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Molecular Complex Formation between Some Azacrown Ethers and 2,4,6-Trinitrophenol

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Abstract. The formation of molecular complexes with 1 : 1 stoichiometry between 2,4,6-trinitrophenol and aza-12-crown-4, aza-15-crown-5 and aza-18-crown-6 in chloroform solution was investigated spectrophotometrically. The resulting complexes were isolated and characterized by microchemical analysis, IR and NMR spectroscopy. The equilibrium constants of the 1 : 1 adducts were evaluated from the non-linear least-squares fitting of the absorbance-mole ratio data. The overall stability of the 2,4,6-trinitrophenol complexes was found to vary in the order aza-15-crown-5 > aza-18-crown-6 ≈ aza-12-crown-4. The kinetics of complex formation between 2,4,6-trinitrophenol and the aza-substituted crown ethers used were investigated and in all cases the results showed the occurrence of an oscillating chemical reaction in solution.

Key words: 2,4,6-trinitrophenol, aza-crown ethers, molecular complexes, spectrophotometry, IR, NMR.

1. Introduction

Macrocyclic crown ethers are known to form intermolecular charge-transfer complexes with neutral molecules [1, 2], although studies on such molecular interactions have been far fewer in number than those on cation-macrocycle interactions. Recent spectroscopic and thermodynamic studies have involved charge-transfer complexes formed between crown ethers and a variety of acceptor molecules such as 2,3-dichloro-5,6-dicycanobenzoquinone (DDQ) [3–5], tetracyanoethylene (TCNE) [3, 4, 6], 7,7,8,8-tetracyanoquinodimethane (TCNQ) [3], *p*-chloranil (CHL) [3, 7], 2,4,6-trinitrophenol (TNP) [8] and, especially iodine [9–15]. Increasing interest in the study of such molecular complexes is mainly due to their possible applications in diverse areas such as separation science, catalysis of chemical re-

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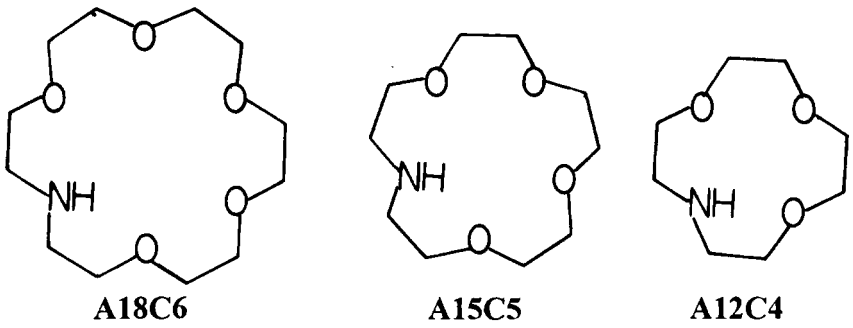

Figure 1. Structures of the azacrown ethers.

actions, biomimetic receptors and conversion of chemical reactions into optical or electronic signals [1].

The cavity formed by the cyclic disposition of the donor atoms in the macrocyclic polyethers provides a very exciting feature to investigate their molecular encapsulation properties [1, 2]. A study of the macrocycle interaction with neutral molecules reveals that complementary positioning of the recognition sites and other active groups in the macrocyclic structure can lead to very strong and specific complexation [16]. Thus, the number, type and arrangement of donor atoms in the macrocyclic cavity are expected to play a key role in the selectivity they show toward guest molecules [1]. It has been recently shown that the substitution of some of the oxygens in the crown ether cavity by nitrogen atoms results in a tremendous enhancement in the stability of their iodine [10, 11, 13, 14] and DDQ [5] complexes over those of ordinary crowns.

Polynitrophenol derivatives can form stable molecular complexes with various electron donors such as aniline and naphthalene [17–20]. The structure of these complexes are shown to be strongly dependent on the type of electron donor [19, 20]. Such charge-transfer complexes are frequently used in the areas of biological chemical analysis and the determination of various drug compounds [21, 22]. It is noteworthy that the formation of both charge-transfer and proton-transfer complexes between polynitrophenols and various amine derivatives have been reported in the literature, although the acid-base interactions are shown to predominate in the solid and molten states [23–32]. However, studies dealing with the complexation of polynitrophenols with aza-substituted crown ethers are quite sparse [8]. In this paper we report the results of spectroscopic investigation of the stoichiometry, formation constant and kinetics of molecular complexes between 2,4,6-trinitrophenol (TNP) and aza-12-crown-4 (A12C4), aza-15-crown-5 (A15C5) and aza-18-crown-6 (A18C6) in chloroform solution. The structures of the azacrowns used are shown in Figure 1.

2. Experimental

Reagent grade A18C6, A15C5, A12C4, 2,4-dinitrophenol (DNP) and TNP (all from Fluka) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Spectroscopic grade chloroform (Merck) was used as received.

All UV-Vis spectra were recorded on a Shimadzu 2100 spectrophotometer equipped with a temperature regulated cell holder. The temperature control was achieved using a Shimadzu TB-85 Therm Bath having an accuracy of $\pm$ 0.5 °C. ^{1}H NMR spectra were recorded on a Jeol JNM-EX90 FT NMR spectrometer at a field of 21.15 kG (90 MHz). In all experiments, TMS was used as an internal standard. The IR spectra were recorded on a Shimadzu 470 spectrometer, using KBr discs. The microanalytical measurements (C, H, N) were made with a Foff Heraus CHNO Rapid Analyzer. Melting points were measured by a Gallenkamp apparatus. All absorbance measurements were made on freshly prepared solutions. Specific details are given in the Results and Discussion section.

The molecular adducts in the crystalline form were prepared by dissolving appropriate amounts of azacrowns and TNP in chloroform. The resulting solutions were filtered and transferred into a crystallization dish. The solutions were allowed to evaporate over a time period of 12 h. The solid compounds were then recrystallized from reagent grade diethyl ether. The resulting solid crystals were collected and dried under vacuum.

3. Results and Discussion

The electronic spectra of 3.0×10^{-5} M TNP in the presence of increasing amounts of the azacrowns used were obtained in chloroform solution. Sample spectra for the A15C5-TNP system and the corresponding mole ratio and continuous variations plots are shown in Figure 2. The corresponding spectra for the A18C6-TNP and A12C4-TNP systems are very similar to those of A15C5-TNP and thus are not included. As is evident from Figure 2A, the overall spectral feature of TNP has greatly changed upon addition of the azacrown ether. The wavelengths of maximum absorption (λ_m) and the corresponding molar absorptivities (ϵ) observed are as follows:

TNP	λ_m = 338 nm; ϵ = 5220 l M^{-1} cm^{-1}
A15C5-TNP	λ_{m1} = 352 nm; ϵ = 16080 l M^{-1} cm^{-1}
	λ_{m2} = 410 nm; ϵ = 9500 l m^{-1} cm^{-1}

Moreover, the spectra show a well defined isosbestic point at 305 nm. It should be noted that the λ_{m1} and λ_{m2} values for the A12C4-TNP and A18C6-TNP complexes are similar to those reported above for A15C5-TNP. The observed pronounced spectral changes could be presumably due to both charge-transfer and proton-

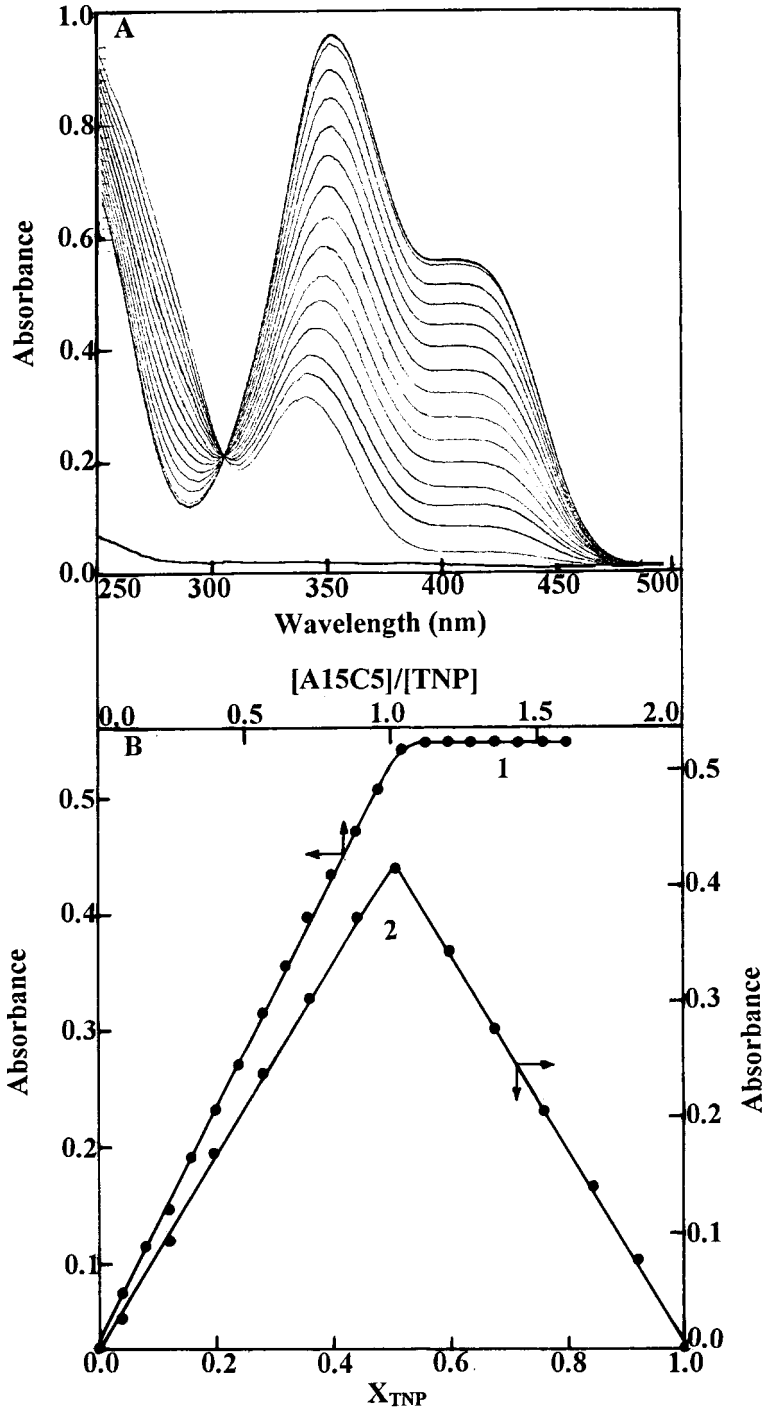

Figure 2. (A) Electronic absorption spectra of 3.0×10^{-5} M TNP in the presence of increasing concentration of A15C5 (A15C5/TNP mole ratio from 0.0 to 1.6). (B) Corresponding mole ratio (1) and continuous variations (2) plots.

transfer in the formation of the molecular complexes, as pointed out previously [23–25, 28, 30, 32]. The occurrence of a proton-transfer from TNP as donor to azacrown ethers as acceptor was also supported by the close spectral resemblance between the azacrown-TNP molecular complexes and the tetrabutylammonium salt of TNP. Consequently, in chloroform solution, one can expect the existence of some electrostatic as well as H-bonding interactions as driving forces responsible for the complexation reactions between the protonated azacrown ethers and trinitrophenolate anion.

The stoichiometry of the resulting molecular complexes was examined by the method of continuous variations [33, 34]. A sample plot is shown in Figure 2B. All continuous variations plots possess a distinct inflection point at a X_{TNP} value of 0.5, emphasizing the formation of 1 : 1 molecular complexes in solution. Moreover, the absorbance vs. azacrown/TNP mole ratio plots show a sharp break at the mole ratio of 1 (see Figures 2B and 4), further supporting the formation of 1 : 1 adducts in solution. Furthermore, the existence of a well defined isosbestic point in the spectra of TNP upon titration with the azacrown ethers (Figure 2A) is also a good indication for a simple complexation equilibrium.

The proton NMR spectra of TNP, A18C6 and their molecular complex A18C6-TNP in deuterated chloroform were obtained and the results are summarized in Table I. As seen, the two phenyl protons of TNP show a considerable upfield shift of about 0.3 ppm upon complexation with A18C6, due to the transfer of charge from the azacrown ether to this molecule. On the other hand, while the —OCH_2— and, especially, the —OCH_2CH_2O— protons of A18C6 show negligible downfield shifts of 0.13 and 0.03 ppm, respectively, upon complexation, there is a considerable downfield shift of 0.28 ppm for the —NCH_2— protons of the crown ether. Such a chemical shift behavior may reveal the involvement of the nitrogen atom of the macrocyclic ring in both the proton-transfer and charge-transfer processes during the molecular complex formation. It is noteworthy that a similar chemical shift behavior was observed in the case of the A15C5-TNP and A12C4-TNP complexes.

For a series of samples in chloroform in which the concentration of TNP was 0.010 M and the A18C6 concentration varied from 0.00 up to approximately 0.03 m the chemical shift of the single NMR signal due to the phenyl protons of TNP was determined at 27 °C. The resulting NMR spectra are shown in Figure 3 and the corresponding chemical shift-mole ratio plot is given in Figure 4. The absorbance-mole ratio plots for the A18C6-TNP and A18C6-DNP systems are also included in Figure 4 for comparison. In the case of the A18C6-TNP system, both the chemical shift and absorbance signals change sharply and linearly upon addition of the crown ether until a mole ratio of 1 is reached. Beyond this mole ratio the signals remain essentially constant. Such mole ratio plots indicate the formation of very stable 1 : 1 complexes with $K_f > 10^7$. On the other hand, the absorbance-mole ratio plot for the A18C6-DNP complex does not slow such a sharp break at the mole ratio of 1 as that of the A18C6-TNP system, indicating the formation of a weaker 1 : 1 complex.

Table I. ^{1}H NMR spectral data of A18C6, TNP and their 1 : 1 molecular complex

Compound	δ (ppm)		
A18C6	—NCH_2—	—OCH_2—	—OCH_2CH_2O—
	2.80 (triplet)	3.63 (triplet)	3.69 (singlet)
A18C6-TNP	3.08	3.76	3.72
TNP	Ph-H	OH	
	9.13 (singlet)	11.80 (broad singlet)	
A18C6-TNP	8.82	very broad	

Table II. Stability constants and molar absorptivities of 1 : 1 complexes between azacrown ethers and polynitrophenols at 10 °C in chloroform solution

Complex	log K_f	ϵ (l M^{-1} cm^{-1})
A12C4-TNP	7.0 ± 0.3	9145
A15C5-TNP	> 7	9500
A18C6-TNP	7.1 ± 0.2	9864
A18C6-DNP	5.75 ± 0.08	9730

The overall equilibrium constants for the resulting molecular complexes at 10 °C were evaluated from the computer fitting of the absorbance-mole ratio data to a previously derived equation for a 1 : 1 complex [35] using a non-linear least-squares program KINFIT [36] and the results are summarized in Table II. Sample computer fits of the mole ratio data for the A18C6-TNP and A18C6-DNP complexes are shown in Figure 5. The fair agreement between the observed and calculated absorbances further supports the occurrence of 1 : 1 complexation between the polynitrophenol derivatives and the azacrown ethers used in chloroform solution.

The data given in Table II reveal that, as expected, TNP as a stronger proton donor and π-acceptor forms a much more stable molecular complex with A18C6 than does DNP. From Table II, it is also evident that the cavity size of the azacrown ethers used would also play a key role in the stability of the resulting molecular complexes. The stability of the TNP complexes vary in the order A15C5 $>$ A18C6 $\approx$ A12C4.

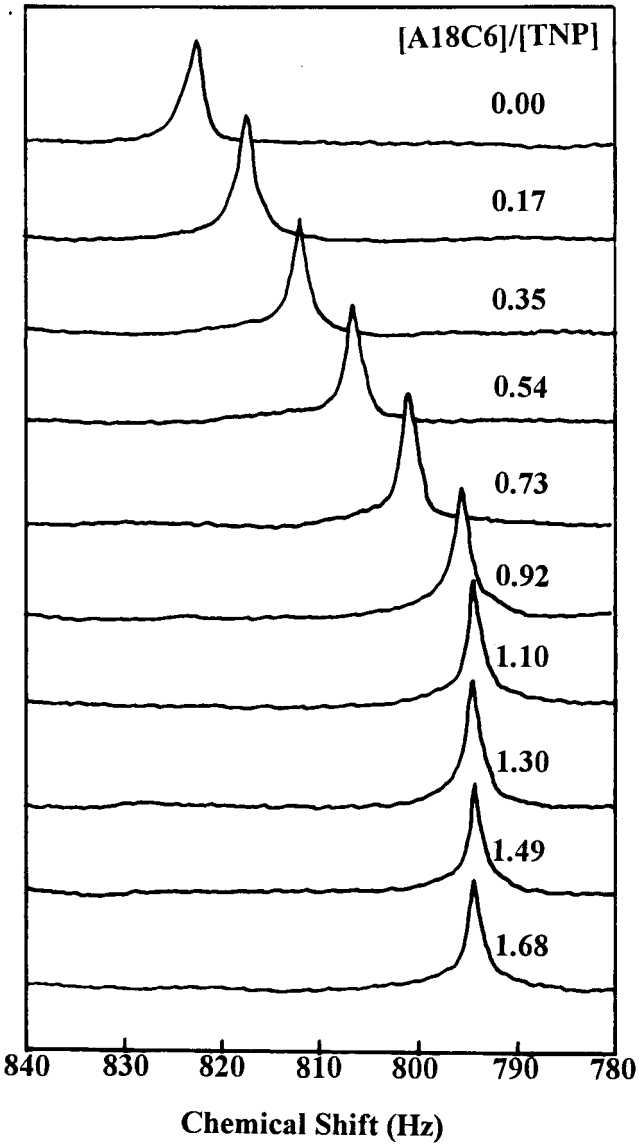

Figure 3. Proton NMR spectra of TNP at various A18C6/TNP mole ratios in chloroform solution at 25 °C.

It is well established that the proton-transfer from TNP to some crown ethers will result in the formation of "crownated" protons [37–40]. In aprotic solvents of low dielectric constant, the TNP ion can form a crown separated ion-pair with the crownated proton whose spectrum resembles that of uncomplexed TNP salts [41]. On the other hand, from the NMR and X-ray data obtained from the complexation studies of 2,4,6-trinitrotoluene (TNT) and 1,3,5-trinitrobenzene (TNB) with some

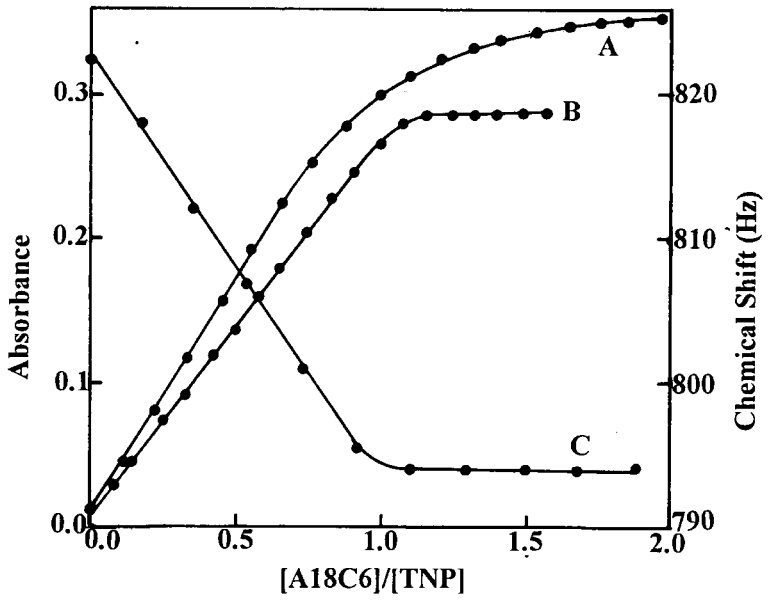

Figure 4. Absorbance-mole ratio plots for A18C6-DNP (A) and A18C6-TNP (B) and chemical shift-mole ratio plot for the A18C6-TNP (C) system in chloroform solution.

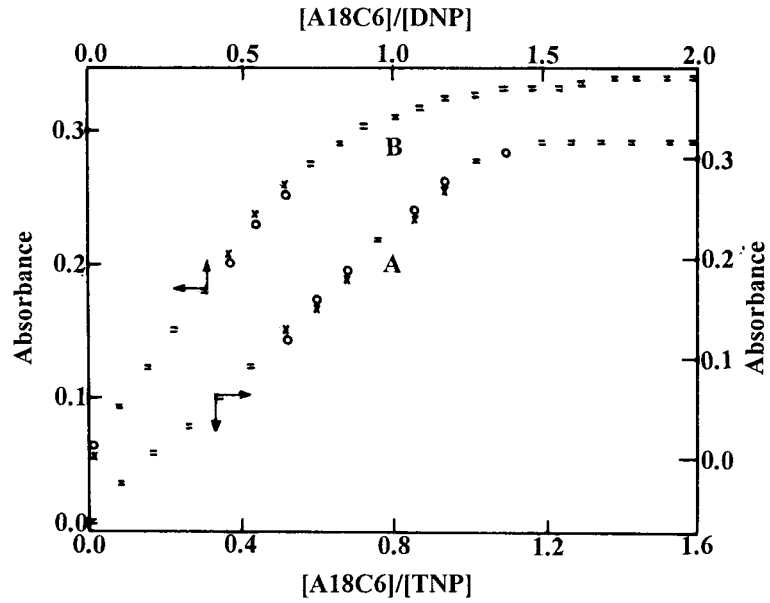

Figure 5. Computer fit of the plots of absorbance vs. [A18C6]/[TNP] (A) and absorbance vs. [A18C6]/[DNP] (B): (×) experimental points; (○) calculated points; (=) experimental and calculated points are the same within the resolution of the plots.

Table III. Microchemical data, colour and melting points of the molecular complexes of TNP with azacrown ethers

Compound	Colour	m.p. (°C)	% Calculated (found)		
			C	H	N
TNP	Yellow	121–122	–	–	–
A12C4	White	58–62	–	–	–
A12C4-TNP	Bright yellow	164–166	41.6 (41.8)	5.0 (5.0)	13.9 (14.1)
A15C5	White	36–38	–	–	–
A15C5-TNP	Dull yellow	115–117	42.8 (43.5)	5.4 (5.4)	12.5 (12.2)
A18C6	White	49–52	–	–	–
A18C6-TNP	Bright yellow	113–114	43.9 (43.5)	5.7 (5.9)	11.4 (10.9)

crown ethers, Jayathirtha and Krishnan [42] concluded that the benzene ring of the acceptor molecule (TNT or TNB) is displaced towards the cavity of the crown ether with the plane of donating oxygens making an angle of 14° with the phenyl ring of the acceptor. Apart from this, one of the NO_2 groups is projected into the cavity suggesting a $n-\pi$ stabilization (n-lone pair electrons of oxygens to π^* of the NO_2 group). This would lead to the deshielding of the ether protons as observed.

Thus, according to the above mentioned picture, in the course of molecular complex formation between TNP and the azacrown ethers used via proton-transfer and charge-transfer processes, it is not surprising to observe that the most stable complex is obtained with a given azacrown ether cavity (i.e. A15C5). It is clear that the azacrown ethers smaller or larger than A15C5 fail to provide such an optimal structural configuration for the molecular complex formation with the TNP molecule.

The crystalline salts of the TNP complexes with different azacrown ethers were prepared, as described in the Experimental section. The physical properties and the CHN analysis of the isolated complexes, given in Table III, clearly indicate the formation of the A12C4-TNP, A15C5-TNP and A18C6-TNP molecular complexes. The infrared spectra of the macrocycles, TNP and the isolated complexes in the wavenumber range 4000–400 cm^{-1} were recorded. The resulting spectral data together with the tentative assignment of the most important IR-frequencies that provide structural evidence for the formation of the 1 : 1 adducts are listed in Table IV. The assignment of the IR-bands of the molecular complexes are based on comparison between the IR spectra of the complexes and those of TNP and the azacrown ethers used as well as on the previously known assignments for the related species [43, 44].

From the data given in Table IV it is clear that most of the fundamental frequencies of TNP and, especially, azacrown ethers show significant shifts, strongly supporting the formation of the macrocycle-TNP molecular complexes. For ex-

Table IV. Infrared frequencies (cm^{-1}) and tentative assignments for TNP, different azacrowns and their 1 : 1 complexes

TNP	A12C4	A12C4-TNP	A15C5	A15C5-TNP	A18C6	A18C6-TNP	Assignments
–	3524 (s)	3415 (w)	3445 (s)	3420 (w)	3455 (s)	3432 (w)	ν(N—H)
3085 (vs)	–	3038 (m)	–	–	3015 (m)	–	ν(N—H) aromatic
–	2905 (vs)	2860 (m)	2895 (vs)	2845 (m)	2891 (vs)	2820 (m)	ν(C—H) aliphatic
1624 (vs), 1600 (sh)	–	1630 (s)	–	1630 (s)	–	1636 (s)	ν (C=C)
1560 (vs), 1524 (sh)	–	1558 (s)	–	1555 (s)	–	1557 (s)	ν (N—O)
1423 (s)	–	1423 (m)	–	1430 (m)	–	1426 (m)	$\nu(\phi$-OH)
1333 (vs)	–	1356 (m)	–	1362 (m)	–	1361 (m)	ν(C—N)
–	1283 (m)	1255 (s)	1285 (m)	1260 (s)	1273 (m)	1255 (s)	ν(C—N)
–	1133 (vs)	1101 (s)	1126 (vs)	1120 (s)	1126 (vs)	1100 (s)	ν(C—O)
700 (vs)	–	706 (s)	–	708 (s)	–	708 (s)	$\nu(\phi$-H) out of plane bending

(vs): very strong; (s): strong; (m): medium; (sh): shoulder.

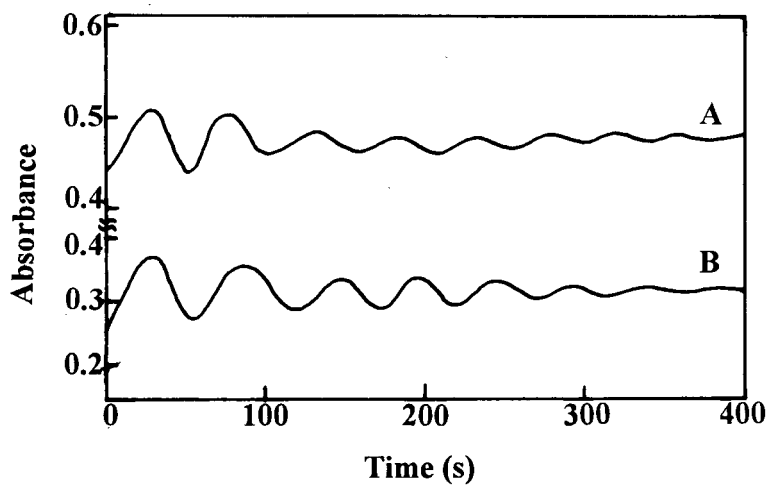

Figure 6. Absorbance-time plots at 440 nm for 1.0×10^{-4} M TNP in the presence of 3.0×10^{-5} M A15C5 (A) and A18C6 (B) in chloroform at 25 °C.

ample ν(C—N) and ν(N—H) of the azacrowns show 10–40 cm^{-1} shifts to lower frequencies upon complexation with TNP, most probably indicating the direct participation of the nitrogen atom of the ring, as proton acceptor and electron pair donor, in the molecular complex formation process. Meanwhile, the TNP frequencies such as ν(C=C) and, especially, ν(C—N) show a relatively large shift to higher frequencies, as a result of complexation with the macrocycles [5, 8].

In order to investigate the kinetics of the molecular complex formation reactions between TNP and azacrown ethers in chloroform solutions, the absorbance-time plots at 410 nm for chloroform solutions containing TNP (1.0×10^{-4} m) and azacrown ethers with an azacrown/TNP mole ratio of about 0.3 were obtained. Some of the resulting absorbance-time plots are shown in Figure 6. It is obvious from Figure 6 that the complex formation between TNP and the azacrown ethers proceed via an oscillating chemical reaction.

Due to their complex mechanisms including an autocatalytic step [45], some far-from-equilibrium chemical systems show an oscillating behavior. Such systems are usually referred to as ‘oscillating reactions’. Oscillating reactions can take place both in the liquid phase [46–48] and in the gaseous phase of heterogeneous catalytic systems [49]. Moreover, there are several references to naturally occurring oscillating reactions like those resulting in periodic changes in the calcium concentration in a variety of cell types, which are very significant to protein phosphorylation [50].

Some work in our research group is now being undertaken to study these oscillating reactions from a physico-chemical point of view in order to elucidate the complex reaction mechanisms behind the oscillations, and to develop some theoretical kinetic models accounting for the experimental results.

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