Side Arm Participation in Crown Phosphonate Monoethyl Ester–Alkali Metal Cation Complexes

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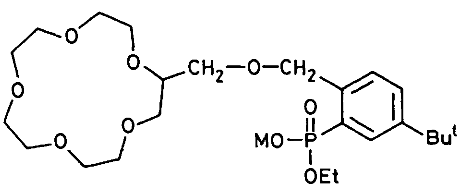
Participation of an anionic side group in complexation of a polyether-bound alkali metal cation in solution is demonstrated by ^{1}H n.m.r. spectroscopy.

Heteroatom-containing side arms on crown ether compounds offer potential additional co-ordination sites for complexation of polyether-bound cations. Although enhanced stability constants for crown ethers with side arm binding sites[1] argue for participation of the pendant functionality in cation complexation in solution, more convincing evidence has been provided by ^{13}C n.m.r. relaxation time (T_1) measurements.[2] In these studies, mobility of carbons within dialkyl and alkyl aryl ether-containing side arms was reduced when a complex was formed. We now report dramatic ^{1}H n.m.r. evidence for co-ordination of an anionic side group with a polyether-bound cation in the crown phosphonate monoethyl ester series (**1**).



(1)
a; M = Na
b; M = H
c; M = K
d; M = Li

Synthesis of (**1a**) involved reaction of *p*-t-butyltoluene with periodic acid dihydrate and iodine in $HOAc–H_2O–H_2SO_4$ (100:20:3) at 60—65 °C to give 85% of 5-t-butyl-2-methyliodobenzene (**2**) (b.p. 92—94 °C at 1.0 Torr). Treatment of (**2**) with triethylphosphite and activated copper powder at reflux gave 72% of diethyl 5-t-butyl-2-methylbenzenephosphonate (**3**) (b.p. 138—141 °C at 0.8 Torr) which was subsequently hydrolysed with NaOH in aq. EtOH at reflux and then neutralized to produce 85% of the monoethyl ester of 5-t-butyl-2-methylbenzenephosphonic acid (**4**) (b.p. 176—179 °C at 0.65 Torr). Reaction of (**4**) with *N*-bromosuccinimide and benzoyl peroxide in CCl_4 at reflux gave 83% of the monoethyl ester of 2-(bromomethyl)-5-t-butylbenzenephosphonic acid (**5**). Reaction of (**5**) with potassium hydride and then hydroxymethyl-15-crown-5[3] in tetrahydrofuran at reflux for 4 days, followed by neutralization, and conversion into the sodium salt for ease of purification by column chromatography yielded 36% of (**1a**) (m.p. 105—108 °C). Neutralization of (**1a**) with 6 M HCl gave (**1b**) which was converted into (**1c**) and (**1d**) by treatment with the appropriate alkali metal carbonates.

The 100 MHz ^1H n.m.r. spectrum of the crown phosphonic acid monoethyl ester (**1b**) in deuteriochloroform exhibited a sharp singlet for the benzylic protons at δ 4.88 downfield from $SiMe_4$. The benzylic proton absorptions of (**1c**) and (**1d**) appeared as broadened singlets centred at δ 5.04 and 5.18, respectively. In sharp contrast, the benzylic proton absorption of (**1a**) was an AB quartet (J_{AB} 12 Hz) centred at δ 5.03.

Differences between the ^1H n.m.r. spectra for the sodium salt (**1a**) on the one hand and the potassium and lithium salts (**1c**) and (**1d**) on the other are readily interpretable in terms of the relationship between the diameters[4] of the polyether cavity (1.7—2.2 Å), and sodium (1.90 Å), potassium (2.66 Å), and lithium (1.20 Å) cations. For (**1a**) the sodium cation is of the appropriate size to bind tightly within the polyether cavity. Simultaneous co-ordination of the phosphonate function markedly restricts mobility of the side group and the two diastereotopic benzylic protons. For (**1c**) and (**1d**) the alkali metal cations are either too large or too small for strong interactions within the polyether cavity. Dominant co-ordination of these alkali metal cations by the phosphonate group would not require loss of side group mobility. The AB pattern observed for the benzylic protons in (**1a**) is a convincing demonstration of anionic side group participation in complexation of a polyether-bound alkali metal cation in solution.

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