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Meta Nitration of Thiacalixarenes

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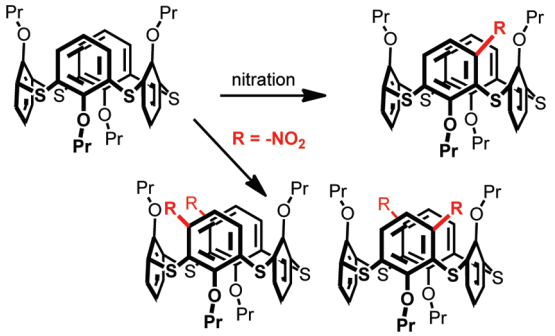

Nitration of thiacalix[4]arene, immobilized in the *1,3-alternate* conformation, leads regioselectively to meta-substituted products. Depending on the reaction conditions, mono- and dinitro-derivatives can be isolated in acceptable yields. This unique substitution pattern is inaccessible in classical calixarene chemistry, and yields inherently chiral compounds, which makes thiacalixarenes very attractive as building blocks or molecular scaffolds.

Introduction

Thiacalix[4]arenes, which were discovered more than a decade ago,[1] represent attractive compounds for many potential applications in supramolecular chemistry. The presence of four sulfur atoms, instead of common $-CH_2-$ bridges, imparts to these molecules[2] many interesting and novel features when compared with classical calix[4]arene analogues. During ongoing research on the chemistry of thiacalixarenes it was demonstrated that these compounds can serve efficiently as complexation agents for transition metals.[3] Thiacalixarenes possess a number of other novel properties, including the ability to have their conformational preferences significantly altered,[4] and to undergo the oxidation of the sulfur bridges to sulfoxides or sulfones.[5]

Electrophilic aromatic substitution represents a straightforward strategy for the derivatization of the upper rim in the classical calixarene series. However, the analogous reactions of thiacalixarenes are, so far, only rarely used. The electrophilic reactions of thiacalixarenes have previously generally been based either on lower-rim unsubstituted thiacalix[4]arenes[6] or on partly alkylated derivatives.[7]

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As we have shown in our previous work, the lower-rim tetraalkylated thiacalix[4]arenes possess unprecedented regioselectivity in electrophilic substitution. As a result, the formylation of a *1,3-alternate* conformer leads unexpectedly to the meta-substituted[8] products—a substitution pattern inaccessible in classical calixarene chemistry. Furthermore, the otherwise identical reaction conditions gave completely different results with the *cone* conformation, where unusual intramolecularly methylene-bridged compounds were formed.[9] This indicates the tremendous difference in the reactivity of the thiacalix[4]arene skeleton when compared with the common calix[4]arene analogues.

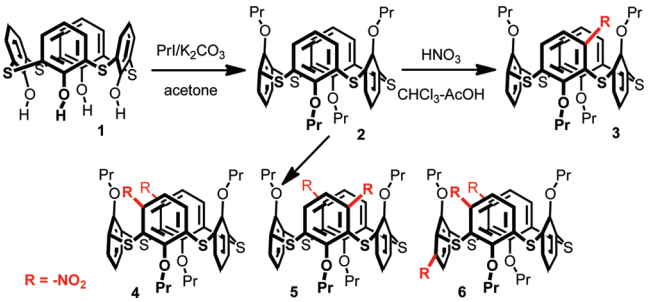
Nitration of classical calix[4]arenes (direct nitration[10] or the *ipso*-substitution[11]) is a well-established procedure, always leading to para-substituted nitro derivatives. These compounds are very useful intermediates in the syntheses of more elaborate systems (usually via reduction to the corresponding amino-derivatives). Unfortunately, nitration of thiacalix[4]arene is not so straightforward, as competitive oxidation of the sulfur bridges can occur.[12] Consequently, other than the direct nitration[13] of starting thiacalix[4]arene **1**, only reactions of diacylated[14] or dialkylated[15] compounds have been described so far.

In this paper we report on the first successful direct nitration of a tetraalkylated thiacalix[4]arene. Contrary to the classical analogues, this reaction yields the mono- or disubstituted compounds with the nitro groups located exclusively in the meta-positions. The unusual regioselectivity of thiacalixarene nitration makes the nitro-derivatives very interesting building blocks for further utilization in supramolecular chemistry.

Results and Discussion

Synthesis. Tetrapropoxy derivative **2**, immobilized in the *1,3-alternate* conformation, was prepared by a known procedure,[16] using alkylation of the starting thiacalixarene **1** with PrI/K_2CO_3 in acetone. The nitration of **2** was carried out in a $CHCl_3$−AcOH mixture, using aqueous 65% HNO_3 as the nitration agent.[17] While using 10 equiv of nitric acid did not lead to any visible reaction after 1 h of stirring at rt, reflux (20 h) of **2** (0.15 mmol) with 80 equiv of HNO_3 in a mixture of 1.5 mL of AcOH and 50 mL of $CHCl_3$ gave

SCHEME 1. Nitration of Thiacalix[4]arenes (*1,3-Alternate*)



mononitro derivative **3** in a yield of 74%. Moreover, the MS and NMR analyses of the crude reaction mixture indicated the presence of only trace amounts of the dinitro isomers. Similar conditions using a higher excess of HNO_3 (340 equivs) gave a mixture of several isomers which were separated by preparative TLC on silica gel plates: monoderivative **3** (10% yield), dinitro derivatives **4** and **5** (both in 26% yields), and trinitro derivative **6** in a 17% yield (Scheme 1). Interestingly, this mixture was obtained only after 0.5 h of reflux, while the longer reaction time led to reduced yields of the nitrated products, probably due to the concurrent oxidation of the sulfur bridges. It is worth mentioning that the ESI MS analyses showed no tetranitrated compounds to be present in any of the crude reaction mixtures.

As the dinitro derivatives are important intermediates in the design of classical calixarene-based receptors, we have carried out the nitration on a bigger scale to show the synthetic usefulness of this reaction. Thus, the gram-scale nitration of thiacalixarene **2** was carried out and the products separated by column chromatography on silica gel to give dinitro and trinitro isomers **4**, **5**, and **6** in 43%, 31%, and 12% yields, respectively.

The ESI MS of compound **3** showed a signal at *m*/*z* 732 corresponding to the mononitrated product with a Na^+ cation $[M + Na]^+$. Similarly, compounds **4**, **5**, and **6** exhibited the molecular peaks $[M + Na]^+$ at *m*/*z* 777 and 812, respectively, proving the presence of two or three nitro groups in the molecules. The ^1H NMR spectrum of **3** shows a doublet at 7.48 ppm with a coupling constant of 8.5 Hz. The complicated splitting pattern of the aromatic part of the spectrum indicates the introduction of a nitro group into the meta position of the thiacalixarene skeleton (para-substitution should lead to a much more symmetrical spectrum). Similar characteristic features can also be seen in the ^1H NMR spectra of **4**−**6**. Theoretically, assuming only meta-substitution, up to five different regioisomers of the dinitro thiacalixarene can be obtained (Figure 1). Unfortunately, the complex splitting pattern of compounds **4** and **5**, together with overlapping signals both in the aromatic and in the aliphatic part of the ^1H NMR spectra, did not allow the unambiguous assignment of the isolated compounds.

Therefore, the final unequivocal structural evidence was obtained by using single-crystal X-ray crystallography. This clearly demonstrated that thiacalix[4]arene **4** corresponds to achiral regioisomer **A** (Figure 2), while derivative **5** represents inherently chiral isomer **B**. Trinitro thiacalixarene **6**, isolated only as a byproduct, is obviously formed by subsequent nitration of symmetrical **4** on the other side of the molecule.

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(17) Use of 100% HNO_3 leads to the oxidation of sulfur bridges as shown by MS spectra of the crude reaction mixture.

Surprisingly, only the isomers possessing nitro groups on the same side of the thiacalixarene skeleton (structures **A** and **B**, Figure 1) are formed in good yields. This makes these compounds promising candidates for further utilization in the design of new receptors as they allow the introduction (after reduction to the amino group) of various functional groups to form well-organized systems. Moreover, while the isomer **A** (compound **4**) represents a symmetrical compound with a previously inaccessible substitution pattern, isomer **B** (compound **5**) is an inherently chiral system with many possible applications in supramolecular chemistry.

To gain deeper insight into the regioselectivity in the thiacalixarene series we have carried out a quantum-chemical prediction of the nitration reaction. The free energy of the corresponding σ complexes was evaluated by using the B3LYP/6-311+G(d,p)//HF/6-31G** method and the results are collected in Table 1. Obviously, the attack of electrophilic species (NO_2^+) is possible from two different directions: (i) inside the cavity (leading to the *endo* σ-complex) and (ii) outside the cavity (leading to the *exo* σ-complex). As can be seen from Table 1, the meta substitution is favored in both cases over the para attack (with a difference greater than 5.3 kcal·mol^{-1}). This result is in accordance with our previous findings[8] and reflects the general preferences of thiacalix[4]arenes in electrophilic aromatic substitution reactions. Interestingly, the *endo* stereochemistry represents the lowest energy state, while the *exo* σ-complex is less stable by 2.45 kcal·mol^{-1}. This indicates the positive role of the thiacalixarene cavity during interactions with electrophilic species in the transition state of the reaction. Unfortunately, all our attempts to explain the regioselective formation of only two dinitro isomers, based on the same quantum-chemical prediction, have failed.

Therefore, we have attempted to analyze the reaction in terms of thermodynamic control and the energy of all theoretically possible dinitro isomers **A**−**E** (Figure 1) was calculated. As can be seen from Table 2, the comparison of relative energies of the corresponding isomers **A**−**E** obtained by the B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) method showed that the most stable is the isomer **D** followed by isomers **E** and **C**. Obviously, the results of theoretical calculations are in contrast to the experimental results, as the only isolated isomers **A** and **B** are those with the highest total energies (Table 2). On the other hand, the energy gap between the corresponding isomers is very small (1.35 kcal·mol^{-1}) and can be easily overridden by the solvation effects under nitration conditions.

In conclusion, the nitration of thiacalix[4]arene, immobilized in the *1,3-alternate* conformation, leads exclusively to the formation of meta-substituted derivatives. The electronic effect of the sulfur bridges gives us a rare opportunity to prepare compounds with an otherwise inaccessible substitution pattern. Depending on the conditions used, mono- or dinitro, inherently chiral derivatives can be obtained in good

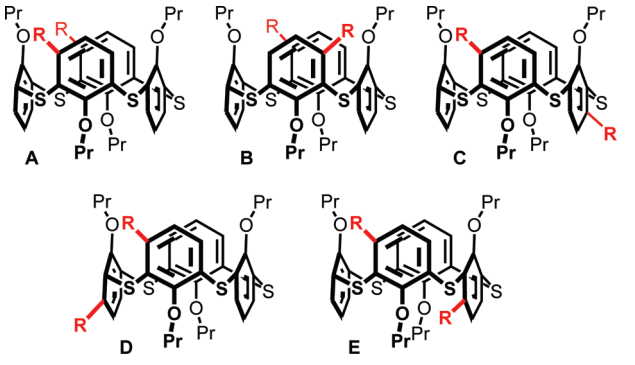
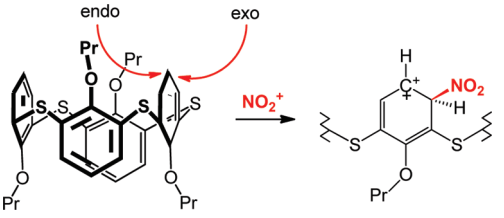


FIGURE 1. Theoretically possible regioisomers of a meta-substituted dinitrothiacalixarene.

TABLE 1. Comparison of Total and Relative Energies of the Corresponding Meta- and Para-Substitution



calculation[a]	total energy[b]	rel energy[c]
m-NO_2-*endo*	−3494.956166	0.0000
m-NO_2-*exo*	−3494.952264	2.4487
p-NO_2-*endo*	−3494.947620	5.3624
p-NO_2-*exo*	−3494.946812	5.8699

[a]B3LYP/6-311+G(d,p)//HF/6-31G** method used. [b]In au. [c]In kcal·mol^{-1}.

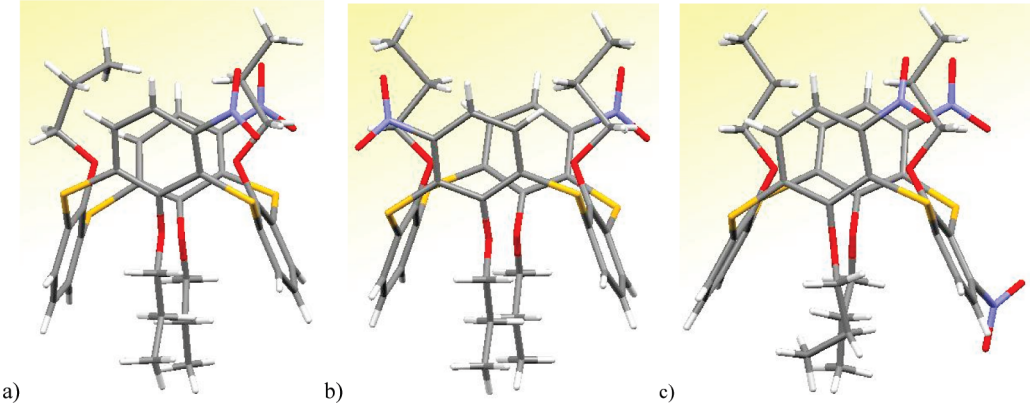


FIGURE 2. Crystallographic structures of compounds **4** (a), **5** (b), and **6** (c).

TABLE 2. Comparison of Total and Relative Energies of the Corresponding Dinitro Isomers A−E (Figure 1)

calculation[a]	total energy[b]	rel energy[c]
A	−3699.167721	1.35
B	−3699.168987	0.56
C	−3699.169543	0.21
D	−3699.169875	0
E	−3699.169609	0.17

[a]B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p) method used. [b]In au. [c]In kcal·mol^{-1}.

yields for further use in the design of novel thiacalixarene-based receptors.

Experimental Section

General Experimental Methods. All reagents and solvents were purchased from commercial sources and used without further purification. NMR spectra for all compounds were accomplished at 298 K on an NMR spectrometer operating at 300 MHz for ^{1}H and 75 MHz for ^{13}C, using solvent peaks of $CDCl_3$ $\delta(^{13}C)$ = 77.0 ppm and $\delta(^1H)$ = 7.26 ppm or TMS as an internal standard. d_1-Chloroform (stabilized over silver wool, 99.8% of deuterium) was used for the spectroscopic studies. Column chromatography was performed with silica gel 60. Thin layer chromatography (TLC) was performed with glass sheets coated with silica gel 60 F_{254}, followed by visualization with UV light. Melting points are uncorrected. IR spectra were measured with a FT-IR spectrometer in KBr tablets. Usually, the 100 scans for one spectrum were accumulated at a spectral resolution of 4 cm^{-1}. Mass spectra were measured with the ESI technique. Samples for elemental analyses were dried in the desiccator over P_2O_5 under vacuum (1Torr) at 80 °C overnight.

4-Nitro-25,26,27,28-tetrapropoxythiacalix[4]arene (*1,3-Alternate*) 3. Thiacalixarene **2** (100 mg, 0.150 mmol) was dissolved in chloroform (50 mL) and glacial acetic acid (1.1 mL) and concd HNO_3 (0.88 mL) were added. The solution was then refluxed for 20 h and after cooling to room temperature water was added. The organic phase was washed five times with water and then it was dried over $MgSO_4$ and evaporated to dryness. Product **3** was obtained by preparative thin layer chromatography (silica gel, eluent hexane−dichloromethane, 50−50) as a yellow solid. Yield 74% (78 mg); mp 249−251 °C (ethyl acetate); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48 (d, 1H, J = 8.5 Hz), 7.31−7.44 (m, 7H), 6.89−6.83 (m, 3H), 3.99−3.73 (m, 7H), 3.58 (q, 1H, J = 7.7 Hz), 1.26−1.11 (m, 4H), 1.10−0.96 (m, 4H), 0.70−0.63 (m, 9H), 0.58 (t, 3H, J = 7.8 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.0, 159.8, 159.5, 149.9, 134.8, 132.8, 132.5, 131.7, 131.49, 131.46, 129.0, 128.9, 128.7, 128.5, 127.8, 127.4, 126.4, 123.0, 123.0, 119.2, 70.7, 70.7, 70.5, 70.3, 22.4, 22.3, 21.6, 10.1, 10.0, 9.6, 9.5 ppm; MS (ES+) calcd for $C_{36}H_{39}NO_6S_4$ 732.16 [M + Na$^+$], found m/z 732.45 [M + Na$^+$]; IR (KBr) ν 2964, 2877, 1631, 1561, 1517, 1465, 1431, 1382, 1345, 1233 cm^{-1}. Elemental Anal. Calcd for $C_{36}H_{39}NO_6S_4$: C, 60.90; H, 5.54; N, 1.97; S, 18.06. Found: C, 60.56; H, 5.11; N, 1.89; S, 17.98.

Compounds 4, 5, and 6. Thiacalixarene **2** (600 mg, 0.900 mmol) was dissolved in chloroform (350 mL) and a mixture of concd HNO_3 (21.1 mL) and glacial acetic acid (27.6 mL) was added. The reaction mixture was then refluxed for 30 min, cooled to room temperature, and quenched by water. The organic phase was washed thoroughly with water, dried over $MgSO_4$, and evaporated to dryness. Products **4**, **5**, and **6** were separated by column chromatography (silica gel, eluent = hexane:dichloromethane 50:50 v/v) as yellow solids.

4,18-Dinitro-25,26,27,28-tetrapropoxythiacalix[4]arene (*1,3-Alternate*) 4: yield 43% (292 mg); mp 188−191 °C (acetone); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (d, 2H, J = 7.5 Hz), 7.45 (d, 2H, J = 7.1 Hz), 7.41−7.36 (m, 4H), 6.94−6.85 (m, 2H), 3.96−3.84 (m, 4H), 3.81−3.74 (m, 2H), 3.58 (t, 2H, J = 7.8 Hz), 1.20−0.85 (m, 8H), 0.71−0.50 (m, 12H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.1, 159.1, 150.2, 134.7, 132.7, 132.5, 132.2, 129.2, 128.1, 128.0, 126.3, 123.7, 119.9, 119.5, 71.0, 70.6, 70.6, 22.7, 22.6, 21.8, 10.4, 9.9, 9.3 ppm; MS (ES+) calcd for $C_{36}H_{38}N_2O_8S_4$ 777.96 [M + Na$^+$], found m/z 777.42 [M + Na$^+$]; IR (KBr) ν 2965, 2877, 1516, 1478, 1429, 1345, 1231 cm^{-1}. Elemenal Anal. Calcd for $C_{36}H_{38}N_2O_8S_4$: C, 57.27; H, 5.07; N, 3.71; S, 16.99. Found: C, 57.05; H, 4.98; N, 3.64; S, 16.77.

4,16-Dinitro-25,26,27,28-tetrapropoxythiacalix[4]arene (*1,3-Alternate*) 5: yield 31% (210 mg); mp 234−236 °C (THF); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.52 (d, 2H, J = 8.5 Hz), 7.45 (d, 2H, J = 9.1 Hz), 7.34 (d, 4H, J = 8.4 Hz), 6.90 (t, 2H, J = 7.6 Hz), 3.94 (q, 2H, J = 7.3 Hz), 3.80 (q, 4H, J = 7.6 Hz), 3.65 (q, 2H, J = 7.9 Hz), 1.11−1.00 (m, 8H), 0.67−0.61 (m, 12H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.2, 160.0, 159.7, 150.3, 134.8, 132.9, 132.6, 132.3, 129.4, 129.1, 128.41, 128.40, 127.6, 126.3, 123.7, 119.9, 71.1, 70.9, 70.8, 70.5, 22.7, 22.6, 22.0, 21.9, 10.3, 9.8, 9.7 ppm; MS (ES+) calcd for $C_{36}H_{38}N_2O_8S_4$ 777.96 [M + Na$^+$], found m/z 777.37 [M + Na$^+$]; IR (KBr) ν 2965, 2877, 1563, 1516, 1428, 1344, 1231 cm^{-1}. Elemental Anal. Calcd for $C_{36}H_{38}N_2O_8S_4$: C, 57.27; H, 5.07; N, 3.71; S, 16.99. Found: C, 57.11; H, 5.01; N, 3.57; S, 16.50.

4,10,24-Trinitro-25,26,27,28-tetrapropoxythiacalix[4]arene (*1,3-Alternate*) 6: yield 12% (86 mg); mp 249−251 °C (acetone); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57 (d, 1H, J = 7.3 Hz), 7.53 (d, 1H, J = 7.3 Hz), 7.51 (s, 2H), 7.46 (d, 1H, J = 1.8 Hz), 7.43 (d, 1H, J = 1.8 Hz), 7.40 (dd, 1H, J = 3.8 and 1.8 Hz), 7.38 (dd, 1H, J = 4.1 and 1.8 Hz), 6.95 (t, 1H, J = 7.7 Hz), 3.92−3.83 (m, 4H), 3.75−3.53 (m, 4H), 1.23−0.78 (m, 8H), 0.73−0.64 (m, 9H), 0.58 (t, 3H, J = 7.3 Hz) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.9, 159.6, 151.1, 150.3, 149.8, 135.0, 134.4, 133.6, 132.4, 132.2, 132.0, 130.5, 130.4, 129.6, 127.6, 125.3, 125.1, 124.9, 123.9, 120.1, 120.0, 71.4, 71.0, 70.7, 70.5, 22.6, 22.2, 22.0, 21.8, 10.3, 9.9, 9.3, 8.9 ppm; MS (ES+) calcd for $C_{36}H_{37}N_3O_{10}S_4$ 822.13 [M + Na$^+$], found m/z 822.15 [M + Na$^+$]; IR (KBr) ν 2965, 2878, 1563, 1519, 1474, 1434, 1346, 1231 cm^{-1}. Elemental Anal. Calcd for $C_{36}H_{37}N_3O_{10}S_4$: C, 54.05; H, 4.66; N, 5.25; S, 16.03. Found: C, 53.90; H, 4.61; N, 5.12; S, 15.95.

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Supporting Information Available: Synthesis and characterization of all new compounds **3**−**6**, copies of ^{1}H, ^{13}C NMR, IR spectra, and MS spectra, quantum chemical calculations, and crystallographic measurements. This material is available free of charge via the Internet at http://pubs.acs.org.