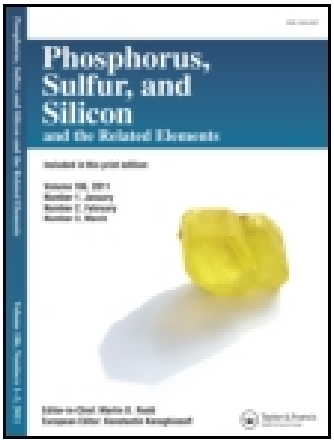


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gpss20

New Calix[4]Resorcinols with Thiophosphoryl-Containing Fragments

Irina R. Knyazeva [a], Alexander R. Burilov [a], Guzyal M. Fazleeva [a], Il'dus A. Nuretdinov [a], Tatyana V. Gryaznova [a], Yulia G. Budnikova [a], Vera V. Khrisanforova [a], Aidar T. Gubaidullin [a], Bulat M. Gabidullin [a], Victor V. Syakaev [a], Michael A. Pudovik [a] & Alexander I. Konovalov [a]

[a] A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Russian Federation

Published online: 24 Aug 2011.

To cite this article: Irina R. Knyazeva, Alexander R. Burilov, Guzyal M. Fazleeva, Il'dus A. Nuretdinov, Tatyana V. Gryaznova, Yulia G. Budnikova, Vera V. Khrisanforova, Aidar T. Gubaidullin, Bulat M. Gabidullin, Victor V. Syakaev, Michael A. Pudovik & Alexander I. Konovalov (2011) New Calix[4]Resorcinols with Thiophosphoryl-Containing Fragments, Phosphorus, Sulfur, and Silicon and the Related Elements, 186:9, 1972-1980, DOI: 10.1080/10426507.2011.554926

To link to this article: http://dx.doi.org/10.1080/10426507.2011.554926

Phosphorus, Sulfur, and Silicon, 186:1972–1980, 2011

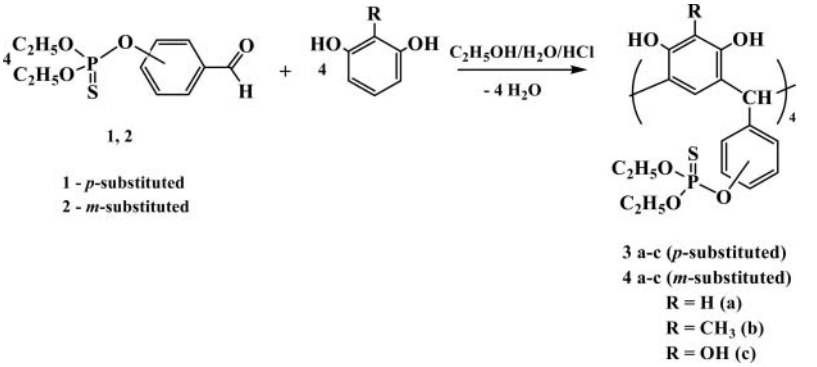
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2011.554926

NEW CALIX[4]RESORCINOLS WITH THIOPHOSPHORYL-CONTAINING FRAGMENTS

Irina R. Knyazeva, Alexander R. Burilov, Guzyal M. Fazleeva, Il'dus A. Nuretdinov, Tatyana V. Gryaznova, Yulia G. Budnikova, Vera V. Khrisanforova, Aidar T. Gubaidullin, Bulat M. Gabidullin, Victor V. Syakaev, Michael A. Pudovik, and Alexander I. Konovalov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Russian Federation

GRAPHICAL ABSTRACT



Abstract *The condensation of thiophosphorylated aldehydes **1** and **2** with resorcinol and its derivatives leads to the formation of the new type of calix[4]resorcinols with four thiophosphoryl groups inserted to the substituents located in methylidene bridges of the molecule. The conformation of these compounds was found to be "flattened partial cone" or "chair," which was determined by NMR methods and a single-crystal X-ray diffraction study.*

Keywords Calix[4]resorcinol; condensation; thiophosphorylated aldehyde; conformation

INTRODUCTION

The chemistry of calixarenes with organoelement fragments, especially with phosphorus-containing functional groups, attracts a great interest of many scientists of the world due to their ability to form complexes with various organic molecules and metal

Received 13 December 2010; accepted 12 January 2011.
The work was supported by the Russian Foundation for Basic Research (grant no. 08-03-00512a).
Address correspondence to Irina R. Knyazeva, A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Arbuzov Street 8, 420088 Kazan, Russian Federation. E-mail: ihazieva@mail.ru

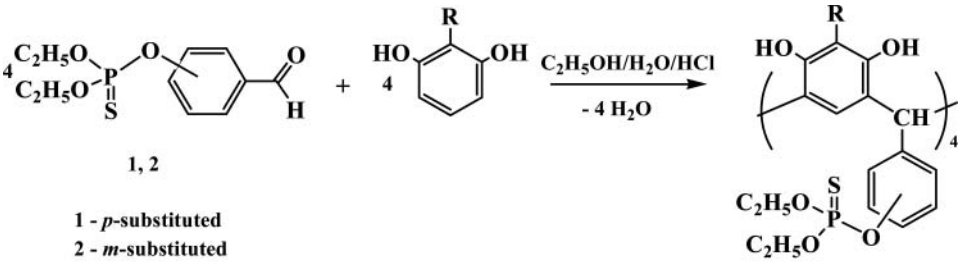
ions, tendency toward self-assembly, which leads to the formation of supramolecular ensembles. Set of the above mentioned properties makes this compound class promising for the creation of new types of complexing agents,[1] metal ion extraction agents,[2] and catalytic systems.[3–5]

The general pathway to the synthesis of calix[4]resorcinols is based on the acidic condensation of resorcinol and aldehydes.[6,7] In order to develop this method, we have recently obtained new calix[4]resorcinols bearing phosphonates and phosphonium fragments on the lower rim of the molecule using phosphorylated derivatives of benzaldehyde as reactants.[8,9]

In the present study, we synthesized the first representatives of calix[4]resorcinols with four thiophosphoryl (P═S) groups inserted to the substituents located in the methylidene bridges of the molecule. It is known that the P═S group actively interacts with salts of different metals[10] and alkyl halides.[11] In addition, while phosphonate (P═O) derivatives have proved to be efficient extractants for hard cationic species,[12,13] for thiophosphonate (P═S) derivatives the different and interesting properties toward soft metal cations may be expected.

RESULTS AND DISCUSSION

Thiophosphorylated aldehydes **1** and **2** with the aromatic spacer between thiophosphoryl and aldehyde groups (thiophosphoryl group located in *para* or *meta* positions in relation to the aldehyde fragment) were used as new starting materials for the synthesis of calixarenes. New thiophosphorylated calix[4]resorcinols **3a–c** and **4a–c** were obtained by the condensation of these aldehydes with resorcinol, 2-methylresorcinol, and pyrogallol in acidic aqueous alcoholic media after prolonged heating (Scheme 1).



Scheme 1

^{31}P, ^{1}H, ^{13}C, electrospray ionization (ESI) mass spectra, and elemental analysis are in a good agreement with the proposed structure. The presence of only one signal at approximately 62 ppm in the ^{31}P NMR spectrum of each from obtained compounds indicates that the four phosphorus atoms are equivalent.

Several conformations with different arrangements of resorcinol rings and substituents in the methylidene bridges with respect to each other and to the macrocycle

plane are known for calix[4]resorcinols to be as *cone*, *flattened cone*, *flattened partial cone*, *1,2-alternate*, and *1,3-alternate.*[14] The preferred conformation of a structure depends on the properties of the introduced functional groups, the nature of the substituent groups in the calixarene matrix, and the reaction conditions.

The calix[4]resorcinol **4b** crystallized in the triclinic crystal system, space group P-1, forms a crystal solvate with two water molecules and four dimethylformamide (DMF) molecules per calixarene macrocycle. The calixarene molecule occupies a special position and has an inversion center. One of the DMF molecules and one of the thiophosphoryl-containing substituents are disordered in the crystal over two positions with relative occupancies 0.65:0.35 and 0.60:0.40, respectively. The calix[4]resorcinol **4b** molecule has *rctt* configuration of its thiophosphoryl-containing substituents and exists in "chair" conformation (Figure 1). The selected bond lengths and angles around the phosphorus atoms are in

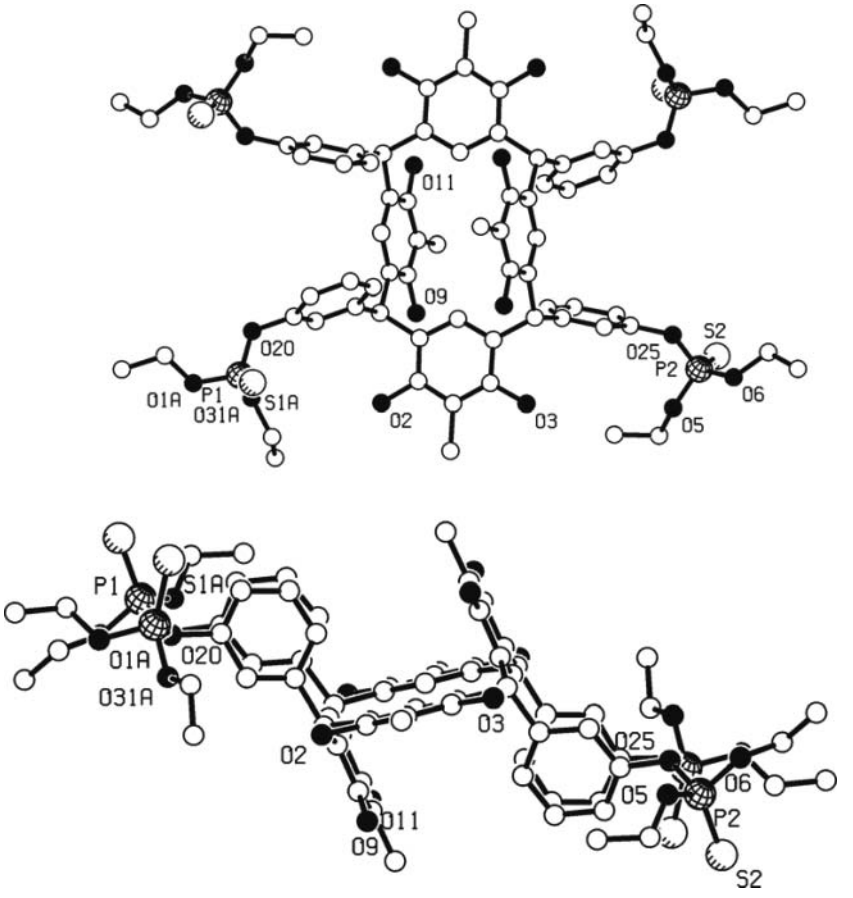


Figure 1 Two different views of the molecule **4b** and partial numbering scheme, hydrogen atoms, and solvate molecules of water and DMF are omitted for clarity. Disordered thiophosphoryl-containing substituents (P1) are shown in the position with the greater occupancy. The selected bond lengths (Å) and angles (°) are P1 O31A 1.542(7), P1 O1A 1.559(7), P1 O20 1.570(5), P1 S1A 1.889(7), P2 O5 1.519(6), P2 O6 1.551(7), P2 O25 1.554(5), P2 S2 1.899(4); O5 P2 O6 98.6(4), O5 P2 O25 102.5(3), O6 P2 O25 101.9(4), O5 P2 S2 118.7(3), O6 P2 S2 117.0(3), O25 P2 S2 115.3(2), C35 O5 P2 125.9(8).

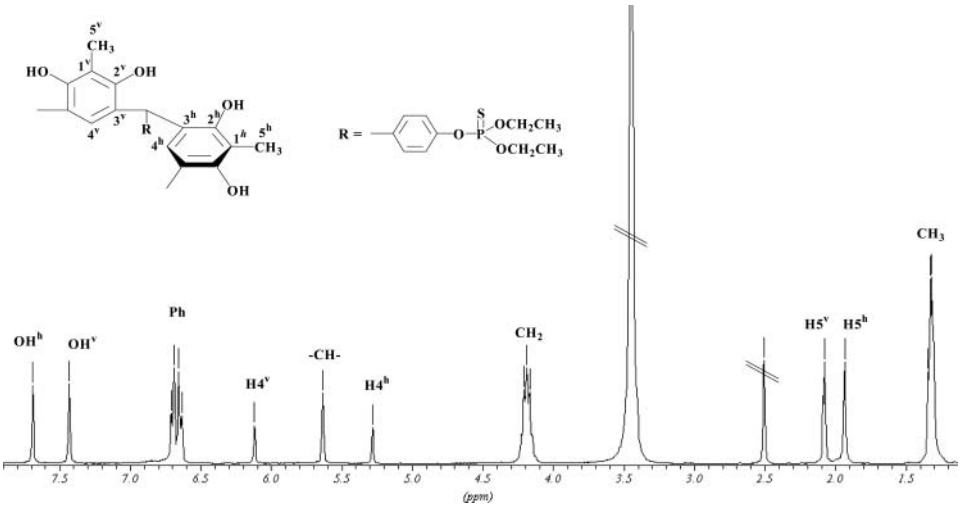


Figure 2 ^{1}H NMR spectrum of calix[4]resorcinol **3b** (600 MHz, DMSO-d_6).

the range of the typical values for thiophosphates and are presented in the description of Figure 1. Two opposite resorcinol rings are coplanar and the other two are antiparallel.

All hydroxyl groups of the calixresorcinol scaffold take part in the classical hydrogen bonding interactions with the solvate molecules. Calixarene macrocycles are connected by hydrogen bonds through water molecules and by $\pi-\pi$ interaction, forming supramolecular pillars along crystallographic axis *Ox*. Due to the nonclassical hydrogen bond interactions, those pillars generate layers parallel to *Oxy* crystallographic plane.

The presented results of the single-crystal X-ray diffraction analysis are in agreement with the NMR spectroscopic data for all obtained compounds. The ^{1}H and ^{13}C NMR spectra of compounds **3a–c** and **4a–c** display the duplication of signals from protons and carbon atoms of resorcinol fragments (Figure 2). This attests to the different (vertical and horizontal) arrangements of opposite resorcinol rings with respect to the macrocycle plane. The NMR ^{1}H 2D NOESY spectrum of compound **3b** (Figure 3) shows the cross-peak between signals of protons of methyl groups from vertically oriented 2-methylresorcinol fragments (CH_3^v), and signals of aromatic protons from substituent in the methylidene bridges (Ph). This indicates that the molecule exists in "flattened partial cone" (or "chair") conformation.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-600 spectrometer (600 and 150 MHz, respectively) in dimethyl sulfoxide (DMSO)-d_6 or acetone-d_6; ^{31}P NMR spectra were recorded on a Bruker MSL-400 NMR-Fourier spectrometer (166.93 MHz). NMR experiments were carried out in solutions (10 mmol $\times$ L^{-1}) at 303 K. The pulse programs of the 2D NOESY experiments were taken from Bruker software library. IR spectra were measured on a Bruker Vector 22 Fourier-transform spectrometer; the solid samples were examined as emulsions in Vaseline. ESI mass spectra were recorded on Esquire-LC 00084 instrument.

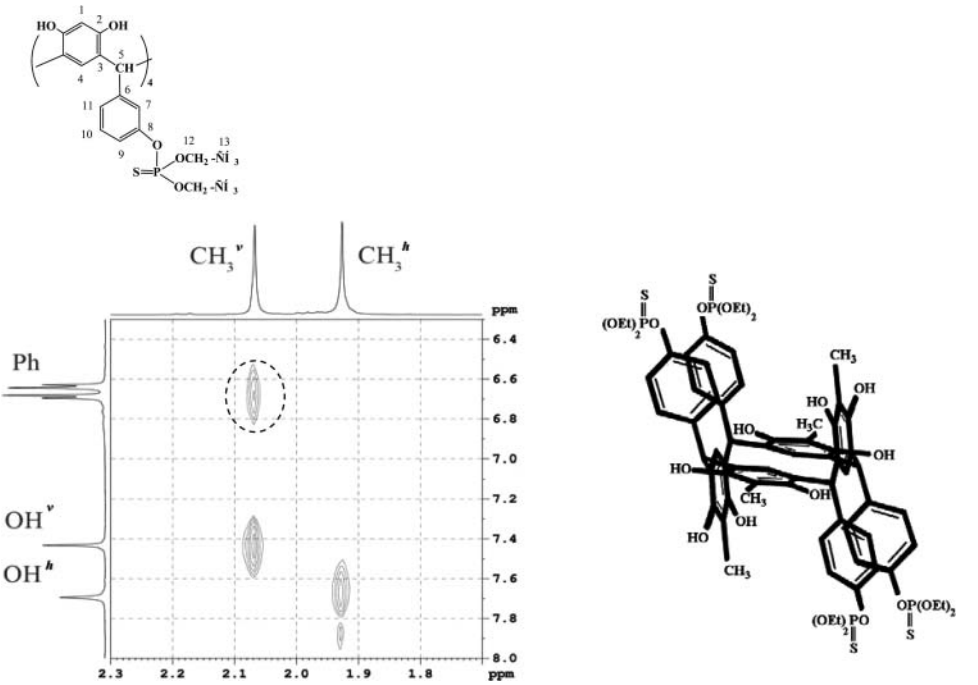


Figure 3 Fragment of ^{1}H NMR 2D NOESY spectrum for compound **3b** (600 MHz, DMSO-d_6).

X-Ray Crystallography

Suitable single crystals were obtained from a solution of **4b** in DMF at ambient temperature. The X-ray diffraction data for crystal of compound **4b**, $C_{72}H_{84}O_{20}P_4S_4 \cdot 4C_3H_7NO \cdot 2H_2O$, were collected at 296 K on a Bruker AXS Smart Apex II CCD diffractometer in the ω and ϕ-scan modes using graphite monochromated MoK_α (λ 0.71073Å) radiation. The crystal data, data collection, and the refinement are given in Table 1. Data were corrected for the absorption effect using SADABS program.[15] The structures were solved by a direct method and refined by the full matrix least squares using SHELXTL[16] and WinGX[17] programs. All nonhydrogen atoms were refined anisotropically. The positions of hydrogen atoms were located from the Fourier electron density synthesis and were included in the refinement in the isotropic riding model approximation.

Data Collections. Images were indexed, integrated, and scaled using the APEX2[18] data reduction package. All figures were made using PLATON.[19]

Crystallographic data (excluding structure factors) for the structure **4b** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 803752. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

Diethyl-(4-formylphenyl)thiophosphate 1 was synthesized according to a known procedure.[20]

Diethyl-(3-formylphenyl)thiophosphate 2. A solution of 3-hydroxybenzaldehyde (2.1 g, 0.017 mol) in tetrahydrofuran (THF) (25 mL) was added dropwise to the suspension

Table 1 Crystallographic data for calix[4]resorcinol **4b**

Empirical formula	$C_{84}H_{116}N_4O_{26}P_4S_4$
Compound formula	$C_{72}H_{84}O_{20}P_4S_4 \cdot 4C_3H_7NO \cdot 2H_2O$
Formula mass	1849.93
Temperature (K)	296(2)
Crystal size (mm)	0.13 × 0.16 × 0.28
Crystal description	Pink prism
Crystal system	Triclinic
Space group	$P-1$
a (Å)	9.1242(12)
b (Å)	16.020(2)
c (Å)	16.550(2)
α (°)	97.343(2)
β (°)	94.394(2)
γ (°)	97.763(2)
V (Å^3)	2366.4(5)
Z	1
ρ_{calc} (g/cm^3)	1.298
μ (cm^{-1})	2.42
$F(000)$	980
θ range (°)	1.92 – 26.25
Index ranges	$-11 \le h \le 11$ $-19 \le k \le 19$ $-20 \le l \le 20$
Reflections collected	18338
Reflections observed ($I > 2\sigma$)	3482
Reflections unique	9337 ($R_{int} = 0.0581$)
R1, wR2 (2σ data)	0.0812, 0.2004
R1, wR2 (all data)	0.2092, 0.2714
Max/min transmission factors	0.9353/0.9692
Data/restraints/parameters	9337/36/586
GooF on F^2	0.950
Largest difference electron density peak/hole (e/Å^3)	0.386/− 0.239

of NaH (0.5 g, 0.0208 mol) in THF (50 mL) at 10 °C and reaction mixture was stirred at room temperature for 40 min. Then, the solution of diethylthiophosphoric acid chloroanhydride (3 g, 0.016 mol) in THF was added and the mixture was stirred at room temperature for 12 h. The reaction mixture was quenched with H_2O and extracted with benzene (5 × 25 mL). After drying over $MgSO_4$ and removal of the solvent by evaporation, the crude product was purified by column chromatography using a mixture of *n*-hexane/ethyl acetate (3:1) as eluent. The desired product was obtained as light yellow oil (3.02 g, 69% yield, $R_f = 0.58$). ^{31}P NMR (166.93 MHz, acetone-d$_6$): $\delta = 61.5$ ppm. ^{1}H NMR (600 MHz, acetone-d$_6$): $\delta =$ 1.37 (t, $^3J_{HH} = 6.97$ Hz, 6H, C$\underline{H}_3$), 4.29 (m, 4H, OC$\underline{H}_2$), 7.54 (d, $^3J_{HH} = 8.07$ Hz, 1H, C$\underline{H}_{ar}$), 7.64 (t, $^3J_{HH} = 7.70$ Hz, 1H, C$\underline{H}_{ar}$), 7.74 (s, 1H, C$\underline{H}_{ar}$), 7.82 (d, $^3J_{HH} = 7.70$ Hz, 1H, C$\underline{H}_{ar}$,), 10.07 (s, 1H, C$\underline{H}$O) ppm. IR (film) ν_{max}: 822 (P=S); 973, 1023 (P−O−C) cm^{-1}. Anal. Calcd. for $C_{11}H_{15}O_4PS$: C, 48.17; H, 5.51; P, 11.29; S, 11.69. Found: C, 48.21; H, 5.34; P, 11.49; S, 11.54.

Calix[4]resorcinol 3a. The mixture of resorcinol (0.31 g, 2.82 mmol) and aldehyde **1** (0.77 g, 2.82 mmol) in ethanol (6 mL), water (6 mL), and concentrated hydrochloric acid (2 mL) was stirred under heating at 70 °C for 3 days. The precipitate was filtered and washed with ethanol and diethyl ether. After drying in vacuo (40 °C, 0.06 Torr), the product

was obtained (0.60 g, 58%) as white powder. mp > 220 °C (dec.). ^{31}P NMR (166.93 MHz, DMSO-d_6): $\delta = 62.3$ ppm. ^{1}H NMR (600 MHz, DMSO-d_6): $\delta = 1.31$ (m, 24H, C$\underline{H}_3$), 4.17 (m, 16H, C$\underline{H}_2$), 5.50 (s, 2H, H4^h), 5.54 (s, 4H, C$\underline{H}$), 6.16 (s, 2H, H4^v), 6.17 (s, 2H, H1^v), 6.33 (s, 2H, H1^h), 6.61 (d, $^3J_{HH} = 8.59$ Hz, 8H, CH−C$_{ar}$−C$\underline{H}_{ar}$), 6.71 (d, $^3J_{HH} = 8.59$ Hz, 8H, O−C$_{ar}$−C$\underline{H}_{ar}$), 8.58 (s, 4H, OH^v), 8.63 (s, 4H, OH^h) ppm. ^{13}C NMR (150 MHz, d_6-DMSO): $\delta = 15.7$ (s, C$\underline{H}_3$), 41.4 (s, C$\underline{H}$), 64.6 (s, C$\underline{H}_2$), 101.8 (s, C1^v), 101.9 (s, C1^h), 119.2 (s, C$\underline{H}_{ar}$), 119.5 (s, C4^v), 120.5 (s, C3^v), 120.8 (s, C3^h), 129.9 (s, C$\underline{H}_{ar}$), 131.4 (s, C4^h), 141.3 (s, C$_{ar}$), 147.5 (c, C$_{ar}$), 150.7 (s, C2^h), 152.9 (s, C2^v) ppm. IR ν_{max}: 830 (P=S); 956, 1016 (P−O−C); 3150–3550 (OH) cm^{-1}. Anal. Calcd. for $C_{68}H_{76}O_{20}P_4S_4$: C, 55.74; H, 5.19; P, 8.47; S, 8.74. Found: C, 54.68; H, 5.22; P, 8.20; S, 8.63. ESI-MS: *m/z* = 1465 [M+H]$^+$ (calcd. M = 1464).

Calix[4]resorcinol 3b. This compound was obtained as white powder by a method analogous to that used to prepare **3a** by treatment of 2-methylresorcinol (0.24 g, 1.93 mmol) with aldehyde **1** (0.53 g, 1.93 mmol). Yield 0.4 g (65%), mp > 255 °C (dec.). ^{31}P NMR (166.93 MHz, DMSO-d_6): $\delta = 62.4$ ppm. ^{1}H NMR (600 MHz, DMSO-d_6): $\delta = 1.31$ (t, $^3J_{HH}$ 6.7 Hz, 24H, C$\underline{H}_3$), 1.93 (s, 6H, H5^h), 2.07 (s, 6H, H5^v), 4.18 (m, 16H, C$\underline{H}_2$), 5.27 (s, 2H, H4^h), 5.62 (s, 4H, C$\underline{H}$), 6.11 (s, 2H, H4^v), 6.63 (d, $^3J_{HH} = 8.4$ Hz, 8H, CH−C$_{ar}$−C$\underline{H}_{ar}$), 6.69 (d, $^3J_{HH} = 8.4$ Hz, 8H, O−C$_{ar}$−C$\underline{H}_{ar}$), 7.43 (s, 4H, OH^v), 7.69 (s, 4H, OH^h) ppm. ^{13}C NMR (150 MHz, d_6-DMSO): $\delta = 9.6$ (s, C5^h), 10.1 (s, C5^v), 15.8 (d, $^3J_{CP} = 5.8$ Hz, CH$_3$), 43.1 (s, CH), 64.7 (d, $^2J_{CP} = 5.8$ Hz, CH$_2$), 110.9 (s, C1^h), 111.1 (s, C1^v), 119.4 (d, $^3J_{CP} = 3.0$ Hz, P−O−C$_{ar}$−C$\underline{H}_{ar}$), 122.0 (s, C3^v), 122.8 (s, C3^h), 125.6 (s, C4^v), 127.8 (s, C4^h), 130.4 (s, CH−C$_{ar}$−C$\underline{H}_{ar}$), 140.5 (s, CH−C$\underline{}_{ar}$), 147.8 (d, $^2J_{CP} = 7.5$ Hz, P−O−C$\underline{}_{ar}$), 150.6 (s, C2^h), 150.7 (s, C2^v) ppm. IR ν_{max}: 818 (P=S); 942, 1020 (P−O−C); 3150–3650 (OH) cm^{-1}. Anal. Calcd. for $C_{72}H_{84}O_{20}P_4S_4$: C, 56.80; H, 5.53; P, 8.16; S, 8.42. Found: C, 56.77; H, 5.52; P, 7.84; S, 8.48. ESI-MS: *m/z* = 1521 [M+H]$^+$ (calcd. M = 1520).

Calix[4]resorcinol 3c. This compound was obtained as dark pink powder by a method analogous to that used to prepare **3a** by treatment of pyrogallol (0.46 g, 3.65 mmol) with aldehyde **1** (1.00 g, 3.65 mmol). Yield 0.84 g (60%), mp > 180 °C (dec.). ^{31}P NMR (166.93 MHz, acetone-d_6): $\delta = 61.5$ ppm. ^{1}H NMR (600 MHz, acetone-d_6): $\delta = 1.37$ (t, $^3J_{HH} = 7.3$ Hz, 24H, CH$_3$), 4.26 (m, 16H, CH$_2$), 5.34 (s, 2H, H4^h), 5.80 (s, 4H, CH), 6.11 (s, 2H, H4^v), 6.76 (d, $^3J_{HH} = 8.4$ Hz, 8H, CH−C$_{ar}$−C$\underline{H}_{ar}$), 6.84 (d, $^3J_{HH} = 8.4$ Hz, 8H, O−C$_{ar}$−C$\underline{H}_{ar}$), 8.01 (s, 12H, OH) ppm. IR ν_{max}: 819 (P=S); 926, 1020 (P−O−C); 3250–3600 (OH) cm^{-1}. Anal. Calcd. for $C_{68}H_{76}O_{24}P_4S_4$: C, 53.40; H, 4.97; P, 8.12; S, 8.38. Found: C, 53.48; H, 4.50; P, 8.17; S, 7.86. ESI-MS: *m/z* = 1529 [M+H]$^+$ (calcd. M = 1528).

Calix[4]resorcinol 4a. The mixture of resorcinol (0.33 g, 3.00 mmol) and aldehyde **2** (0.82 g, 3.00 mmol) in ethanol (10 mL), water (10 mL), and concentrated hydrochloric acid (5 mL) was stirred under heating at 70 °C for 3 days. The solvent was removed in vacuo and the residue was dissolved in ethanol and reprecipitated in water. After drying (40 °C, 0.06 Torr), the product was obtained (0.94 g, 86%) as white powder. mp > 140 °C (dec.). ^{31}P NMR (166.93 MHz, acetone-d_6): $\delta = 61.4$ ppm. ^{1}H NMR (600 MHz, acetone-d_6): $\delta =$ 1.25 (t, $^3J_{HH} = 7.3$ Hz, 24H, CH$_3$), 4.14 (m, 16H, CH$_2$), 5.75 (s, 2H, H4^h), 5.82 (s, 4H, CH), 6.17 (s, 2H, H4^v), 6.21 (s, 2H, H1^v), 6.31 (s, 2H, H1^h), 6.53 (d, $^3J_{HH} = 7.6$ Hz, 4H, P−O−C$_{ar}$−C$\underline{H}_{ar}$−CH$_{ar}$), 6.59 (s, 4H, C$_{ar}$−C$\underline{H}_{ar}$−C$_{ar}$), 6.83 (d, $^3J_{HH} = 8.0$ Hz, 4H, CH−C$_{ar}$−C$\underline{H}_{ar}$−CH$_{ar}$), 7.10 (t, $^3J_{HH} = 7.9$ Hz, 4H, P−O−C$_{ar}$−CH$_{ar}$−C$\underline{H}_{ar}$), 7.34 (br. m., 8H, −OH) ppm. IR ν_{max}: 820 (P=S); 956, 1022 (P−O−C); 3100–3550 (OH) cm^{-1}. Anal. Calcd. for $C_{68}H_{76}O_{20}P_4S_4$: C, 55.74; H, 5.19; P, 8.47; S, 8.74. Found: C, 55.22; H, 5.38; P, 7.98; S, 8.77. ESI-MS: *m/z* = 1465 [M+H]$^+$ (calcd. M = 1464).

Calix[4]resorcinol 4b. This compound was obtained as white powder by a method analogous to that used to prepare **4a** by treatment of 2-methylresorcinol (0.38 g, 3.06 mmol) with aldehyde **2** (0.84 g, 3.06 mmol). Yield 0.67 g (56%), mp > 250 °C (dec.). ^{31}P NMR (166.93 MHz, DMSO-d_6): δ = 61.4 ppm. ^{1}H NMR (600 MHz, DMSO-d_6): δ = 1.22 (t, $^3J_{HH}$ = 7.0 Hz, 24H, CH_3), 1.95 (s, 6H, H6^h), 2.10 (s, 6H, H6^v), 4.10 (m, 16H, CH_2), 5.25 (s, 2H, H4^h), 5.69 (s, 4H, CH), 6.14 (s, 2H, H4^v), 6.42 (d, $^3J_{HH}$ = 7.5 Hz, 4H, P−O−C_{ar}−C$\underline{H}_{ar}$−CH_{ar}), 6.48 (s, 4H, C_{ar}−C$\underline{H}_{ar}$−C_{ar}), 6.73 (d, $^3J_{HH}$ = 8.2 Hz, 4H, CH−C_{ar}−C$\underline{H}_{ar}$−CH_{ar}), 6.90 (t, $^3J_{HH}$ = 7.9 Hz, 4H, P−O−C_{ar}−CH_{ar}−C$\underline{H}_{ar}$), 7.32 (s, 4H, OH^v), 7.71 (s, 4H, OH^h) ppm. IR ν_{max}: 821 (P=S); 953, 1022 (P−O−C); 3100–3600 (OH) cm^{-1}. Anal. Calcd. for $C_{72}H_{84}O_{20}P_4S_4$: C, 56.80; H, 5.53; P, 8.16; S, 8.42. Found: C, 56.89; H, 5.58; P, 8.33; S, 8.41. ESI-MS: 1521 $[M+H]^+$ (calcd. M = 1520).

Calix[4]resorcinol 4c. This compound was obtained as dark pink powder by a method analogous to that used to prepare **4a** by treatment of pyrogallol (0.27 g, 2.14 mmol) with aldehyde **2** (0.59 g, 2.14 mmol). Yield 0.53 g (65%), mp > 140 °C (dec.). ^{31}P NMR (166.93 MHz, acetone-d_6): δ = 61.8 ppm. ^{1}H NMR (600 MHz, acetone-d_6): δ = 1.26 (m, 24H, CH_3), 4.15 (m, 16H, CH_2), 5.32 (s, 2H, H4^h), 5.84 (s, 4H, CH), 6.12 (s, 2H, H4^v), 6.61 (d, $^3J_{HH}$ = 7.6 Hz, 4H, P−O−C_{ar}−C$\underline{H}_{ar}$−CH_{ar}), 6.65 (s, 4H, C_{ar}−C$\underline{H}_{ar}$−C_{ar}), 6.85 (d, $^3J_{HH}$ = 8.3 Hz, 4H, CH−C_{ar}−C$\underline{H}_{ar}$−CH_{ar}), 7.00 (t, $^3J_{HH}$ = 7.93 Hz, 4H, P−O−C_{ar}−CH_{ar}−C$\underline{H}_{ar}$), 8.02 (br. m., 12H, −OH) ppm. IR ν_{max}: 819 (P=S); 972, 1018 (P−O−C); 3100–3600 (OH) cm^{-1}. Anal. Calcd. for $C_{68}H_{76}O_{24}P_4S_4$: C, 53.40; H, 4.97; P, 8.12; S, 8.38. Found: C, 53.63; H, 4.58; P, 8.04; S, 8.63. ESI-MS: 1529 $[M+H]^+$ (calcd. M = 1528).

REFERENCES

1. G. A. Gainanova, E. P. Zhil'tsova, L. A. Kudryavtseva, S. S. Lukashenko, A. P. Timosheva, A. R. Burilov, I. R. Knyazeva, and A. I. Konovalov, *Russ. J. Gen. Chem.*, **76,** 1788–1794 (2006).
2. A. Mustafina, J. Elistratova, A. Burilov, I. Knyazeva, R. Zairov, R. Amirov, S. Solovieva, and A. Konovalov, *Talanta*, **68,** 863–868 (2006).
3. T. N. Pashirova, S. S. Lukashenko, E. M. Kosacheva, M. V. Leonova, I. R. Knyazeva, A. R. Burilov, L. A. Kudryavtseva, and A. I. Konovalov, *Colloid J.*, **70,** 202–209 (2008).
4. T. N. Pashirova, S. S. Lukashenko, E. M. Kosacheva, L. Z. Rizvanova, G. A. Gainanova, I. R. Knyazeva, A. R. Burilov, L. A. Kudryavtseva, and A. I. Konovalov, *Russ. Chem. Bull., Int. Ed.*, **56,** 959–966 (2007).
5. G. A. Gainanova, E. P. Zhiltsova, L. A. Kudryavtseva, S. S. Lukashenko, I. R. Knyazeva, A. R. Burilov, V. I. Kovalenko, L. V. Avvakumova, and A. I. Konovalov, *Russ. J. Gen. Chem.*, **77,** 40–46 (2007).
6. L. M. Tunstad, J. A. Tucker, E. Dalcanale, J. Weiser, J. A. Bryant, J. C. Sherman, R. C. Helgeson, C. B. Knobler, and D. J. Cram, *J. Org. Chem.*, **54,** 1305–1312 (1989).
7. E. U. Thoden van Velzen, J. F. Engbersen, and D. N. Reinhoudt, *J. Am. Chem. Soc.*, **116,** 3597–3598 (1994).
8. E. L. Gavrilova, A. A. Naumova, A. R. Burilov, M. A. Pudovik, E. A. Krasilnikova, and A. I. Konovalov, *Izv. Acad. Nauk SSSR, Seriya Khim. (Engl. Transl.)*, **11,** 2269–2271 (2007).
9. E. L. Gavrilova, A. A. Naumova, N. I. Shatalova, A. R. Burilov, M. A. Pudovik, E. A. Krasilnikova, and A. I. Konovalov, *Phosphorus Sulfur Silicon Relat. Elem.*, **183,** 561–565 (2008).
10. N. M. Karayannis, C. M. Mikulski, and L. L. Pytlewski, *Inorg. Chim. Acta Rev.*, **5,** 69–105 (1971).
11. P. S. Pishchimuka, *Zh. Russ. Fiz.-Khim. Obshch., Ser. Khim. (Russ. J. Phys. Chem. Soc., Ser. Chem.)*, **44,** 1406–1554 (1912).

12. P. Delange, J.-C. Mulatier, B. Tinant, J.-P. Declercq, and J.-P. Dutasta, *Eur. J. Org. Chem.*, 3695–3704 (2001).
13. B. Bibal, B. Tinant, J.-P. Declercq, and J.-P. Dutasta, *Supramol. Chem.*, **15,** 25–32 (2003).
14. V. I. Maslennikova, O. S. Serkova, M. Gruner, S. Goutal, I. Bauer, W. D. Habicher, K. A. Lyssenko, M. Yu. Antipin, and E. E. Nifantyev, *Eur. J. Org. Chem.*, 4884–4893 (2004).
15. G. M. Sheldrick, *SADABS, Program for Empirical X-ray Absorption Correction* (Bruker-Nonius, Göttingen, Germany, 2004).
16. G. M. Sheldrick, *SHELXTL v.6.12, Structure Determination Software Suite* (Bruker AXS, Madison, WI, 2000).
17. L. J. Farrugia, *J. Appl. Crystalogr.*, **32,** 837–838 (1999).
18. *APEX2 (Version 2.1), SAINT Plus, Data Reduction and Correction Program (Version 7.31A)* (Bruker Advanced X-ray Solutions, Bruker AXS, Inc., Madison, WI, 2006).
19. A. L. Spek, *J. Appl. Cryst.*, **36,** 7–13 (2003).
20. G. M. Fazleeva, V. P. Gubskaya, F. G. Sibgatullina, V. V. Yanilkin, N. V. Nastapova, S. K. Latypov, A. A. Balandina, I. E. Ismaev, V. V. Zverev, Y. Y. Efremov, and I. A. Nuretdinov, *Izv. Acad. Nauk SSSR, Seriya Khim. (Engl. Transl.)*, **3,** 489–497 (2006).