SHORT COMMUNICATION

COMPUTATIONAL INVESTIGATION ON THE STRUCTURE AND NMR CHEMICAL SHIFTS OF ENDO-CONE [CS$_2$(p-METHYLCALIX[4]ARENE)] COMPLEX

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ABSTRACT

The structure and NMR chemical shifts of endo-cone [CS$_2$(p-methylicalix[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 $^{13}$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$_2$(p-methylicalix[4]arene)] complex are in good agreement with experimental solid-state NMR data.

Keywords: computational investigation, structure, NMR chemical shifts, [CS$_2$(p-methylicalix[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 $^{13}$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 $^1$H NMR spectra have been used to determine three-dimensional structural models for supramolecular complexes [2, 10-11]. $^1$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 $^1$H and $^{13}$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 $^{13}$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 $^{13}$C NMR spectroscopy [8]. TGA experiments indicated that CS$_2$ is bound very strongly in the p-methylcalix[4]arene cavity. Crosspolarisation magic angle spinning (CP-MAS) $^{13}$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$_2$ in the calixarene cavity to be highly symmetrically oriented directly on the C$_4$ axis of the
Table 1. Comparison between calculated structural parameters and crystal structure

<table>
<thead>
<tr>
<th>Method</th>
<th>BIO+</th>
<th>RHF/6-311G++(d,p)</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_A$/Å</td>
<td>7.95</td>
<td>8.38</td>
<td>8.34</td>
</tr>
<tr>
<td>$d_O$/Å</td>
<td>2.80</td>
<td>2.72</td>
<td>2.69</td>
</tr>
<tr>
<td>$d_S$/Å</td>
<td>1.62</td>
<td>1.55</td>
<td>1.55</td>
</tr>
<tr>
<td>$\alpha$°</td>
<td>61</td>
<td>56</td>
<td>56.5</td>
</tr>
<tr>
<td>$I$ (°)</td>
<td>88</td>
<td>57</td>
<td>92</td>
</tr>
</tbody>
</table>

* $\alpha$ is defined as the angle between a phenyl ring and plane A (plane of the methylene bridges).
* The inclusion $I$ is defined as: $I = d_S^- - d_S^+ - 100\%$. Plane B represents the top of the calix[4]arene cavity.

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

<table>
<thead>
<tr>
<th></th>
<th>Complex</th>
<th>Free guest</th>
<th>CIS $^a$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{exp}$</td>
<td>191.3</td>
<td>192.5</td>
<td>-1.2</td>
</tr>
<tr>
<td>$\delta_{calc}$</td>
<td>204.4</td>
<td>205.5</td>
<td>-1.1</td>
</tr>
</tbody>
</table>

* CIS = complex-induced chemical shift = $\Delta \delta = \delta$ (complex) - $\delta$ (free guest).
* 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–CS$_2$ complex

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

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–CS$_2$ complex, the $^{13}$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 $\Delta \delta = \delta(CS_2 \text{complexed}) - \delta(CS_2)$ 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.

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REFERENCES