

RING PUCKERING IN CROWN ETHER COMPLEXATION STUDIED BY 2D NOESY

S.V. Santhana Mariappan, G.V. Visalakshi,
and S. Subramanian

Department of Chemistry, Indian Institute of Technology,
Madras 600036, India

ABSTRACT

The conformational changes in the complexation of dibenzo-18-crown-6 (DB18C6) with K⁺ have been investigated through 2D NOESY. Results indicate that the complexation leads to a folding of benzo groups away from the plane of the crown or a puckering of the crown part.

INTRODUCTION

Crown ethers are important class of compounds since they pertain to an unusual property of complexation with alkali and alkaline earth metal cations and the mechanism of complexation has a close resemblance with the ion selective transport in membrane physiology (1). It is very important to have information about the structural changes the molecules undergo due to complexation to understand their various functions clearly. Thermodynamic and kinetic parameters of complexation of various combinations of crown ethers and cations have been derived by NMR method in recent days (2). On the other hand the structural changes due to complexation are not well studied.

The complexation of DB18C6 with KI was studied with the view to understand the structural changes through the vicinal coupling constants and the salt-induced chemical shifts of the -OCH₂CH₂O- fragment; nevertheless the changes in the relative position of the benzo group with respect to crown is not well understood. In order to understand the specific structural changes, we have undertaken NOE studies on the spatial connectivity of the benzo protons and the proximal methylene protons of the ether fragment.

EXPERIMENTAL

1:1 complex of DB18C6 with KI was prepared in freshly distilled DMSO-d₆. The solution of pure crown and its complex were sealed into two NMR tubes and were used for all NMR measurements. A Bruker WP 270 NMR spectrometer was used for the steady state NOE experiments, while a Bruker AM 500 was used for all the 2D NOE experiments, which were performed in the absolute value mode. J cross peaks arising from zero quantum coherence evolving during the mixing period were suppressed by the method of m-scrambling (3).

DISCUSSION

Figure 1 shows the ¹H NMR spectra of normal and complexed DB18C6 with potassium iodide taken in 500 MHz. The signals around 4.0 are assigned to the two groups of methylene protons attached to ether oxygens (-OCH₂CH₂O-) the deshielded bunch corresponding to the methylene protons nearer to the benzo group. The signals around 7.0 are assigned to the protons of the benzo group (4), where deshielded group is assigned to the protons which are closer to the ether oxygen.

We observed NOE for benzo α - protons, when we saturated the transitions corresponding to the protons 1 for both uncomplexed and complexed crown ether; it was noticed that there is a small increase in the percentage NOE for complexed crown ether (15% and 18% for uncomplexed and complexed respectively). 2D Nuclear Overhauser Effect Spectroscopy (NOESY) experiments were done for the same samples for six mixing times in order to estimate the

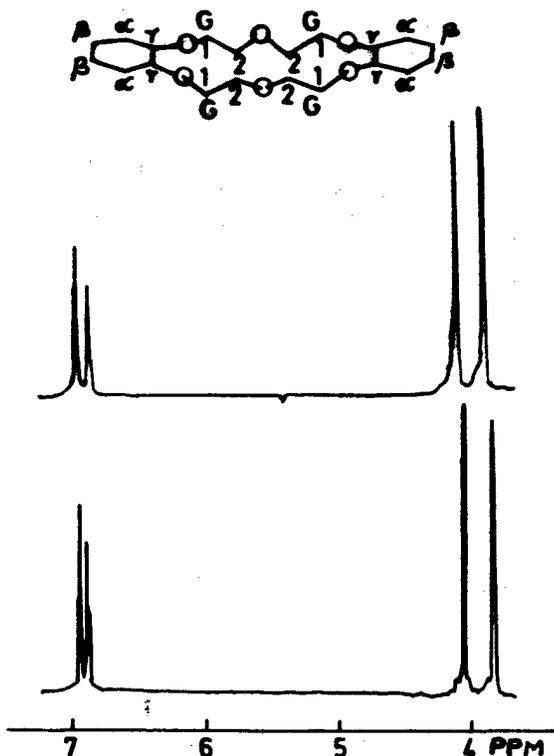


Fig. 1 One dimensional ¹H NMR spectra of pure and complexed DB18C6 recorded at 500 MHz. On the top of the spectra the solution conformation of the uncomplexed DB18C6 is also given.

distance between the benzo and proximal ether methylene protons accurately. Fig. 2 shows a typical NOE contour map with respect to a mixing time of 800 ms for uncomplexed crown ether.

Table 1 reports the NOE intensities taken at the maximum NOE cross section for the mixing time range under consideration. The intensities were fitted to the following equation (5):

$$a_1(\tau_m) = - (n_\alpha M_0 q_1 \tau_c \exp(-R_L \tau_m) (1 - \exp(-R_C \tau_m)) / (NR_C)) \dots [1]$$

keeping $M_0 q_1 \tau_c$, R_C , and R_L as the unknown parameters.

In equation [1] $a_1(\tau_m)$ denotes the intensity of the 1- α cross peak, M_0 is the equilibrium magnetization and τ_c denotes the isotropic rotational tumbling correlation time. n_α and N

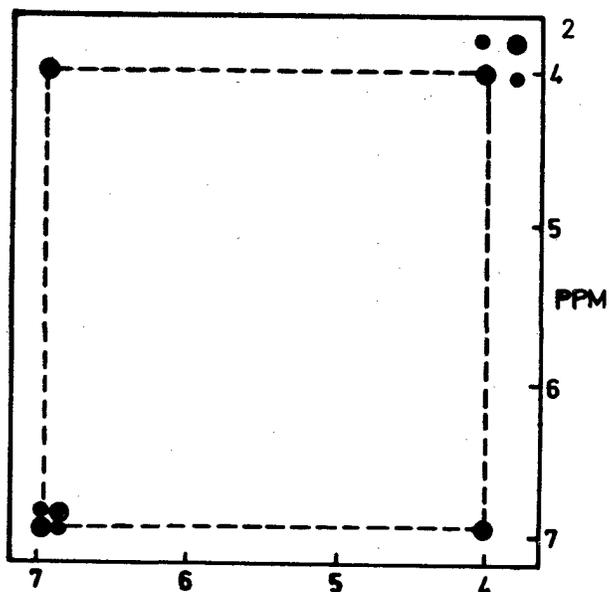


Fig. 2 Contour plot of 500 MHz NOESY spectrum of uncomplexed DB18C6 for a mixing time of 0.800 sec. The symmetric cross peaks between 1 and 4 protons are denoted by dotted lines

Table 1. 2D NOESY 1- α cross peak intensities

state of crown ether	cross-mixing time (ms)	intensity	$R_C (s^{-1})$
uncomplexed	0.25	0.449	1.12
	0.35	0.608	
	0.40	0.629	
	0.60	1.215	
	0.80	1.585	
	1.20	0.434	
complexed	0.25	1.394	2.53
	0.30	1.898	
	0.40	2.212	
	0.60	2.627	
	0.80	2.153	
	1.20	1.543	

are respectively the number of α -protons and the total number of protons of the NOE detected dipolar network. R_C and R_L are respectively the cross relaxation and leakage rate constants (for the actual expressions of R_C , R_L , and $q_{1\alpha}$ see reference 5).

The cross relaxation constants were found to be 1.12 and 2.53 sec⁻¹ respectively for uncomplexed and complexed DB18C6. Assuming a constant isotropic molecular tumbling correlation time, the distance between protons 1 and α before and after complexation can be related to each other by the following equation:

$$R_C(U)r_{1-\alpha}^6(U) = R_C(C)r_{1-\alpha}^6(C) \dots [2]$$

We derived an internuclear distance of 1.95Å between 1 and α by using a Dreiding model with all gauche conformation for DB18C6 (solution conformation reported in the literature) for uncomplexed molecule and is used to arrive at the distance between the same in the complexed state. The decrease in distance was estimated to be 0.25±0.05Å.

The reduction in distance may be attributed to the possibility that upon complexation the crown puckers with respect to benzo group in such a way that there is a decrease in distance or due to a decrease in C(γ)-O-CH₂(1) bond angle making 1 and α closer. Any 'folding' of the benzo group away from the plane leads to slightly unequal distances for the protons in the 1 position with respect to the benzo α -proton. The nonequivalence that might be caused by this is still unresolved within the line width of the slightly broadened resonances of 1-protons and as such it is likely that the benzo group could undergo a 'fluttering' motion by way of folding 'up' or 'down' relative to the plane. If this is what happens in

effect, then the 'fluttering' frequency may correspond to the frequency of exchange between complexed and 'free' cation in the medium.

If the benzene ring does not fold, then the alternative inference is that upon complexation the crown part elongates about an axis in the plane of the ring perpendicular to the axis joining the benzo group. This would also account for the observed NOE results.

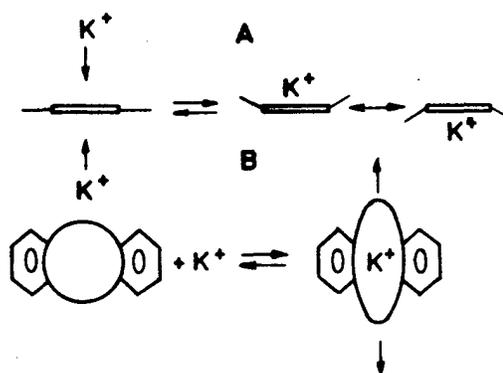


Fig. 3 Two possible models to explain the observed reduction of the distance between 1 and α . (A) fluttering motion of the benzene ring and (B) stretching of the crown ring.

Note: Recent molecular mechanics calculation do indicate that the crowns undergo a V-shaped puckering around the alkali metal ion (6).

ACKNOWLEDGEMENTS

Thanks are due to IIT, Madras for a scholarship to SVSM and to the SIF, Bangalore and TIFR, Bombay for help in the high frequency NMR measurements.

REFERENCES

1. P.B. Chock and E.O. Titus Prog. Inorg. Chem. 18, 287 (1973)
2. R.M. Izat, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen, Chem. Rev., 85, 271 (1985)
3. S. Macura, Y. Huang, D. Suter and R.R. Ernst, J. Magn. Reson. 43, 259 (1981)
4. D. Live and S.I. Chan, J. Am. Chem. Soc. 98, 3769 (1976)
5. S. Macura and R.R. Ernst, Mol. Phys. 41, 95 (1980)
6. P.D.J. Grootenhuis and P.A. Kollman, J. Am. Chem. Soc., 111, 2152 (1989)