

Molecular complexes of macrocyclic polyethers with 1, 3, 5-trinitrobenzene

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Abstract. The interaction of six macrocyclic polyethers with 1, 3, 5-trinitrobenzene has been studied by spectroscopic methods. The association constants have been evaluated by ^1HMR chemical shift method. There is evidence that major contribution to the interaction is *via* n and π electrons. The donor strengths of the polyethers have been evaluated.

Keywords. Molecular complexes; macrocyclic polyethers; association constants; ^1HMR chemical shifts; donor strengths.

1. Introduction

Macrocyclic polyethers synthesised by Pedersen (1967) have been the subject of much study due to their ability to solubilize alkali and alkaline earth metal ions in organic solvents (Pedersen and Frensdorf 1972) and their close resemblance to naturally occurring antibiotics (Szabo *et al* 1973). As model systems for peptide antibiotics, their complexation behaviour with alkali and alkaline earth metal ions has been well studied (Christiansen *et al* 1974; Truter 1973). However, very little attention has been paid to their ability to form molecular complexes. This would be particularly relevant to the study of these ethers as model systems for antibiotics, since interaction with the membrane would precede the complexation and this interaction is very likely to be of electron donor-acceptor type. It would then be of interest to study whether the polyethers which exhibit permselective conductance behaviour in the membrane, would form molecular complexes and the nature of stabilisation forces responsible for the formation of such complexes. Goldberg (1975) has shown from x-ray structural studies that hydrogen bonding and geometric factors form the stabilisation forces in the molecular complexes of two polyethers. No information is available about their stabilities and structures in solution which would have been useful in assessing the nature of binding sites and conformations of ethers in solution.

We have examined here the ability of six macrocyclic polyethers (figure 1) to form molecular complexes with 1, 3, 5-trinitrobenzene (TNB) in chlorinated hydrocarbons.

2. Experimental

The I.U.P.A.C. nomenclature and the widely used names of these polyethers are: 2, 3-benzo-1, 4, 7, 10, 13-pentaoxacycloptadeca-2-ene, benzo-15-Crown-5, (I);

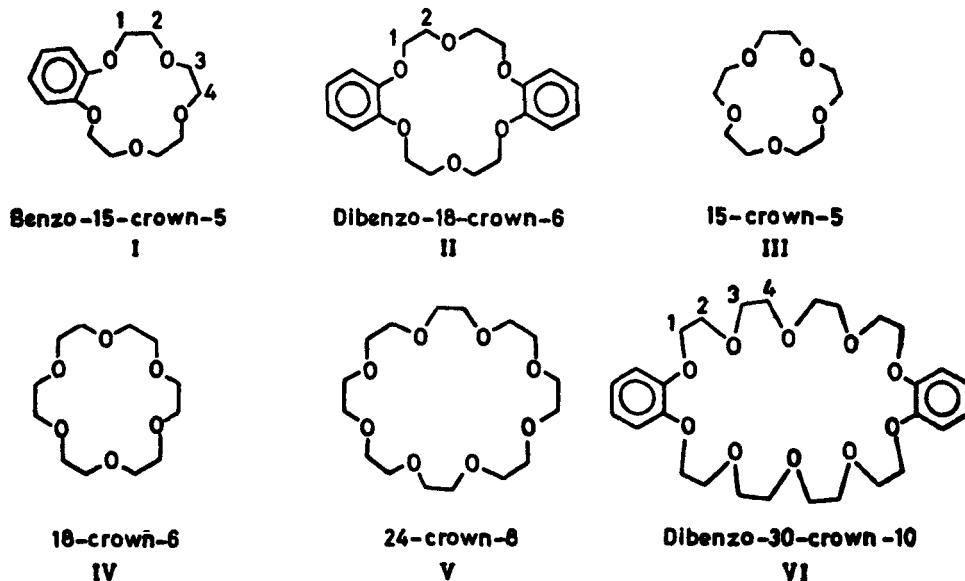


Figure 1. Structural formulas for macrocyclic polyethers

2, 3, 11, 12-dibenzo-1, 4, 7, 10, 13, 16-hexaoxacyclooctadeca-2, 11-diene, dibenzo-18-Crown-6, (II); 1, 4, 7, 10, 13-pentaoxacyclopentane, 15-Crown-5, (III); 1, 4, 7, 10, 13, 16-hexaoxacyclooctadecane, 18-Crown-6, (IV); 1, 4, 7, 10, 13, 16, 19, 22-octaoxacyclotetracosane, 24-Crown-8, (V); 2, 3, 17, 18-dibenzo-1, 4, 7, 10, 13, 16, 19, 22, 25, 28-decaoxacyclotriaconta-2, 17-diene, dibenzo-30-Crown-10, (VI). The ethers were synthesised and purified according to published procedures (Pedersen 1967; Dale and Kristiansen 1972; Cook *et al*; Gokel *et al* 1974). 1, 3, 5-trinitrobenzene (TNB) was obtained from BDH and twice crystallised from benzene. All the solvents used were of spectroscopic grade.

The ¹HMR measurements were carried out on a Varian HA 100 NMR spectrometer using C²HCl₃ and C₂H₄Cl₂ as solvents with TMS as internal standard. The electronic absorption spectra were recorded on a Unicam SP700A spectrophotometer with CH₂Cl₂ as solvent. The infrared spectra were taken on a Carl Zeiss UR 10 spectrometer using KBr and KRS cells.

The association constants have been evaluated by ¹HMR shift method as described in the literature (Foster and Fyfe 1965). The ether (I)—TNB complexation was followed under the condition (ether)₀, (donor) > (TNB), (acceptor)₀ and phenyl signal of TNB (0.06 M) at 958 Hz was monitored in C²HCl₃ solutions containing large excess of ether (0.9–5.5 M). In the case of other ethers (II) and (VI) owing to the poor solubility of these ethers in C²HCl₃, C₂H₄Cl₂ was used as a solvent under the condition (acceptor)₀ > (donor)₀. The shifts in phenyl signals of these ethers (0.02 M) were monitored in solutions containing excess of TNB (0.2–1.7 M). These shifts were analysed graphically and by computation to calculate the association constants K and Δ₀, the chemical shift of TNB or phenyl protons signals of the ethers in the complex relative to the shift in pure components. MINDS programme was used for computation work (Dodson *et al* 1971). The values of K and Δ₀ obtained from graphical method compares favourably with the computed values. The

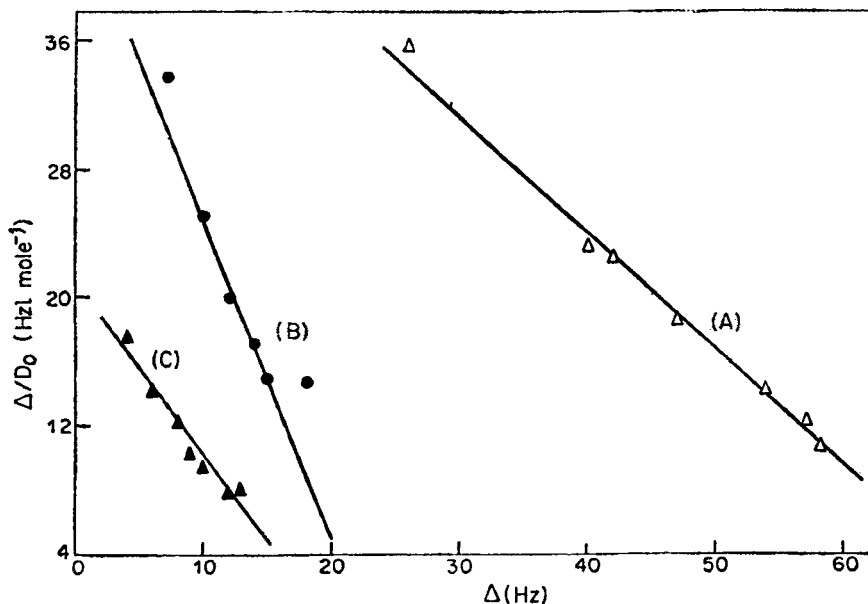


Figure 2. Plots of Δ/D_0 against Δ for the complexes of TNB with A. Benzo-15-crown-5; B. Dibenzo-30-crown-10 and C. Dibenzo-18-crown-6 at 31.5°C.

linearity of the plots (figure 2) suggests a 1 : 1 complexation of ethers with TNB. It was found possible to carry out temperature dependence studies at two temperatures for two ethers only due to the limited solubility of the ethers in solvents used.

The charge transfer maxima of the complexes (1 : 1), ν_{CT} , were measured according to the method of Krishna and Bhowmick (1968) since the charge transfer absorptions lie beneath the absorptions of TNB. The ionisation of the donor ethers (I^D) were calculated using the relationship

$$h\nu_{CT} = aI^D + b$$

The values of a and b are taken from Foster (1959). The results are given in table 2.

3. Results and discussion

The ¹HMR resonances of the polyethers and their assignments are given in table 1. The ¹HMR spectrum of benzene substituted ether (I) yield valuable information due to ring current magnetic anisotropy and this led to spatial relationship of ether protons and aromatic group. The 100 MHz ¹HMR spectra of benzene substituted ethers, (I), (II) and (VI), though not well resolved in the phenyl signals (singlets are observed), the ether protons signals show multiplets. It has been found possible to identify two multiplets (AA' BB') arising from each of the 1, 1' and 2, 2' protons in ethers (I) and (VI) while these are not well resolved in ether (II) (only a doublet is observed). These assignments agree well with the work of Live and Chan (1976). The nonbenzenoid ether proton resonances occur as singlets and yield very little information concerning the protons environments. The data presented in table 2

Table 1. ¹HMR spectral data of macrocyclic polyethers and their assignments.

Ether	(Hz) in C ³ HCl ₃	assignments
Benzo-15-Crown-5, (I)	374	3,4
	394	2,2'
	408	1,1'
	686	aryl
Dibenzo-18-Crown-6 (II)	414	1,1'
	420	2,2'
	696	aryl
15-Crown-5, (III)	366	ether
18-Crown-6, (IV)	356	ether
24-Crown-8, (V)	360	ether
Dibenzo-30-Crown-10, (VI)	376, 378	3,4
	393	2,2'
	420	1,1'
	694	aryl

Table 2. Measured properties of macrocyclic polyether—TNB interaction

Donor ether	Association constant (1 mole ⁻¹)	Δ_o (Hz)	ν_{CT} (cm ⁻¹)	I^D (ev)
I	0.632†	77	25,320	8.29
	0.514‡			
II	1.091†	19	23,530	8.05
III	—	—	23,225	8.01
IV	—	—	25,640	8.34
V	—	—	23,810	8.09
VI	2.000†	22	22,990	7.98
	1.370*			

†at 31°5° ‡at 50° *at 45°

have been helpful in arriving at the possible geometry of the molecular complexes in solution (vide infra).

The low values of association constants suggest weak interaction of the ethers with TNB. Lack of data on the nonbenzenoid ethers is due to small shifts of the TNB signals on addition of large excess of ethers and these could not be monitored with sufficient accuracy. However, the fact that they form molecular complexes is shown by the appearance of charge transfer absorptions. The magnitudes of association constants obtained in the present study show that larger cyclic ether (VI) forms a stabler complex in solution, relative to the ethers (I) and (II). The limited temperature dependance studies of association constants in the ethers (I) and (VI) permit us to compare the thermodynamic parameters. Thus at 304.6° the ΔF^θ , ΔH^θ and $T\Delta S$ values of ether (I) and ether (VI) are 1.16 kJ/mol, -12.10 kJ/mol and -13.24 kJ/mol and -1.75 kJ/mol, -20.43 kJ/mol and -18.66 kJ/mol respectively. The

magnitude of enthalpy and entropy of complexation of ether (VI) relative to those of ether (I) suggests that increased size of the ether and presence of an additional benzene ring favours better complexation.

Attempts to isolate the molecular complexes in crystalline state have so far been unsuccessful except in the case of ether (I)—TNB. The HMR spectrum of the isolated complex in C^2HCl_3 is very similar to the spectrum obtained from a solution containing equimolar concentration of ether (I) and TNB. This permits us to compare the proton resonances of other ethers in the 1 : 1 solutions containing TNB. It is observed that the phenyl protons of TNB and of the ethers (I), (II) and (VI) occur in a shielded region. Further, the 2 and 2' protons of these ethers are similarly shielded as a result of complexation. This suggests that TNB is situated predominantly over the phenyl ring of the ether at a distance away from the mutual deshielding zones of the two rings. Construction of CPK molecular models for the complexes showed that such an arrangement would lead one of the nitro groups of TNB projected over the cavity and in proximity to one of each of the 2, 2'-protons. This leads to preferential shielding of these protons. It is suggested that in the case of nonbenzenoid ethers, the TNB is situated over the cavity. The CH_2-O-CH_2 -signal in these ethers do not change appreciably (1-2Hz) when compared to benzene substituted ethers (5-8 Hz). The possibility of cage structures for these molecular complexes is ruled out since molecular dimensions of these ethers do not permit this.

The infrared spectra of the complexes, 1 : 1 solid mixtures were compared with the vibrations of the individual components. It is found that vibrations in the region $1300-1200\text{ cm}^{-1}$ arising from the CH_2-O-CH_2 groups of the ethers are shifted to higher frequencies while the band at 640 cm^{-1} of TNB is shifted in lower frequencies in the complexes. The latter band has been assigned to δNO_2 of TNB. The lowering of this band has been attributed to the decreased bending force constant as a consequence of reduced π -bond order of the NO_2 group of TNB resulting from the charge donation to π^* orbital. It is difficult to identify this effect in the NO_2 stretching frequency due to overlapping of $-CH_2-O-CH_2$ -vibrations. The band at 980 cm^{-1} of the pure ether (I) is absent in the isolated complex. This band has been assigned as complex sensitive band since the band is absent in the complexes (Poonia 1974). We assign this band as conformation sensitive band arising from the CH_2 rocking vibration of a *gauche* $O-CH_2-O$ group similar to that ethylene glycols (Miyake 1960). The absence of this band in the complex is attributed to a conformer of the ether (I) in which the $O-CH_2-CH_2-O$ group is in *trans* configuration. In the complexes of other ethers the presence of a band in this region suggests a *gauche* configuration of the $O-CH_2-CH_2-O$ group.

The donor strengths of these ethers expressed as ionization potentials (table 2) do not show significant variation in going from benzene substituted ethers to simple ones. The smallness of Δ_0 values and their apparent independence of donor strengths suggest that the ring current effects may form the stabilisation force in these complexes. Since the ethers possess both increvalent n sites (lone pair electrons of ether oxygens) and π sites, the molecular complexes formed can be classified as sacrificial $\pi-\pi$ type, in the case of (I), (II) and (VI) and $n-\pi$ type in the case of (III), (IV) and (V). The latter type of complexation gains support from the observation that fluoranil (π -acceptor) forms complexes with (III) (IV) and (V) (unpublished). The data presented here affords the first example of molecular complexation of macrocyclic polyethers with π -acceptors.

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