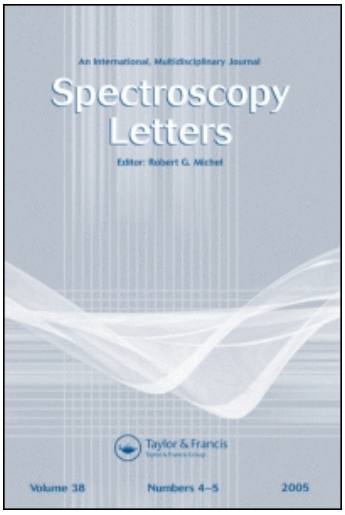

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Synthesis and Spectroscopic Studies of the Charge-Transfer Complexes of 2,3-Diaminopyridine and π-Electron Acceptors

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ABSTRACT

The spectrophotometric properties of the charge transfer (CT)-complexes formed between 2,3-diaminopyridine (DAPY) and π-acceptors tetrachloro-*p*-benzoquinone (chloranil) and tetracyanoethylene (TCNE) have been studied in chloroform. The stoichiometry of these CT-complexes is shown to be 1 : 1, (DAPY : chloranil) and 1 : 3 (DAPY : TCNE) forming complexes with the general formula [(DAPY)(chloranil)] and [(DAPY)$(TCNE)_3$]. The two complexes were isolated as solids and further characterized by elemental analysis and infrared measurements.

Key Words: CT-complexes; 2,3-Diaminopyridine; Chloranil; TCNE; Electronic spectra; Infrared spectra.

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INTRODUCTION

The intermolecular charge transfer (CT)-complexes of aza-organic bases and π-organic electron acceptors have been the subjects of many investigations.[1–6] However, studies of these complexes in the solid state appear to be limited, as most of the studies were focused on the formation constants of the CT-complexes in different solvents. The solvent effects were assumed to be mainly due to solvent interactions with electron acceptors.[7]

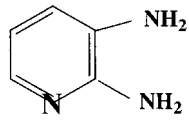
To continue our studies of CT-complexes,[2,8–10] the present paper represents the results of a study of the formation of new CT-complexes obtained in the reaction of the electron donor 2,3-diaminopyridine (DAPY), shown in Sch. 1, which contains two different donation sites. They are the NH_2 groups and N of the pyridine ring with the two π-electron acceptors tetrachloro-*p*-benzoquinone (chloranil) and tetracyanoethylene (TCNE) in chloroform as a solvent.

The aim of the work is to investigate the nature and structure of each of the new CT-complexes in both solution and solid states.

EXPERIMENTAL

All chemicals were high pure grade and were used without further purification. DAPY and chloranil were obtained from Aldrich Chemical Co., while TCNE was obtained from Merck Chemical Co.

The electronic absorption spectra of the donor, DAPY, the acceptors chloranil and TCNE, and the resultant complexes in chloroform were recorded using a Perkin–Elmer double beam spectrometer, model EZ-210, with quartz cell of 1-cm path length. In order to determine the stoichiometry of the CT-complexes, photometric titrations were performed for each of the π-acceptors and the donors in $CHCl_3$ at 22°C according to a known method.[11] The concentration of the donor, DAPY, in the reaction mixture was kept fixed at 1×10^{-3}–2×10^{-4} mol L^{-1}, in the cases of the reaction with chloranil and TCNE, respectively, while the concentration of chloranil was changed over



Scheme 1.

the range 0.25×10^{-3}–6×10^{-3} mol L^{-1}, and that of TCNE over the range 0.5×10^{-4}–12×10^{-4} mol L^{-1}.

The solid CT-complexes were isolated as follows. The (DAPY–chloranil) complex was isolated as a very dark brown solid by the addition of the reactants, 0.109 g (0.001 mol) of DAPY in 20 mL $CHCl_3$ to 0.246 g (0.001 mol) of chloranil in 35 mL $CHCl_3$ with constant stirring for 5 min. The reaction mixture was left to evaporate at room temperature to about 25 mL volume. The very dark brown solid was filtered, washed several times with minimum amounts of $CHCl_3$, and dried under vacuum. The second CT-complex (DAPY–TCNE) has an intensive violet color. It was isolated using a similar method, 0.001 mol of DAPY (0.109 g in 20 mL $CHCl_3$) was added to 0.003 mol of TCNE (0.384 g in 60 mL $CHCl_3$). The change in the reactants ratio from 1 : 1 in case of chloranil to 1 : 3 in case of TCNE was based on the stoichiometry of each reaction determined from the photometric titration method as will be seen later in the text. The formed CT-complexes were characterized by their spectroscopic data as well as elemental analysis and given the molecular formulas [(DAPY)(chloranil)] and [(DAPY)$(TCNE)_3$]. Analysis for [(DAPY)(chloranil)]: C, 36.46% (37.18); H, 1.85% (1.97); and N, 12.00% (11.83%) and for [(DAPY)$(TCNE)_3$]: C, 55.43 (55.98); H, 1.8% (1.42); and N, 42.72% (42.60%) (calculated values are shown in brackets).

The infrared spectra of the reactants and the formed CT-complexes were recorded from KBr discs using a Nicolet FT-IR model 670 spectrometer.

RESULTS AND DISCUSSION

New strong broad bands in the visible spectra are observed immediately upon mixing solutions of the donor DAPY and the π-acceptors chloranil and TCNE in $CHCl_3$ at 22°C. These bands are ascribed to CT electronic transitions of the formed complexes. Neither the donor nor the π-acceptors absorb in these regions. Figures 1 and 2 show the electronic absorption spectra for the DAPY, chloranil, TCNE, and the formed CT-complexes. These figures clearly demonstrate that the CT-transition in the DAPY–chloranil complex occurs at 496 nm while such a transition occurs at two main bands at 412 and 531 nm in the case of the DAPY–TCNE complex. Photometric titration measurements of the reactions in $CHCl_3$ based on the electronic absorption bands at 496 nm for the DAPY–chloranil complex and at 412 and 531 nm for the DAPY–TCNE complex are shown in Figs. 3 and 4. These figures reveal that the stoichiometry of the DAPY–chloranil reaction is 1 : 1 and of the DAPY–TCNE is 1 : 3 forming the CT-complexes [(DAPY)(chloranil)] and [(DAPY)$(TCNE)_3$], respectively. These structures agree quite well with the

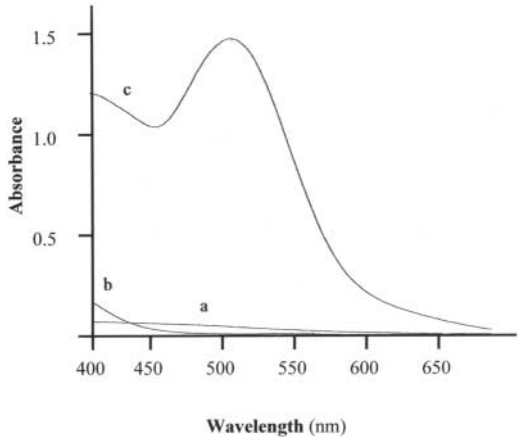


Figure 1. Electronic absorption spectra of DAPY–chloranil reaction (a: [DAPY] = 1×10^{-3} M; b: [chloranil] = 1×10^{-3} M; and c: 1 : 1, DAPY–chloranil mixture; [DAPY] = [chloranil] = 1×10^{-3} M).

elemental analysis data of the isolated solid CT-complexes. It is of interest to see that the [(DAPY)(chloranil)] has only one band while the [(DAPY)$(TCNE)_3$] has two main bands with some shoulder structures, but they belong to the same product, Fig. 4. This fact supports the conclusion that DAPY reacts with one chloranil or three TCNE.

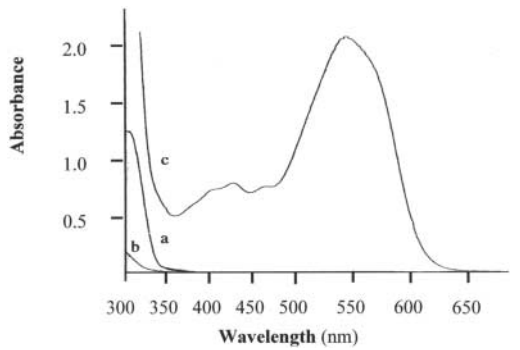


Figure 2. Electronic absorption spectra of DAPY–TCNE reaction (a: [DAPY] = 2×10^{-4} M; b: [TCNE] = 2×10^{-4} M; and c: 1 : 3, DAPY–TCNE mixture; [DAPY] = 2×10^{-4} M and [TCNE] = 6×10^{-4} M).

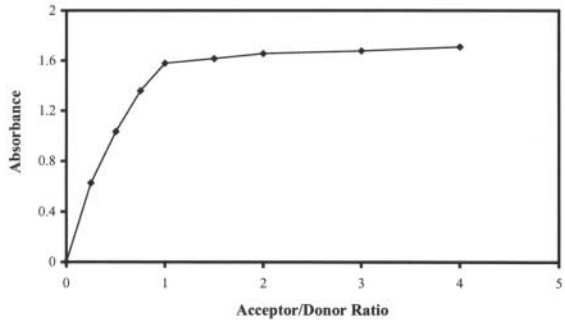


Figure 3. Photometric titration curve for the DAPY–chloranil reaction based on the 496 nm absorption.

The infrared spectra of the CT-complexes [(DAPY)(chloranil)] and [(DAPY)$(TCNE)_3$] are shown in Fig. 5 while their band assignments along with those of the free DAPY are given in Table 1. The spectra of each of the product complexes contain the main characteristic bands of both DAPY and chloranil in the case of [(DAPY)(chloranil)] and of DAPY and TCNE in case of [(DAPY)$(TCNE)_3$] and this represents an additional support of the formation of the DAPY–acceptor CT-complexes. However, interestingly, the υ (N–H) vibrations of the free DAPY are shifted to lower wavenumber values in the spectra of the complexes (Table 1). This

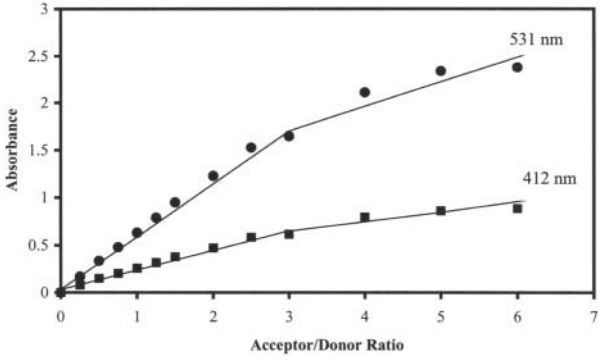


Figure 4. Photometric titration curves for the DAPY–TCNE reaction based on the 412 and 531 nm absorptions.

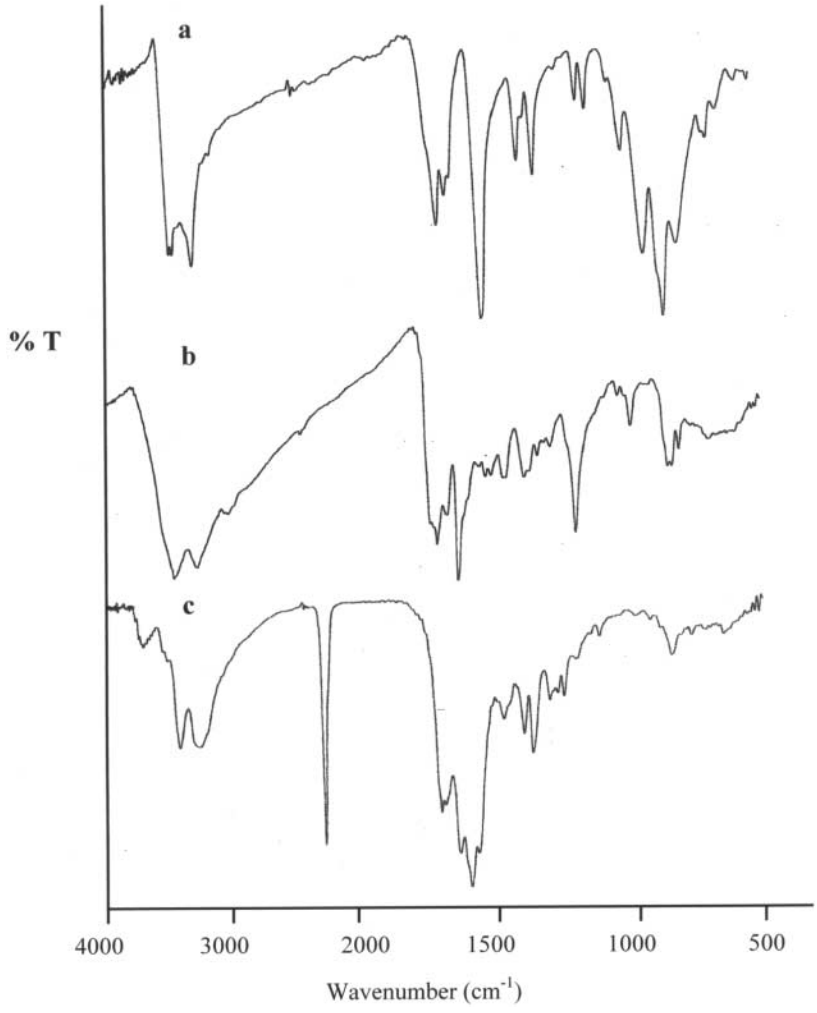


Figure 5. Infrared absorption spectra for a: DAPY, b: [(DAPY)(chloranil)], and c: [(DAPY)$(TCNE)_3$].

shows that the complexation of DAPY with the acceptor takes place via the DAPY two $-NH_2$ groups rather than the pyridine ring. The vibrations of the pyridine ring do not show any measurable changes upon complexation.

Since the concentrations of the reactants are very small in magnitude and comparable, calculations of the formation constant, K_C, and the absorptivity,

Table 1. Infrared wavenumbers[a] (cm^{-1}) and assignments for DAPY, [(DAPY)(chloranil)], and [(DAPY)$(TCNE)_3$].

DAPY	[(DAPY)(chloranil)]	[(DAPY)$(TCNE)_3$]	Assignments[b]
3,360s	3,322s	3,322s	υ (N–H); DAPY
3,344s	—		
3,280w	3,269w	3,232sh	
3,178s	3,176s	3,177s	υ (C–H); aromatic
3,062w, 3,017w	3,113sh, 3,055w	3,096sh	
—	—	2,211vs	υ (C≡N); TCNE
—	1,678vs	—	υ (C═O); chloranil
1,633sm	1,649m	1,650s	υ (C═C), ring
—	1,614m	1,628m	stretching
1,594m	1,567s	1,578m	vibrations; DAPY and chloranil
—	—	1,528s	υ (C═C); TCNE
1,482vs	1,486w	1,499m	υ (C═C), ring
1,467vs	1,461w	—	stretching vibrations; DAPY and chloranil
—	1,438w	1,406mw	δ (NH_2) and δ(CH)
—	1,389m	—	deformations;
1,305m	1,305m	1,328m	DAPY and
1,282wm	—	1,283ms	chloranil
—	—	1,191w, 1,167wm	υ (C–N); TCNE
—	1,111vs	—	chloranil characteristic band
1,072m	—	—	υ (C–N); DAPY
1,034m	—	1,033w	
949w	947w	—	δ (C–H) deformation;
900m	900m	889w	aromatic; DAPY and chloranil
828s	—	837w	δ (C–H); out of plane
776m	—	—	wag; aromatic
750m	750ms	750m	
—	711m	—	υ (C–Cl); chloranil
700m	—	—	NH_2 deformations;
589mw	—	—	free DAPY
578mw	—	—	δ (CH), out of plane
522w	554w	550w, 530w	ring bending; aromatic

[a]m, medium; s, strong; sh, shoulder and w, weak.

ε_C, were performed for the CT-complex [(DAPY)(chloranil)] using the modified Benesi–Hildebrand equation[12] for the 1 : 1 reaction;

$$\frac{[A_0][D_0]}{A} = \frac{1}{K_C \varepsilon_C} + \frac{[A_0] + [D_0]}{\varepsilon_C}$$

where A is the absorbance of the CT-transition of [(DAPY)(chloranil)] at 496 nm, $[A_0]$ and $[D_0]$ are the initial concentrations of the acceptor and the donor, respectively. A straight line is obtained from the plot of $[A_0]\,[D_0]/A$ vs. $[A_0] + [D_0]$ confirming our conclusion of the formation of 1 : 1 complex. The obtained values of K_C and ε_C are 1.65×10^{-4} L mol^{-1} and 3.89×10^3 L mol^{-1} cm^{-1}, respectively. The high value of K_C indicates the higher stability of the [(DAPY)(chloranil)] complex while the high value of ε_C is characteristic for CT-complexes. An unsuccessful attempt was made to calculate the corresponding values for the 1 : 3 CT-complex, [(DAPY)$(TCNE)_3$]. The 1 : 3 stoichiometry equation has many complicated terms to deal with and we hope to overcome this problem and to publish these results in the future.

CONCLUSION

The donor DAPY reacts at room temperature with the π-electron acceptors chloranil and TCNE in $CHCl_3$ to form the solid stable CT-complexes [(DAPY)(chloranil)] and [(DAPY)$(TCNE)_3$], respectively, where the reaction stoichiometry is 1 : 1 and 1 : 3.

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