

See discussions, stats, and author profiles for this publication at:  
<https://www.researchgate.net/publication/239160627>

# Theoretical study of vibrational spectra of p-tert-butylcalix[4]crown-6-ether complexed with ethyl ammonium cation

ARTICLE *in* CHEMICAL PHYSICS LETTERS · JUNE 2003

Impact Factor: 1.9 · DOI: 10.1016/S0009-2614(03)00753-X

---

CITATIONS

6

---

READS

12

5 AUTHORS, INCLUDING:



**Jong-In Choe**

Chung-Ang University

77 PUBLICATIONS 732 CITATIONS

SEE PROFILE



**Shinkoh Nanbu**

Sophia University

107 PUBLICATIONS 898 CITATIONS

SEE PROFILE

# Theoretical study of vibrational spectra of *p*-*tert*-butylcalix[4]crown-6-ether complexed with ethyl ammonium cation

Satoshi Minamino <sup>a</sup>, Jong-In Choe <sup>b</sup>, Suk-Kyu Chang <sup>b</sup>,  
Fumiyasu Mizutani <sup>a</sup>, Shinkoh Nanbu <sup>a,\*</sup>

<sup>a</sup> Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan

<sup>b</sup> Department of Chemistry, Chung-Ang University, Seoul 156-756, Republic of Korea

Received 19 March 2003

## Abstract

Theoretical infrared (IR) absorption spectra were calculated for *p*-*tert*-butylcalix[4]crown-6-ether (**1**) in the cone conformer and its ethyl ammonium complex. The IR spectra were obtained by restricted Hartree–Fock (RHF) calculations with the 6-31G basis set. For the purpose of an absorption band assignment on the host molecule, guest molecule, and complexes thereof, we discussed a way to distinguish a specific molecule by comparing the calculated vibrational spectra. The theoretical result for the host molecule **1** and its ethyl ammonium complex were preliminarily compared with the experimental result, and found that the calculated result agrees well with the features of the experimental spectra.

© 2003 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Crown ethers are cyclic polyethers discovered by Pedersen in 1967 [1,2], and has fascinated researchers for a long time as a basic skeleton of a wide variety of intriguing supramolecular systems. The characteristic chemistry of the crown ether involves complexation of the ether oxygen with various ionic species. This molecular interaction is termed ‘host–guest’ chemistry, with the crown ether as host and the ionic species as guest [3].

From the viewpoint of theoretical chemistry, the chemical bond involved in the complexation is characterized with a through-space interaction between the ionic species and the non-bonding orbitals of the ether oxygen that is similar to the complexation of benzene with ammonium cations [4]. The selectivity and strength of the molecular binding are strongly depending on the electronic structures both of the active sites of the guest and host molecules. Furthermore, this recognition mechanism is quite important in many vital processes of biological systems; the enzyme recognizes the substrates within its active sites by taking the similar molecular binding mechanism. Thus, there is an important aspect of the host–guest chemistry

\* Corresponding author. Fax: +81-564-55-7025.  
E-mail address: [nanbu@ims.ac.jp](mailto:nanbu@ims.ac.jp) (S. Nanbu).

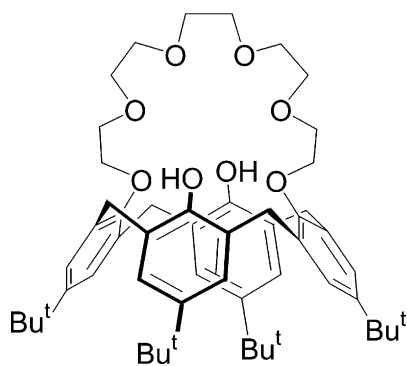


Fig. 1. Structure of *p*-tert-butylcalix[4]crown-6-ether (**1**).

for the purpose of a simplified simulation of much more complex biological systems [5].

On the other hand, a great progress for computational facilities provides us an opportunity to study the relatively large and complicated supramolecular system. Wipff [6] have reported the computational studies on a series of important ionophores derived from calixarenes. We also have reported the structures and energies of isomers for *p*-tert-butylcalix[4]crown-6-ether (**1**) (Fig. 1) [7,8]. In the present work, we report the vibrational spectra for the cone conformation of the host **1** and its ethyl ammonium complex using ab initio molecular orbital method, and provide a theoretical information for the infrared (IR) absorption spectra in order to distinguish the complexed state from the isolated host molecule.

## 2. Ab initio molecular orbital calculations

Restricted Hartree–Fock (RHF) calculations on the host molecule, guest molecule, and complex were carried out using 6-31G basis set. Molecular geometries were fully optimized, and vibrational frequencies were obtained by using analytic second derivative technique. To directly compare with the experimental data, the calculated frequencies were also scaled following the recommended scale factor of 0.893 [9]. Furthermore, the broadened IR spectra were presented assuming a Lorentzian line width of 50 cm<sup>-1</sup>. All calculations were performed with the GAUSSIAN 98 program package [10]. The computers were a Fujitsu VPP5000

owned by the Research Center for Computational Science at Okazaki and Compaq DS20E in our laboratory, and the frequency analysis was quite time-consuming step in the calculations because there are 147 nuclei for the complex conformation, and the number of vibrational modes is 435 (147 × 3 – 6). Using our Compaq DS20E machine, it was possible to determine them over two weeks of calculation.

## 3. Results and discussion

The theoretical IR spectrum for the host-molecule in cone conformer is shown in Fig. 2a. It is clearly seen that the spectrum is characterized with the two vibrational groups, which consist of (i) the

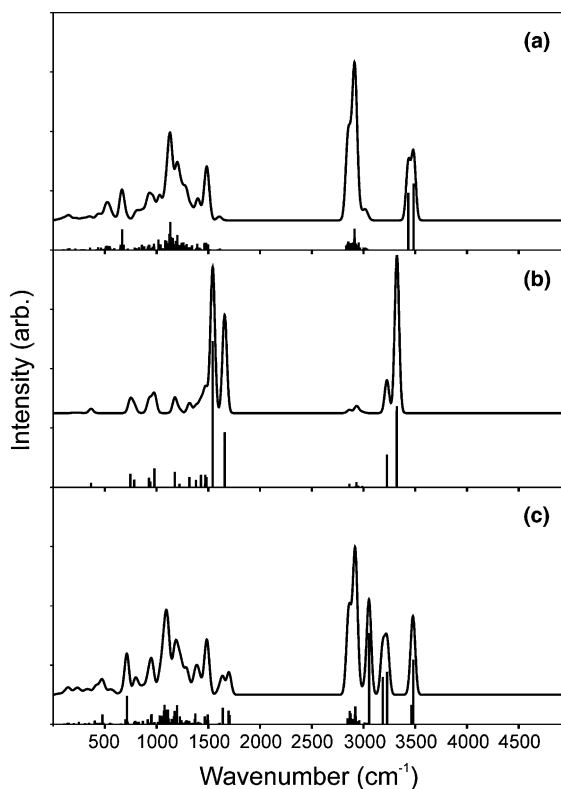


Fig. 2. Theoretical IR absorption spectra: (a) *p*-tert-butyl calix[4]crown-6-ether as the host molecule, (b) ethyl ammonium cation as the guest molecule, and (c) its complex. The broadened absorptions show the simulation with Lorentzian broadening; the line width is 50 cm<sup>-1</sup>.

lower vibrational frequencies than  $1600\text{ cm}^{-1}$  and (ii) the high frequencies above  $2900\text{ cm}^{-1}$ . The lower vibrational frequencies were mainly assigned to the cooperative nuclear motions of the crown ether moiety and benzene-ring. On the other hand the high frequencies around  $3000\text{ cm}^{-1}$  consist of the two parts; the frequencies just around  $2900\text{ cm}^{-1}$  corresponds to the CH stretching motions of the tertiary butyl groups, and the two strong peaks,  $3483$  and  $3433\text{ cm}^{-1}$ , correspond to the two OH stretching motions in the benzene-ring. Thus, the IR spectrum of the host-molecule is well characterized with these two vibrational groups. Note that the broad spectrum is not completely same as the bar spectrum, because some peaks overlapped each other due to the degenerate or almost degenerate vibrational states; for example, although there are lots of small peaks around  $2900\text{ cm}^{-1}$ , the corresponding peak becomes strong after broadening the bar spectrum using the assumption of a Lorentzian line shape.

The corresponding experimental spectrum for the host-molecule is shown in Fig. 3a [11]. Our theoretical spectrum could almost reproduce the features of the experimental result; there are two vibrational groups, and the strong and broad peak

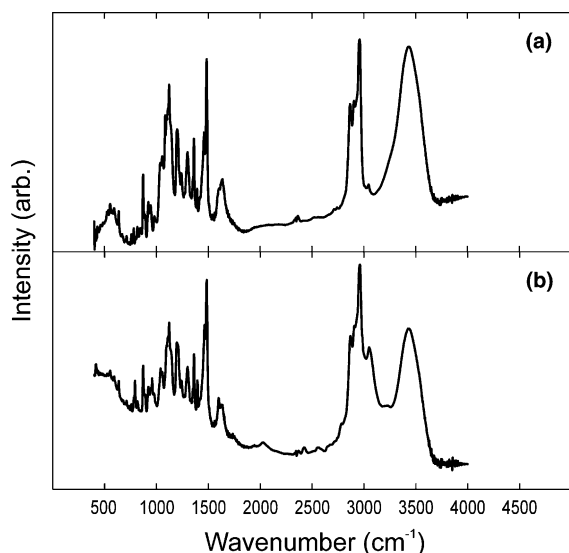


Fig. 3. Experimental IR spectra: (a) the *p*-*tert*-butylcalix[4]-crown-6-ether [10] and (b) its ethyl ammonium complex.

around  $3500\text{ cm}^{-1}$  corresponds to the two OH stretching motions of the benzene-ring. However, the spectral structure of lower frequency region is slightly different from the calculated result although the general appearance duplicates relatively well.

The theoretical IR spectrum for the guest molecule of the ethyl ammonium cation is shown in Fig. 2b. The IR spectrum also consists of the two parts; one is the lower frequency group than  $1650\text{ cm}^{-1}$ , while the second is the high frequency group around  $3200\text{ cm}^{-1}$ . The strong peak at  $1542\text{ cm}^{-1}$  corresponds to the  $\text{NH}_3$  umbrella motion, and also the strong peak at  $1658\text{ cm}^{-1}$  corresponds to the degenerate vibrational motions of the  $\text{NH}_2$  and  $\text{NH}$  bending motions; one is a symmetric motion, while the other is an anti-symmetric motion. The peaks lower than  $1650\text{ cm}^{-1}$  are mainly due to the cooperative motions of the ethyl and the ammonium groups. While, the strong peak located at  $3323\text{ cm}^{-1}$  corresponds to the degenerate vibrational motions of the  $\text{NH}$  stretching and  $\text{NH}_2$  anti-symmetric stretching motions, and the medium peak at  $3226\text{ cm}^{-1}$  corresponds to the  $\text{NH}_3$  symmetric stretching motion. The weak peaks around  $2900\text{ cm}^{-1}$  correspond to the vibrational motions of the ethyl group.

The theoretical IR spectrum calculated for the complex comprising of calix[4]-crown host compound and ethylammonium guest ions is shown in Fig. 2c. The two new peaks which consist of  $3053$ ,  $3185$ , and  $3228\text{ cm}^{-1}$  appear in the frequency region between  $2900$  and  $3500\text{ cm}^{-1}$  of the free host spectrum shown in Fig. 2a, and these two peaks could be the fingerprint of the complex formation. That is because the sharp peak located at  $3323\text{ cm}^{-1}$  shown in Fig. 2b should be split into two peaks ( $3185$  and  $3228\text{ cm}^{-1}$ ) due to the complex formation, and finally the broad peak could appear because of the condensed phase. Moreover, the medium peak at  $3226\text{ cm}^{-1}$  shown in the guest spectrum should be transformed into a strong peak ( $3053\text{ cm}^{-1}$ ) upon formation of the complex. Thus, the complexation of calix-crown molecule with ethylammonium guest ions could be confirmed by the presence of these diagnostic bands in the IR spectra.

The corresponding experimental spectrum for the ammonium complex is shown in Fig. 3b [11].

Table 1  
Main features of vibrational modes depending on the molecular structures

Vibrational modes	Host (Energy/cm <sup>-1</sup> )	Guest (Energy/cm <sup>-1</sup> )	Complex (Energy/cm <sup>-1</sup> )
OH stretching	3483		3481
OH stretching	3433		3462
NH stretching		3323 <sup>a</sup>	3228
NH <sub>2</sub> anti-symmetric stretching		3323 <sup>a</sup>	3185
NH <sub>3</sub> symmetric stretching		3226	3053
<i>tert</i> -Butyl motions	~2900		~2900
NH <sub>2</sub> bending		1658 <sup>a</sup>	1705
NH bending		1658 <sup>a</sup>	1695
NH <sub>3</sub> umbrella motion		1542	1639
Cooperative motions	~1100		~1100
OH twisting	666		713

<sup>a</sup> Degenerate vibrational states.

As expected in the theoretical spectrum, the new two peaks appear in the valley of the two big peaks of the host; the NH<sub>3</sub> symmetric stretching peak (3053 cm<sup>-1</sup>) is clearly shown on the shoulder of the big peak at 2900 cm<sup>-1</sup>, and moreover NH<sub>2</sub> anti-symmetric stretching (3185 cm<sup>-1</sup>) and NH stretching (3228 cm<sup>-1</sup>) peaks are observed as the shallow broad hill in the valley of the two big peaks. Thus, we could reproduce the feature of the experimental spectrum for the complex by theoretical one obtained by ab initio molecular orbital calculation.

The expected spectral features for the host–guest system are summarized in Table 1. Since the complex should be formed from the interaction between the ammonium cation unit (–NH<sub>3</sub><sup>+</sup>) of the guest molecule and the non-bonding orbitals of the oxygen atom of the crown-6-ether moiety, the vibrational motions related with the ammonium cation unit are confined in the crown-6-ether ring. Especially, the three NH stretching motions were quite affected, while the bending motions were not. The degenerate vibrational state consisted of the NH stretching and NH<sub>2</sub> anti-symmetric stretching motions (3323 cm<sup>-1</sup>) should be shifted and split into the two peaks (3228 and 3185 cm<sup>-1</sup>). The calculated energy shift is more than 100 cm<sup>-1</sup>. However, if we assume the interactions in condensed phase, the two peaks should be merged into a broader single peak as shown in Fig. 2c. This situation is

also similar to the two strong OH stretching states for the host and complex molecules. Moreover, the NH<sub>3</sub> symmetric stretching motion (3226 cm<sup>-1</sup>) could be shifted with changing its IR intensity. Although the intensity of the band is medium in the guest molecule, it became strong by forming the complex. On the other hand, the peak for the NH<sub>3</sub> umbrella motion changed in opposite manner compared to the NH<sub>3</sub> symmetric stretching motion, because the intensity of the umbrella motion for the complex should be small comparing with the three NH stretching modes. Thus, we found the characteristic of the vibrational states of the host, guest, and complex molecules for the present system. The diagnostic differences in the IR spectra should provide us the key to understand more deeply the host–guest molecular structures by enabling to assign and distinguish the individual and complexed molecular states.

### Acknowledgements

This work was supported by a Grant-in-Aid from the Ministry of Education, Science, and Culture (No. 13740336), Japan. The large portions of the computations were carried out with use of the computer facilities at the Research Center for Computational Science of The Okazaki National Research Institutes.

## References

- [1] C.J. Pedersen, J. Am. Chem. Soc. 89 (1967) 2495.
- [2] C.J. Pedersen, J. Am. Chem. Soc. 89 (1967) 7017.
- [3] D.J. Cram, J.M. Cram, Acc. Chem. Res. 11 (1978) 8.
- [4] K.S. Kim, J.Y. Lee, S.J. Lee, T.-K. Ha, D.H. Kim, J. Am. Chem. Soc. 116 (1994) 7399.
- [5] M.T. Reetz, C.M. Neimeyer, K. Harms, Angew. Chem. Int. Ed. Engl. 30 (1991) 1474.
- [6] G. Wipff, in: Kluwer (Ed.), Computational Approaches in Supramolecular Chemistry, Academic Publishers, Dordrecht, 1994.
- [7] J.-I. Choe, K. Kim, S.-K. Chang, Bull. Korean Chem. Soc. 21 (2000) 465.
- [8] J.-I. Choe, S.-K. Chang, S.W. Ham, S. Nanbu, M. Aoyagi, Bull. Korean Chem. Soc. 22 (2001) 1248.
- [9] J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Methods, second ed., Gaussian, Inc, Pittsburgh, PA, 1996.
- [10] M.J. Frisch et al., GAUSSIAN 98, Revision A.9, Gaussian, Inc, Pittsburgh, PA, 1998.
- [11] J.-I. Choe, J.H. Kim, S.-K. Chang, S. Minamino, F. Mizutani, S. Nanbu, Chung-Ang University, Seoul, 2003, to be published.