

# Thiophosphorylation of Calix[4]resorcinarenes with 2,4-Diaryl-1,3-dithia-2λ<sup>5</sup>,4λ<sup>5</sup>-diphosphetane 2,4-Disulfides

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**Abstract**—Reactions of 2,4-diaryl-1,3-dithia-2λ<sup>5</sup>,4λ<sup>5</sup>-diphosphetane 2,4-disulfides with tetraheptylcalix[4]-resorcinarene and octa-*O*-(2-hydroxyethyl)tetraoctylcalix[4]resorcinarene gave the corresponding octakis(aryl-dithiophosphonic acids).

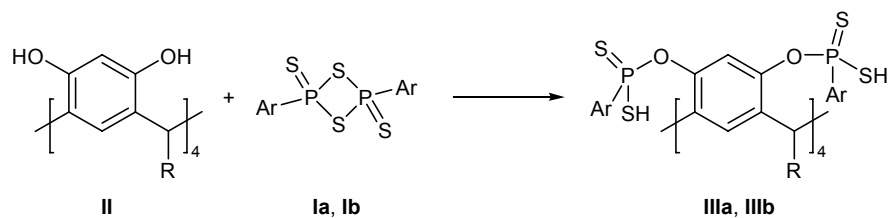
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Calixarenes can be functionalized at the hydroxy groups to change the size and geometric shape of the cavity and its ability to effectively and selectively bind ions and neutral molecules. In the series of calixarenes functionalized at the hydroxy groups by heteroatom moieties, much attention is given to cavitands phosphorylated at lower and upper rims [1–14]. On the other hand, thiophosphorylated calixarene derivatives were studied to a considerably lesser extent. They were synthesized mainly via addition of sulfur to the corresponding phosphorylated calixarene derivatives with three-coordinate phosphorus atoms [15]. Prior to our studies dithiophosphorylated calixarenes were not reported in the literature. Nevertheless, such compounds attract interest as complexing agents, extractants, antioxidants, corrosion inhibitors, etc. We propose to obtain such compounds via reactions of calixarenes with 2,4-diaryl-1,3-dithia-2λ<sup>5</sup>,4λ<sup>5</sup>-diphosphetane 2,4-disulfides as thophosphorylating agents. It is known that

2,4-dialkyl- or 2,4-diaryl-1,3-dithia-2λ<sup>5</sup>,4λ<sup>5</sup>-diphosphetane 2,4-disulfides react with alcohols, diols, and other polyhydric alcohols at the O–H bonds with formation of aryldithiophosphonic, bis-aryldithiophosphonic, and poly-aryldithiophosphonic acids [16–24]. Calix[4]resorcinarene **II** reacted with 2,4-diaryl-1,3-dithia-2λ<sup>5</sup>,4λ<sup>5</sup>-diphosphetane 2,4-disulfides **Ia** and **Ib** at a molar ratio of 1:4 in benzene to give octa-*O*-(2,4,6,8-tetraheptyl-1,3,5,7(1,3)-tetrabenzenacyclooctaphane-1<sup>4</sup>,1<sup>6</sup>,3<sup>4</sup>,3<sup>6</sup>,5<sup>4</sup>,5<sup>6</sup>,7<sup>4</sup>,7<sup>6</sup>-octayl) octakis(hydrogen aryl-phosphonodithioates) **IIIa** and **IIIb** (Scheme 1).

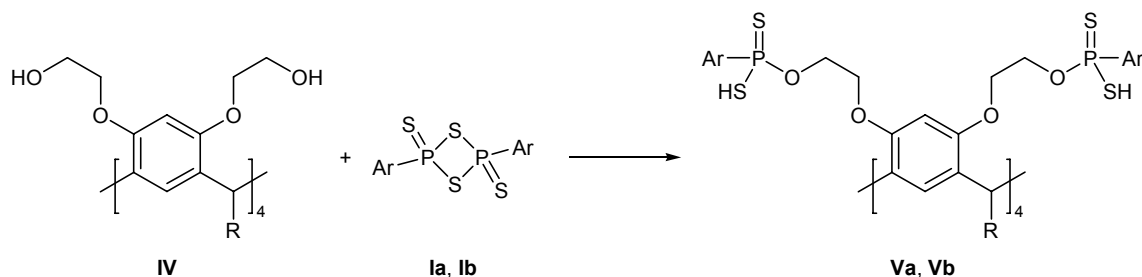
The reaction with diphosphetane disulfide **Ia** was complete in 10 h at 20°C, whereas heating of the reaction mixture for 20 h at 60°C was necessary to obtain compound **IIIb**. The <sup>31</sup>P NMR spectrum of **IIIa** contained a singlet at δ<sub>p</sub> 88.1 ppm, while the signal of compound **IIIb** with 4-phenoxyphenyl substituents on the phosphorus atoms was displaced upfield (δ<sub>p</sub> 81.7 ppm). Such chemical shifts are typical of di-

**Scheme 1.**



R = C<sub>7</sub>H<sub>15</sub>; Ar = 3,5-di-*tert*-butyl-4-hydroxyphenyl (a), 4-phenoxyphenyl (b).

Scheme 2.



R = C<sub>8</sub>H<sub>17</sub>; Ar = 3,5-di-*tert*-butyl-4-hydroxyphenyl (a), 4-phenoxyphenyl (b).

thiophosphonic acids [25]. The IR spectra of cavitands **IIIa** and **IIIb** lack broad absorption band at 3306 cm<sup>-1</sup> typical of stretching vibrations of the O–H bonds in initial calixarene **II**. In the IR spectrum of **IIIa**, a narrow absorption band with medium intensity was observed at 3633 cm<sup>-1</sup> due to stretching vibrations of OH groups in the 3,5-di-*tert*-butyl-4-hydroxyphenyl substituents on the phosphorus atom. Stretching vibrations of the S–H bonds in acids **IIIa** and **IIIb** gave rise to weak broad absorption bands in the region 2403–2540 cm<sup>-1</sup>, in keeping with published data for thioacids of four-coordinate phosphorus [26]. The IR spectra of **IIIa** and **IIIb** also contained absorption bands at 664–694 and 505–526 cm<sup>-1</sup>, which belong to stretching vibrations of the P=S and P–S bonds, respectively [26]. In the <sup>1</sup>H NMR spectrum of **IIIb**, SH protons resonated as a multiplet at δ 2.18 ppm, and the strong singlet at δ 1.45 ppm in the <sup>1</sup>H NMR spectrum of **IIIa** was assigned to methyl protons in the *tert*-butyl groups.

With a view to enlarge the cavity in cavitands and the number of reaction centers therein capable of interacting with guest molecules we recently improved the procedure for the synthesis of calix[4]resorcinarenes functionalized by 2-hydroxyethyl groups at the upper rim via reaction of 1,3-bis(2-hydroxyethoxy)benzene with aldehydes [27]. Octa-*O*-(2-hydroxyethyl) derivatives of calix[4]resorcinarenes having eight hydroxy groups were also expected to undergo thiophosphorylation by the action of 1,3-dithia-2λ<sup>5</sup>,4λ<sup>5</sup>-diphosphetane 2,4-disulfides. In fact, the reaction of octa-*O*-(2-hydroxyethyl)tetraoctylcalix[4]resorcinarene **IV** with dithiadiphosphetane disulfides **Ia** and **Ib** at a molar ratio of 1:4 in benzene afforded octakis(aryldithiophosphonic acids) **Va** and **Vb** (Scheme 2).

The reactions were carried out at 20 (with compound **Ia**) or 60°C (**Ib**), the reaction time being 6 days. More severe conditions could favor formation of by-products. Acids **Va** and **Vb** displayed only one signal

in the <sup>31</sup>P NMR spectrum at δ<sub>p</sub> 89.8 or 80.9 ppm, respectively. The IR spectrum of **Vb** contained two weak broadened absorption bands at 2439 and 2311 cm<sup>-1</sup> due to stretching vibrations of free and associated S–H groups, respectively. In the <sup>1</sup>H NMR spectrum of **Vb** protons in the ethylene fragment resonated as a multiplet at δ 4.50 ppm. The molecular ion peak (*m/z* 3400) was observed in the MALDI TOF mass spectrum of **Vb**.

Thus we have synthesized new calix[4]resorcinarenes functionalized at the upper rim by dithiophosphoryl groups, which attract interest as compounds possessing practically important properties.

## EXPERIMENTAL

The IR spectra (400–4000 cm<sup>-1</sup>) were recorded on a Bruker Vector 22 spectrometer with Fourier transform from films between KBr plates or KBr pellets. The <sup>1</sup>H NMR spectra were measured on Bruker Avance-400 (400 MHz) and Bruker Avance-600 instruments (600 MHz) from solutions in CDCl<sub>3</sub>, and the <sup>31</sup>P NMR spectra were recorded on a Bruker CXP-100 spectrometer (36.5 MHz) from solutions in benzene; the <sup>31</sup>P chemical shifts were determined relative to 85% H<sub>3</sub>PO<sub>4</sub> as external reference. The mass spectra (MALDI TOF) were obtained on a Bruker Ultraflex mass spectrometer (UV laser, λ 337 nm).

**O',O'',O''',O''''',O''''',O''''',O''''',O'''''' - [2,4,6,8-Tetraheptyl-1,3,5,7(1,3)-tetrabenzenacyclo-octaphane-1<sup>4</sup>,1<sup>6</sup>,3<sup>4</sup>,3<sup>6</sup>,5<sup>4</sup>,5<sup>6</sup>,7<sup>4</sup>,7<sup>6</sup>-octayl] octakis(hydrogen 3,5-di-*tert*-butyl-4-hydroxyphenylphosphonodithioate) (IIIa).** Compound **Ia**, 1.4 g (2.3 mmol), was dispersed in 8 ml of anhydrous benzene, and 0.5 g (0.6 mmol) of calix[4]resorcinarene **II** was added in portions at 20°C under dry argon. The mixture was stirred for 10 h at 20°C and filtered, the filtrate was evaporated under reduced pressure (0.5 mm) at 40°C for 1 h, and the residue was evacu-

ated for 1 h at a residual pressure of 0.02 mm. Yield 1.5 g (79%), mp 190–191°C. IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 3626 m (O–H), 3082 w (C–H<sub>arom</sub>); 2957 v.s., 2926 v.s., 2871 s, 2857 s (CH<sub>2</sub>, CH<sub>3</sub>); 2540 w, br (S–H), 1584 m, 1488 s (C=C<sub>arom</sub>), 1430 s ( $\delta_{\text{as}}\text{CH}_3$ ), 1363 m ( $\delta_{\text{s}}\text{CH}_3$ ), 1073 m, br [(P)O–C], 900 s, br (O–C), 664 m, br (P=S), 505 m (P–S). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.90 t (12H, CH<sub>3</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 1.43 m [40H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>], 1.45 br.s (144H, *t*-Bu), 2.31 m (8H, CH<sub>3</sub>CH<sub>2</sub>), 4.15 t (4H, CH, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 5.88 m (4H, 5'-H), 7.54 m (4H, 2'-H), 7.76 d (16H, 2-H, 6-H, <sup>3</sup>J<sub>PH</sub> = 15.9 Hz). Found, %: C 61.13; H 7.89; P 7.33; S 15.99. C<sub>168</sub>H<sub>248</sub>O<sub>16</sub>P<sub>8</sub>S<sub>16</sub>. Calculated, %: C 61.43; H 7.61; P 7.54; S 15.62.

**O',O'',O''',O'''' ,O''''' ,O'''''' ,O''''''' ,O'''''''' -** {2,4,6,8-Tetraheptyl-1,3,5,7(1,3)-tetrabenzenacyclo-octaphane-1<sup>4</sup>,1<sup>6</sup>,3<sup>4</sup>,3<sup>6</sup>,5<sup>4</sup>,5<sup>6</sup>,7<sup>4</sup>,7<sup>6</sup>-octayl} octakis(hydrogen 4-phenoxyphenylphosphonodithioate) (**IIIb**) was synthesized in a similar way (the reaction mixture was heated for 20 h at 60°C). Yield 71%, thick resinous substance. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 2927 v.s., 2855 v.s. (CH<sub>3</sub>, CH<sub>2</sub>), 2403 w, br (S–H), 1585 v.s., 1488 v.s. (C=C<sub>arom</sub>), 1466 m, 1455 m ( $\nu_{\text{as}}\text{CH}_3$ ), 1043 s, br [(P)O–C], 982 s, br (O–C), 694 s (P=S), 526 m (P–S). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.90 t (12H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 5.8 Hz), 1.29 m [40H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>], 2.18 m (8H, SH), 3.47 m and 3.70 m (8H, CH<sub>2</sub>CH), 4.10 m (4H, CH<sub>2</sub>CH), 6.36 m (4H, 5''-H), 6.92 d.d (16H, 3'-H, 5'-H, <sup>3</sup>J<sub>HH</sub> = 5.2 Hz), 7.00 m (16H, 3-H, 5-H), 7.15 d.d (8H, 4'-H, <sup>3</sup>J<sub>HH</sub> = 5.8 Hz), 7.33 d.d (16H, 2'-H, 6'-H, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz), 7.68 d.d and 7.82 d.d (16H, 2-H, 6-H, <sup>3</sup>J<sub>HH</sub> = 7.4, <sup>3</sup>J<sub>PH</sub> = 14.1 Hz). Found, %: C 61.22; H 5.15; P 7.87; S 16.90. C<sub>152</sub>H<sub>152</sub>O<sub>16</sub>P<sub>8</sub>S<sub>16</sub>. Calculated, %: C 60.94; H 5.11; P 8.27; S 17.13.

**O',O'',O''',O'''' ,O''''' ,O'''''' ,O''''''' ,O'''''''' -** {2,4,6,8-Tetraoctyl-1,3,5,7(1,3)-tetrabenzenacyclo-octaphane-1<sup>4</sup>,1<sup>6</sup>,3<sup>4</sup>,3<sup>6</sup>,5<sup>4</sup>,5<sup>6</sup>,7<sup>4</sup>,7<sup>6</sup>-octayl} octakis(oxyethane-2,1-diyl) octakis(hydrogen 3,5-di-*tert*-butyl-4-hydroxyphenylphosphonodithioate) (**Va**). Compound **Ia**, 0.56 g (0.9 mmol), was added in portions at 20°C under argon to a suspension of 0.3 g (0.2 mmol) of calixresorcinarene **IV** in 10 ml of anhydrous benzene. The mixture was stirred for 6 days at 20°C and filtered, the filtrate was evaporated under reduced pressure (0.5 mm, 40°C, 1 h), and the residue was evacuated at 0.02 mm (1 h). Yield 0.8 g (93%), mp 86–87°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3626 m (O–H); 2926 s, 2871 m, 2856 m (CH<sub>3</sub>, CH<sub>2</sub>); 2394 w, br (S–H), 1584 m, 1500 m (C=C<sub>arom</sub>), 1430 s ( $\nu_{\text{as}}\text{CH}_3$ ), 1364 m ( $\nu_{\text{s}}\text{CH}_3$ ), 1041 s, br [(P)O–C], 954 s, br, 898 m, br (O–C), 654 m, br (P=S), 503 m (P–S). <sup>1</sup>H NMR spec-

trum,  $\delta$ , ppm: 0.87 t (12H, CH<sub>3</sub>CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 7.0 Hz), 1.43 m [40H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>], 1.47 br.s (144H, *t*-Bu), 1.76 m (8H, CH<sub>3</sub>CH<sub>2</sub>), 1.94 m (8H, SH), 2.60 d.t (8H, CH<sub>2</sub>CH, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz), 3.77 m (4H, CH<sub>2</sub>CH), 4.56 m and 4.58 m (32H, OCH<sub>2</sub>CH<sub>2</sub>O), 6.18 m (4H, 5'-H), 7.01 m (4H, 2'-H), 7.77 d (16H, 2-H, 6-H, <sup>3</sup>J<sub>PH</sub> = 15.6 Hz). Mass spectrum (MALDI TOF, 1,8,9-trihydroxyanthracene matrix): *m/z*: 3581 [*M* + H – 2*Bu-t*]<sup>+</sup>. Found, %: C 60.78; H 7.92; P 6.56; S 14.32. C<sub>188</sub>H<sub>288</sub>O<sub>24</sub>P<sub>8</sub>S<sub>16</sub>. Calculated, %: C 61.14; H 7.86; P 6.71; S 13.89. *M* 3693.

**O',O'',O''',O'''' ,O''''' ,O'''''' ,O''''''' ,O'''''''' -** {2,4,6,8-Tetraoctyl-1,3,5,7(1,3)-tetrabenzenacyclo-octaphane-1<sup>4</sup>,1<sup>6</sup>,3<sup>4</sup>,3<sup>6</sup>,5<sup>4</sup>,5<sup>6</sup>,7<sup>4</sup>,7<sup>6</sup>-octayl} octakis(oxyethane-2,1-diyl) octakis(hydrogen 4-phenoxyphenylphosphonodithioate) (**Vb**) was synthesized in a similar way (the reaction mixture was heated for 6 days at 60°C). Yield 88%, mp 50–52°C. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 3065 w (C–H<sub>arom</sub>), 2925 m, 2853 m (CH<sub>3</sub>, CH<sub>2</sub>), 2439 w, br (S–H, free), 2311 w, br (S–H, assoc.), 1584 v.s., 1488 v.s. (C=C<sub>arom</sub>), 1455 m ( $\nu_{\text{as}}\text{CH}_3$ ), 1044 s, br [(P)O–C], 962 s, br (O–C), 695 s (P=S), 519 m (P–S). <sup>1</sup>H NMR spectrum,  $\delta$ , ppm: 0.86 m (12H, CH<sub>3</sub>CH<sub>2</sub>), 1.25 m and 1.27 m [40H, CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>], 1.95 m (8H, CH<sub>2</sub>CH), 3.50 m (4H, CH<sub>2</sub>CH), 4.50 m (32H, OCH<sub>2</sub>CH<sub>2</sub>O), 6.10 m (4H, 5''-H), 7.02 m (32H, 3-H, 3'-H, 5-H, 5'-H), 7.20 m (8H, 4'-H), 7.36 m (16H, 2'-H, 6'-H), 7.84 d.d (16H, 2-H, 6-H, <sup>3</sup>J<sub>HH</sub> = 7.9, <sup>3</sup>J<sub>PH</sub> = 12.5 Hz). Mass spectrum (MALDI TOF, nicotinic acid matrix): *m/z*: 3400 [*M*]<sup>+</sup>. Found, %: C 61.17; H 5.35; P 7.20; S 14.76. C<sub>172</sub>H<sub>192</sub>O<sub>24</sub>P<sub>8</sub>S<sub>16</sub>. Calculated, %: C 60.69; H 5.68; P 7.28; S 15.07. *M* 3401.

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