Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **28:** 245–258, 1997.

Infrared Spectroscopic Study of the Role of Water in Crown Ethers and Their Molecular Complexes with 3- and 4-Nitrophenol

B. I. EL-ESWED, M. B. ZUGHUL and G. A. W. DERWISH*
Department of Chemistry, Faculty of Science, University of Jordan, Amman 11942, Jordan

(Received: 12 July 1996; in final form: 2 October 1996)

Abstract. The IR spectra of the crystalline complexes of 3- and 4-nitrophenol with crown ethers were studied, viz., 18-crown-6 (18C6), benzo-18-crown-6 (B18C6), dibenzo-18-crown-6 (DB18C6), dicyclohexano-18-crown-6 (DC18C6) and dibenzo-24-crown-8 (DB24C8). The spectra of uncomplexed crown ethers showed water absorption bands which indicate the presence of two types of bound water molecules, viz., cavitant water enclosed by the strong ether-cavity field and outer-layer hydrogen-bonded water molecules. Upon complexation with 3- and 4-nitrophenol, the bands attributed to cavitant water disappeared, leaving the outer layer water to act as a bridge between the host crown ether and the guest phenols. The results further showed that of the crown ethers and of the phenols, B18C6 and DC18C6 and 3-nitrophenol, have the strongest interaction. The behaviour of the phenols was explained by the increased contribution of the inductive σ-moment over the resonance π-moment in the complexes.

Key words: Solid molecular complexes, crown ethers, water in crown ethers, 3-nitrophenol, 4-nitrophenol, IR spectra.

1. Introduction

The study of well-defined complexes formed between neutral molecules and crown ethers is an area of active interest [1, 2]. A number of complexes with phenolic compounds have been reported in the literature in which water molecules seem to form an integral part of the crystalline structure, as shown by X-ray crystallographic studies [3–7]. Thus, in the phenolic complexes, the water molecules act as bridges between the host ether molecules and the guests, i.e. a hydrogen bond links the phenolic hydrogen with the water molecule and the hydrogens of the water molecule are bonded to the crown ether.

Furthermore, the presence of water in crown ethers has received some attention in regard to the nature of its attachment to the ether molecules [2]. Water was shown to be encircled by macrocyclic ethers containing pyridine and ketone moieties, such as the hexaethylene glycol bis (2-pyridyl) ketone macrocycle, but not by 18C6 or related compounds [8]. This was attributed to the influence of the heteroaromatic moiety on the conformation and the size of the polyether ring.

---

* Author for correspondence.

In continuation of our studies of crown ether molecular complexes [9–11], the present work was planned in order to investigate the spectral characteristics of 3- and 4-nitrophenol complexes with crown ethers, viz., 18C6, B18C6, DB18C6, DC18C6 and DB24C8; and to shed some light on the possible host-guest interaction, and the role played by water molecules in these complexes, as well as in the uncomplexed ethers.

2. Experimental

IR spectra were recorded in the region 4000–400 cm^{-1} using a Nicolet Impact 400 FTIR spectrometer. A polystyrene film was used to calibrate the spectrometer. KBr discs were used for all samples and handled under dry conditions. Melting points were determined using a Harris melting point apparatus with a Gold Brand thermometer (Brand, Germany). All melting points were reported as measured without correction.

m-Nitrophenol (general purpose reagent, B.D.H.), p-nitrophenol (puriss, Fluka), 18-crown-6, benzo-18-crown-6, dibenzo-18-crown-6, dicyclohexano-18-crown-6 (all for synthesis, Merck), dibenzo-24-crown-8 (purum, Fluka), chloroform and ether (AR, C.B.H.) were all used without further purification.

2.1. PREPARATION OF COMPLEXES

The crown ether (1 mmol) in 2 mL of chloroform was added to 1 mmol of the guest in 10 mL of hot chloroform. The solution was allowed to evaporate at room temperature. For most samples crystals were formed, but semisolids were obtained for some. These were the complexes of B18C6 and DC18C6 with 3-NP and B18C6 and 18C6 with 4-NP. The latter was successfully crystallized from a solution in diethylether which was then allowed to evaporate and crystals were formed. The other semisolids persisted in spite of all attempts at obtaining well defined crystals. Table I summarizes some of the physical properties of the prepared complexes. The only complex that has previously been reported in the literature, is the 18C6 complex with 3-NP [3] with a melting point over the range 49–56 °C as compared with the much sharper and higher melting point of 55–58 °C obtained in the present work.

2.2. REMOVAL OF WATER FROM CROWN ETHERS

It has been reported that 18C6 is a hygroscopic compound [12]. Attempts were made to obtain dry 18C6 either by drying over P_2O_5 or recrystallization from such solvents as acetonitrile, methanol/ether, chloroform-methanol/ether or chloroform/ether. These procedures were found to be ineffective in removing all traces of water as judged by the observation of the water absorption band in the 3450 cm^{-1} and 1620 cm^{-1} regions.

Table I. Physical properties of crown ether complexes.

	Complex	M.P. °C	Colour
1	18C6/3-NP[#]	55–58	light yellow
2	B18C6/3-NP	*	light yellow
3	DB18C6/3-NP	126–136	yellow
4	DC18C6/3-NP	*	light yellow
5	DB24C8/3-NP	67–69	gray
6	18C6/4-NP	40–49	yellow
7	B18C6/4-NP	*	yellow
8	DB18C6/4-NP	123–125	yellow
9	DC18C6/4-NP	89–94	yellow
10	DB24C8/4-NP	65–66	gray

[#] Reported in Ref. [3] m.p. 49–56 °C and ratio (1 : 2 : $2H_2O$).

[*] Semisolids.

Key. 3-NP: 3-nitrophenol, 4-NP: 4-nitrophenol.

DC18C6, which gave well resolved water absorption bands, was selected to show that these bands belong to water associated with DC18C6 and not to water in KBr or due to sorbed atmospheric vapor. Several spectra were taken with different amounts of DC18C6 in KBr pellets, and they all show that, following the increase in the amount of DC18C6, the intensity of the bands assigned to water molecules increased in a uniform manner, as did those of the ether bands, thus showing that water is associated with the crown ether.

3. Results and Discussion

3.1. WATER IN CROWN ETHERS

Although, in general, the appearance of the water bands differed from one crown ether to another, as shown in Figure 1, there are many features in common among them, as can be judged from Table II.

However, because of the rather sharp bands shown in the spectrum of hydrated DC18C6, they will be discussed first. The band at 3566 cm^{-1} can be assigned to $\nu_{as}OH_2$, the one at 3397 cm^{-1} to $\nu_{s}OH_2$ and that at 3251 cm^{-1} to the first overtone of the β_{O-H} vibration. These may be compared with those of water in the gas phase i.e., at 3756, 3652 and 3151 cm^{-1} [13]. The β_{O-H} vibration of water in the crown ether appeared at 1651 cm^{-1} giving for the first overtone the calculated value of 3302 cm^{-1} compared with the observed value of 3251 cm^{-1}, a situation similar to that for water in the gas phase which has the fundamental at 1595 cm^{-1} and the overtone observed at 3151 cm^{-1}. Similar bands in the crown ethers, 18C6 and B18C6 were observed and assigned accordingly, Table II.

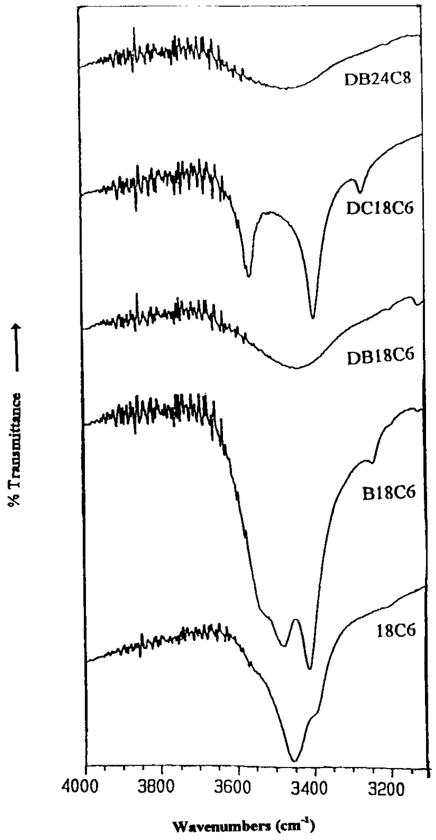


Figure 1. IR spectra for water in crown ethers in the region (4000–3100 cm^{-1}.

If one considers the ν_{as}, ν_{s} and $\beta_{\text{O}-\text{H}}$ bands of water in the gas, the liquid, and in hydrated DC18C6 phases (Table III), then comparing the ν_{m} values of the centres of the ν_{as} and ν_{s} bands for each of these three phases, as in Scheme 1, it becomes apparent that the changes shown in DC18C6 are greater than those in the liquid water phase. This can be judged by the values of ν_{as}, ν_{s} and the shift suffered by the centres of these two bands, viz., $\Delta\nu_{\text{m}}$ = 222 cm^{-1} in DC18C6 as compared to 171 cm^{-1} in the liquid phase. Taking this together with the relative shifts to higher frequencies, with reference to gaseous water, of $\beta_{\text{O}-\text{H}}$, i.e., 56 and 45 cm^{-1}, respectively, lead to the conclusion that the water in DC18C6 is in a stronger (hydrogen) bonding environment than in liquid water.

Furthermore, water in solid DC18C6 seems to differ markedly from that of solid phase water (see Table III), $\Delta\beta_{\text{O}-\text{H}}$, as measured from the gas phase value, is larger for water in DC18C6 than for water in the solid phase. This fact, therefore, excludes the consideration of water associated with crown ethers to be in a similar

Table II. Infrared vibrations (in cm^{-1}) of water in uncomplexed crown ethers.

Assignment	**18C6**	**B18C6**	**DB18C6**	**DC18C6**	**DB24C8**
$\nu_{\text{as O-H}}$ of H_2O enclosed inside the ether ring	3563 (sh)	3541 (sh)		3566 (m)	
$\nu_{\text{O-H}}$ of outer-layer hydrogen bonded water	3453 (br,s)	3467 (br,m)	3450 (br)		3450 (br)
$\nu_{\text{s O-H}}$ of H_2O enclosed inside the ether ring.	3397 (sh)	3403 (s)		3397 (s)	
First overtone of $\beta_{\text{O-H}}$					
observed:	3202 (w)	3260 (w)		3251 (w)	
calculated:	3234	3266		3302	
$\beta_{\text{O-H}}$	1617 (m)	1633 (m)	*	1651 (m)	*

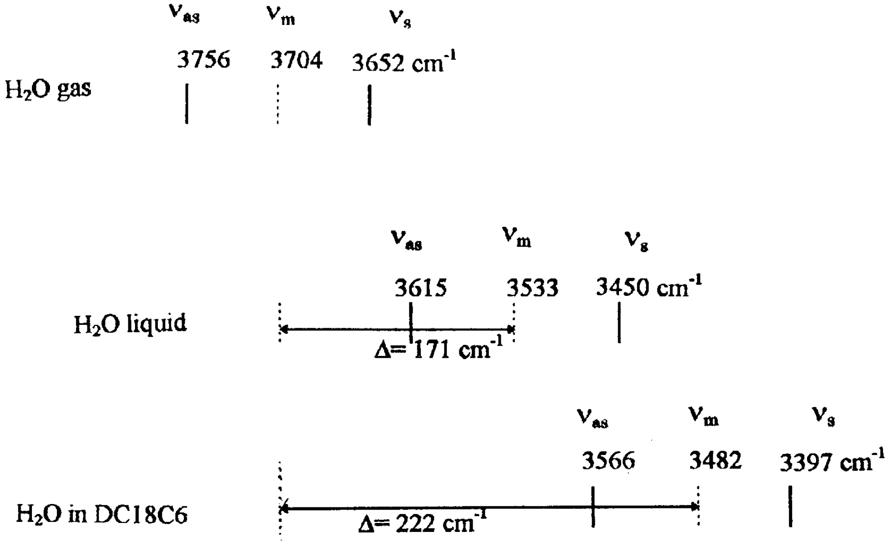
* The band may be overshadowed by crown ether absorption.
Key. See footnote to Table V.

Table III. Water vibrations (in cm^{-1}) in the gas, liquid, solid phases and in DC18C6.

Assignment	Gas phase Ref. [13]	Liquid phase Ref. [21]	Solid phase Ref. [21]	DC18C6
ν_{as}O—H	3756	3615	3220	3566
ν_{s}O—H	3652	3450	3400	3397
$\beta_{\text{O-H}}$	1595	1640	1620	1651
First overtone of $\beta_{\text{O-H}}$				
observed:	3151			3251
calculated:	3190			3302

environment to that of solid water i.e. an extensively hydrogen bonded network of water molecules.

The fact that water in DC18C6 is in a (hydrogen) bonding environment and still shows the characteristic ν_{as}, ν_{s} and $\beta_{\text{O-H}}$ bands of water in the gas phase, may lead one to consider the water vibrations in DC18C6 to be those of cavitant water in a uniform field enclosed by the ether ring, such that it forms nonspecific hydrogen bonds with the oxygen atoms of the ring, as depicted in Figure 2. Such an arrangement of the water molecule inside the ether cavity seems to be plausible in the light of the recently reviewed studies that showed the possible accommodation of the larger hydronium ion inside the 18C6 cavity [2].



Scheme 1. ν_{as} and ν_s of H_2O in the gas phase, in the liquid phase and in hydrated DC18C6.

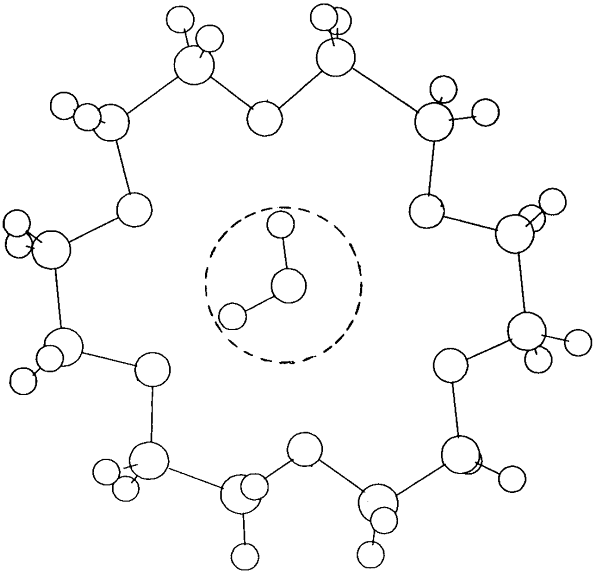


Figure 2. Representation of cavitant water in 18C6

Besides the absorption bands assigned to cavitant water inside the crown ethers, a prominent broad band at about 3450 cm^{-1} appeared in all spectra, except for DC18C6. This band could be assigned to outer layer hydrogen bonded water (Table II). This assignment is supported by the work of Kolthoff and Chantooni [5] on the ternary complexes 18C6 : H_2O : P (P = 4,4′-biphenol, 3-nitrophenol, 2,4-

Table IV. νOH_2 stretching vibrations (in cm^{-1}) in free and complexed crown ethers.

Free ethers	Crown-ether complexes with: 4-nitrophenol (this work)	3-nitrophenol (this work)	3-nitrophenol [5]*	2,4-dinitrophenol [5]**
18C6				
3563 (sh)			3500.8	3529 (sh)
3453 (br,s)	3423 (br)	3425 (br)	3458.6	3423.4
3397 (sh)				
B18C6				
3541 (sh)				
3467 (br,m)	3432 (br)	3393 (br)		
3403 (s)				
DB18C6				
3450 (br)	3430 (br)	3450 (br)		
DC18C6				
3566 (m)				
	3450 (br)	3440 (br)		
3397 (s)				
DB24C8				
3450 (br)	3450 (br)	3435 (br)		

*3-Nitrophenol: H_2O: 18C6 (2 : 2 : 1).
**2,4-Dinitrophenol: H_2O: 18C6 (2 : 2 : 1).
Key: as in Table V.

dinitrophenol and dichloropicric acid) in which they identified water acting in a dual manner as a hydrogen bond acceptor to the acidic O—H of the phenol and a hydrogen bond donor to the crown ether oxygens. They reported that ν_{O-H} of water in these complexes appeared in the 3550–3350 cm^{-1} region. Similar bands were also found in the present work in the spectra of crown ether complexes with 3- and 4-nitrophenols (Table IV). It is interesting to note that the bands assigned to cavitant water are absent in the spectra of these complexes.

In order to test for the presence of the cavitant water in the crown ether molecules when the latter are present in solution, ^{1}H-NMR spectra were measured in $CDCl_3$ and DMSO-d_6 solvents. The results were inconclusive in identifying any water signals. This may indicate that in such solutions, as in the case of the solid ether complexes, the cavitant water is absent.

3.2. EFFECT OF COMPLEXATION ON THE SPECTRA OF 3- AND 4-NITROPHENOL

The absorption bands of 3- and 4-nitrophenol complexes in the range 4000–400 cm^{-1} are given in Tables V and VI, respectively.

The prominent bands at 3477 and 3397 cm^{-1} in 3-nitrophenol, and at 3382 and 3333 cm^{-1} in 4-nitrophenol, which are usually assigned to ν_{O-H} are absent,

Table V. IR absorption bands of 3-nitrophenol complexes in the region (4000–400 cm^{-1}).[a]

Assignment[b]	3-NP	18C6/3-NP	B18C6/3-NP	DB18C6/3-NP	DC18C6/3-NP	DB24C8/3-NP
Free ν_{O-H}	3477 (m)	*	*	*	*	*
Bonded ν_{O-H}	3397 (s)					
$\nu_{OH_2 \cdots CE}$		3425 (br)	3393 (br)	3450 (br)	3440 (br)	3435 (br)
$\nu_{OH \cdots water \cdots CE}$		3125 (br)	3055 (br)	3110 (br)	3055 (br)	3125 (br)
ν_{C-H}	3122 (w)	*	*	3118 (m)#	3120 (m)#	3120 (m)#
	3009 (w)	*	*	*	*	
$\nu_{C=C}$	1623 (m)	1618 (m)	1623 (m)	1618(m)	1618 (m)	1618 (m)
$\nu_{C=O}$		1583 (m)	1584 (m)	1582 (sh,m)	1581(m)	1575 (sh,m)
$\nu_{as}NO_2$	1523 (vs)	1529 (vs)	1535 (vs)	1527(vs)	1527 (vs)	1527 (vs)
$\nu_{C=C}$	1483 (m)	*	*	1488 (sh)	*	1482 (sh)
	1467 (m)	1465 (m)	*	1474 (m)	1470 (m)	1475 (sh)
$\nu_{s}NO_2$	1352 (vs)	1352 (vs)	1346 (s)	1350 (s)	1350 (s)	1350 (s)
δ_{O-H}	1336 (m-s)		*			
ν_{C-O}	1299 (s)	1305 (m)	1301 (m)	1301 (m)	1303 (m)	1301 (m)
δ_{C-H}	1272 (m)	*	1275 (m)	*	1274 (w)	*
δ_{O-H}	l213 (m-s)		*	*	1208 (m)	1210 (sh)
δ_{C-H}	1164 (w-m)	1158 (vw)	1166 (vw)	1166 (vw)	*	1166 (sh)
δ_{C-H}	1080 (m)	*	*	1082 (w-m)	*	*
Ring breathing	999 (m)	997 (w-m)	999 (w-m)	*	*	999 (w)
γ_{C-H}	935 (m)	933 (w-m)	933 (w-m)	*	*	935 (s)
δ_{NO_2}	873 (m)	877 (w-m)	877 (w-m)	875(w-m)	877 (m)	879 (w-m)
γ_{C-H}	817 (s)	813 (s)	813 (s)	813 (s)	813 (s)	813 (s)
	794 (m-s)	798 (m)	796 (m)	794 (w)	800 (sh,m)	798 (w-m)
γ_{NO_2}	742 (m-s)	736 (m-s)	738 (m-s)	738 (s)	740 (s)	*
	673 (m)	678 (m)	673 (m)	675 (m)	679 (m)	675 (m)
Bonded γ_{O-H}	599 (br,m)				601 (vw)	
ρ_{NO_2}	555 (w-m)		576 (vw)	554 (vw)		
			541 (vw)			

*The band was overshadowed by other absorptions.

The intensity was amplified by other absorptions.

[a] *Key.* ν_{as}, asymmetric stretching; ν_s, symmetric stretching; δ, in plane bending; ρ, rocking; γ, wagging; (s), strong; (m), medium; (w), weak; (sh), shoulder; (br), broad.

[b] References for assignment are [22–25].

or are overshadowed by the stronger and broader neighboring bands in all the complexes in the regions 3450–3400 cm^{-1} and 3125–3050 cm^{-1}. Note that the former occupied the position of free ν_{O-H} of 3- and 4-nitrophenol, but are too broad to be assigned to such a vibration.

Kolthoff and Chantooni [5] observed two bands in this region of the spectra of the 18C6 : water : P (P = 4,4′-biphenol, 3-nitrophenol, etc.) complexes. One lies in the region 3500–3450 cm^{-1} assigned to the O—H stretching of water bonded to crown ether oxygens, and the other in the region 3150–3100 cm^{-1} assigned to the O—H stretching of the phenol which is bonded to water oxygen. The good agreement with the present work, as can be judged from Table VII, leads to a similar assignment for these bands in the 3- and 4-nitrophenol complexes.

The difference (Δ) between the free ν_{O-H} bands in 3- and 4-nitrophenol and the bands assigned to the O—H stretching of the phenol bonded to water oxygen in the complexes [$\nu(O—H)_{P \cdots water \cdots CE}$ (P = 3- or 4-nitrophenol)] are given in Table

Table VI. IR absorption bands of 4-nitrophenol complexes in the region (4000–400 cm^{-1}).[a]

Assignment[b]	4-NP	18C6/4-NP	B18C6/4-NP	DB18C6/4-NP	DC18C6/4-NP	DB24C8/4-NP
Free ν_{O-H}	3382 (sh,m)	*	*	*	*	*
Bonded ν_{O-H}	3333 (s)					
$\nu_{OH_2 \cdots CE}$		3423 (br)	3432 (br)	3430 (br)	3450 (br)	3445 (br)
$\nu_{OH \cdots water \cdots CE}$		3090 (br)	3055 (br)	3110 (br)	3090 (br)	3100 (br)
ν_{C-H}	3132 (w)	*	*	3136 (m)#	*	*
	3080 (w)	*	*	3079 (w)	3079 (m)#	
$\nu_{C=C}$	1614 (m-s)	1614 (m)	1614 (m)	1614 (m)	1614 (m)	1612 (m)
	1591 (s)	1591 (s)	1591 (s)	1595 (s)	1593 (s)	1593 (s)
	1515 (m-s)	1515 (m-s)	*	*	1515 (s)	1512 (s)
$\nu_{as}NO_2$	1498 (s)	1498 (m-s)	1500 (s)	*	1500 (s)	1498 (s)
δ_{O-H}	1346 (s)	1350 (s)	1350 (s)			
$\nu_{s}NO_2$	1326 (vs)	1336 (vs)	1338 (vs)	1336 (vs)	1336 (s)	1336 (vs)
ν_{C-O}	1286 (s)	1288 (s)	1288 (s)	1286 (s)	1288(s)	1288(s)
δ_{O-H}	1218 (s)		*	*		*
δ_{C-H}	1166 (m-s)	1166(m)	1164 (m)	1164 (m)	1166 (m)	1164 (m)
	1112 (s)	*	1112 (s)	1112 (s)	1110 (s)	1110 (s)
γ_{C-H}	960 (w)	*		*		*
δ_{NO_2}	865 (m)	868 (m)	862(m)	868 (m)	866 (m)	864 (sh)
γ_{C-H}	852 (s)	855 (m)	852 (m)	854 (m)	854 (m-s)	854 (m-s)
γ_{NO_2}	756 (m)	756 (m)	750 (s)	750 (s)	756 (m-s)	754 (m-s)
γ_{O-H}	694 (m-s)	696 (w)	694 (w-m)	694 (w-m)	694 (w-m)	694 (w-m)
	630 (m)	628 (m)	628 (m)	628 (m)	628 (m-s)	628(m)
	536 (w)	532 (w)	534(w)	535 (w)	534 (w)	
ρ_{NO_2}	497 (m)	499 (w)	501 (w)	503 (w)	499 (w)	501 (w)

*The band was overshadowed by other absorptions.

\# The intensity was amplified by other absorptions.

[a] *Key*: as in Table V.

[b] References for assignment are [23–27].

Table VII. O—H stretching vibrations (in cm^{-1}) of crown ether complexes with phenols.

Complex	$\nu OH_2 \cdots CE$	$\nu(O—H)_P \cdots water \cdots CE$
18C6.4,4′-biphenol.$(H_2O)_2$ [Ref. 5]	3529 3487	3142.2
18C6(3-nitrophenol.$H_2O)_2$ [Ref. 5]	3500.8 3458.6	3128
18C6/3-nitrophenol [this work]	3425 (br)	3125 (br)
18C6/4-nitrophenol [this work]	3423 (br)	3090 (br)

Table VIII. The differences Δ (cm^{-1}) between the stretching frequencies of free and complexed O—H of 3- and 4-nitrophenol.

	$\Delta = \nu(O—H)_{free} - \nu(O—H)_{P \cdots water \cdots CE}$				
Guest/Host	18C6	B18C6	DB18C6	DC18C6	DB24C8
3-nitrophenol	352	422	368	422	352
4-nitrophenol	292	327	272	292	282

VIII. From Table VIII, the following trends can be inferred for the strength of these hydrogen bond interactions in the complexes, from which both B18C6 and DC18C6 complexes showed the strongest interactions: for 3-nitrophenol complexes

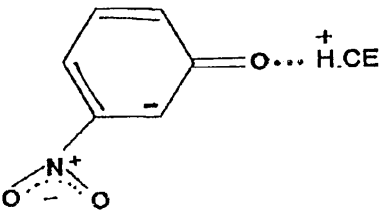
B18C6 = DC18C6 > DB18C6 > 18C6 = DB24C8

and for 4-nitrophenol complexes:

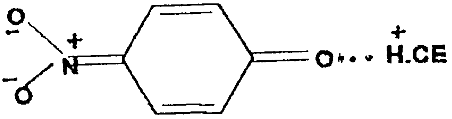
B18C6 > DC18C6 = 18C6 > DB24C8 > DB18C6.

Table VIII also indicates that hydrogen bonding is stronger in the complexes of 3-nitrophenol than of 4-nitrophenol. This is in the opposite direction to the trends of the acidity [14] and the dipole moment [15] (pK_a and dipole moment = 8.28 and 3.9D, respectively, for 3-nitrophenol and 7.15 and 5.1D, respectively, for 4-nitrophenol). This trend may indicate that the strength of the hydrogen bonding interaction between the ethers and the guest molecules is not determined by the acidity or the dipole moment of the guest. Consideration of other spectral characteristics of the complexes offers a possible explanation for the observed trend, as given in the following paragraphs.

Another common feature of 3- and 4-nitrophenol complexes is the disappearance or weakening of δ_{O-H} and γ_{O-H} absorption bands. This may be related to the contribution of the quinonoidal structures **I** and **II** for the 3- and 4-nitrophenol complexes, respectively.



I



II

In 3-nitrophenol complexes, the $\nu_{\mathrm{C-O}}$ band at 1299 cm^{-1} was weakened to a large extent and new bands were observed at about 1580 cm^{-1} which are absent in the spectra of both uncomplexed 3-nitrophenol and crown ethers. These new bands can be assigned to the contribution of $\nu_{\mathrm{C-O}}$ of the quinonoidal structure **I**. The fact that NO_2 vibrations in 3-nitrophenol were hardly affected in the complexes further indicates the predominance of structure **I**.

In the 4-nitrophenol complexes, no new bands similar to those in 3-nitrophenol complexes were observed and the $\nu_{\mathrm{C-O}}$ vibration still occupied its original position of the uncomplexed 4-nitrophenol. Furthermore, the ν_{as}, δ, and γ and $\rho_{\mathrm{NO_2}}$ vibrational bands were hardly affected, but $\nu_{\mathrm{s\,NO_2}}$ was shifted to higher values. All these indicate that structure **II** is of little importance. So, since structure **II** is expected to be responsible for the higher acidity and dipole moment of 4-nitrophenol, the lower contribution of this structure in the complexes may be responsible for 4-nitrophenol complexes having lower $\Delta\nu$ values than 3-nitrophenol. This is further supported by the σ-moment and π-moment of 3- and 4-nitrophenol which are (2.68, 2.02D) and (1.65, 4.46D), respectively [15]. The σ-moment being higher in 3-nitrophenol than in 4-nitrophenol is consistent with the higher values for $\Delta\nu$ of the former complexes. Thus, it would seem that complexation of the nitrophenol molecules with the ether does not operate through a π-resonance form such as II, but rather through the operation of the inductive effect. A similar observation was made in the crown ether complexes with 4-nitroaniline [16].

3.3. EFFECT OF COMPLEXATION ON THE IR SPECTRA OF CROWN ETHERS

Very few changes in the spectra of the crown ethers in the complexes were observed, thus the ether C—O stretching vibrations were hardly affected. In the case of 18C6, no extra bands, or splitting of the C—O—C, C—C stretching or CH_2CH_2 rocking bands were observed; thus indicating the preference of the molecule for D_3d conformation in the hydrated crown ether and its complexes with nitrophenols. This is in agreement with both crystallographic and theoretical work on 18C6 complexes with water and other neutral molecules [17–19]. However, the exception is in the CH_2 stretching vibrations which showed marked distortions when compared with those of the uncomplexed ethers, as shown by the examples given in Figure 3.

No marked changes were observed in the vibrational bands of the aromatic moieties of the benzo-substituted ethers. However B18C6, which showed the strongest

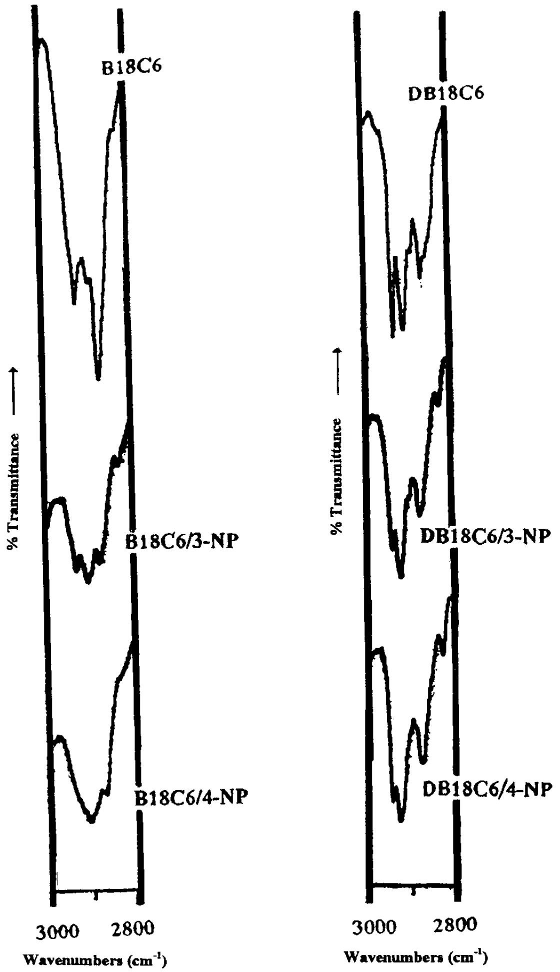


Figure 3. The CH_2 stretching bands in free and complexed crown ethers

interaction, gave prominent shifts to higher values in the in-phase γ_{C-H} absorption band upon complexation.

4. Concluding Remarks

The present spectral study showed two distinctive sets of bands attributed to the water molecules present in the crown ethers. The first set is that of typical hydrogen-bonded water molecules, the so-called outer-layer water, which persisted in the crown ether complexes with phenols and acted as a bridge between the latter and the ether oxygens.

The second set exhibited all the characteristic OH_2 vibrations of water molecules with relative shifts indicating their presence in a uniform strong-field environment.

These so called cavitant water molecules do not form specific hydrogen bonds to any of the ether oxygens and therefore are quite distinct from water in the liquid or solid phase which is typified by extensive hydrogen-bonded networks. Unlike the outer-layer water, the cavitant water bands disappeared upon complexation.

These results seem to give credence to the view that, in some uncomplexed crown ethers, water molecules may be held in the uniform field of the oxygens within the ether cavity. So far this has only been demonstrated in the case of macrocylic ethers containing a hetero-aromatic moiety which provided the necessary conformation and cavity size to encircle the water molecule [8].

DC18C6, which was previously reported to accommodate the larger hydronium ion [20], is shown in the present work to have the required flexibility and space for cavitant water. The other crown ethers varied in this respect as demonstrated, on one hand, by the absence of the bands assigned to cavitant water in the case of the rigid DB18C6 and DB24C8, and, on the other hand, by the presence of the two sets of bands in 18C6 and B18C6, both known to be flexible and thus able to provide sites for both types of water attachments.

References

1. F. Vögtle and E. Weber (Eds.): *Host Guest Complex Chemistry of Macrocycles: Synthesis, Structure, Applications*, Springer-Verlag, Berlin (1985).
2. G. Gokel: *Crown Ethers and Cryptands*, Royal Society of Chemistry, London (1991).
3. F. Vögtle and W.M. Muller: *Chem. Ber.* **114**, 3179 (1981).
4. W.H. Watson, J. Galloy, D.A. Grossie, F. Vögtle and W.M. Muller: *J. Org. Chem.* **49**, 347 (1984).
5. I.M. Kolthoff and M.K. Chantooni: *Can. J. Chem.* **70**, 177 (1992).
6. A. Elbasyouny, H.J. Brugge, K. von. Deuten, M. Dickel, A. Knöchel, K.U. Koch, J. Kopf, D. Melzer, and G. Rudolph: *J. Am. Chem. Soc.* **105**, 6568 (1983).
7. B. Belamri, C. Bavoux, and A. Thozet: *J. Incl. Phenom.* **8**, 383 (1990).
8. G.R. Newkome, H.C.R. Taylor, F. R. Fronczek, T. J. Delord, D. K. Kohli, and F. Vögtle: *J. Am. Chem. Soc.* **103**, 7376 (1981).
9. G.A.W. Derwish, S.R. Salman, and S.M. Al-Marsoumi: *J. Incl. Phenom.* **20**, 123 (1995).
10. G.A.W Derwish, S.R. Salman, and S.M. Al-Marsoumi: *J. Incl. Phenom.* **23**, 175, (1995).
11. B.I. El-Eswed, M.B. Zughul, and G.A.W. Derwish: *J. Incl. Phenom.* **24**, 325 (1996).
12. H.S. Gold and M.R. Rice: *Talanta* **29**, 637 (1982).
13. G. Herzberg: *Molecular Spectra and Molecular Structure*, Vol. 2: *Infrared and Raman Spectra of Polyatomic Molecules.* Van Nostrand, New York (1966).
14. R.C. Weast and M.J. Astle: *Handbook of Chemistry and Physics.* CRC Press, Florida, U.S.A. (1980).
15. A.J. Owen: *Tetrahedron* **25**, 3693 (1969).
16. B.I. El-Eswed, M.B. Zughul, and G.A.W. Derwish: *Spectroscopy Letter* **30** (in press).
17. J.W.H.M. Uiterwijk, S. Harkema, and D. Feil: *J. Chem. Soc. Perkin Trans. 2*, 721 (1987).
18. G. Ranghino, S. Romano, J.M. Lehn, and G. Wipff: *J. Am. Chem. Soc.* **107**, 7873 (1985).
19. D. Mootz, A. Albert, S. Schaefgen, and D. Stäben: *J. Am. Chem. Soc.* **116**, 12045 (1994).
20. R.M. Izatt, B.L. Haymore, and J.J. Christensen: *J. Chem. Soc.* 1308 (1972).
21. K. Nakamoto: *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York and London (1963).
22. A.R Katritzky and P. Simmons: *J. Chem. Soc.* 2058 (1959).
23. J.F. Brown: *J. Am. Chem. Soc.* **77**, 6341 (1955).
24. J.H.S. Green, D.J. Harrison, and W. Kynaston: *Spectrochim. Acta* **27A**, 2199 (1971).
25. J.H.S Green and D.J. Harrison: *Spectrochim. Acta* **26A**, 1925 (1970).

26. H.A. Szymanski: *Interpreted Infrared Spectra.* Vol. 3, Plenum Press, New York (1967).
27. A.R. Katritzky and P. Simmons: *J. Chem. Soc.* 2051 (1959).