



Figure 1. ^1H N.m.r. (400 MHz) spectra in CDCl_3 : (a) (2), (b) Na^+ -(2), (c) K^+ -(2).

singlet resonances at *ca.* δ 4.3 can be assigned to oxyethylene protons by the chemical shift and intensity. \ddagger The non-terminal oxyethylene protons are equivalent on the n.m.r. time scale because of rapid interconversion between the conformers. The poorly-resolved, non-terminal aromatic resonance at *ca.* δ 6.9 also suggests conformational flexibility of the molecule at ambient temperature. \S Eight resolved signals with identical intensities were observed at δ 3.26, 3.51, 3.88, 3.93, 3.96, 4.04, 4.42, and 4.53 for K^+ -(2). This separation of the

\ddagger The A_2B_2 pattern at *ca.* δ 3.9–4.1 and the sharp singlet signals at δ 5.3–5.5 were assigned to the terminal oxyethylene protons and the methylene protons of the oxybenzyl group, respectively.

\S Resonances of terminal aromatic protons for (2) and Na^+ -(2) appeared in the range δ 7.2–7.9.

aliphatic resonances results from the different environments of the methylene protons when fixed in a three-dimensional structure in K^+ -(2). Additionally, the multiplicity of the aromatic resonance is probably caused by a mutual ring current effect of the aromatic rings held at definite positions in the complex. From these results, it is inferred that the K^+ -(2) complex has a definite coiled conformation with co-ordination of the ether oxygen atoms to the potassium ion.

A CPK (Corey–Pauling–Koltun) model of (2) in a *gauche* conformation gave a coiled structure with a cavity (2.9 Å diameter) which did not require head-to-tail hydrogen bonding to form the pseudo cyclic structure found in natural ionophores and (1).^{1,2} The size of the cavity of the coil corresponds well with the diameter of K^+ (2.66 Å) but is larger than Na^+ (1.96 Å), as in the case of (1). The longer polyether chain of (2) over (1) makes K^+ -(2) more lipophilic than the pseudo cyclic polyether chain structure of K^+ -(1). The high solubility of the complex in the dichloroethane liquid membrane is probably due to the stability of the coiled structure which in turn causes the high K^+ -selectivity.

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