Spectroscopic Study of the Complexation of DDQ with 1,10-Diaza-18-crown-6 in Chloroform Solution

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Abstract. The formation of charge transfer complexes with 1 : 1 and 2 : 1 stoichiometries (acceptor-to-donor) between DDQ and 1,10-diaza-18-crown-6 in chloroform solution was investigated spectrophotometrically. The stepwise formation constants of the resulting complexes were evaluated from the non-linear least-squares fitting of the absorbance-mole ratio data. The enthalpies and entropies of the complexation reactions were determined from the temperature dependence of the stepwise formation constants. The resulting 1 : 1 and 2 : 1 complexes were isolated in crystalline form and characterized. The results are consistent with the ionic structure of the resulting charge transfer complexes.

Key words: Diaza-18-crown-6, DDQ, charge transfer complexes, spectrophotometry, IR, NMR.

1. Introduction

Crown ethers are macrocyclic polyethers [1] well known for their ability to form selective and stable inclusion complexes with many cations in solution [2, 3]. However, more recently increasing attention has been focused on the study of the interactions of these ligands with various neutral molecules [4]. Among different crown ethers used for such donor–acceptor complexation, aza-substituted crown ethers show very interesting features [5–9]. We have recently noticed that the substitution of the oxygen atoms in a crown ether ring by NH groups results in a drastic enhancement in the stability of their molecular complexes with iodine in chloroform solution over the corresponding crown-iodine complexes [8, 9].

Although there are several published papers on the complexation of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and some other π-acceptors with crown ethers and benzocrown ethers in solution [10–16], to the best of our knowledge, there is no previous report on the complexation of DDQ with azacrowns. In this paper we wish to report the results of a spectroscopic investigation of the stoichiometry, characteristics and thermodynamics of DDQ complexes with 1,10-diaza-18-crown-6 (DA18C6, **I**) in chloroform solution.

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2. Experimental

Reagent grade DA18C6 (Fluka) and DDQ (Merck) 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 Philips PUB700 spectrophotometer and the absorbance measurements at various temperatures were made with a Philips PU875 spectrophotometer. At all temperatures, the cell was thermostatted with a Lo-temprol 154 thermostat to $\pm 0.5\,^{\circ}$C. The IR spectra were recorded on a Perkin Elmer 181 spectrometer using KBr pellets. The proton NMR spectra were recorded on a Jeol JNM-EX90 FTNMR spectrometer operating at a field of 21.15 kG (90 MHz). Melting points were measured by a Gallenkamp apparatus.

3. Results and Discussion

The existence of new bands in the visible region of the electronic spectrum of the mixtures of DDQ and DA18C6 in chloroform (Figure 1) must be associated with the charge transfer complexes, since neither the π-acceptor nor the crown ether absorbs significantly in this region. The formation of such molecular complexes between DDQ and a variety of nitrogen-donating molecules such as aliphatic amines [17], anilines [18], aminopyridines [19], aromatic amines [20], indolyldiene aniline derivatives [20] and imidazoles [21] has been reported in the literature.

In order to determine the stoichiometry of the molecular complexes, the spectra of a series of solutions containing a constant concentration of DDQ (3.0×10^{-4} M) and varying amounts of DA18C6 (up to a DA18C6/DDQ mole ratio of 6) were obtained (Figure 2). From Figure 2 one can distinguish two distinct behaviours, one at low DA18C6/DDQ mole ratios (spectra 1–5) with one isosbestic point at about 414 nm, indicating the presence of one equilibrium step. The second spectral behaviour, associated with spectra 6–11, reveals two other isosbestic points at about 450 nm and 516 nm, indicating the possibility of two equilibrium steps. The spectra show that DA18C6 can form at least two complexes of 1 : 1 and 2 : 1 (acceptor-to-donor) stoichiometries with DDQ in chloroform solution. While the $(DDQ)_2 \cdot DA18C6$ complex absorbs at about 485 nm, the DDQ·DA18C6 adduct shows two absorption maxima at about 370 nm and 510 nm (see Figures 1 and 2). The resulting absorbance vs. DA18C6/DDQ mole ratio plots at two different wavelengths are shown in Figure 3, indicating the stepwise formation of 2 : 1 and 1 : 1 complexes in solution.

The stoichiometries of the resulting charge transfer complexes were further examined by the method of continuous variations [23, 24] and the resulting plot is shown in Figure 4. As seen, the plot possesses two distinct inflection points at X_{DDQ} values of 0.50 and 0.66 which emphasize the formation of DDQ·DA18C6 and $(DDQ)_2 \cdot DA18C6$ adducts in solution, respectively. It should be noted that the
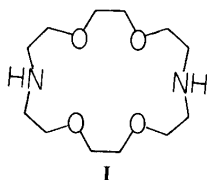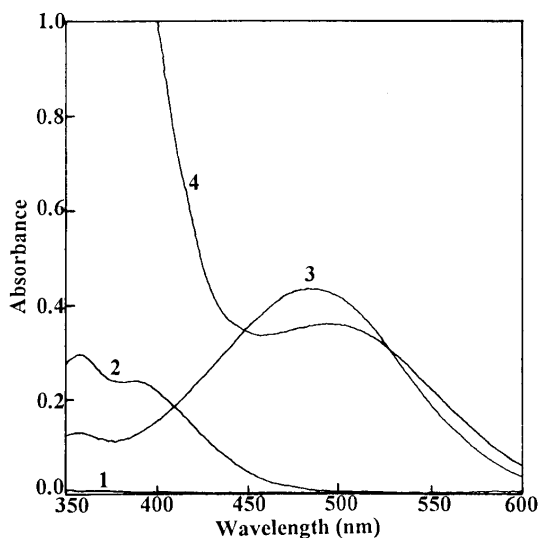
Figure 1. Visible spectra of DA18C6 (1), DDQ (2), $(DDQ)_2 \cdot DA18C6$ (3) and DDQ. DA18C6 (4) in chloroform solution.

formation of such A_2D complexes between DDQ and some indolyldiene aniline derivatives has recently been reported [21].

For the evaluation of the stepwise formation constants of the resulting $1:1$ and $2:1$ molecular complexes (i.e. K_1 and K_2, respectively) from the absorbance–mole ratio data, a non-linear least-squares curve fitting program, KINFIT, was used [25]. The program is based on the iterative adjustment of calculated to observed absorbance values by using either the Wentworth matrix technique [26] or the Powell procedure [27]. Adjustable parameters are K and ϵ values (ϵ = molar absorption coefficient of the complexes).

The observed absorbance is given by Equation (1) and the mass balance Equations are written as Equations (2) and (3).

$$A_{\mathrm{obs}} = \epsilon_{\mathrm{DDQ}}[\mathrm{DDQ}] + \epsilon_1\,[\mathrm{DDQ \cdot DA18C6}] + \epsilon_2[(\mathrm{DDQ})_2 \cdot \mathrm{DA18C6}] \qquad (1)$$

$$C_{\mathrm{DDQ}} = [\mathrm{DDQ}] + [\mathrm{DDQ \cdot DA18C6}] + 2[(\mathrm{DDQ})_2 \cdot \mathrm{DA18C6}] \qquad (2)$$

$$C_{\mathrm{DA18C6}} = [\mathrm{DA18C6}] + [\mathrm{DDQ \cdot DA18C6}] + [(\mathrm{DDQ})_2 \cdot \mathrm{DA18C6}]. \qquad (3)$$
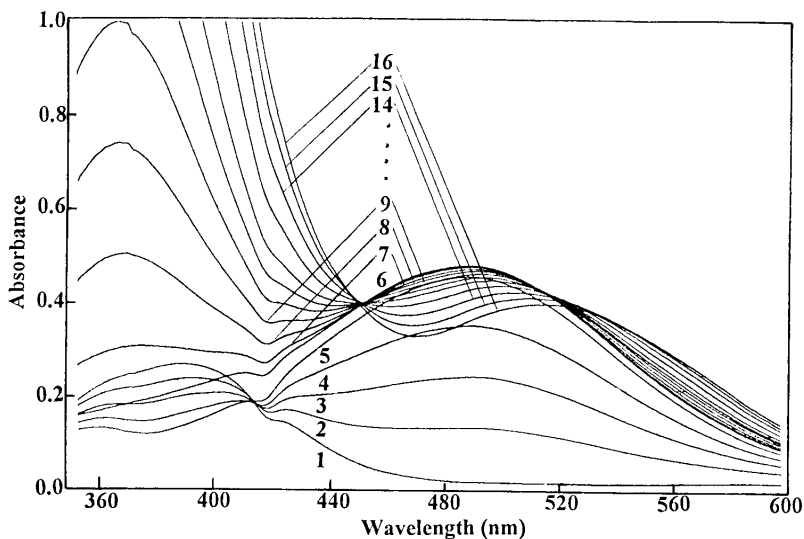
Figure 2. Visible spectra of 3.0×10^{-4} M of DDQ in chloroform in the presence of varying concentration of DA18C6. The DA18C6/DDQ mole ratios are: 1, 0.0; 2, 0.1; 3, 0.2; 4, 0.3; 5, 0.4; 6, 0.5; 7, 0.6; 8, 0.7; 9, 0.8; 10, 0.9; 11, 1.0; 12, 1.2; 13, 2.0; 14, 3.0; 15, 4.0; 16, 6.0.
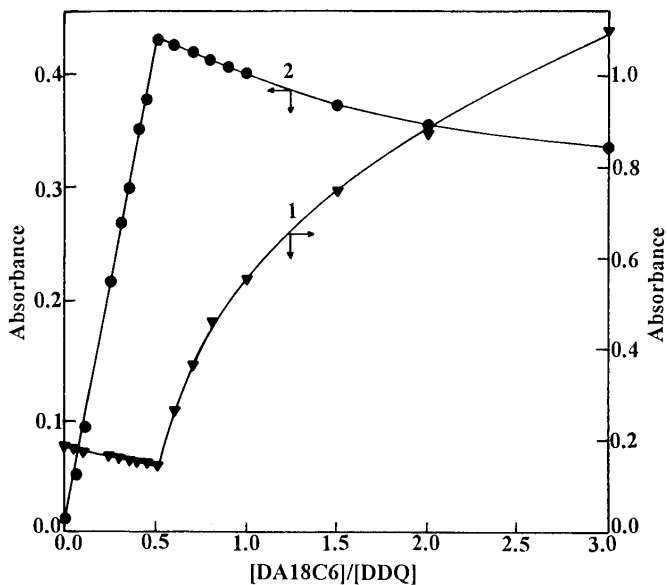

Figure 3. Plots of absorbance vs. DA18C6/DDQ mole ratio in chloroform solution obtained at 411 nm (1) and 485 nm (2).

The stepwise formation constants for the formation of 1 : 1 and 2 : 1 complexes are also given by Equations (4) and (5), respectively.

$$K_1 = \frac{[\text{DDQ} \cdot \text{DA18C6}]}{[\text{DDQ}][\text{DA18C6}]} \tag{4}$$
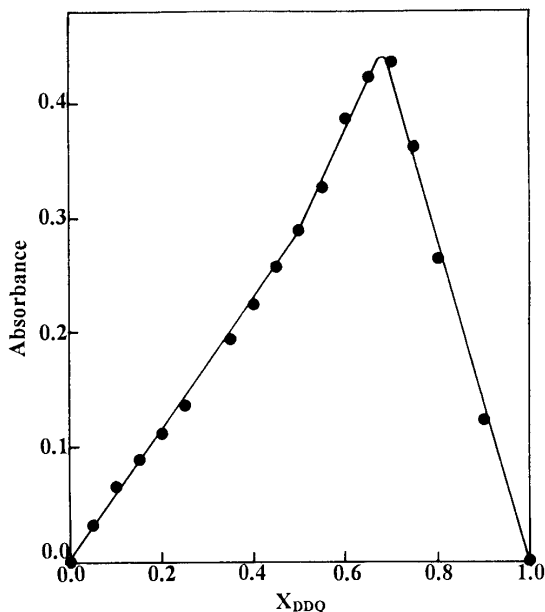
Figure 4. Continuous variations plot for DDQ–DA18C6 system in chloroform solution; $\lambda = 485$ nm.

$$K_2 = \frac{[(DDQ)_2 \cdot DA18C6]}{[DDQ \cdot DA18C6][DDQ]}. \tag{5}$$

Substitution of Equations (4) and (5) into Equations (2) and (3) and rearrangement yields Equation (6):

$$K_1 K_2 [DDQ]^3 + [K_1(1 + K_2(2C_{DA18C6} - C_{DDQ}))][DDQ]^2$$

$$+ (1 + K_1(C_{DA18C6} - C_{DDQ}))[DDQ] - C_{DDQ} = 0. \tag{6}$$

The free DDQ concentrations, [DDQ], were calculated from Equation (6) by means of a Newton–Raphson procedure. Once the value of [DDQ] had been obtained, the concentration of all other species involved were calculated from the corresponding mass balance equations by using the estimated values of K_1 and K_2 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 absorbance values for all experimental points was minimized. The output of the program KINFIT comprises the refined parameters, the sum-of-squares and the standard deviations of the data.

   In order to evaluate the enthalpies and entropies of formation of the result-ing charge transfer complexes, the absorbance-mole ratio plots were obtained at four different temperatures (Figure 5). The stepwise formation constants K_1 and K_2 at various temperatures, obtained by computer fitting of the corresponding

Table I. Thermodynamic data for the stepwise formation of 1 : 1 and 2 : 1 charge transfer complexes between DDQ and DA18C6 in chloroform solution

Wavelength (nm)	$\log K$				
		5 °C	15 °C	25 °C	35 °C
485	$\log K_1$	7.54 ± 0.03	7.17 ± 0.08	7.05 ± 0.09	6.70 ± 0.09
	$\log K_2$	6.73 ± 0.02	6.38 ± 0.11	6.21 ± 0.10	5.96 ± 0.14
449	$\log K_1$	7.54 ± 0.02	7.22 ± 0.08	7.04 ± 0.07	6.64 ± 0.10
	$\log K_2$	6.73 ± 0.02	6.55 ± 0.11	6.29 ± 0.14	5.95 ± 0.14
	$\Delta H_1 = -45 \pm 4 \text{ kJ mol}^{-1}$			$\Delta H_2 = -42 \pm 2 \text{ kJ mol}^{-1}$	
	$\Delta S_1 = -17 \pm 8 \text{ JK}^{-1} \text{ mol}^{-1}$			$\Delta S_2 = -21 \pm 7 \text{ JK}^{-1} \text{ mol}^{-1}$	

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 2 : 1 complexation between DDQ and DA18C6 in chloroform solution. Plots of $\log K$ vs. $1/T$ were linear for both complexes (i.e. with a regression coefficient >0.99). 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.

The data given in Table I clearly show that the stepwise formation constants, at various temperatures, evaluated from the computer fitting of the absorbance–mole ratio data at two different wavelengths are in excellent agreement with each other. This is indicative of the high degree of reliability of the method used for the evaluation of the K_1 and K_2 values.

Furthermore, the stability of the resulting complexes are exceptionally high, as compared with the molecular complexes formed between DDQ and ordinary and benzo-substituted crown ethers [4, 10–16]. Similarly, it has been recently shown that the substitution of the oxygen atoms in a crown ether ring by NH groups results in a drastic increase in the stability of iodine complexes [8, 9, 28, 29] over those of ordinary crowns [4]. It should be noted that the reported formation constants for iodine complexes with azasubstituted crown ethers [8, 9] and cryptands [30] are of about the same order as that obtained for the DDQ·DA18C6 complex in this study (Table I).

As can be seen from Table I, both 1 : 1 and 2 : 1 complexes are enthalpy stabilized but entropy destabilized. Similar behavior has been frequently reported for the interaction of macrocyclic ligands with neutral molecules in solution [4, 9, 10, 12]. Although a detailed interpretation of all parameters including solvation–desolvation of the reaction partners is not possible, it is very likely that part of the unfavorable entropy contribution is related to a decrease in the conformational entropy of DA18C6 upon formation of charge transfer complexes with DDQ. Large macrocycles such as DA18C6 should be rather flexible in the free state. The extent of flexibility is expected to vary with the extent of macrocycle–solvent interac-
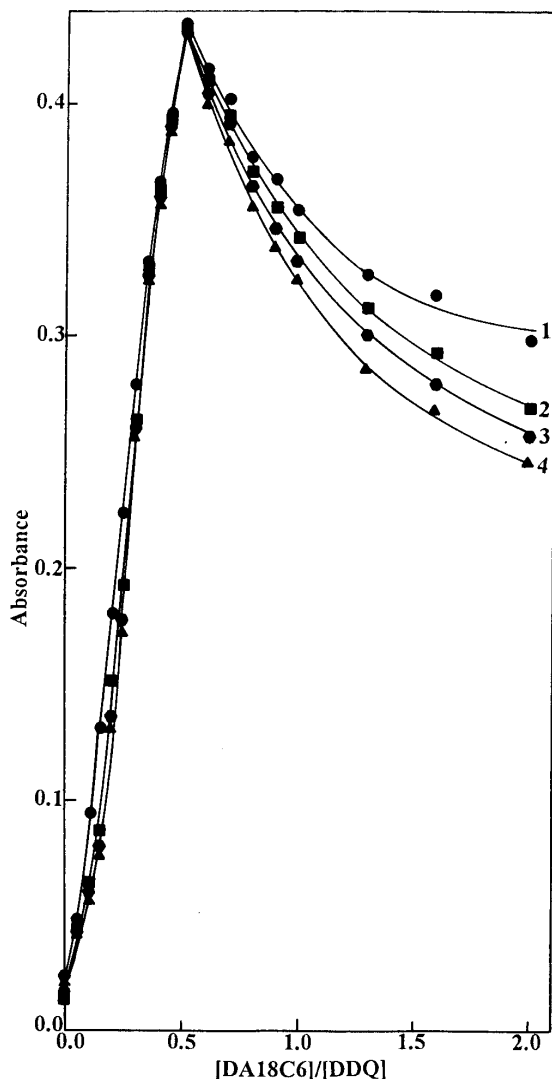
Figure 5. Plots of absorbance vs. DA18C6/DDQ mole ratio in chloroform solution ($\lambda = 485$ nm) at various temperatures: 1, 5 °C; 2, 15 °C; 3, 25 °C; 4, 35 °C.

tion. Interaction of the planar DDQ molecule with the flexible DA18C6 molecule presumably results in the formation of a rigid charge transfer adduct in which the preferred conformation of the two component molecules for maximum overlap will lead to a negative entropy change during the complexation reaction. Since, in the formation of a 2:1 $(DDQ)_2 \cdot DA18C6$ complex, two planar DDQ molecules can trap a DA18C6 molecule inside a kind of 'sandwich' structure, the resulting entropy change is more negative than that observed for a 1:1 complex.
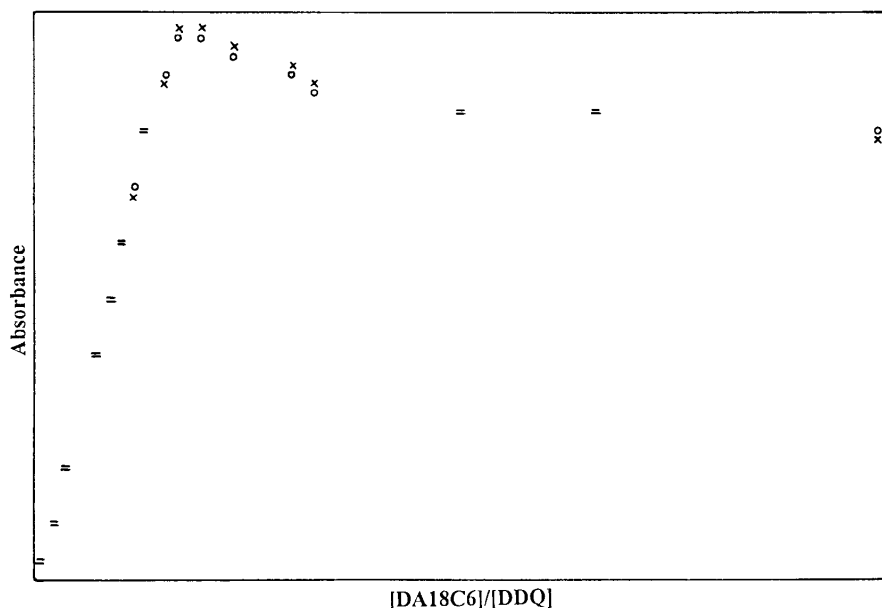
Figure 6. Computer fit of the plot of absorbance vs. DA18C6/DDQ mole ratio obtained at 485 nm and 15 °C: (×), experimental points; (○) calculated points; (=), experimental and calculated points are the same within the resolution of the plot.

Table II. Melting points and IR spectral data of DDQ and DA18C6 and their charge transfer complexes

Compound:	DDQ	DA18C6	DDQ·DA18C6	(DDQ)$_2$·DA18C6
MeltingPoint (°C)	213	113	153	184
ν_{NH} (cm^{-1})	–	3240	3040 (broad)	3040 (shoulder)
ν_{CN} (cm^{-1})	2230	–	2200	2200
ν_{CO} (cm^{-1})	1675	–	1545 (broad)	1555

In order to prepare the charge transfer complexes of DDQ with 18C6 in crystalline form, 10 mL of solutions containing 15 mg DA18C6 and the appropriate amount of DDQ for the formation of DDQ·DA18C6 and (DDQ)$_2$·DA18C6 adducts were prepared in chloroform. After filtration, the solutions were allowed to evaporate over about 15 h. The resulting solid crystals were collected and dried under vacuum for 10 h. The melting points and IR spectral data of DDQ, DA18C6 and their 1 : 1 and 2 : 1 complexes are presented in Table II. A comparison between the IR spectra of the reagents and of the resulting charge transfer complexes shows two points.

(a) The 3240 cm^{-1} ν_{NH} band of DA18C6 shifts strongly to a lower wavenumber in the presence of DDQ. This effect can be explained by the contribution of the
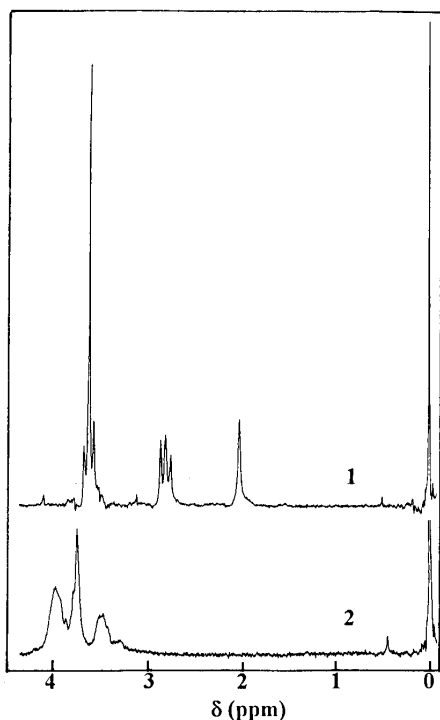
Figure 7. ^{1}H-NMR spectra of DA18C6 (1) and its 1:1 complex with DDQ (2) in CDCl$_3$ solution.

Table III. Equivalent conductances of the equimolar solutions (3.0×10^{-4} M) of the free donor, free acceptor and their charge transfer complexes in chloroform solution at 25 °C

Compound	Λ (S cm^2 mol^{-1})
DDQ	0.007
DA18C6	0.006
DDQ·DA18C6	0.103
(DDQ)$_2$·DA18C6	0.113

NH groups of DA18C6 with the acceptor via n-electrons of the nitrogen atoms, so that the charge migration from the crown ether to the acceptor molecule results in lower charge density on the N—H bonds.

(b) The CO and, to a lower extent, the CN stretching of DDQ in the 1:1 and 2:1 complexes show a bathochromic shift to lower frequencies. This effect is indicative of a high charge density on the carbonyl and cyano groups of the π-acceptor [14, 16], as a result of charge transfer from the highest occupied molecular orbital

(HOMO) of the donor to the lowest unoccupied molecular orbital (LUMO) of the π-acceptor. The above results show the strong pattern due to the DDQ anion radical [31].

Moreover, the molar conductance of the equimolar solutions of DDQ, DA18C6 and their 1 : 1 and 2 : 1 complexes in chloroform were determined and the results are given in Table III. It is seen that the equivalent conductances of the charge transfer complexes are largely increased compared with those obtained for the free reagents, supporting the above conclusion.

Interesting results are obtained from the ^{1}H-NMR spectra of DA18C6 and its DDQ complex (Figure 7). The spectrum of DA18C6 (Figure 7-1) consisted of a triplet due to —OCH$_2$— (at about 3.65 ppm), a singlet for —OCH$_2$CH$_2$O— (at about 3.60 ppm), a triplet for —NCH$_2$— (at about 2.8 ppm) and a singlet for —NH— (at about 2.05 ppm). On the other hand, the ^{1}H-NMR spectrum of the DDQ·DA18C6 complex shows a quite different pattern (Figure 7-2). As seen, the —NCH$_2$—, and especially the —NH— signals, are shifted very strongly downfield so that the spectrum shows no signal in the chemical shift range of 2–3 ppm. It seems reasonable to assume that such a tremendous shift is due to the charge migration mainly from the n-electrons of the —NH— groups of the macrocycle to the π-acceptor, strongly supporting the results obtained from the IR studies. However, other protons of the macrocycle (i.e. —OCH$_2$— and —OCH$_2$CH$_2$O— protons) also show some downfield shifts upon complexation with DDQ, although to a much lower extent.

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