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Phosphorus-bridged calixarene phosphites: dramatic influence of a *tert*-butyl group at the upper rim of the macrocycle upon anion binding

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Experimental

2-H-*5,15-Di(*tert-*butyl)-7,13-dimethyl-2-oxodibenzo[*d,g*]-1,3,2-dioxaphosphocin* **2**. Bis(1-hydroxy-4-methyl-6-*tert*-butylphenyl)methane **1** (0.50 g, 1.46 mmol) and ethylene chlorophosphite (0.26 ml, 2.92 mmol) in 10 ml of *p*-bromotoluene in an argon atmosphere were heated for 6 h at 150 °C. The solvent was evaporated *in vacuo*. A pure product **2** (0.57 g, 96%) was obtained by recrystallization from *n*-octane. ^{1}H NMR ($CDCl_3$) δ: 7.31 (d, 1H, PH, $^1J_{PH}$ 730.9 Hz), 7.06 (s, 2H, H_{Ar}), 7.03 (s, 2H, H_{Ar}), 4.42 (d, 1H, Ar–CH_2–Ar, $^2J_{HH}$ 10.0 Hz), 3.65 (d, 1H, Ar–CH_2–Ar, $^2J_{HH}$ 10.0 Hz), 2.30 (s, 6H, Ar–*Me*), 1.40 (s, 18H, Ar–C*Me*$_3$). ^{31}P NMR ($CDCl_3$) δ: 0.5 (d, $^1J_{PH}$ 730.9 Hz). Found (%): C, 70.93; H, 8.24; P, 7.85. Calc. for $C_{23}H_{31}O_3P$ (%): C, 71.48; H, 8.08; P, 8.01.

Proximal bridged p-tert-*butylcalix[4]arene bis(hydrogen phosphite)* **5**. Method A: *p-tert*-Butylcalix[4]arene **4** (1.00 g, 1.54 mmol) and ethylene chlorophosphite (0.55 ml, 6.16 mmol) in 20 ml of *p*-bromotoluene in an argon atmosphere were heated for 6 h at 150 °C. The solvent was evaporated *in vacuo*. A pure product **5** (0.90 g, 82%, mp 293 °C) was obtained by recrystallization from chloroform–tetrachloromethane. Method B: *p-tert*-Butylcalix[4]arene **4** (1.00 g, 1.54 mmol) and ethylene chlorophosphite (0.27 ml, 3.08 mmol) in 20 ml of *p*-bromotoluene in an argon atmosphere were heated for 6 h at 150 °C. The solvent was evaporated *in vacuo*. Yield of product **5**, 1.10 g (100%), mp 293 °C. IR (KBr, ν/cm^{-1}): 931 [O–P(O)–O], 1193 (P–O–Ph), 1278 (P=O), 2458 (P–H). ^{1}H NMR ($CDCl_3$) δ: 7.26 (d, 4H, H_{Ar}, $^4J_{HH}$ 2.4 Hz), 7.18 (dd, 4H, H_{Ar}, $^4J_{HH}$ 2.4 Hz, $^5J_{PH}$ 1.5 Hz), 5.30 (d, 1H, PH, $^1J_{PH}$ 779.3 Hz), 4.47 (d, 2H, Ar–CH_2–Ar, $^2J_{HH}$ 14.9 Hz), 4.12 (s, 4H, Ar–CH_2–Ar), 3.59 (d, 2H, Ar–CH_2–Ar, $^2J_{HH}$ 14.9 Hz), 1.32 (s, 36H, Ar–C*Me*$_3$). ^{31}P NMR ($CDCl_3$) δ: –0.4 (d, $^1J_{PH}$ 779.3 Hz). MS (CI), *m*/*z*: 740.6 (M^+·). Found (%): C, 70.93; H, 7.81; P, 9.00. Calc. for $C_{44}H_{54}O_6P_2$ (%): C, 71.33; H, 7.35; P, 8.36.

Proximal bridged calix[4]arene bis(hydrogen phosphite) **7**. Calix[4]arene **6** (1.00 g, 2.35 mmol) and ethylene chlorophosphite (0.84 ml, 9.40 mmol) in 20 ml of *p*-bromotoluene in an argon atmosphere were heated for 6 h at 150 °C. The solvent was evaporated *in vacuo* and extracted by a small amount of chloroform. Undissolved powder was filtered off, washed with hot chloroform and dried to give 0.73 g (62%) of product **7** (mp 353 °C). IR (KBr, ν/cm^{-1}): 934 [O–P(O)–O], 1197 (P–O–Ph), 1270 (P=O), 2457 (P–H). ^{1}H NMR ($CDCl_3$) δ: 7.11–7.24 (m, 12H, H_{Ar}), 5.42 (d, 1H, PH, $^1J_{PH}$ 783.8 Hz), 4.53 (d, 2H, Ar–CH_2–Ar, $^1J_{HH}$ 15.4 Hz), 4.16 (s, 4H, Ar–CH_2–Ar), 3.64 (d, 2H, Ar–CH_2–Ar, $^1J_{HH}$ 15.4 Hz). ^{31}P NMR ($CDCl_3$) δ: –0.3 (d, $^1J_{PH}$ 783.8 Hz). MS (CI), *m*/*z*: 515.9 (M^+·). Found (%): C, 65.61; H, 4.44; P, 11.58. Calc. for $C_{28}H_{22}O_6P_2$ (%): C, 65.12; H, 4.29; P, 12.00.