Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Photoregulated-metal binding with an azobenzene-capped calix[4]arene

Fumio Hamada[a]; Toru Masuda[a]; Yoshihiko Kondo[a]
[a] Department of Material Engineering and Applied Chemistry, Mining College, Akita University, Tegata, Akita, Japan

To cite this Article Hamada, Fumio , Masuda, Toru and Kondo, Yoshihiko(1995) 'Photoregulated-metal binding with an azobenzene-capped calix[4]arene', Supramolecular Chemistry, 5: 2, 129 — 131

To link to this Article: DOI: 10.1080/10610279508029484

URL: http://dx.doi.org/10.1080/10610279508029484

SUPRAMOLECULAR CHEMISTRY, Vol. 5, pp. 129–131
Reprints available directly from the publisher
Photocopying permitted by license only

Photoregulated-metal binding with an azobenzene-capped calix[4]arene

FUMIO HAMADA*, TORU MASUDA and YOSHIHIKO KONDO

Department of Material Engineering and Applied Chemistry, Mining College, Akita University, Tegata, Akita 010, Japan

(Received January 24, 1994)

The photoresponsive calix[4]arene(1), which is modified with an azobenzene moiety on the lower rim of the calix, has been prepared. Photoisomerization of 1 was performed with photoirradiation by a 500W-Xe lamp using a Corning 7 -37 filter. The liquid-liquid extraction of various ions by 1 in the form of both cis and trans isomers using picrate counter ion has been studied. Calixarene 1 shows a higher binding ability to the metal cations examined in the trans form than for cis isomer and exhibits over twice the binding ability, except for Cu^{2+} and Al^{3+}, compared to the non-modified calix[4]arene (2), which has same structure on the upper rim of the calix.

INTRODUCTION

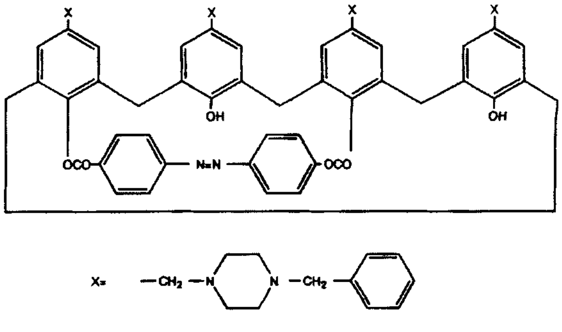
Photochemical control of complexation phenomena is a recent topic in a host-guest chemistry, and various photoresponsive ligands have been used to regulate the binding of organic compounds or metal cations in an on-off fashion.[1] The class of versatile macrocyclic host known as calixarenes has recently received increasing attention. Calixarenes are composed of benzene moieties whose functionalization of the upper and lower rim of the calix can be expected to improve or alter their inclusion properties.[2] From this point of view, many derivatives of calixarenes have been prepared and studied with regard to host-guest behavior. However, to our best knowledge, the area of photoregulated calixarenes, with a view to complexing metal cations has been slow to develop. In this contribution we would like to present the synthesis of a new photoresponsive calix[4]arene (1), which is modified with an azobenzene moiety on the lower rim of the calix. The extractability of 1 in the form of cis-trans isomers for alkali and transition metal cations in a liquid-liquid extraction system has been studied.

EXPERIMENTAL SECTION

Preparation of azobenzene-capped calix[4]arene (**1**). A reaction mixture of 5,11,17,23-tetrakis[(N'-benzyl-N-piperazino)methyl-25,26,27,28-tetrahydroxy-calix[4]arene (**2**)[3] (2.94 g, 2.5 mmol) and azobenzene-4,4'-dicarboxyl chloride (**3**) (1.19 g, 3.9mmol)[4] in the presence of triethylamine in chloroform (50 mL) was stirred at room temperature for 6 h. The reaction mixture was washed twice with water and the organic layer was dried over Na_2SO_4. After filtration, the organic layer was evaporated in vacuo to yield an orange powder, which was purified with silica gel column chromatography using a chloroform-methanol mixture, and finally methanol was used as eluting solvent. The methanol eluting fractions were combined and evaporated to yield pure **1**. Yield: 15.2%. ^{1}H-NMR ($CDCl_3$): 8.43 (4H, d, J=8.57, azonenzene-H), 8.05 (4H,d, J = 8.58, azobenzene-H), 7.30 (20H,m, ArH), 6.94 (4H, s, ArH), 6.70 (4H, s, ArH), 3.90 (4H, d, J = 14Hz, $ArCH_2Ar$), 3.55 (4H, d, J = 14Hz, $ArCH_2Ar$), 3.49, 3.47, 3.29 and 3.14 (4s, 16H, $ArCH_2N$), 2.4 and 2.22 (2br. s, 32H, NCH_2). Found: C, 74.88; H, 6.83; N, 10.02. Calcd. for $C_{90}H_{94}N_{10}O_6 \bullet 2\,H_2O$: C, 74.66; H, 6.82; N, 9.67 Fab-MS: 1412 (M^+) IR(KBr): 1710 cm^{-1}.

Photoisomerization of 1

A dichloromethane solution containing **1** (2.0 mL, 1 × 10^{-3} mol dm^{-3}) was UV-photoirradiated with a 500W-Xe lamp using a USHIO ELECTRIC INC DBS-501A with a Corning 7–37 filter.



---

*To whom correspondence should be addressed.

Liquid-liquid extraction ability of 1

After 12 h photoirradiation of a dichloromethane solution of **1** (2 mL, 1 × 10^{-3} mol dm^{-3}), an aqueous solution (2 mL) containing 2 × 10^{-5} mol dm^{-3} of picric acid and 1 × 10^{-2} mol dm^{-3} of metal nitrate were added and stirred for 30 min under UV-photoirradiation. An aliquot of the upper aqueous solution was withdrawn, and the UV spectrum was recorded. The extractability was determined on the basis of the absorbance of picrate ion in aqueous solutions by the following equation[5,6];

$$\text{Extractability (\%)} = [(A_0 - A)/A_0] \times 100$$

where A and A_0 are the absorbance at 354 nm in the presence and the absence of **1**, respectively.

RESULTS AND DISCUSSION

The synthesis of the new calix[4]arene, which was modified with azobenzene on the lower rim, is shown in Scheme 1. 5,11,17, 23—tetrakis[(N'-benzyl-N-piperazino) methyl]-25,26,27,28-tetrahydroxy calix[4]arene (**2**) has been reported by the Gutsche group.

We selected this compound for our study because **2** might be an excellent ligand for complexation with alkali and transition metal cations[3]. The ^{1}H-NMR of **1** shows a pair of doublets at 3.90 and 3.55 ppm arising from the hydrogen on the bridging methylene groups with J_{AB} = 14 Hz at 25°C, which means **1** exists in the cone conformation.[7] The photoisomerization of **1** was performed with photoirradiation with a 500W-Xe lamp using a Corning 7–37 filter, which selects the UV region (310 < λ < 390 nm). Figure 1 shows the absorbance spectra of **1** obtained by UV-photoirradiation and non-photoirradiation of **1**. After UV irradiation, the absorption spectra at around 260 nm was increased and that around 330 nm was decreased, which means trans-to-cis isomerization occurred. **1** exhibits isosbestic points at 303 nm during the whole course of the trans-to-cis isomerization. The photostationary state was almost performed by UV-photoirradiation for 12 h. The cis percentage of **1** at the photostationary state was calculated to be 30% using the absorbance at 330 nm[8]. The cis form is converted back into the original trans one if kept in the dark, with a half life time of 21 h at 25°C. When the non-UV photoirradiated **1** was kept in the dark, the absorption spectrum was not changed. This suggests that non-photoirradiated **1** exists more in the trans than in the cis isomer.

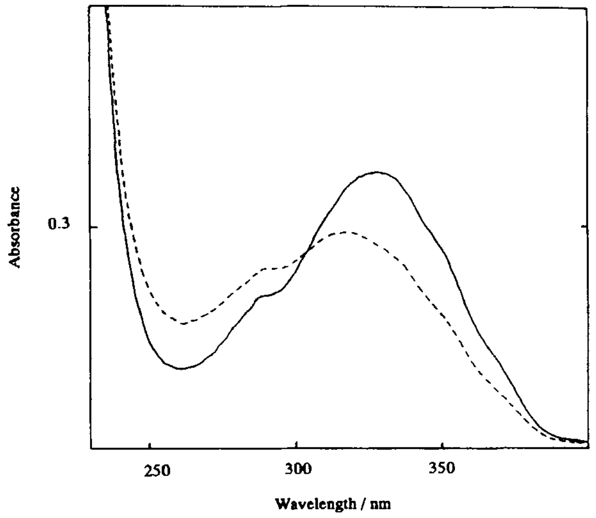
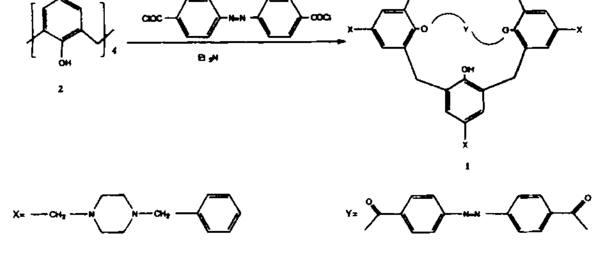


Figure 1 Absorption spectra of the trans (———) and the photoirradiated (— — —) form of **1** in dichloromethane (1 × 10^{-5} mol•dm^{-3}).



Scheme 1

Photoisomerization of the capped moiety on the lower rim of **1**, probably works to change the configuration at the upper rim of **1**. This might effect regulation of the metal affinity of **1**. We studied the affinity of **1** for several metal cations in the cis and trans isomers. Table 1 shows the liquid-liquid extractability (Ex) of the trans form of **1**, photoirradiated **1**, the cis form of **1**, and the non-modified calix[4]arene(**2**). Here, the trans form of **1** is the non-photoirradiated fraction; photoirradiated **1** is obtained by UV photoirradiation for 12 h, and cis **1** is calculated from Eq.1:

$$Ex_{cis-1} = (Ex_{photoirradiated-1} - 0.7Ex_{trans-1})/0.3 \quad \text{(Eq.1)}$$

The extractability of **1** in the trans form are ranges from 71% to 52.3%. On the other hand, the extractability of the non-modified calix (**2**) exhibits high selectivity for

Table 1 Extraction of metal picrates with ligands

Ligands	*Picrate salt extracted (%)*						
	Na^+	*K^+*	*Ni^{2+}*	*Cu^{2+}*	*Zn^{2+}*	*Cd^{2+}*	*Al^{3+}*
trans-**1**	76.3	71	58.3	53.6	52.3	69.4	59.9
photo-irradiated-**1**	46.8	38	30.1	42.4	33.9	30.6	49.7
cis-**1**	0	0	0	4.8	0	0	7.7
2	16	4.5	19.9	54	20.2	16.5	59.9

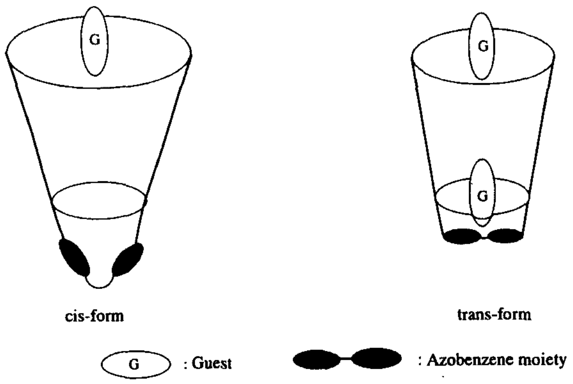


Figure 2 Schematic representation for the complexed species of the trans and cis forms of **1**.

Cu^{2+} and Al^{3+}, which is almost the same efficiency as for those of **1** in the photo-irradiated and trans form, but shows small extractability for the other metal cations examined. This means that the appended moiety on the lower rim of the calix could be the region which complexes with all the metal cations except Cu^{2+} and Al^{3+}. Nomura and co-workers reported the extractability for metal cations of a calix[6]arene derivative containing an azo group on the upper rim[5]. The extractability of the photo-irradiated form of **1** is lower than for trans form of **1**. The cis-form shows small extractability for only Cu^{2+} and Al^{3+} metal cations. This fact suggests that the trans isomer of **1** has a more favorable configuration for complexation of metal cations than has the cis isomer.

We determined the ratio of **2** and copper ion in the complex is 1:1 by the continuous variation method[9]. It suggests that **1** in the fashion of the trans isomer complexes with two metal cations on the upper and lower rim areas. On the other hand, **1** in the fashion of the cis form cannot complex with metal cations except Cu^{2+} and Al^{3+} on the upper rim and lower rim areas, because the ligands on the upper rim are too spread out to effectively complex with the metal cations. A schematic representation for the complexed species of trans and cis forms of **1** is shown in Fig. 2. In conclusion, the present results show that photo-regulated, selective metal cations extraction can be realized by the use of photo-responsible calix[4]arene derivative (**1**).

REFERENCES

1 a) S. Shinkai; T. Ogawa; T. Nakaji; Y. Kusano and O. Manabe; *Tet. Lett.*, **1979**, 4569.
b) A. Ueno; H. Yoshimura and T. Osa; *J. Am. Chem. Soc.*, **1979**, *101*, 2779.
c) M. Inouye; M. Ueno and T. Kitao; *J. Am. Chem. Soc.*, **1990**, *112*, 8977.
d) M. Fukushima; T. Osa and A. Ueno; *Chem. Lett.*, 709, **1991**.
e) F. Hamada; M. Fukushima; T. Osa and A. Ueno;, *Makromol. Chem., Rapid Commun.*, **1993**, *14*, 279 .
f) F. Hamada; M. Fukushima; T. Osa; H. Ikeda; F. Toda and A. Ueno; *Makromol. Chem. Rapid Commun.*, **1993**, *14*, 287.
2 J. Vicenns and V. Böhmer, "Calixarenes, a Versatile Class of Macrocyclic Compounds", Kluwer Academic Publishers, Dordrecht; **1991**.
3 C. David Gutsche; Kye Chu Nam; *J. Am. Chem. Soc.*, **1988**, *110*, 6153.
4 M.L. Tomlinson; *Helv. Chim. Acta*, **1959**, 1653.
5 E. Nomura; H. Taniguchi and S. Tamura; *Chem. Lett.*, **1989**, 1125.
6 F. Hamada; T. Fukugaki; K. Murai; G.W. Orr and J.L. Atwood; *J. Incl. Phenom.*, **1991**, *10*, 57.
7 K. Araki; S. Shinkai and T. Matsuda; *Chem. Lett.*, **1989**, 581.
8 A. Ueno; J. Anzai; T. Osa and Y. Kadoma; *Bull. Chem. Soc. Jpn.*, **1977**, *50*, 2995.
9 S. Shinkai; H. Koreishi; K. Ueda; T. Arimura and O. Manabe; *J. Am. Chem. Soc.*, **1987**, *109*, 6371.