er acidity of both of the latter types. Another possibility is that the latter types have a more exposed surface area of the H(D) atom simply for steric reasons. Models suggest this might be so. It has been shown that hydrophobic binding effects (not isotope effects) in phase transfer equilibria are proportional to the surface area of the molecule.[17]

If the isotope effects only involve more freedom of motion in the hydrophobic phase, then in more ordered systems such as the current models for biomembrane structure,[18,19] isotope effects would be attenuated. On the other hand, if a real lipophilic effect produces red shifts, perhaps through van der Waals interactions, more ordered systems ought to produce increased isotope effects. Therefore, further experiments to explore the effect of order in the stationary phase, and in particular to produce columns which will serve as closer models for biomembrane structure and binding, are in progress.

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Cesium-133 Nuclear Magnetic Resonance Study of Crown and Cryptate Complexes of Cs^+ Ion in Nonaqueous Solvents

Sir:

In recent years the study of complexes of alkali metal ions with macrocyclic polyether ligands became a popular and important field of research. We have shown recently that alkali metal NMR is a powerful technique for the exploration of the formation and the solution properties of alkali cryptates with lithium[1] and sodium[2] ions. The extent of complexation is strongly dependent on the cationic and macrocyclic dimensions as well as on the solvent in which the reaction takes place. The polyethers used in this research were 18-crown-6 (I) (18C6) and monobenzo-222-cryptand (II) (C222B).

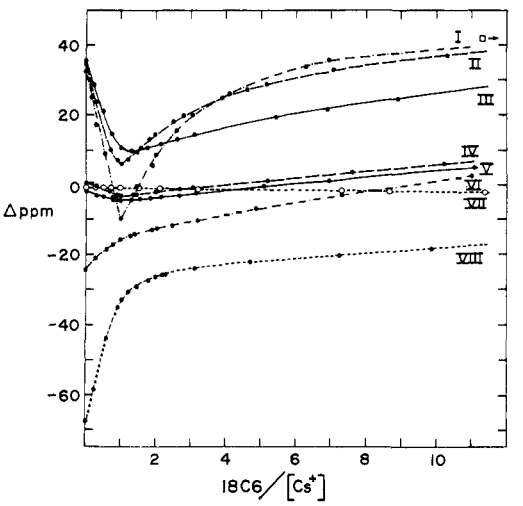
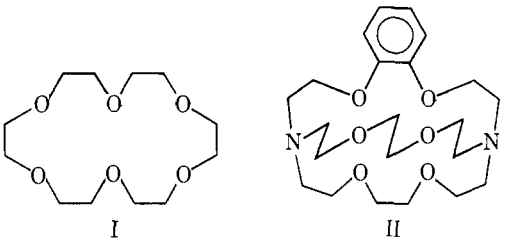


Figure 1. Plot of cesium-133 chemical shift vs. 18-crown-6/Cs^+ mole ratio in different solvents. Concentration of cesium salts is 0.01 M in all cases: (I) $CsBPh_4$ in PY, (II) $CsBPh_4$ in Me_2CO, (III) $CsBPh_4$ in PC, (IV) $CsBPh_4$ in DMF, (V) CsI in DMF, (VI) $CsBPh_4$ in MeCN, (VII) CsI in H_2O, (VIII) $CsBPh_4$ in Me_2SO.



Most inorganic cesium salts are only sparingly soluble in nonaqueous solvents. Cesium tetraphenylborate and, to some extent, cesium iodide, however, are sufficiently soluble to permit an NMR investigation. Measurements were carried out in propylene carbonate (PC), pyridine (PY), acetone (Me_2CO), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (Me_2SO), and acetonitrile (MeCN). These solvents covered a dielectric constant range from $D = 12.4$ to $D = 65$. The solvents were purified by previously described techniques.[1] Karl Fischer titrations and gas chromatographic analysis showed that they contained less than 100 ppm of water.

The measurements were made at 7.8709 MHz in the pulsed Fourier-transform mode. The field was locked with a home-built lock probe[3] which used the Varian DA-60 console to lock on a proton resonance. The NMR spectrometer is interfaced to a Nicolet 1083 computer for time averaging of spectra and also for on-line Fourier transformation of data. A 0.5 M cesium bromide solution was used as external reference. All ^{133}Cs chemical shifts are referred to an infinitely dilute aqueous Cs^+ solution as reference and are corrected for the differences in the bulk diamagnetic susceptibility of the solvents. A positive value of Δ indicates a shift to higher field.

The variation of the ^{133}Cs chemical shift as a function of the 18C6/Cs^+ mole ratio in different solvents is shown in Figure 1. It is immediately obvious that the solvent plays an extremely important role in the complexation process. The behavior in pyridine, acetone, and propylene carbonate solutions is especially interesting in that the ^{133}Cs resonance shifts *linearly downfield* until a 1:1 ligand/Cs^+ mole ratio is reached and then gradually shifts *upfield* as the concentration of ligand is increased. The data seem to indicate a two-step reaction, first the formation of a stable 1:1 complex and then the addition of a second molecule of the li-

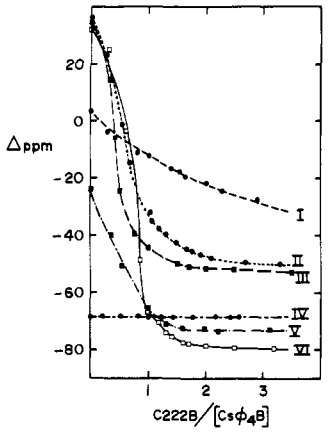


Figure 2. Plot of cesium-133 chemical shift vs. C222B/$CsBPh_4$ mole ratio in different solvents. Concentration of $CsBPh_4$ is 0.01 M in all cases: (I) DMF, (II) PC, (III) Me_2CO, (IV) Me_2SO, (V) MeCN, (VI) PY.

gand to form a "sandwich" complex.[4] In Me_2SO and MeCN solutions the ^{133}Cs resonance shifts only upfield with some indication of a weak "break" at 1:1 mole ratio. No clear-cut evidence for a 2:1 complex is observed. It should be noted, however, that the resonance continues to shift upfield, even after the formation of a 1:1 complex.

Cryptand C222B, with a tridimensional cavity, might be expected to form a stronger complex than does a two-dimensional crown. However, it is known[5] that in methanol the complex between C222B and Cs^+ ion is weaker than the corresponding dicyclohexyl-18-crown-6 complex. The variation of the chemical shift with ligand/Cs^+ mole ratio is shown in Figure 2. In all solvents, except Me_2SO, the ^{133}Cs resonance shifts downfield with increasing concentration of the ligand. From the shape of the curves it can be concluded that the resulting complex is less stable than the 18C6 complex. However, the magnitude of the chemical shift upon complexation is much larger with the cryptand than with the crown. Similar results were observed in a study of Cs^+ complexes with cryptand C222.[6] Strong solvent dependence of the chemical shift of a 1:1 ligand/Cs^+ mole ratio also indicates that, in contrast to the Li^+-C211 case,[1,7] the metal ion is not insulated from the solvent. These observations suggest that either the Cs^+ ion is not completely enclosed in the ligand cavity or that the solvent can interact with Cs^+ through the openings in the ligand.

With both ligands the extent of complexation is strongly dependent on the nature of the solvent. For example, it appears that in Me_2SO solutions the cryptand complex is much weaker than the crown complex and the binding ability of C222B is not strong enough to displace the primary solvation shell around the Cs^+ ion (Figure 2). A similar behavior is observed for the Cs^+-18C6 system in water (Figure 1).

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A New Method of Enantiomeric Purification via a Topochemical Photodimerization Reaction. Application to Three 1-Aryl Ethanols

Sir:

The preparation of enantiomerically pure products in the absence of a general method of resolution is still a challenge in synthetic organic chemistry.[1] We wish to describe here a novel method of enantiomeric purification based on the difference of a topochemical solid-state reaction of an enantiomeric crystal and the corresponding racemic compound.

Systematic studies on photodimerization of planar vinyl or aromatic molecules in the solid state have shown the necessity of a contact of about 4.0 Å between the reactive sites.[2] Such contacts may be achieved either via a short translation axis [β-type packing] or by antiparallel pairwise arrangement of the molecules, most commonly related by a crystallographic center of inversion [α-type packing]. Pairing via a twofold symmetry axis is very rarely observed[2b] since it does not lead to a close packed crystal[3] for a molecule of arbitrary shape. Photodimerizable molecules containing a chiral group may crystallize only in an α structure or in a light-stable γ structure, since a short distance of 4.0 Å [β-type packing] is precluded by the bulky nature of the chiral groups. A resolved sample of such molecules, which crystallize in a chiral crystal and thus in a structure lacking centers of inversion, will most probably appear in the light-stable γ form. On the other hand, a racemic compound may crystallize either in an α structure, where two heterochiral molecules make plane-to-plane contact across a center of inversion, or in a γ structure. Consequently, attachment of a photodimerizable handle to an enantiomerically enriched sample such as an alcohol, amine, acid, etc., will yield materials which may give a mixture of crystals in which the racemic compound appears in the photoactive α form and the enantiomer in the γ form. Upon irradiation of such a mixture the former will yield a meso photodimer, whereas the latter will remain unaffected, and will be easily separated from the reaction mixture.[4]

We describe here the use of this approach in the enantiomeric purification of three 1-aryl ethanols by condensing them with 9-anthroic acid to the corresponding anthroates **1–3**, followed by irradiation and extraction (Scheme I).[5] The crystallographic constants are summarized in Table I.

The anthracene handle was selected because its α form crystals, easily detected by a characteristic excimer emission, react almost quantitatively. The unaffected monomer may be simply extracted from the sparingly soluble dianthracenes.[6,7] The dimer on heating at its melting point splits back to a monomer, and so allows a simple recovery of the anthracene reagent.

Partially enriched alcohols were obtained either by asymmetric reduction of the corresponding benzophenone with $LiAlH_2(quinine)_2$,[8,9] or by partial resolution via the phthalic acid ester. These were treated with 9-anthroyl chloride and the crystalline esters exposed to uv irradiation at re-