Synthesis and Conformation Analysis of New Perphosphorylated Calix[4]resorcinarenes

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The octaphosphorylation of calix[4]resorcinarenes **1** by 2-dialkylamino-1,3,2-diheterophosphorinanes **2** is described, and the effect of different factors on the structures of the resulting perphosphorylated products **3**–**5** was studied. Conformation analysis of these compounds by correlated 2D NMR spectroscopy and X-ray diffraction analysis was performed, and it was found that compounds **3**–**5**, like the initial resorcinarenes **1**, each have the *all-cis* configuration of the R groups in the methylidene bridges of the calixarene system, but different orientations of benzene rings and phosphorinane fragments with respect to one another and to the macrocycle plane. Perphosphorylated resorcinarenes **3a**–**c**, **4a** and **5a** with R = alkyl exist in *flattened cone* conformations with the phosphorinane fragments on the same side of the macrocycle plane. The conformations of the perphosphorylated resorcinarenes **3d**, **4b** and **5b** with R = Ph change to forms intermediate between *flattened cone* and *1,3-alternate*. The phosphorus fragments in these compounds are located on opposite sides of the macrocycle plane. It was shown that the oxidation and sulfurisation of phosphocalixarenes **3** proceed without any change in the spatial organisation of the macrocyclic system.

Introduction

The chemistry of calixarenes is one of the most intensively developed branches of organic chemistry, dealing with *the unlimited modification possibilities*[1] of these compounds and the design of complex organic molecules and related coordination and supramolecular systems.[1,2] The presence of a molecular cavity, which varies in size and properties depending on the nature and arrangement of functional groups introduced into the calixarene, indicates wide prospects for the use of modified calixarenes as self-adjusting ligands, receptor systems, efficient extractants etc.

New octaphosphorylated calix[4]resorcinarene derivatives containing sterically hindered phosphorinane fragments at the peripheries of their macrocyclic systems are described in this paper. The main attention is given to study of the structures of the compounds synthesised.

The perphosphorylation of calix[4]resorcinarenes **1** was first studied by Markovskii et al. in the early 1990s.[3] More recently, trivalent phosphorus derivatives − phenyldichlorophosphane[4] and simple triamidophosphites[5] − were introduced into this reaction. From ^{1}H and ^{31}P NMR spectroscopic data, the authors[3b,4,5b] supposed that octaphosphorylated calix[4]resorcinarenes existed in the *flattened cone* conformation. No detailed conformation analysis was performed for the compounds obtained.

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Results and Discussion

Several conformations with different arrangements of benzene rings and R groups in the methylidene ridges with respect to one another and to the macrocycle plane are known for calix[4]resorcinarenes:[6] *cone*, *flattened cone*, *flattened partial cone*, *1,2-alternate* and *1,3-alternate* (Figure 1).

The preferred conformation of a structure should depend on the properties of the inserted functional groups, the nature of the R groups in the calixarene matrix and the reaction conditions.[6]

We studied the effect of the R groups on the structures of perphosphorylated products by the use of calix[4]resorcinarenes **1** containing alkyl (**1a**−**c**) and phenyl (**1d**) substituents in the methylidene bridges as substrates. They all existed in *flattened cone* conformations and had *all-cis* R group configurations. To examine the effect of functional groups, 2-dialkylamino-1,3,2-diheterophosphorinanes **2**,

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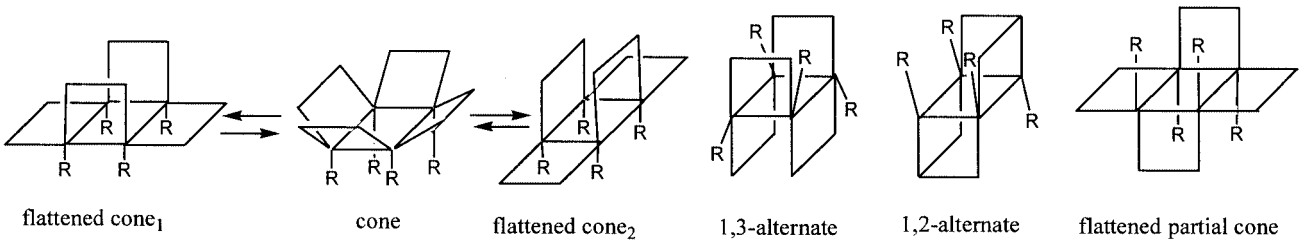


Figure 1. Conformations of calix[4]resorcinarenes

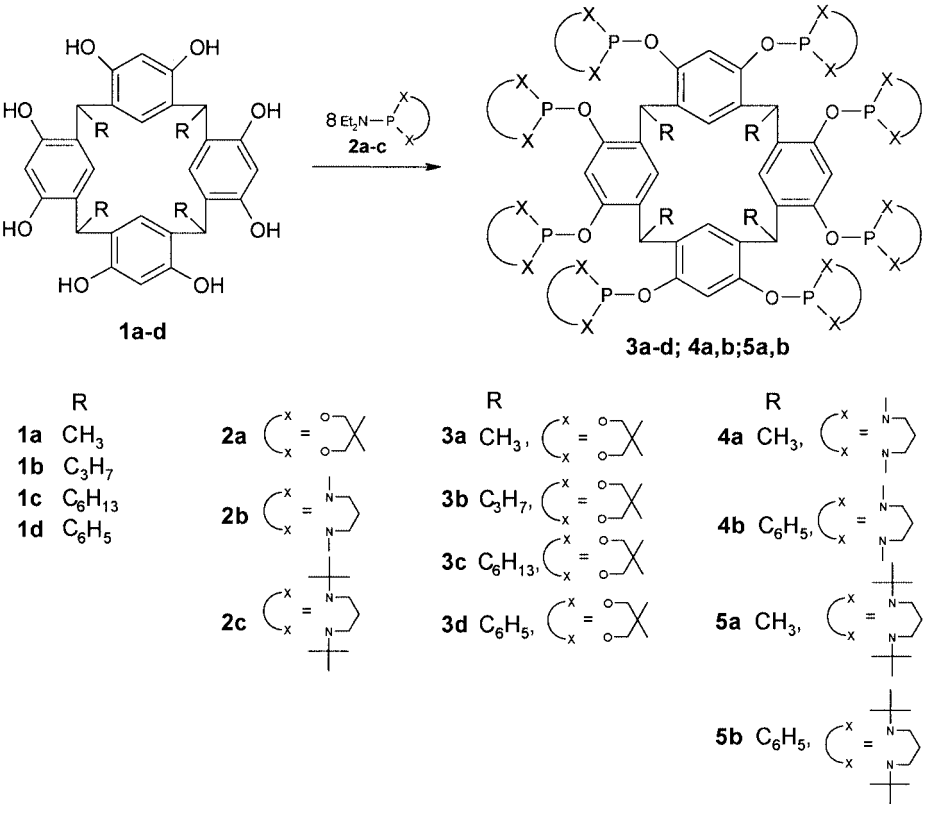
differing in the nature of the phosphoric fragment and the steric load in the phosphorinane cycle, were introduced into the reaction. Dioxaphosphorinane **2a** was a monoamidophosphite and contained a sterically hindered fragment at the periphery of the phosphorinane cycle with respect to the phosphorus atom. Diazaphosphorinanes **2b** and **2c** were triamidophosphites containing sterically hindered fragments at the phosphorus atoms.

Octaphosphorylation of Calix[4]resorcinarenes 1 by 2-Dialkylamino-1,3,2-Diheterophosphorinanes 2

The phosphorylation of resorcinarenes **1** by phosphorinanes **2** was carried out in dioxane with varying reagent ratios, temperature, and reaction time (Scheme 1).

According to the classical concepts of organophosphorus chemistry,[7] the phosphorylating capacity of amidophosphites increases in the sequence monoamidophosphites < diamidophosphites < triamidophosphites. Interaction between the resorcinarenes **1a**−**d** and dioxaphosphorinane **2a** at room temperature therefore proceeded slowly even in the presence of a large excess of phosphorylating agent and resulted in the formation of a mixture of products with different degrees of phosphorylation. The best conditions were found to be at 90−95 °C. At the same time, the octaphosphorylation of **1a** and **1d** by diazaphosphorinanes **2b** and **2c** was completed at 20−25 °C, and an increase in temperature only accelerated the process while having no effect on its selectivity.

Note that the perphosphorylation of resorcinarenes **1** by phosphorinanes **2a** and **2b** proceeded at the stoichiometric reagent ratio. At the same time, the reactions of resorcinarenes **1a** and **1d** with phosphorinane **2c**, which were conducted at the stoichiometric reagent ratio, had stopped 1 hour after the reagents were mixed. A downfield shift of the signal from **2c** ($\delta = -11$ ppm) was observed in the ^{31}P NMR spectra of the reaction mixtures. Probably, **2c** forms a complex with partly phosphorylated resorcinarene, which hampers the further development of the process. When an excess



Scheme 1. Synthesis of perphosphorylated calix[4]resorcinarenes **3**−**5**

of **2c** was added, the phosphorylation of the resorcinarene continued, the complex decomposed, and the reaction was complete in several hours. At the end of the reaction, a signal from the free original amide **2c** (δ = 98 ppm) and two singlets from phosphorylated products were observed in the ^{31}P NMR spectra of the reaction mixtures.

Under the conditions used, the synthesised compounds **3**−**5** usually precipitated from the reaction mixture, which facilitated their isolation.

The phosphocalixarenes **3a**−**d**, **4a**, **4b**, **5a** and **5b** were isolated as individual stereomers in yields of 52−76%. They were white, crystalline compounds with high melting points. The elemental analysis and molecular weight data for compounds **3**−**5** as determined by the MALDY method corresponded to the calculated values. Two singlets with equal integral intensities and very similar chemical shifts observed in the ^{31}P NMR spectra of compounds **3**−**5** indicated the presence of two magnetically non-equivalent phosphorus atoms in their molecules.

Conformation Analysis of Perphosphorylated Calix[4]-resorcinarenes 3−5

The conformations of phosphocalixarenes **3a**−**d**, **4a**, **4b**, **5a** and **5b** were determined by ^{1}H and ^{13}C NMR spectroscopy. The exact assignment of all proton and carbon signals of compounds **3a**, **3d**, **5a** and **5b** was achieved by COSY, HMBC, HSQC and ROESY measurements. The assignment of the ^{1}H and ^{13}C NMR spectra for **3b**, **3c**, **4a** and **4b** was carried out in accordance with those of **3a** and of **5a** and **5b**, respectively.

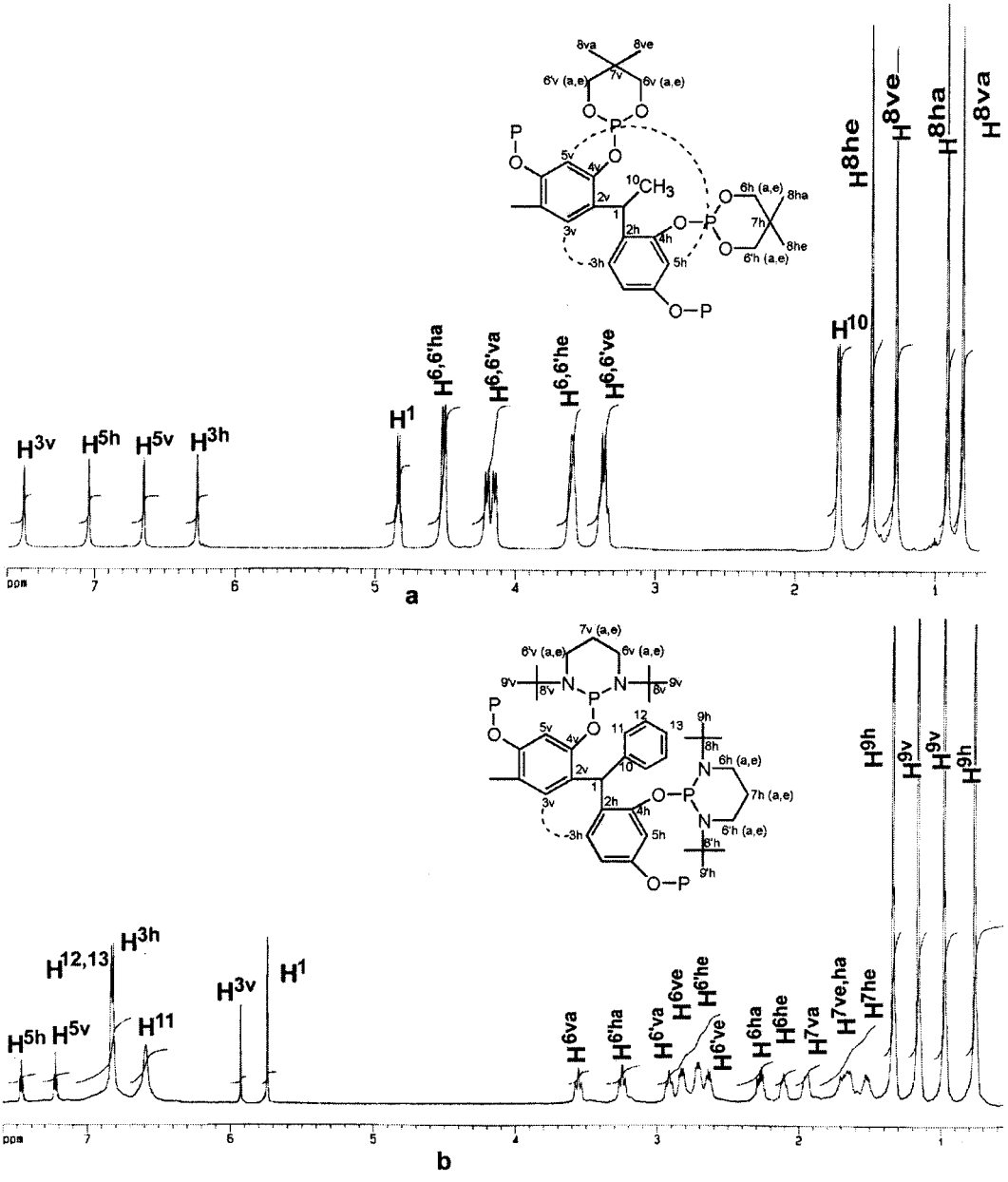


Figure 2. ^{1}H NMR spectra of compounds **3a** (a) and **5b** (b)

The ^{1}H NMR spectra of compounds **3a**−**c**, with alkyl groups in the methylidene bridges and dioxaphosphorinane substituents on the benzene rings, each display four singlets from the H^5 and H^3 protons of the benzene rings and four signals from the $H^{6,6'}$ and H^8 protons of the phosphorinane cycles (Figure 2, a). This attests to different (vertical and horizontal) arrangements of aromatic and phosphorinane cycles relative to the macrocycle plane.

The methyl protons ($H^{1\circ}$) of **3a** give rise to ROESY peaks, which differ in intensity from the H^3 protons of the vertical (H^{3v}) and planar (H^{3h}) benzene rings (see a in Figure 3). The H^{10}/H^{3h} proton pair has lower ROESY intensities than the H^{10}/H^{3v} proton pair, which indicates the axial orientation of the methyl groups and the vertical and planar assignment of the H^3 protons. This supposition is confirmed by an opposite ratio of ROESY intensities observed for the H^3 protons and the methine proton (H^1) of the hydrocarbon bridge: $H^1/H^{3h} > H^1/H^{3v}$. The presence of strongly negative exchange cross-peaks for H^{3v}/H^{3h} and H^{5v}/H^{5h} in the ROESY spectrum of **3a** (see b in Figure 3) suggests interconversion typical for the *flattened cone* conformation (Figure 1) and indicates the *all-cis* configuration of the R groups.

The presented NMR spectroscopic data agree with the results of an X-ray diffraction study of phosphocalixarene **3a**, which showed the molecule to exist in a *flattened cone* conformation and to have the *all-cis* configuration of its methyl groups (see a in Figure 4). The vertical benzene rings are almost parallel; the dihedral angle between them is 7.9°, while the planar benzene rings are arranged at an angle of 17.9°. All phosphorinane cycles are in the *chair* conformation; they are located at the periphery of the molecule and leave the molecular cavity open.

The introduction of the more sterically loaded diazaphosphorinane substituents into the molecule of resorcinarene **1a** hampers interconversion, which results in the non-equivalence of the two sides of phosphorinane cycles in the phosphocalixarenes **4a** and **5a**. In the ^{1}H NMR spectra, differences are observed between the signal parameters of the methylene protons in the 6- and 6′-positions of the vertically oriented phosphorinane cycles. In the ^{13}C NMR spectra, different chemical shifts are observed for carbon atoms in the 6- and 6′-positions of the phosphorinane cycles in both vertical and planar fragments of the molecules. Positive cross-peaks are observed for the H^{3v}/H^{3h} pair in the ROESY spectra of **5a**, but the H^{5v}/H^{5h} proton pair displays weakly negative exchange signals, which indicate very weak interconversion for this *all-cis* resorcinarenes with very long lifetimes of the *flattened cone*$_1$ and *flattened cone*$_2$ conformations (Figure 1).

The perphosphorylated resorcinarenes **3a**−**c**, **4a** and **5a** with alkyl substituents in their methylidene bridges thus all have *all-cis* alkyl group configurations and exist in *flattened cone* conformations. All the phosphorus fragments in these compounds are located on the same side of the macrocycle plane.

In the ^{1}H and ^{13}C NMR spectra of phosphocalixarenes **3d**, **4b** and **5b**, with phenyl groups in the alkylidene bridges, the non-equivalence of protons and carbon atoms on two sides of phosphorinane cycles is manifested in both the ver-

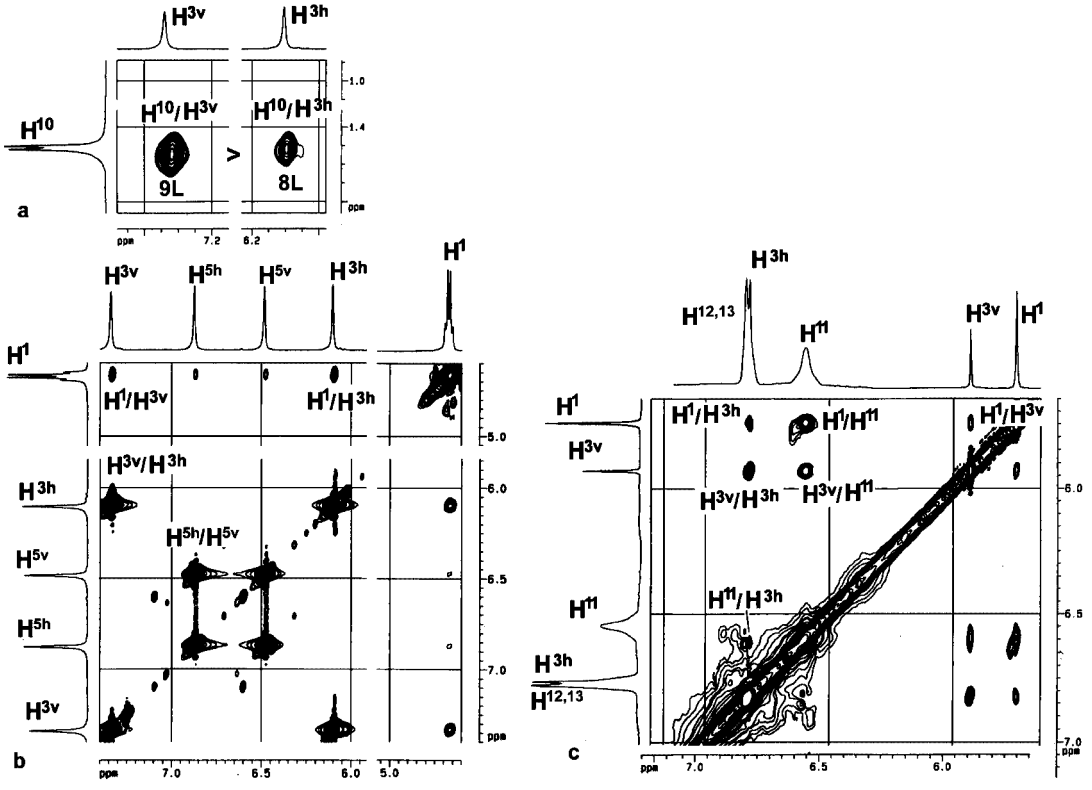
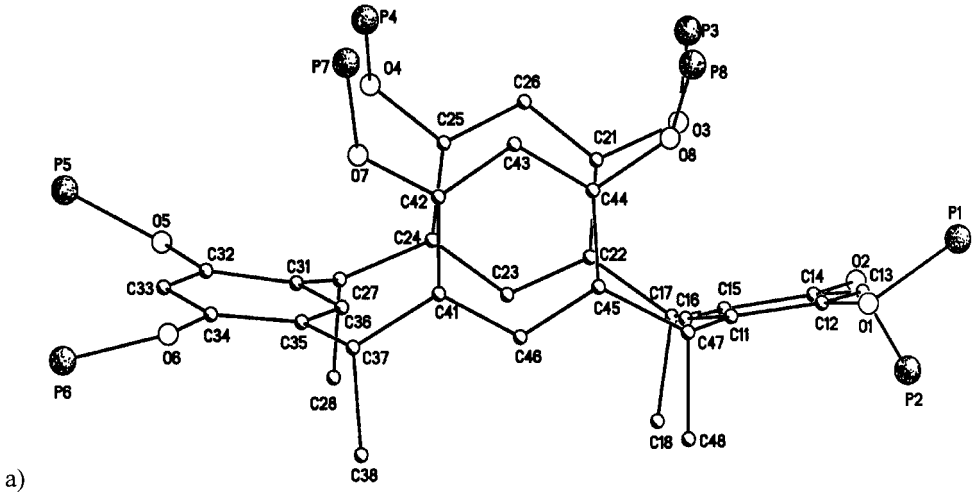


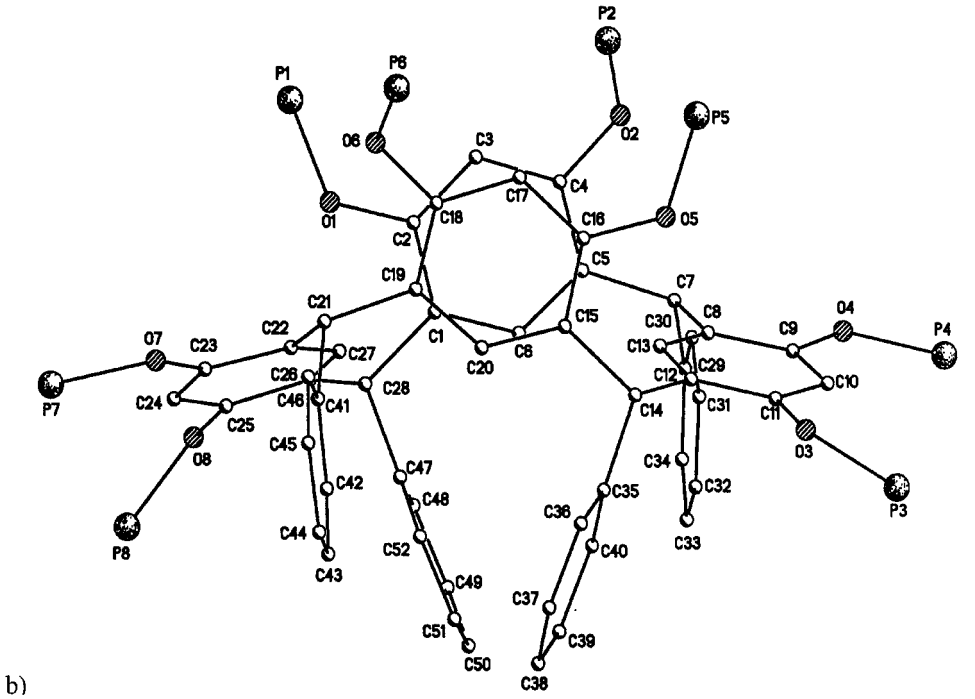
Figure 3. ROESY spectra of **3a** (a,b) and **5b** (c)

tical and the horizontal fragments of the molecule. Eight well resolved proton multiplets are observed in the ^{1}H NMR spectra of these compounds (Figure 2, b), and four carbon atom signals in the phosphorinane cycle 6- and 6′-positions are observed in their ^{13}C NMR spectra. The H^{11}/H^{3h} proton pair has a lower ROESY peak intensity than the H^{11}/H^{3v} pair (Figure 3, c), while the H^{1}/H^{3h} proton pair has a higher intensity than the H^{1}/H^{3v} pair, which indicates the axial orientation of phenyl groups in the internuclear bridges of the calixarenes. In the ROESY spectra of **3d** and **5b**, strongly positive cross-peaks are observed for the H^{3v}/H^{3h} pair and no peaks are found for the H^{5v}/H^{5h} pair (see c in Figure 3), which attests to the absence of interconversion typical for the *flattened cone* conformation. Hence, the conformations of compounds **3d**, **4b** and **5b**, which contain phenyl groups in the calixarene matrix, differ from those of alkyl derivatives **3a**−**c**, **4a** and **5a** discussed above.

In order to establish the calix[4]resorcinarene conformation in these compounds, the X-ray diffraction analysis (XRD) of single crystals of **5b**, obtained by two different synthetic routes, was undertaken. Surprisingly, it was found that the phosphocalixarene conformation is almost the same in both crystals with only slight variation of the mutual disposition of the diazaphosphorinane cycles in respect to the phenyl rings, so these crystals can be regarded as polymorph modifications. It should be noted that both crystals contain a solvate dioxane molecule and crystallised in the same $P\bar{1}$ space group with one and two independent



a)



b)

Figure 4. General views of **3a** (a) and **5b** (b), the phosphorinane cycles are omitted for clarity: a) The dihedral angles between aromatic rings are (°): C21-C26/C41−C46 7.9, C11−C16/C31−C36 17.9. C11−C16/C21−C26 87.7, C11−C16/C41−C46 84.6, C31−C36/C21−C26 75.4, C31−C36/C41−C46 119.2. b) The dihedral angles between aromatic rings are (°): C1−C6/C15−C20 25.1, C8−C13/C22−C27 39.5. C1−C6/C8−C13 116.1, C8−C13/C15−C20 89.2, C1−C6/C22−C27 84.7, C15−C20/C22−C27 119.2.

molecules in the unit cell (α- and β-modification, respectively). Since we obtained more accurate data for the α-polymorph and the geometry for two polymorphs is almost identical, all data given below are for the α-modification.

Comparison of **5b** and **3a** (b and a in Figure 4, respectively) revealed that the introduction of phenyl groups results in a significant distortion of the calix[4]resorcinarene *flattened cone* conformation. First of all, the dihedral angle between two vertical rings becomes as large as 25.1° and their mutual orientation is changed from eclipsed to staggered. Although the alkylidene carbon atoms, which form the *base of the cone*, are non-coplanar in both molecules, the puckering angle in **5b** is as large as 34.2° (compare with 11.2 ° in **3a**).

The main differences between **5b** and **3a**, however, are observed for the horizontal rings. The dihedral angle between the horizontal rings in **5b** is increased to 39.5° and these rings are oriented in the opposite direction, in contrast to **3a**, in which the upper parts of these rings are slightly inclined into the cavity. The non-equivalence of the phenyl rings can also be easily illustrated by comparison of the dihedral angles between the vertical and the horizontal rings, which vary in the ranges of 84.7−119.2° and 75.4−87.7° in **5b** and **3a**, respectively.

Although the Ph rings are in the *all-cis* configuration, the conformation for the C−Ph bonds in **5b** is close to synclinal, with the pseudotorsion angles varying in the 21.5−37.6° range, while the same values for the C−Me bonds in **3a** are 7.6−11.7°.

The diazaphosphorinane cycles in **5b** are located at the periphery of the molecule and leave the molecular cavity open, as in **3a**.

Thus, the perphosphorylated resorcinarenes **3d**, **4b** and **5b**, with phenyl substituents in the methylidene bridges, have the *all-cis* R group configuration, as do their alkyl analogues **3a**−**c**, **4a** and **5a**. However, their conformations have changed to intermediate between *flattened cone* and *1,3-alternate* because of the *repulsion* of four spatially close and axially oriented phenyl groups. The phosphorus fragments in these compounds are located on the opposite sides of the macrocycle plane.

Oxidation Reactions of P^{III}-Phosphocalixarenes 3

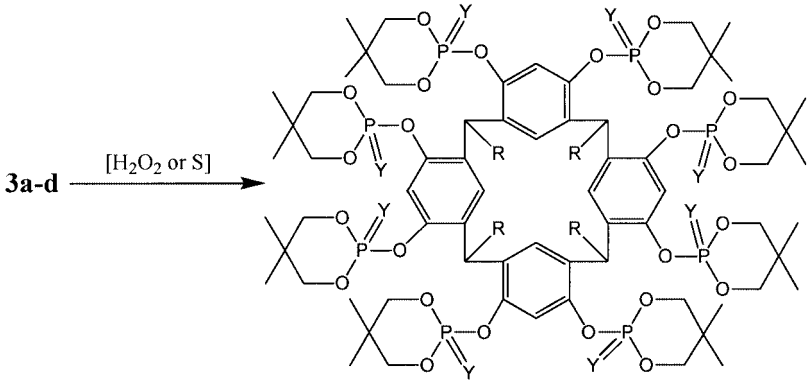
Octaphosphorylated calixarenes containing eight trivalent phosphorus atoms easily enter into oxidation reactions, which can serve as a selective method for the preparation of perphosphorylated calixarenes with pentavalent phosphorus atoms in their molecules.

The oxidation of P^{III}-phosphocalixarenes **3a**−**d** by an adduct of hydrogen peroxide and urea was performed at the stoichiometric reagent ratio (Scheme 2). Methylene chloride was used as solvent. The reactions was monitored by ^{31}P NMR spectroscopy, and at the end of the reaction the ^{31}P NMR spectra of reaction mixtures had no signals from initial phosphites **3** and showed signals in the range between −14 and −16 ppm typical for phosphates.

The sulfurisation of calixarenes **3a** and **3d** was performed by treatment of equimolar amounts of reagents in a chloroform/benzene mixture (1:1) at 80 °C for 5 h. At the end of the reaction, the ^{31}P NMR spectra of reaction mixtures showed signals in the $\delta = 51-55$ ppm range typical of thiophosphate derivatives.

Octaphosphates **6a**−**d** and octathiophosphates **7a** and **7b** were obtained in yields of 70−96%. Two singlets with similar chemical shifts and equal integral intensities were detected in the ^{31}P NMR spectra of phosphates **6a** and **6d** and thiophosphate **7b**; a broadened singlet was observed in the spectra of phosphates **6b** and **6c** and thiophosphate **7a**. The averaging of signals for calixarenes **6b**, **6c** and **7a** is due to interconversion (Figure 1).

Parameters typical for the ^{1}H and ^{13}C NMR spectra of P^{III}-phosphocalixarenes **3** remain in the spectra of P^{V}-phosphocalixarenes **6** and **7**, which indicates a structural analogy to the corresponding P^{III}- and P^{V}-octaphosphorylated resorcinarenes.



6, 7

6 Y = O, R = CH_3 (a), C_3H_7 (b), C_6H_{13} (c), C_6H_5 (d)
7 Y = S, R = CH_3 (a), C_6H_5 (b)

Scheme 2. Oxidation reactions of P^{III}-phosphocalixarenes **3**

Conclusion

Perphosphorylated calix[4]resorcinarenes with alkyl groups (**3a**−**c**, **4a**, **5a**, **6a**−**c**, **7a**) in the methylidene ridges exist in *flattened cone* conformations regardless of the steric loads of the phosphorinane fragments and the size of the alkyl groups. The substitution of alkyl groups by phenyl groups (**3d**, **4b**, **5b**, **6d**, **7b**) results in a significant distortion of the *flattened cone* conformations of the resorcinarenes, which become intermediate between the *flattened cone* and *1,3-alternate* conformations because of the *repulsion* of four spatially close axially oriented phenyl groups. The increase in the steric load of diheterophosphorinane fragments hampers interconversion (Figure 1) by stabilising one of the conformations of calix[4]resorcinarene.

Experimental Section

General: ^{1}H NMR (TMS internal reference), ^{13}C NMR (TMS internal reference) and ^{31}P NMR spectra (85% H_3PO_4 external reference) of **3b**,**c**; **4a**,**b** and **3a**,**d**, **5a**,**b** were recorded with Bruker AC 300, AMX 400 and DRX 500 spectrometers, respectively; those of **6a**−**d** and **7a** and **7b** were performed with a Bruker WM 200 spectrometer. Exact assignment of ^{1}H and ^{1}H NMR spectra was carried out by two-dimensional NMR techniques (COSY, ^{1}H/^{13}C correlated HSQC, ^{1}H/^{13}C correlated HMBC, ROESY) for **3a** and **3d** and for **5a** and **5b**.

MALDI-TOF mass spectra were measured with a Kratos Kompact MALDI II (Shimadzu Europa GmbH) with N_2-laser source (λ = 337 nm), positive polarity and 20 kV acceleration voltage. All syntheses were operated in dry solvents under argon. Calix[4]resorcinarenes **1** were synthesised by the procedures described previously.[8] 2-Amido-1,3,2-diheterophosphorinanes **2** were synthesised by the procedures described in.[9]

X-ray Crystallographic Study: Crystallographic data for **3a**, **5b** (α-form) and **5b** (β-form) are presented in Table 1. All structures were solved by direct methods and refined by full-matrix, least-squares against F^2 in the anisotropic (H-atoms isotropic) approximation, with use of the SHELXTL-97 package. The absorption correction was applied semiempirically from equivalent reflections. The positions of hydrogen atoms were calculated from the geometrical point of view and included in refinement in riding model approximation.

1. Phosphoresorcinarene 3a: A mixture of **1a** (0.231 g, 0.42 mmol) and **2a** (0.87 g, 4.25 mmol) in dioxane (1 mL) was heated at 90−95 °C for 40.5 h. The precipitate was filtered, washed with dioxane and maintained at 85−90 °C and 1 Torr for 10 h for the complete removal of dioxane and dialkylamine. Yield 68%. M.p. 283−284 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 0.64 (s, 12 H, H^{8va}), 0.75 (s, 12 H, H^{8ha}), 1.12 (s, 12 H, H^{8ve}), 1.29 (s, 12 H, H^{8he}), 1.47 (d, $^3J_{H,H}$ = 7.19 Hz, 12 H, $H^{1°}$), 3.21 (dd, $^2J_{H,H}$ = 10.39, $^3J_{P,H}$ = 23.03 Hz, 8 H, $H^{6,6've}$), 3.43 (dd, $^2J_{H,H}$ = 10.4, $^3J_{P,H}$ =

Table 1. Crystal data and structure refinement for **3a** and **5b**

	3a	**5b** (α-form)	**5b** (β-form)
Molecular formula	$C_{72}H_{104}O_{24}P_8$	$C_{140}H_{224}N_{16}O_8P_8 \cdot (C_4H_8O_2)$	$C_{140}H_{224}N_{16}O_8P_8 \cdot 3/4(C_4H_8O_2)$
Molecular mass	1601.31	2595.22	2604.20
Colour, shape	colourless, prism	yellow, prism	yellow, prism
Dimension (mm)	0.41 × 0.31 × 0.15	0.50 × 0.30 × 0.20	0.53 × 0.33 × 0.16
Diffractometer	Nonius-CCD	SMART CCD	SMART CCD
Temperature (K)	198(2) K	120(2)	120(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	21.325(4)	15.050(1)	19.712(8)
b (Å)	22.248(4)	19.334(1)	27.681(12)
c (Å)	18.951(4)	27.208(2)	29.571(13)
α (°)		100.283(2)	80.410(10)
β (°)	113.55(3)	101.892(2)	72.641(9)
γ (°)		99.586(2)	89.716(9)
V (Å^3)	8242(3)	7450.7(10)	15168(11)
Z (Z')	4(1)	2(1)	4(2)
F(000)	3392	2816	5642
$\rho_{calcd.}$ (g·cm^{-1})	1.290	1.157	1.146
Radiation, λ(Mo-K_α) (Å)	0.71073	0.71073	0.71073
Linear absorption, μ(cm^{-1})	2.40	1.54	1.52
$T_{min.}/T_{max.}$	0.9648/0.9079	0.9313/0.85291	0.9624/0.87248
Scan type	ω	ω	ω
θ range (°)	3.57−22.00	1.29−25.00	1.29−24.00
Completeness of dataset (%)	99.5	98.4	99.2
measured	77423	47914	62160
unique	10062 [R(int.) = 0.1130]	25814 (0.0443)	36904 (0.0882)
with [$I > 2\sigma(I)$]	6531	11378	16544
Parameters	988	1600	3308
final $R(F_{hkl})$: R_1	0.0528	0.0855	0.0997
wR_2	0.1045	0.2187	0.2318
GOF	1.073	1.087	1.060
$\rho_{max.}/\rho_{min.}$ (e·Å^{-3})	0.376/−0.544	0.725/−0.407	0.619/−0.415

11.00 Hz, 8 H, $H^{6,6'he}$), 4.01 (dd, $^2J_{H,H}$ = 10.11, $^3J_{P,H}$ = 27.17 Hz, 8 H, $H^{6,6'va}$), 4.35 (d, $^2J_{H,H}$ = 9.92 Hz, 8 H, $H^{6,6'ha}$), 4.67 (q, $^3J_{H,H}$ = 7.0 Hz, 4 H, H^1), 6.10 (s, 2 H, H^{3h}), 6.49 (s, 2 H, H^{5v}), 6.88 (s, 2 H, H^{5h}), 7.34 (s, 2 H, H^{3v}) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 20.55 (s, C^{1o}), 22.45 (s, C^{8e}), 22.63 (s, C^{8a}), 31.62 (s, C^1), 32.53 (s, C^{7v}), 32.70 (d, $^3J_{P,C}$ = 3.68 Hz, C^{7h}), 69.19 (s, $C^{6,6'v}$), 69.27 (s, $C^{6,6'h}$), 108.46 (t, $^3J_{P,C}$ = 10.33 Hz, C^{5h}), 110.50 (t, $^3J_{P,C}$ = 13.62 Hz, C^{5v}), 125.83 (s, C^{3h}), 126.15 (s, C^{3v}), 129.21 (s, C^{2v}), 133.09 (s, C^{2h}), 147.12 (d, $^2J_{P,C}$ = 7.16 Hz, C^{4h}), 149.12 (s, C^{4v}) ppm. ^{31}P NMR (202.47 MHz, $CDCl_3$, 25 °C): δ = 114.54, 115.01 ppm. MS (MALDI): *m/z* (%) = 1602 (10) [M^+],1666 (100) [M^+] + Na^+ + K^+. $C_{72}H_{104}O_{24}P_8$ (1601.37): calcd. C 54.00, H 6.55, P 15.47; found C 54.09, H 6.61, P 15.50.

2. Phosphoresorcinarene 3b: This compound was obtained analogously to **3a**, by treatment of **1b** (0.06 g, 0.91 mmol) with **2a** (0.14 g, 7.28 mmol) for 38 h. Yield 65%. M.p. 234−235 °C. ^{1}H NMR (300.17 MHz, $CDCl_3$, 25 °C): δ = 0.66 (s, 12 H, H^{8va}), 0.79 (s, 12 H, H^{8ha}), 0.92 [t, $^3J_{H,H}$ = 7.26 Hz, 12 H, $(CH_2)_2CH_3$], 1.15 (s, 12 H, H^{8ve}), 1.25 (s, 12 H, H^{8he}), 1.31 (m, 8 H, $CH_2CH_2CH_3$), 1.87 (m, $^3J_{H,H}$ = 7.61 Hz, 8 H, $CH_2CH_2CH_3$), 3.24 (dd, $^3J_{H,H}$ = 9.82, $^3J_{P,H}$ = 8.25 Hz, 8 H, $H^{6,6've}$), 3.47 (dd, $^3J_{H,H}$ = 9.94, $^3J_{P,H}$ = 8.75 Hz, 8 H, $H^{6,6'he}$), 4.0 (br. s, 8 H, $H^{6,6'va}$), 4.38 (d, $^3J_{H,H}$ = 9.69 Hz, 8 H, $H^{6,6'ha}$), 4.59 (t, $^3J_{H,H}$ = 7.34 Hz, 4 H, H^1), 6.21 (s, 2 H, H^{3h}), 6.57 (s, 2 H, H^{5v}), 6.93 (s, 2 H, H^{5h}), 7.31 (s, 2 H, H^{3v}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 14.21 [s, $(CH_2)_2CH_3$], 21.11 (s, $CH_2CH_2CH_3$), 22.47 (s, C^{8e}), 22.64 (s, C^{8a}), 28.74 (s, $CH_2CH_2CH_3$), 32.64 (s, C^7), 37.47 (s, C^1), 69.23 (s, $C^{6,6'}$), 108.11 (t, $^3J_{P,C}$ = 12.80 Hz, C^{5h}), 110.45 (t, $^3J_{P,C}$ = 14.40 Hz, C^{5v}), 126.60 (s, C^{3h}), 126.80 (s, C^{3v}), 127.07 (s, C^{2v}), 132.04 (s, C^{2h}), 147.96 (d, $^2J_{P,C}$ = 7.1 Hz, C^{4h}), 149.72 (s, C^{4v}) ppm. ^{31}P NMR (121.48 MHz, $CDCl_3$, 25 °C): δ = 114.30, 114.76 ppm. MS (MALDI): *m/z* (%) = 1715 (30) [M^+], 1779 (100) [M^+] + Na^+ + K^+. $C_{80}H_{120}O_{24}P_8$ (1713.58): calcd. C 56.07, H 7.06, P 14.46; found C 56.12, H 7.03, P 14.51.

3. Phosphoresorcinarene 3c: The compound was obtained analogously to **3a** by treatment of **1c** (0.099 g, 0.12 mmol) with **2a** (0.19 g, 9.7 mmol) for 20 h. The product was precipitated with acetonitrile (5 mL). Yield 52%. M.p. 151−152 °C. ^{1}H NMR (300.17 MHz, $CDCl_3$, 25 °C): δ = 0.66 (s, 12 H, H^{8va}), 0.79 (s, 12 H, H^{8ha}), 0.84 [t, $^3J_{H,H}$ = 6.59 Hz, 12 H, $(CH_2)_5CH_3$], 1.15 (s, 12 H, H^{8ve}), 1.24 (s, 12 H, H^{8he}), 1.33 [m, 32 H, $CH_2(CH_2)_4CH_3$], 1.94 [m, $^3J_{H,H}$ = 7.24 Hz, 8 H, $CH_2(CH_2)_4CH_3$], 3.24 (dd, $^3J_{H,H}$ = 10.33, $^3J_{P,H}$ = 10.26 Hz, 8 H, $H^{6,6've}$), 3.46 (dd, $^3J_{H,H}$ = 8.50, $^3J_{H,H}$ = 7.71 Hz, 8 H, $H^{6,6'he}$), 4.00 (d, $^3J_{H,H}$ = 9.91 Hz, 8 H, $H^{6,6'va}$), 4.39 (d, $^3J_{H,H}$ = 9.95 Hz, 8 H, $H^{6,6'ha}$), 4.60 (t, $^3J_{H,H}$ = 7.13 Hz, 4 H, H^1), 6.20 (s, 2 H, H^{3h}), 6.58 (s, 2 H, H^{5v}), 6.94 (s, 2 H, H^{5h}), 7.31 (s, 2 H, H^{3v}) ppm. ^{13}C NMR (75.47 MHz, $CDCl_3$, 25 °C): δ = 14.02 [s, $(CH_2)_5CH_3$], 22.54 [s, $(CH_2)_4CH_2CH_3$, H^{8e}], 22.76 (s, H^{8a}), 28.74 [s, $(CH_2)_3CH_2CH_2CH_3$], 29.87 [s, $(CH_2)_2CH_2(CH_2)_2CH_3$], 31.94 [s, $CH_2CH_2(CH_2)_3CH_3$], 32.62 (s, C^{7v}), 32.77 (s, C^{7h}), 35.94 [s, $CH_2(CH_2)_4CH_3$], 37.15 (s, C^1), 69.31 (s, $C^{6,6'}$), 108.12 (t, $^3J_{P,C}$ = 15.09 Hz, C^{5h}), 110.54 (t, $^3J_{P,C}$ = 15.09 Hz, C^{5v}), 126.52 (s, C^{3h}), 126.80 (s, C^{3v}), 127.10 (s, C^{2v}), 132.12 (s, C^{2h}), 148.11 (d, $^2J_{P,C}$ = 7.08 Hz, C^{4h}), 149.77 (s, C^{4v}) ppm. ^{31}P NMR (121.48 MHz, $CDCl_3$, 25 °C): δ = 114.27, 114.71 ppm. MS (MALDI): *m/z* (%) = 1885 (18) [M^+],1949 (100) [M^+] + Na^+ + K^+. $C_{92}H_{144}O_{24}P_8$ (1881.90): calcd. C 58.72, H 7.71, P 13.17; found C 58.75, H 7.78, P 13.12.

4. Phosphoresorcinarene 3d: The compound was obtained analogously to **3a** by treatment of **1d** (0.121 g, 0.15 mmol) with **2a** (0.25 g, 1.42 mmol) for 37.5 h. Yield 72%. M.p. 318−319 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$, 25 °C): δ = 0.34 (s, 12 H, H^{8ha}), 0.63 (s, 12 H, H^{8va}), 1.07 (s, 12 H, H^{8he}), 1.15 (s, 12 H, H^{8ve}), 2.99 (dd, $^2J_{H,H}$ = 10.45, $^3J_{P,H}$ = 10.45 Hz, 4 H, $H^{6'he}$), 3.12 (dd, $^2J_{H,H}$ = 10.62, $^3J_{P,H}$ = 10.68 Hz, 4 H, H^{6he}), 3.21 (dd, $^2J_{H,H}$ = 10.62, $^3J_{P,H}$ = 10.59 Hz, 4 H, $H^{6've}$), 3.28 (dd, $^2J_{H,H}$ = 10.62, $^3J_{P,H}$ = 10.39 Hz, 4 H, H^{6ve}), 3.43 (dd, $^2J_{H,H}$ = 10.57, $^3J_{P,H}$ = 2.37 Hz, 4 H, $H^{6'ha}$), 3.72 (dd, $^2J_{H,H}$ = 10.45, $^3J_{P,H}$ = 2.23 Hz, 4 H, H^{6ha}), 4.00 (dd, $^2J_{H,H}$ = 10.75, $^3J_{P,H}$ = 1.81 Hz, 4 H, $H^{6'va}$), 4.06 (dd, $^2J_{H,H}$ = 10.62, $^3J_{P,H}$ = 1.70 Hz, 4 H, H^{6va}), 5.79 (s, 4 H, H^1), 5.85 (s, 2 H, H^{3v}), 6.34 (s, 2 H, H^{3h}), 6.66 (s, 2 H, H^{5v}), 6.72 (br. s, 8 H, H^{11}), 6.86 (s, 2 H, H^{5h}), 6.93- 6.99 (m, 12 H, $H^{12,13}$) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 22.15 (s, C^{8ha}), 22.27 (s, C^{8he}), 22.39 (s, C^{8ve}), 22.60 (s, C^{8va}), 32.29 (d, $^3J_{P,C}$ = 4.73 Hz, C^{7h}), 32.56 (d, $^3J_{P,C}$ = 4.21 Hz, C^{7v}), 43.96 (s, C^1) 68.61 (s, $C^{6'h}$), 69.27 (s, C^{6h}), 69.29 (s, $C^{6'v}$), 69.33 (s, C^{6v}), 106.32 (t, $^3J_{P,C}$ = 18.25 Hz, C^{5h}), 109.46 (t, $^3J_{P,C}$ = 15.69 Hz, C^{5v}), 125.53 (s, C^{13}), 127.14 (s, C^{2h}), 127.82 (s, C^{12}), 128.22 (s, C^{2v}), 128.46 (s, C^{11}), 129.71 (s, C^{3h}), 133.77 (s, C^{3v}), 143.48 (s, C^{1o}), 149.20 (d, $^2J_{P,C}$ = 7.79 Hz, C^{4v}), 149.44 (d, $^2J_{P,C}$ = 6.75 Hz, C^{4h}) ppm. ^{31}P NMR (202.47 MHz, $CDCl_3$, 25 °C): δ = 113.76, 115.88 ppm. MS (MALDI): *m/z* (%) = 1852 (50) [M^+],1916 (100) [M^+] + Na^+ + K^+. $C_{92}H_{112}O_{24}P_8$ (1849.65): calcd. C 59.74, H 6.10, P 13.40; found C 59.85, H 6.18, P 13.47.

5. Phosphoresorcinarene 4a: The compound was obtained analogously to **3a** by treatment of **1a** (0.1046 g, 0.192 mmol) with **2b** (0.3982 g, 1.54 mmol) at 20−25 °C for 48 h. Yield 73%. M.p. 222−223 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.50 (d, $^3J_{H,H}$ 7.20 Hz, 12 H, C^{1o}), 1.51 (m, 4 H, H^{7ve}), 1.68 (m, 4 H, H^{7he}), 1.86 (m, 4 H, H^{7va}), 2.08 (m, 4 H, H^{7ha}), 2.37 (d, $^3J_{H,H}$ = 16.00 Hz, 12 H, $N-CH_3^v$), 2.40 (m, 4 H, $H^{6've}$), 2.49 (m, 4 H, H^{6va}), 2.59 (d, $^3J_{H,H}$ = 16.40 Hz, 12 H, $N-CH_3^v$), 2.65 (m, 8 H, $H^{6,6'he}$), 2.72 (d, $^3J_{H,H}$ = 16.81 Hz, 12 H, $N-CH_3^h$), 2.73 (d, $^3J_{H,H}$ = 16.01 Hz, 12 H, $N-CH_3^h$), 2.78 (m, 4 H, H^{6ve}), 3.08 (m, 4 H, H^{6va}), 3.31 (m, 8 H, $H^{6,6'ha}$), 4.70 (q, $^3J_{H,H}$ = 6.82 Hz, 4 H, H^1), 6.44(s, 2 H, H^{3h}), 6.83 (t, $^4J_{P,H}$ = 2.8 Hz, 2 H, H^{5v}), 6.95 (t, $^4J_{P,H}$ = 2.8 Hz, 2 H, H^{5h}), 7.27 (s, 2 H, H^{3v}) ppm. ^{13}C NMR (100.61 MHz, $CDCl_3$, 25 °C): δ = 22.00 (s, C^{1o}), 24.81 (s, C^{7h}), 25.43 (s, C^{7v}), 30.77 (s, C^1), 39.84 (d, $^2J_{P,C}$ = 31.69 Hz, $N-CH_3^h$), 39.89 (d, $^2J_{P,C}$ = 31.79 Hz, $N-CH_3^v$), 40.09 (d, $^2J_{P,C}$ = 31.39 Hz, $N-CH_3^v$), 43.86 (d, $^2J_{P,C}$ = 5.53 Hz, $C^{6'v}$), 44.47 (d, $^2J_{P,C}$ = 5.73 Hz, C^{6v}), 44.58 (d, $^2J_{P,C}$ = 5.73 Hz, $C^{6'h}$), 44.77 (d, $^2J_{P,C}$ = 5.73 Hz, C^{6h}), 107.56 (t, $^3J_{P,C}$ = 21.23 Hz, C^{5v}), 107.65 (t, $^3J_{P,C}$ = 18.01 Hz, C^{5h}), 124.72 (s, C^{3h}), 125.91 (s, C^{2v}), 129.11 (s, C^{3v}), 130.24 (s, C^{2h}), 151.18 (s, C^{4h}), 151.79 (s, C^{4v}) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 123.21, 123.55 ppm. MS (MALDI): *m/z* (%)= 1589 (30) [M^+]. $C_{72}H_{120}N_{16}O_8P_8$ (1585.62): calcd. C 54.54, H 7.63, N 14.13, P 15.63; found C 54.50, H 7.66, N 14.15, P 15.60.

6. Phosphoresorcinarene 4b: The compound was obtained analogously to **4a** by treatment of **1d** (0.1378 g, 0.174 mmol) with **2b** (0.2825 g, 1.39 mmol). Yield 76%. M.p. 228−229 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 1.31 (m, 4 H, H^{7he}), 1.51 (m, 4 H, H^{7ve}), 1.78 (m, 4 H, H^{7ha}), 1.90 (m, 4 H, H^{7va}), 1.98 (d, $^3J_{P,H}$ = 16.81 Hz, 12 H, $N-CH_3^h$), 2.09 (m, 4 H, H^{6he}), 2.28 (m, 4 H, H^{6ha}), 2.40 (m, 4 H, $H^{6've}$), 2.44 (d, $^3J_{P,H}$ = 16.01 Hz, 12 H, $N-CH_3^v$), 2.53 (m, 4 H, $H^{6'he}$), 2.55 (d, $^3J_{P,H}$ = 16.80 Hz, 12 H, $N-CH_3^v$), 2.60 (m, 4 H, H^{6ve}), 2.65 (d, $^3J_{P,H}$ = 16.41 Hz, 12 H, $N-CH_3^h$), 2.73 (m, 4 H, $H^{6'ha}$), 2.93 (m, 4 H, $H^{6'va}$), 3.11 (m, 4 H, H^{6va}), 5.80 (s, 4 H, H^1), 5.93 (s, 2 H, H^{3v}), 6.60 (s, 2 H, H^{3h}), 6.73 (br. s., 8 H, H^{11}), 6.85 (t, $^4J_{P,H}$ = 2.4 Hz, 2 H, H^{5v}), 6.92 (m, 12 H, $H^{12,13}$), 7.06 (t, $^4J_{P,H}$ = 2.8 Hz, 2 H, H^{5h}) ppm. ^{13}C NMR (100.61 MHz, CDC_3, 25 °C): δ = 24.98 (s, C^{7h}), 25.25 (s, C^{7v}), 39.11 (d, $^2J_{P,C}$ = 30.59 Hz, $N-CH_3^h$), 39.76 (d, $^2J_{P,C}$ = 30.28 Hz, $N-CH_3^h$), 40.01 (d, $^2J_{P,C}$ = 30.28 Hz, $N-CH_3^v$), 40.31 (d, $^2J_{P,C}$ = 30.01 Hz, $N-CH_3^v$), 40.77 (s, C^1), 43.59 (d, $^2J_{P,C}$ = 5.53 Hz, C^{6h}),

43.86 (d, $^2J_{P,C}$ = 5.43 Hz, $C^{6'h}$), 44.23 (d, $^2J_{P,C}$ = 5.33 Hz, $C^{6'v}$), 44.77 (d, $^2J_{P,C}$ = 5.83 Hz, $C^{6}{}_{v}$), 105.02 (t, $^3J_{P,C}$ = 23.04 Hz, C^{5h}), 107.01 (t, $^3J_{P,C}$ = 19.62 Hz, C^{5v}), 124.55 (s, C^{13}), 124.60 (s, C^{2h}), 126.02 (s, C^{2v}), 127.57 (s, $C^{11,12}$), 129.64 (s, C^{3h}), 135.70 (s, C^{3v}), 145.99(s, $C^{1\circ}$), 151.28 (d, $^2J_{P,C}$ = 6.04 Hz, C^{4v}), 152.56 (d, $^2J_{P,C}$ = 6.04 Hz, C^{4h}) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$, 25 °C): δ = 121.76, 123.51 ppm. MS (MALDI): *m/z* (%) = 1830 (20) [M^+]. $C_{92}H_{128}N_{16}O_8P_8$ (1833.89): calcd. C 60.25, H 7.04, N 12.22, P 13.51; found C 60.20, H 6.99, N 12.10, P 13.55.

7. Phosphoresorcinarene 5a: The compound was obtained analogously to **4a** by treatment of **1a** (0.1046 g, 0.192 mmol) with **2c** (0.3982 g, 1.54 mmol). Yield 63%. M.p. 250−252 °C. ^{1}H NMR (500 MHz, CDC_3, 25 °C): $\boldsymbol{\delta}$ = 1.00 (s, 12 H, $H^{9'v}$), 1.11 (s, 12 H, H^{9v}), 1.22 (s, 12 H, H^{9h}), 1.31 (s, 12 H, $H^{9'h}$), 1.42 (d, $^3J_{H,H}$ = 6.87 Hz, 12 H, $H^{1\circ}$), 1.68 (m, 4 H, H^{7ve}), 1.85 (m, 8 H, $H^{7he,va}$), 2.20 (m, 4 H, H^{7ha}), 2.57 (m, 4 H, $H^{6'ev}$), 2.73 (m, 4 H, $H^{6'va}$), 2.77 (m, 4 H, H^{6ve}), 2.94 (m, 8 H, $H^{6,6'he}$), 3.39 (m, 8 H, $H^{6,6'ha}$), 3.50 (m, 4 H, H^{6va}), 4.52 (q, $^3J_{H,H}$ = 6.98 Hz, 4 H, H^1), 6.64 (s, 2 H, H^{3h}), 7.16 (s, 2 H, H^{3v}), 7.21 (t, $^4J_{P,H}$ = 4.23 Hz, 2 H, H^{5v}), 7.49 (t, $^4J_{P,H}$ = 4.10 Hz, 2 H, H^{5h}) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): $\boldsymbol{\delta}$ = 23.94 (s, $C^{1\circ}$), 26.60 (s, C^{7h}), 27.63 (s, C^{7v}), 29.44 (d, $^3J_{P,C}$ = 14.91 Hz, $C^{9\ or\ 9'}$), 29.65 (d, $^3J_{P,C}$ = 15.28 Hz, $C^{9\ or\ 9'}$), 29.90 (d, $^3J_{P,C}$ = 14.57 Hz, $C^{9\ or\ 9'}$), 29.92 (d, $^3J_{P,C}$ = 14.56 Hz, $C^{9\ or\ 9'}$), 31.37 (s, C^1), 38.28 (s, $C^{6'v}$), 38.63 (s, C^{6v}), 39.38 (s, $C^{6'h}$), 39.60 (s, C^{6h}), 54.66 (d, $^3J_{P,C}$ = 20.00 Hz, $C^{8\ or\ 8'}$), 54.83 (d, $^3J_{P,C}$ = 18.16 Hz, $C^{8\ or\ 8'}$), 55.01 (d, $^3J_{P,C}$ = 19.38 Hz, $C^{8\ or\ 8'}$), 55.03 (d, $^3J_{P,C}$ = 19.38 Hz, $C^{8\ or\ 8'}$), 106.59 (t, $^3J_{P,C}$ = 28.42 Hz, C^{5v}), 107.66 (t, $^3J_{P,C}$ = 25.77 Hz, C^{5h}), 124.81 (s, C^{2v}), 125.90 (s, C^{3h}), 129.16 (s, C^{2h}), 130.24 (s, C^{3v}), 151.46 (d, $^2J_{P,C}$ = 10.22 Hz, C^{4h}), 151.64 (d, $^2J_{P,C}$ = 10.43 Hz, C^{4v}) ppm. ^{31}P NMR (202.47 MHz, $CDCl_3$, 25 °C): $\boldsymbol{\delta}$ = 113.23, 114.93 ppm. MS (MALDI): *m/z* (%) = 2258 (100) [M^+]. $C_{120}H_{216}N_{16}O_8P_8$ (2258.89): calcd. C 63.75, H 9.56, N 9.92, P 10.98; found C 63.69, H 9.55, N 9.13, P 10.57.

8. Phosphoresorcinarene 5b. Method A: The compound was obtained analogously to **3a** by treatment of **1d** (0.1046 g, 0.17 mmol) with **2c** (0.3574 g, 1.74 mmol) for 3 h. Yield 70%. m.p. 267−269 °C. **Method B:** The compound was obtained analogously to **4a** by treatment of **1d** (0.1029 g, 0.15 mmol) with **2c** (0.2692 g, 1.54 mmol). Yield 76%. M.p. 267−269 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.79 (s, 12 H, H^{9h}), 1.07 (s, 12 H, $H^{9'v}$), 1.20 (s, 24 H, $H^{9v,9'h}$), 1.54 (m, 4 H, H^{7he}), 1.67 (m, 8 H, $H^{7ve,ha}$), 1.95 (m, 4 H, H^{7va}), 2.12 (m, 4 H, H^{6he}), 2.28 (m, 4 H, H^{6ha}), 2.65 (m, 4 H, $H^{6'ev}$), 2.72 (m, 4 H, $H^{6'he}$), 2.84 (m, 4 H, H^{6ve}), 2.93 (m, 4 H, $H^{6'va}$), 3.26 (m, 4 H, $H^{6'ha}$), 3.57 (m, 4 H, H^{6va}), 5.75 (s, 4 H, H^1), 5.93 (s, 2 H, H^{3v}), 6.60 (br. s., 8 H, H^{11}), 6.83 (s, 2 H, H^{3h}), 6.84 (m, 12 H, $H^{12,13}$), 7.24 (t, $^4J_{P,H}$ = 4.26 Hz, 2 H, H^{5v}), 7.48 (t, $^4J_{P,H}$ = 5.51 Hz, 2 H, H^{5h}) ppm. ^{13}C NMR (125.77 MHz, $CDCl_3$, 25 °C): δ = 26.80(s, C^{7h}), 27.26(s, C^{7v}), 29.50 (d, $^3J_{P,C}$ = 14.69 Hz, $C^{9\ or\ 9'}$), 29.56 (d, $^3J_{P,C}$ = 15.54 Hz, $C^{9\ or\ 9'}$), 29.69 (d, $^3J_{P,C}$ = 15.73 Hz, $C^{9\ or\ 9'}$), 29.93 (d, $^3J_{P,C}$ = 15.14 Hz, $C^{9\ or\ 9'}$), 38.04 (s, C^{6h}), 38.69 (s, $C^{6'h,v}$), 38.98 (s, C^{6v}), 43.09 (s, C^1), 54.30 (d, $^3J_{P,C}$ = 24.22 Hz, C^{8h}), 54.77 (d, $^3J_{P,C}$ = 22.96 Hz, $C^{8'h}$), 55.02 (d, $^3J_{P,C}$ = 20.59 Hz, C^{8v}), 55.07 (d, $^3J_{P,C}$ = 21.76 Hz, $C^{8'v}$), 105.39 (t, $^3J_{P,C}$ = 27.86 Hz, C^{5h}), 106.06 (t, $^3J_{P,C}$ = 29.06 Hz, C^{5v}), 122.93 (s, C^{2h}), 123.76 (s, C^{13}), 125.01 (s, C^{2v}), 127.38 (s, C^{12}), 127.57 (s, C^{11}), 130.65 (s, C^{3h}), 136.97 (s, C^{3v}), 147.93 (s, $C^{1\circ}$), 151.41 (d, $^2J_{P,C}$ = 10.89 Hz, C^{4v}), 152.48 (d, $^2J_{P,C}$ = 10.20 Hz, C^{4h}) ppm. ^{31}P NMR (202.47 MHz, $CDCl_3$, 25 °C): δ = 111.99, 115.85 ppm. MS (MALDI): *m/z* (%) = 2511 (100) [M^+]. $C_{140}H_{228}O_8N_{16}P_8$ (2507.17): calcd. C 66.94, H 9.15, N 8.92, P 9.84; found C 60.11, H 9.74, N 8.63, P 9.73.

9. Phosphoresorcinarene 6a: A solution of phosphocalixarene **3a** (0.1478 g, 0.0923 mmol) in CH_2Cl_2 (1 mL) was added to an adduct of hydrogen peroxide and urea (0.0694 g, 0.738 mmol). The reaction mixture was maintained at 20−25 °C for 4 h. The precipitate was filtered off, the filtrate was washed with water, and the organic layer was separated. The solvent was completely removed, and the product was dried in vacuo (1 Torr) at 85−90 °C. Yield 70%. M.p. 209−210 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 0.81 (s, 12 H, H^{8va}), 0.90 (s, 12 H, H^{8ha}), 1.15 (s, 12 H, H^{8ve}), 1.33 (s, 12 H, H^{8he}), 1.53 (d, $^3J_{H,H}$ = 7.25 Hz, 12 H, $H^{1\circ}$), 3.84 (m, 8 H, $H^{6,6've}$), 4.04 (d, $^3J_{H,H}$ = 12.81 Hz, 8 H, $H^{6,6'he}$), 4.34 (d, $^3J_{H,H}$ = 11.10 Hz, 8 H, $H^{6,6'va}$), 4.48 (d, $^3J_{H,H}$ = 9.39 Hz, 8 H, $H^{6,6'ha}$), 4.75 (q, $^3J_{H,H}$ = 7.25 Hz, 4 H, H^1), 5.95 (s, 2 H, H^{3h}), 6.95 (s, 2 H, H^{5v}), 7.39 (s, 2 H, H^{5h}), 7.44 (s, 2 H, H^{3v}) ppm. ^{31}P NMR (80.97 MHz, $CDCl_3$, 30 °C): δ = −14.18, −14.40 ppm. $C_{72}H_{104}O_{32}P_8$ (1729.37): calcd. C 50.01, H 6.06, P 14.33; found C 50.06, H 6.12, P 14.37.

10. Phosphoresorcinarene 6b: The compound was obtained analogously to **6a** by treatment of **3b** (0.078 g, 0.0446 mmol) with an adduct of hydrogen peroxide and urea (0.0335 g, 0.357 mmol). Yield 70%. M.p. 289−290 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 0.85 (br. s, 24 H, H^{8a}), 0.97 [t, 12 H, $^3J_{H,H}$ = 7.61 Hz, $(CH_2)_2CH_3$], 1.25 (br. s, 24 H, H^{8e}), 1.35 (m, 8 H, $CH_2CH_2CH_3$), 1.83 (m, $^3J_{H,H}$ = 6.59 Hz, 8 H, $CH_2CH_2CH_3$), 3.9−4.36 (m, 32 H, $H^{6,6'}$), 4.64 (t, $^3J_{H,H}$ = 6.59 Hz, 4 H, H^1), 6.10 (s, 2 H, H^{3h}), 6.57 (s, 2 H, H^{5v}), 7.05 (s, 2 H, H^{5h}), 7.44 (s, 2 H, H^{3v}) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$, 30 °C): δ = 13.83 [s, $(CH_2)_2CH_3$] 19.63 (s, $CH_2CH_2CH_3$), 21.04 (s, C^{8e}), 21.44 (s, C^{8a}), 29.36 (s, $CH_2CH_2CH_3$), 36.17 (s, C^1), 36.48 (s, C^7), 76.36 (s, $C^{6,6'v}$), 77.00 (s, $C^{6,6'h}$), 108.73 (br. s, C^{5h}), 111.49 (br. s, C^{5v}), 126.49 (s, C^{3h}), 126.71 (s, C^{3v}), 128.21 (s, C^{2v}), 132.29 (s, C^{2h}), 145.89 (br. s, C^{4h}), 147.33 (br. s, C^{4v}) ppm. ^{31}P NMR (80.97 MHz, $CDCl_3$, 30 °C): δ = −14.41 ppm. $C_{80}H_{120}O_{32}P_8$ (1841.58): calcd. C 52.18, H 6.57, P 13.46; found C 52.21, H 6.53, P 13.41.

11. Phosphoresorcinarene 6c: The compound was obtained analogously to **6a** by treatment of **3c** (0.0516 g, 0.027 mmol) with an adduct of hydrogen peroxide and urea (0.0205 g, 0.218 mmol). Yield 95.8%. M.p. 152−153 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 0.85 (br. s, 24 H, H^{8a}), 0.88 [t, $^3J_{H,H}$ = 6.81 Hz, 12 H, $(CH_2)_5CH_3$], 1.25 (br. s, 24 H, H^{8e}), 1.33 [m, 32 H, $CH_2(CH_2)_4CH_3$], 1.95 [m, $^3J_{H,H}$ = 6.73 Hz, 8 H, $CH_2(CH_2)_4CH_3$], 3.98−4.30 (m, 32 H, $H^{6,6'}$), 4.61 (t, $^3J_{H,H}$ = 6.59 Hz, 4 H, H^1), 6.00 (s, 2 H, H^{3h}), 6.58 (s, 2 H, H^{5v}), 7.00 (s, 2 H, H^{5h}), 7.45 (s, 2 H, H^{3v}) ppm. ^{31}P NMR (80.97 MHz, $CDCl_3$, 30 °C): δ = −14.23 ppm. $C_{92}H_{144}O_{32}P_8$ (2009.90): calcd. C 54.98, H 7.22, P 12.33; found C 54.94, H 7.26, P 12.36.

12. Phosphoresorcinarene 6d: The compound was obtained analogously to **6a** by treatment of **3d** (0.065 g, 0.0351 mmol) with an adduct of hydrogen peroxide and urea (0.028 g, 0.294 mmol). Yield 87%. M.p. 243−244 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 0.54 (s, 12 H, H^{8ha}), 0.87 (s, 12 H, H^{8va}), 1.15 (s, 12 H, H^{8he}), 1.22 (s, 12 H, H^{8ve}), 3.57−3.97 (m, 32 H, $H^{6,6'}$), 5.83 (s, 2 H, H^{3v}), 5.96 (s, 4 H, H^1), 6.15 (s, 2 H, H^{3h}), 6.70 (br. s., 8 H, C^{11}), 7.04 (m, 12 H, $C^{12,13}$), 7.29 (s, 2 H, H^{5v}),.7.64 (s, 2 H, H^{5h}) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$, 30 °C): δ = 19.63 (s, C^{8h}), 21.47 (s, C^{8v}), 31.59 (d, $^2J_{P,C}$ = 5.88 Hz, C^{7h}), 31.9 (d, $^2J_{P,C}$ = 5.80 Hz C^{7v}), 43.80 (s, C^1), 76.36 (s, $C^{6,6'h}$), 77.00 (s, $C^{6,6'v}$), 108.48 (br. s, C^{5h}), 111.48 (br. s, C^{5v}), 126.39 (s, C^{13}), 127.66 (s, C^{2h}), 127.84 (s, C^{12}), 128.18 (s, C^{2v}), 129.43 (s, C^{11}), 130.06 (s, C^{3h}), 133.77 (s, C^{3v}), 140.78, (s, $C^{1\circ}$), 146.95 (d, $^2J_{P,C}$ = 6.92 Hz, C^{4v}), 147.13 (d, $^2J_{P,C}$ = 6.94 Hz, C^{4h}) ppm. ^{31}P NMR (80.97 MHz, $CDCl_3$, 30 °C): δ = −14.50, −15.56 ppm. $C_{92}H_{112}O_{32}P_8$ (1977.64): calcd. C 55.87, H 5.71, P 12.53; found C 55.85, H 5.73, P 12.50.

13. Phosphoresorcinarene 7a: Sulfur (0.0237 g, 0.74 mmol) was added to a solution of phosphocalixarene **3a** (0.1473 g, 0.092 mmol) in a chloroform/benzene mixture (1:1, 1 mL). The reaction mixture was maintained at 75−80 °C for 4 h. Hexane (4 mL) was added to the reaction mixture, and the precipitate was filtered off and dried in vacuo (1 Torr) at 85−90 °C. Yield 80%. M.p. 327−328 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 0.81 (s, 12 H, H^{8va}), 0.93 (s, 12 H, H^{8ha}), 1.17 (s, 12 H, H^{8ve}), 1.35 (s, 12 H, H^{8he}), 1.57 (d, $^3J_{H,H}$ = 7.02 Hz, 12 H, $H^{1°}$), 3.96−4.40 (m, 32 H, $H^{6,6'}$), 4.78 (q, $^3J_{H,H}$ = 7.33 Hz, 4 H, H^1), 6.36 (s, 2 H, H^{3h}), 6.94 (s, 2 H, H^{5v}), 7.42 (s, 2 H, H^{5h}), 7.46 (s, 2 H, H^{3v}) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$, 30 °C): δ = 20.54 (s, $C^{1°}$), 21.21 (s, C^{8e}), 21.95 (s, C^{8a}), 31.23 (s, C^1), 32.07 (s, C^7), 76.35 (s, $C^{6,6'v}$), 76.99 (s, $C^{6,6'h}$), 110.93 (br. s., C^{5h}), 113.11 (br. s, C^{5v}), 126.22 (s, C^{3h}), 126.99 (s, C^{3v}), 130.89 (s, C^{2v}), 133.52 (s, C^{2h}), 146.06 (s, C^{4h}), 147.09 (s, C^{4v}) ppm. ^{31}P NMR (80.97 MHz, $CDCl_3$, 30 °C): δ = 54.77 ppm. $C_{72}H_{104}O_{24}P_8S_8$ (1857.90): calcd. C 46.55, H 5.64, P 13.34, S 13.81; found C 46.58, H 5.69, P 13.41, S 13.86.

14. Phosphoresorcinarene 7b: The compound was obtained analogously to **7a** by treatment of **3d** (0.1461 g, 0.079 mmol) with sulfur (0.0202 g, 0.63 mmol). Yield 84%. M.p. 344−345 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 30 °C): δ = 0.88 (s, 12 H, H^{8ha}), 1.18 (s, 12 H, H^{8va}), 1.26 (s, 12 H, H^{8he}), 1.26 (s, 12 H, H^{8ve}), 3.61−4.47 (m, 32 H, $H^{6,6'}$), 6.02 (s, 4 H, H^1), 6.17 (s, 2 H, H^{3v}), 6.55 (s, 2 H, H^{3h}), 7.00 (s, 2 H, H^{5v}),7.08 (br. s, 8 H, H^{11}), 7.48 (m, 12 H, $H^{12,13}$), 7.56 (s, 2 H, H^{5h}) ppm. ^{13}C NMR (50.32 MHz, $CDCl_3$, 30 °C): δ = 20.05 (s, C^{8h}), 21.94 (s, C^{8v}), 31.73 (d, $^2J_{P,C}$ = 6.20 Hz, C^{7h}), 32.11 (d, $^2J_{P,C}$ = 6.40 Hz, C^{7v}), 43.43 (s, C^1), 76.38 (s, $C^{6,6'h}$), 77.01 (s, $C^{6,6'v}$), 109.82 (br. s, C^{5h}), 114.31 (br. s, C^{5v}), 126.23(s, C^{13}), 127.97 (s, C^{2h}), 128.14 (s, C^{12}), 128.33 (s, C^{2v}), 129.75 (s, C^{11}), 130.61 (s, C^{3h}), 133.91 (s, C^{3v}), 142.15(s, $C^{1°}$), 147.19 (d, $^2J_{P,C}$ = 7.81 Hz, C^{4v}), 147.31 (d, $^2J_{P,C}$ = 7.79 Hz, C^{4h}) ppm. ^{31}P NMR (80.97 MHz, $CDCl_3$, 30 °C): δ = 51.94, 53.56 ppm. $C_{92}H_{112}O_{24}P_8S_8$ (2106.18): calcd. C 52.46, H 5.36, P 11.76, S 12.18; found C 52.49, H 5.39, P 11.81, S 12.20.

CCDC-237719 (for **3a**), -238030 (for **5b α-form**) and -238031 (for **5b β-form**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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