Geometry and GIAO-DFT chemical shift calculations of calixarene complexes—the inclusion of carbon disulfide in *p-tert*-butylcalix[4]arene †

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Quantum chemical GIAO-DFT NMR calculations [B3LYP/6-311G(d,p)//RHF/6-31G(d)] of the host–guest complex *p-tert*-butylcalix[4]arene–carbon disulfide are in good agreement with experimental solid-state NMR data.
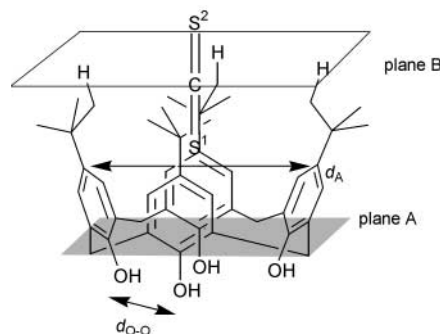
Introduction

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.[1–5] When no crystallographic data[6] are accessible, alternative methods are used to gain structural information on the host–guest complexes or clathrates. CP-MAS ^{13}C NMR spectroscopy[7–16] and thermochemical methods[17–20] are applicable for the investigation of crystalline materials. Other NMR techniques, such as solvent-induced chemical shifts, aromatic solvent-induced shifts (ASIS) and titration experiments, 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.[2,21,22] [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.[22] 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. This approach however 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, GIAO-DFT NMR calculations[23–26] 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.
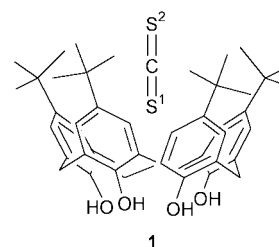
Herein, we want to report the first comparison of *ab initio* NMR chemical shift calculations for a calix[4]arene inclusion complex with solid-state ^{13}C NMR chemical shifts based on the 1:1 complex (**1**) of *p-tert*-butylcalix[4]arenes with carbon disulfide. This complex has been characterised recently by thermogravimetric analysis (TGA) and solid-state ^{13}C NMR spectroscopy.[18] TGA experiments indicated that CS_2 is bound very strongly in the *p-tert*-butylcalix[4]arene cavity. Cross-polarisation magic angle spinning (CP-MAS) ^{13}C NMR spectroscopy showed a significant complexation-induced chemical shift (CIS = −2.2 ppm) compared to solution data.[18] 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 host. Due to the relatively small size and the high symmetry of the guest molecule this system is suitable for quantum chemical investigations.

Table 1 Comparison between calculated structural parameters and crystal structure

Method	SYBYL[27]	MM+[28]	RHF/6-31G(d)[29]	Crystal structure
d_A/Å	7.35, 8.17	7.95	8.48	8.34
d_{O-O}/Å	2.79, 2.86	2.80	2.73	2.69
d_{S^2-C}/Å	1.58	1.62	1.55	1.55
a^a/°	55, 75	61	54	56.5
I^b (%)	100	88	57	92

^{a} a is defined as the angle between a phenyl ring and plane A (plane of the methylene bridges). ^{b} The inclusion I is defined as:

$$I = \frac{d_{S^1-S^2} - d_{S^2-\text{plane B}}}{d_{S^1-S^2}} \times 100\%.$$ Plane B represents the top of the calix[4]-arene cavity.

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Results and discussion

Geometry optimisations were performed on an initial geometry obtained from the experimental data for the crystal structure, using SYBYL[27] and MM+[28] force fields, semi-empirical (PM3) and *ab initio* (RHF/6-31G(d)) calculations.[29] Table 1 summarises important calculated and experimental data for the inclusion complex **1**. 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-tert*-butylcalix[4]arene and carbon disulfide. In the course of the PM3 optimisation cycles host and guest are separated. *Ab initio*

Table 2 Comparison between calculated and experimentally obtained chemical shift data

	δ_C		
	Complex	Free guest	CIS[a] (ppm)
δ_{exp}	190.1	192.3	−2.2
δ_{calc}[b]	204.4	205.5	−1.1

[a] CIS = complex-induced chemical shift = $\Delta\delta = \delta$ (complex) − δ (free guest). [b] GIAO-DFT calculated chemical shift [B3LYP/6-311G(d,p)//RHF/6-31G(d)] referenced to TMS calculated on the same level of theory.
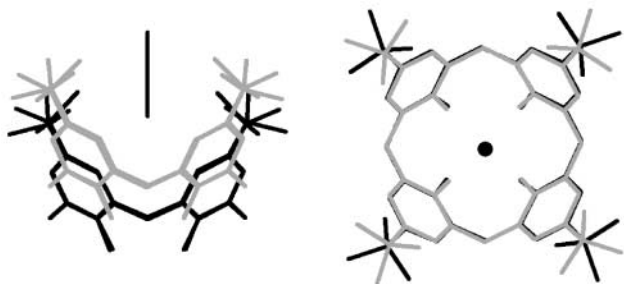

Fig. 1 Molecular structure of the 1:1 *p-tert*-butylcalix[4]arene–CS$_2$ complex obtained by crystallography (black) and by RHF/6-31G(d) geometry optimisation (grey); enclosed CS$_2$ molecules overlaid.

RHF/6-31G(d) geometry optimisations in general give a very good description of the calixarene and carbon disulfide moieties, but underestimate the attractive intermolecular forces.§ At RHF/6-31G(d) level the inclusion of the guest is calculated to be 57% as compared to 92% calculated from the experimental data (Table 1 and Fig. 1).

Based on the RHF/6-31G(d) geometry for the *p-tert*-butylcalix[4]arene–CS$_2$ complex, the ^{13}C NMR chemical shift of the guest molecule was calculated using the GIAO-DFT method [B3LYP/6-311G(d,p)][29] and compared to the chemical shift of carbon disulfide calculated at the same level [GIAO-DFT (B3LYP/6-311G(d,p) at RHF/6-31G(d) geometry)]. The difference $\Delta\delta = \delta(CS_2$ 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 (−2.20 ppm), taking into account the different geometries for the calculated and the experimental crystal structure.

The results obtained for the *p-tert*-butylcalix[4]arene–carbon disulfide (1:1) complex (**1**) show the feasibility of high level *ab initio* calculations for host–guest complexes of calix[4]-arenes. *Ab initio* GIAO-DFT 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 modelling methods. Further comparisons of GIAO-DFT calculated and experimental solid-state or solution NMR chemical shifts of other host–guest complexes are currently under investigation.

Notes and references

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§ Frequency calculations for characterisation of the optimised structure to be an energy minimum would require >6 weeks of CPU time and were not performed.

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