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LETTERS TO THE EDITOR

Calix[4]resorcinolarenes with Thioamide Groups at the Upper Rim of the Molecule

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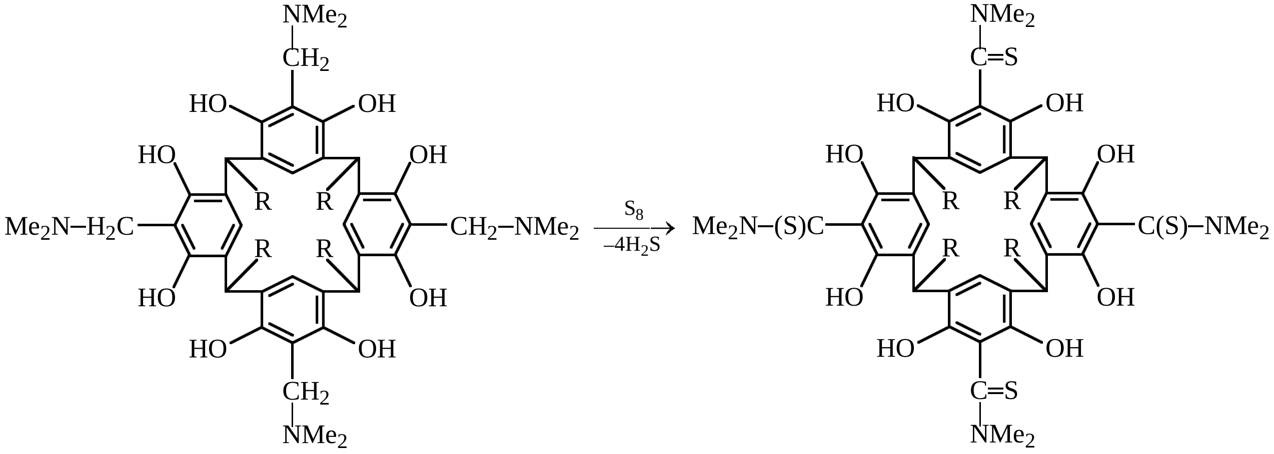
With the aim to prepare previously unknown calix[4]resorcinolarenes containing thioamide groups in the *o*-position of the aromatic ring, we studied thionation of dimethylaminomethylated calix[4]resorcinolarenes **Ia** and **Ib**. We found that heating of caix[4]resorcinolarenes **Ia** and **Ib** with elemental sulfur in DMF at 150°C gives new calixarenes **IIa** and **IIb** in high yield. The composition and structure of **IIa** and **IIb** were confirmed by elemental analysis and by IR and ^{1}H NMR spectroscopy. The IR spectra of calixarenes **IIa** and **IIb** contain the following absorption bands, cm^{-1}: 1540 (C=S in thioamides), 1605 (aromatic ring), and 3300–3500 (OH). The ^{1}H NMR spectra of **IIa** and **IIb** have no proton signals in the region of methylene groups (3.00–3.20 ppm). At the same time, the signal of the dimethylamino group protons is shifted from 1.65 ppm in the initial calixarenes **Ia** and **Ib** to 3.25–3.32 ppm in **IIa** and **IIb**.



Ia, **Ib**

IIa, **IIb**

I, **II**, R = Me (**a**), C_6H_{13} (**b**).

4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,19-tetra(*N*,*N*-dimethylaminothiocarbonyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene IIa. A mixture of 0.2 g of calixarene **Ia** and 0.1 g of elemental sulfur in 0.25 ml of DMF was heated at 150°C until hydrogen sulfide evolution ceased. Then 3 ml of chloroform was added, unchanged sulfur was filtered off, and the solid product was precipitated by pouring into pentane. The precipitate was dried in a vacuum (0.04 mm Hg). Compound **IIa** (0.18 g, 78%) was obtained, mp 300°C (dec.). ^{1}H NMR spectrum (acetone-d_6), δ, ppm (*J*, Hz): 1.78 d (12H, CH_3CH, $^3J_{HH}$ 7.0), 3.32 br.s (24H, CH_3N), 4.66 q (4H, CH_3CH, $^3J_{HH}$ 6.9), 7.63 s (4H, *m*-CH_{arom}), 8.25 s (8H, OH). Found, %: C 58.68; H 5.88; N 4.76; S 13.91. $C_{44}H_{52}N_4O_8S_4$. Calculated, %: C 59.19; H 5.83; N 6.27; S 14.35.

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4,6,10,12,16,18,22,24-Octahydroxy-5,11,17,19-tetra(*N*,*N*-dimethylaminothiocarbonyl)-2,8,14,20-tetramethylpentacyclo[19.3.1.1^{3,7}.1^{9,13}.1^{15,19}]octacosa-1(25),3,5,7(28),9,11,13(27),15,17,19(26),21,23-dodecaene IIb was prepared similarly from 0.3 g of calixarene **Ib** and 0.07 g of elemental sulfur. Yield 0.25 g (75%), mp 205–210°C. ^{1}H NMR spectrum (chloroform-*d*), δ, ppm (*J*, Hz): 0.85 br.m (12H, CH_3CH_2), 1.24–1.26 m [32H, $CH_3(CH_2)_4$], 2.13 m (8H, $CHCH_2$), 3.25 br.s (24H, CH_3N), 4.29 q (4H, CH_3CH), $^3J_{HH}$ 7.0), 7.25 s (4H, *m*-CH_{arom}), 8.01 s (8H, OH). Found, %: C 65.12; H 7.70; N 5.25; S 11.50. $C_{64}H_{92}N_4O_8S_4$. Calculated, %: C 65.52; H 7.85; N 4.77; S 10.92.

The IR spectra were taken on a UR-20 spectrometer in the range 400–3600 cm^{-1} (mulls in mineral oil). The ^{1}H NMR spectra were recorded on a Varian WM-250 (250.13 MHz) spectrometer relative to the residual proton signals of deuterated solvents (chloroform-*d* and acetone-d_6).

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