

## SHORT COMMUNICATION

COMPUTATIONAL INVESTIGATION ON THE STRUCTURE AND NMR CHEMICAL SHIFTS OF ENDO-CONE [CS<sub>2</sub>(p-METHYLCALIX[4]ARENE)] COMPLEXHanggara Sudrajat<sup>1,\*</sup>, Muhammad S. Saefullah<sup>2</sup>, Danis Sriwijaya<sup>1</sup>, Mirta A. Putri<sup>1</sup>, and Ria Armunanto<sup>3</sup><sup>1</sup>Undergraduate Student, <sup>3</sup>Austrian-Indonesian Center for Computational Chemistry, Department of Chemistry, Faculty of Mathematics and Natural Sciences Gadjah Mada University, Sekip Utara Yogyakarta 55281<sup>2</sup>Laboratory of Computational Physics, Physics Education Department, Faculty of Mathematics and Natural Sciences, State University of Yogyakarta, Karangmalang, Yogyakarta 55283<sup>3</sup>Department of Chemistry, Gadjah Mada University, Sekip Utara Yogyakarta, 55281

Received December 1, 2008; Accepted March 24, 2009

## ABSTRACT

The structure and NMR chemical shifts of endo-cone [CS<sub>2</sub>(p-methylcalix[4]arene)] complex have been computationally investigated using BIO+ force fields, semi-empirical (PM3) and *ab initio* (RHF/6-311G++(d,p)) calculations. The first comparison of *ab initio* NMR chemical shift calculations for a calix[4]arene inclusion complex with solid-state <sup>13</sup>C NMR chemical shifts based on the 1:1 complex of p-methylcalix[4]arenes with carbon disulfide in endo-cone complexation mode has been reported. The results showed that *ab initio* (RHF/6-311G++(d,p)) NMR calculations of the host-guest [CS<sub>2</sub>(p-methylcalix[4]arene)] complex are in good agreement with experimental solid-state NMR data.

**Keywords:** computational investigation, structure, NMR chemical shifts, [CS<sub>2</sub>(p-methylcalix[4]arene)].

## INTRODUCTION

Calix[*n*]arenes are interesting host molecules which can be easily functionalised to enclose neutral organic molecules, cations or anions, both in solution and in the solid state [1-2]. When no crystallographic data are accessible, alternative methods are used to gain structural information on the host-guest complexes or clathrates. CP-MAS <sup>13</sup>C NMR spectroscopy [3-7] and thermochemical [8-9] methods are applicable for the investigation of crystalline materials. Other NMR techniques, such as titration experiments, solvent-induced chemical shifts (SICS), aromatic solvent-induced shifts (ASIS), complexation-induced shifts (CIS), are useful methods to study the complexation behaviour in solution [1-2].

Complexation-induced shifts (CIS) in <sup>1</sup>H NMR spectra have been used to determine three-dimensional structural models for supramolecular complexes [2, 10-11]. <sup>1</sup>H chemical shifts were estimated based on models for the aromatic ring current for various force field calculated geometries of a host-guest complex [11]. Good agreement of derived NMR data was found for force field calculated models of the complexes which showed similar geometries to X-ray crystal structures. However, this approach lacks general applicability

because the model for the ring current depends on the host and has to be adapted for different host structures. In contrast, Gauge Including Atomic Orbitals (GIAO)-NMR calculations are independent of such model assumptions and can be used for any host-guest system and for both <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts [12-15].

Taking into account this information, herein, we want to report the first comparison of *ab initio* GIAO-NMR chemical shift calculations for a calix[4]arene inclusion complex with solid-state <sup>13</sup>C NMR chemical shifts based on the 1:1 complex of p-methylcalix[4]arenes with carbon disulfide and to ascertain the feasibility of this approach for host-guest complex of calix[4]arene. This complex has been characterised by thermogravimetric analysis (TGA) and solid-state <sup>13</sup>C NMR spectroscopy [8]. TGA experiments indicated that CS<sub>2</sub> is bound very strongly in the p-methylcalix[4]arene cavity. Crosspolarisation magic angle spinning (CP-MAS) <sup>13</sup>C NMR spectroscopy showed a significant complexation-induced chemical shift (CIS = -1.2 ppm) compared to solution data. The low temperature (173 K) X-ray crystal structure analysis of the complex indicated the inclusion of CS<sub>2</sub> in the calixarene cavity to be highly symmetrically oriented directly on the C<sub>4</sub> axis of the

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**Table 1.** Comparison between calculated structural parameters and crystal structure

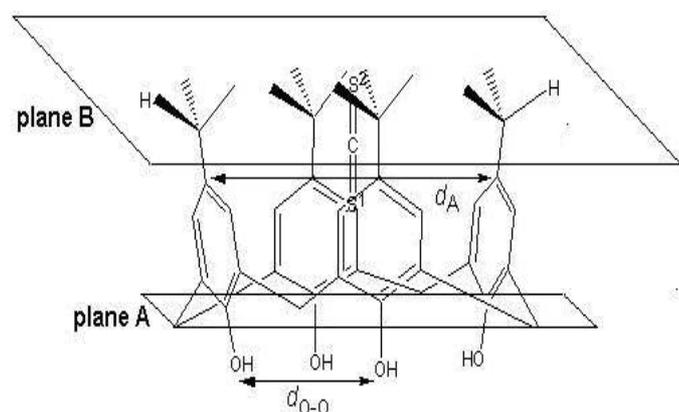
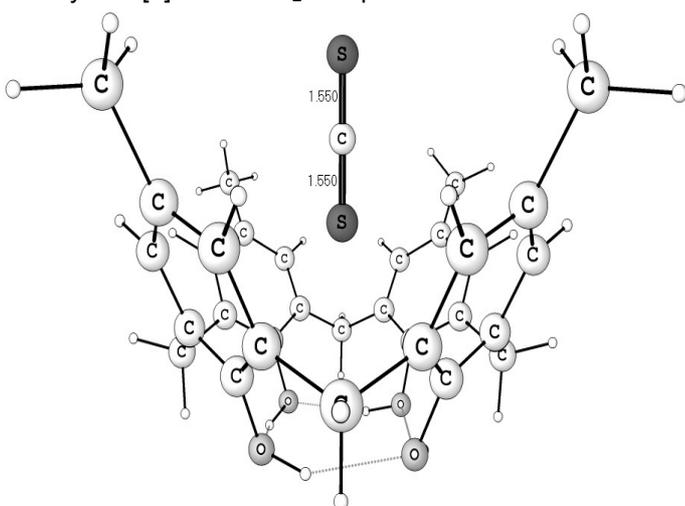
	Method		
	BIO+	RHF/6-311G++(d,p)	Crystal Structure
$d_A/\text{\AA}$	7.95	8.38	8.34
$d_{O-O}/\text{\AA}$	2.80	2.72	2.69
$d_{S^2-C}/\text{\AA}$	1.62	1.55	1.55
$\alpha^a/^\circ$	61	56	56.5
$I^b(\%)$	88	57	92

<sup>a</sup> $\alpha$  is defined as the angle between a phenyl ring and plane A (plane of the methylene bridges). <sup>b</sup>The inclusion  $I$  is defined as:  $I = d_{S^1-S^2} - d_{S^2-\text{plane B}} / d_{S^1-S^2} \times 100\%$ . Plane B represents the top of the calix[4]arene cavity.

**Table 2.** Comparison between calculated and experimentally obtained chemical shift data

	$\delta_C$		
	Complex	Free guest	CIS <sup>a</sup> (ppm)
$\delta_{\text{exp}}^b$	191.3	192.5	-1.2
$\delta_{\text{calc}}$	204.4	205.5	-1.1

<sup>a</sup>CIS = complex-induced chemical shift =  $\Delta\delta = \delta(\text{complex}) - \delta(\text{free guest})$ . <sup>b</sup>GIAO calculated chemical shift [RMP2/6-311G++(d,p)//RHF/6-311++G(d,p)] referenced to TMS calculated on the same level of theory.

**Figure 1.** Structural parameters of the 1:1 p-methylcalix[4]arene- $\text{CS}_2$  complex**Figure 2.** Molecular structure of the 1:1 p-methylcalix[4]arene- $\text{CS}_2$  complex obtained by RHF/6-311++G(d,p) geometry optimisation.

host. Due to the relatively small size and the high symmetry of the guest molecule this system is suitable for quantum chemical investigations.

## COMPUTATIONAL METHODS

Geometry optimisations were performed on an initial geometry obtained from the experimental data for the crystal structure, using BIO+ force fields and semi-empirical (PM3) with the HyperChem 7.5 program [16] and *ab initio* (RHF/6-311G++(d,p)) calculations with the GAUSSIAN 98 program [17]. Details of the X-ray crystal structure determination are deposited at the Cambridge Crystallographic Data Centre (CCDC 136/840 and CCDC 136/841).

## RESULT AND DISCUSSION

Table 1 summarises important calculated and experimental data for the inclusion complex. Force field methods give fast access to a qualitative picture of the complex but important structural features like the symmetry and the C=S bond length are not adequately described. PM3 calculations fail to describe the attractive host-guest interactions between p-methylcalix[4]arene and carbon disulfide. In the course of the PM3 optimisation cycles host and guest are separated. *Ab initio* RHF/6-311G++(d,p) geometry optimisations in general give a very good description of the calixarene and carbon disulfide moieties, but underestimate the attractive intermolecular forces. At RHF/6-311G++(d,p) level of theory, the inclusion of the guest is calculated to be 57% as compared to 92% calculated from the experimental data (Table 1, Figure 1 and Figure 2).

Based on the RHF/6-311G++(d,p) geometry for the p-methylcalix[4]arene- $\text{CS}_2$  complex, the  $^{13}\text{C}$  NMR

chemical shift of the guest molecule was calculated using the GIAO method (RMP2/6-311G++(d,p)) and compared to the chemical shift of carbon disulfide calculated at the same level (GIAO-RMP2/6-311G++(d,p) at RHF/6-311G++(d,p) geometry). The difference  $\Delta\delta = \delta(\text{CS}_2 \text{ complexed}) - \delta(\text{CS}_2)$  was calculated to be -1.10 ppm (Table 2). This shift difference is in good agreement with the experimentally determined complex-induced shift (-1.20 ppm), taking into account the different geometries for the calculated and the experimental crystal structure.

## CONCLUSION

The results obtained for the p-methylcalix[4]arene-carbon disulfide (1:1) complex show the feasibility of high level *ab initio* calculations for host-guest complexes of calix[4]arenes. *Ab initio* GIAO chemical shift calculations provide a useful tool for the comparison of experimentally observed complexation-induced shifts (CIS) with CIS data estimated for structures obtained using molecular modeling methods.

## ACKNOWLEDGEMENT

Part of this work was supported by grant from the *Kompetisi Karya Tulis Mahasiswa bidang Ilmu Pengetahuan Alam* (KKTMM-IPA) 2007. The large portions of the computations were carried out with use of the computer facilities at the Indonesian Higher Education Network-INHERENT (*i-hpc-portal komputasi paralel*) of the Gadjah Mada University.

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