

DFT Study for *p*-*tert*-Butylcalix[4]arene Crown Ether Bridged at the Lower Rim with Pyridyl Unit Complexed with Potassium Ion

Jong-In Choe

Department of Chemistry, Chung-Ang University, Seoul 156-756, Korea. E-mail: choeji@cau.ac.kr

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Stable molecular conformations were calculated for the *p*-*tert*-butylcalix[4]arene crown ether bridged at the lower rim with pyridyl unit (**1**) in the various conformers and their potassium-ion complexes. The structures of three distinct conformations have been optimized using DFT B3LYP/6-31G(d,p) method. Relative stability of free host **1** is in following order: cone (most stable) > partial-cone > 1,3-alternate conformer. For two different kinds of complexation mode, the potassium cation in the crown-ether moiety (*cr*) has much better complexation efficiency than in the benzene-rings (*bz*) pocket for all three kinds of conformation of host molecule **1**. The relative stability of complex (**1**+K⁺) in the *cr*-binding mode is in following order: partial-cone (most stable) ~ cone > 1,3-alternate conformer.

Key Words : 1,3-Dimethoxycalix[4]crown-ether with pyridyl unit, Complexation, Potassium cation, DFT B3LYP/6-31G(d,p)

Introduction

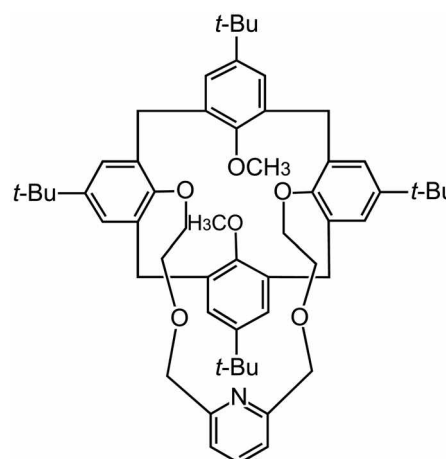
Calix[4]arene-based receptors that possess unusual cavity dimensions have been synthesized *via* 'upper' and 'lower' rim functionalization, and host compounds based on the calix-crown framework, including selective chromoionophores for potassium ion have been prepared and their interesting ionophoric properties were investigated.¹ The complexation properties of these molecules appear to be highly dependent upon the nature and number of donor atoms and also upon the conformation of the calix[4]arene moiety.²

The selective 1,3-dialkylation of *p*-*tert*-butylcalix[4]arene followed by the introduction of suitable polyether bridges on the two remaining OH groups has generated a new family of potassium selective ionophores.³ In particular the 1,3-dimethyl ether of *p*-*tert*-butylcalix[4]crown-5-ether (**1**) has shown a surprisingly high K⁺/Na⁺ selectivity in extraction.^{3(b)} Recently, *endo*- or *exo*-complexation of calix[4]arene with alkali metal cations has been analyzed by HF, MP2 and DFT calculations.⁴

We have undertaken the relative binding affinity study of cone-shaped *p*-*tert*-butylcalix[4]aryl esters toward alkali metal cations focusing on the binding site of upper or lower-rim pocket of the host molecule using DFT calculation method.⁵ The B3LYP/6-31G(d) calculation suggested that *exo*-complexation efficiency of potassium ion inside the cavity of lower rim of *p*-*tert*-butylcalix[4]aryl esters was better than the *endo*-complexation inside the upper rim (four aromatic rings).

Recently, Kim *et al.* calculated the relative stabilities of various conformers for the calix[4]hydroquinone⁶ compound, which were in following order: cone (most stable) > partial-cone > 1,2-alternate conformer ~ 1,3-alternate conformer.

We have reported the relative stabilities and stable



Scheme 1. Chemical drawing of *p*-*tert*-butylcalix[4]arene crown ether bridged at the lower rim with pyridyl unit (**1**).

structures of three different (cone, partial cone, and 1,3-alternate) conformers for the 1,3-dialkyl ether of *p*-*tert*-butylcalix[4]crown-5-ether and their potassium-cation complexes using the B3LYP/6-31G(d,p) calculation method.⁷

The ability of pyridine-containing crown ethers to form complexes with a variety of guests has been studied.⁸ However, pyridine moieties have been incorporated into the lower rim of calixarenes only relatively recently.⁹ Alkali metal picrate extraction studies of *p*-*tert*-butylcalix[4]arene crown ether bridged at the lower rim with pyridyl unit (**1**) shows peak selectivity toward K⁺.¹⁰

The objectives of this research is to determine the relative stability of different conformational isomers for the host (**1**) by using the DFT method, to calculate the relative complexation efficiencies of the various kinds of potassium complexes (**1**+K⁺), and to investigate the characteristics of cation-oxygen (nitrogen) and cation- π interactions¹¹ in these complexes. These calculation results might provide a basis

for the utilization of the unique molecular frameworks of calix[4]crown-ethers in the designing of other functional ionophores having various conformational isomers and supramolecular functions.

Computational Methods

The initial conformations of 1,3-dimethoxy-*p-tert*-butyl-calix[4]arene crown-ether bridged at the lower rim with pyridyl unit (**1**) were constructed by HyperChem.¹² In order to find optimized structures, we executed conformational search by simulated annealing method.¹³ The potassium complexes of **1** were fully re-optimized using DFT B3LYP/6-31G(d,p) methods to estimate the absolute and relative energies for the different complexes after semi-empirical AM1 energy minimization. The DFT optimizations of various conformers of host **1** and their K⁺-complexes of **1** by Gaussian 98¹⁴ were done with error limit of less than 0.01 kcal/mol (2×10^{-6} atomic unit (A.U.)) for each structure.

Results and Discussion

The DFT B3LYP/6-31G(d,p) calculations without any constraint were carried out for the conformers of the host **1**.

Table 1 reports the DFT B3LYP/6-31G(d,p) optimized energies of the three different conformations of **1**. The calculations suggest that cone-shape conformer of **1** is found to be 4.70 and 6.26 kcal/mol more stable than partial cone and 1,3-alternate analogues, respectively. These relative stabilities of three conformers of **1** are similar to the values (3.1 and 6.2) of 1,3-dimethyl ether of *p-tert*-butylcalix[4]crown-5-ether,^{7a} bigger than the values (2.0 and 1.8) of 1,3-diethyl ether of *p-tert*-butylcalix[4]crown-5-ether,^{7b} but much less than the values (11.6 and 19.8) of the calix[4]-hydroquinone.⁶

The DFT B3LYP/6-31G(d,p) optimizations were also carried out for two kinds of complexation mode for each conformer: combining cone, partial-cone, or 1,3-alternate conformer of the *p-tert*-butylcalix[4]crown-ether (**1**) with potassium ion in two different locations (the crown-ether (*cr*) or benzene-rings (*bz*) pocket) of **1**.

Table 2 reports the B3LYP/6-31G(d,p) calculated complexation energies of the six different complexes in two different binding modes. When one compares the relative stabilities of the complexes for the different guest positions in Table 2, the potassium cation in the crown-ether moiety

Table 1. DFT B3LYP/6-31G(d,p) Calculated Energies of Different Conformations of Host (**1**)

Host (1)	Figure ^a	A.U.	kcal/mole	ΔE^b
Cone	Fig. 1(a,b)	-2722.1922	-1708201.59	0.00
Partial cone	Fig. 2(a,b)	-2722.1847	-1708196.89	4.70
1,3-alternate	Fig. 3(a,b)	-2722.1822	-1708195.33	6.26

^aFigure 1(a) is the side view, and Figure 1(b) is the front view of cone conformer, etc. ^b ΔE is the relative energy (kcal/mol) with respect to the most stable conformation of the free host.

Table 2. DFT B3LYP/6-31G(d,p) Complexation Energies of Different Complexes of Host (**1**) with Potassium Ion

Binding mode ^a	Figure	E_{complex}^b	$\Delta E_{\text{complex}}^c$	ΔE_{ref}^d
Host(cone)•K ⁺ (<i>cr</i>)	Fig. 1(c,d)	-3322.0423	-78.48	3.05
Host(cone)•K ⁺ (<i>bz</i>)	Fig. 1(e,f)	-3322.0151	-61.43	20.09
Host(pc)•K ⁺ (<i>cr</i>)	Fig. 2(c,d)	-3322.0471	-81.53	0.00
Host(pc)•K ⁺ (<i>bz</i>)	Fig. 2(e,f)	-3322.0160	-62.00	19.53
Host(1,3-alt)•K ⁺ (<i>cr</i>)	Fig. 3(c,d)	-3322.0143	-60.95	20.58
Host(1,3-alt)•K ⁺ (<i>bz</i>)	Fig. 3(e,f)	-3321.9991	-51.38	30.14

^a*cr* indicates crown-ether pocket binding, and *bz* means benzene-rings pocket mode. Host(pc) means the partial cone conformation of host(**1**). Host(1,3-alt) denotes the 1,3-alternate conformation. ^b E_{complex} (a.u.) is the total energy of the complex. ^c $\Delta E_{\text{complex}}$ (kcal/mol) is defined as the total energy of the complex minus the sum of the total energies of the cation and the most stable free ligand conformation. $\Delta E_{\text{complex}}$ are with respect to the cone conformation of the bare host. ^d ΔE_{ref} is defined as the binding energies relative to that of the most strongly bound complex.

(*cr*) has much better (20-30 kcal/mole) complexation efficiency than in the benzene-rings (*bz*) pocket for all kinds of conformation of host molecule **1**.

Figures 1(a) and 1(b) show the front and side views of the cone conformation of the host **1**, Figures 1(c) and 1(d) display its potassium complexes in *cr*-mode, and Figures 1(e) and 1(f) are its potassium complexes in *bz*-mode. When one sees the front view (Fig. 1(a)) of free host **1**, two of the oxygen atoms in the crown-ether moiety are not converged to the center of the crown-ether ring, but randomly pointing outward. However, all of the nitrogen and oxygen atoms in the crown-ether moiety at the front view (Fig. 1(c)) of cone *cr*-mode complex (**1**•K⁺) are symmetrically converged to the center of the crown-ether ring due to the strong electrostatic attractions from potassium cation. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.¹⁵ The side view (Fig. 1(d)) of the cone *cr*-mode complex displays the two additional cation-oxygen interactions from potassium to the methoxy-oxygen atoms. When one sees the side view (Fig. 1(f)) of the cone *bz*-mode complex, two *tert*-butyl-anisole groups in the calix[4]arene moiety are vertically coordinated with the potassium guest due to the strong cation- π interactions.^{16,17}

Figures 2(a) and 2(b) show the front and side views of the partial-cone conformation of the host **1**, Figures 2(c) and 2(d) display its potassium complexes in partial-cone *cr*-mode, and Figures 2(e) and 2(f) are in partial-cone *bz*-mode. When one sees the Figures 2(c) and 2(d), all of the nitrogen and oxygen atoms in the crown-ether moiety are symmetrically converged to the center of the crown-ether ring due to the strong electrostatic attractions from potassium cation with an additional cation-oxygen interaction from potassium to the methoxy oxygen.

Figures 3(a) and 3(b) show the front and side views of the 1,3-alternate conformation of the host **1**, Figures 3(c) and 3(d) display its potassium complexes in *cr*-mode, and Figures 3(e) and 3(f) are in *bz*-mode. When one sees the Figures 3(c) and 3(d) of 1,3-alternate *cr*-mode of host **1**, the

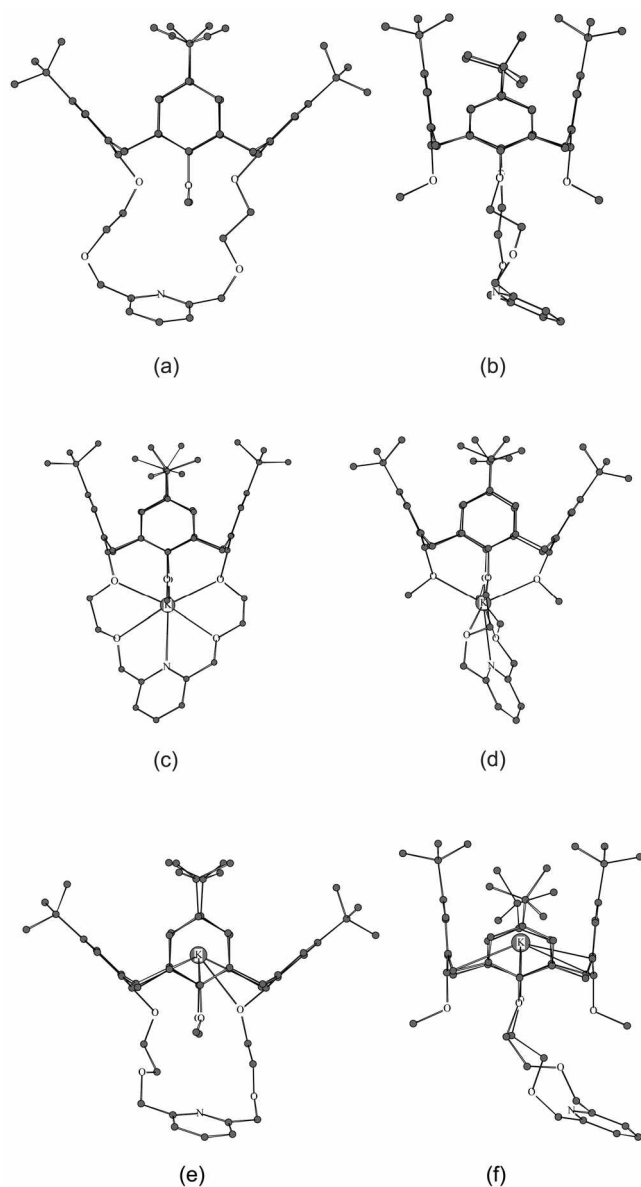


Figure 1. DFT calculated structures of cone conformer of **1**. (a) Side view and (b) front view of the cone host **1**, (c) side view and (d) front view of the cone *cr*-complex **1**•K⁺, (e) side view and (f) front view of the cone *bz*-complex **1**•K⁺. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.¹⁵

nitrogen and two oxygen atoms in the crown-ether moiety are converged to the potassium cation. The side view (Fig. 3 (f)) of the 1,3-alternate *bz*-mode complex, displays the two additional cation-oxygen interactions from potassium to the methoxy oxygen atoms.

The strong binding energies in the *cr*-complexations of K⁺ with the host **1** are coming from K⁺-oxygen (nitrogen) interactions in crown-ether ring and additional interactions from methoxy group and/or benzene rings. The MP2/6-311+G* calculations suggest that cation-oxygen binding energy is -19.4 kcal/mol when K⁺ is binding to the anisole oxygen, and that cation- π interaction energy is -18.7 kcal/mol for K⁺ with the benzene ring of anisole.^{16,17} The weaker

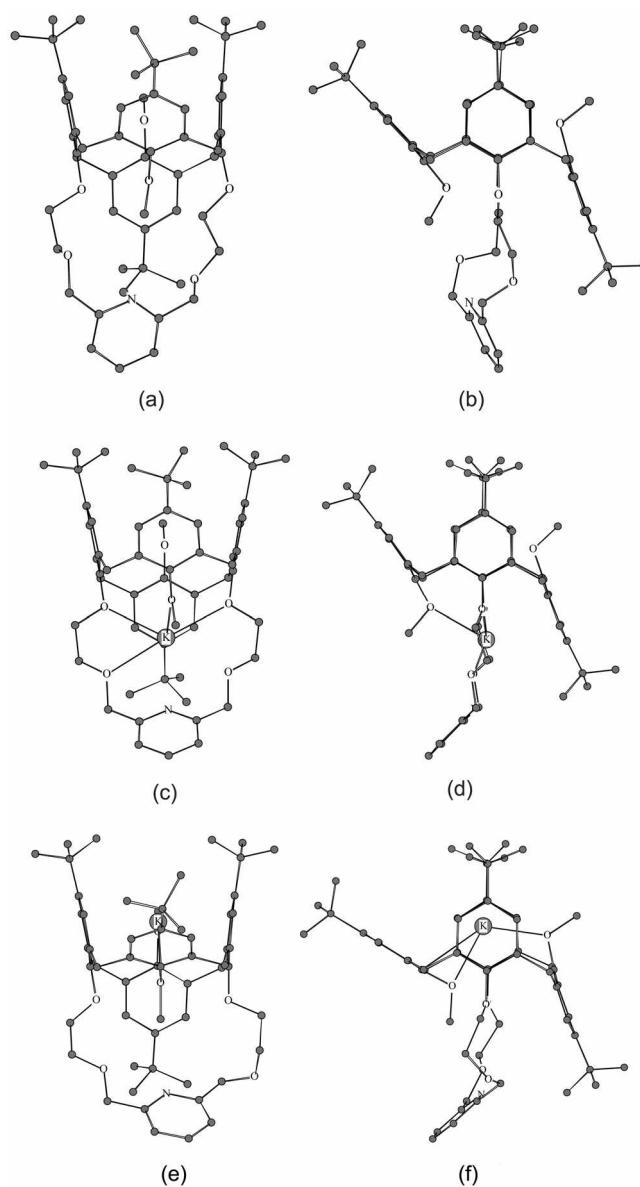


Figure 2. DFT calculated structures of partial-cone conformer of **1**. (a) Side view and (b) front view of the partial-cone host **1**, (c) side view and (d) front view of the partial-cone *cr*-complex **1**•K⁺, (e) side view and (f) front view of the partial-cone *bz*-complex **1**•K⁺.

bz-complexation efficiencies in Table 2 are originated from the fewer number of electrostatic interactions of potassium cation with the ligand sites of oxygen atom and π -electrons of benzene ring.

When one investigates $\Delta E_{complex}$ and ΔE_{rel} of the B3LYP/6-31G(d,p) calculations for *cr*-binding mode in Table 2, the cone complex (-78.48 kcal/mol) is found to be 3.05 kcal/mol less stable than the most stable partial-cone complex (**1**•K⁺) (-81.53 kcal/mol). These complexation energies of the host **1** toward to potassium ion show better binding efficiencies than the values (-72.1 ~ -74.5 kcal/mol) of the 1,3-dialkyl ether of *p-tert*-butylcalix[4]crown-5-ether.^{6,7} However the 1,3-alternate complex (-60.95 kcal/mol) in *cr*-moiety between two benzene rings is 20.58 kcal/mol less stable than the partial-cone complex.

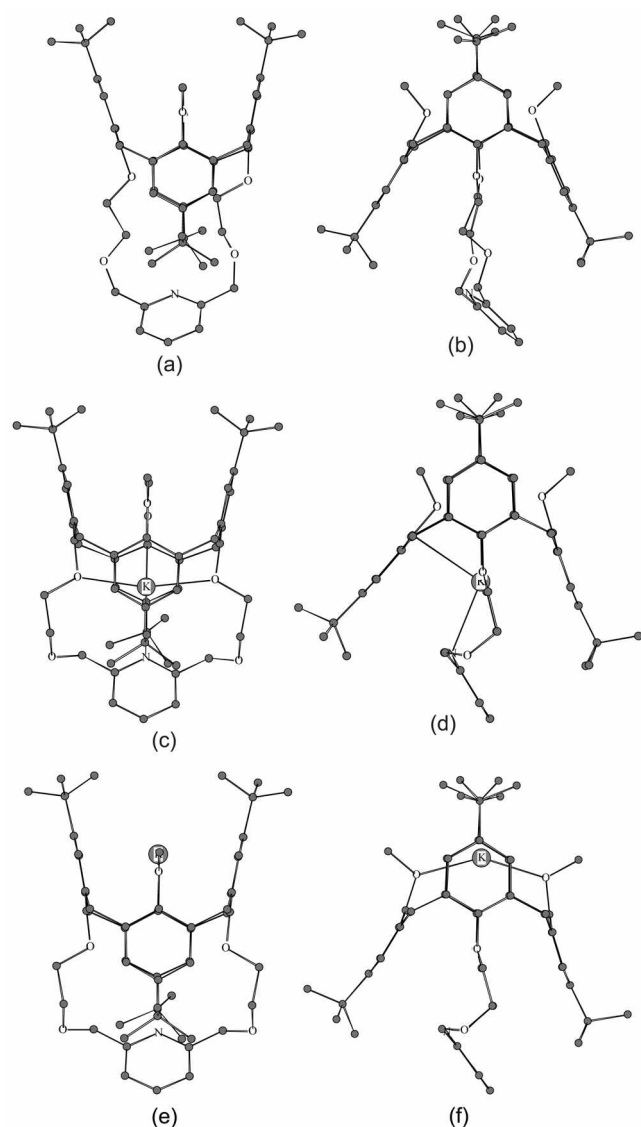


Figure 3. DFT calculated structures of 1,3-alternate conformer of **1**. (a) Side view and (b) front view of the 1,3-alternate host **1**, (c) side view and (d) front view of the 1,3-alternate *cr*-complex **1**•K⁺, (e) side view and (f) front view of the 1,3-alternate *bz*-complex **1**•K⁺.

To explain the relative binding energies of the different complexes, we have measured the distances from the potassium cation to the nitrogen and oxygen atoms of the host **1**. (See Table 3)

An interesting fact deduced from the Table 3 is that the average distance (2.650 Å) between K⁺ and the methoxy oxygen atoms of cone-shaped host in *cr*-binding mode is 0.138 Å shorter than the average value (2.788 Å) between K⁺ and the crown-ether-oxygen atoms of the host. These cation-oxygen distances suggest that the electrostatic attraction between K⁺ and the methoxy-oxygen is stronger than the ether-oxygen atom, since the movement of methoxy-oxygen atom is relatively free compared to the oxygen atoms of the crown-ether framework. MP2/6-311+G* calculation suggests that the optimized binding distance between K⁺ and the oxygen atom of an anisole is 2.617 Å.¹⁶ Another point noticed in the Table 3 is that the average distance (2.640 Å) between K⁺ and the crown-ether-oxygen atoms of 1,3-alternate *cr*-complex is shorter by 0.238 Å than the value (2.878 Å) of partial-cone analog. This is another explanation for the reasonable binding efficiency of 1,3-alternate *cr*-complex with K⁺ with fewer ligating oxygen atoms.

Overall, the DFT calculated complexation energies and the K⁺-oxygen distances of the complexes (**1**•K⁺) suggest that *p-tert*-butylcalix[4]arene crown ether bridged at the lower rim with pyridyl unit (**1**) gives better binding efficiency toward to potassium ion than other similar hosts such as the 1,3-dialkyl ether of *p-tert*-butylcalix[4]crown-5-ether.

Conclusion

DFT B3LYP/6-31G(d,p) calculations suggest that the relative stability of the different conformers of *p-tert*-butylcalix[4]arene crown ether bridged at the lower rim with pyridyl unit (**1**) is in following order: cone (most stable) > partial-cone > 1,3-alternate conformer. The binding efficiencies of potassium cation in the crown-ether moiety (*cr*) has much better (20-30 kcal/mol) than the values of the benzene-rings (*bz*) pocket for all three kinds of conformation of host molecule **1**. The relative stability of three confor-

Table 3. Calculated Distances (Å) between K⁺ and the Nitrogen and Oxygen Atoms of **1**

Distance from K ⁺	<i>cr</i> -Complex			<i>bz</i> -Complex		
	I _(cone) •K ⁺	I _(pc) •K ⁺	I _(1,3alt) •K ⁺	I _(cone) •K ⁺	I _(pc) •K ⁺	I _(1,3alt) •K ⁺
Nitrogen	2.920	3.030	2.881			
Ether-Oxygen (1)	2.716	2.951	2.639	2.814		
Ether-Oxygen (2)	2.817	2.920	2.640	2.945		
Ether-Oxygen (3)	2.715	2.774				
Ether-Oxygen (4)	2.903	2.865				
Ave. Ether-Oxygen	2.788	2.878	2.640	2.880		
Methoxy Oxygen (1)	2.688				2.736	2.583
Methoxy Oxygen (2)	2.612				2.621	2.567
Ave. Methoxy Oxygen	2.650				2.679	2.575

*The distance (Å) data which are too far to interact with potassium ion are omitted. Atoms that are within a bond proximate distance (2.950 Å for the O...K⁺ pair) from one another were automatically marked as bonded in Figures 2 and 3.¹⁵

mations for *cr*-complex ($1 \cdot K^+$) is: partial-cone (most stable) \sim cone $>$ 1,3-alternate conformer. The number of cation-oxygen interactions in crown-ether ring and methoxy groups with potassium cation was crucial to the stability of the different conformation of $1 \cdot K^+$ complex. The host **1** toward to potassium ion shows better binding efficiencies than the 1,3-dialkyl ether of *p-tert*-butylcalix[4]crown-5-ether.

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