Journal of Inclusion Phenomena and Molecular Recognition in Chemistry **32:** 439–451, 1998.

Spectroscopic Study of the Complexation of 5,6,14,15-Dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene with Some Polynitrophenol Derivatives in Chloroform Solution

SUSAN SADEGHI
Department of Chemistry, Shahid Beheshti University, Tehran, Iran.

MOJTABA SHAMSIPUR*
Department of Chemistry, Razi University, Kermanshah, Iran.

(Received: 11 August 1997; in final form: 20 November l997)

Abstract. The complex formation between 5,6,14,15-dibenzo-1,4-dioxa-8, 12-diazacyclopentadeca-5,14-diene (DBDA15C4) and 4-nitrophenol (MNP), 2,4-dinitrophenol (DNP) and 2,4,6-trinitrophenol (TNP) have been studied spectrophotometrically in chloroform solution. The resulting proton transfer-charge transfer complexes are formulated as DBDA15C4·TNP and DBDA15C4·$(TNP)_2$, confirming characterizations by microchemical analysis and IR spectroscopy. The equilibrium constants for the resulting complexes (K_1 and K_2) were evaluated from the non-linear least-squares fitting of the absorbance–mole ratio data. The overall stability of the resulting complexes was found to vary in the order TNP > DNP > MNP. The enthalpies and entropies of the successive complexation reactions for the DBDA15C4–TNP system were determined from the temperature dependence of the equilibrium constants.

Key words: DBDA15C4, polynitrophenol, proton transfer–charge transfer complexes, chloroform, spectrophotometry, IR.

1. Introduction

Since the discovery of crown ethers in 1967 [1], most thermodynamic and kinetic studies have been directed toward their complexing ability with different metal ions in aqueous and nonaqueous solvents [2, 3]. Investigations of adduct formation between crown compounds and neutral species are quite recent [4]. The cavity formed by the cyclic disposition of oxygen atoms in crown ethers provides a very exciting feature for studying their molecular encapsulation properties. Recently, there has been increasing interest in the study of the charge transfer complexes between macrocyclic crown ethers and a wide variety of acceptors such as 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) [5–7], tetracyanoethylene (TCNE) [5, 6], 7,7,8,

* Author for correspondence.

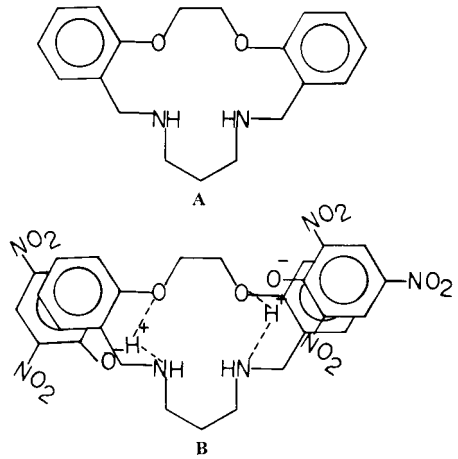

Figure 1. Structure of DBDA15C4 (A) and its 1 : 2 complex with TNP (B).

8-tetracyanoquinodimethane (TCNQ) [5], chloranil [5, 8], 2,4,6-trinitrotoluene (TNT) [9], picric acid [10] and, especially, iodine [11–16]. It has been shown that the substitution of some of the oxygen atoms in a crown ether ring by —NH— groups results in a tremendous increase in the stability of their iodine [11, 12, 14, 15] and DDQ [7] complexes over those of ordinary crowns.

Crown ethers have also been found to behave as powerful proton solvating agents in anhydrous aprotic solvents which are poor or moderately poor H-bond acceptors [17–22]. Possible applications of such solubilization and ionization of acids mediated by crown ethers in low dielectric constant aprotic solvents include acid–base catalysis, electrochemical processes, solvent extraction and other separation methods [18].

The anions of polynitrophenol derivatives, and especially picrate ion, are well known as versatile chelating counter ions for complexation, extraction and transport through membranes of alkali and alkaline earth cations by neutral and synthetic ionophores [23]. Moreover, polynitrophenols form a wide range of molecular complexes with a variety of electron donor molecules [24]. However, although the formation of charge transfer and proton transfer complexes between polynitrophenol derivatives and various amine derivatives has been reported in the literature [15–33], studies dealing with the molecular complexes of these compounds with aza-substituted crown ethers are quite sparse [10, 34].

We have recently commenced a spectroscopic study of molecular complexes of ordinary crowns [16], benzocrowns [6] and azacrown ethers [7, 14, 15] with some neutral acceptor molecules. In this paper we report the results of a spectroscopic investigation of the stoichiometry and thermodynamics of complex formation of 2,4,6-trinitrophenol (TNP), 2,4-dinitrophenol (DNP) and 4-nitrophenol (MNP) with 5,6,14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadeca-5,14-diene (DBDA15C4, Figure 1) in chloroform solution.

2. Experimental

Reagent grade DBDA15C4, TNP , DNP and MNP (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 0.5°C. The infrared spectra were recorded on a Shimadzu 410 spectrometer. The microanalytical measurements (C, H, N) were made with a Foss Heraus CHNO Rapid Analyzer. Melting points were measured by a Gallenkamp apparatus. All 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 the crown ether 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

Figure 2 shows the electronic absorption spectra of 5.0×10^{-5} M of TNP (A), DNP (B) and MNP (C) in the presence of increasing amounts of DBDA15C4 in chloroform solutions. It is immediately obvious that the overall spectral feature of the nitrophenol derivatives used has greatly changed upon addition of the crown ether. The wavelengths of maximum absorption observed are as follows:

TNP: 336 nm	DBDA15C4–TNP: 353 and 415 nm; isosbestic point at 300 nm
DNP: 340 nm	DBDA15C4–DNP: 360 and 400 nm; isosbestic point at 318 nm
MNP: 318 nm	DBDA15C4–MNP: 318 and 390 nm; isosbestic point at 333 nm

Such pronounced spectral changes, especially in the case of TNP and DNP, are presumably due to the occurrence of both charge transfer and proton transfer during the formation of the corresponding molecular complexes, as pointed out previously [25–27, 31, 33]. The transfer of a proton from TNP to DBDA15C4 was also supported by the close spectral resemblance between the DBDA15C4–TNP system and the tetrabutylammonium salt of TNP [20].

The absorbance vs. crown/nitrophenol mole ratio plots for all three nitrophenol derivatives used, obtained at 410 nm, are shown in Figure 3A. While the mole ratio plots for TNP and DNP show two distinct breaks at the mole ratios of about 0.5 and 1.0, the absorbance of the DBDA15C4–MNP system shows only a gradual increase with the mole ratio, indicating the formation of weak molecular adducts in the latter

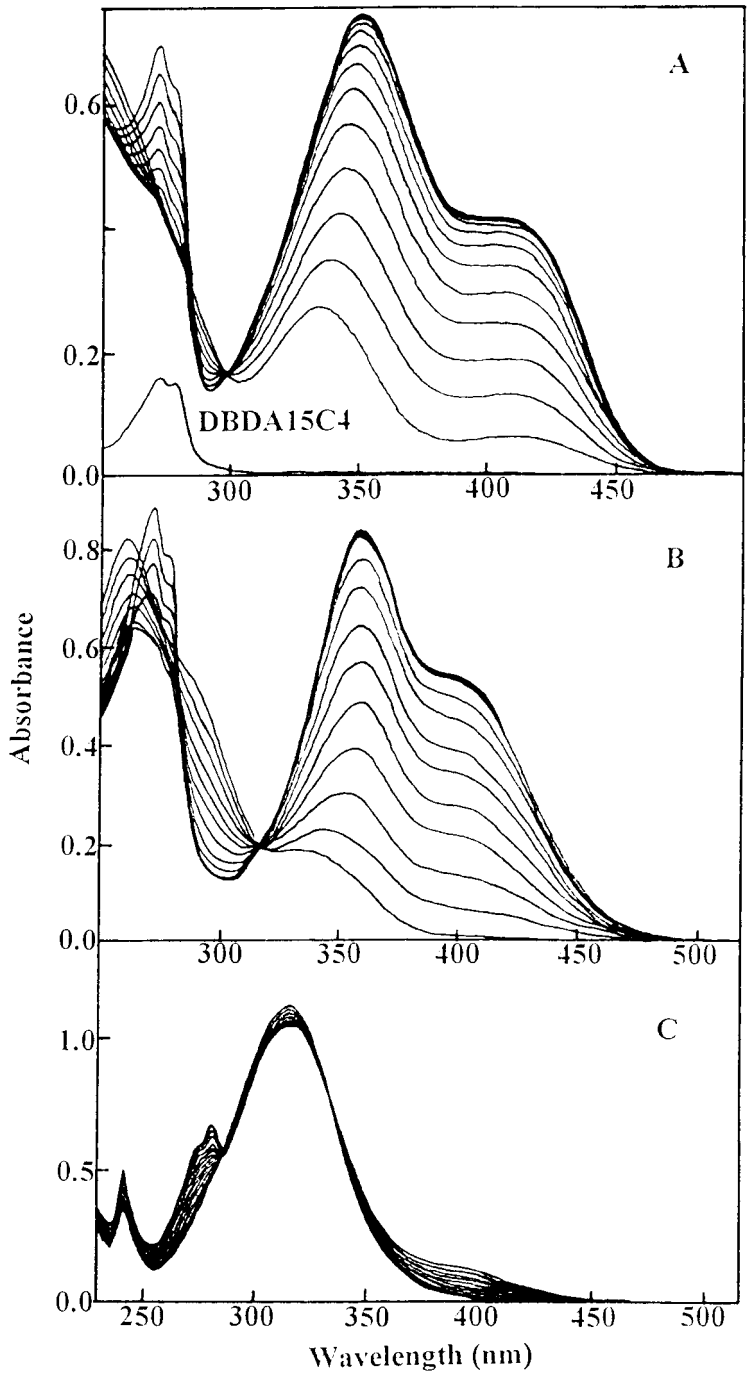

Figure 2. Absorption spectra at 20 °C of different nitrophenol derivatives in chloroform in the presence of various concentrations of DBDA15C4 (DBDA15C4/nitrophenol from 0 to about 1.7): A, TNP (5.0×10^{-5} M); B, DNP (5.2×10^{-5} M); C, MNP (3.2×10^{-5} M).

(as it is also obvious from Figure 2C). However, the observed mole ratio behavior for the case of TNP and DNP strongly emphasizes the successive formation of 1 : 1 and 1 : 2 (crown-to-nitrophenol) species in chloroform solution. The formation of these adducts was further supported by observing two sharp breaks in absorbance vs. nitrophenol/crown plots (Figure 3B) at the nitrophenol : crown ratios of 1.0 and 2.0, respectively.

It is well established that the proton transfer from TNP to some 18-crowns will result in the formation of 'crownated' protons [18–22]. In aprotic solvents of low dielectric constant, the picrate ion can form a crown separated ion pair with the crownated proton whose spectrum resembles that of uncomplexed picrate salts [35]. On the other hand, it is well known that benzocrown ethers can form 1 : 1 charge transfer complexes with different π acceptors such as DDQ, TCNE and TCNQ [5, 6]. In this case, the Ph—O—CH_2—CH_2— group of the benzocrowns was found to act as an electron donor group in the resulting molecular complexes with the π acceptors used. Based on the above established conclusions, and those reported elsewhere [25–27, 31, 33], the simultaneous operation of the proton transfer and charge transfer interactions between DBDA15C4 and TNP and DNP could be explained according to the following picture. The transfer of protons from two nitrophenol molecules to the crown ether, presumably one from the top and one from the bottom of the rigid plane of the crown ether, will be followed by the formation of crown-separated ion pairs with the nitrophenolate anions. The formation of such ion pairs can consequently bring the nitrophenolate ions into close proximity to the benzo groups of the crown ether, so that the transfer of charge from the Ph—O—CH_2—CH_2— group of the macrocyclic ligand to the nitrophenolate ions will be facilitated. It should be noted that, in this picture, the dissociation of DBDA15C4·$(TNP)_2$ into the corresponding free nitrophenolate ion and protonated crown ether has been neglected, due to the low dielectric permittivity of chloroform used as solvent. The formation of the homoconjugate salt DBDA15C4H^+·HTNP·TNP^- is also unlikely. A possible structure of the resulting DBA15C4·$(TNP)_2$ adduct is shown in Figure 1B.

In order to investigate the influence of temperature on the stoichiometry and stability of the resulting molecular adducts, the absorbance–mole ratio data for the DBDA15C4–TNP system were obtained at four different temperatures and the results are shown in Figure 4. On increasing the temperature from 10 to 50 °C, the curvature of the plots at the mole ratio of about 0.5 reduces at the expense of the increased sharpness of the breaks at a mole ratio of about 1.0. In other words, formation of the 1 : 2 adduct seems to be preferred at lower temperatures, while a more stable 1 : 1 adduct is formed at higher temperatures.

The stoichiometries of the resulting molecular adducts were further examined by the method of continuous variations [36] and some of the resulting plots are shown in Figure 5. As seen, the plots possess two distinct inflection points at X_{TNP} values of 0.50 and 0.66 which emphasize the formation of both DBDA15C4·TNP and DBDA15C4·$(TNP)_2$ complexes in solution, respectively. It is interesting to

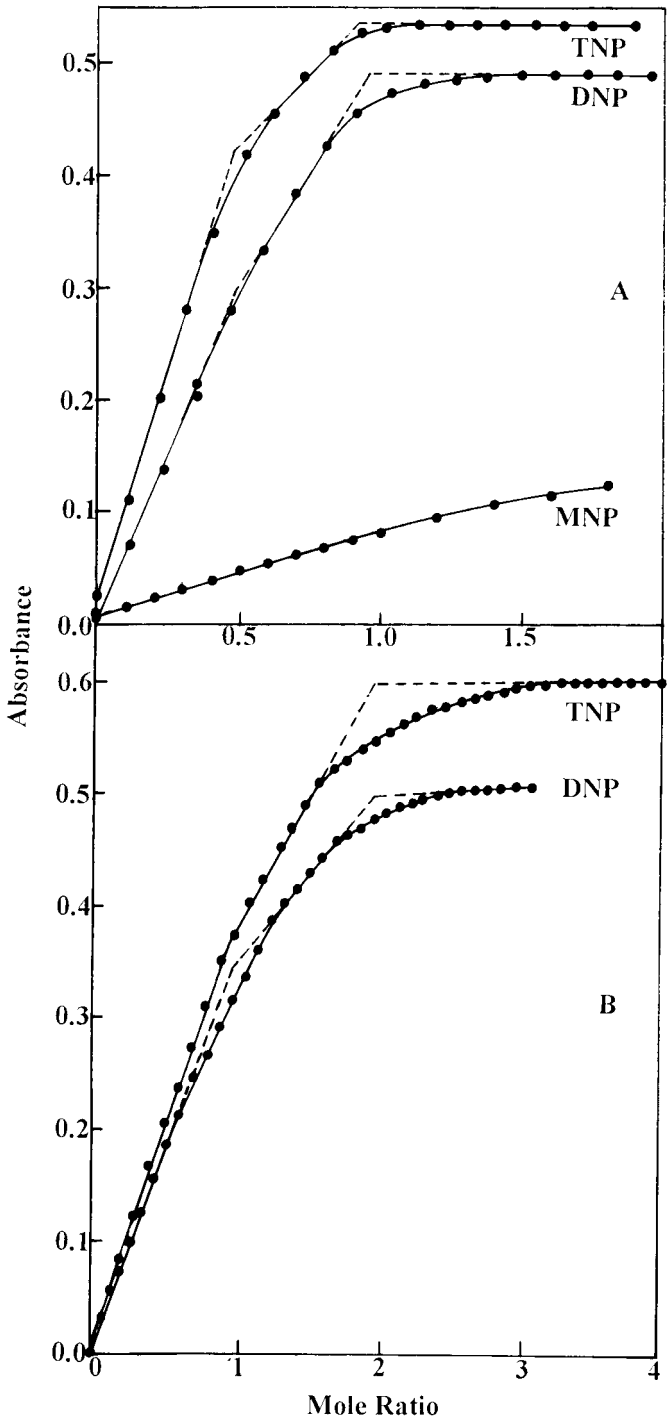

Figure 3. Absorbance–mole ratio plots at 20 °C and $\lambda = 410$ nm in chloroform solution: A, absorbance vs. [DBDA15C4]/[nitrophenol] plots ([nitrophenol] = 5.0×10^{-5} M); B, absorbance vs. [nitrophenol]/[DBDA15C4] plots ([DBDA15C4] = 5.2×10^{-5} M).

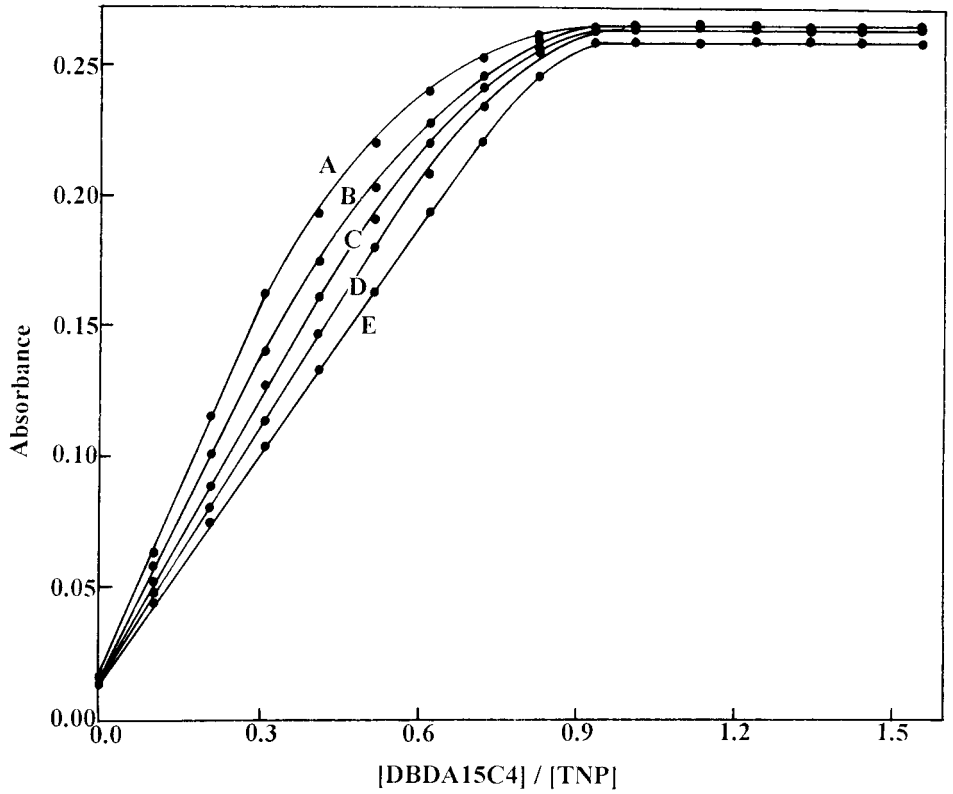

Figure 4. Plots of absorbance vs. [DBA15C4]/[TNP] mole ratio at various temperatures in chloroform solution ([TNP] = 3.0×10^{-5} M, $\lambda = 410$ nm): A, 10 °C; B, 20 °C; C, 30 °C; D, 40 °C; E, 50 °C.

note that the continuous variation plot obtained at 50 °C (Figure 5A) shows a sharper break at $X_{\mathrm{TNP}} = 0.66$, while at 10 °C, the break at $X_{\mathrm{TNP}} = 0.50$ is more distinct (Figure 5B). This nicely supports the observed temperature effect on the absorbance–mole ratio plots (Figure 4).

The stability constants of the 1 : 1 and 1 : 2 adducts at various temperatures were evaluated from the corresponding absorbance-mole ratio data as follows. When DBDA15C4 reacts with TNP, it may form both 1 : 1 and 1 : 2 complexes as

$$\mathrm{DBDA15C4} + \mathrm{TNP} \overset{K_1}{\rightleftharpoons} \mathrm{DBDA15C4} \cdot \mathrm{TNP}$$

$$K_1 = \frac{[\mathrm{DBDA15C4{\cdot}TNP}]}{[\mathrm{DBDA15C4}][\mathrm{TNP}]} \tag{1}$$

$$\mathrm{DBDA15C4} \cdot \mathrm{TNP} + \mathrm{TNP} \overset{K_2}{\rightleftharpoons} \mathrm{DBDA15C4} \cdot (\mathrm{TNP})_2$$

$$K_2 = \frac{[\mathrm{DBDA15C4} \cdot (\mathrm{TNP})]}{[\mathrm{DBDA15C4} \cdot \mathrm{TNP}][\mathrm{TNP}]}. \tag{2}$$

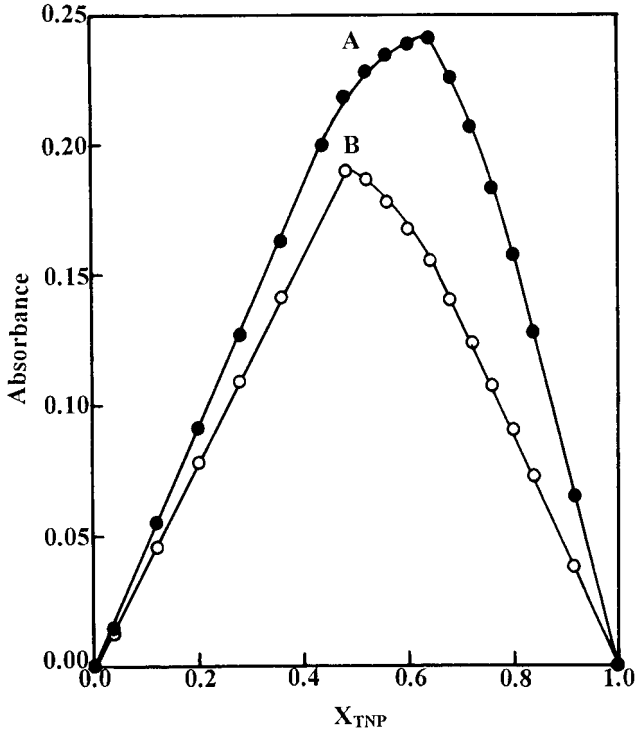

Figure 5. Continuous variations plots for DBDA15C4–TNP system in chloroform at 10 °C (A) and 50 °C (B) and $\lambda = 410$ nm.

The mass balance equations are written as Equations (3) and (4).

$$C_{\mathrm{DBDA15C4}} = [\mathrm{DBDA15C4}] + [\mathrm{DBDA15C4 \cdot TNP}] + [\mathrm{DBDA15C4 \cdot (TNP)_2}] \quad (3)$$

$$C_{\mathrm{TNP}} = [\mathrm{TNP}] + [\mathrm{DBDA15C4 \cdot TNP}] + 2[\mathrm{DBDA15C4 \cdot (TNP)_2}]. \quad (4)$$

Substitution of Equations (1) and (2) into Equations (3) and (4) and rearrangement yields Equation (5):

$$0 = K_1K_2[\mathrm{TNP}]^3 + [K_1(1 + K_2(2C_{\mathrm{DBDA15C4}} - C_{\mathrm{TNP}}))][\mathrm{TNP}]^2 + (1 + K_1(C_{\mathrm{DBDA15C4}} - C_{\mathrm{TNP}}))[\mathrm{TNP}] - C_{\mathrm{TNP}}. \quad (5)$$

The observed absorbance of the solution is also given by

$$A_{\mathrm{abs}} = \epsilon_{\mathrm{TNP}}[\mathrm{TNP}] + \epsilon_{\mathrm{DBDA15C4 \cdot TNP}}[\mathrm{DBDA15C4 \cdot TNP}] + \epsilon_{\mathrm{DBDA15C4 \cdot (TNP)_2}}[\mathrm{DBDA15C4 \cdot (TNP)_2}] \quad (6)$$

where the ϵ values are the molar absorptivities of the species denoted. For evaluation of the formation constants from the absorbance–mole ratio data, a nonlinear

Table I. Equilibrium constants for the formation of 1 : 1 and 1 : 2 adducts between DBDA15C4 and different nitrophenol derivatives at various temperatures in chloroform.

Nitrophenol derivative	Temperature (°C)	log K_1	log K_2
MNP	20	<3	<2
DNP	20	6.78 ± 0.10	3.68 ± 0.05
TNP	10	6.05 ± 0.06	4.73 ± 0.10
	20	7.10 ± 0.03	4.22 ± 0.02
	30	8.00 ± 0.10	3.75 ± 0.14
	40	9.00 ± 0.06	2.81 ± 0.03
	50	10.36 ± 0.12	2.22 ± 0.03
	$\Delta H_1 = 184 \pm 8$ kJ mol^{-1}		$\Delta H_2 = -112 \pm 7$ kJ mol^{-1}
	$\Delta S_1 = 762 \pm 27$ J mol^{-1} K^{-1}		$\Delta S_2 = -303 \pm 23$ J mol^{-1} K^{-1}

least-squares curve fitting program KINFIT was used [37]. The program is based on the iterative adjustment of calculated values of absorbance to observed values. The adjustable parameters are stepwise equilibrium constants of all complexes present and the corresponding molar absorptivities.

The procedure used for the evaluation of the K_1 and K_2 values from the absorbance–mole ratio is as follows. The free TNP concentrations, [TNP], were calculated by means of a Newton–Raphson procedure. Once the value of [TNP] had been obtained, the concentrations of other species involved are calculated from the corresponding mass balance equations by using the estimated values of the formation constants at the current iteration step of the program. Refinement of the parameters was continued until the sum-of-squares of the residuals between calculated and observed values of the absorbance for all experimental points was minimized. The output of the KINFIT program comprises the refined parameters, the sum-of-squares and the standard deviation of the data. All the stepwise equilibrium constants, obtained by computer fitting of the corresponding absorbance-mole ratio data, are listed in Table I. A sample computer fit of the mole ratio data is shown in Figure 6. The fair agreement between the observed and calculated absorbances further supports the occurrence of both 1 : 1 and 1 : 2 adducts between DBDA15C4 and TNP in chloroform solution.

From the data given in Table I, it is immediately obvious that the overall stability of the resulting molecular complexes between DBDA15C4 and different nitrophenol derivatives used varies in the order TNP > DNP $\gg$ MNP. The observed trend is not unexpected, since TNP is the strongest proton donor and π acceptor in the series, while NMP is the weakest one in both respects. In order to have a better understanding of the thermodynamics of the molecular complexation reactions studied, it is useful to consider the enthalpic and entropic contributions to these

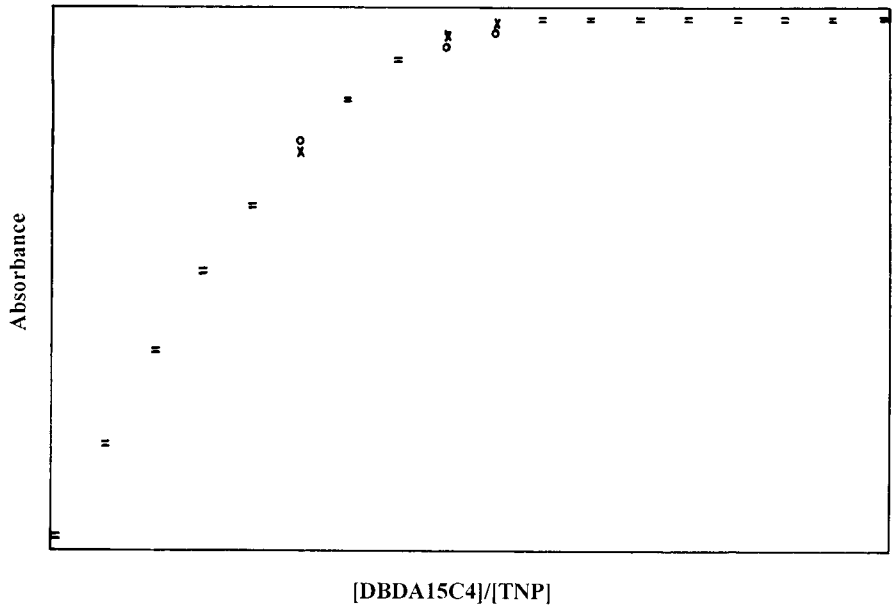

Figure 6. Computer fit of the plot of absorbance vs. [DBDA15C4]/[TNP] mole ratio at 410 nm and 20 °C: (×) experimental points; (○) calculated points; (=) experimental and calculated points are the some within the resolution of the plot.

reactions. The enthalpies and entropies for the complexation equilibria (1) and (2) in chloroform solution were determined by measuring the formation constants K_1 and K_2 as a function of temperature [38, 39]. Plots of log K vs. $1/T$ were linear ($r > 0.99$) for both equilibria. The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots, respectively, and the results are also included in Table I. As seen, while equilibrium (1) is enthalpy destabilized and entropy stabilized, the second equilibrium (2) shows the opposite behavior; it is enthalpy stabilized, but entropy destabilized. In Equation (1), positive entropy may possibly reveal the stronger solute–solvent interaction of the initial reactants with a low polarity solvent such as chloroform, as compared with that of the partially ionized 1 : 1 adduct with the solvent molecules. While, in Equation (2), the increased rigidity of the final product DBDA15C4·$(TNP)_2$ (see Figure 1B) seems to be primarily responsible for the negative value of ΔS_2, as compared to the possibly low contribution of the desolvation of the reactants in the second step.

The crystalline DBDA15C4·TNP and DBDA15C4·$(TNP)_2$ adducts were prepared, as described in the Experimental section. The physical properties and the results of chemical analysis (C, H, N) of the isolated complexes, given in Table II, clearly reveal the formation of the above mentioned species. The infrared spectra of the macrocycle used, TNP and the isolated solid complexes have been recorded in the wavenumber range 4000–700 cm^{-1}. The resulting spectral data together

Table II. Microchemical data, colour and melting points for the two molecular adducts of DBDA15C4 with TNP.

Compound	Colour	m.p. (°C)	% Calculated (Found) C	H	N
DBDA15C4	White	144	–	–	–
TNP	Yellow	121–122	–	–	–
DBDA15C4·TNP	Dull yellow	163–165	54.6 (54.4)	12.8 (12.9)	4.9 (5.0)
DBDA15C4·$(TNP)_2$	Deep yellow	196–200	48.3 (48.3)	14.1 (14.5)	4.0 (3.9)

Table III. Infrared frequencies (cm^{-1}) and tentative assignments for DBDA15C4, TNP and their 1 : 1 and 1 : 2 adducts.

DBDA15C4	TNP	DBDA15C4·TNP	DBDA15C4·$(TNP)_2$	Assignments
3325(vs)	–	3280(w)	3215(w)	ν(N—H)
3058(s)	3085(s)	3055(w)	3015(w)	ν(C—H) aromatic
2944(s), 2900(s), 2827(s)	–	2910(w), 2795(w)	2935(w), 2805(w)	ν(C—H) aliphatic
1607(vs)	1632(vs) 1609(vs)	1628(s), 1584(s)	1626(s), 1563(s)	ν(C=C)
–	1550(sh), 1520(vs)	1551(s), 1516(sh)	1550(m), 1509(sh)	ν(N—O)
	1424(s)	1437(m)	1441(m)	$\nu(\phi$—OH)
–	1343(vs)	1352(w)	1353(w)	ν(C—N)
	1326(vs)	1315(s)	1311(s)	ν(C—C)
1221(vs)	–	1152(m)	1154(m)	ν(C—N)
1087(vs)	–	1073(m)	1068(m)	ν(C—O)
–	707(s)	712(m)	715(m)	$\nu(\phi$—H) out of plane bending

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

with the tentative assignment of the most important IR frequencies that provide structural evidence for the formation of the 1 : 1 and 1 : 2 adducts are listed in Table III. The assignments of the molecular complexes' bands are based on a comparison between the spectra of the complexes and the spectra of DBDA15C4 and TNP as well as on the previously known assignments for the related species [40, 41].

From the data given in Table III it is obvious that, while the IR frequencies of the macrocycle DBDA15C4 such as ν(C—H) (aliphatic), ν(C—C) and ν(C—O) show

a shift of about 10–30 cm^{-1} to lower frequencies upon complexation with TNP, the shift in frequencies of C—N and N—H stretchings is of order of about 45–110 cm^{-1}. This is most probably due to the direct participation of the nitrogen atoms of the crown ether, as proton acceptor and electron pair donor, in the molecular complexation process, as mentioned previously. On the other hand, the relatively large shifts observed in ν(C—H) (aromatic) and ν(C=C) frequencies (in the order of about 20–70 cm^{-1}), can be reasonably related to the process of charge-transfer from the benzo ring of the crown ether to the TNP ring (as a strong π acceptor). Thus, the observed changes in the IR spectra of DBDA15C4 and TNP brought about upon molecular complexation is nicely in support of the proposed structure for the 1 : 1 and 1 : 2 adducts (Figure 1B).

References

1. C.J. Pedersen: *J. Am. Chem. Soc.* **89**, 7017 (1967).
2. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen, and D. Sen: *Chem. Rev.* **85**, 271 (1985).
3. R.M. Izatt, K. Pawlak, J.S. Bradshaw, and R.L. Bruening: *Chem. Rev.* **91**, 1721 (1991).
4. R.M. Izatt, J.S. Bradshaw, K. Pawlak, R.L. Bruening, and J. Tarbet: *Chem. Rev.* **92**, 1261 (1992).
5. A.M. Nour El-Din: *Spectrochim. Acta* **42A**, 637 (1986).
6. A. Semnani and M. Shamsipur: *Spectrochim. Acta* **49A**, 411 (1993).
7. M. Hasani and M. Shamsipur: *J. Incl. Phenom.* **28**, 39 (1997).
8. L.J. Andrews and R.M. Keefer: *J. Org. Chem.* **53**, 537 (1988).
9. Y. Jayathirtha and V. Krishnan: *Indian J. Chem.* **20A**, 249 (1981).
10. A.H. Rady: *Spectrosc. Lett.* **25**, 327 (1992).
11. E.M. Nour and L.A. Shahada: *Spectrochim. Acta* **44A**, 1277 (1988).
12. E.M. Nour: *Spectrochim. Acta* **47A**, 743 (1991).
13. W. Hirsch, J. Greenman, and R. Pizer: *Can. J. Chem.* **71**, 2171 (1993).
14. A. Semnani and M. Shamsipur: *J. Incl. Phenom.* **22**, 99 (1995).
15. A. Semnani and M. Shamsipur: *J. Chem. Soc. Dalton Trans.* 2215 (1996).
16. A. Semnani and M. Shamsipur: *Polish J. Chem.* **71**, 134 (1997).
17. E. Shchori and J. Jagar-Grodzinski: *J. Am. Chem. Soc.* **94**, 7957 (1972).
18. N. Nae and J. Jagur-Grodzinski: *J. Am. Chem. Soc.* **99**, 489 (1977).
19. I.M. Kolthoff; W. Ji-Wang, and M.K. Chantooni: *Anal. Chem.* **55**, 1202 (1983).
20. M.K. Chantooni and I.M. Kolthoff: *J. Solution Chem.* **21**, 683 (1992).
21. M.K. Amini and M. Shamsipur: *J. Solution Chem.* **21**, 275 (1992).
22. M.K. Amini and M. Shamsipur: *Iran. J. Chem. & Chem. Eng.* **11**, 12 (1992).
23. U. Olsher, H. Feinberg, F. Frolow, and G. Shoham: *Pure Appl. Chem.* **68**, 1195 (1996) and references therein.
24. R. Foster: *Organic Charge Transfer Complexes*, Academic Press, London (1969).
25. N. Inoue and Y. Matsunaga: *Bull. Chem. Soc Jpn.* **45**, 3478 (1972).
26. G. Saito and Y. Matsunaga: *Bull. Chem. Soc Jpn.* **46**, 714 (1973).
27. R.M. Issa and M.M. El-Essawey: *Z. Phys. Chem.* **253**, 96 (1973).
28. P.A. Johansson: *Acta Pharm. Suec.* **14**, 345 (1977).
29. K.M. Issa, S. Abu-El-Wafa, M. Gaber, and E.H.A. Mohamed: *Acta Chim. Hung.* **118**, 179 (1985).
30. A. Togashi and Y. Matsunaga: *Bull. Chem. Soc Jpn.* **60**, 1171 (1987).
31. J. Csaszar and N.M. Bizong: *Acta Phys. Chem.* **33**, 37 (1987).

32. S.F. Bureiko, V.P. Oktyabrskii, and K. Philaya: *Zh. Fiz. Khim.* **67**, 315 (1993); *Chem. Abstr.* 120-163323t (1994).
33. B. Stojceva-Radovanovic: *Anal. Lab.* **2**, 255 (1993).
34. H. M. Colquhoun *et al.*: *J. Chem. Soc., Perkin Trans. 2*, 250 (1980).
35. M. Bourgoin, K.H. Wong, J.Y. Hui, and J. Smid: *J. Am. Chem. Soc.* **97**, 3462 (1975).
36. P. Job: *Ann. Chim. (Paris)* **9**, 113 (1928).
37. V.A. Nicely and J.L. Dye: *J. Chem. Educ.* **49**, 443 (1971).
38. M. Shamsipur, G. Rounaghi, and A.I. Popov: *J. Solution Chem.* **9**, 701 (1980).
39. M. Hasani and M. Shamsipur: *J. Incl. Phenom.* **16**, 123 (1993).
40. L.J. Bellamy: *The Infrared Spectra of Complex Molecules*, Chapman-Hall, London (1975).
41. R.M. Silverstein, G.C. Bassler, and T.C. Morill: *Spectroscopic Identification of Organic Compounds*, Wiley & Sons, New York (1981).