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Multicavitands III: Synthesis and NMR Studies of a Tri-directional Koiland Composed of Three *p-tert-butyl*calix[4]arene Units Fused by two Silicon Atoms

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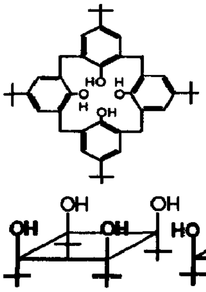
Abstract: The synthesis of a divergent trireceptor composed of three hydrophobic cavities was achieved by fusing three *p-tert*-butylcalix[4]arene units in their cone conformation with two silicon atoms. Complete structural analysis was possible using multidimensional NMR techniques. Variable temperature NMR studies between 40°C and -90°C revealed that all three calix units were in their cone conformation and that the only conformational change observed was a rotation around the silicon-oxygen bonds with a $\Delta G^{\neq}$ of ca. 46 kJ mol^{-1}.

The use of non-covalent interactions to assemble koilands and connectors may be a means of obtaining new plastic (flexible) networks in the solid state. We defined koilands[1,2] as multicavity receptor molecules composed of at least two cavities arranged in a divergent fashion. The directionality of the assembling process between the koiland and connectors may be controlled either by the number and the disposition of the cavities within the structure of the hollow brick, or by the shape of the connector. In our earlier work we succeeded in preparing linear centrosymetric[1] and non-centrosymetric[2] koilands possessing two divergent cavities with an angle of 180° between them. We report here the first example of a tri-directional koiland composed of three *p-tert*-butylcalix[4]arenes[3] **1** directly fused by two silicon atoms **2**. The only other two triscalixarenes reported are those in which three calixarenes are interconnected by aromatic[4] or by ferrocene[5] moieties.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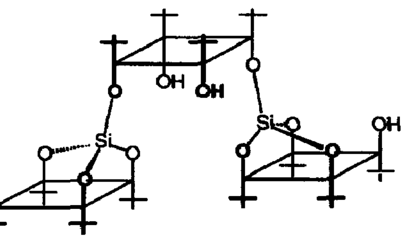
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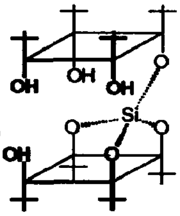
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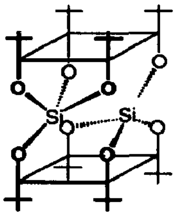
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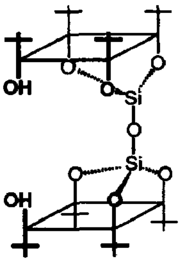
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Compound **2** was prepared by reacting **1**[6] with $SiCl_4$ and NaH in dry THF. In order to optimise the synthesis of **2**, the effect of the solvent (THF, CH_3CN, CH_3Ph), the base (NaH, Et_3N), the reagent ($SiCl_4$, $Si(OMe)_4$), the ratio base/**1** (2,4), the ratio reagent/**1** (0.6-3), the reaction time (1h-17 days) and the reagent addition time (at once-50 min.) was investigated (see table). No trace of **2-5** was observed for the reaction of **1** with $SiCl_4$ in CH_3CN or with $Si(OMe)_4$ in THF. However, in toluene, although no trace of **4** was detected, rather poor yields of **2** (4%) and **3** (9%) were obtained. The best yield (60-69%, repeated several times) for the synthesis of **2** was achieved by dropwise addition (45 min) of diluted $SiCl_4$ (10% solution) in THF with ratio of base/**1** and of $SiCl_4$/**1** of 4 and 1.2 respectively.[7] The yield of **2** when pure $SiCl_4$ was added at once never exceeded 1%. The highest yields for **3**[2] (36%, 4 eq. of NaH, 0.6 eq. of $SiCl_4$) and for **4**[1] (52%, 5 eq. of NaH, 1.2 eq. of $SiCl_4$) were obtained in THF by immediate addition of pure reagent. In some cases, low yields of **5** (1-4%)[8] were observed, probably due to the presence of moister.

Table: Reaction conditions and yields of products.

Solvent	Base	Eq of base	Reagent	Eq of Reagent	Time	2	3	4	5
THF	NaH[a]	2	$Si(OMe)_4$[b]	0.6	17 d	0 %	0 %	0 %	0 %
THF	NaH[a]	2	$SiCl_4$[c]	0.6	1 h	12 %	9%	0 %	3 %
THF	NaH[a]	2	$SiCl_4$[b]	0.6	1 h	<1 %	15%	0 %	<1 %
THF	NaH[d]	5	$SiCl_4$[b]	1.2	2 h	0 %	0 %	52 %	0 %
THF	NaH[a]	4	$SiCl_4$[e]	1.2	1 h	69 %	0 %	0 %	0 %
THF	NaH[a]	4	$SiCl_4$[b]	0.6	3 h	<1 %	36 %	0 %	3.4 %
CH_3CN	NaH[a]	4	$SiCl_4$[b]	1.1	1 h	0 %	0 %	0 %	0 %
CH_3Ph	Et_3N[f]	4	$SiCl_4$[b]	3.0	38h	4 %	9 %	0 %	0 %

a: 25 °C, 17h. b: immediate addition. c: 10% solution of $SiCl_4$ (THF) added over 50 min. d: 25 °C, 20h e: 10% solution of $SiCl_4$ (THF) added over 45 min. f: Et_3N, $SiCl_4$ and **1** were stirred in CH_3Ph at 25 °C.

Mass spectrometry (FAB^+, 1993.7) indicated that **2** contained 3 calix units, 2 Si atoms and 4 OH groups. At 25 °C, the presence of Si atoms was further confirmed by ^{29}Si NMR (-107.8 ppm). The presence of OH groups was also observed by IR (3528 cm^{-1}) and by ^1H NMR (3.53, 7.70 ppm). The structure of **2** was investigated by ^1H and ^{13}C NMR spectroscopy. At 25 °C, the ^1H spectrum indicated that **2** was composed of two types of calix units with 1/2 ratio (Fig. 1) and thus possessed a plane of symmetry. Both types of calix were in cone conformation. These observations were further confirmed by ^{13}C NMR. The complete structural assignment at 25 °C in solution was achieved by ROESY experiments. Thus, **2** was composed of three calix units, all in cone conformations, fused by two Si atoms. The top calix containing two OH groups (Fig. 1) was connected twice at 1,3 positions to both Si atoms. At 25 °C, the other two equivalent calix units, each possessing one OH group, were each triply coordinated to Si atoms, thus completing their coordination spheres. Due to the flexibility induced by the presence of hydroxy groups, one could expect three different conformations (cone, partial cone, 1,3-alternate) for the top calix and two conformers (cone, partial cone) for the two bottom calix units. Furthermore, because of the possible free rotations around both Si-O bonds interconnecting the calix units, many rotamers could exist in solution. Therefore, a systematic conformational analysis of **2** using variable temperature ^1H NMR was performed (Fig. 1). By decreasing the temperature from 40 °C to -80 °C, all three calix units, although maintaining their cone conformations, were differentiated and, thus, three sets of proton signals with 1/1/1 ratio were observed. Furthermore, ^{29}Si NMR showed two distinct signals at -80 °C (-108.7, -108.9 ppm) revealing two slightly different Si atoms. The observed coalescence temperatures Tc for all signals , except for the OH groups, ranged from -60 °C to -30 °C. The free energy of activation $\Delta G^{\ddagger}$ calculated from different Tc values ranged from 44.3 to 46.4 kJ mol^{-1}. These almost identical values suggested a unique or a correlated "wiper" type process. The structure of **2** at -80 °C was again elucidated by ROESY experiments which revealed that, as expected, upon cooling no changes in the connectivity of the three calix units by Si atoms or of their cone conformation occurred. The effect of decreasing the temperature from 40 to -80 °C was to slowdown the equilibrium between the two equivalent rotamers (Fig. 2). In such a rotamer, perhaps due to possible hydrogen bonding between the OH groups, the two equivalent calix units at 25 °C were differentiated.

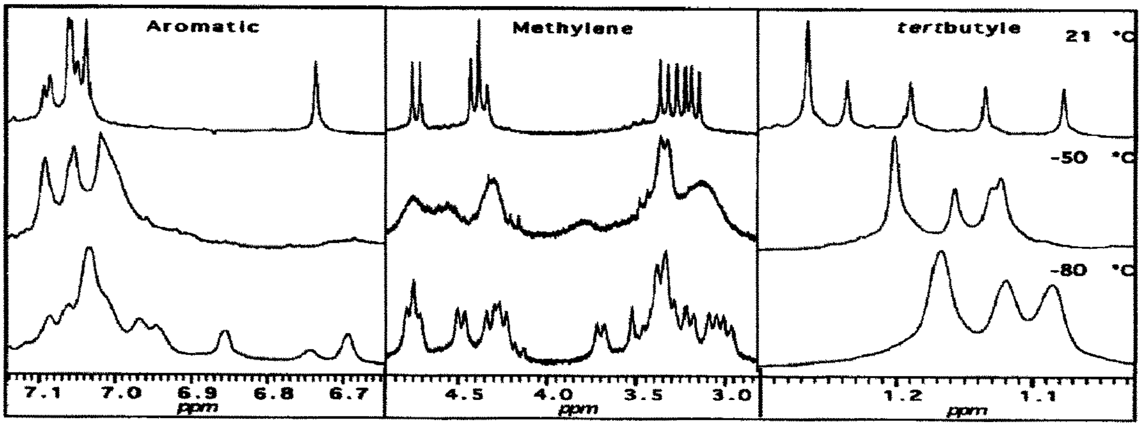

Fig. 1. Selected ^{1}H NMR signals of **2** at different temperatures.

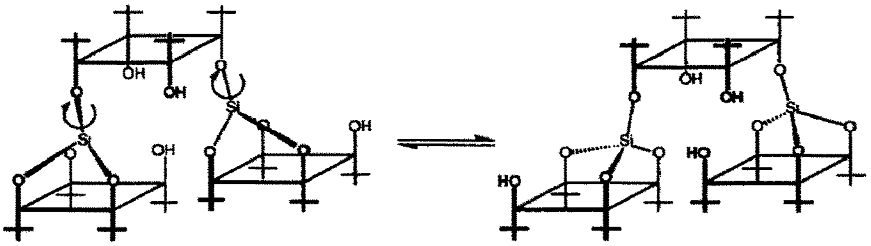

Fig. 2. "wiper" type equilibrium between two rotamers of **5**.

In conclusion, we were able to fuse with remarkably high yield three *p-tert*-butylcalix[4]arenes with two Si atoms. Structural analysis revealed that all three calix units were in their cone conformation with the only conformational process taking place between 40 °C and -80 °C being the rotation around Si-O bond.

The assembling of tridirectional koilands with linear connectors in the solid state may lead to non-covalent dendrimers, work in the elaboration of such networks in the solid state using **2** as a unit is under progress.

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7. In a 100 ml round bottom flask, a suspension of **1**[6] (2g, 2.7 mmoles) and NaH (260 mg, 1.1 mmol) in dry THF (50 ml) was stirred at r. t. for 17 h. To the white slurry thus obtained a solution of $SiCl_4$ (0.35 ml, 3 mmol) in dry THF (3 ml of THF) was added dropwise (45 mn.) and stirring was continued for another 1 h. The solid was removed by filtration and washed with $CHCl_3$ (2x20 ml); the washes and the filtrate were combined before the mixture was evaporated to dryness under reduced pressure. The pure compound **2** (1.218 g, 69%) was obtained as a white solid after a short chromatography (SiO_2, rf= 0.5, CH_2Cl_2/hexane 30/70). M. p. 318-320 °C; ^1H NMR (CD_2Cl_2, 400.135 MHz, 25 °C): δ 1.09, 1.14, 1.20, 1.25 4x (s, 18H, CH_3), 1.28 (s, 36H, CH_3), 3.19 (d, J=13.5 Hz, 4H, CH_2), 3.26 (d, J=13.2 Hz, 4H, CH_2), 3.36 (d, J=13.3 Hz, 4H, CH_2), 4.38 (d ,J=13.5 Hz, 4H, CH_2), 4.42 (d, J=13.5 Hz, 4H, CH_2), 4.75 (d, J=13.2 Hz, 4H, CH_2), 6.76, 7.05 2x (s, 4H, arom), 7.06 (AB, J=2.6 Hz, 4H, arom), 7.08 (s, 8H, arom.), 7.11 (AB, J=2.6 Hz, 4H, arom), 7.43 (s, 2H, OH); ^1H NMR (CD_2Cl_2, 400.135 MHz, -80 °C): δ 0.94, 0.98 2x (s, 9H, CH_3), 1.08, 1.12 2x (s, 27H, CH_3), 1.17 (s, 36H, CH_3), 2.99 (d, J= 12.2 Hz, 2H, CH_2), 3.08 (d, J=13.4 Hz, 2H, CH_2), 3.20 (d, J=12.3 Hz, 2H, CH_2), 3.31-3.37(br., 6H, CH_2), 3.53 (s, 1H, OH), 3.69 (d, J=11.2 Hz, 2H, CH_2), 4.25 (d, J=12.8 Hz, 2H, CH_2), 4.31 (d, J=12.2 Hz, 2H, CH_2), 4.48 (d, J=11.4 Hz, 2H, CH_2), 4.73 (d, J=13 Hz, 2H, CH_2), 4.77 (d, J=13 Hz, 2H, CH_2), 6.56, 6.70 2x (s, 2H, arom.), 6.75 (s, 1H, OH), 6.86, 6.95, 6.98, 7.02 4x (s, 2H, arom.), 7.04 (s, 8H, arom.), 7.07, 7.10 2x (s, 2H, arom.), 7.70 (s, 2H, OH); ^{13}C NMR ($CDCl_3$, 100.614 MHz , 25 °C): δ 29.7 (CH_2), 31.04, 31.33, 31.42, 31.51, 31.74 (CH_3), 33.08 (CH_2), 33.73, 33.80, 33.88, 33.95, 34.27 (C), 34.72 (CH_2), 124.42, 124.67, 124.97, 125.32, 125.4 (C, arom.), 126.33, 126.39 (CH, arom.), 128.89, 129.48, 130.31, 130.36, 132.71, 141.84, 152.25, 144.45, 144.64, 144.90, 145.44, 146.53, 147.82, 147.87, 150.67 (C, arom.); ^{29}Si NMR (CD_2Cl_2, 79.495 MHz, 25 °C): δ -107.86; ^{29}Si NMR (CD_2Cl_2, 79.495 MHz, -80 °C): δ -108.71, -108.90; Positive ion FAB (*m*-nitrobenzylalcohol), m/z=1993.7 ($M^{+\cdot}$, 100%), 1977.9 (M^+-CH_3 + H^+, 30%); IR (KBr) 3528 (m, l, OH), 990 (s, Ph-O-Si); UV 280 nm (22860 l mol^{-1} cm^{-1}); Found: H 8.26, C 79.29; calcd for $C_{132}H_{160}O_{12}Si_2$: H 8.09, C 79.47%.
8. To a suspension of *p-tert*-butylcalix[4]arene **1**[6] (2 g, 2.70 mmol) in dry THF (50 ml), NaH (260 mg, 10.82 mmol) was added under argon and the mixture was stirred at r. t. over a period of 17 h. To the slurry $SiCl_4$ (0.2 ml, 1.7 mmol) was added and the mixture further stirred for another 3 h. THF was removed and the pure compound **5** (63 mg, 3.4%) was obtained as a white solid after chromatography (SiO_2, rf=0.05, CH_2Cl_2/hexane 10/90). ^1H NMR ($CDCl_3$, 300.133 MHz, 25 °C): δ 1.03, 1.19 2x (s, 18H, CH_3), 1.31 (s, 36H, CH_3), 3.29 (d, J=14.1 Hz, 4H, CH_2), 3.30 (d, J=13.8 Hz, 4H, CH_2), 4.25 (d, J=13.9 Hz, 4H, CH_2), 4.52 (d, J=13.7 Hz, 4H, CH_2), 6.13 (s, 2H, OH), 6.76 (s, 4H, arom.), 7.02 (AB, 2.5 Hz, 4H, arom.), 7.06 (s, 4H, arom.), 7.09 (AB, 2.4 Hz, 2H, arom.); ^{13}C NMR ($CDCl_3$, 100.61 MHz, 25 °C): δ 31.3, 31.4, 31.5 (CH_3); 33.0, 33.7, 34.0, 34.3, 34.7 (C, CH_2); 124.5, 124.6, 124.9, 126.5, 126.6, 130.0, 130.4, 132.5, 142.3, 144.9, 145.0, 146.6, 147.7, 148.0 (arom.); ^{29}Si NMR ($CDCl_3$, 79.495 MHz, 26 °C): δ –130.53; IR (KBr) 3568 (m,l, OH), 994.9 (s, Ph-O-Si), Positive ion FAB (*m*-nitrobenzylalcohol), m/z 1362.5 ($M^{+\cdot}$, 100%), 1347.5 ($M^{+\cdot}$-CH_3, 40%); Found: H 8.01, C 77.3; calcd for $C_{88}H_{106}O_9Si_2$: H 7.83, C 77.49%.

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