Detection of Alkali Metal Ions *via* Optical Rotatory Dispersion; a Sensitive Test for Sodium in the Presence of Lithium and Potassium

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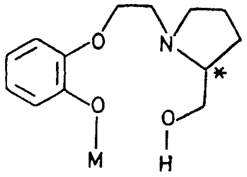
Summary A chiral, alkali metal ligand exhibits unusual cation dependent optical rotatory dispersion curves.

In the course of our work on chiral crown compounds,[1] we prepared compound (**1**). This compound had the requisite number of heteroatoms for the formation of stable co-ordination complexes with lithium cation[2] and its lithium salt is a stable crystalline solid.[3]



(1)

a; M = H
b; M = Li
c; M = Na
d; M = K

We report the o.r.d. curve dependence of (**1**) on the counterions (M).

The semicrown (**1a**) was prepared by two independent routes in an overall yield of *ca.* 40% (*cf.* Scheme). It is a white, crystalline solid†, m.p. 99—101°; $[\alpha]_D^{24\cdot7°}$ − 17·0° ($c = 1$, CH_2Cl_2).

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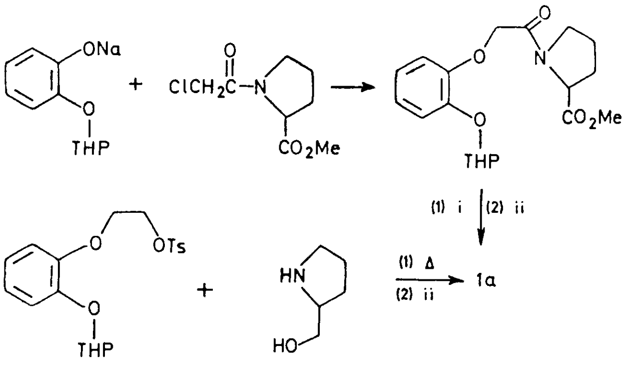
† This compound gave correct elemental analysis.

The difference in o.r.d. curves (Figure) implies that lithium and sodium are probably encapsulated (in methylene chloride solvent) and that potassium is not. This is supported by the fact that the tetraethylammonium counter ion exhibits a similar o.r.d. curve to that of potassium. Also, addition of lithium cations to the potassium salt of (**1**) transforms the potassium o.r.d. curve into the lithium curve.



i, $LiAlH_4$; ii, aqueous HCl

SCHEME

The interaction of (**1**) with sodium is stronger than with potassium or lithium. As a result, when sodium ions are added to the lithium complex (in methylene chloride solution), one obtains the o.r.d. curve corresponding to the sodium complex. Addition of one equiv. of lithium ions to the sodium complex does not change the sodium o.r.d. curve. An excess of four equiv. of lithium cations is required to cause a noticeable change in the sodium o.r.d. curve.

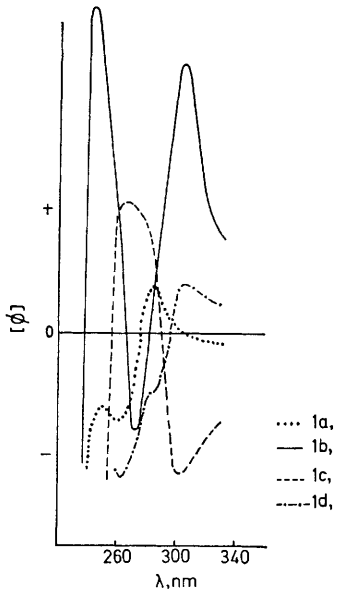


FIGURE. *Cation dependent Cotton effects.*

Since these determinations were performed at ligand concentrations of 10^{-3} to 10^{-4}M, this complexing agent should prove applicable for spectropolarimetric determinations[4] of alkali metal ions; especially sodium in the presence of potassium and lithium.

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[1] F. Wudl and F. Gaeta, *J.C.S. Chem. Comm.*, 1972, 107.

[2] C. J. Pedersen, *J. Amer. Chem. Soc.*, 1967, **89**, 7017. Compound (**1**) is of the monensin type where a cyclic conformation is maintained *via* hydrogen bonds.

[3] F. Wudl, to be published in *J. Amer. Chem. Soc.*

[4] R. J. Palma, P. E. Reinbold, and K. H. Pearson, *Chem. Comm.*, 1969, 254.