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Synthesis and Conformational Properties of Bis(calix[4]arene)

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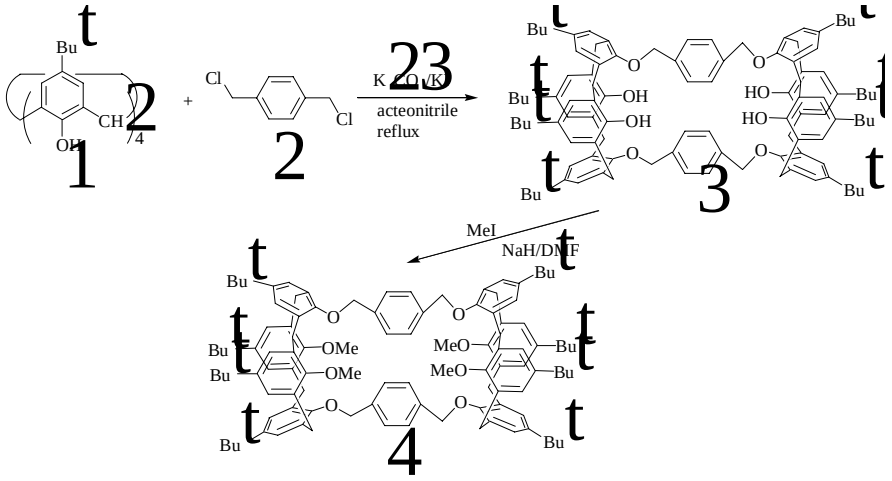
Abstract: The bis(calix[4]arene) **3** was synthesized in moderate yield by the reaction of *p-tert*-butylcalix[4]arene (**1**) with 1,4-bis(chloromethyl)benzene (**2**). The conformation of all alkylated product **4** was investigated by the variable-temperature ^{1}H-NMR.

Keywords: Bis(calix[4]arene), conformation, receptor.

Calixarenes are very useful building blocks or molecular platforms in supramolecular chemistry[1]. In recent years, there are lots of achievements in the field of molecular recognition and self-assembly based on the calixarene skeleton[2]. In order to enlarge the cavity of calixarenes, the synthesis of calixarene derivatives with multi-cavity or oligo-calixarenes have absorbed increasing interests. Among these calixarene derivatives, bis(calixarenes) were useful artificial receptors and can be as the mimics of ion channel of biological system[3]. Here, we wish to report a facile method to synthesize bis(calix[4]arenes) and their conformational properties.

Scheme 1

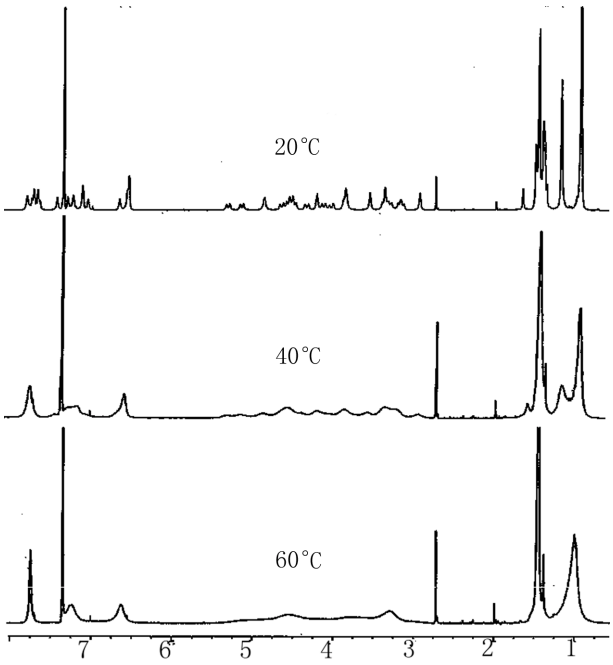


Bis(calix[4]arene) **3** linked by two *p*-phenylene groups could be conveniently synthesized with *p-tert*-butylcalix[4]arene (**1**) and 1,4-bis(chloromethyl)benzene (**2**) in

moderate yield (50%)[4]. Other than the linkage, *e.g.* crown ether, bis(calix[4]arene) **3** as the main product has been obtained instead of intramolecular linkaged product because of the rigid structure of *p*-phenylene.

3 has adopted cone conformation in $CDCl_3$ at room temperature owing to the presence of intramolecular hydrogen-bonding at the lower rim. It can be confirmed from the signals of protons of methylene between two phenol rings, which showed AB system. However, compound **4**[4], which are the all-methylated product of **3**, may possess seven conformations in the same condition and its ^{1}H-NMR spectrum signals are difficult to be ascribed. The different conformational isomers of **4** can interconverse with the oxygen-through-the annulus rotation mode, and this interconversion will be faster at higher temperature[1c]. So, when temperature is raised above 60°C, the resolution of the spectrum of **4** became worse due to the rapid interconversion of the signals of all possible conformers at high temperature. And the structure can be determined from the type and integral of signals in the spectrum. (**Figure 1**)

Figure 1 ^{1}H NMR spectra of bis(calix[4]arene) **4** at different temperatures.



The effect of complexation for the change of conformations will be investigated in the following work.

Acknowledgments

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References and Notes

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4. **3**: yield 50%; mp 285°C (dec.); MS (maldi-TOF): *m/z* 1523 (M^++Na). ^{1}H-NMR ($CDCl_3$) δ 0.95 (s, 36H, $C(CH_3)_3$),1.27 (s, 36H, $C(CH_3)_3$), 3.29 and 4.32 (AB-d, ^2J = 13.0 Hz, 16H, $ArCH_2Ar$), 5.13 (s, 8H, $ArOCH_2$), 6.80 (s, 8H, ArH), 7.03 (s, 8H, ArH), 7.42 (s, 4H, OH), 7.82 (s, 8H, Ar'H); ^{13}C-NMR ($CDCl_3$) δ 31.02, 31.72 ($C(CH_3)_3$), 31.99 ($ArCH_2Ar$), 33.78, 33.92 ($C(CH_3)_3$), 77.82 ($ArOCH_2$), 124.91, 125.53, 126.95, 127.66, 132.58, 137.22, 141.12, 146.88, 150.69, 150.92 (ArC); IR (KBr) ν 3424, 1599, 1484, 1462, 1207 cm^{-1}. Anal. Calcd. for $C_{104}H_{124}O_8$: C, 83.16; H, 8.32. Found: C, 83.01; H, 8.63. **4**: yield 75%; mp 260-262°C; MS (maldi-TOF): *m/z* 1579 (M+Na). ^{1}H-NMR ($CDCl_3$, 60°C) δ 0.99 (s, 36H, $C(CH_3)_3$),1.45 (s, 36H, $C(CH_3)_3$), 3.00-5.20 (br, 36H, OCH_3, $ArCH_2Ar$, $ArOCH_2$), 6.62 (s, 8H, ArH), 7.24 (s, 8H, ArH), 7.74 (s, 8H, Ar'H); IR (KBr) ν 1585, 1482, 1195 cm^{-1}. Anal. Calcd. for $C_{108}H_{132}O_8$: C, 83.25; H, 8.54. Found: C, 82.77; H, 8.62.

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