Phosphorylation of *p-tert*-butylthiacalix[4]arene: reaction with phosphorous triamides

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The reaction of *p-tert*-butylthiacalix[4]arene **1** with PCl_3 gives the phosphorous diester chloride **2** which could be transformed into the double cyclic phosphorous diester amide **3**. The conformation of this derivative was found to be *1,2-alternate* with two magnetically different phosphorus atoms. The reaction of **1** with $P(NEt_2)_3$ gives the asymmetric phosphorus thiacalix[4]arene **4**. The conformations of the phosphorus thiacalix[4]arenes **3** and **4** were determined by NMR methods. Phosphorus thiacalixarene **3** was investigated by temperature-dependent ^{1}H NMR and ^{31}P NMR spectroscopy in a range from −80 °C to +120 °C. In this range, no conformational changes could be detected. Due to their different environments, the phosphorus atoms in compound **3** show different reactivities in oxidation experiments with cumene hydroperoxide.

Introduction

Calixarenes, cyclic condensation products of phenols with formaldehyde, are important building blocks in supramolecular chemistry. There are many examples in the literature dealing with the use of calixarenes as a molecular scaffold for the synthesis of more elaborate molecules, supramolecular assemblies, sensors, receptors *etc*.[1–3]

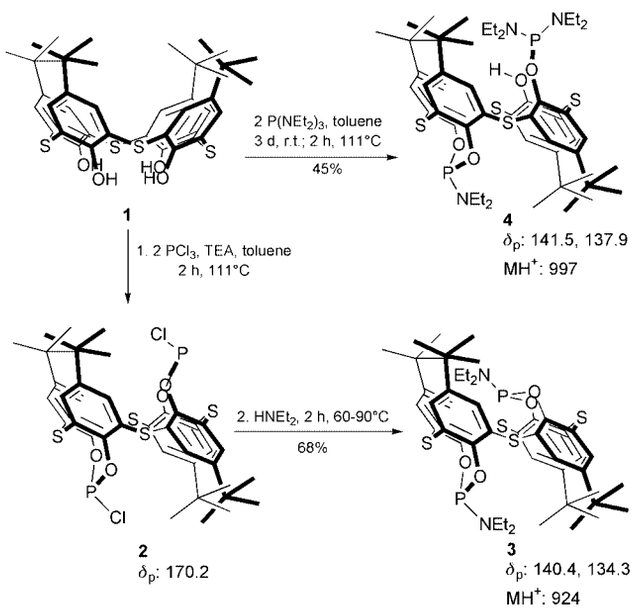
In 1997 the first one-pot synthesis of *p-tert*-butylthiacalix[4]arene (**1**) was published[4] which allows the preparation of this new calixarene in substantial quantities. The sulfur bridges in the molecule cause some differences in the chemical and physical properties compared to common *p-tert*-butylcalix[4]arene. For example, *p-tert*-butylthiacalix[4]arene strongly complexes transition metal ions.[5] A chirally modified derivative of **1** used as the chiral stationary phase for gas chromatography excellently separates enantiomeric amino acids, amines and alcohols in contrast to the corresponding *p-tert*-butylcalix[4]arene derivative.[6] The research on thiacalixarene chemistry is just beginning.

While many phosphorus containing calixarenes were synthesized during the last decade,[7–9] only one derivative of the thiacalixarene **1** is known.[10] Herein we report the synthesis of phosphorus thiacalixarenes containing phosphamidite moieties.

Results and discussion

For the phosphorylation reaction of *p-tert*-butylthiacalix[4]arene (**1**) we used phosphorous trichloride and hexaethylphosphorous triamide, compounds which have been already applied in phosphorylation reactions of *p-tert*-butylcalix[*n*]arenes and calixresorc[4]arenes.[8,11,12]

The reaction of **1** with PCl_3 gives the double cyclic phosphorous diester chloride **2**[10] which we could convert into the double cyclic phosphorous diester amide **3** by reaction with diethylamine in good yield. The phosphorylation of *p-tert*-butylthiacalix[4]arene **1** with hexaethylphosphorous triamide at room temperature followed by rapid heating up to 111 °C leads to the biphosphorylated thiacalixarene **4** in moderate yield. Following this reaction by ^{31}P NMR spectroscopy, the appearance of hexacoordinated phosphorus as reported for *p-tert*-butylcalix[4]arene[11] was not observed (Scheme 1).



Scheme 1 Syntheses of the phosphorus thiacalixarenes **3** and **4**.

The determination of the structures was carried out by 2D NMR spectroscopy. *p-tert*-Butylthiacalix[4]arene (**1**) is a highly symmetric molecule which exists in solution as the *cone*-conformer.[4] In the ^{1}H NMR spectrum, singlets are found for all protons. However, the phosphorus thiacalixarene **3** shows two singlets for the *tert*-butyl protons and four signals for the aromatic protons. In the ^{31}P NMR spectrum we observe two different chemical shifts for the phosphorus atoms, indicating the presence of two magnetically different phosphorus atoms. This suggests that the compound has C_S symmetry which would hold for a *cone* or a *1,2-alternate* conformation. The phosphorus thiacalixarene **4** gives two signals in the ^{31}P NMR spectrum which are different from that of compound **3**. Furthermore, the four singlets for the *tert*-butyl protons and the

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Table 1 Multiplicity and intensity of ^{1}H NMR signals of compounds **1**, **3** and **4**

Groups	**1**	**3**	**4**
tert-Butyl	1 s, 36 H	2 s, 18 H each	4 s, 9 H each
Ph	1 s, 8 H	4 s, 2 H each	8 d, 1 H each
O*H*	1 s, 4H	—	1 s, 1 H
$N(CH_2CH_3)_2$	—	2 m, 4 H each	4 m, 12 H in total
$N(CH_2CH_3)_2$	—	2 t, 6 H each	3 t, 6 H each

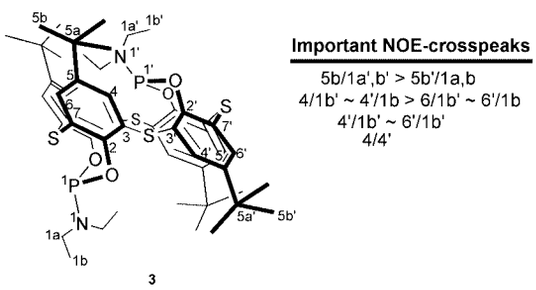


Fig. 1 Phosphorus thiacalix[4]arene **3** and the most important NOE-crosspeaks.

eight doublets for the aromatic protons indicate that the phosphorus thiacalixarene **4** must have C_1 symmetry. The multiplicity and intensity of the ^{1}H NMR signals of compounds **1**, **3** and **4** are shown in Table 1.

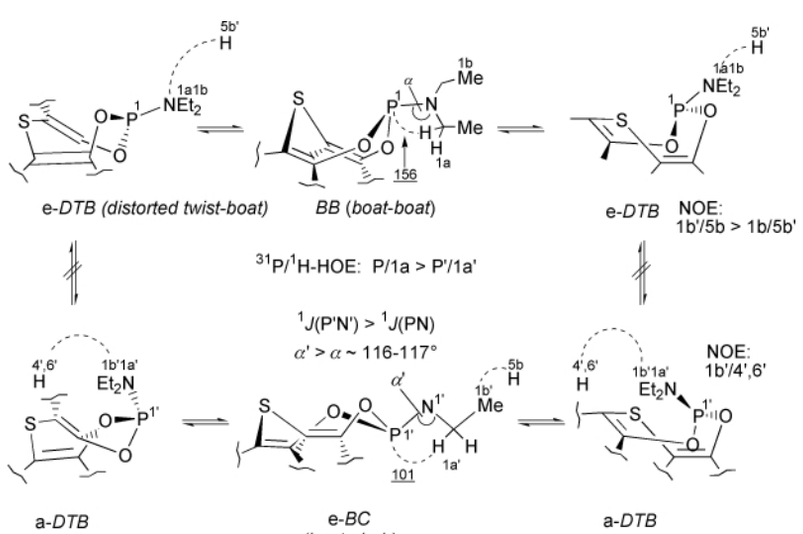
In the NOESY spectrum of phosphorus thiacalix[4]arene **3**, the protons of the methyl and the methylene groups of the diethylamino moieties show strong NOE's with the opposite *tert*-butyl and aromatic protons (see Fig. 1). Furthermore, the NOE of the aromatic protons 5/5′ is very weak, so the distance through space between both protons must be long. This is only possible if the phosphorus thiacalixarene **3** has a *1,2-alternate* conformation. That is a remarkable difference compared to the already known phosphorus derivatives of the *p-tert*-butylcalix[4]arene, of which the *cone*-conformers have been reported in most cases,[7–9,11,12] but not the *1,2-alternate*-conformers.

In the bicyclic amidite **3**, two different types of phosphorus atoms must be present according the two ^{31}P NMR signals. The two phosphocine ring systems must have different conformations which cannot interconvert, as follows from the structure of **3** (Fig. 1). In Scheme 2, a simplified transformation scheme of the eight-membered ring conformers of **3** is shown, which was established in its general version by Renaud *et al.*[13] and investigated by Arshinova and co-workers.[14]

Because of the NOE effects 5b/1a′,b′ > 5b′/1a,b, it is obvious that one of the phosphocine rings of **3** represents an equatorial *boat-chair* (e-*BC*) conformation with a ^{31}P NMR shift of 140.4 ppm for the 1′-P atom undergoing a fast conformational change to the axial *distorted-twist-boat* (a-*DTB*) conformation as indicated by the 4′,6′/1b′ crosspeaks. The other ring has an equatorial *boat-boat* (e-*BB*) conformation with a ^{31}P NMR shift of 134.3 ppm for the 1-P atom, which is transformed to some extent into the energetically lower e-*DTB* conformers with strong 4′/1a,b NOE's. The usual conformational inversion e-*BB*↔e-*BC* is not possible in the case of phosphorus thiacalixarene **3**. For this process, the bulky diethylamino moieties would have to thread simultaneously through the calixarene rim. Hence, both phosphorus atoms remain magnetically different.

Lowering the temperature down to −80 °C, in the ^{1}H NMR spectra of **3** the signals of the two diethylamino moieties, 1a,b-H as well as 1a′,b′-H, split to give two signals for each methylene and methyl group. In the NOESY spectrum, even at −70 °C, the orientations of the two phosphocine rings were found to be unchanged. However, the splitting of the diethylamino signals is the result of the hindrance of rotation of the diethylamino moieties around the P–N bond, even though the solution conformation could not be determined unambiguously. The rotational barriers, $\Delta G_{190}^{\ddagger} = 8.9$ kcal mol^{-1} for the 1′-P–N bond and $\Delta G_{223}^{\ddagger} = 10.2$ kcal mol^{-1} for the 1-P–N bond, were calculated on the basis of the chemical shift differences and the coalescence temperatures.[15] On increasing the temperature up to 120 °C, no dynamic conformational processes could be observed. At 100 °C, the 1-P atom was oxidized by air as indicated in the ^{31}P NMR spectrum by the disappearance of the signal at 134 ppm and the appearance of a new signal at −5.5 ppm.

The structure of phosphorus thiacalixarene **4** as shown in Fig. 2 could also be determined by 2D NMR experiments. In this compound, the 14a′,b′-protons of the diethylamino moieties show strong NOE's with the opposite protons of the *tert*-butyl groups (see Fig. 2). The NOE's of the aromatic protons 11/24 and 4/17, respectively, are very weak. The *1,2-alternate* conformation of **4** can be compared with that of phosphorus thiacalix[4]arene **3**. Additionally, we found an NOE-crosspeak between the OH-proton and the 18b-*tert*-butyl protons of **4**, which indicates that the OH-group is able to swing through the calixarene rim. The ^{31}P NMR shifts were assigned by the 2D-^{31}P/^{1}H-HOESY and ^{1}H/^{31}P-HMBC methods, respectively. The 14-P atom of **4** gives a shift at 141.5 ppm, the



Scheme 2 Conformational transformations of the two different thiaphosphocine fragments of the phosphorus thiacalixarene **3** according to Renaud *et al.*[13] and the NOE effects observed (volume integrals A_{ij}).

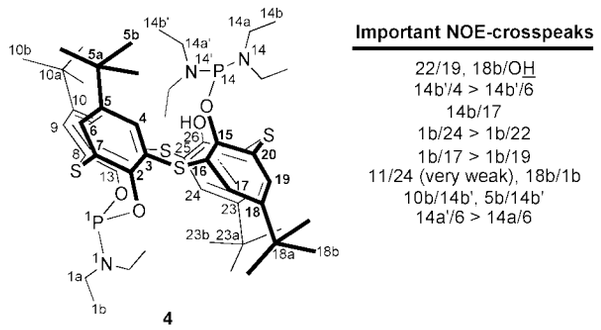
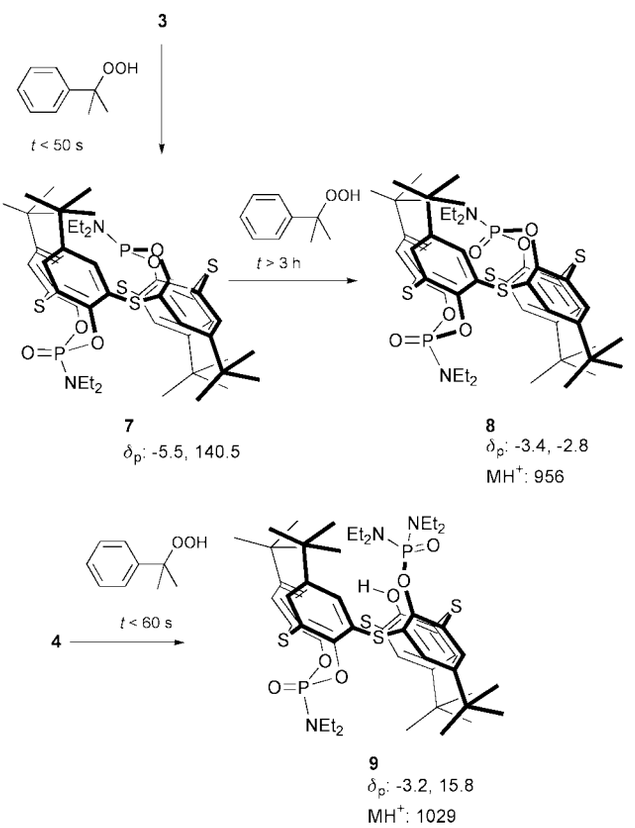


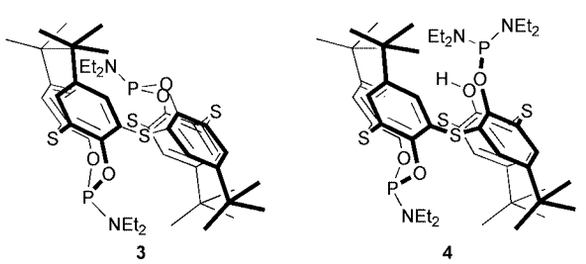
Fig. 2 Phosphorus thiacalix[4]arene **4** and the most important NOE-crosspeaks.

ring-closed 1-P atom at 137.9 ppm in a *BB*-phosphocine conformation (Fig. 2).

The conformation stipulated reactivities of the phosphorus atoms in the ring systems of **3** and **4** were proven by oxidation experiments with cumene hydroperoxide (Scheme 3). In compound **3**, the 1-P atom in which the lone electron pair is not shielded was completely oxidized within 50 seconds to give compound **7**. The complete oxidation to compound **8**, however, required 3 hours because of the shielding of the 1′-P atom. The phosphorus thiacalixarene **4** was completely oxidized within 1 min. This reaction behavior supports the proposed structures of **3** and **4** as shown in Scheme 1. Oxidation reactions at the sulfur atoms were not observed under the conditions used. The molecular weights of the products were determined by MALDI-TOF spectrometry.



Scheme 3 Oxidation of phosphorus thiacalixarenes **3** and **4**.



Experimental

All melting points were determined with a Kofler melting point apparatus and are corrected.

The NMR experiments were performed on a Bruker DRX-500 spectrometer operating at 500.13 MHz (^{1}H), 125.77 MHz (^{13}C), 202.45 MHz (^{31}P) and 50.69 MHz (^{15}N). Pulsed *z*-gradients were used for the COSY, HSQC and HMBC measurements. The spectra were recorded as solutions in $CDCl_3$ using for ^{1}H NMR and ^{13}C NMR TMS as an internal standard, for ^{31}P NMR 85% H_3PO_4 as an external standard and for ^{15}N NMR $CH_3{}^{15}NO_2$ as an internal standard with $\delta = 0.00$ ppm. The temperature-dependent ^{1}H NMR and ^{31}P NMR experiments with phosphorus thiacalix[4]arene **3** were carried out in CD_2Cl_2 in a range from −80 °C to −10 °C, and in 1,1,2,2-tetrachloroethylene-d_2 in a range from +30 °C to +120 °C.

The 2D experiments were acquired with proton spectral widths of 4000 Hz in both dimensions and 2K data points in the t_2 domain. Furthermore the following parameters were used:

(a) COSY: 512 t_1 spectra with 8 scans, recycling delay $D1 = 2.0$ s, sine bell window functions prior to Fourier transformation.

(b) The ^{1}H/^{13}C correlated spectra were recorded with 350 t_1 increments, 8 or 32, respectively, transients for each t_1, $D1 = 2.0$ s and a long-range delay $\Delta = 65$ ms for HMBC. π/3-shifted sine-squared functions for HSQC and, respectively, sine bell functions for HMBC in both dimensions and a zero-filled 2K × 1K data matrix were used for processing.

(c) The phase-sensitive NOESY and ROESY spectra were obtained in the TPPI mode from 512 experiments in t_1, 32 scans in t_2 and $D1 = 2.0$ s. Mixing times τ_m (NOE) = 800 ms, spin-lock-τ_m (ROE) = 250 ms. The data were zero-filled to 2K × 2K points before applying a π/2-shifted sine-squared bell function in both dimensions.

(d) ^{1}H/^{31}P-HMBC: 350 t_1 increments at a phosphorus sweep width of 40 ppm, 8 scans in t_2, $D1 = 3.0$ s, long-range delay $\Delta = 50$ ms.

(e) ^{1}H/^{15}N-HMBC: 350 t_1 spectra with a nitrogen sweep width of 100 ppm, 40 scans in t_2, $D1 = 3.0$ s, long-range delay = 60 ms. Processing of all HMBC data with sine bell window functions in a zero-filled 2K × 1K matrix.

(f) The ^{31}P/^{1}H correlated HOESY spectra were recorded in the phase-sensitive mode using the TPPI method. 256 t_1 experiments, 28 scans for each FID in t_2, $D1 = 3.0$ s and the mixing time $\tau_m = 1.5$ s were applied. The sweep widths are 40 ppm in the phosphorus t_2 domain and 4000 Hz in t_1 for protons. π/2 shifted sine-square bell window functions in both dimensions and zero-filling to give a 2K × 1K matrix were used for processing.

Elemental analyses have been carried out with a Fa. Carlo Erba elemental analyzer. The molecular mass spectra were recorded on a Kratos Compact MALDI II mass spectrometer. Solvents were dried prior to use with appropriate drying agents. Hexaethylphosphorous triamide[16] and *p-tert*-butylthiacalix[4]arene (**1**)[4] were synthesized according to the given methods.

Synthesis of phosphorus thiacalixarene 3

A suspension of *p-tert*-butylthiacalix[4]arene **1** (1.44 g, 2.00 mmol) and phosphorous trichloride (0.55 g, 4.00 mmol) was stirred in toluene (50 cm^3) for 10 min. Triethylamine (0.82 g, 8.00 mmol) was added and the mixture was refluxed for 2 h. After cooling to 60 °C, diethylamine (0.60 g, 8.20 mmol) was added and the suspension was stirred for 2 h. During this period the temperature was increased to 90 °C. After cooling to

room temperature, the amine hydrochlorides were filtered and the solvents were removed *in vacuo*. The residue was dissolved in methylene chloride (5 cm^3) and crystallized after addition of acetonitrile (20 cm^3) to give **3** (1.26 g, 68%) as a colorless solid, mp 229–231 °C (Found: C, 62.35; H, 7.0; N, 3.0; S, 13.7%; MH^+, 924. $C_{48}H_{64}N_2O_4P_2S_4$ requires C, 62.4; H, 7.0; N, 3.0; S, 13.9%; *M*, 923.2); δ_N (50 MHz; $CDCl_3$) −300.3 (d, J_{PN} 94, 1-N), −298.4 (d, J_{PN} 85, 1′-N); δ_P (202 MHz; $CDCl_3$) 134.30 (1-P), 140.35 (1′-P); ^1H NMR: δ_H (500 MHz; $CDCl_3$) 0.38 (6 H, t, *J* 7, 1b′-N(CH_2CH_3)$_2$), 0.86 (6 H, t, *J* 7, 1b-N(CH_2CH_3)$_2$), 1.25 (18 H, s, 5b-C(CH_3)$_3$), 1.29 (18 H, s, 5b′-C(CH_3)$_3$), 2.58 (4 H, m, 1a′-N(CH_2CH_3)$_2$), 2.75 (4 H, m, 1a-N(CH_2CH_3)$_2$), 7.35 (2 H, d, *J* 2, 6′-Ph), 7.42 (2 H, d, *J* 2, 4′-Ph), 7.55 (2 H, d, *J* 3, 6-Ph), 7.62 (2 H, d, *J* 2, 4-Ph); δ_C (125 MHz; $CDCl_3$) 13.62 (1′-N(CH_2CH_3)$_2$), 14.52, 14.54 (1-N(CH_2CH_3)$_2$), 31.26, 31.31 (C(CH_3)$_3$), 34.15, 34.37 ($C(CH_3)_3$), 36.70 (d, J_{PC} 28, 1-N(CH_2-CH_3)$_2$), 36.91 (d, J_{PC} 27, 1-N(CH_2CH_3)$_2$), 121.74 (d, J_{PC} 3, 7-Ph), 122.49 (3-Ph), 127.73 (7′-Ph), 128.02 (4′-Ph), 128.68 (d, J_{PC} 6, 3′-Ph), 129.89 (6′-Ph), 134.49 (6-Ph), 135.37 (4-Ph), 144.41 (5-Ph), 146.26 (5′-Ph), 151.55 (d, J_{PC} 13, 2′-Ph), 157.57 (dd, J_{PC} 9, J_{PC} 5, 2-Ph); *m*/*z* 924 (MH^+, 100%).

Synthesis of phosphorus thiacalixarene 4

p-tert-Butylthiacalix[4]arene **1** (1.44 g, 2.00 mmol) and hexaethylphosphorous triamide (0.99 g, 4.00 mmol) were stirred in toluene (30 cm^3) at room temperature for 3 d and afterwards refluxed for an additional 2 h. The liquids were removed *in vacuo* and the residue was stirred with acetonitrile (20 cm^3). The solid was filtered off, dissolved in methylene chloride (5 cm^3) and crystallized after addition of acetonitrile (20 cm^3) to give **4** (0.90 g, 45%) as a colorless solid, mp 204–206 °C (decomp.) (Found: C, 62.25; H, 7.6; N, 4.1; S, 12.7%; MH^+, 997. $C_{52}H_{75}N_3O_4P_2S_4$ requires C, 62.6; H, 7.6; N, 4.2; S, 12.9%; *M*, 996.3); δ_N (50 MHz; $CDCl_3$) −321.1 (14-N), −297.9 (d, J_{PN} 66, 14′-N); δ_P (202 MHz; $CDCl_3$) 137.92 (1-P), 141.35 (14-P); δ_H (500 MHz; $CDCl_3$) 0.61 (6 H, t, *J* 7, 14b′-(N(CH_2CH_3)$_2$)$_2$), 0.64 (6 H, t, *J* 7, 14b-(N(CH_2CH_3)$_2$)$_2$), 0.76 (6 H, br s, 1b-N(CH_2CH_3)$_2$), 1.17 (9 H, s, 18b-C(CH_3)$_3$), 1.24 (9 H, s, 10b-C(CH_3)$_3$), 1.28 (9 H, s, 23b-C(CH_3)$_3$), 1.32 (9 H, s, 5b-C(CH_3)$_3$), 2.00–2.20 (2 H, br m, 1a-N(CH_2CH_3)$_2$), 2.44 (2 H, m, 14a′-N(CH_2CH_3)$_2$), 2.54 (2 H, m, 14a′-N(CH_2CH_3)$_2$), 2.84 (6 H, m, 1a-N(CH_2CH_3)$_2$ and 14a-N(CH_2CH_3)$_2$), 6.02 (1 H, s, O*H*), 7.14 (1 H, d, *J* 2, 24-Ph), 7.27 (1 H, d, *J* 2, 17-Ph), 7.29 (1 H, d, *J* 2, 19-Ph), 7.39 (1 H, d, *J* 2, 22-Ph), 7.41 (1 H, d, *J* 2, 6-Ph), 7.55 (1 H, d, *J* 2, 9-Ph), 7.56 (1 H, d, *J* 2, 4-Ph), 7.68 (1 H, d, *J* 2, 11-Ph); δ_C (125 MHz; $CDCl_3$) 14.20 (1b-N(CH_2CH_3)$_2$ and 14b-N(CH_2CH_3)$_2$), 14.88 (14b′-N(CH_2CH_3)$_2$), 31.09 (18b-C(CH_3)$_3$), 31.31 (10b-C(CH_3)$_3$), 31.36 (5b-C(CH_3)$_3$), 31.40 (23b-C(CH_3)$_3$), 34.06 (10a-*C*(CH_3)$_3$), 34.10 (23a-*C*(CH_3)$_3$), 34.20 (18a-*C*(CH_3)$_3$), 34.26 (5a-*C*(CH_3)$_3$), 36.34 (br, 1a-N(CH_2CH_3)$_2$), 39.37 (d, J_{PC} 23, 14a-N(CH_2CH_3)$_2$), 39.54 (d, J_{PC} 21, 14a′-N(CH_2CH_3)$_2$), 116.62 (8-Ph), 122.85 (25-Ph), 123.64 (12-Ph), 124.03 (d, J_{PC} 12, 21-Ph), 125.21 (24-Ph), 125.61 (3-Ph), 125.68 (d, J_{PC} 5, 7-Ph), 126.95 (17-Ph), 127.09 (d, J_{PC} 5, 20-Ph), 127.56 (16-Ph), 127.69 (22-Ph), 129.33 (6-Ph), 130.24 (4-Ph), 133.11 (19-Ph), 136.33 (9-Ph), 138.08 (11-Ph), 142.30 (23-Ph), 144.03 (10-Ph), 144.36 (5-Ph), 145.57 (18-Ph), 151.92 (26-Ph), 152.06 (d, J_{PC} 6, 15-Ph), 153.28 (d, J_{PC} 5, 2-Ph), 159.44 (d, J_{PC} 14, 13-Ph); *m*/*z* 997 (MH^+, 100%).

Oxidation of phosphorus thiacalix[4]arenes 3 and 4

In an NMR tube, 20 mg samples of the phosphorus thiacalixarenes **3** or **4** dissolved in 1 cm^3 of $CDCl_3$ were mixed at room temperature with 0.2 cm^3 of cumene hydroperoxide (94%). The oxidation reactions were followed by ^{31}P NMR.

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