



Molecular Complexes of Crown Ethers, Part 5: Complexes of DB18C6 with Some Acceptors

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Abstract. The UV-Visible spectra of DB18C6 as a donor with TCNE (Tetracyanoethylene), and DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) as acceptors were studied. Charge transfer spectra were obtained for these systems from which it was possible to calculate the formation constant, K_c . The effects of potassium halides were studied. This study shows that in the presence of the anion there is an electron transfer from the anion to the acceptor. This process is enhanced by the presence of the crown ether, CE. The formation of the anion salt with the acceptor, in the presence of the CE, follows the trend $F = I > Br > Cl$. It is also indicated in this study that the interaction between DB18C6 and the acceptor follow the trend $DDQ > TCNE$.

Key words: UV-visible spectra, charge transfer complex, formation constant, DB18C6, TCNE, DDQ, halides, electron transfer

1. Introduction

Although most of the work on crown ethers (CE) has been focused on their complexation with metal ions, a number of papers related to the study of charge-transfer complexes between crown ethers with acceptor molecules have been reported [1–10].

Shchori and Jaguar-Grodzinski [1] observed molecular complex formation of CE with bromine during the bromination of stilbene in the presence of dicyclohexano-18C6. Hopkins et al. [2] reported that the stabilities for the formation of molecular complexes between 12C4, 15C5, and 18C6 with iodine are two or three times larger than those reported for iodine complexes of monoethers and diethers. Malini and Krishnan [3] reported the formation of molecular complexes between B15C5, DB18C6, and DB24C8 with DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone). Nour El-Din [4] reported the formation of 1:1 complexes between DB18C6 and different acceptors. Semnani and Shamsipur [5] showed that the CT complex of TCNE (tetracyanoethylene) with DB18C6 in the presence of KCl is less stable than that formed in the absence of the salt.

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Salman et al. [6] studied the intermolecular complexes of four CEs (B15C5, B18C6, DB18C6 and DB24C8) as donors with three acceptors (7,7,8,8-tetracyanoquinodimethane, TCNE) and *p*-chloranil in DCE (dichloroethane). Their results indicate that the position of the CT band blue shifts while the formation constant increases following the systematic change of the electron affinity of the acceptors. They also reported the intermolecular CT complex of DB18C6 and B15C5 with different acceptors in DCE in the presence and absence of KCl salt [7].

No systematic trend has been observed due to the influence of anions upon the interaction between cations and ligand. However, the interaction between the anion and complexed cation may affect the complex stability [7]. In highly solvating media the charged complex and the counter ion are strongly solvated; no anion effect on the complex stability was observed. In poorly solvating media, anion effects were observed [11], which depends on the charge, size, shape and polarizability of the anion.

The aim of this work is to study the charge transfer complexation between different crown ethers such as 18C6 and DB18C6 with different acceptors such as TCNE and DDQ and to calculate K_c whenever possible.

The effect of using different halide anions with the same cation on the CT complexation of the CE with the acceptor is also studied. The mode of addition of CE, acceptor and the salt is varied to investigate if the different systems are interchangeable.

The Benesi–Hildebrand equation [12] was found to be applicable for most complexes. Formation constants and molar absorptivity coefficients of the CT complexes were calculated.

2. Experimental

Infrared (IR) spectra were recorded on a Pye-Unicam SP 300 instrument as potassium bromide discs. Ultraviolet-visible spectra were recorded for the CE and their complexes as solutions in dichloroethane solvent on a DMS-100 spectrophotometer.

All chemicals used in this work were of pure grade purified before use (BDH, Fluka, and Aldrich). TCNE was recrystallized from chlorobenzene and then sublimed, m.p (198-200 °C). DDQ was recrystallized twice from benzene, m.p. (214–216 °C).

Attempts were made to obtain solid CT complexes by mixing equimolar quantities of each acceptor with the donor dissolved in a small amount of DCE, and then the solution was filtered and allowed to evaporate slowly at room temperature. The solid complexes were collected and dried. In order to prepare ternary complexes (CE + salt + acceptor), an excess amount of the salt was dissolved in the CE solution, then the acceptor solution was added. The reaction mixture was left for one hour and then the solution was filtered and allowed to evaporate slowly at room temperature. Then a solid precipitate was formed.

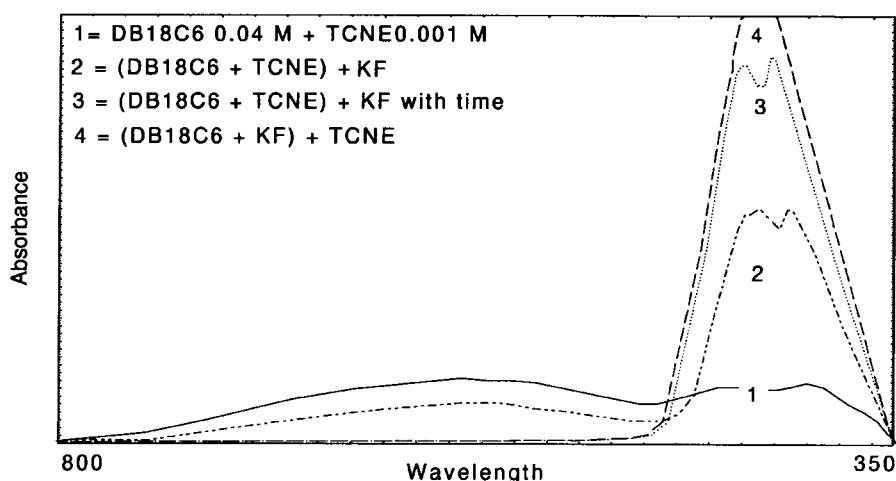


Figure 1. Absorption spectra of DB18C6-TCNE-KF in DCE.

The stability constant of the CT complexes, K_c , can be calculated from the Benesi-Hildebrand equation [12].

3. Results and Discussion

3.1. DB18C6 + TCNE

A mixed DCE solution of DB18C6 and TCNE immediately exhibits a dark blue color due to the formation of a CT complex. The absorption spectrum of this solution displays two main absorption bands. The shorter wavelength band appears as a doublet ($\lambda_{\max} = 395, 415$ nm). The second absorption band appears as a broad band at 586 nm (Figure 1). Neither TCNE nor DB18C6 has any measurable absorption in this region. However, the broad absorption band located at 586 nm could be ascribed to the formation of an intermolecular CT complex [3-4]. The Benesi-Hildebrand plot (Figure 2) indicates a 1:1 stoichiometry for the complex with a value of $K_c = 2.9 \text{ dm}^3 \text{ mol}^{-1}$. The results obtained for this system in this study are in accord with those of reference [6].

When any one of the salts (i.e. KF, KCl, KBr and KI) was added to the DCE solution containing DB18C6 and TCNE, the blue color of the complex became less intense and vanished almost completely with time and a new color developed. This change of color depended on the salt used.

Treatment of the dark blue solution of the complex with KF resulted in an immediate color change to yellow, and the band located at 586 nm disappeared with time, while the intensity of the band located at 395 and 415 nm increased sharply (Figure 1). This was assigned to a CT band of a complex of TCNE with the fluoride anion. This result was confirmed by an experiment in which 18C6 was used instead of DB18C6 solution, the DCE solution of this CE, which cannot

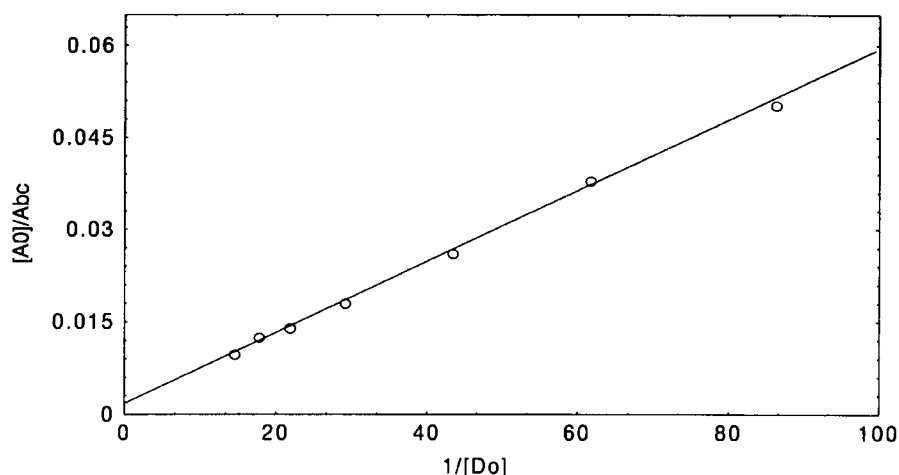


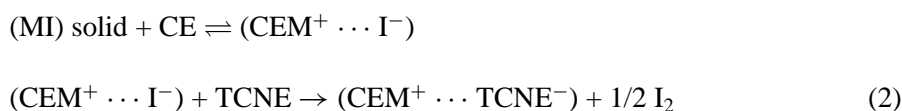
Figure 2. Typical Benesi–Hildebrand plot of the CT complex of 0.001 M TCNE with different concentrations of DB18C6 in DCE.

form a π -CT complex with TCNE, exhibited the same absorption at 395 nm and 415 nm. Salman et al. [7] showed that the sequence of addition of the cation to the CE and the acceptor is very important and that the resulting complex might be different and variable. Therefore another case was studied where the mode of addition was (DB18C6 + KF) + TCNE in DCE. When TCNE solution was added to that of (CE+KF) a new band appeared immediately ($\lambda_{\max} = 395, 415$ nm) (Figure 1), the intensity of the band was time dependent and the CT band of the complex between DB18C6 and TCNE did not appear. This may be attributed to the greater nucleophilicity of the fluoride anion as compared with the $\text{PhOCH}_2\text{CH}_2$ group in the presence of CE [13]. When adding KF to TCNE solution no band appeared at 395, 415 nm. This suggested that the interaction is:

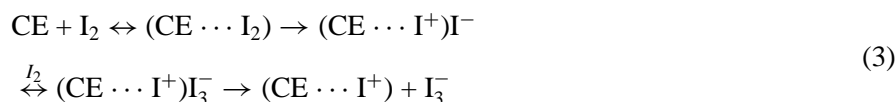


The same band at 395 and 415 nm was obtained when KI was mixed with a solution of (TCNE + DB18C6) or (TCNE + 18C6) together with a new band at ($\lambda_{\max} = 365$ nm).

Webster et al. [14] reported that the iodine anion (from MI) reacts with TCNE in acetonitrile to yield the TCNE anion, and they concluded that free iodine is formed in this reaction. Eastman [15] studied the ESR spectrum of the ion pair formed by the complexation of the salt of TCNE and the crown ether, which is dissolved in benzene and proposed the following mechanism:

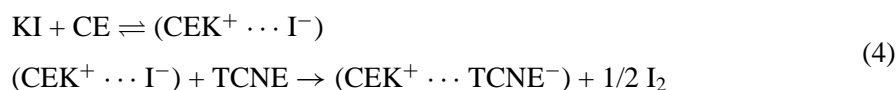


Therefore, according to Webster and Eastman iodine will be formed, but according to Webster there is no need for the crown ether to form iodine. Muchova and Holba [16] during their studies of the CT complex between crown ethers and iodine suggested the following mechanism Equation (3).

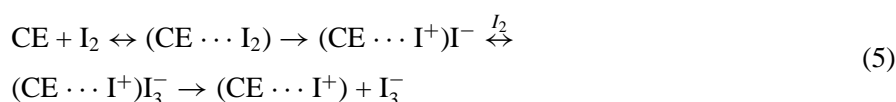


This result was supported by the appearance of two absorption bands located at 292 and 365 nm, which were assigned to the triiodide anion.

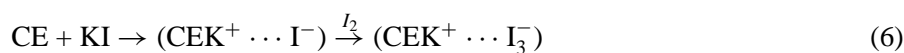
Iodine in DCE has an absorption at 520 nm [17]. In the present work this band did not appear when a TCNE solution was added to a solution of (CE + KI). This may suggest the following possibilities. The first is that iodine did not form in this system. The second is that iodine was formed in a small quantity and in a slow step according to the following equations:



This was followed by a fast step represented by the following equation:



This mechanism is supported by two observations. The first is that we did not observe the iodine absorption at 520 nm, and the second is that we observe the band at 365 nm, which may be assigned to the triiodide anion, which was present in the system before the addition of TCNE. We did not observe the other band which belongs to the triiodide anion at 292 nm because it coincides with the band at 300 nm which is assigned to the formation of the tricyanoethenolate anion [14] by the conversion of TCNE^- in the presence of oxygen or a trace amount of water present in the solvent and the intensity of this band increased with time. The third possibility is that I_2 was formed in a slow step followed by a fast step in which CE will complex with KI according to the following mechanism:



It is difficult to decide which of the mechanisms listed above is dominant.

To study the effect of KBr salt on the formation and stability of the intermolecular complex, an excess amount of the salt was added to the (DB18C6 + TCNE) solution resulting in a color change from blue to red, and the band located at 586 nm disappeared slowly with time. This process was accompanied by the appearance of

a new band at ($\lambda_{\max} = 420$ nm) and the intensity of this band increases with time, and this band was shifted to 460 nm. In another experiment TCNE was added to (DB18C6 + KBr). In this case a red color formed immediately, and a new band appeared in the visible region which was located at 460 nm, while the band attributed to the CT complex between the CE and TCNE did not appear. Briegle et al. [18] have reported a charge transfer absorption at 460 nm for the LiBr-TCNE complex in acetonitrile. The same absorption at 460 nm was obtained in this work in an experiment in which 18C6 was used instead of DB18C6. These results prove that the interaction of 18C6 and TCNE with KBr can be attributed to the CT from the bromide anion to TCNE. The above two systems were found to be interchangeable, but the time required to obtain the same results usually is about two hours. This may be due to the steric factor of the complex (CE + TCNE) which may prevent the salt from complexing with the CE and consequently to react with the acceptor. This may be another proof of the importance of the participation of $\text{PhOCH}_2\text{CH}_2$ in the complexation of the acceptor with benzo substituted crown ethers. The decay of the CT band between bromide anion and TCNE may be assumed to follow a first order correlation.

In order to investigate the effect of the concentration of the acceptor in complex formation, a large excess of TCNE was used. On mixing a DCE solution of DB18C6 and TCNE a dark blue color forms immediately due to the formation of a CT complex. The absorption spectrum of this solution displays two main absorption bands ($\lambda_{\max} = 395, 415$) and a broader band at 586 nm. The Benesi-Hildebrand plot indicates a 1 : 1 ratio for the complex with a value of $K_c = 2.63 \text{ dm}^3 \text{ mol}^{-1}$. The result obtained for this system was close to the results obtained when excess DB18C6 was used.

The effect of KBr salt on the formation of the CT complex was studied by adding an excess amount of salt to 0.001 M DB18C6, the mixture was left for half an hour then 0.02 M of TCNE was added. The following results were obtained: a new band appeared immediately after the addition. This band which is located at 505 nm decreased rapidly in intensity with time and became very broad. The resulting broad band increased with time then developed into three bands located at 464, 505 and 586 nm accompanied by the appearance of a new sharp band at 395 nm which has a larger intensity compared with the other bands. Initially the bands located at 464, 505 and 586 nm have the same intensity relative to each other, then the band at 586 nm increases with time more than the other bands and red shifts to 620 nm. After about three hours the two bands at 505 and 464 nm increase in intensity more than the other bands. The band at 505 nm coincides with the band at 464 nm and its intensity increased with time. Finally only two bands at 620 and 464 nm exist in the range 400–800 nm. Figure 3 summarizes these results.

To explain these results we suggest the following steps.

Initially there is a large excess of TCNE in solution and a small amount of KBr complexed with CE, therefore the band located at 505 nm may be attributed to charge migration from the bromide anion to two molecules of TCNE

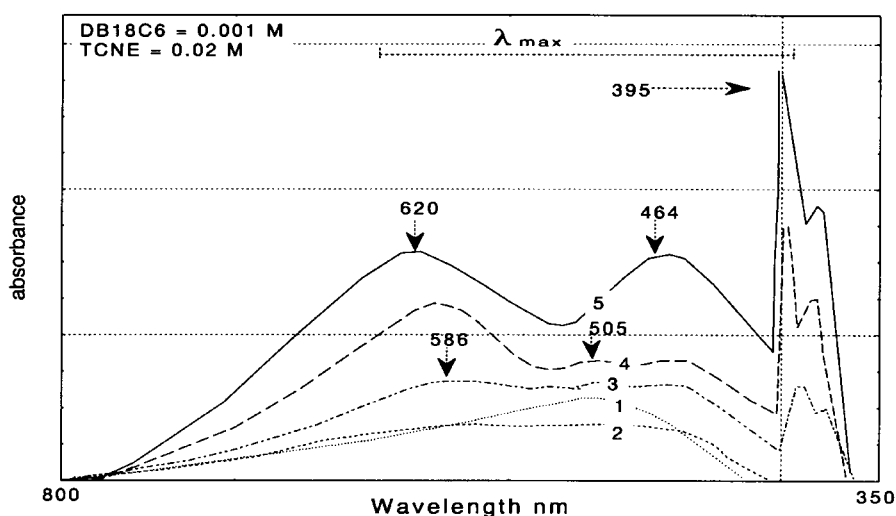


Figure 3. Time dependent spectra of (DB18C6+KBr) + TCNE in DCE.

to form $[\text{DB18C6K}^+ \cdots \text{Br}^-(\text{TCNE})_2]$, since the CT band attributed to charge migration from bromide anion to TCNE did not appear. The red shift of the 1 : 2 complex between the bromide anion and TCNE, as compared with the 1 : 1 complex studied before in this work, may be explained by the distribution of charge between two anti bonding orbitals of two molecules of the acceptor. Thus an electron can move and overlap through the π -electron clouds in these complexes [20]. The complex $[\text{DB18C6K}^+ \cdots \text{Br}^-(\text{TCNE})_2]$ may be converted to $[\text{TCNE} \cdots \text{DB18C6K}^+ \cdots \text{Br}^- \cdots \text{TCNE}]$. This suggestion explains why the band at 505 nm decreases and at the same time the band at 586 nm starts to emerge which may be attributed to CT from the $\text{PHOCH}_2\text{CH}_2$ group to TCNE. The complex $[\text{TCNE} \cdots \text{DB18C6K}^+ \cdots \text{Br}^- \cdots \text{TCNE}]$ may interact with more TCNE to form the $[\text{TCNE} \cdots \text{DB18C6K}^+ \cdots \text{Br}^- \cdots (\text{TCNE})_2]$ complex. This may explain the increase in intensity of the band at 505 nm. Finally the complex $[\text{TCNE} \cdots \text{DB18C6K}^+ \cdots \text{Br}^- \cdots (\text{TCNE})_2]$ may be converted to the $[(\text{TCNE})_2 \cdots \text{DB18C6K}^+ \cdots \text{Br}^- \cdots \text{TCNE}]$ complex. This can be explained by the disappearance of the 505 nm band, and the increase of the intensity of the bands at 464 nm and 586 nm which then shifts to 620 nm with time. This shift is due to the flattening of DB18C6 in the presence of potassium salt [17], which improves the overlap between CE and the acceptor, since the position of the CT band depends on the integral overlap [12]. The large increase in the intensity of the band at 620 nm in the presence of the salt as compared with its absence at the same concentration may support this suggestion.

To study the effect of KCl on the formation of the CT complex (DB18C6 – TCNE), an excess amount of KCl was added to the (DB18C6 – TCNE) solution. The bands at 395 and 415 nm increased in intensity and the band at 586 nm decreased in intensity slowly. After one day the intensity of this band increased slowly

Table I. Absorption maxima of the systems TCNE, salt, and CE complexes.

System	λ_{\max} nm
DB18C6 + TCNE	586
DB18C6 + TCNE + KF	395, 415
(DB18C6 + KCl) + TCNE	395, 415, 566 \rightarrow 620
(DB18C6 + TCNE) + KCl	395, 415, 586 \rightarrow 620
(DB18C6 + TCNE) + KBr	460
(DB18C6 + KBr) + TCNE	460
(DB18C6 + KBr) + TCNE (excess)	395, 464, 505, 586 \rightarrow 620
DB18C6 + TCNE + KI	365, 395, 415

with time and red shifted to 620 nm. The color of the solution changed gradually with time to green-yellow and a new band appeared at 300 nm which is assigned to the formation of the tricyanoethenolate anion [14] by the converted TCNE⁻, which was due to the formation of a CT complex from the halide anion to TCNE, in the presence of a trace amount of water or oxygen. When a TCNE solution was added to the (DB18C6 + KCl) solution a different result was obtained. A new band appeared at 566 nm in addition to the two bands at 415 and 395 nm attributed to the CT complex from CE to TCNE. This band was red shifted to 620 nm after one day and another band appeared at 300 nm indicating that the two systems are interchangeable. The blue shift observed for the CT band in the presence of the salt in the system [(CE + KCl) + TCNE], as compared with that in its absence, might suggest a decrease in the electron donor ability of CE, since the K⁺ is bound very tightly to the unshared pair of electrons on the oxygen atom [19] and fits into the cavity of CE leading to a decrease in the donor ability of CE. The observed red shift for the 566 nm band with time may be attributed to the flattening of DB18C6 in the presence of the potassium salt [20], which improves the overlap between CE and the acceptor, since the position of the CT band depends on the integral overlap [12]. The long time required for the two systems to be interchangeable as compared with KBr or KF can be explained by a weak nucleophilic property of the chloride anion.

Table I summarizes the absorption maximum of the systems TCNE, salt, and CE complexes.

The IR spectra of the solid complexes between DB18C6 with TCNE and (DB18C6 + TCNE + salt) were determined in KBr pellets and compared with those of the separate compounds. The comparison shows the following: for (DB18C6 + TCNE) ν_{CN} in the complex shows a small shift to a lower frequency. This shift is indicative of a higher charge density on the cyano group. For ternary complexes (DB18C6 + TCNE + Salt) ν_{CN} in the complex showed a larger shift to lower

frequency (2196 cm^{-1}). This may be explained by the formation of the TCNE anion radical. Since the addition of the electron from the salt is accompanied by a decrease in the bond order and in the force constant, caused by the antibonding character of the odd electron orbital [21, 22]. The $2985\text{--}2810\text{ cm}^{-1}$ peaks (assigned to the methylene stretching of the ethoxy groups coupled with the ring vibration in CE) shifted to a lower frequency ($2980\text{--}2800\text{ cm}^{-1}$) upon complex formation with TCNE. This is probably due to a very small contribution of the ethoxy group of DB18C6 in the interaction with TCNE. Pooni and Truter [23] reported that one of the criteria for complex formation between CE and the salt is the disappearance of the aliphatic $\nu_{\text{C-O-C}}$ band at 997 cm^{-1} , this is probably due to the fact that the complex causes the two aliphatic C—O—C bonds to be arranged symmetrically about the center of symmetry of the DB18C6 molecule so that the net change in dipole moment become close to zero, i.e. the absorption becomes IR inactive. Only in the system (DB18C6 + KI + TCNE) is the disappearance of this band an indication of the different geometry of this complex which is formed for this ternary system. The interaction of the anion with TCNE may effect the structure of the CE. The $^1\text{H-NMR}$ spectra for all the above complexes show a very slight shift in the position of the aromatic protons and methylene groups in CE.

3.2. DDQ AND DB18C6

DDQ has been found to be a typical electron acceptor and forms stable CT complexes with various benzo substituted crown ethers [4–6]. In the present study, the CT complex of DDQ with DB18C6 in DCE solution was studied. A new broad band at $\lambda_{\text{max}} = 635\text{ nm}$ was obtained in the visible region of the spectrum which appeared after mixing the above solutions.

The Benesi–Hildebrand plot indicated a 1 : 1 stoichiometry for the complex. The K_c value for this complex was $6.6\text{ dm}^3\text{ mol}^{-1}$.

To study the effect of potassium halides (i.e. KF, KCl, KBr and KI) on the formation of the CT complex, the absorption spectra were recorded after the addition of excess amount of the salt. A new multiple CT absorption was obtained corresponding to the formation of a CT complex from the halide anion to DDQ to form DDQ^- in the presence of CE.

The IR spectrum of the crystalline complex (DB18C6 + DDQ + salt) was recorded as a KBr pellet and compared with those of the separate compounds shows the following features: A shift of ν_{CN} from 2260 and 2238 to 2226 cm^{-1} is observed. This may be explained as being due to strong charge donation from the halide anion to the antibonding orbital, causing a weakening of the CN bond. The ν_{CO} peak at 1672 cm^{-1} in DDQ disappears upon complex formation. This may be explained as being due to strong charge donation to DDQ. The complex involving the strong donor and acceptor appear to be almost wholly dative, and the IR spectrum is simply the sum of the spectra of the corresponding ions. Joel et al. suggested [24] resonance structures for DDQ^- (Figure 4).

Table II. Absorption maxima of DDQ, Salt, and CE complexes.

Complex	λ_{\max} nm
DB18C6 + DDQ	635
DB18C6 + DDQ + KF	410, 463, 500, 540, 586
DB18C6 + DDQ + KCl	410, 463, 500, 540, 586
DB18C6 + DDQ + KBr	463, 500, 540, 586
DB18C6 + DDQ + KI	410, 463, 500, 540, 586

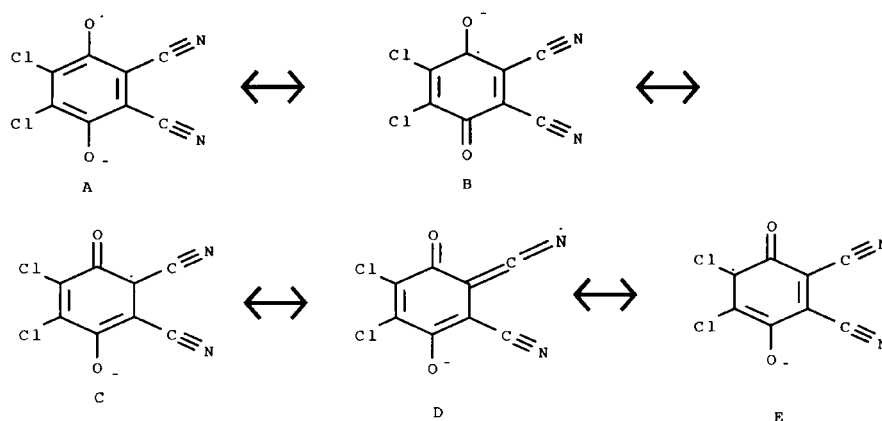


Figure 4. The resonance structures of DDQ^- .

They concluded that resonance structure (A) is the most stable resonance structure followed by D and C. Structures B and E do not make major contributions. These results explain why CN shifted to lower wave number and the CO peak disappeared from the IR spectrum.

For comparison, the halide salts were added to (18C6 – DDQ) and the same results were obtained. This indicates that the new band is due to the formation of a CT complex from the salt anion to DDQ. Since the (DDQ – 18C6) solution did not show any spectral changes upon the addition of DDQ solution to 18C6, it indicates that either no complex or a very weak complex was formed.

4. Conclusion

In the present work, the CT processes involve a charge transfer from the n -bonding molecular orbital or π system in the benzene ring in the CEs, or from the anion of the salt in the presence of CEs, to the π system in the acceptors.

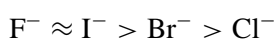
The charge transfer from non-bonding molecular orbitals of 18C6 to different π acceptors (TCNE and DDQ) shows no characteristic band in the UV-Visible

Table III. The IR absorption of the system (CE + DDQ + salt).

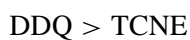
	$\nu_{\text{CN}} \text{ cm}^{-1}$	$\nu_{\text{CO}} \text{ cm}^{-1}$	$\nu_{\text{COC}} \text{ cm}^{-1}$
DB18C6	–	–	996
DDQ	2238	1672	–
	2260		
DB18C6-DDQ	2234	1690	996
	2245		
DB18C6-DDQ-KI	2226	–	–

spectrum indicating the absence of a CT complex between 18C6 and different acceptors. This may be due to the high electronegativity of the oxygen atom in the structure of CEs, which prevents charge transfer to the anti bonding orbital of the acceptors.

The addition of a salt (KF, KCl, KBr, KI) to the mixture of 18C6 and one of the acceptors (TCNE and DDQ), shows a characteristic band in the visible region. This is due to a migration of the charge from the anion to the acceptors. Both KF and KI show new CT bands in the visible region due to a strong interaction between the anion and the acceptor. From the position of the CT band we can suggest the following trend for the interaction of the anion salt with the acceptor in the presence of 18C6,



In contrast to 18C6, DB18C6 shows characteristic CT bands when it is mixed with the acceptor in DCE solution. This band is due to a CT from the π system of the donor molecule to the anti bonding orbital of the acceptor. IR and NMR give little information about the molecular interaction, indicating a weak interaction between DB18C6 and the acceptor. So the presence of the phenyl group is essential to form a CT complex. The extent of the interaction between DB18C6 and the acceptors may be derived from the position of the CT band in the visible region. Therefore the following trend in λ_{max} may be noted.



This sequence completely follows the order expected from the electron affinity of the acceptors.

When excess acceptor was added to the DB18C6 new bands appeared in the UV-Visible spectra. In this work it was suggested that this is due to the formation of a 1 : 2 complex between the bromide anion and TCNE. There is a need to run this experiment with 18C6 to support this suggestion and this is in progress.

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