

Phosphate Doubly Capped Tetrahomodioxacalix[6]arene

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Abstract: A bisphosphate-bridged tetrahomodioxacalix[6]arene with a C_{2v} symmetry at the ambient temperature was obtained by the reaction of tetrahomodioxacalix[6]arene with POCl_3 .

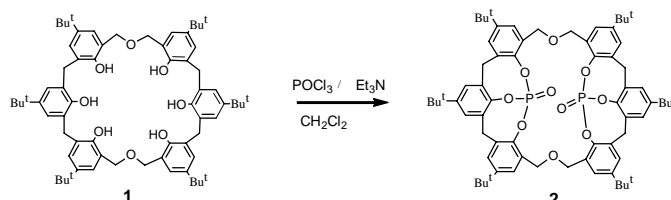
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Calixarenes are conformationally flexible cyclic condensation products of *p*-substituted phenol and formaldehyde which are capable of including small molecules¹. In order to recognize guest molecule efficiently, it is usually desirable to freeze the conformation of calixarene, especially in case of higher member of the calixarene family, such as calix[6]arenes. Capping the calix[6]arenes with trifunctional reagent² or doubly bridging it with bifunctional reagents³ are efficient routes to reduce the mobility of the conformation of calix[6]arene, especially, doubly capping it with trifunctional reagent. Only two examples were known. Biali *et al.* synthesized bisphosphate-bridged calix[6]arene by pyrolysis of the product of calix[6]arene and $\text{ClPO}(\text{OEt})_2$.⁴ Leeuwen *et al.* obtained diphosphite-bridged calix[6]arene from calix[6]arene and PCl_3 directly⁵. Both phosphorus bridged calix[6]arene existed in *syn* and *anti* conformation, and two conformers are noninterconvertable.

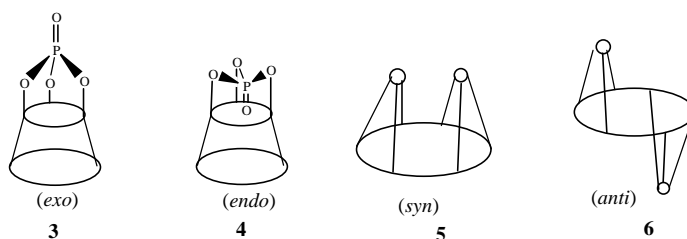
Homooxacalixarenes are calixarene analogues in which CH_2 bridges are replaced by CH_2OCH_2 bridges partly or completely. More recently, a new parent homooxacalixarenes, tetrahomodioxacalix[6]arene **1** was reported by Masci⁶. Little is known about its derivatives. Here we report the synthesis of its doubly capping product, bisphosphate-bridged tetrahomodioxacalix[6]arene. The synthetic route is depicted as **Scheme 1**.

After reacting tetrahomodioxacalix[6]arene **1** with 4 equivs. of POCl_3 in the presence of Et_3N in dichloromethane for 24 h under nitrogen atmosphere, the solvent was distilled, and the residue was washed with distilled water and then extracted with chloroform. After removal of the solvent, the crude product was passed through a silica gel column. Bisphosphate-bridged tetrahomodioxacalix[6]arene **2** was isolated as a white solid in 35% yield, mp 265-6°C.

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Scheme 1 The synthetic route of the titled compound

The multiple bridged system **2** can be viewed as having two subunits, each formed by three proximal phenolic oxygens bridged by a phosphorus atom. Depending on the mutual orientation of the two subunits, two conformers are possible (*syn* **5** or *anti* **6**). Another conformer based on the orientation of the P=O moieties towards the cavity seems impossible as the P-O bond is too short [towards the cavity (*endo*) **3** or away from it (*exo*) **4** as shown in **Figure 1**]. A single singlet at -21.2 ppm in the ^{31}P NMR spectrum of **2** indicated the existence of only one conformer. ^1H NMR spectroscopy suggests a two mutually perpendicular mirror planes in the titled compound with C_{2v} -symmetry giving rise to two AB systems in a 1:1 ratio. Thus, a *syn* conformer is more plausible.

Figure 1 The possible conformers of the titled compound

References and Note

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- Analytic data of compound **2** ^1H NMR (300 MHz, CDCl_3 , δ ppm): 1.26 (s, 18H, C(CH₃)₃), 1.30(s, 36H, C(CH₃)₃), 3.65 (d, 4H, J = 13.5 Hz, ArCH₂Ar), 4.65 (d, 4H, J=12.0 Hz, ArCH₂OAr), 4.78 (d, 4H, J=12.0 Hz, ArCH₂OAr), 5.20 (d, 4H, J = 13.5 Hz, ArCH₂Ar), 7.21 (s, 8H, ArH), 7.39 (s, 4H, ArH) MS(FAB): m/z 1,118 (M^+ -2H). Anal. calcd. for C₆₈H₈₂P₂O₁₀ (%): C, 72.84; H, 7.37; found: C, 72.85; H, 7.42.

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