Bulgarian Chemical Communications, Volume 48, Number3 (pp. 403– 413) 2016

Spectroscopic studies of charge-transfer complexes of 2,3-dichloro-5,6-dicyano-p-benzo-quinone with p-nitroaniline

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Received August 2, 2015, Accepted October 5, 2015

The charge-transfer complexes of the donor p-nitroaniline (PNA) with the acceptor 2, 3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) were studied spectrophotometrically in various solvents such as CH_2Cl_2, $CHCl_3$, and CCl_4 at different temperatures. Two charge-transfer bands were observed in each case. The results indicate that the formation of the CT-complex in a less polar solvent is comparatively high. The stoichiometry of the CT-complex was found to be 1:1. The physical parameters of the CT-complex were evaluated by the Benesi–Hildebrand equation. The data are discussed in terms of the formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy (ΔG^o), oscillator strength (f), transition dipole moment (μ_{EN}), resonance energy (R_N) and ionization potential (I_D). The results indicate that the formation constant (K_{CT}) for the complex is dependent upon the nature of electron acceptor, donor and polarity of solvents used. The formation of the complex was confirmed by UV-visible, FT-IR, and ^{1}H–NMR techniques. The possible structure of the CT-complex between DDQ and PNA was proposed.

Keywords: Charge-transfer complex; 2, 3-dichloro-5, 6-dicyano-p-benzo-quinone (DDQ); p-nitro aniline (PNA); UV-Visible, FT-IR, ^{1}H–NMR.

INTRODUCTION

Various aromatic molecules can behave as electron donors and form molecular complexes with electron acceptor molecules such as halogens, nitro compounds and quinines [1-2]. Extensive works have been carried out to elucidate the nature of intermolecular interactions in these molecular complexes. Mulliken has developed the theory of the intermolecular CT interactions, which has been successfully applied to the interpretation of the absorption bands characteristic of molecular complexes in various systems [3]. DDQ is a strong electron acceptor having electron affinity of 1.9 e.v. [4].

In the present paper, spectrophotometric studies were carried out for CT complexes of DDQ with p-nitroaniline, special attention being paid to the appearance of two CT bands. Orgel first reported two bands in the case of methylbenzene complexes of chloranil and 1, 2, 5-trinitrobenzene [5]. Orgel related the two ionization potentials of the donor molecules to the frequencies of the CT bands.

This paper presents studies of the charge-transfer interaction between DDQ and p-nitroaniline in both liquid and solid states. The aim of the work is to determine the reaction stoichiometry, the nature of bonding between DDQ and PNA, and also some physical parameters. In addition, the nature and structure of the reaction product (CT–complex) in both solution and solid states can be estimated using spectroscopic techniques like FT-IR, ^{1}H NMR and UV-Vis electronic absorption to obtain the stoichiometry, molecular structure and nature of interaction for the CT-complexes [6-9].

EXPERIMENTAL

Materials

Analytical grade (AR) chemicals were used throughout. 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) and p-nitro aniline (PNA) were obtained from Sigma Aldrich, (CDH). Dichloromethane (Merck), chloroform (Merck) and carbon tetrachloride (Merck) were used without further purification.

Preparation of standard solutions

Solutions of the donor of different concentrations, 0.01M, 0.02M, 0.03M, 0.04M, and 0.05M, were prepared in different volumetric flasks by dissolving accurately weighed amounts of p-nitro aniline in different solvents such as carbon tetrachloride, chloroform and dichloromethane.

A standard solution of the acceptor, DDQ (0.01M) was prepared by dissolving accurately weighed amounts of the acceptor in the above solvents in different volumetric flasks.

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Synthesis of solid CT- complex

Analar R grade samples of DDQ and p-nitroaniline were employed for the synthesis of the title compound. Equimolar solutions of the two reactants were separately prepared in methanol and mixed together. The resulting solution was stirred well for about thirty min.

The precipitated adduct was filtered off at the pump and repeatedly recrystallised from methanol to enhance the degree of purity of the synthesized compound.

Analyses

The electronic absorption spectra of the donor P-nitroaniline, acceptor DDQ and the resulting complex in dichloromethane, chloroform and carbon tetrachloride were recorded at different temperatures, i.e. 20^0C, 25^0C and 30^0C in the visible range 200 nm–600 nm using a UV- visible spectrophotometer Perkin-Elmer- λ-850 with a 1 cm quartz cell path length. The FT-IR spectra of the reactants and the resulting CT-complex were recorded with the help of the FT-IR spectrometer INTERSPEC– 2020 (spectra lab U.K.) in KBr pellets. The ^{1}H NMR spectrum of the CT-complex was measured in acetone using Bruker Advance II 400 NMR spectrometer.

RESULTS AND DISCUSSION

Observation of CT- bands

3-ml volumes of the donor and the acceptor were scanned separately by spectrophotometric titration [10] at their wavelengths of maximum absorption: 280 nm for DDQ, 400 nm for PNA, 320 nm for the blank solvent (dichloromethane) and 440 nm and 560 nm for the CT-complex of 0.01M PNA and 0.01M DDQ in dichloromethane, as shown in Fig 1. The reaction mixture of the donor (10 ml) and the acceptor (10 ml) in the different solvents, viz., carbon tetrachloride, chloroform and dichloromethane, formed a yellow colored charge transfer complex. The complex for each of the reaction mixtures was let to standing overnight at different temperatures i.e. 20^0C, 25^0C and 30^0C to form a stable complex before analysis at the maximum absorbance 440 nm and 560 nm for dichloromethane, 430 nm and 550 nm for chloroform and 420 nm and 540 nm for carbon tetrachloride.

The concentration of the donor in the reaction mixture was kept higher than that of the acceptor, $[D_0] >> [A_o]$ [11, 12] and changed over a wide range of concentrations from 0.01M to 0.5M while the concentration of the π-acceptor (DDQ) was kept fixed [11] at 0.01M in each solvent; these produced solutions with donor: acceptor molar ratios varying from 1:1 to 50:1, these concentration ratios were used to obtain a straight line diagram for determination of the formation constants of the CT-complex.

The spectra of the solutions of 0.01M PNA, and 0.01M DDQ in different solvents were recorded with solvents used as a reference, the longest wavelength peak was considered as the CT–peak [13]. The changes of the absorption intensity to higher values for all complexes in this study when adding the donor were detected and investigated, as shown in Table 5. These measurements were based on the CT-absorption bands exhibited in the spectra of the above mentioned systems given in Figs. 2- 4. In all systems studied the absorption spectra are of similar nature except for the position of the absorption maxima (λ_{CT}) of the complexes. The CT–complex absorption spectra were analyzed by fitting to the Gaussian function

$$y = y_0 + [A/ w\sqrt{(\pi/2))}]\ \exp [-^2 (x- x_c)^2/w^2]$$

where x and y denote wavelength and absorbance, respectively. The results of the Gaussian analysis for all systems under study are shown in Table 1. The wavelengths of these new absorption maxima ($\lambda_{CT} = x_c$) and the corresponding transition energies (hν) are summarized in Tables 2-4.

Determination of the ionization potentials of the donor

The ionization potentials of the donor (I_D) in the charge transfer complexes were calculated using the empirical equation derived by Aloisi and Piganatro [14]

$$I_D \text{ (eV)} = 5.76 + 1.53 \times 10^{-4}\ \nu_{CT} \quad (1)$$

where ν_{CT} is the wave number in cm^{-1} of the complex determined in different solvents, viz., carbon tetrachloride, chloroform and dichloromethane. The data are summarized in Tables 2-4.

Determination of oscillator strength, (f), and transition dipole moment, (µEN)

From the CT-absorption spectra, one can determine the oscillator strength. The oscillator strength *f* is estimated using the formula

$$f = 4.32 \times 10^{-9} \int \varepsilon_{CT} d\nu \quad (2)$$

where $\int \varepsilon_{CT} d\nu$ is the area under the curve of the extinction coefficient of the absorption band in question vs. frequency. To a first approximation

$$f = 4.32 \times 10^{-9}\ \varepsilon_{CT}\ \Delta\nu_{1/2} \quad (3)$$

where ε_{CT} is the maximum extinction coefficient of the band and $\Delta\nu_{1/2}$ is the half-width, i.e., the width of the band at half the maximum extinction. The observed oscillator strengths of the CT-bands are summarized in Tables 2-4.

The extinction coefficient is related to the transition dipole by

$$\mu_{EN} = 0.0952\ [\varepsilon_{CT}\ \ \Delta\nu_{1/2}/\Delta\nu]^{1/2} \quad (4)$$

where $\Delta\upsilon \approx \upsilon$ at εCT and μ_{EN} is defined as $-e \int \psi ex \sum i r i \psi g\ d\tau$. μEN for the complexes of PNA with DDQ is given in Tables 2-4.

Determination of resonance energy (R_N)

Briegleb and Czekalla [15] theoretically derived the relation

$$\varepsilon_{CT} = 7.7 \times 10^{-4}\ /\ [h\nu_{CT}/\ [R_N] - 3.5\ ], (5)$$

where ε_{CT} is the molar extinction coefficient of the complex at the maximum of the CT absorption, ν_{CT} is the frequency of the CT-peak and R_N is the resonance energy of the complex in the ground state, which is obviously a contributing factor to the stability constant of the complex (a ground state property). The values of R_N for the complexes under study are given in Tables 2-4.

Table 1. Gaussian curve analysis for the CTC in the spectra of DDQ with PNA in different polar solvents.

Complex	Solvent	Temperature	A	W	Xc	Y_0
DDQ + PNA	CH_2Cl_2	20^0C	34.75 ± 6.66	95.74±15.05	419.37	0.8232±0.0235
DDQ + PNA	$CHCl_3$	20^0C	28.28 ± 4.52	67.84±9.66	421.56	0.9350±0.0197
DDQ + PNA	CCl_4	20^0C	32.42 ± 4.69	49.17±6.18	423.69	1.042±0.0290

Table 2. CT-complex absorption maxima *(λ_{CT})*, transition energies *($h\nu_{CT}$)*, of the DDQ+PNA complexes, experimentally determined values of ionization potentials *(I_D)*, oscillator strength (*f*), dipole moments *(μ_{EN})*, and resonance energies (*R_N*) of the complexes in dichloromethane.

Complex	Solvent	Temp.	λ_{CT} (nm)	f ×10^{-5}	μ_{EN} (Debye)	R_N (ev)	$h\nu_{CT}$ (ev)	I_D(ev)	ΔG
DDQ + PNA	CH_2Cl_2	20^0C	419.37nm	3.63×10^{-5}	0.892	0.00671	2.96	9.40	13.408
DDQ + PNA	CH_2Cl_2	20^0C	549.17nm	3.48×10^{-5}	0.757	0.00370	2.26	8.54	14.721
DDQ + PNA	CH_2Cl_2	25^0C	423.39nm	2.36×10^{-5}	0.912	0.00694	2.93	9.37	13.465
DDQ + PNA	CH_2Cl_2	25^0C	558.46nm	1.73×10^{-5}	0.775	0.00381	2.22	8.49	14.778
DDQ + PNA	CH_2Cl_2	30^0C	428.15nm	2.64×10^{-5}	0.934	0.00720	2.90	9.32	13.636
DDQ + PNA	CH_2Cl_2	30^0C	530.30nm	6.58×10^{-5}	0.798	0.00425	2.34	8.63	14.492

Table 3. CT-complex absorption maxima *(λ_{CT})*, transition energies *($h\nu_{CT}$)*, of the DDQ+PNA complexes, experimentally determined values of ionization potentials *(I_D)*, oscillator strength (*f*), dipole moments *(μ_{EN})*, and resonance energies (*R_N*) of the complexes in chloroform.

Complex	Solvent	Temp.	λ_{CT} (nm)	f $\times10^{-5}$	μ_{EN} (Debye)	R_N (ev)	hν_{CT} (ev)	I_D(ev)	ΔG
DDQ + PNA	$CHCl_3$	20^0C	421.56nm	2.65×10^{-5}	0.905	0.00690	2.95	9.38	13.808
DDQ + PNA	$CHCl_3$	20^0C	563.95nm	2.42×10^{-5}	0.801	0.00403	2.20	8.47	14.549
DDQ + PNA	$CHCl_3$	25^0C	425.36nm	$1.93.\times10^{-5}$	0.914	0.00695	2.92	9.35	14.549
DDQ + PNA	$CHCl_3$	25^0C	575.23nm	6.75×10^{-5}	0.736	0.00334	2.16	8.40	15.120
DDQ + PNA	$CHCl_3$	30^0C	425.23nm	2.13×10^{-5}	0.930	0.00718	2.92	9.35	14.778
DDQ + PNA	$CHCl_3$	30^0C	579.73nm	7.57×10^{-5}	0.752	0.00345	2.14	8.39	15.006

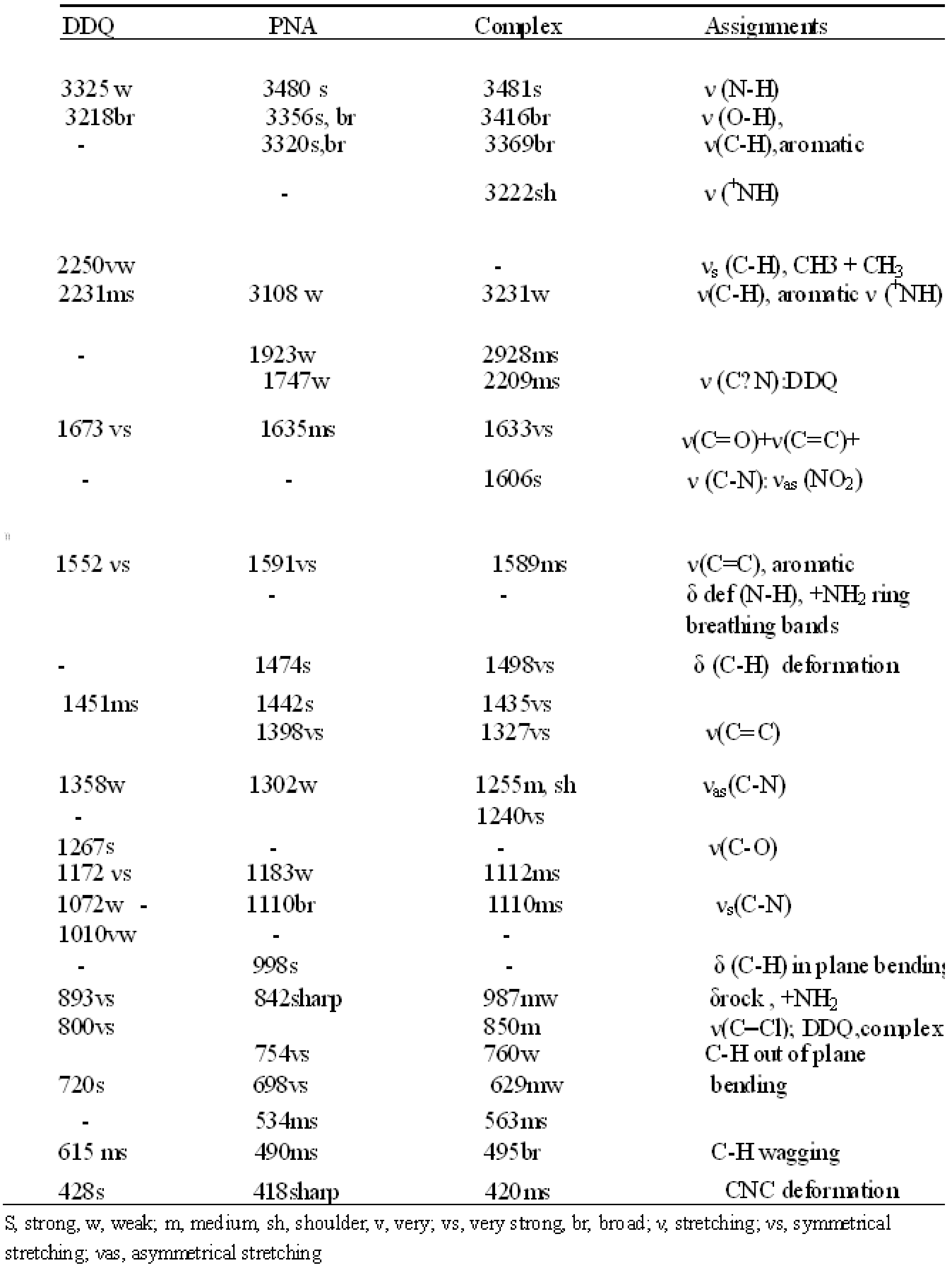
Table 4. CT-complex absorption maxima *(λ_{CT})*, transition energies *($h\nu_{CT}$)*, of the DDQ+PNA complexes, experimentally determined values of ionization potentials *(I_D)*, oscillator strength (*f*), dipole moments *(μ_{EN})*, and resonance energies (*R_N*) of the complexes in carbon tetrachloride

Complex	Solvent	Temp.	λ_{CT} (nm)	f $\times10^{-5}$	μ_{EN} (Debye)	R_N (ev)	hν_{CT} (ev)	I_D(ev)	ΔG
DDQ + PNA	CCl_4	20^0C	423.69nm	2.07×10^{-5}	0.939	0.00735	2.93	9.37	15.120
DDQ + PNA	CCl_4	20^0C	572.066nm	6.26×10^{-5}	0.775	0.00372	2.17	8.43	14.835
DDQ + PNA	CCl_4	25^0C	421.65nm	$1.87.\times10^{-5}$	0.949	0.00753	2.94	9.38	15.291
DDQ + PNA	CCl_4	25^0C	512.78nm	1.54×10^{-5}	0.798	0.00440	2.42	8.74	14.435
DDQ + PNA	CCl_4	30^0C	418.89nm	2.27×10^{-5}	0.972	0.00795	2.96	9.40	15.291
DDQ + PNA	CCl_4	30^0C	513.89nm	$1.22.\times10^{-5}$	0.829	0.00474	2.42	8.72	14.093

Table 5. Absorption maxima λ_{CT} , association constants (K), molar absorptivities (ε), of the CT-complex of DDQ and PNA in dichloromethane, chloroform and carbon tetrachloride at 20^0C, 25^0C and 30^0C.

Systems	Solvent	λ_{CT} (nm)		K_{20} (l mol^{-1})		K_{25} (l mol^{-1})		K_{30} (l mol^{-1})		ε_{20} (l mol^{1}cm^{-1})		ε_{25} (lmol^{1}cm^{-1})		ε_{30} (lmol^{1}cm^{-1})	
DDQ + PNA	CH_2Cl_2	440	560	228	383	234	393	247	351	176	127	184	133	193	141
DDQ + PNA	$CHCl_3$	430	550	269	362	356	455	393	434	181	142	185	120	191	125
DDQ + PNA	CCl_4	420	540	453	399	482	340	488	301	195	133	199	141	209	152

Table 6. Characteristic infrared frequencies*(cm^{-1}) and tentative assignments for DDQ, PNA and their complex.



DDQ	PNA	Complex	Assignments
3325 w	3480 s	3481s	ν (N-H)
3218br	3356s, br	3416br	ν (O-H),
-	3320s,br	3369br	ν(C-H),aromatic
	-	3222sh	ν ($^+$NH)
2250vw		-	ν_s (C-H), CH3 + CH_3
2231ms	3108 w	3231w	ν(C-H), aromatic ν ($^+$NH)
-	1923w	2928ms	
	1747w	2209ms	ν (C?N):DDQ
1673 vs	1635ms	1633vs	ν(C=O)+ν(C=C)+
-	-	1606s	ν (C-N): ν_{as} (NO_2)
1552 vs	1591vs	1589ms	ν(C=C), aromatic
	-	-	δ def (N-H), +NH_2 ring breathing bands
-	1474s	1498vs	δ (C-H) deformation
1451ms	1442s	1435vs	
	1398vs	1327vs	ν(C=C)
1358w	1302w	1255m, sh	ν_{as}(C-N)
-		1240vs	
1267s	-	-	ν(C-O)
1172 vs	1183w	1112ms	
1072w -	1110br	1110ms	ν_s(C-N)
1010vw	-	-	
-	998s	-	δ (C-H) in plane bendin
893vs	842sharp	987mw	δrock , +NH_2
800vs		850m	ν(C–Cl); DDQ,complex
	754vs	760w	C-H out of plane
720s	698vs	629mw	bending
-	534ms	563ms	
615 ms	490ms	495br	C-H wagging
428s	418sharp	420ms	CNC deformation

S, strong, w, weak; m, medium, sh, shoulder, v, very; vs, very strong, br, broad; v, stretching; vs, symmetrical stretching; vas, asymmetrical stretching

Determination of standard free energy changes (ΔG^o) and energy (E_{CT}) of the π-π interaction between donor and acceptor*

The standard free energy changes of complexation (ΔG^o) were calculated from the association constants by the following equation derived by Martin, Swarbrick and Cammarata [16].

$$\Delta G^o = -\,2.303\ RT \log K_{CT} \quad (6)$$

where ΔG^o is the free energy change of the CT–complexes (KJ mol^{-1}), R is the gas constant (8.314 $Jmol^{-1}K$), T is the temperature and K_{CT} is the association constant of the complex (l mol^{-1}) in different solvents at different temperatures 20^{0}C, 25^{0}C and 30^{0}C, shown in Tables 2-4.

The energy (E_{CT}) of the π–π* interaction between donor (PNA), and acceptor (DDQ), is calculated using the following equation derived by G. Briegleb and Z. Angew [17]:

$$E_{CT} = 1243.667/\ \lambda CT \quad (7)$$

where λ_{CT} is the wavelength of the CT band.

The calculated values of E_{CT} are given in Tables 2-4.

Spectrophotometric study of the formation constants of the charge transfer complexes in different polar solvents

The stoichiometries and the formation constants of the charge transfer complex of p-nitroaniline with DDQ were determined in different polar solvents, viz., carbon tetrachloride, chloroform and dichloromethane at different temperatures 20^{0}C, 25^{0}C and 30^{0}C using the Benesi–Hildebrand equation [18, 19]. The spectrophotometric data were employed to calculate the values of the formation constants, K_{CT} of the complexes. The changes in the absorbance upon addition of PNA to a solution of DDQ of fixed concentration follow the Benesi-Hildebrand equation [18, 19] in the form:

$$[A]_o / A = (1 / K_{CT}\varepsilon_{CT}) \times 1 / [D]_0 + 1/\varepsilon_{CT} \quad (8)$$

where $[D]_o$ and $[A]_o$ are the concentrations of the PNA donor, and DDQ acceptor, respectively, A is the absorbance of the donor-acceptor mixture at λ_{CT}, against the solvents as reference, K_{CT} is the formation constant and ε_{CT} is the molar extinction coefficient, different from that of the complex in eq.(8) [18,19], which is valid under the condition $[D]_o >> [A]_o$ [11, 12] for 1:1 donor-acceptor complexes. The concentration of the donor PNA was changed over a wide range from 0.01M to 0.5M while he concentration of the π acceptor DDQ was kept fixed at 0.01M in each reaction mixture. These produced solutions with donor: acceptor molar ratio varying from 1:1 to 50:1. The experimental data are given in Table 3.

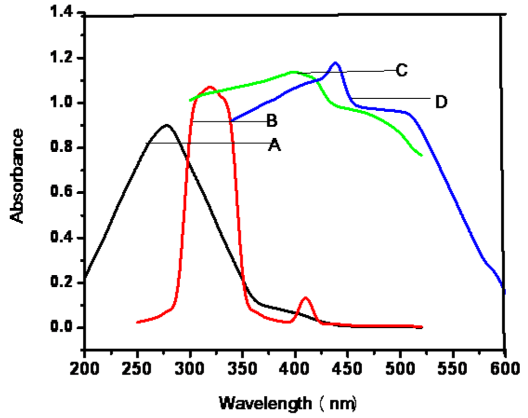


Fig. 1. Absorption spectra of (A) 0.01M DDQ (B) Blank solvent (dichloromethane) (C) 0.01 M p-nitro aniline (D) CT-complex of 0.01 M PNA and 0.01 M DDQ in dichloromethane.

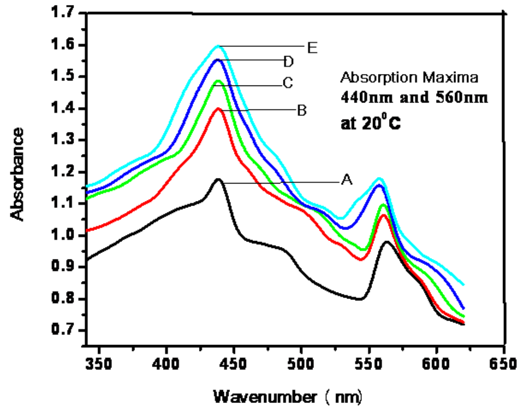


Fig. 2. Absorption spectra of DDQ (1 × 10^{-2}M) in dichloromethane at 20^{0}C with addition of p-nitroaniline concentrations ranging from 0.01M to 0.05M with increasing concentrations from bottom to top.

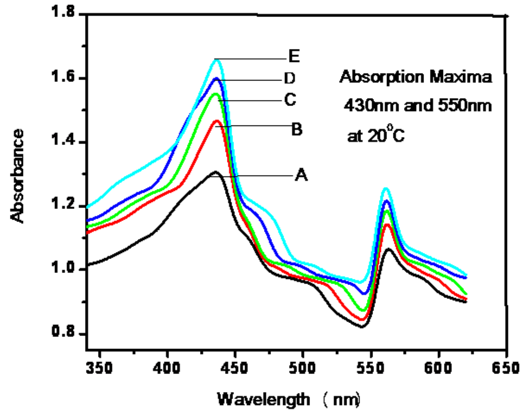


Fig. 3. Absorption spectra of DDQ (1 × 10^{-2}M) in chloroform at 20^{0}C with addition of p-nitroaniline concentrations ranging from 0.01M to 0.05M with increasing concentrations from bottom to top.

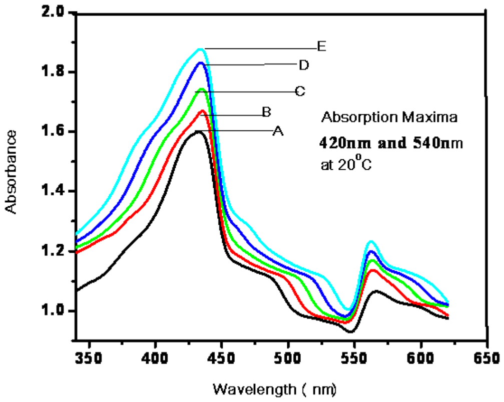


Fig. 4. Absorption spectra of DDQ (1 × 10^{-2}M) in carbon tetrachloride at 20^{0}C with addition of p-nitroaniline concentrations ranging from 0.01M to 0.05M with increasing concentrations from bottom to top.

The Benesi – Hildebrand [18, 19] method is an approximation that has been used many times and gives decent results. The intensity in the visible region of the absorption bands, measured against the solvent as reference, increases with the increase in the polarity and addition of PNA. The typical absorbance data for the charge transfer complexes of PNA with DDQ in different polar solvents at different temperatures 20^{0}C, 25^{0}C and 30^{0}C are reported in Table 5. In all systems very good linear plots according to eq. (8) [18, 19] were obtained, as shown in Figs 5-7.

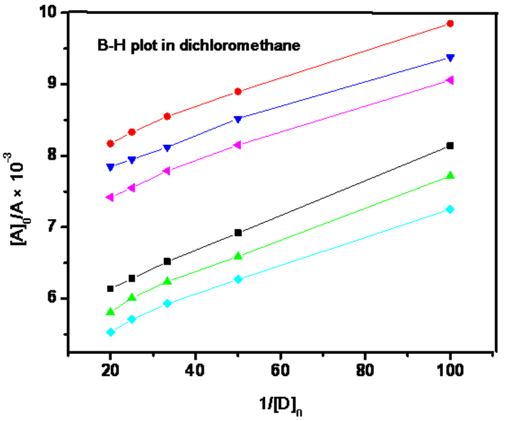


Fig. 5. Relation between [A] $_0$/A and 1/ [D] $_0$ of DDQ+PNA in CH_2Cl_2.

Formation constants for the complexes in different polar solvents at different temperatures 20^{0}C, 25^{0}C and 30^{0}C determined from the BH plots are summarized in Table 5. The correlation coefficients of all plots were above 0.99. Plots of $[A]_0/A$ against $1/[D]_o$ were found to be linear in all systems in Figs. 5-7 showing 1:1 charge transfer complexes, i.e. the straight lines are obtained with the slopes $1/K_{CT}\varepsilon_{CT}$. These results are an evidence of 1:1 CT-complexes. From the slope $1/K_{CT}\varepsilon_{CT}$ and the intercept, $1/\varepsilon_{CT}$, K_{CT} and ε_{CT} of the CT–complex were calculated in different polar solvents.

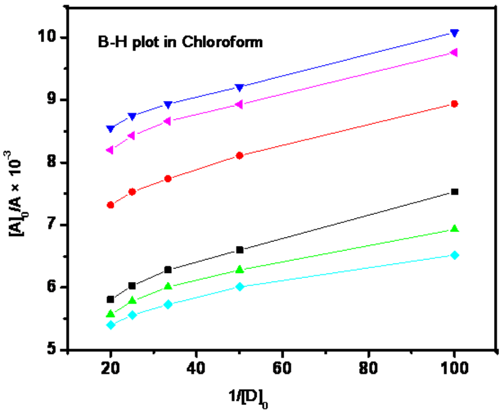


Fig. 6. Relation between $[A]_0/A$ and $1/[D]_0$ of DDQ+PNA in $CHCl_3$.

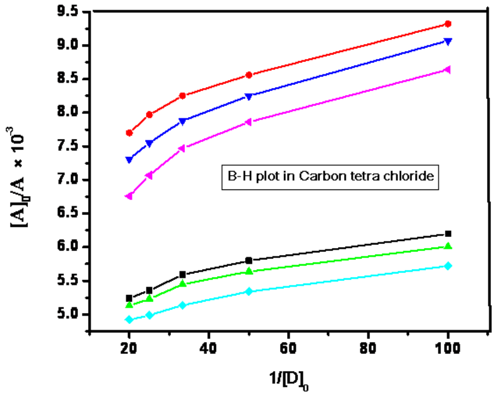


Fig. 7. Relation between [A] $_0$/A and 1/[D] $_0$ of DDQ+PNA in CCl_4..

Appearance of two CT-bands

The two absorption peaks of the CT-complex in each system and their λmax are given in Table 5.

Well defined absorption peaks of the two CT bands were observed for the DDQ complexes with PNA. Multi-CT absorption bands have been found in the CT complexes containing strong electron acceptors such as chlorine, bromanil and TCNE [20].

The origin of the multi-CT bands observed in the case of DDQ/PNA complex can be explained by the existence of two closely located occupied orbitals of the donors [21].

Effect of temperature on the formation constant

Temperature affects the values of K_{CT}, generally K_{CT} for DDQ complexes increases with the increase in temperature. But in some cases, such as the complexes of DDQ with PNA at 25^{0}C, and λmax 540 nm in CCl_4, at 30^{0}C, and λmax 560 nm in CH_2Cl_2, at 30^{0}C, and λmax 550 nm in $CHCl_3$, and at 30^{0}C, and λmax 540 nm in CCl_4, its value decreases with the increase in temperature, as shown in Table 5. There may be a decrease in the stability of the complex with the increase in temperature in these systems. This trend is similar to that reported in many systems, such as TCNB-benzene complexes and DDQ and acetanilide, biphenyl and naphthalene systems [21].

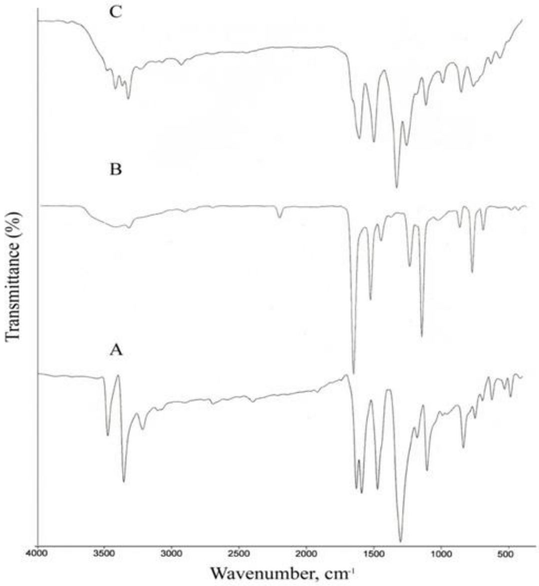


Fig. 8. FT-IR spectrum of (A) complex of DDQ and PNA, (B) acceptor DDQ and (C) donor (PNA).

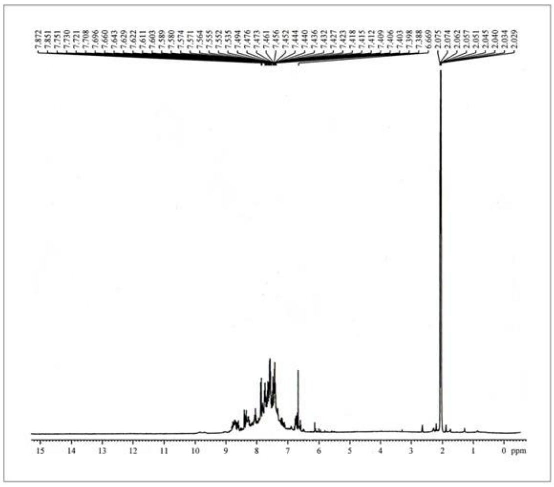


Fig. 9. ^{1}HNMR spectrum of the CT-complex

Effect of solvents on the formation of CT-complexes

The spectroscopic properties were markedly affected by varying solvent polarity. In the present investigation, the K_{CT} values increased significantly from dichloromethane to carbon tetrachloride with decreasing solvent polarity. The values of the association constant K_{CT} and the values of molar extinction coefficient are shown in Table 5. Moreover, the experimental results of the CT interaction between DDQ with PNA in different polar solvents reveal that the values of the association constant K_{CT}, in dichloromethane at λ_{CT} 440 nm and 560 nm are 228 (1 mol^{-1}), 383 (1 mol^{-1}) at 20^{0}C, 234 (1 mol^{-1}), 393 (1 mol^{-1}) at 25^{0}C and 247 (1 mol^{-1}) and 351 (1 mol^{-1}) at 30^{0}C. In chloroform the values of the association constant K_{CT}, at λ_{CT} 430 nm and 550 nm are 269 (1 mol^{-1}), 362 (1 mol^{-1}) at 20^{0}C, 356 (1 mol^{-1}), 455(1 mol^{-1}) at 25^{0}C and 393 (1 mol^{-1}), 434(1 mol^{-1}) at 30^{0}C. In carbon tetrachloride the values of the association constant $K_{CT,}$ at λ_{CT} 420 nm and 540 nm are 453 (1 mol^{-1}), 399 (1 mol^{-1}), at 20^{0}C 482 (1 mol^{-1}), 340 (1 mol^{-1}), at 25^{0}C, 488 (1 mol^{-1}), 301 (1 mol^{-1}), at 30^{0}C. The values of the molar extinction coefficients $\varepsilon_{20,}$ $\varepsilon_{25,}$ and ε_{30} in dichloromethane are 176 (1 mol^{-1}cm^{-1}), 127 (1 mol^{-1}cm^{-1}) and 184 (1 mol^{-1}cm^{-1}), 133 (1 mol^{-1}cm^{-1}) and 193 (1 mol^{-1}cm^{-1}), 141 (1 mol^{-1}cm^{-1}), respectively. The values of the molar extinction coefficients $\varepsilon_{20,}$ $\varepsilon_{25,}$ and ε_{30} in chloroform are 181 (1mol^{-1}cm^{-1}), 142 (1mol^{-1}cm^{-1}), 185 (1mol^{-1}cm^{-1}), 120(1mol^{-1}cm^{-1}), and 191(1mol^{-1}cm^{-1}), 125 (1mol^{-1}cm^{-1}), respectively, as shown in Table 5. The values of the molar extinction coefficients $\varepsilon_{20,}$ $\varepsilon_{25,}$ and ε_{30} in carbon tetrachloride are 195 (1 mol^{-1}cm^{-1}), 133 (1 mol^{-1}cm^{-1}), 199 (1 mol^{-1}cm^{-1}), 141 (1 mol^{-1}cm^{-1}), 209 (1 mol^{-1}cm^{-1}), 152 (1 mol^{-1}cm^{-1}), respectively, as represented in Table 5. The increase in the K_{CT} values with decreasing solvents polarity may also be due to the fact that the CT-complex should be stabilized in less polar solvents [22].

The influence of solvent polarity on the spectroscopic and thermodynamic properties of molecular electron-donor-acceptor (EDA) complexes is discussed. The data given in Table 5 show that DDQ interacts more strongly with PNA in carbon tetrachloride than in the other two solvents.

The experimentally determined values of oscillator strength, (f) in dichloromethane at 20^{0}C are 3.63×10^{-5} and 3.48×10^{-5}; at 25^{0}C are 2.36×10^{-5}, and 1.73×10^{-5}; and at 30^{0}C are 2.64×10^{-5} and 6.58×10^{-5}, as given in Table 2. The values of the oscillator strength, (f) in chloroform at 20^{0}C are 2.65×10^{-5} and 2.42×10^{-5}; at 25^{0}C are 1.93×10^{-5} and 6.75×10^{-5}; and at 30^{0}C are 2.13×10^{-5} and 7.57×10^{-5}, respectively, as shown in Table 3. In carbon tetrachloride the values of the oscillator strength, (f) at 20^{0}C are 2.07×10^{-5} and 6.26×10$^{-5;}$ at 25^{0}C are 1.87×10^{-5} and 1.54×10^{-5}; and at 30^{0}C are 2.27×10^{-5} and 1.22 ×10^{-5}, respectively (Table 4).

The values of the transition dipole moment, (μ_{EN}) in dichloromethane are 0.892 Debyes and 0.757 Debyes at 20^{0}C; 0.912 Debyes and 0.775 Debyes at 25^{0}C; and 0.934 Debyes and 0.798 Debyes at 30^{0}C (see Table 2). In chloroform the values of the transition dipole moment, (μ_{EN}) are 0.905 Debyes and 0.801 Debyes at 20^{0}C; 0.914 Debyes and (0.736 Debyes at 25^{0}C; and 0.930 Debyes and 0.752 Debyes at 30^{0}C (Table 3). In carbon tetrachloride the values of the transition dipole moment, (μ_{EN}) are 0.939 Debyes and 0.775 Debyes at 20^{0}C; 0.949 Debyes and 0.798 Debyes at 25^{0}C; and 0.972 Debyes and 0.829 Debyes at 30^{0}C (Table 4), which indicate that the complex should be more stable in the less polar solvent CCl_4 than in the other two solvents.

The free energy change of the complexation also reveals that the CT-complex formation between the donor (PNA) and the acceptor (DDQ) is exothermic in nature. The values of ΔG^o in dichloromethane: -13.408 KJmol^{-1} and -14.721 KJmol^{-1} at 20^{0}C; -13.405 KJmol^{-1} and -14.778 KJmol^{-1} at 25^{0}C; and -13.636 KJmol^{-1} and -14.492 KJmol^{-1} at 30^{0}C are shown in Table 2. In chloroform the values of ΔG^o at 20^{0}C are -13.808 KJmol^{-1} and -14.549 KJmol^{-1}; at 25^{0}C are -14.549 KJmol^{-1} and -15.120 KJmol^{-};^{1} and at 30^{0}C – -14.778 KJmol^{-1} and -15.006 KJmol^{-1} (Table 3). In carbon tetrachloride the values are -15.120 KJmol^{-1} and -14.835 KJmol^{-1} at 20^{0}C; -15.291 KJmol^{-1} and -14.435 KJmol^{-1} at 25^{0}C; and -15.291 KJmol^{-1} and -14.093 KJmol^{-1} at 30^{0}C (Table 4). The values of ΔG^o generally become more negative as the association constants of the molecular complex increase.

The calculated values of I_D of the DDQ/PNA system in dichloromethane at 20^{0}C are 9.40(*ev*), 8.54(*ev*); 9.37(*ev*) and 8.49 (*ev*) at 25^{0}C and 9.32(*ev*) and 8.63(*ev*) at 30^{0}C (Table 2). In chloroform the values of I_D at 20^{0}C are 9.38 (*ev*) and 8.47 (*ev*); at 25^{0}C are 9.35 (*ev*) and 8.40 (*ev*); and at 30^{0}C are 9.35 (*ev*) and 8.39 (*ev*) (Table 3). The calculated values of I_D in carbon tetrachloride at 20^{0}C are 9.37 (*ev*) and 8.43 (*ev*); at 25^{0}C are 9.38 (*ev*) and 8.74 (*ev*); and at 30^{0}C are 9.40 (*ev*) and 8.72 (*ev*) (Table 4). The approximate constancy of the I_D values indicates that the ionization potential has a negligibly small effect on the K_{CT} value.

FT-IR spectra of CT-complex and reactants

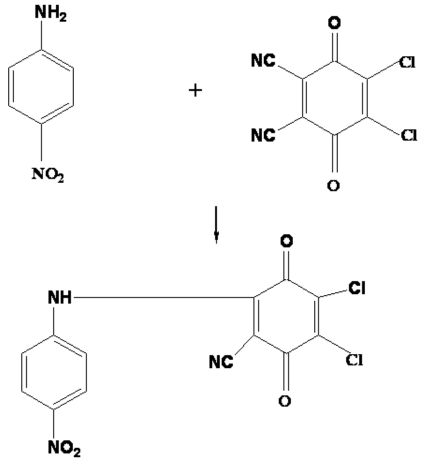
FT-IR spectra of p-nitroaniline (donor), DDQ (acceptor) and their CT-complex are shown in Fig 8. while the assignments of their characteristic FT-IR spectral bands are reported in Table 6. The formation of the charge transfer complex during the reaction of DDQ with PNA is strongly evidenced by the presence of the main characteristic infrared bands of the donor and acceptor in the spectrum of the product. There are changes in their intensities compared with those of the free donor and acceptor. This shift was attributed to the charge transfer from donor to acceptor upon complexation.

The FT-IR spectrum of the DDQ/PNA complex indicated that the band that results from the ν (C≡N) vibration of the free DDQ acceptor changed in frequency and decreased in intensity in the complexes upon CT complexation. Free DDQ shows two ν (C≡N) vibrations at 2250 and 2231 cm^{-1}, while in its complex ν (C≡N) occurs at a lower wave number value, 2209 cm^{-1}. It is clear that ν (C≡N) of DDQ is decreased upon complexation [23]. The characteristic band of ν (N-H) of PNA is observed at 3480 cm^{-1} (strong) and 3356 cm^{-1} (strong). In the CT-complex a new band is observed at 3481 cm^{-1}(strong). The band at 3076 cm^{-1}(weak) is due to the aromatic C-H stretching vibration. The $–NH_2$ deformation mode is observed by the absorption at 1633 cm^{-1} (very strong) in the CT-complex, whereas in free PNA this is observed at 1635 cm^{-1} (medium strong). This band overlaps with the aromatic C=C stretching vibrations. The $–NO_2$ group is observed at 1606 cm^{-1}(strong) in the CT complex, whereas in free PNA this is observed at 1591 cm^{-1} (very strong). The group of bands assigned to ν (C-Cl) vibrations, which appeared at 893 cm^{-1} and 800 cm^{-1} in the free DDQ, exhibited a shift to lower wave numbers at 862 cm^{-1} and 780 cm^{-1} and a decrease in intensity of the characteristic peaks [23]. These observations clearly confirm that the (C≡N) group in the DDQ acceptor participates in the complexation process. Because DDQ lacks acidic centers, the molecular complex can be assumed to form through π-π* and/or n-π* charge migration from the HOMO of the donor to the LUMO of the acceptor. The π-π* CT complex is formed *via* the benzene ring (electron-rich group) of the PNA and DDQ reagents (electron- acceptor).

The cyano group (C≡N) is an electron-withdrawing group that exists in DDQ in a conjugated bonding system. The 2 CN groups in DDQ withdraw electrons from the aromatic ring, and such a process will make the aromatic ring an electron-accepting region. The π*–CN electron density appears to increase and more easily accept a proton from the donor because of the electron-withdrawing process and the conjugated electron system. So, the interaction mode between PNA and the DDQ acceptor also occurs through migration of an H^+ ion to one of the cyano groups in the DDQ acceptor to form a positive ion ($-C≡N^+H$) that associates with the $–NH_2$ group in PNA.

^{1}*H- NMR spectrum of the CT- complex*

The ^{1}H-NMR spectrum of the 2, 3-dichloro-5, 6-dicyano-*p*-benzoquinone and p-nitro aniline product in acetone is shown in Figure 9. P-nitro aniline ring system was specified in the region δ = 8.40–6.66 ppm. The NH_2 group of p-nitroaniline occuring at δ= 6.71 in the free donor was shifted to δ= 6.66. This indicates that one of the CN groups of DDQ has been eliminated by the amino group of the p-nitroaniline donor eliminating HCN [24] (Scheme 1). The doublet peaks at δ= 8.40 ppm and the triplet peaks at δ = 7.62 ppm assigned to the rest of protons of p-nitroaniline are in the same kind in DDQ moiety in the CT-complex. The intensities and chemical shifts of the aromatic signals were significantly affected by the elimination and the accompanying changes in the structured configuration. Mechanism and structure of the CT-complex of acceptor and donor is given in Scheme 1.



Scheme 1. Mechanism of the interaction between p-nitroaniline and DDQ

CONCLUSION

The UV –Vis spectrophotometric method for the study of the CT-complex of DDQ with PNA ascertains the formation of a 1:1 (A:D) complex in all three solvents, viz., carbon tetrachloride, chloroform and dichloromethane. In all systems the stoichiometry is unaltered by changing the solvent. The association constants, K_{CT} and molar extinction coefficients, ε_{CT}, of all systems were evaluated by the Benesi-Hildebrand method. The spectroscopic and thermodynamic parameters of the CT-complexes were found to be dependent on the polarity of the solvents. The values of oscillator strengths, (f) transition dipole moments, (μ_{EN}) resonance energies, (R_N) and standard free energies, (ΔG^o) were estimated for the PNA/DDQ systems in different polar solvents. The results show that the investigated CT-complex is stable, exothermic and spontaneous. From the trends in the CT absorption bands, the ionization potentials of the donor molecules were estimated. The FT-IR and ^{1}H NMR spectra revealed that the charge transfer complex is present as an ion pair and there are few free ions in solution.

Acknowledgements: *Authors thank Dr. Sakir Ali, Chairman of Chemistry Department, Aligarh Muslim University, India, for providing the facilities of instruments of FT-IR spectrometer,UV-Visible spectrophotometer. Financial assistance from the UGC, New Delhi extended through the Women-PDF fellowship is also gratefully acknowledged. The authors also thank the learned referee for making valuable comments.*

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СПЕКТРОСКОПСКИ ИЗСЛЕДВАНИЯ НА КОМПЛЕКСИ С ПРЕНОС НА ЗАРЯДА ОТ 2,3-ДИХЛОРО-5,6-ДИЦИАНО-p-БЕНЗОХИНОН С p-НИТРОАНИЛИН

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Постъпила на 2 август, 2015 г.; приета на 5 октомври, 2015 г.

(Резюме)

Комплекси с пренос на заряда (CT-комплекси) с донор p-нироанилин (PNA) и акцептор 2,3-дихлоро-2,6-дициано-p-бензохинон (DDQ) са изследвани спектро-фотометрично в различни разтворители, като CH_2Cl_2, $CHCl_3$ и CCl_4 при различни температури. Във всички случаи са наблюдавани по две линии на пренос на заряда. Резултатите показват, че образуването на CT-комплекс в по-малко поляреn разтворителе сравнително високо. Стехиометрията на CT-комплекса е 1:1. Физичните параметри на CT-комплекса са оценени по уравнението на Benesi–Hildebrand. Данните са обсъдени в смисъла на константите на образуване (K_{CT}), коефициента на моларна екстинкция (ε_{CT}), стандартния термодинамичен потенциал (ΔG^o), силата на осцилатора (f), преодния диполен момент (μ_{EN}), рзонансната енергия (R_N) и йонизационния потенциал (I_D). Резултатите показват, че константата на образуване на комплекса (K_{CT}) е зависима от природата на акцептора на електрони, на донора и от полярността на използвания разтворител. Образуването на комплекса се потвърждава чрез UV-Vis – спектроскопия, FTIR и ^{1}H–ЯМР. Предложена е структура на CT-комплекса между DDQ и PNA.