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SOLVENT EFFECT IN NMR SPECTRA OF DB30C10, DB18C6 AND B18C6 CROWN ETHER MOLECULES

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ABSTRACT

NMR spectra of various Crown compounds (DB30C10), DB18C6 and B18C6) determined using different solvent to know what is the solvent impact on Coupling constants. The present study is Highly valuable to know why multiplet changes in same compound in different solvent.

KEYWORDS: Chemical shift anisotropy, Aromatic Protons, Rotamer Conversion,Gauche conformation, Coupling constants

DB 18C6 has the simplest spectrum of the cyclic ether studies. However all of the crown ether examined, exhibit the same basic spectral characteristic. The ^{1}HNMR spectra of DB18C6 in acetone and $CDCL_3$ consist of two multiplets in the ether region at about 4.1 ppm downfield from Me_4Si and another multiplet due to the aromatic protons at about 7.0 ppm another multiplet due to the aromatic proton at about 7.0 ppm downfield from Me4Si. The spectra of B18C6 and DB30C10 in the ether region are more complex due to the greater number of chemically non-equivalent ether fragment.

MATERIALS AND METHODS

All the NMR samples (DB30C10, DB18C6 and B18C6) and solvent (Acetone,Chloroform-d ($CDCL_3$), Deuterium oxide (D_2O)) chemical were obtained from commercial sources and used as received. All crown ether and salts were independently soluble in acetone to perform the ^{1}HNMR experiments. All NMR spectra were taken on a varian HR-220 equipped with Fourier transform accessory for ^{1}H . The proton spectra were taken at 220MHz, either in the CW Or FT mode at 15 ºC. Noise and single frequency proton decoupling were used. A varian 620i computer with 16k memory (8 K for FT data) was employed to carry out the fourier transform.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

All Crown ethers were independently soluble in acetone to perform 1H NMR experiments.Ether resonance separated due to Chemical shift anisotropy of the benzo group.Ether fragments are undergoing conversion between the SYN- and ANTI gauche rotamers.By X-Ray data of DB30C10 and DB18C6 it concludes that interconversion between the Syn and Anti gauche rotamers must be faster than 10^3s-1.

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The spectral parameter for B18C6 and DB30C10 in 29 mol%D_2O in acetone are not a great deal different from those observed in acetone but when B18C6 is studied in D_2O the other coupling constants were found to be significantly different from those observed in the other media used in this work.The results in D_2O are much more typical of those found in the complexes. For DB30C10 and DB18C6 in $CDCL_3$ and B18C6 in $CDCL_3$ and acetone,there observed no spectral changes over a concentration range of $2X10^{-3}$ to $2X10^{-1}$ M.

DISCUSSION

The main reason for the separation of the ether resonances is the chemical shift anisotropy of the benzo group. However, comparing the shifts of the individual ether protons relative to internal Me4Si, it was found that there is also an upfield shift of these resonance in acetone relative to that in $CDCL_3$.This shift is more pronounced at position 2,3 and 4 in the cases of B18C6 and DB30C10 the magnitude for these shifts all being about the same(0.06-

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0.09 ppm). Because of the strong distance dependence of the ring current effect. It is being realized that this rules out a benzo group reorientation effect.The behaviors attributed to chemical shift anisotropy of the acetone solvent molecules.The effect is stereospecific presumably either because there is poreferential orientation of the acetone molecules in the proximity of the ether linkages or these parts of the crown ether molecule are more exposed to the solvent.

Both the multiples for the ether and aromatic protons are characteristic of a four-spin AA'BB' coupled system. The aromatic region is typical of the spectra found for 1, 2- disubstituted benzenes($J_{AA'}$=0.2, J_{AB}=8.0, $J_{A'B}$=1.6, $J_{BB'}$=7.4Hz). These coupling constant show no variation between the various compounds studied or upon ion complexion.The ether multiplet of DB18C16 is typical of what is observed for a XCH_2CH_2Y fragment undergoing rapid rotamer conversion.On analysis of the coupling constants (Table 01) with relation for such systems,It is concluded that the ether fragments are undergoing conversion between the Syn- and anti-gauche rotamers.1,4-Dioxane,which is known to undergo ring inversion resulting in similar rotamer interconversions,exhibits analogous coupling constants. A comparisons of the proton vicinal coupling constant for the (C(1), C(2))and(C(3), C(4)) either fragment of B18C6 and DB30C10 with those of DB18C6 (Table 02) show them to be the same and hence it was surprise that the ether fragments in these two molecules are in the gauche conformation with rapid interconversion as well. A lower limit to the rate of interconversion between the gauche rotamers can be estimates form the possible chemical shift difference between the methylene proton within a geminal pair assuming that the crown ring system is frozen in one configuration.

Under these circumstances, a chemical shift difference between these protons due to the slightly different just a position of the two methylene protons relative to the benzo groups is being expected.The chemical shift difference can be estimated from Johnson and Bovey's theory on the ring current shifts and was found to be ~100Hz. For these calculations the interatomic distances 1derived from X-ray data has been used for DB30C10 and DB18C6.Since only narrow resonances are observed in the experiments with uncomplexed molecules,these results indicate that the interconversion between the syn-and anti-gauche rotamers must be faster than 10^3s-1.

Rapid rotamers interconversion of the ether linkage is found in the study for complexes crown molecules, except some of the ion complexes in $CDCL_3$. In the latter cases, slight broadening is observed in the ether spectrum, suggesting that the rate of rotamer interconversion has become more comparable to the NMR time scale,no doubt a refelection of the slower dissociation rate for the ion comlexes in this solvent system.

In contrast to the above conclusion the x-ray results for the free DB18C6 indicate the presence of the both trans and gauche rotamers. Similar studies of DB30C10 however shows only the syn-and anti-gauche rotamers with dihedral angles about 60º in agreement with present NMR observations. In the case of DB18C6 aside from the coupling constant data which have presented above detailed ring current calculation assuming various configurations also indicate that the observed experimental data here are best accounted for by a rapid interconversion with gauche rotamers. In Table 03, for example comparison has been made for the chemical shift difference between C(1) and C(2), or C(3) and C(4) protons predicted by two structures, one provide by the x-ray data and the other the syn↔anti-gauche structural model proposed here with the observed ether multiple- seperation.The experimental result is in closer agreement with the proposed structure.

The reliability of these computations cans be assessed by performed similar calculations based on the all gauche crystallographic structural data for DB30C10. Excellent agreement is obtained between the calculated and experimental shift difference for the ether multiple in the C (1) C (2) fragment here.

A further confirmation of the similarity of the DB18C6,B18C6, and DB30C10 structures is found by combining the shifts of the ether protons in the latter two cases [$(\delta H_1 + \delta H_4)$- $(\delta H_2 + \delta H_3)$],to estimate the result for ether multiplet seperations in DB18C6. This means of combining the shifts Compensates for the presence of the only one aromatic group in B18C6 and negligible effect of the more distant aromatic group on the ether proton shifts in DB30C10.Thus H_1 in DB18C6 seas an effect similar to the

H_1,S in B18C6 and DB30C10 from the proximal benzo group and an additional contribution similar to that seen for the H_4'S from the distal aromatic moiety. A similar argument hold for H_2 and H_3.The results for DB30C10 are 50 and 38 Hz in $CDCl_3$ and acetone.

There is a close correspondence between these numbers and ether multiplet separation for DB18C6.

The spectral parameter for B18C6 and DB30C10 in 29 mol%D_2O in acetone are not a great deal different from those observed in acetone (Table 1 and 2)) but when B18C6 is studied in D_2O the other coupling constants were found to be significantly different from those observed in the other media used in this work.The results in D_2O are much more typical of those found in the complexes. The formation of a complex with H_3O^+,previously reported for dicyclohexyl-18-crown,is unlikely here ,since the P^H of the solution in this studies was neutral. A more likely possibility is the hydration of the ether oxygens For DB30C10 and DB18C6 in $CDCL_3$ and B18C6 in $CDCL_3$ and acetone, there observed no spectral changes over a concentration range of $2X10^{-3}$ to $2X10^{-1}$ M.

Table 1: Ether Multiplet Seperation

		Experimental			Calculated δH2-δH1	
Crown ether	Solvent	δH2- δH1	δH3- δH2	δH4- δH3	From Proposed Structure	From X Ray Structure
DB18C6	Acetone	40.0			49	62
	$CDCl_3$	30.0				
B18C6	Acetone	59.8	33.4	14.0		
	$CDCl_3$	57.2	33.8	12.0		
DB30C10	Acetone	67.0	25.2	16.1		61
	$CDCl_3$	58.4	21.6	20.0		

Table 2: Protons Chemicals shifts of Uncomplexed Crown Ethers in Various Solvents

		Ether Protons[B]					Aromatic protons[A]	
Crown ether	Solvent	1	2	3	4	5	,	α
DB18C6	Acetone	-4.147	-3.965	-----	-----	-----	-6.876	-6.944
	$CDCl_3$	-4.177	4.041	-----	-----	-----	-6.877	-6.899
B18C6	Acetone	-4.124	3.852	-3.700	-3.633	-3.596	-6.882	-6.950
	$CDCl_3$	-4.163	-3.930	-3.776	-3.722	-3.692	-6.887	-6.905
	29 mol%D_2O in Acetone	-4.149	-3.879	-3.752	-3.688	-3.688	-6996	-7.032
	D_2O	-4.223	3.900	3.727	3.709	-3.661	6.898	6.953
DB30C10	Acetone	-4.131	-3.826	-3.712	-3.632	-----	-6.879	-6.953
	$CDCl_3$	-4.153	-3.887	-3.799	-3.698	-----	-6.881	-6.899
	29 mol%D_2O in Acetone	-4.148	-3.859	-3.734	-3.661	------	-6.896	-6.976

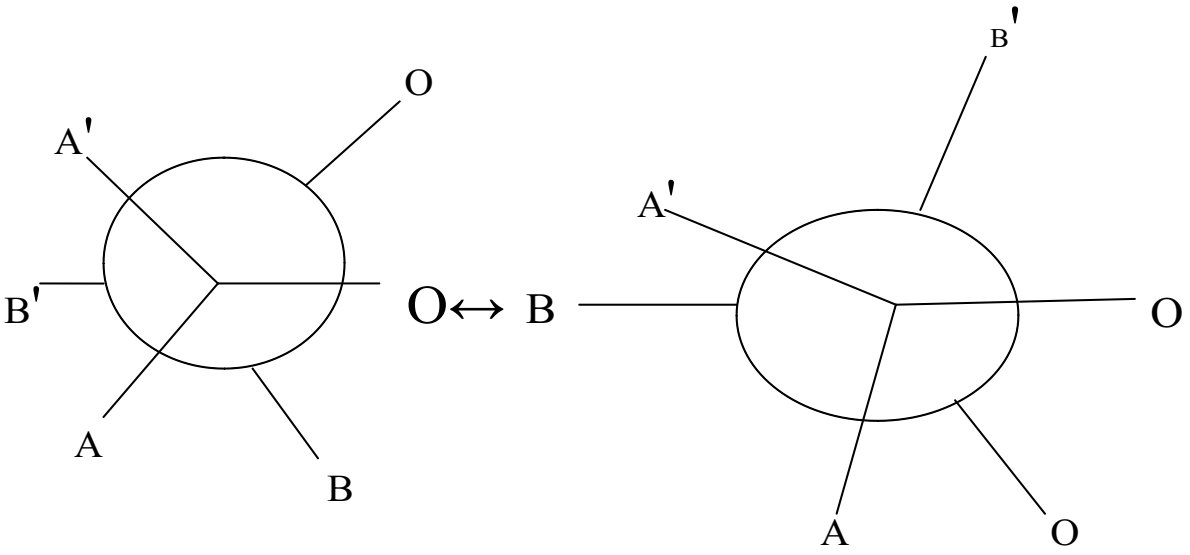
Where

A = All chemicals shifts are given in parts per million and are referred to internal Me_4Si.

B=Protons are designated by the number of the cation to which they are attached.

Table 3: Vicinal Coupling Constant for Ether Fragments (Hz)

Crown Ether	Solvent	C(1)-C(2) Fragment[a]		C(1)-C(2) Fragment[a]	
		$J_{A'B}$	J_{AB}	$J_{A'B}$	J_{AB}
DB18C6	Acetone	3.5	5.8	---------	-------
	$CDCl_3$	3.3	5.7	---------	--------
B18C6	Acetone	3.3	6.1	3.2	6.2
	$CDCl_3$	3.2	6.1	3.3	6.1
	29 mol%D_2O in Acetone	2.5	6.1	3.0	6.1
	D_2O	1.8	6.2	--------	------
DB30C10	Acetone	3.1	6.2	3.3	6.0
	$CDCl_3$	3.0	6.0	3.3	6.0
	29 mol%D_2O in Acetone	3.0	6.1	3.2	6.0
1,4 Dioxane		2.7		6.05	



[a]$J_{A'B} = J_{AB'}$, $J_{AB} = J_{A'B'}$

Abbreviation:

DB18C6 : Dibenzo-18-crown-6
B18C6 : Benzo-18-crown-6
DB30C10 : Dibenzo-30-crown-10

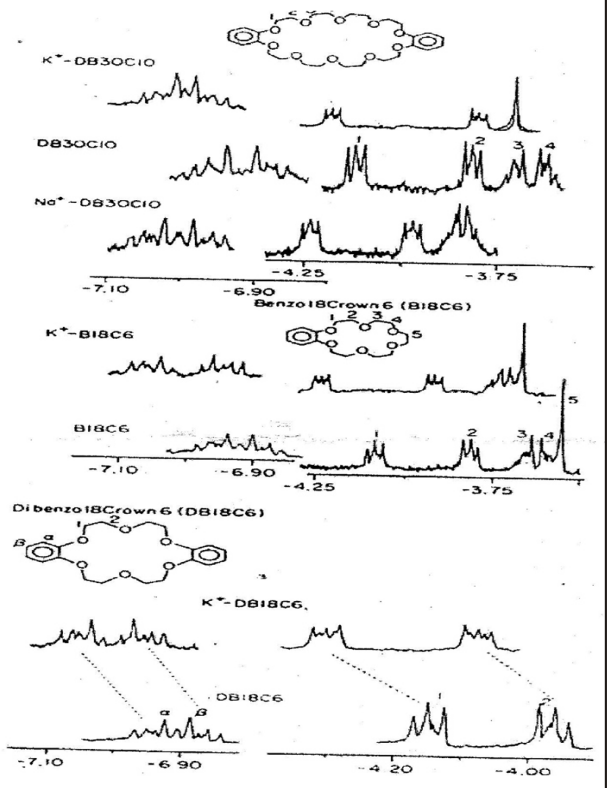


Figure 1: ^{1}H NMR spectra of dibenzo- 10-crown-6 (DB 18c6), benzo 18-crown-6 (B18C6), and dibenzo-30-crown-10 (DB30C10), and then KSCN or $NaClO_4$ complexes in acetone-d6. Shifts are relative to Me_4Si

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