

Spectroscopic Study of the Interaction Between TCNQ and Cryptand 222 in Chloroform Solution

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ABSTRACT: *The interaction between 4, 7, 13, 16, 21, 24 - hexaoxa-1,10 - diazabicyclo [8.8.8] hexacosane (C222) and 7,7,8,8- tetracyanoquinodimethane (TCNQ) has been studied in chloroform at 25°C. The results indicate a two step mechanism. At the first step, two adducts (assign as P1 and P2) are formed through equilibrium reactions. In continue and through nonequilibrium reactions the adducts are converted to a final product (assign as P3). Based on the comparison of the spectra of C222-TCNQ mixture with that of Na-18C6-TCNQ mixture, the $C222^+TCNQ^-$, $C222^+TCNQ^-TCNQ^0$ and $(C222^+)_2(TCNQ^-)_2$ are suggested as the P1, P2, and P3, respectively. IR spectra of C222 and TCNQ are compared with the spectrum of solid 1:1 TCNQ-C222 complex and the effect of complexation on absorption bands are discussed.*

KEY WORDS: *C222, TCNQ, Spectrophotometry, Molecular complex, Chloroform.*

INTRODUCTION

Hundreds of different molecular complexes containing TCNQ as the acceptor have been made and studied [1-7]. Some of the complexes which exhibit the highest conductivity observed for organic compounds [8,9]. Although the molecular complexes of TCNQ with different donors have been investigated quite extensively, few reports on the complexes of crown ethers and TCNQ have appeared [10-11], and it seems that most studies have been concentrated on physical properties of complex in solid state. The magnetic and optical properties

of Na-DB18C6-TCNQ and K-DB18C6-TCNQ are investigated in solid state [12]. The electrical resistivities and electronic reflection spectra of complexes of alkali metal-TCNQ with crown ether polymers and alkaline earth metal cation-TCNQ-crown ether were studied [13,14]. So, more study in this field is needed. We recently discussed the behavior of the molecular complexes of different crown ethers and cryptands [15-20]. In this paper we report the results of spectroscopic study of complexation of TCNQ with C222 in chloroform solution.

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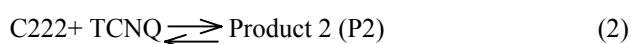
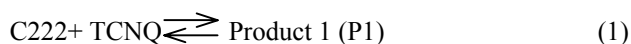
EXPERIMENTAL

4, 7, 13, 16, 21, 24 - Hexaoxa - 1, 10 - diazabicyclo [8.8.8] hexacosane (C222) from Merck company was recrystallized from reagent grade n-hexane and dried under vacuum over P_2O_5 . 7, 7, 8, 8 - Teracyanoquinodimethane (TCNQ) from Merck company was used without any further purification except for vacuum drying. 18-Crown-6 (18C6, Merck) was precipitated as its acetonitrile complex [22]. The crystals were filtered and the solvent was removed by placing the complex under vacuum for at least 24h. The complex of Na^+ -18C6-TCNQ $^-$ was obtained by melting appropriate amounts of Na-18C6-TCNQ followed by cooling and then dissolving in chloroform.

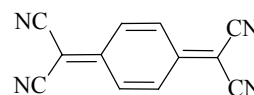
All UV-vis spectra were recorded on a Perkin Elmer Lambda 2 spectrophotometer. All of the IR spectra recorded on a Shimadzu IR- 470 spectrophotometer using KBr pellets. Solid complex of TCNQ-C222 was isolated from the solution containing 1:1 amount of TCNQ-C222 in chloroform followed by solvent vaporization.

RESULTS AND DISCUSSION

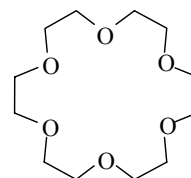
The electronic absorption spectrum of 5.07×10^{-5} MTCNQ in chloroform is shown in Fig. 1.1. This spectrum shows a λ_{max} at 400 nm and a shoulder at 370 nm. It was found in Fig. 1.2-1.12 that during addition of excess C222, about 5.46×10^{-5} M, the intensity of TCNQ bands has reduced gradually. New bands appeared at 332 and 437 nm, which is shown in Fig. 1 in the region of spectra from bottom to top at 300-350 and 425-450 nm regions, respectively. The reduction of TCNQ bands as well as the appearance of two new bands and the observation of two isosbestic points [23] can be attributed to the formation of two adducts through the equilibrium reaction of C222 and TCNQ. The corresponding equilibrium can be written as follows:



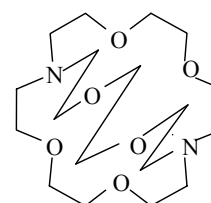
As seen in Fig. 2, it is interesting to note that after 48 hours, the TCNQ bands disappeared completely and the intensity of the bands due to the new products were increased. Also, two λ_{mad} at 415 nm and 430 nm were cleared and a new band was appears at 480 nm. The disappearance of TCNQ bands beside the increasing of



7,7,8,8-teracyanoquinodimethane



18-crown-6



4,7,13,16,21,24 - hexaoxa-1,10 - diazabicyclo [8.8.8] hexacosane

the intensity of the bands due to the products (P1 and P2) can be assigned to the complete conversion of TCNQ to P1 and P2. The appearance of new band at 480 nm can also be attributed to the further conversion of P1 and P2 to the new product P3.



The above reaction is further supported by the observation of the spectrum of TCNQ-C222 mixture after 120 hours (Fig. 3). As it can be seen, the P1 and P2 bands were disappeared and the intensity of P3 band was increasing.

The spectrum of a mixture of Na-18C6 and TCNQ is also shown in Fig. 3. As it can be seen four bands were appeared at 340 nm, 415 nm, 430 nm, and 480 nm. Comparison of the recent bands with that of P1, P2 and P3 band (Fig. 3) indicates that the position of the bands was similar. Such similarity can be attributed to the formation of the identical adduct in the interaction of Na-18C6 and TCNQ and C222-TCNQ.

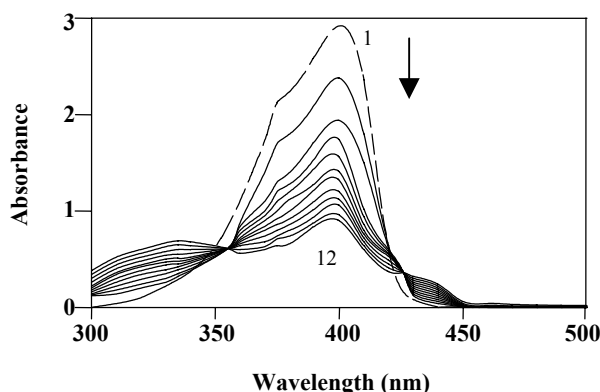


Fig. 1: Absorption spectra of 5.07×10^{-5} M of TCNQ (1) and 5.07×10^{-5} M of TCNQ in the presence of 5.46×10^{-5} M of C222 (2-12). The spectra No. 2 to 12 have been recorded after 5, 10, 15, ... and 55 minutes respectively.

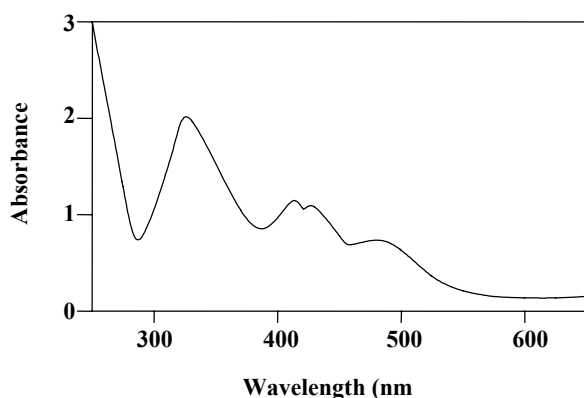


Fig. 2: Absorption Spectrum of 5.01×10^{-5} M of TCNQ in the presence of 5.46×10^{-5} M of C22 after 48 hours.

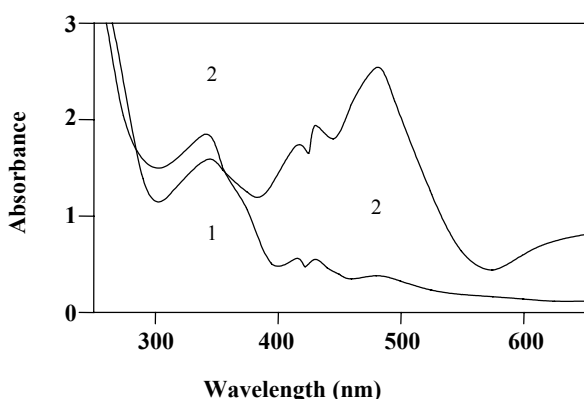
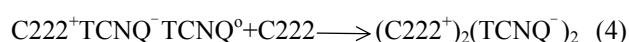
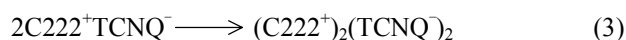
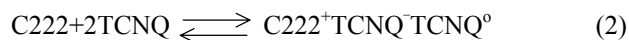


Fig. 3: Absorption spectrum of 5.01×10^{-5} M of TCNQ in the presence of 5.46×10^{-5} M of C222 after 120 hours (1) and absorption spectrum of a mixture of heated Na-18C6 and TCNQ (2).

It has been mentioned previously that TCNQ forms two series of stable salts and salt like derivatives so that each involving complete transfer of an electron to TCNQ with the formation of anion radical TCNQ^- [24]. The first series was represented by the simple salt formula $\text{M}^{n+}(\text{TCNQ}^-)_n$ in which M may be a metallic or organic cation [1]. Members of the second of the salt-like series, the complex salts represented by the formula $\text{M}^{n+}(\text{TCNQ}^-)_n(\text{TCNQ}^0)$, contain a molecule of formally neutral TCNQ beside TCNQ^- radical anion [24]. In addition, it has been shown that 18C6 complexes of potassium form brick work stacks of TCNQ dimmers at each end which were co-ordinate (18-crown-6) encapsulated metal ions [25]. So it can be concluded that the observed bands in the mixture of Na-18C6-TCNQ are due to $\text{Na}^+18\text{C6TCNQ}^-$, $\text{Na}^+18\text{C6TCNQ}^-\text{TCNQ}^0$, and $(\text{Na}^+18\text{C6})_2(\text{TCNQ}^-)_2$. In a similar fashion the observed bands in C222-TCNQ mixtures can be assigned to the $\text{C222}^+\text{TCNQ}^-$, $\text{C222}^+\text{TCNQ}^-\text{TCNQ}^0$ and $(\text{C222}^+)_2(\text{TCNQ}^-)_2$. It seems that the dimerization is a time consuming process. So it is suggested that $(\text{C222}^+)_2(\text{TCNQ}^-)_2$ is the final product (P3) of the interaction of TCNQ and C222. The $\text{C222}^+\text{TCNQ}^-$ and $\text{C222}^+\text{TCNQ}^-\text{TCNQ}^0$ are also assigned to P1 and P2, respectively. According to above discussions, the Eqns. 1- 4 can be rewritten as follows:



It is interesting to note that the λ_{max} of final product (P3) is more than the initial ones (P1 and P2). This can be attribute to the increase in the length of radical anion. In fact, upon dimerization of TCNQ and production of $(\text{TCNQ}^-)_2$, a new ion with increased length of conjugation is formed. Such structural variation affects the absorption maximum and shifts it to red region [26].

To investigate the effect of other mole ratios on the results, the spectral variation of mixtures of 5.07×10^{-5} M of TCNQ in the presence of 5.46×10^{-4} M of C222 (the TCNQ/C222 mole ratio=0.09) and 5.46×10^{-5} M of TCNQ in the presences of 6.23×10^{-6} M of C222 (the TCNQ/C222 mole ratio=8.80) were also followed. In each case, the variation similar to 1:1 C222:TCNQ mixtures (Figs.1-3)

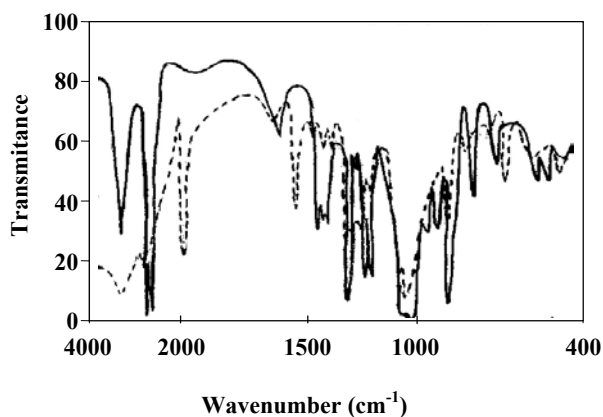


Fig. 4: IR Spectra of TCNQ (-) and 1:1 TCNQ-C222 complex (...).

were observed. However, the rate of variation was different. This means that adduct are independent of TCNQ/C222 mole ratios.

IR Spectrum of the 1:1 TCNQ-C222 complex is compared with that of TCNQ in Fig. 4. As it can be seen the CN stretching frequency at 2220 cm^{-1} has been shifted to 2117 cm^{-1} . This shift to lower frequency indicates a higher charge density of CN [27]. The C=C stretching band at 1540 cm^{-1} has also been shifted to 1560 cm^{-1} . This can be assigned to the shortening of conjugation system through complexation [28].

Comparison of the IR spectrum of TCNQ-C222 complex with that of C222 in Fig. 5 shows reduction of the intensity of the bands and the shift of C-N stretching band at 1100 to 1150 cm^{-1} . The first effect can be attributed to the increasing of the symmetry of molecule during complexation [29], and the second effect indicates the direct involvement of nitrogen's, in fact, the electron donating ability of oxygen lowers the charge density on it. This results in lowering the force constant and shift to lower frequencies [30].

Finally, the suggested mechanism and identification of proposed products can be further confirmed by techniques such as ESR (Electron Spin Resonance), FAB (Fast Atom Bombardment) and ENDOR (Electron-Nuclear-Double-Resonance) [31-34]. ENDOR spectroscopy can best be described as a nuclear magnetic resonance experiment of free radicals.

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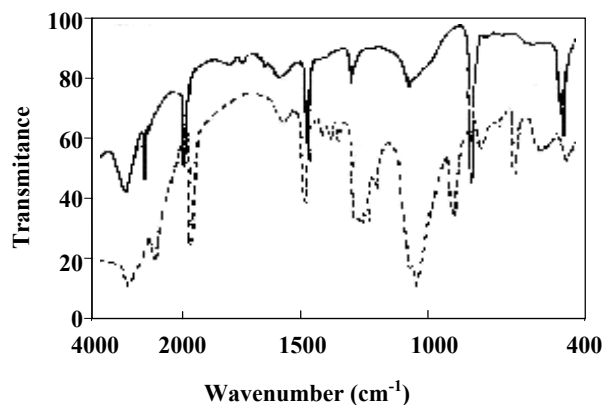


Fig. 5: IR Spectra of C222 (-) and 1:1 TCNQ-C222 complex (...).

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