

STUDY OF CONFORMATIONAL SENSITIVITY THROUGH ^{13}C NMR CHEMICAL SHIFTS AND ^{13}C SPIN LATTICE RELAXATION TIME IN CROWN ETHER MOLECULES

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ABSTRACT

The ^{13}C Chemical shifts are less sensitive to perturbations such as solvent effect than ^1H NMR Chemical shifts. The spectra of B18C6 and its complex with Na^+ and K^+ shows the similarity in both the solvent CDCl_3 and Acetone, same closeness reported for DB18C6 in CD_2Cl_2 and also the ether ring conformation are found same for both of these molecules. The ^{13}C NMR spectra of DB30C10 are very similar to ^1H NMR but when these molecule complexed with K^+ , ^{13}C NMR spectra are grossly different which indicate different structure in the complex form. The ^{13}C spin lattice relaxation time (T_1 's) for all the protonated carbon of DB30C10 in uncomplexed form are very similar but different in complexed forms.

KEYWORDS: Chemical Shifts, Spin Lattice Relaxation Time, Segmental Motion, Gauche Rotamers, Aromatic Carbons, Ether Ring Conformation, Proton-Proton Coupling Constants

The one of the most important property for crown ether is complexation with alkali metal. Crown ether holds the Na^+ and K^+ by some ion dipole forces just as solvent but the forces are much stronger here. The ^1H NMR and ^{13}C NMR spectra are mainly used to explain the structure of a number of cyclic crown ether such as Benzo 18 crown 6 (B18C6), Dibenzo 30 crown 10 (DB30C10), Dibenzo 18 crown 6 (DB18C6) and its interaction with alkali metal are examined. The solvent used to performed this study are CDCl_3 , Acetone and CD_2Cl_2 . Structural information deduced from detail analysis of NMR spectra and chemical shifts. The main aim of study is to check conformational sensitivity by dissolving different crown ether (B18C6, DB30C10 and DB18C6) in different solvent (CD_2Cl_2 , CDCl_3 and Acetone) by complexing with Na^+ and K^+ Alkali metal. The ^{13}C Spin lattice relaxation time (T_1 's) of DB30C10 and DB18C6 are also studies.

MATERIALS AND METHODS

All the NMR samples and solvent were obtained from commercial sources and used as received. DB18C6 and B18C6 crown ether and salts were independently soluble in acetone and CDCl_3 to perform the ^1H NMR experiments. Complexing in CDCl_3 were made by evaporating the acetone and redissolving the crystalline complex. All the NMR spectra were taken on a varian HR-220 equipped with Fourier transform accessory for ^1H NMR. The proton spectra were taken at 220 MHz either in the CW or FT mode at $\sim 15^\circ\text{C}$.

The ^{13}C spectra were done in the Mode at 553 MHz and at $\sim 47^\circ\text{C}$. Noise and single frequency proton decoupling were used. Assignment of the ^{13}C spectra were made from both resonance and off resonance decoupling. A varian 620 i computer with 16 k memory (8 K for FT data) was employed to carry out the Fourier transform. T_1 's were determined by progressive saturation and inversion recovery sequence. Peak intensities were determined by weighing cut-out spectra. Vicinal proton-proton coupling constants are good to ± 0.2 Hz. A negative shift indicates a downfield shift.

RESULTS AND DISCUSSION

The ^{13}C chemical shifts are known to be sensitive to conformation and relatively less sensitive to perturbations such as solvent effects. Although the understanding of the ^{13}C shifts is not sufficient to establish the details of small structural changes on the basis of the spectral positions of the ^{13}C resonance alone. There are distinctive shifts characteristics of the complexed forms of the crown ethers which present a more simplified picture than the proton results.

The chemical shifts spectra and peak assignment for the ether region of B18C6 and some of its complexes in CDCl_3 and acetone are given in Table 1 and Figure 1. As can be seen the spectra of the uncomplexed molecule are similar in both solvents. The KI-B18C6 spectra indicate changes on complexation that are alike in both solvent and are shared by other complexes in CDCl_3 and acetone. From these results it was reaffirmed the similarity of the K^+ and

Na^+ complexes and of B18C6 itself in both solvents. The chemical shifts of the ether carbons of DB18C6 in CDCl_3 are very similar to those for position 1 and 2 of B18C6 (Table 1). They also match closely to those reported for DB18C6 in CD_2Cl_2 . The KSCN-DB18C6 complex indicates the same changes on complexation as B18C6. From this it has been again concluded that the two ether ring conformation in the uncomplexed and complexed forms are the same for both of these molecules.

When free B18C6 NMR spectra is observed in D_2O a Spectrum similar to that for the complexed molecule in other solvents was found (Figure 1) this also suggested by the ether proton coupling constants. The K^+ complex of B18C6 in D_2O shows almost the same ^{13}C NMR spectrum as the uncomplexed molecule giving the typical pattern for a B18C6 complex which then conclude that the same bond conformation persists in all solvents studied. The D_2O result indicates the rather minor role that the cation plays in the ^{13}C NMR shift as opposed to the effect of conformational changes.

The ^{13}C NMR spectra of B18C6 and DB30C10 (Table 1) are very similar (Figure 1 and 2) as were the

respective ^1H NMR spectra. However when these molecules are complexed with K^+ , the ^{13}C NMR spectra are grossly different an observation which is consistent with earlier conclusion of different structure in the complexed form.

The ^{13}C spin-lattice relaxation times (T_1 's) of DB30C10 have been measured in both free and complexed forms. For uncomplexed DB30C10 the T_1 's of all the protonated carbons are very similar while in the complex the ether carbons relax about twice as fast as the protonated aromatic carbons (Table 2). If the molecule is rigid can tumble rapidly and isotropically then carbon T_1 's should be proportional to the number of protons attached. These results thus imply segmental motion in the ether fragments of the free crown ether on a time scale of 10^{-11} s, while on this time scale the complex appears rigid. Fedarko has come to the same conclusions for DB18C6 and its K^+ complex. The ether segmental motion of the uncomplexed molecules may be related to the inversion gauche rotamers observed in the proton spectra. This process slow down in the complex to a point where it can no longer contribute to the relaxations process.

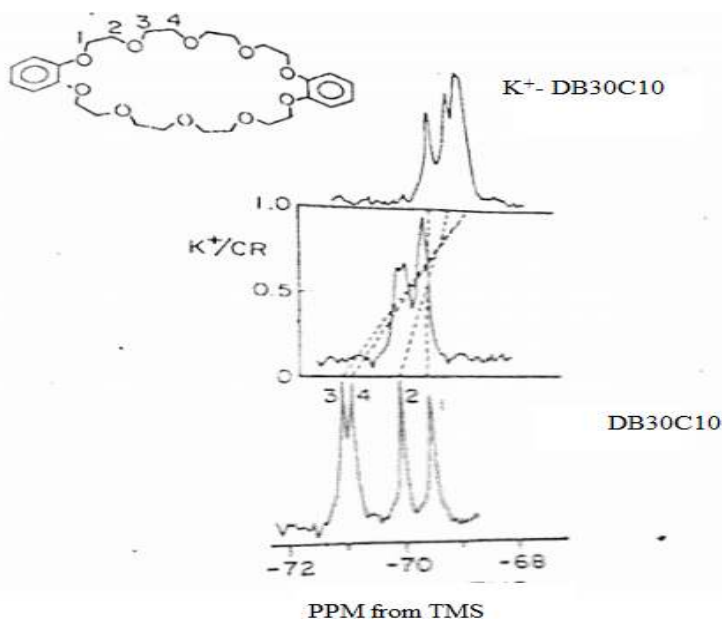


Figure 1: ^{13}C NMR spectra of the ether region of DB30C10 (bottom), 50% K^+ complexed DB30C10 (middle), and KSCN- DB30C10 in CDCl_3 shifts are relative to internal Me_4Si .

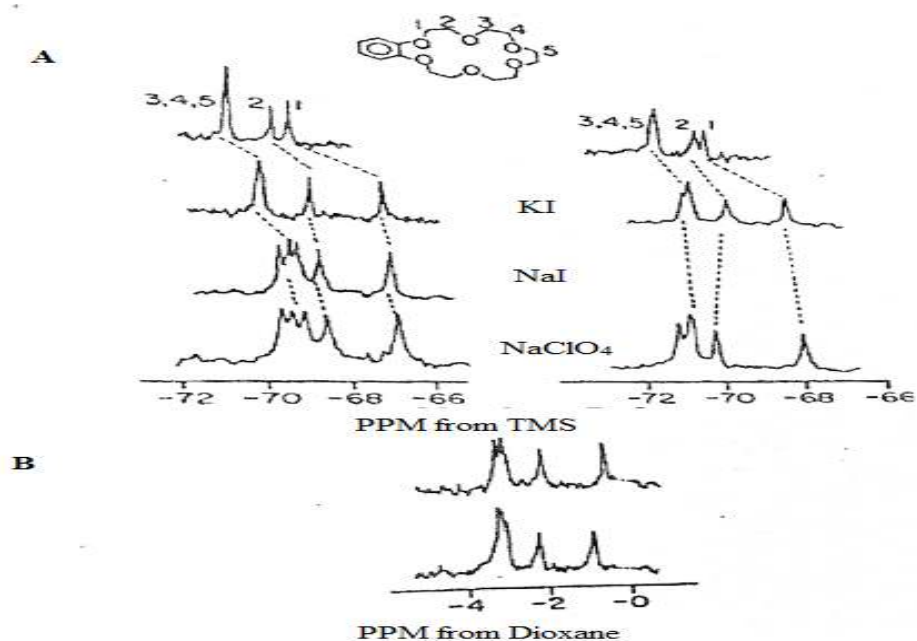


Figure 2: (A) ^{13}C NMR spectra of the ether region of B18C6 and some of its complexes in acetone (right side) and CDCl₃ (left side) shifts are relative to internal Me₄Si. (B) ^{13}C NMR spectra of B18C6 (upper) and KCl-B18C6 (lower) in D₂O shifts are relative to dioxane.

Table 1: ^{13}C NMR shifts from Me₄Si for B18C6, DB18C6 and DB30C10 in free and Complexed form

Crown ether	Solvent	C(1)	C(2)
B18C6	Acetone	-70.25	-70.49
B18C6	CDCl ₃	-69.44	-69.87
KSCN-B18C6	CDCl ₃	-67.10	-68.90
DB18C6	CDCl ₃	-69.39	-70.19
KSCN-DB18C6	CD ₂ Cl ₂	-67.50	-69.20
DB30C10	CDCl ₃	-69.50	-70.30
KSCN-DB30C10	CDCl ₃	-69.40	-69.07

Table 2: Carbon T₁'s for DB18C6 and DB30C10 in seconds

Crown ether	Solvent	C(1)	C(2)
DB30C10	CDCl ₃	1.18	1.05
KSCN-DB30C10	CDCl ₃	0.82	0.77
DB18C6	CD ₂ Cl ₂	1.24	1.19
KSCN-DB18C6	CD ₂ Cl ₂	0.50	0.50

CONCLUSIONS

In conclusion we demonstrated conformational sensitivity in crown ether molecules by ^{13}C NMR Chemical

shifts and ^{13}C Spin Relaxation time. This is found that ^{13}C NMR spectra of B18C6 in CDCl₃, Acetone and its complexes with K⁺ show similarity. On the other hand

^{13}C NMR and ^1H NMR spectra for DB30C10 and B18C6 are also very similar but complexed with K^+ , ^{13}C NMR spectra are different indicating that different structure in complex forms.

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