ORGANIC LETTERS

2005
Vol. 7, No. 16
3401−3404

Stilbene-Bridged *tert*-Butylcalix[4]arene as Photoswitchable Molecular Receptors

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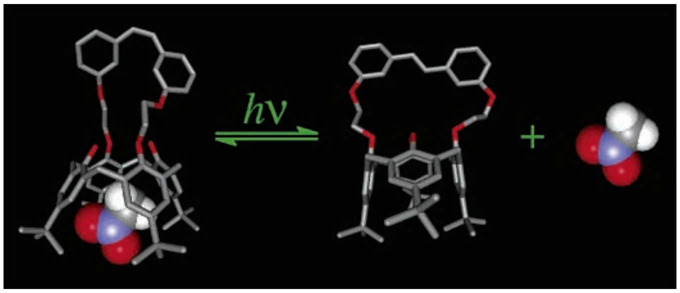
Received April 18, 2005

ABSTRACT



Using a designed control of conformations of *tert*-butylcalix[4]arene between cone and pinched cone, a highly selective receptor for small electron-deficient molecules with photoswitching binding ability was attained.

Calix[4]arenes are one of the most intriguing platforms for constructing selective receptors because of their preorganized basket structure assembled from four phenol rings. Flipping one or more phenol rings can convert the calix[4]arene basket from the most stable cone conformation into a partial-cone, 1,2 alternating-cone and 1,3 alternating-cone conformation.[1] Even a small movement of the phenol rings can distort the cone structure to a pinched cone conformation in which two opposite phenyl rings are almost parallel.[2] Each conformation of calix[4]arenes can be attained by incorporating appropriate substituents on either rim of the basket structure.[3]

As a result of the electron-rich character of its four phenol rings, the cavity of a calix[4]arene is a good π-donor that can form complexes with electron-poor species.[4] The binding selectivity can be achieved through adjustment of the size and shape of the cavity as well as the types of substituents.[5] To manipulate the binding selectivity, we have engaged in the synthesis of calix[4]arene derivatives possessing substituents that can control the change of conformations via a simple external stimulation such as irradiation with light.[6] Although many photoswitchable ionophores have been reported, there were only few reports concerning photoswitchable receptor for molecules.[7]

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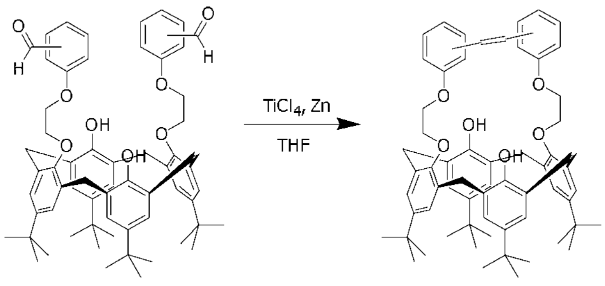
10.1021/ol050854u CCC: $30.25

Five stilbene-bridged calix[4]arenes (**1**) were synthesized through a modified McMurry reductive coupling reaction using $TiCl_4$/Zn in THF as a reducing agent (Scheme 1).[8] Both *cis*- and *trans*-isomer of *o*-**1** and *m*-**1** can be obtained from the reductive coupling of *o*- and *m*-bis-benzaldehyde calix[4]arenes, but the coupling of *p*-bis-benzaldehyde calix[4]arene yielded only *cis*-*p*-**1**. All calix[4]arene derivatives obtained were in the cone conformation.[9]

Scheme 1. Synthesis of Stilbene-Bridged *p*-*tert*-Butyl Calix[4]arenes



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The complexation of these five isomers of **1** with molecular compounds in $CDCl_3$ was investigated by using ^1H NMR spectroscopy (400 MHz). Among five host ligands and eight guest molecules tested, the host−guest complexes were clearly observed between *o*-**1** or *cis*-*m*-**1** and acetonitrile or nitromethane as evidenced by the shift ($|\Delta\delta_g|$) of the signals of the methyl protons in the guest molecules (Figure 1).

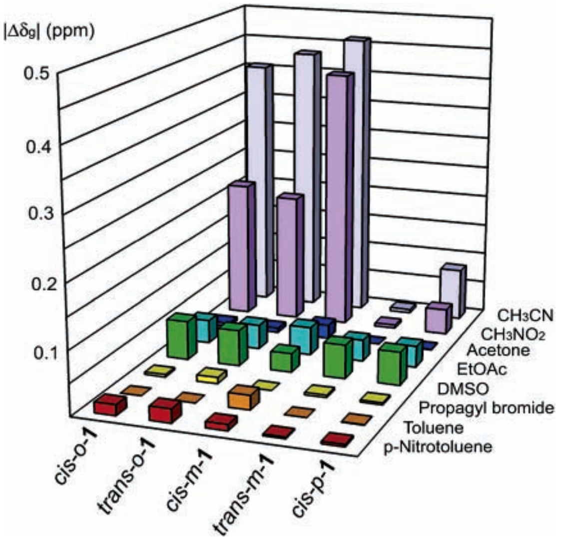

Figure 1. Shift ($|\Delta\delta_g|$) of the signals of the methyl group in the guest compounds (1:1 ratio) after addtion into the host solutions.

Since all ligands were in the cone conformation, the difference in binding abilities among the ligands must derive from the variation between the cone and pinched cone conformation. Transitioning from the cone to pinched cone conformation, the normally circular wider rim of calix[4]arene is likely to reshape into an oval ring. For *p*-*tert*-butylcalix[4]arene derivatives, this minor conformational change can cause the entrance via the wider rim to close. Ligands *o*-**1** and *cis*-*m*-**1** were thus likely to retain the cone conformations, which allowed a guest molecule to enter the cavity, whereas the *trans*-*m*-**1** and *p*-**1** assumed the pinched cone conformations, in which the entrance to the cavity was closed. The structures of five isomers of **1** obtained from AM1 semiempirical molecular modeling optimization agree well with this hypothesis (Figure 2). Although we have not been able to obtain the X-ray structure of all five isomers of **1**, the X-ray structures of *cis*-*o*-**1** and two isomers of azobenzene bridged calixarenes, *trans*-*o*-**2** and *trans*-*m*-**2**,[9] analogous to the *trans*-*o*-**1** and *trans*-*m*-**1** confirmed the proposed cone and pinched cone conformations (Figure 3).

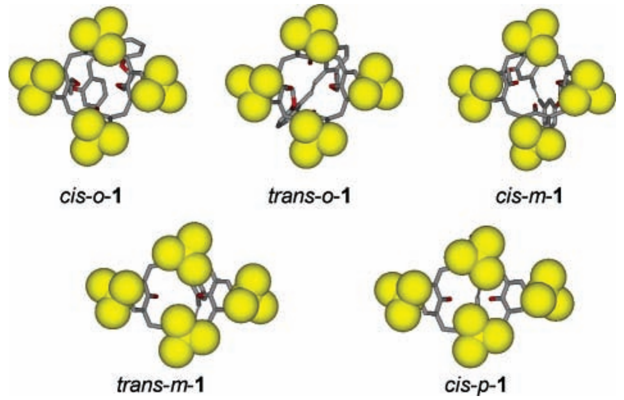

Figure 2. Structures of five isomers of **1** optimized by AM1 semiempirical molecular modeling, viewed from the wider rim of calix[4]arenes. The yellow balls represent carbon atoms of *tert*-butyl groups.

As the cavity of *tert*-butyl-calix[4]arene is rather small, the selectivity of the *o*-**1** and *cis*-*m*-**1**, binding with only two (out of eight) least bulky guests, is not totally surprising. The protons of *o*-**1** and *cis*-*m*-**1** showed variation in the shift ($|\Delta\delta_h|$) of the chemical shift values after the complexation with nitromethane and acetonitrile. The greatest shift was observed at the signal of the aromatic protons of calix[4]arene, suggesting that the guest molecule was situated within the calix[4]arene π-cavity.[10] A Job's plot between the mole fraction of the guest compound (X) and $(1 - X)\ |\Delta\delta_h|$ indicated a formation of a 1:1 host−guest complex. The result is in good agreement with our previous observation from the X-ray structure of the similar calix[4]arene deriva-

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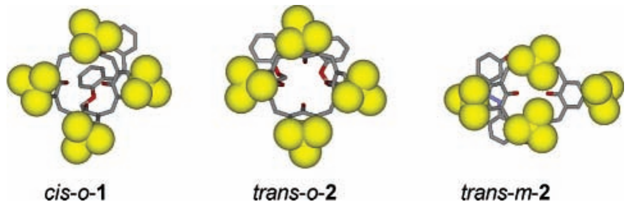

Figure 3. X-ray Structures of stilbene and azobenzene bridged calix[4]arenes, **1** and **2**, respectively, viewed from the wider rim of calix[4]arenes. The yellow balls represent carbon atoms of *tert*-butyl groups.

tives revealing that the calix[4]arene cavity can accommodate only one guest molecule of this size.[6a]

The complexation constant (K_{eq}) for these 1:1 complexes were computed from EQNMR program using the chemical shift of the host protons (δ_h) having the highest $|\Delta\delta_h|$ values.[11] All K_{eq} fell within the range of $10-100\ M^{-1}$ corresponding to a dynamic complexation (Table 1).

Table 1. Complexation Constants of *o*-**1** and *cis*-*m*-**1** with Acetonitrile and Nitromethane from NMR Titration Computed with EQNMR

host	selected signal (ppm)	K_{eq} for CH_3CN (M^{-1})	K_{eq} for CH_3NO_2 (M^{-1})
cis-*o*-**1**	6.89	57	38
trans-*o*-**1**	6.98	57	45
cis-*m*-**1**	6.98	58	45

The difference in binding ability between *cis*-*m*-**1** and *trans*-*m*-**1** together with the photoisomerizable property of their stilbene unit has provided us the molecular tools to demonstrate a photoswitching ability between the complexing and noncomplexing states. The photoswitching process was studied by observing the movement of the signal of methyl protons in the guest compounds. The mixture of acetonitrile or nitromethane with *cis*-*m*-**1** at a 1:1 mole ratio showed a considerable upfield shift of the signal (compare *b* with *a* and *f* with *e* in Figure 4) indicating the existence of host−guest complexation. On the other hand, the signal remained almost at the same position of that of the free guest when it was mixed with *trans*-*m*-**1**, indicating the absence of complexation. When the mixtures of the guest compounds and *cis*-*m*-**1** were exposed to a dose of broad band UV irradiation to attain the photostationary state, the signal retreated somewhat toward the original positions of the free guests (Figures 4, *d* and *h*), indicating a release of some guest molecules from the complexes.

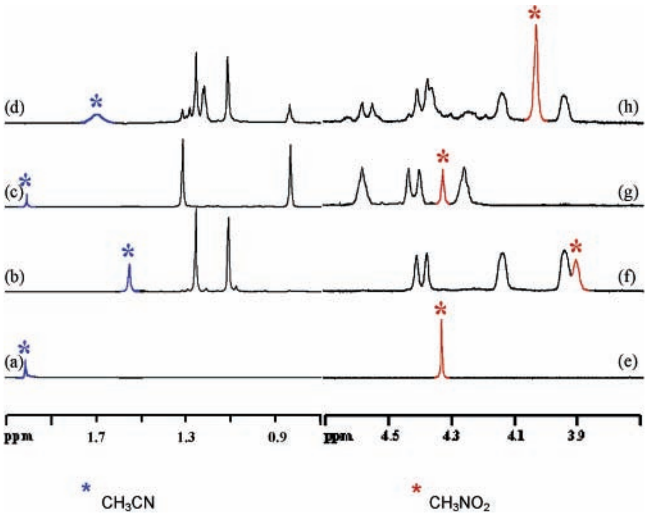

Figure 4. ^1H NMR spectra of a 1:1 mixture of host and guest: (a) CH_3CN, (b) *cis*-*m*-**1**/CH_3CN, (c) *trans*-*m*-**1**/CH_3CN, (d) photostationary state *m*-**1**/CH_3CN, (e) CH_3NO_2, (f) *cis*-*m*-**1**/CH_3NO_2, (g) *trans*-*m*-**3**/CH_3NO_2, (h) photostationary state *m*-**1**/CH_3 NO_2.

The percentages of guest molecules being released were estimated on the basis of the changes of chemical shift values. Assuming that the guest molecules complexed within the *cis*-*m*-**1** cavity would be completely released if all of the host molecules were converted to the *trans* geometry, the monitored signal would shift to the position observed for the mixture of the guests and *trans*-*m*-**1**. Experimentally, the mixture of the guests and *cis*-*m*-**1** showed an approximately 30% shift after irradiation (Table 2) for both acetonitrile and nitromethane cases, indicating 30% conversion of *cis*-*m*-**1** to *trans*-*m*-**1** and thus a 30% reduction in binding ability of the ligand. The opposite process was also performed by starting from the mixture of the guests and *trans*-*m*-**1** that exhibited the photoswitching from noncomplexing to 70% complexing at the photostationary state. The 70:30 complexing:noncomplexing ratio observed here is identical to the *cis*:*trans* ratio observed at the photostationary state of *m*-**1** in the absence of guest compound.[9]

Table 2. Shifts $|\Delta\delta_g|$ of Signals of Methyl Protons in Acetonitrile and Nitromethane at Initial and Photostationary States (p.s.)

	$\|\Delta\delta_g\|$ for CH_3CN (ppm)			$\|\Delta\delta_g\|$ for CH_3NO_2 (ppm)		
ligand	initial	p.s.	% at p.s	initial	p.s.	% at p.s.
cis-*m*-**1**	0.461	0.320	69.1	0.417	0.295	70.4
trans-*m*-**1**	0.006	0.320	30.9	0.005	0.295	29.6

In conclusion, *m*-**1** can be used to convert photo energy into a mechanical force that controls its complexation ability. The compound may be applied for transportation of specific compounds and in separation technology. In an attempt to confirm our hypothesis, we are endeavoring to grow X-ray quality single crystals of our complexes in order to study them in the solid state using X-ray diffraction.

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Acknowledgment. This work was financially supported by the Thailand Research Fund (TRF) (RSA4580026), Ministry of University Affairs (UDC39/2543), and National Science and Technology Development Agency (NSTDA) (CO-B-11-11-09-202D).

Supporting Information Available: Experimental details and NMR data for the complexation study. This material is available free of charge via the Internet at http://pubs.acs.org.

OL050854U