RECENT APPLICATION OF ab initio CALCULATIONS ON CALIXARENES AND CALIXARENE COMPLEXES. A REVIEW

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This review is dedicated to Professor Ivan Stibor on the occasion of his 60th birthday in recognition of his outstanding contributions to supramolecular chemistry.

1. Introduction 1169
2. Results and Discussion 1171
2.1. Conformations of Free Calixarenes 1171
2.2. Calculations on Calixarene Complexes 1179
2.3. Calculations on Reaction or Geometrical Interconversion Pathways. 1183
2.4. Calculation of Molecular Properties. 1186
3. Conclusions. 1191
4. References 1192

In this short review the application of ab initio quantum chemical calculations on calixarenes and calixarene complexes is highlighted. The main focus lies on results obtained mainly during the last 2–3 years. A review with 92 references.

Keywords: Calixarenes; Inclusion compounds; Ab initio calculations; DFT; Conformation analysis; Quantum chemistry; Computer chemistry; Supramolecular chemistry.

1. INTRODUCTION

Syntheses and application of supramolecular systems depend strongly on the spatial arrangement of the corresponding building blocks. To understand how and why the “superstructure” is formed, good structural models are crucial and such three-dimensional representations of a supramolecular entity are the basis for evaluation of intermolecular forces which are decisive for the cohesion of all structural elements.

During the last 25 years, calix[*n*]arenes have aroused much interest because of their convenient application as receptor molecules for cations, anions, and neutral molecules or as ligands and catalytic systems[1–8].

For the determination of three-dimensional arrangement of such supramolecular entities in the solid state, usually single-crystal X-ray structure determination is regarded as the ultimate structure proof. However, this methodology strongly depends on the accessibility of single-crystalline material. If such crystalline material is not available, ^{13}C CP-MAS NMR [9–18], vibrational spectroscopy[1,20–26], or thermochemical methods[27–30] are applicable. In solution, NMR titration experiments have found widespread use for the characterisation of inclusion processes[1,2,31,32].

Except the use of single-crystal structure analysis, which gives direct access to the three-dimensional coordinates of the supramolecular system of interest, most spectroscopic methodologies depend strongly on interpretation and sometimes also on "chemical intuition". At this point the use of computer chemistry, i.e. molecular modeling and quantum chemical calculations, comes into play. The use of force-field and semiempirical calculations as well as molecular dynamics simulations are well-established, very useful methods in the field of calixarene chemistry[33–35]. All these methods depend strongly on the choice of parameters describing bond length, angles, dihedrals, and intermolecular forces. In principle, ab initio calculations are free of such model assumptions and would therefore be appropriate for the description of any calixarene or calixarene complex. However, the much higher effort in computer time necessary for the application of high ab initio methods has limited the use of such calculations until recently. But the actual improvements both in computer hardware and software makes it more and more attractive to apply high-level quantum chemical methods to gain structural insight into supramolecular systems.

Because quantum chemical calculations on alkali metal complexes of calixarenes have been reviewed recently[36], this article is focused on recent examples of the use of such calculations in the field of calixarene chemistry. It is not intended to give a comprehensive overview but to highlight some examples how ab initio calculations can contribute to this field.

This review is divided into several parts, namely results dealing with various conformers of free calixarenes and related compounds, calculations on calixarene complexes with cations, anions and neutral molecules, followed by some examples of the use of quantum chemical methods exploring reaction pathways catalysed by calixarenes and finally calculations of properties (vibrational and NMR spectra). Furthermore, it is not intended to give an in-

troduction to quantum chemistry in general but to give an overview of the possibilities of such methods in the daily routine of a calixarene chemist.

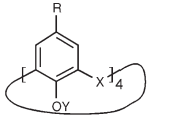
2. RESULTS AND DISCUSSION

2.1. Conformations of Free Calixarenes

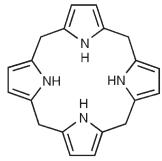
The conformation of a macrocyclic receptor is a key feature which determines the utilisation of such molecules in all applications of supramolecular chemistry of today. Therefore, the study of the conformational behaviour of calix[*n*]arenes has been in the focus since the beginning of their chemistry. Experimental data are usually obtained by dynamic NMR spectroscopy[37,38]. Parallel to the experimental characterisation of all possible conformers of the calixarene family, computational methods have been also widely used to support and interpret the experiment. Many molecular mechanics and semiempirical studies were dealing with the relative energy of the conformations as well as interconversion pathways between them and were reviewed recently[33,35]. In general, the relative energy increases from cone < partial cone (paco) < 1,2-alternate (1,2-alt) < 1,3-alternate (1,3-alt) as calculated by force-field methods (Table I, entries 3–5). The calculated relative energies seemed to be in agreement with the $\Delta G^{\ddagger}$ of about 15 kcal mol^{-1} obtained experimentally by NMR spectroscopy for 4-*tert*-butylcalix[4]arene (**1**) and calix[4]arene (**2**) (Table I, entries 1, 2). Depending on the force-field used, the C_4 symmetrical cone conformation was sometimes identified as a transition state lying 0.6 kcal mol^{-1} (MM3) above the real minimum of this series, the pinched cone conformer (C_2 symmetry).

Inspired by that research is was obvious that ab initio calculations have been also used to study the conformational behaviour of calixarenes. Some recent results concerning the basic calix[4]arene skeleton (**2**) are summarised in Table I, entries 6–16, a graphical representation of these results[39,40] is shown in Fig. 1. Based on Hartree–Fock (HF) geometry optimisations mainly on levels up to HF/3-21G(d,p) or by density functional theory (DFT) up to BLYP/6-31G(d) single point energy calculations were performed using HF (Table I, entries 6–10), Moller–Plesset (MP) perturbation theory (Table I, entry 11), or DFT (Table I, entries 12–16) up to a 6-31G(d,p) level. In general, most methods seem to overestimate the relative energies of the four calix[4]arene conformers, although the values tend to converge towards realistic data when using higher basis sets such as 6-31G(d,p) in combination with DFT or MP methods. For the time-consuming geometry optimisations,

TABLE I
Calculated relative stability of conformers of calixarene derivatives (energies in kcal mol^{-1})



1 (R = *t*-Bu, X = CH_2, Y = H)
2 (R = H, X = CH_2, Y = H)
3 (R = H, X = S, Y = H)
4 (R = H, X = SO_2, Y = H)
5 (R = *t*-Bu, X = SO_2, Y = H)
6 (R = PPh_2, X = CH_2, Y = Me)



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Entry	Compound	Energy	Geometry	cone	paco	1,2-alt	1.3-alt	Ref.
1	**1**	experiment	–	0		15.7; 14.8[a]		37
2	**2**	experiment	–	0		14.9; 13.8[a]		37
3		MM3(89)	MM3(89)	0	9.9	11.7	18.7	91
4		MM3(92)	MM3(92)	0	5.6	6.1	10.6	91
5		CHARMM	CHARMM	0	8.9	11.5	17.2	92
6		HF/3-21G	HF/3-21G	0	18.3	21.9	31.9	39
7		HF/6-31G	HF/3-21G	0	11.6	20.9	23.1	39
8		HF/3-21G(d,p)	HF/3-21G(d,p)	0	16.0	26.3	28.1	39
9		HF/6-31G(d,p)	HF/3-21G(d,p)	0	7.0	14.7	13.6	39
10		HFB/6-31G	HFB/6-31G	0	12.1	20.4	20.9	40
11		MP2/6-31G(d,p)	HF/3-21G(d,p)	0	9.4	18.9	17.1	39
12		BLYP/6-31G	BLYP/6-31G	0	16.0	26.2	27.8	40
13		BLYP/6-31G(d)	BLYP/6-31G	0	9.7	17.2	16.3	40
14		BLYP/6-31G(d,p)	BLYP/6-31G	0	10.0	17.4	16.6	40
15		BLYP/6-31G(d)	BLYP/6-31G(d)	0	10.7	18.6	18.1	39,40
16		B3LYP/6-31G(d,p)	BLYP/6-31G(d)	0	10.5	18.4	17.6	39,40
17	**3**	HF/3-21G	HF/3-21G	0	22.1	33.7	30.8	41
18		HF/3-21G(d,p)	HF/3-21G(d,p)	0	19.4	29.9	27.8	41
19		B3LYP/3-21G	B3LYP/3-21G	0	24.6	44.5	36.1	41
20		B3LYP/3-21G(d,p)	B3LYP/3-21G(d,p)	0	21.3	30.9	31.9	41
21		B3LYP/6-31G(d,p)	B3LYP/6-31G(d,p)	0	10.1	16.5	13.8	41
22		B3LYP/6-311G(d,p)	B3LYP/6-31G(d,p)	0	9.1	15.6	12.3	41
23		G96LYP/6-311G(d,p)	B3LYP/6-31G(d,p)	0	8.2	13.9	11.5	41
24	**4**	B3LYP/6-31G(d)	AM1	8.3	10.4	0.0	5.1	43
25	**5**	B3LYP/6-31G(d)	AM1	0.57	2.02	0.0	4.87	43
26	**6**	HF/G-31G(d)	HF/STO-3G	2.7	0.0	18.0	4.5	44
27	**7**	BLYP/6-31G+G(d,p)	BLYP/3-21G	16.0	4.8	6.7	0.0	46

[a] $\Delta G^{\ddagger}$ in chloroform and benzene, respectively.

HF/3-21G(d,p) is currently the method of choice weighing accuracy against CPU time[39].

The cone (pinched cone) conformation is identified by all calculations as the most stable conformer of calix[4]arene (**2**); the partial cone isomer lies about 10.7 kcal mol^{-1} (median of all calculations, entries 6–16) above the minimum. The picture is not as clear when one has to distinguish which conformer is the next. Some calculations (Table I, entries 6–8, 10, 12) do prefer the 1,2-alternate conformation (median 21.9) over the 1,3-alternate (median 27.8 kcal mol^{-1}). This finding parallels most force-field calculations. In contrast, all other simulations using 6-31G(d) or 6-31G(d,p) basis sets (Table I, entries 9, 11, 13–16) exhibited a weak preference of about 1 kcal mol^{-1} for the 1,3- over the 1,2-alternate conformation. Treating both sets of calculations separately, the following median relative energies could be obtained: cone (0.0), paco (16.0), 1,2- (21.9) and 1,3-alt (27.8 kcal mol^{-1}); using basis sets 6-31G(d) or 6-31G(d,p): cone (0.0), paco (9.9), 1,2- (17.9) and 1,3-alt (16.9 kcal mol^{-1}).

Taking all data for calix[4]arene (**2**) into account, the median values (dashed grey line in Fig. 1) practically coincide nearly with the results obtained by the BLYP/6-31G(d,p) based on a BLYP/6-31G(d) geometry.

A more homogeneous picture is obtained for thiacalix[4]arene (**3**) (Table I, entries 17–23, Fig. 2)[41]. Again, the relative differences between conformers are overestimated using basis sets up to 3-21G(d,p). Reasonable results were obtained by DFT calculations; similar to calix[4]arene, a 6-31G(d,p) level or

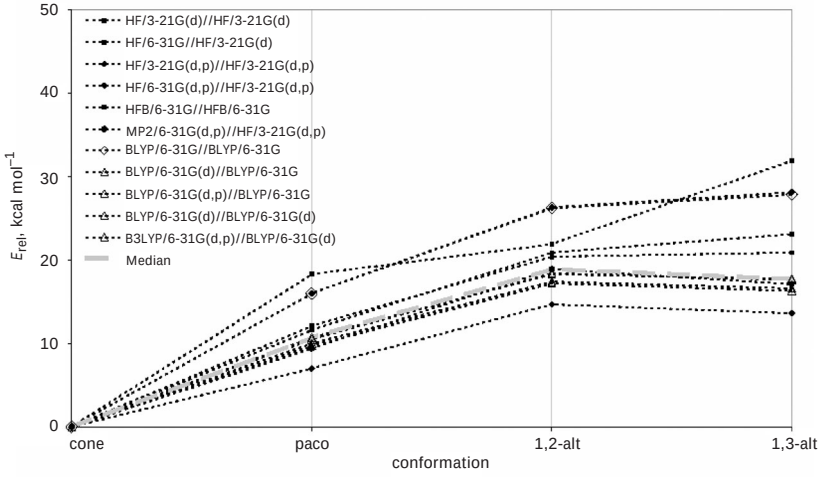


FIG. 1
Plot of the calculated relative energy (kcal mol^{-1}) of the conformations of calix[4]arene (**2**)

higher seems to be appropriate. The stability of all the four conformers for thiacalix[4]arene (**3**) is calculated to be: cone (0.0) < paco (median 19.4) < 1,3- (27.8) < 1,2-alt (29.9 kcal mol^{-1}).

When one compares calix[4]arene (**2**) and thiacalix[4]arene (**3**) on the basis of similar calculation levels, e.g. Table I, entries 16 and 21, the 1,2- and

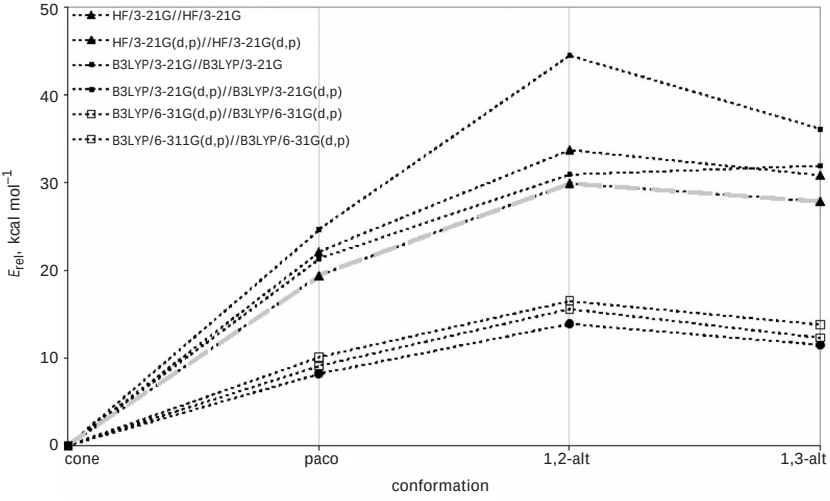


FIG. 2
Plot of the calculated relative energy (kcal mol^{-1}) of the conformations of thiacalix[4]arene (**3**)

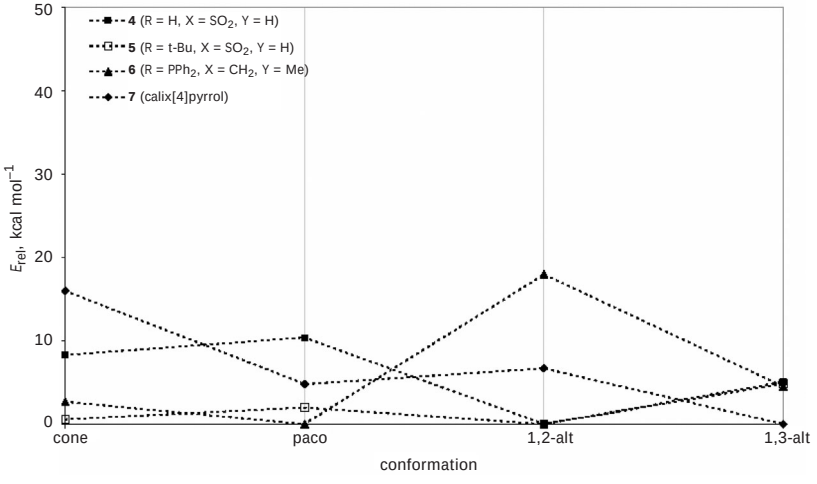


FIG. 3
Plot of the calculated relative energy (kcal mol^{-1}) of the conformations of calixarenes **4**–**7**

1,3-alternate conformation of calix[4]arene are about 2–4 kcal mol^{-1} less stable than the corresponding isomers of the thia analogue **3**. This is in agreement with the experimental observation by Stibor et al. that thiacalix[4]arene is more flexible in solution compared with calix[4]arene[42].

The distribution of the conformers of sulfonylcalix[4]arene (**4**; 4 possible conformers) and 4-*tert*-butylsulfonylcalix[4]arene (**5**; 35 possible conformers) were studied by Ruangpornvisitu and co-workers[43]. Based on an AM1 semiempirical potential energy surface scan, ab initio single-point calculations were performed to obtain relative energies for all possible structures (cf. Table I, entries 24, 25, and Figs 3 and 4). In both sulfonylcalix[4]arene derivatives **4** and **5**, the 1,2-alternate configuration is the most stable. Compared with thiacalix[4]arene, the energy surface for the oxidised derivative is very shallow (Table I, entries 21 and 25); the difference between lowest and highest energy conformers is 4.87 and 16.5 kcal mol^{-1}, respectively, corresponding to a factor of ≈3.4[43].

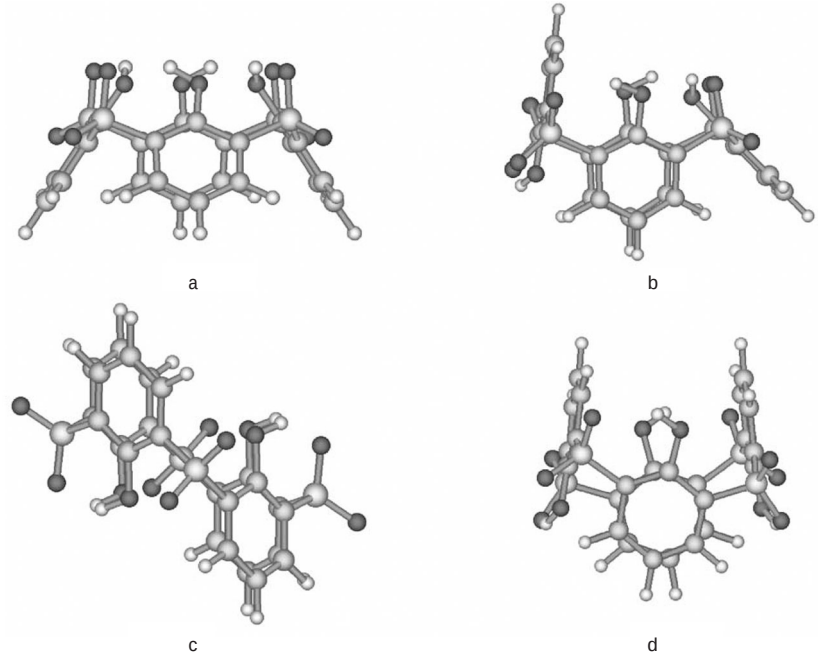


FIG. 4
Calculated conformers of the sulfonylcalix[4]arene **4**: a cone, b partial cone, c 1,2-alternate and d 1,3-alternate[43] (reprinted from: Wanno B., Sang-aroon W., Tuntulani T., Polpoka B., Ruangpornvisitu V.: *J. Mol. Struct. (THEOCHEM)* **2003**, *629*, 137, with permission from Elsevier)

Not only changing the bridges between the benzene rings can change conformational preferences but also modifications at the wide rim of a calix[4]arene skeleton. Tsuji et al. were interested in the calix[4]arene tetramethyl ether **6** bearing four diphenylphosphino groups at the upper rim[44]. Hartree–Fock calculations (cf. Table I, entry 26 and Fig. 3) identified the partial cone conformation as the most stable arrangement flanked by cone and 1,3-alternate with small differences in relative energy (<4.5 kcal mol^{-1}) while the 1,2-alternate is considerably unstable by 18 kcal mol^{-1}.

Calculations of various conformations of both calix[4]arene and calix[6]arene using the HF/STO-2G and HF/6-31G(d,p) methods were reported by Gren and co-workers[45]. These calculations identified the compressed cone conformation of calix[6]arene as the most stable one, thus, maximising hydrogen bonding at the narrow rim.

Similar to calix[4]arenes and derivatives, calix[4]pyrrole (**7**) as a powerful receptor for anions came into the focus for the use of quantum chemical methods[46,47]. Again the conformational characterisation was performed by Sessler and Wu using ab initio calculations (cf. Table I, entry 27, and Figs 3 and 5)[46]. This time, the 1,3-alternate conformation was recognised as the most stable one. The stability sequence could be predicted to be 1,3-alt > paco > 1,2-alt > cone. The same sequence is also true when solvent effects were taken into account using a self-consistent isodensity polarised continuum solvent model (SCIPCM)[46].

Resorcinarenes (resorcarenes) complete the class of all compounds related to calixarenes. Recently, Vainiotalo[48] focused on the intramolecular hydro-

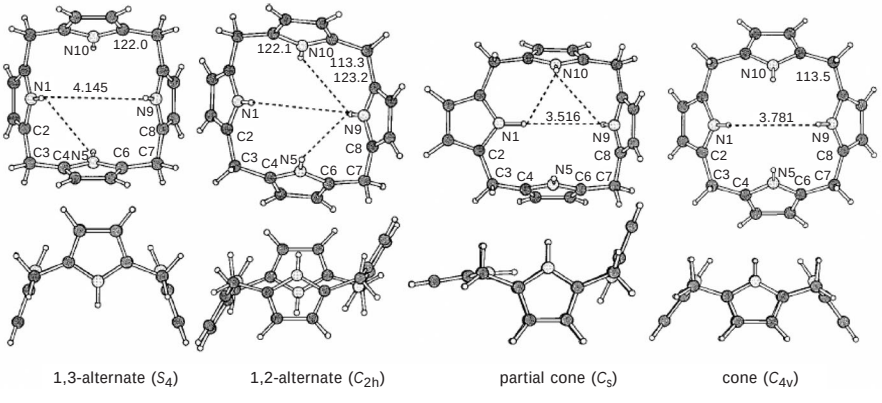
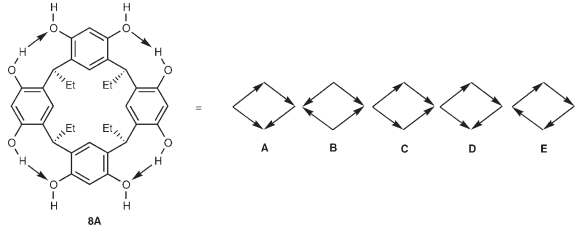


FIG. 5
Calculated conformers of calix[4]pyrrole[46] **7** (reprinted from: Wu Y.-D., Wang D.-F., Sessler J. L.: *J. Org. Chem.* **2001**, *66*, 3739, with permission from American Chemical Society)

gen bonds of tetraethyl resorcarene **8** (Table II). Five different conformations of resorcarene are possible: crown, boat, chair, saddle and diamond (Fig. 6). Neglecting any hydrogen bonding possibility, the crown conformation could not be located as a minimum structure by any computational method used by the authors. The overall stability order of the non-hydrogen bonded conformations is boat > diamond > chair > saddle. A more realistic picture was obtained taking possible intramolecular H-bonds

TABLE II
Calculated relative stability of conformers and intramolecular hydrogen bond possibilities of tetraethylresorcarene[48] **8**



8A

Structure	Energy, kcal mol^{-1}			
	HF/3-21G[a]	HF/3-21G & 6-31++G(d,p)[a,b]	HF/ 6-311++G(d,p)[c]	B3LYP/ 6-311++G(d,p)[c]
Without H-bonds				
Saddle	43.1	40.8	23.8	29.0
Chair	39.9	35.4	18.0	23.6
Diamond	36.2	30.0	13.2	18.0
Boat	34.7	29.2	12.1	17.0
With H-bonds				
Pinched crown **A**	8.5	7.9	5.1	5.4
Pinched crown **B**	8.0	7.5	4.1	5.9
Pinched crown **C**	6.0	5.3	3.3	3.8
Pinched crown **D**	5.1	4.6	2.9	3.1
Crown **E**	0.0	0.0	0.0	0.0

[a] Structures optimised at the same level of theory as used for the energy calculations. [b] The 6-31++G(d,p) basis set was used for the oxygen atoms, for carbon and hydrogen 3-21G. [c] Structures were optimised using the split HF/3-21G and 6-31++G(d,p) basis set.

into account. Because all four pairs of OH groups can be treated independently, 16 structures with a maximum number of four hydrogen bonds are possible and 5 of them were discussed. As one might expect, the C_4 symmetrical arrangement **8E** ("perfect crown") possesses the lowest energy. All other directions of the hydrogen bond array lead to a "pinched crown" structure of lower symmetry. Supposedly, additional stabilisation energy is provided by the direction of the hydrogen bonds. Changing the direction of one hydrogen bond leads to a loss of ≈1–2 kcal mol^{-1} of stabilisation energy.

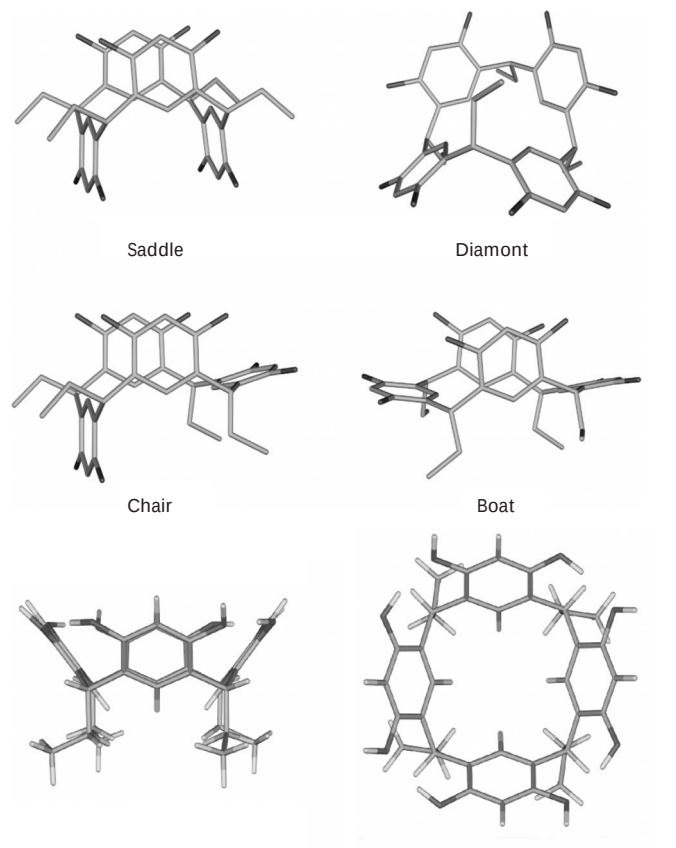


FIG. 6
Calculated conformers of resorcinarene[48] **8** (reprinted from: Mäkinen M., Jalkanen J.-P., Vainiotalo P.: *Tetrahedron* **2002**, *58*, 8591, with permission from Elsevier)

2.2. Calculations on Calixarene Complexes

The literature of quantum chemical calculations on alkali metal complexes until the year 2000 was published recently[36]. Therefore, only some newer examples and results on the inclusion of anions and neutral compounds as well as self-assembly are discussed in the following.

Evanseck[49] studied the influence of cation/π interaction and conformation on the receptor selectivity of dehydroxylated calix[4]arene (metacyclophane) towards Li^+, Na^+ and K^+. Benzene–cation complexes served as models to validate the use of the B3LYP/6-31G(d) level as an accurate method to calculate association energies of benzene and alkali metals. Calculation of the binding energy of metacyclophane to alkali metals revealed that the gas-phase cation selectivities parallel the selectivity of benzene, namely $Li^+ > Na^+ > K^+$.

In a series of publications Choe and co-workers dealt with the inclusion of ammonium cations in calix[4]arene[50,51] and calix[5]arene[52] derivatives. The data compiled in Fig. 7 clearly show that the primary binding site for ammonium cations is the crown ether part of the receptor molecule with a selectivity which is consistent with experimental data.

Only recently, Cabral and Bernardino[39] presented a thorough study of the complexation behaviour of calix[4]arene (**2**) towards cations such as a proton and alkali metals (Table III). Some general trends could be deduced from the calculations. For example, the proton prefers the 1,2-alternate conformation of the calix[4]arene. The MP2 and B3LYP methods gave a stabilisation of –4.1 and –4.5 kcal mol^{-1}, respectively, compared with the cone conformer. For Li^+ and Na^+, no clear preference could be obtained. The 1,2- and 1,3-alternate conformation show similar stabilities. In general, the complexation energies of the 1,3-alternate calix[4]arene with Na^+ are about 30 kcal mol^{-1} lower than those calculated for the smaller cation Li^+. This finding is in accordance with the general selectivity $Li^+ > Na^+ > K^+ > Rb^+$. For smaller cations, such as Li^+ and K^+, the complexation with calix[4]arene is mainly due to electrostatic interactions with the oxygen atoms of the narrow rim of the calix[4]arene adopting an 1,2- or 1,3-alternate conformation. The bigger cations (K^+, Rb^+ and Cs^+) are enclosed in the π-cavity of the macrocycle in the cone conformation[39].

The host–guest chemistry of calix[4]pyrrole **7** is in the focus of a computational study of Sessler, Wu and co-workers[46]. After evaluation of the conformational behaviour of the anion receptor (vide supra), the binding of the fluoride and chloride anion by this host was characterised. The calculated binding energies for both complexes are summarised in Table IV.

Although the experimentally observed anion selectivity ($F^- > Cl^-$) is reproduced by the calculations, the difference between both binding strengths, which is about 15 kcal mol^{-1}, is far too high compared with the experimental value 2.3 kcal mol^{-1} [46].

An inclusion of neutral molecules in the hydrophobic cavity of calixarenes is mainly based on hydrophobic, CH/π, and similar weak interactions, semiempirical methods usually cannot be applied successfully[53]. Due to the small size of the guest molecule limiting the computational effort and known crystal structures the inclusion complexes of 4-*tert*-butylcalix[4]arene with CS_2 [19] and toluene[54] seemed to be ideal candidates for testing

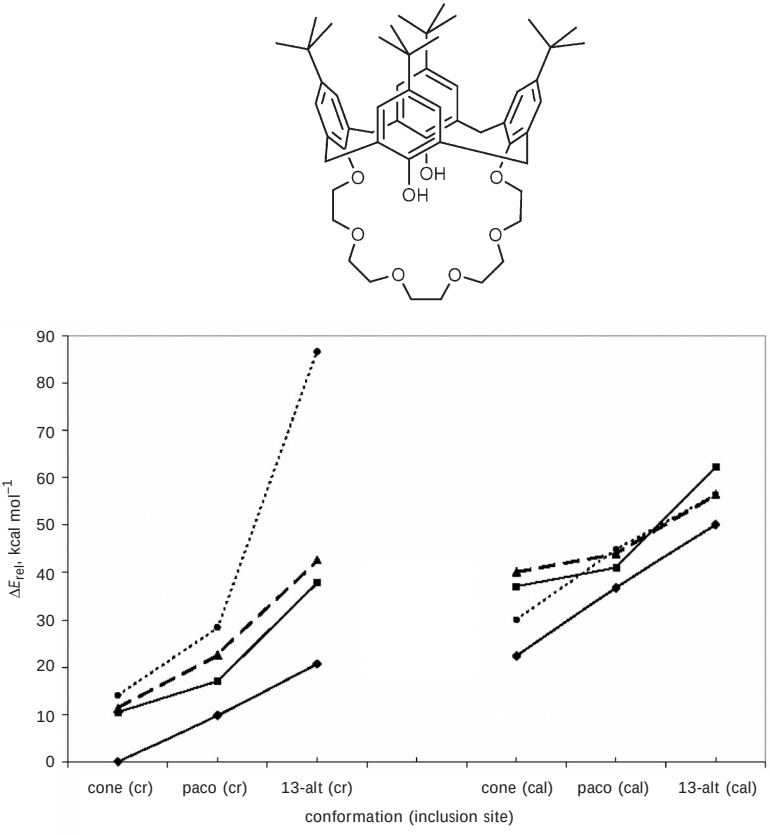


FIG. 7

Plot of calculated relative binding energies for calix[4]crown-6–cation complexes for various conformations and locations of cation binding (binding sites: cr, the cation is contained in the crown ether part of the macrocycle; cal, the cation is contained in the calixarene cavity of the macrocycle). Ammonium cations: ◆ NH_4, ■ NMe_4, ▲ NEt_4, ● NPr_4

TABLE III
Selected calculated relative binding energies ΔE_{rel} (kcal mol^{-1}) of calix[4]arene (**2**) with cations[39]

Conformation	Energy	Geometry	H^+	Li^+	Na^+	K^+
cone	HF/3-21G	HF/3-21G	0	0	0	0
paco			5.8	–8.2	–13	5.6
1,2-alt			–12.7	–19.2	–24	4.7
1,3-alt			15.1	–28.1	–25.8	3.5
cone	HF/3-21G(d,p)	HF/3-21G(d,p)	0	0	0	0
paco			6.3	–3.2	–13.7	6.4
1,2-alt			–9	–12.9	–24.3	3.5
1,3-alt			14.5	–20.9	–27.7	–0.2
cone	HF/6-311G(d,p)	HF/3-21G(d,p)	0	0	0	0
paco			12.3	1.4	–6	5.7
1,2-alt			0	–3.6	–7.4	15.5
1,3-alt			8.5	–6.1	–5.5	13
cone	MP2/6-31G(d,p)	HF/3-21G(d,p)	0	0	0	–
paco			12	–2.7	–18.5	–
1,2-alt			–4.1	–15.3	–25.1	–
1,3-alt			6.7	–17.8	–25.5	–
cone	B3LYP/6-31G(d,p)	HF/3-21G(d,p)	0	0	0	0
paco			12.9	–6.6	–13.5	9.1
1,2-alt			–4.5	–15.2	–21.4	15.6
1,3-alt			2.7	–21.3	–25.7	6.7

TABLE IV
Calculated binding energy (kcal mol^{-1}, BLYP/6-31+G(d,p)) of calix[4]pyrrole in the cone conformation with fluoride and chloride

Conditions	ΔE (F^-)	ΔE (Cl^-)	$\Delta\Delta E = \Delta E$ (F^-) – ΔE (Cl^-)
Gas phase	29.3	42.1	–12.8
CH_2Cl_2 [a]	–21.6	–6.4	–15.2

[a] Isodensity value set to 0.0003.

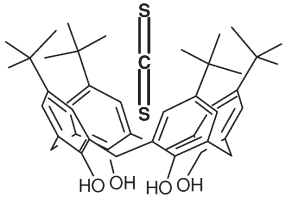
the performance of various quantum chemical methods. Therefore, these neutral host–guest complexes were studied in our group[19,28,53,55], as well as by Ogden, Gale and Rohl[56]. The results of both groups are summarised in Table V.

In the crystalline state[19], the CS_2 molecule is located deep in the cavity of the calixarene, 92% of its length in the macrocycle. The extend of the inclusion is underestimated by the quantum chemical calculations, e.g. the HF/6-31G(d) calculations give only an inclusion of 57%. Using density functional instead of Hartree–Fock methods, the complexation of carbon disulfide was described more realistically, especially when crystal packing effects were taken into account (Table V, SIESTA calculations). However, the HF methods give better agreement of some bond lengths such as the C–S double bond.

Quantum chemical calculations can even help to study bigger assemblies. Kim et al. used DFT methods to evaluate self-assembling phenomena of calix[4]hydroquinone which form nanotube bundles by hydrogen bonds and π–π stacking[57].

TABLE V

Depth of inclusion of carbon disulfide in 4-*tert*-butylcalix[4]arene calculated by various methods (O_4-plane refers to the plane defined by the oxygen atoms of the four phenolic OH groups)



Distance, Å	SIESTA (gas phase)[56]	SIESTA (crystal)[56]	HF/6-31G(d)[53]	X-ray[19]
$C(CS_2)$–O_4-plane	5.93	5.75, 5.80	6.51	5.34
C–S, Å	1.59, 1.60	1.58, 1.60	1.55	1.55

2.3. Calculations on Reaction or Geometrical Interconversion Pathways

Dynamic processes converting various conformations of a molecule one into another are ideal candidates for the application of quantum chemical calculations. Location and characterisation of special points on the interconversion pathway gives rise to an energy profile of such a "reaction". Experimentally only the overall change in energy, i.e. the activation parameters of such a process is accessible. Therefore, calculations give very useful additional information about the process of concern.

The known fact that the experimentally observed C_{4v} symmetry of calix[4]arenes in solution stems from an averaged pinched cone–pinched cone interconversion equilibrium and the inaccessibility of reasonable parameters of Ar–S or S–Ar–S– systems in molecular mechanics force-fields, inspired Lhoták, Stibor and co-workers to perform ab initio calculation on the conformational interconversion of thiacalix[4]arenes in comparison with calix[4]arenes (cf. Fig. 8)[58].

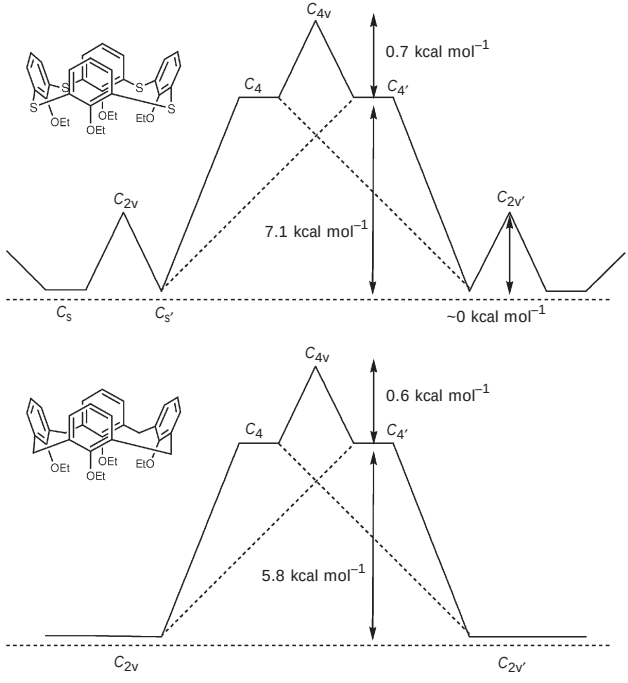


FIG. 8

Calculated energy diagrams for the pinched cone–pinched cone interconversion of tetraethoxythiacalix[4]arene (top) and tetraethoxycalix[4]arene (bottom). The given energy values were obtained on a B3LYP/6-31G(d,p) level[58]

In contrast to tetraethoxycalix[4]arene, the most stable conformer for the thia derivative possesses only C_s symmetry as indicated by the geometry optimisation on a HF/STO-3G level. The interconversion of the conformers proceeds via two C_4 symmetric transition states connected with a C_{4v} symmetric saddle point. Furthermore, the two C_s minima are connected by a C_{2v} saddle point. However, this process has a very low calculated activation barrier (HF/STO-3G: 0.12, HF/G-31G(d,p): 10^{-3} and B3LYP/6-31G(d,p) ≈0 kcal mol^{-1})[58]. In the case of tetraethoxycalix[4]arene, no such C_s–C_{2v} pre-equilibrium could be located.

Comparing the difference between the calculated activation barriers for the pinched cone–pinched cone interconversion of both tetraethoxythiacalix[4]arene and tetraethoxycalix[4]arene ($\Delta\Delta E$ = 1.4 kcal mol^{-1}) with experimental values obtained by temperature dependent NMR spectroscopy ($\Delta\Delta E$ > 4.2 kcal mol^{-1}) reveals that the difference between both systems is underrated by the ab initio calculations. The authors attribute this difference mainly to the solvation of transition states and stacking effects[58].

Fluxional conformational behaviour is also in the focus of Tsuji et al., who is interested in tetrakis- and bis(diphenylphosphino)calix[4]arenes[44,59]. Starting from the bis(diphenylphosphino)calix[4]arenes **9**–Bz bearing benzyl (Bz) groups at the lower rim a platinum complex **9**–$PtCl_2$ could be isolated. Dynamic ^{31}P NMR spectroscopy could prove a conformational equilibrium ($\Delta H^{\ddagger} \approx 9.8$ kcal mol^{-1}). With respect to the transition metal the optimisation of the ground state of the model platinum complex **9**–$PtCl_2$ had to be performed at a HF/LANL2MB level yielding a C_1 symmetrical structure. The result (Fig. 9, GS) indicated the same inclination of the metal fragment against the calixarene skeleton. A similar calculation yielded a structure of the transition state (Fig. 9, TS) for the flipping process of the metal fragment. Here, the P–Pt–P plane is nearly parallel to the central axis of the macrocycle. The calculated energy difference between GS and TS underestimates the measured activation barrier by a factor of ≈1.8.

With ligand **9**, a palladium–allyl complex was accessible as well. Again, the complex **9**–PdC_3H_3 showed a fluxional behaviour in solution as proven by NMR spectroscopy. A twist (T) and a rollover (R) motion could be identified. Both motions occur simultaneously with similar activation enthalpies (T: 10.3, R: 9.8 kcal mol^{-1}). Optimisation of both possible ground states (GS-1 and GS-2, Fig. 9), the transition state as before and single-point energy calculations using HF/LANL2DZ showed a small difference of 0.7 kcal mol^{-1} between both ground state structures and an activation barrier of 8.6 kcal mol^{-1} which is in nice agreement with the experimental value[59].

Quantum chemical calculation can not only be used to understand conformational interconversion pathways but also chemical transformations. Such investigations are widespread when dealing with small systems which serve as models for a certain chemical reaction. Because of the size of macrocyclic ligands and the resulting expenses of the CPU time, mechanistic studies using ab initio calculations on "real" supramolecular systems are rare. One example deals with stereoselectivity of the copper(I)-catalysed cyclopropanation of olefins using a calix[6]arene-based concave catalyst[60]. Optimisation (RI-BP86/SDD) of the flexible calix[6]arene **10**–$Cu(CHCO_2Me)^+$ complex must deal with many possible energy minima on the energy hypersurface. Therefore, this reactive intermediate was built starting from

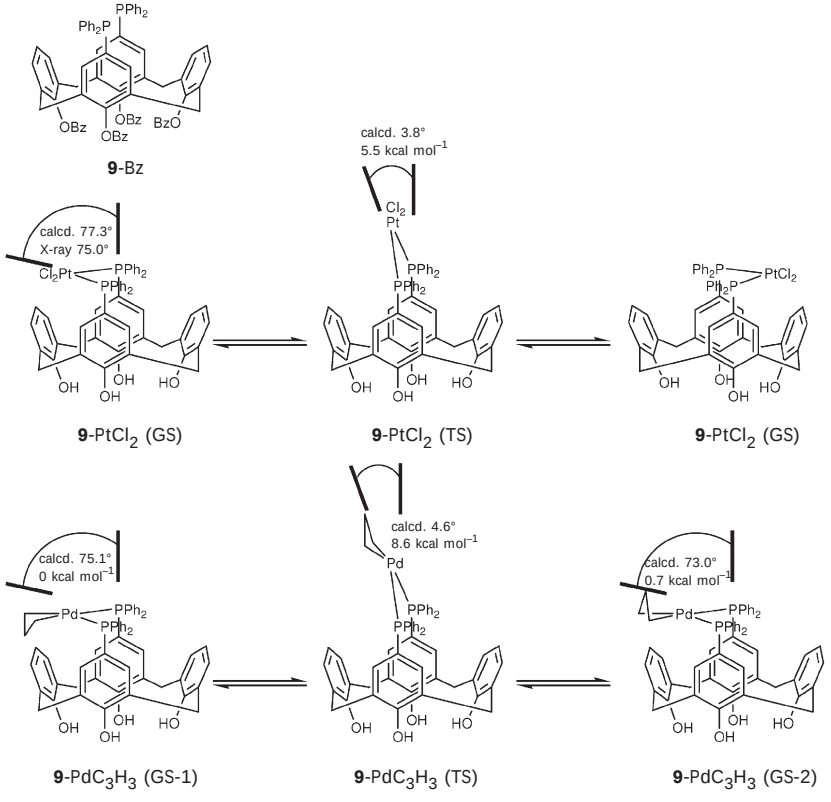


FIG. 9

Conformational equilibria of the platinum (**9**–$PtCl_2$) and palladium allyl complexes (**9**–PdC_3H_3) of bis(diphenylphosphino)calix[4]arene[59] **9** (geometries optimised at HF/LANL2MB, energies calculated at B3LYP/LAN2DZ level)

known geometries of the ligand, adding the metal-carbene fragment and full optimisation of such structures (Fig. 10). The structure obtained by the geometry optimisation clearly shows that the side of the reactive metal centre is blocked by the calix[6]arene skeleton and therefore, the olefin must approach from the same side as the carboxy group. Such an arrangement would lead to a *cis*-cyclopropane which is consistent with the experimentally observed *cis* selectivity exhibited by such catalysts. Similar calculations on reactive intermediates may lead to a better understanding and design of macrocyclic catalysts.

2.4. Calculation of Molecular Properties

The prediction of molecular properties has always been an important application of computer chemistry; this is also true for calixarene chemistry. For example, Garcia and colleagues[61] used RHF/STO-3G calculations to evaluate the electrostatic potential around the most stable conformer of a dimethylsilyl-bridged calix[4]arene.

PM3-tm and DFT calculations of Ru/M (M = Cu, Ni, Co, Zi) heterometallic complexes with a calix[4]arene phosphine oxide by Wipff et al. helped to interpret EXAFS, IR, UV and MS data[62].

The collaboration of Floriani, Re, Rizzoli and Sgamellotti[63–65] as well as the group of Radius[66–69] is interested in transition metal complexes of calixarenes in which the macrocyclic skeleton serves as a model of an oxo-surface. In this area extended Hückel, DFT and MP2 calculations are extremely helpful to understand the geometry, binding mode, or catalytic activity of such metal complexes.

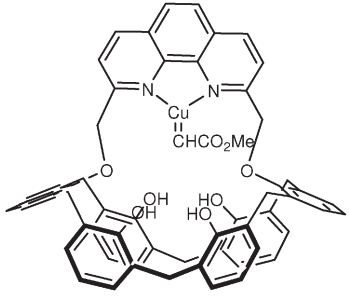


FIG. 10
Calix[6]arene-based concave Cu catalyst **10**

Spectroscopic methods, such as infrared and NMR spectroscopy, are used routinely by the supramolecular chemist. Such data can provide a good interface between theory and experiment. Based on a structural model obtained by any conceivable theoretical or experimental means, spectral data can be calculated using ab initio methods. If the theoretically deduced spectral data are in good agreement with experimental values one can assume that a similar correspondence is true for the underlying geometries. Therefore, various model structures can be checked against experimental data merging theory and experiment.

Vibrational spectroscopy is a simple, fast and reliable approach to characterise supramolecular systems both in the solid state and in solution. Additionally, due to its time-scale, it can be used as a tool in conformational analysis. However, thorough analyses of infrared and Raman spectra of calixarene–guest complexes are somewhat scarce. Because of the complex structure of such complexes, the analysis of the obtained vibrational data is quite tedious. On the basis of DFT calculations quite accurate vibrational frequencies can be obtained. However, in our own experience, frequency calculations of calixarenes on a reasonable level of theory (e.g. B3LYP/6-31G etc.) are very expensive owing to CPU time[53].

Consistently, Katsyuba, Schmutzler et al. are using a stepwise process in analysing fully the vibrational spectra of various calixarene building blocks (Fig. 11)[70–73]. The $\nu(CH_2)$ vibrations of the bridging methylene group of the model compounds are very sensitive to conformational changes thus providing a probe to study the conformational distribution of 2-benzylphenol (**11**) in solution. Based on B3LYP/6-31G(d) and HF/6-31G(d) optimisations, four stable conformers of model phenol **11** could be identified, two with nearly the same and one with quite a high relative energy. The last high-lying conformer could not be observed experimentally. Therefore, only three of those conformations could be quantified in the spectra in CCl_4 solution. The overall conformer distribution observed experimentally is also reflected by the quantum chemical calculations. In addition, the vibra-

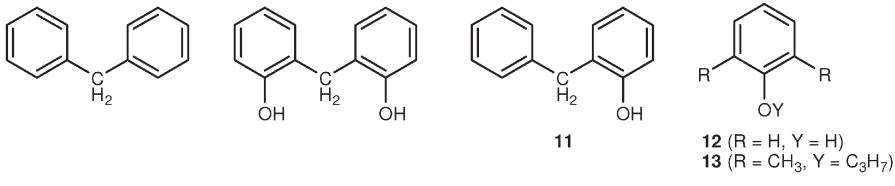


FIG. 11
Calixarene building blocks used for the calculation of vibrational data

tional frequencies calculated by scaled quantum mechanical methods are in good agreement with experimental values.

Using the $\nu(CH_2)$ vibrations as a probe such an approach merging theory, infrared spectroscopy and statistical treatment of experimental data may lead in future to a quantitative relationship that describes the conformational distribution of calixarenes and other diphenylmethane derivatives.

Due to the size of the calixarene moiety, one has to study model systems on a reasonable high level of theory as described before or one is limited to somewhat smaller basis sets to perform calculations in a reasonable time span. Billes and Mohammend-Ziegler used a HF/4-31G(d) basis to calculate geometry and vibrational frequencies for calix[4]arene (**2**)[74]. Starting with geometries possessing C_{4v}, C_{2v} or C_s symmetry, a C_2 symmetrical arrangement was identified as the minimum structure during the optimisation process. For the resulting structure, a full vibrational analysis was performed on the HF/4-31G(d) level. As shown in Fig. 12, a very good agreement between calculated and observed vibrational frequencies can be achieved after a complex scaling of the calculated force constants. The scaling factors vary from 0.86 to 0.91 leading to a small mean deviation of about 9 cm^{-1} (1.7%).

Recently, Kovalenko et al. presented a combined ab initio (HF/3-21G and PBE/TZ2P) and infrared spectroscopic study of thiacalix[4]arene (**3**) in cone conformation[75]. Combining both methods, the authors could show that in the thiacalixarene the cooperative hydrogen bonds are weakened compared

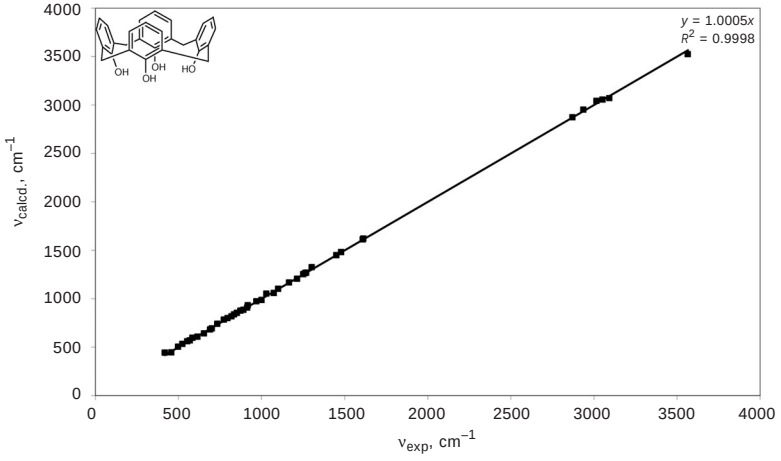


FIG. 12
Correlation of calculated (HF/4-31G(d)) and experimentally observed vibrational frequencies of calix[4]arene[74]

with the parent calix[4]arene. This is due to the fact that the O–O distance is lengthened by ca. 0.1–0.2 Å and O···H···S bifurcated hydrogen bond formation is possible[75].

Since the beginning of calixarene chemistry, NMR spectroscopy both in the solid state and especially in solution has played an important role in elucidation of structures and interactions of supramolecular entities. Usually, changes of certain absorptions of host, guest or both on complexation are used to determine the host–guest geometry and to evaluate the binding strength of the association process. However, such complexation-induced shifts (CIS) are commonly interpreted on a qualitative basis when used for the development of structure models[76].

On the road to quantitative approaches in the evaluation of observed NMR shifts in supramolecular chemistry, classic descriptions of the aromatic ring current and linear electric field effects for various calculated geometries of a host–guest complex can be applied[32,76,77]. A good agreement of experimentally derived and calculated NMR data were found for force-field calculated models of the complexes having geometries similar 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[78–81] 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[82–88].

In a model study, Schatz et al. calculated CIS values of the 4-*tert*-butylcalix[4]arene–CS_2 inclusion complex (**1**–CS_2) at the GIAO-DFT B3LYP/6-311G(d,p) level based on a RHF/6-31G(d) geometry (Table VI). For the en-

TABLE VI
GIAO-DFT calculated and experimentally derived CIS values of the 4-*tert*-butylcalix[4]arene–CS_2 complex[55]

CIS[a]	Geometry	$\Delta\delta_c$[a], ppm
B3LYP/3-21G	experimental geometry	–4.28
B3LYP/6-31G(d)	experimental geometry	–4.69
B3LYP/6-31G(d,p)	experimental geometry	–3.63
B3LYP/6-311G(d,p)	HF/6-31G(d)	–1.10
Experiment		–2.20

[a] CIS, complexation-induced chemical shift of the guest: $\Delta\delta = \delta$ (solid state) – δ (solution).

closed carbon disulfide molecule, a CIS of –1.1 ppm could be calculated; in the solid state a change in chemical shift on complexation of the central carbon atom of CS_2 could be determined amounting to –2.2 ppm, showing a reasonable qualitative agreement[53]. However, calculations based on the experimental geometry of the complex obtained by single crystal structure determination overestimated the complexation-induced chemical shifts to some extent.

High-level geometry optimisations require about 5–10 times more CPU time than the chemical shift calculation[53,85]. Therefore, the crucial point in using NMR shift calculations is to provide good starting geometries, which can be used for the calculation of properties. A combination of the calculation of magnetic properties on ab initio level using geometries optimised with force-field methods or obtained by molecular dynamics simulations seems to be a promising approach for a comparison of experimental theoretical NMR data[55,83,85,89] of large systems.

A model study based on various 4-*tert*-butylcalix[4]arene–solvent complexes indicated that for so far calculated CIS values have reflected the reality only in a qualitative manner[55]. Various starting geometries of the host–guest complex (a functional group of the guest pointing inside or outside or a guest not located in the cavity) were optimised with a Merck94 force-field (MMFF) and the CIS values were calculated ab initio (Table VII). Although the quantitative agreement is not sufficient, a comparison of the CIS pattern for all arrangements made it possible to identify promising candidates for a correct host–guest structure.

TABLE VII
Selected ^{13}C CP-MAS NMR data of 4-*tert*-butylcalix[4]arene–solvent complexes compared to calculated CIS values[28,55]

Guest	δ_c				
	solid	solution	$\Delta\delta_c$[a], ppm	$\Delta\delta_c$[b], ppm	$\Delta\delta_c$[c], ppm
Toluene	15.2	21.4	–6.2	–3.65	–4.47
THF	67.5	67.7	–0.2	–0.27	–0.18
	66.8	67.7	–0.9	–0.68	–0.69
	24.2	25.5	–1.3	–1.93	–1.75
	23.7	25.5	–1.8	–2.79	–2.99

[a] CIS, complexation-induced chemical shift of the guest: $\Delta\delta = \delta$ (solid state) – δ (solution). [b] CIS calculated by GIAO-DFT B3LYP/3-21G//MMFF. [c] GIAO-DFT B3LYP/6-31G(d)//MMFF.

Using CIS values obtained by NMR titration experiments, this approach can yield also host–guest structure models in solution[89].

In summary, GIAO-DFT calculations of complexation-induced chemical shifts of supramolecular host–guest complexes is a fast and sensitive computational approach to identification of possible spatial arrangements of such assemblies. This methodology does not require specialised software and is not limited to certain classes of compounds, any NMR-active nucleus (e.g. ^{1}H, ^{13}C, ^{19}F) for which experimental CIS values are available can be used as probe either in the solid state or in solution. However, the applicability is limited by the quality of the experimental data available because only stationary geometries can be studied. In such cases, statistical treatment of the systems using molecular dynamics simulations followed by NMR calculations might be an appropriate method of simulation of the experimental averaging of the CIS. A further improvement could be achieved by an iterative process to adapt theory and experiment by small changes of the starting geometry followed by calculation of properties.

The second important peace of information that can be evaluated by NMR spectroscopy are spin-spin coupling constants. Bagno, Saielli and Scorrano[90] calculated through-space J_{HH} and J_{CH} coupling constants for an acetonitrile–calix[4]arene complex (**2**–CH_3CN). The coupling occurs between the methyl group of the guest and the neighbouring benzene rings of the calix[4]arene. The J_{CH} values ranging from 0.09–0.19 Hz were obtained, which are well in the range (0.1–0.3 Hz) observed for CH/π bonded model systems. The corresponding J_{HH} couplings are much smaller. This approach lacks an experimental validation because such through-space couplings are difficult to observe in mobile host–guest complexes, but may prove very valuable in future[90].

3. CONCLUSIONS

In general, the use of high-level ab initio quantum chemical calculations in calixarene chemistry seems to be somewhat in its infancy. The systems of interest are quite big; this is a fact that sometimes might hamper the use of a reasonably high level of theory. However, useful contributions have been already made studying all aspects of the supramolecular chemistry of calixarenes.

In future, computational resources will be getting cheaper and cheaper and high level calculations for all problems in structure elucidation of supramolecular systems will be routinely available. In particular the methods which are based on a combination of experiment and theory will make

it easier for the non-computational expert to rely on computer chemistry results because of the common basis. Furthermore, novel computational methods such as linear scaling DFT, ONIOM models, effective solvent models or calculations using periodic boundary conditions will have a serious impact on the applicability of quantum chemical calculation in the field of calixarene chemistry.

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