); 7.08 (d, J=2.3 Hz, arom., 2H); 7.11 (d, J=2.6 Hz, arom., 2H); 7.12 (s, arom., 2H); 7.15-7.60 (m, arom., 28H); ^{13}C (CDCl$_3$, 75 MHz, 25 °C): δ(ppm): 31.4, 31.6 (CH$_3$); 33.7, 34.0, 34.4 (CH$_2$); 122.2, 125.4, 126.7, 126.8, 127.0, 127.3, 128.6, 128.8 (CH arom.); 126.3, 127.5, 128.9, 129.9, 130.3, 130.7, 132.4, 133.3, 135.6, 140.6 (C arom.); 145.0, 145.2, 146.9, 148.3, 150.3 (C; C-O).

11 The X-ray data for all three structures as well a complete structural analysis in terms of packing in the solid state will be published elsewhere.

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