RECENT ADVANCES IN THE FUNCTIONALIZATIONS OF THE UPPER RIMS OF THIACALIX[4]ARENES. A REVIEW

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Received December 31, 2003
Accepted February 17, 2004

Dedicated to Professor Ivan Stibor on the occasion of his 60th birthday.

The chemistry of the thiacalixarenes is very recent compared to that of similar calixarenes. Several papers have recently reported interesting progress in the chemistry of thiacalixarenes. Until recently most of the reactions concerned the substitutions of the lower rims while only very few were dealing with the upper rims. Indeed it was shown that the macrocycles often behave in a very different way compared to the similar calixarenes, and the well-known reactions such as nitration, bromination or formylation could not be directly transposed to the thiacalixarenes. However many important intermediates for upper-rim substitution were recently reported and are resumed in this paper together with further functionalizations of the upper rims and potential developments in the chemistry and applications of thiacalixarenes. A review with 40 references.

Keywords: Calixarenes; Thiacalixarenes; Upper rims; Macrocycles; Thioethers; Sulfides; Electrophilic substitutions; Halogenations; Cross-coupling reactions.

1. INTRODUCTION

The chemistry of calixarenes has been one of the most extensively developed in the field of supramolecular chemistry during the 20 past years[1]. More recently Miyano et al. described the first synthesis of similar macrocycle, the *p-tert*-butylthiacalix[4]arene, with sulfur bridges between the phenolic units instead of the CH_2 [2]. Even if thiacalixarenes present very interesting potential in different fields of applications, such as neutral or ionic complexation, optical and electronic properties, biomedical developments or self-assembling processes, their chemistry remains very poorly documented compared to similar calixarenes. The investigations were essentially focused on thiacalix[4]arenes since the synthesis of larger cavities with 5 or 6 cycles, which would be extremely interesting, remains very problematic[3]. Indeed the yields of their synthesis are very low and there is no efficient method available at the moment for the preparation of larger macrocycles. The first investigations on the chemistry of thiacalix[4]arenes were essentially realized on the modifications of the lower rims. Several studies were reported by the groups of Hosseini, Miyano and Lhoták concerning for example various substitutions of the lower rims, the synthesis of sulfanylthiacalixarenes or oxidation of the sulfur bridges[4–17]. The lower-rim substitutions together with complexing properties of these macrocycles were previously reviewed[18].

The first modifications of the upper rims were the synthesis of the tetrahydroxythiacalix[4]arene from the *p-tert*-butylthiacalix[4]arene and its tetrasulfonation[19,20].

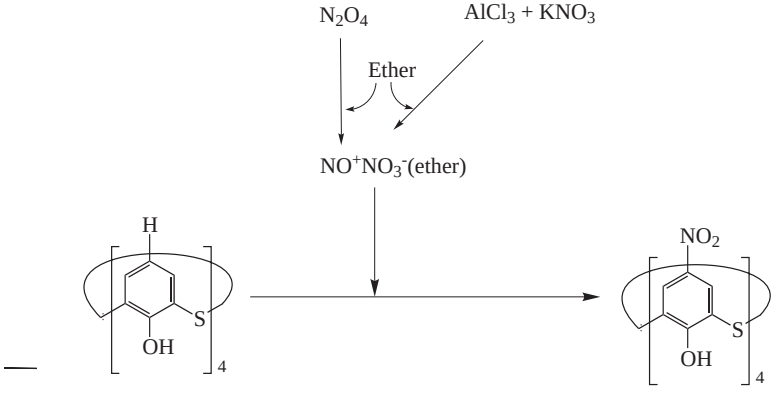
Then, the upper-rim functionalizations with phenylazo or 4-nitrophenylazo groups for non-linear optical applications were described[21]. These macrocycles showed very promising optical properties and encouraged us to develop the upper-rim substitution with extended electron delocalization for optical purposes. We investigated the chemistry of thiacalix[4]-arenes with the perspectives to functionalize the macrocycles for applications as optical limiters not only on the basis of their electron delocalization and their complexing properties, which are very important parameters for cubic nonlinear optical properties, but also for their thermal stability allowing harsh treatment and therefore easy inclusion in a solid-state matrix for device development. Very crucial steps on the way to upper-rim substituted thiacalixarenes are the synthesis of intermediates, the tetranitro, tetraamino, tetrahalo and tetraformylthiacalix[4]arenes. These functional groups open the way to the formation of –C=N–, –C=C–, or –C≡C– bonds, for example. The synthesis of these intermediates and some further

reactions will be discussed in this paper as well as the other few examples of upper-rim modified thiacalixarenes.

2. DISCUSSION

2.1. Tetranitrothiacalix[4]arene

While many articles are dealing with the nitration of calixarenes[22–26], very little is known as far as thiacalixarenes are concerned. Several routes to the synthesis of nitrocalixarenes are reported using conventional nitrations. All these reactions using the classic methods of nitration were investigated for thiacalixarenes and failed. The reaction using a $KNO_3/AlCl_3$ mixture as nitration agent failed in most organic solvents (THF, acetonitrile, toluene ...) but surprisingly worked in the presence of di, tri- or tetraglyme and allowed isolation of the 25,26,27,28-tetrahydroxy-5,11,17,23-tetranitrothiacalix[4]-arene for the first time[27]. Indeed, only the presence of an ether with complexing properties could induce the reaction. Considering the knowledge of nitration reactions, three mechanisms were possible to explain the nitration of the thiacalixarene[27]. Among these mechanisms, the reaction between a nitrosonium nitrate complex with the ether and the thiacalixarene was proposed and demonstrated (Scheme 1). It was evidenced that the complex between nitrosonium nitrate and the ether was prepared by reaction at low temperature between N_2O_4 and 18-crown-6 or glyme. The complex was then reacted stoichiometrically with tetrahydroxythiacalix[4]arene in chlo-



SCHEME 1
Synthesis of 25,26,27,28-tetrahydroxy-5,11,17,23-tetranitrothiacalix[4]arene

roform. The 25,26,27,28-tetrahydroxy-5,11,17,23-tetranitrothiacalix[4]-arene was precipitated instantaneously and was isolated in good yield (67%) by a simple filtration. The $NO^+NO_3^-$ species responsible for the nitration is unstable at room temperature where the stable forms are the molecular entities NO_2 and N_2O_4. When the reaction mixture contains the complexing ether, the ionic species is stabilized enough to induce nitration on the macrocycles. The nitration in the presence of a $KNO_3/AlCl_3$/ether mixture can be thus explained by the in situ formation of N_2O_4 (KNO_3 + $AlCl_3$) and then the $NO^+NO_3^-$(ether) stable complex, which is not obtained in the absence of stabilizing agent. The ^1H NMR spectrum of the nitrated species, prepared from the tetrahydroxythiacalix[4]arene and the $AlCl_3$/KNO_3 mixture in the presence of tetraglyme, shows one singlet at 8.44 ppm corresponding to the two aromatic protons of thiacalixarene. This indicates that the substitution with the nitro group takes place in the para position. A multiplet at 3.55–3.31 ppm shows that the thiacalixarene is solvated by tetraglyme. The presence of four nitro groups attached to the thiacalixarene was confirmed by mass spectrum data, which exhibit only the parent molecular ion. 25,26,27,28-Tetrahydroxy-5,11,17,23-tetranitrothiacalix[4]-arene was characterized by single-crystal X-ray diffraction. The macrocycle possesses a centre of symmetry and adopts a *1,2-alternate* conformation. The usual cyclic intramolecular hydrogen bonds disappear but there are strong hydrogen bonds with the guest molecule (DMSO). This situation shows interactions between the hydroxy group and the sulfur bridges.

One should mention that Lhoták reported investigations of nitration by conventional reactions leading essentially to the oxidation of the sulfur bridges and demonstrating again that no nitrated species can be prepared in this way[28].

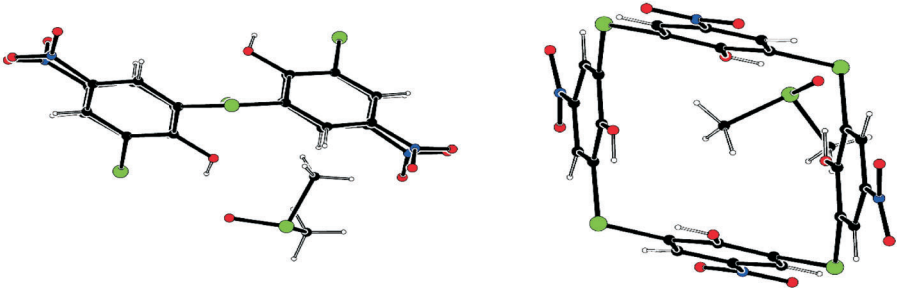
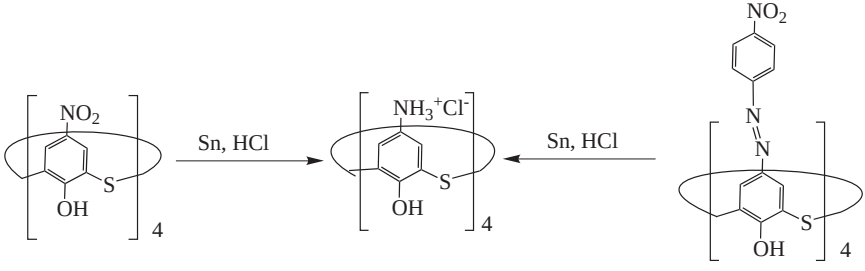


FIG. 1
Structure of the tetranitrothiacalix[4]arene showing the *1,2-alternate* conformation

The reaction using the nitrosonium nitrate complex is thus the only method available at the moment for the preparation of tetranitrothiacalix[4]arene (Fig. 1) and could probably be extended to other macrocycles.

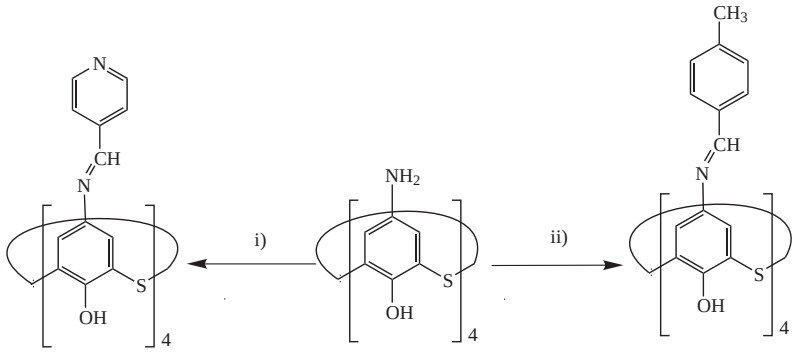
2.2. Aminothiacalix[4]arenes and Thiacalix[4]arene Aldimines

The tetraaminothiacalix[4]arene, which is the intermediate in the formation of tetraiminothiacalixarene, was easily prepared by reduction of the NO_2 groups using metallic Sn in acid (HCl) medium (Scheme 2). The reaction was instantaneous and 5,11,17,23-tetraamino-25,26,27,28-tetrahydroxythiacalix[4]arene stabilized as hydrochloride was obtained in a good yield[27]. The infrared spectra evidenced the replacement of the NO_2 vibration bands (697 cm^{-1}) by those of $NH_3^+Cl^-$ (3131, 2834, 2575 cm^{-1}). This was confirmed by the mass spectrum. The tetraaminothiacalix[4]arene was also easily prepared from tetrakis(4-nitrophenylazo)tetrahydroxythiacalix[4]arene which was reduced with Sn in concentrated HCl in a nearly quantitative yield (95%)[27,29]. However, it seems that the direct reduction of tetranitrothiacalix[4]arene provides a more stable aminothiacalixarene than the route using the phenylazo derivative and is more efficient.



SCHEME 2
Synthesis of 5,11,17,23-tetraamino-25,26,27,28-tetrahydroxythiacalix[4]arene

The tetraaminothiacalix[4]arene can be used for reactions with aldehydes for the preparation of thiacalixarene aldimines. Some examples were reported (Scheme 3). The tetraamine was reacted with pyridine-4-carbaldehyde in the presence of triethylamine. The tetrahydroxytetrakis-[(4-pyridylmethyliden)amino]thiacalix[4]arene could be isolated[27]. The ^1H NMR spectrum shows two doublets at 8.79 and 7.70 ppm which are attributed to pyridyl groups (16 H), one singlet at 8.06 ppm for the phenyl groups of the thiacalixarene (8 H) and one singlet at 8.37 ppm for the methylidene group (4 H).



SCHEME 3
Example of synthesis of thiacalix[4]arene aldimines from tetraaminothiacalixarene: (i) pyridine-4-carbaldehyde, ethanol, Et_3N, N_2; (ii) 4-methylbenzaldehyde, toluene

The tetrakis[(4-methylbenzylidene)amino]thiacalix[4]arene was prepared by reacting 4-methylbenzaldehyde with tetraaminothiacalix[4]arene[29]. It was characterized by mass spectrometry and ^{1}H NMR, which shows a singlet at 9.33 ppm for OH, a singlet at 8.36 ppm for the CH of the imino bond (very similar to the chemical shift observed for the previous imino derivative at 8.37 ppm), singlet at 7.58 ppm for the calixarene, doublets at 7.73 and 7.24 ppm for the phenyls, and a singlet at 2.39 ppm for the methyls.

These are at the moment the only two macrocycles derived from the tetraaminothiacalix[4]arene.

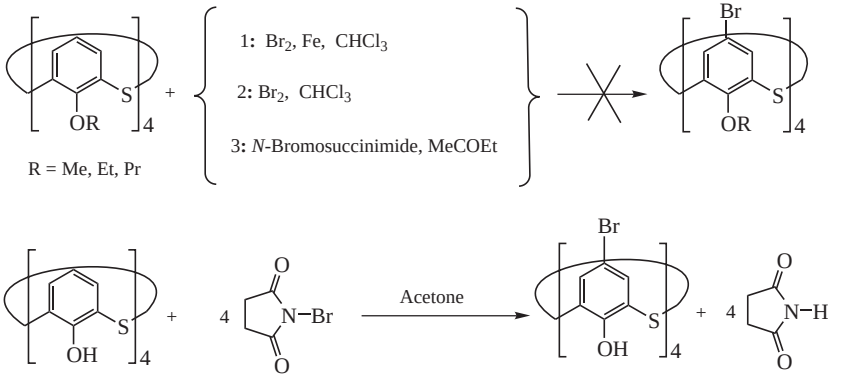
2.3. Tetrahalothiacalix[4]arenes

2.3.1. The Tetrabromothiacalix[4]arene

Tetrahalothiacalix[4]arenes and in particular tetrabromo or tetraiodo derivatives are very important intermediates for the formation of alkynyl derivatives using the Sonogashira reaction. Bromination of the upper rims of the thiacalixarenes is thus an important step in the functionalization of thiacalixarenes as it was extensively demonstrated on similar calixarenes. The well-known classic reactions, which work very well for the family of calixarenes fail for thiacalixarenes. Two different ways of synthesis are reported for the bromination[30,31]. The first method consists in a two-step pathway[31]. The dibromodipropoxythiacalix[4]arene was prepared by reacting 25,27-dipropoxythiacalix[4]arene with bromine in chloroform. A sec-

ond step was then necessary to provide the tetrabrominated species. The tetrabromotetrapropoxythiacalix[4]arene adopts a *1,3-alternate* conformation in the solid state. It was also demonstrated that other conformers, such as the partial cone, were present in solution.

We reported then for the first time the reaction between *N*-bromosuccinimide and tetrahydroxythiacalix[4]arene, using acetone instead of butan-2-one as solvent, which leads directly to the 5,11,17,23-tetrabromo-25,26,27,28-tetrahydroxythiacalix[4]arene in a one-step reaction (Scheme 4)[30]. After modification of the lower rim with a propyl group, the *1,3-alternate* conformer is the majority product as it has been demonstrated by further functionalizations, all the derived species adopting the same *1,3-alternate* conformation.



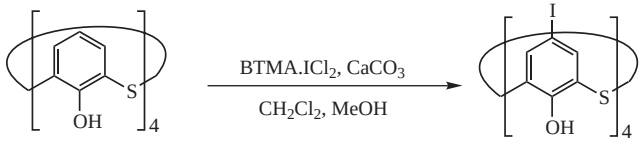
SCHEME 4
Bromination of thiacalix[4]arene

2.3.2. The Tetraiodothiacalix[4]arene

The tetraiodotetrahydroxythiacalix[4]arene was obtained by reaction between the tetrahydroxythiacalix[4]arene and the benzyltrimethylammonium dichloroiodate ($BTMA{\cdot}ICl_2$) in the presence of calcium carbonate (Scheme 5)[32,33]. The NMR spectrum shows one singlet at 9.95 ppm for the hydroxy groups and one singlet at 7.85 ppm for the aromatics, consistently with the tetraiodo derivative. This was confirmed by the mass spectrum with a molecular parent peak at 998.7.

Both tetrabromo- and tetraiodothiacalix[4]arenes are important intermediates that can be used for grafting functional groups on the upper rims of the macrocycle through, for example, carbon–carbon triple bonds. Some examples of utilization of these intermediates for the synthesis of alkynyl-

thiacalixarenes were presented and will be discussed here, but further reactions are expected to be investigated in the near future.

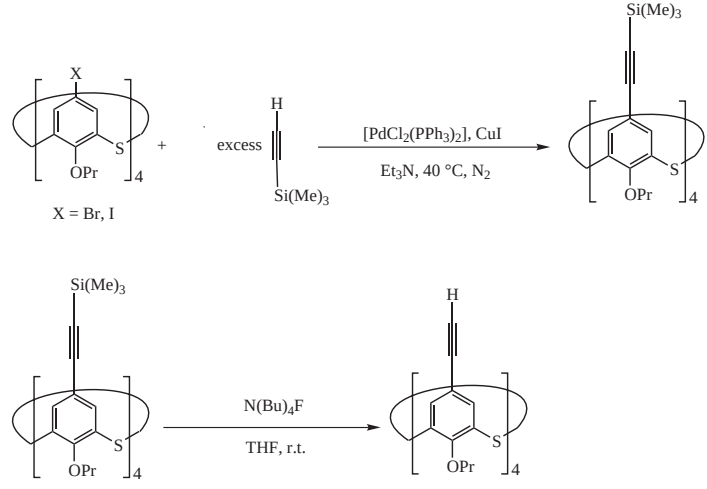


SCHEME 5
Synthesis of tetraiodothiacalix[4]arene

2.4. Synthesis of Alkynylthiacalixarenes

We reported the synthesis of several alkynylthiacalix[4]arenes for nonlinear optical applications[30,32–34]. They were prepared using the Sonogashira reactions. The hydroxy groups had to be previously alkylated in order to prevent them from reacting with the catalyst. The O-alkylation is achieved using propyl iodide in acetone in the presence of cesium carbonate[4,5].

Tetraethynylthiacalix[4]arene was prepared by reaction between (trimethylsilyl)acetylene and the tetrabromotetrapropoxythiacalix[4]arene in triethylamine under nitrogen. The reaction was catalysed by dichlorobis(triphenylphosphine)palladium(II) and copper(I) iodide. The final tetraethynylthiacalix[4]arene was obtained by removal of trimethylsilyl groups with tetrabutylammonium fluoride (Scheme 6). The ^{1}H NMR spectrum



SCHEME 6
Reaction pathway to tetraethynylthiacalix[4]arene

shows a singlet at 7.52 ppm for the phenolic units of the calixarene, one triplet at 3.90 ppm for the O-CH_2 group, one singlet at 3.01 ppm for the ethynyl proton, and the proton signals of the CH_2-CH_3 groups at 1.33 and 0.73 ppm. The solid-state molecular structure was determined by single crystal X-ray diffraction[32,33]. The macrocycle adopts a *1,3-alternate* conformation (Fig. 2). This was actually expected since the bromo derivative shows the same conformation, and this will be a trend for all the derived alkynylthiacalix[4]arenes.

The same reaction between (4-pentylphenyl)acetylene and tetrabromotetrapropoxythiacalix[4]arene gives the 5,11,17,23-tetrakis[(4-pentylphenyl)ethynyl]-24,25,26,27-tetrapropoxythiacalix[4]arene (Scheme 7). The ^{1}H NMR spectrum shows a singlet at 7.57 ppm for the phenolic units of the calixarene, two doublets at 7.42 and 7.17 ppm for the aromatic rings, and the signals for the protons of the propyl and pentyl groups between 3.95 and 0.78 ppm with integrations which are consistent with tetrafunctionalization. The structure of the 5,11,17,23-tetrakis[(4-pentylphenyl)ethynyl]-24,25,26,27-tetrapropoxythiacalix[4]arene was determined using single crystal X-ray diffraction (Fig. 3). The conformation of the macrocycle is also *1,3-alternate*. The packing shows the formation of linear molecular wires in the solid state (Fig. 4).

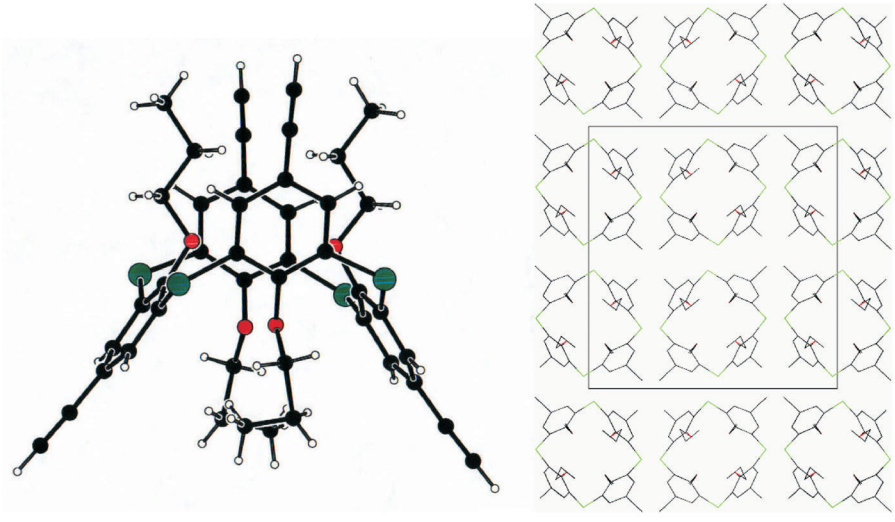
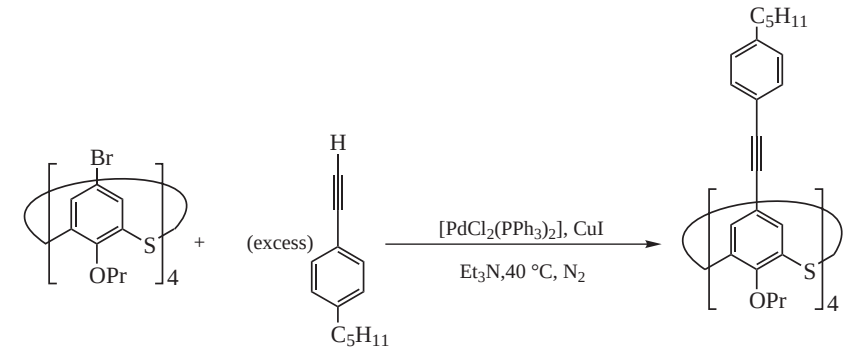


FIG. 2
Structure of the tetraethynylthiacalix[4]arene (a) and packing view along *b*-axis (b)



SCHEME 7
Synthesis of the 5,11,17,23-tetrakis[(pentylphenyl)ethynyl]-24,25,26,27-tetrapropoxythiacalix[4]arene

A thiophene derivative was prepared by the reaction between 2-iodo-5-(phenylethynyl)thiophene and tetraethynylthiacalix[4]arene in triethylamine under nitrogen atmosphere (Scheme 8). The reaction was catalyzed with copper(I) iodide and tetrakis(triphenylphosphine)palladium(0) instead of the classic dichlorobis(triphenylphosphine)palladium(II). This prevents from the formation of the dimer of the thiacalixarene, which was difficult to separate from the final compound. The yield after purification was 60%.

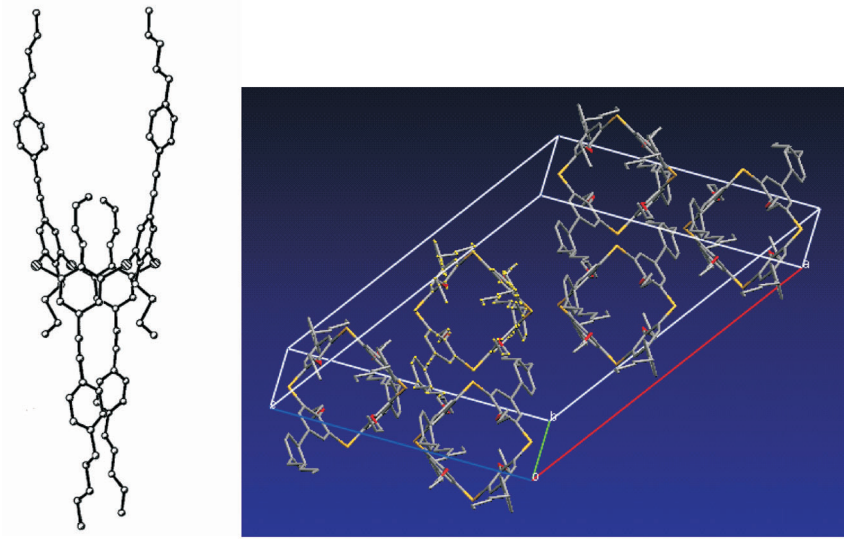
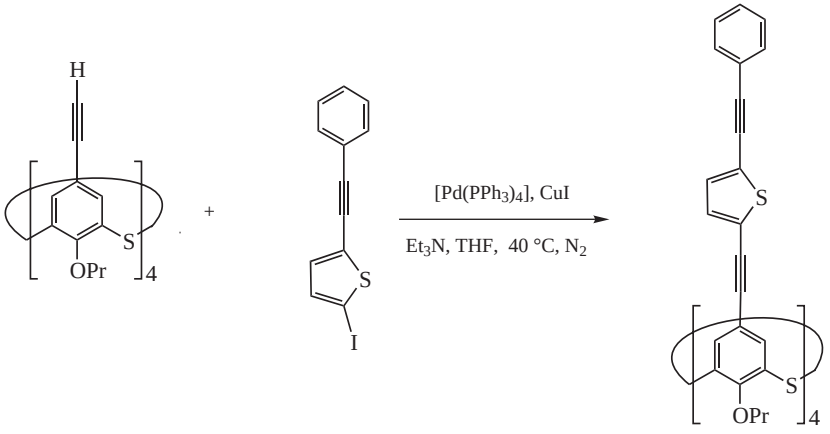


FIG. 3
Structure of the 5,11,17,23-tetrakis[(pentylphenyl)ethynyl]-24,25,26,27-tetrapropoxythiacalix[4]arene and packing view of the structure



SCHEME 8
Synthesis of thiophene derivative

The ^{1}H NMR spectrum in $CDCl_3$ is consistent with the tetrasubstitution of the thiacalixarene. It shows a singlet at 7.59 ppm for phenolic units of the calixarene, two doublets at 7.54 and 7.37 ppm for protons of the aromatic rings, two doublets at 7.16 and 7.15 ppm for protons of the thiophene groups and the signals for protons of the propyl groups between 3.98 and 0.82 ppm with appropriate integrations.

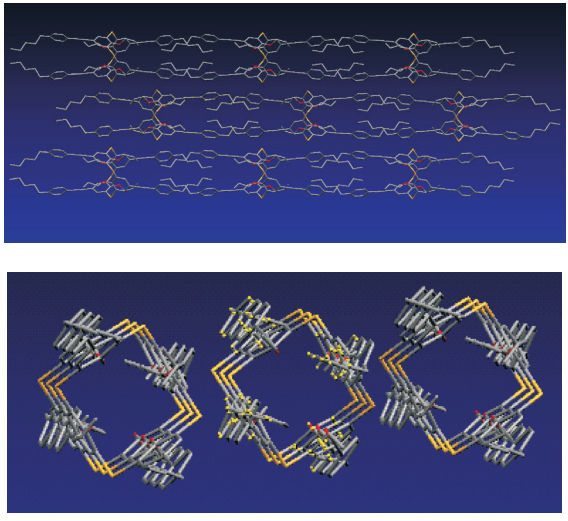
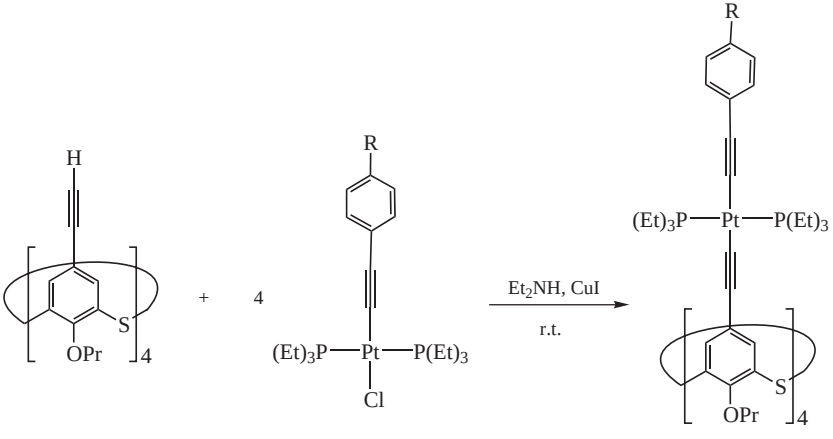


FIG. 4
View along *a*- and *b*-axis showing molecular wires in the structure of the tetrakis[(pentylphenyl)ethynyl]tetrapropoxythiacalix[4]arene

The reaction between the tetraethynylthiacalix[4]arene and the *trans*-chloro(phenylethynyl)bis(triethylphosphine)platinum(II) or the *trans*-chloro[(pentylphenyl)ethynyl]bis(triethylphosphine)platinum(II) in the presence of copper(I) iodide gave platinum complexes of the thiacalix[4]-arene, namely the 5,11,17,23-tetrakis[*trans*-ethynyl(phenylethynyl)bis-(triethylphosphine)platinum(II)]-25,26,27,28-tetrapropoxythiacalix[4]arene and the 5,11,17,23-tetrakis{*trans*-ethynyl[(4-pentylphenyl)ethynyl]bis(tri-ethylphosphine)platinum(II)}-25,26,27,28-tetrapropoxythiacalix[4]arene (Scheme 9). The ^{1}H NMR and ^{13}C NMR spectra with heteronuclear multiple bond correlation experiment in CD_2Cl_2 were consistent with the tetra-substitution of the thiacalixarene. The ^{1}H NMR spectrum showed a singlet at 7.21 ppm for phenolic units of the calixarene, two doublets at 7.12 and 7.01 ppm for aromatic groups, two triplets at 3.79 and 2.52 ppm for the O-CH_2 and the Ar-CH_2, respectively, a multiplet at 2.14 ppm for the P-CH_2 groups, a multiplet between 1.51 and 1.21 ppm for the CH_2 of the pentyl groups, and three triplets at 1.21, 0.87 and 0.64 ppm for the methyl groups. The ^{31}P NMR in CD_2Cl_2 showed a singlet at 12.78 ppm for the phosphine.

The solid-state structure of the 5,11,17,23-tetrakis[*trans*-ethynyl(phenyl-ethynyl)bis(triethylphosphine)platinum(II)]-25,26,27,28-tetrapropoxy-thiacalix[4]arene was determined using X-ray diffraction. The conformation is also *1,3-alternate* (Fig. 5).



SCHEME 9
Synthesis of platinum complexes (R = H, pentyl)

2.5. Formylation of Thiacalix[4]arene

The formylation of the upper rims of the thiacalixarene is an interesting way to achieve functionalization using, for example, Wittig reactions for substitution through ethylenic bonds, imino bonds, or modification with alkoxy groups.

Once again, the conventional reactions that work well for calixarenes such as the Gross reaction[35–37] do not work on thiacalixarenes[38]. Indeed, the Gross reaction, which consists in the reaction between the thiacalix[4]arene and Cl_2CHOCH_3 in the presence of titanium tetrachloride, leads in the case of the tetrapropoxythiacalix[4]arene to a monosubstituted macrocycle with a chloromethyl group in the meta position, together with the removal of one propoxy group (Scheme 10), while it gave no reaction when starting from the tetrahydroxythiacalix[4]arene[38].

Other reactions such as the Vilsmeier–Haack or the Reimer–Tiemann formylation were also investigated without success. The 5,11,17,23-tetraformyl-25,26,27,28-tetrapropoxythiacalix[4]arene could be isolated in good yield (70%) from the reaction between tetrabromotetrapropoxythiacalix[4]arene, butyllithium and *N*-formylpiperidine (Scheme 11)[38].

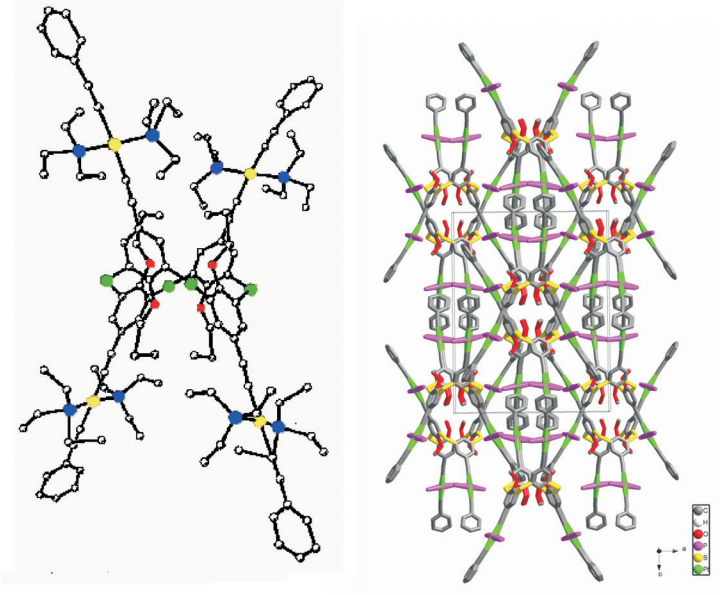
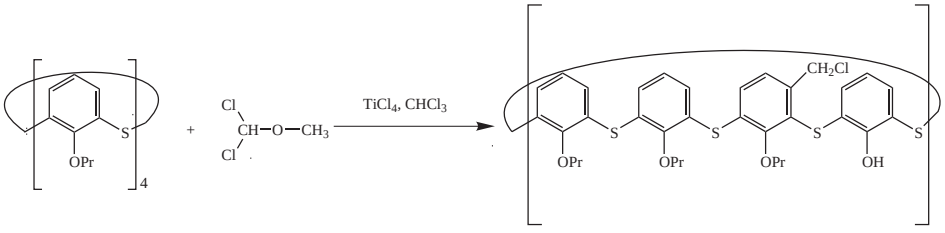
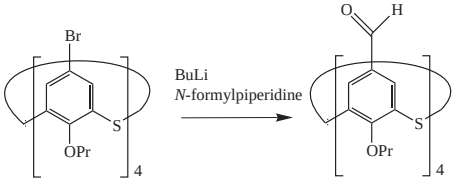


FIG. 5
Structure of the 5,11,17,23-tetrakis[*trans*-ethynyl(phenylethynyl)bis(triethylphosphine)platinum(II)]-25,26,27,28-tetrapropoxythiacalix[4]arene and packing view



SCHEME 10
Synthesis of 18-(chloromethyl)-28-hydroxy-25,26,27-tripropoxythiacalix[4]arene



SCHEME 11
Synthesis of 5,11,17,23-tetraformyl-25,26,27,28-tetrapropoxythiacalix[4]arene

This was confirmed by the ^{1}H NMR spectrum, which shows one singlet at 9.84 ppm for the formyl group, one singlet at 7.96 ppm for aromatic protons, a triplet at 4.03 ppm, a multiplet at 1.33 ppm and a triplet at 0.69 ppm for the OCH_2, CH_2 and CH_3, respectively, of the propyls. The integrations are in perfect agreement with tetrafunctionalization of the macrocycle. The macrocycle probably adopts a *1,3-alternate* conformation since the tetrabromotetrapropoxythiacalix[4]arene adopts the same conformation and rotation is blocked by steric hindrance of propoxy groups.

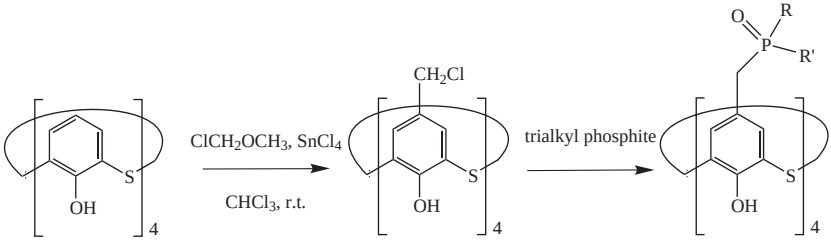
The tetraformylthiacalix[4]arene is a very interesting intermediate for upper-rim functionalizations as it has been demonstrated previously on the calixarenes and we can expect further significant developments in the future.

2.6. (Chloromethyl)thiacalixarenes

Chloromethylation of the upper rim of the macrocycle in the para[39] or meta[38] position was recently described in the literature. The chloromethylation in the meta position was obtained in a good yield (nearly 70%) while attempting to prepare the tetraformylthiacalix[4]arene as previously described (Scheme 10). The structure, which was determined using

single-crystal X-ray diffraction, is original and can be considered as a "pseudo partial cone" since the sulfur plane and the phenolic unit bearing the hydroxy group are almost coplanar, with a very low angle (26.1(3)°) (Fig. 6). The conformation is stabilized by hydrogen bonds between the OH and the oxygen of the nearest propoxy groups. In solution the macrocycle adopts several conformations due to the rotation of the phenolic units, which becomes possible because of the presence of one hydroxy group.

The tetrakis(chloromethyl)thiacalix[4]arene was obtained through reaction of tetrahydroxythiacalix[4]arene and the chloromethyl methyl ether in the presence of $SnCl_4$ [39]. The authors use that intermediate for the formation of phosphorylated thiacalix[4]arene (Scheme 12). Once again it has been observed a strong difference in reactivity compared with the similar calixarene. The phosphorylated species was shown to adopt a cone conformation both in solution and in the solid state according to NMR and X-ray diffraction experiments.



SCHEME 12
Synthesis of phosphorylated thiacalixarenes[39]

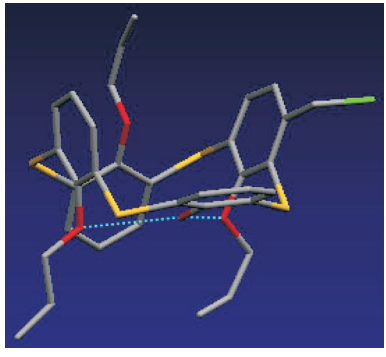
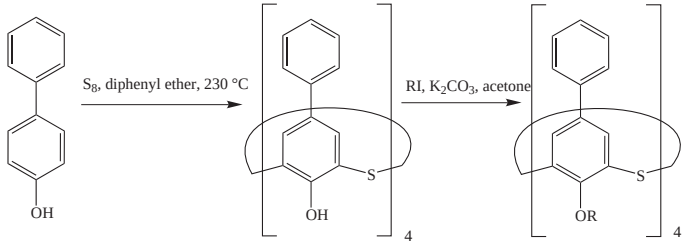


FIG. 6
Structure of the 18-(chloromethyl)-28-hydroxy-25,26,27-tripropoxythiacalix[4]arene

2.7. Tetraphenylthiacalix[4]arene

A tetraphenyl-substituted thiacalixarene was recently prepared by Lhoták et al.[40] This was not a direct functionalization of the upper rim of the macrocycle since it was synthesized directly from cyclization of the biphenyl-4-ol in the presence of sulfur and diphenyl ether, with a 22% yield (Scheme 13). However, it can be also used as intermediate for further functionalizations on phenyl rings. The solid-state structure of the tetraphenyltetrahydroxythiacalix[4]arene was determined as a cone conformer stabilized through intramolecular hydrogen bonds. NMR studies show that the same conformation is maintained in solution. This is an important parameter for some applications involving, for example, molecular inclusion phenomena for which cone conformers are often preferred.



SCHEME 13
Direct synthesis of tetraphenylthiacalix[4]arenes[40]

Alkylation was then performed to prepare the tetraalkoxy derivatives. Different conformers were evidenced using dynamic and two-dimensional NMR experiments. In the case of methyl-substituted thiacalixarene, fast chemical exchanges are observed between the four possible conformers. When increasing the size of the alkoxy group from ethyl to propyl, the exchange rate decreased and the main conformers, *1,3-alternate* and *partial cone*, were isolated.

3. CONCLUSION

We have shown that several important intermediates for the upper-rim functionalization of thiacalixarenes are now available, namely the nitro, amino, bromo, iodo and formyl derivatives. It was clearly evidenced that the chemistry of thiacalixarenes is often very different from that of calixarenes and the former will be certainly much more developed in the future. One can expect many further developments in this field, as it was

observed for the well-known similar calixarenes, since thiacalixarenes possess interesting properties which are often very different from those of calixarenes. They have shown, for example, very nice cubic nonlinear optical properties, which, combined with their solubility and thermal stability, make them interesting candidates for optical applications. Some devices for optical limiting based on thiacalixarenes are already under development in our laboratory. Their complexing properties need to be more investigated with, for example, new multidentate groups grafted on the upper rims for selective complexation. An interesting prospect for complexation would be to increase the size of the cavity of the macrocycles, which has been so far limited only to 4 aromatic rings, and in some cases 5 or 6, but they are still obtained with too low yields to expect important developments. We can expect that the chemistry of the thiacalixarenes will be soon extended to many more compounds. Significant advances in the knowledge of the chemistry of those macrocycles have recently been reported and will arise in the near future. The thiacalixarenes should thus find interesting applications for example in chemical sensors for molecular recognition, optical devices or biomedical developments.

The authors would like to thank their co-workers at the LMI and in particular Prof. J. Bouix and P. Miele, Dr J. M. Letoffe for help with the thermal analysis. We are very grateful to Dr V. G. Kessler (SLU Uppsala) for help with structural characterization, Dr C. Lopes and his colleagues from the Swedish Defence Research Agency (FOI). Prof. M. W. Hosseini and Dr E. Graf (Strasbourg), Prof. I. Stibor and Dr P. Lhoták (Prague), Prof. R. Ungaro and his group (Parma) are also gratefully acknowledged for very fruitful and stimulating discussions.

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