



Synthesis, Spectroscopic and Thermal Studies on Solid Charge-Transfer Molecular Complexes Formed in the Reaction of 5-Amino-1-Methyl-3-Phenylpyrazole with π - and σ - Acceptors

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ABSTRACT

The spectrophotometric characteristics of the solid charge-transfer molecular complexes (CT) formed in the reaction of the electron donor 5-amino-1-methyl-3-phenylpyrazole (AMPP) with the π -acceptors tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) and σ -acceptor iodine have been studied in chloroform at 25 °C. These were investigated through electronic and infrared spectra as well as elemental analysis. The results show that the formed solid CT- complexes have the formulas [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻ in full agreement with the known reaction stoichiometry in solution as well as the elemental measurements. The formation constant k_{CT} , molar extinction coefficient ϵ_{CT} , free energy change ΔG^0 and ECT energy have been calculated for the CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻.

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1. Introduction

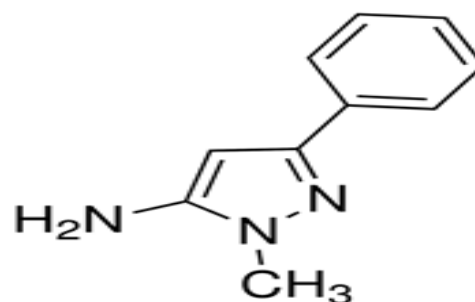
Pyrazoles are a class of compounds that have the ring C₃N₂ with adjacent nitrogen atoms [1]. The molecular interactions between electron donors and acceptors are generally associated in the formation of intensity colored charge-transfer (CT) complexes that absorb radiation in the visible region [2-9]. The photometric methods based on these interactions are usually simple and convenient because of the rapid formation of the complexes. The chemical and physical properties of charge-transfer (CT) complexes formed in the reactions of π - and σ - electron acceptors with different donors like amines, crown ethers, polysulfur bases and oxygen-nitrogen mixed bases have been the subjects of many studies both in solution and in solid state [10-14]. It was found that the reaction stoichiometries as well as the structure of these CT- complexes depend strongly on the number of nitrogen donor atoms as well as on their terminal attached groups, hydrogen or donating groups like alkyl or withdrawing atoms like halogens. Electron donating like alkyl groups were found to enhance the acceptor: donor stoichiometry.

Interestingly, most of the CT- complexes have many applications in chemical analysis like quantitative drug estimation and some complexes have interesting physical properties like electrical conductivities [15-18].

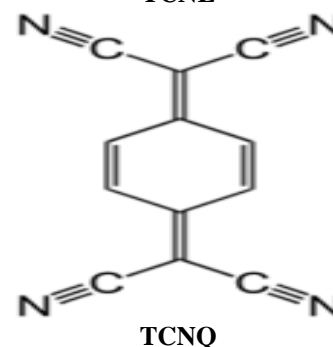
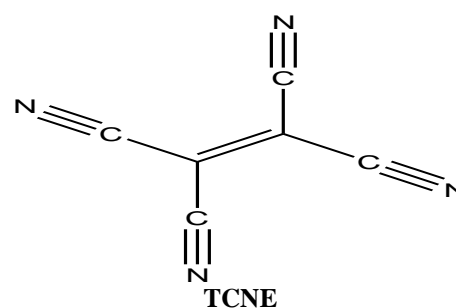
In this paper, we report the formation of three new CT-complexes formed on the reaction of 5-amino-1-methyl-3-phenylpyrazole (AMPP) with different types of π - and σ -electron acceptors.

The π -acceptors are tetracyanoethylene (TCNE) and 7,7,8,8-Tetracyanoquinodimethane (TCNQ) and the σ -electron acceptor is iodine.

All reactions were carried out in CHCl₃ as a solvent. The obtained results enabled us to investigate the stoichiometries and structure inherent in these formed new CT- complexes.



5-Amino-1-methyl-3-phenylpyrazole (AMPP)



2. Experimental

2.1. Materials and instrumentation

The chemicals used in this study were of high grade and purchased from Sigma-Aldrich, USA, and used without further purification. The UV/Vis spectra of the CHCl_3 solutions of the solid CT-complexes formed in the reactions of the donor 5-amino-1-methyl-3-phenylpyrazole and the acceptors tetracyanoethylene (TCNE), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and iodine as well as the reaction products were checked in the region 1000-250 nm using Perkin Elmer UV-Vis-NIR spectrometer model lambda 950 with quartz cell of 1.0 cm path length. Elemental analysis was done using a Perkin Elmer CHNS/O Elemental Analyzer model 2400 series II. The infrared spectra of the reactants, (AMPP), TCNE, TCNQ and iodine and the obtained CT-complexes (KBr pellets) were recorded using Perkin Elmer FTIR spectrometer model spectrum one. The complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻ have been checked using Agilent LC MS/MS model 4620 triple quadrupole while thermogravimetric analysis (TG & DTG) were performed using Perkin Elmer computerized thermal analyzer model Pyris 6 TGA under flow of nitrogen gas (20 ml min⁻¹) with heating rate of 10°C min⁻¹.

2.2. Photometric titration

Photometric titration measurements were performed for the reactions between the donor (AMPP) and each of the acceptors TCNE, TCNQ, and iodine in CHCl_3 at 25 °C in order to determine the reaction stoichiometries according to a literature method [4, 19]. The measurements were conducted under the conditions of fixed donor (AMPP) concentration while those of the acceptors TCNE, TCNQ or iodine were changed over a wide range, to produce in each case reaction solutions where the molar ratio of donor: acceptor varies from 1: 0.25 to 1: 4. The peak absorbance of the formed CT-complexes were measured for all solutions in each case and plotted as a function of the acceptor to donor molar ratio. The infrared spectra of the reactants and the formed CT-complexes (KBr pellets) were recorded on Perkin-Elmer FTIR spectrophotometer model spectrum one.

2.3. Preparation of CT- complexes

The three solid CT- complexes formed in the reaction of (AMPP) with each of TCNE, TCNQ and iodine were prepared in CHCl_3 by the drop wise addition of a saturated solution (95 ml) of the donor to a saturated solution (105 ml) of each of the acceptors. In each case, the mixing of reactants was associated with a strong change in color. The resulting precipitate in each case was filtered off, washed with minimum amounts of chloroform and dried in vacuum over P_2O_5 . The complexes were characterized using spectroscopic techniques (FTIR and UV-Vis) and by elemental analysis: (theoretical values are shown in brackets):

5-amino-1-methyl-3-phenylpyrazole (AMPP) CT-complexes: [(AMPP)(TCNE)] yellow complex (M/W: 301.29); C, 63.31% (63.73.29%) H, 3.59% (3.65%); N, 32.48% (32.53%); [(AMPP)(TCNQ)] dark blue complex (M/W:377.39g); C, 69.89% (69.95%); H, 3.91% (3.98%); N, 25.89% (25.97%); [(AMPP) I]⁺ I₃⁻ dark brown complex (M/W: 680.8g); C, 17.16% (17.2%); H, 1.56% (1.62%); N, 6.13% (6.17%).

3. Results and discussion

3.1. UV-Vis absorption spectra

Fig.1 shows the electronic absorption spectra of the reaction of tetracyanoethylene (TCNE) with the donor AMPP. While none of the reactants' spectra display any measurable absorption in the region 300 – 1000 nm, the

resulting CT-complexes show strong absorptions centered on 540 nm for AMPP-TCNE reactions. These absorptions are associated with the strong change in color observed upon mixing of reactants (yellow) from colorless solution for AMPP-TCNE and reflect the electronic transitions in the formed CT- complexes.

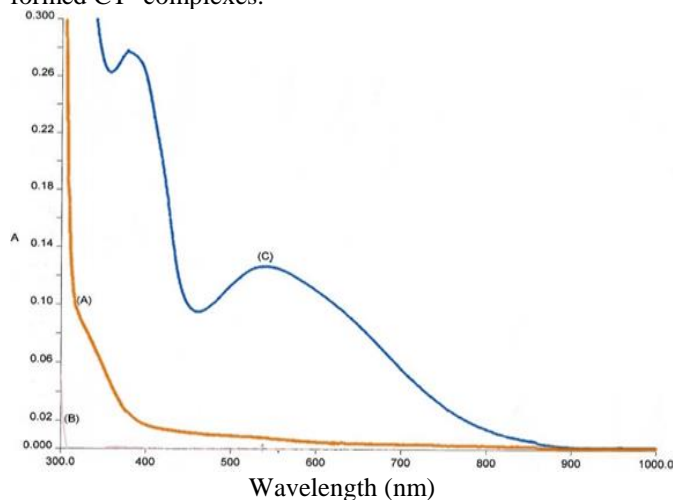


Fig1. Electronic absorption spectra of 5-amino-1-methyl-3-phenylpyrazole-TCNE reaction in CHCl_3 . (A) [AMPP] = $5 \times 10^{-3}\text{M}$; (C) [TCNE] = $5 \times 10^{-3}\text{M}$; 1:1 AMPP- TCNE mixture, [AMPP] = [TCNE] = $5 \times 10^{-3}\text{M}$.

Photometric titration measurements based on these absorptions were performed in order to determine the reaction stoichiometry in CHCl_3 (Fig. 2). The results showed that the donor: TCNE molar ratio was found to be 1:1 for the donor. This is in good agreement with the obtained elemental analysis of the three solid CT- complexes. Based on these experimental data, the complex obtained can be formulated as [(AMPP)(TCNE)].

Interestingly, the reaction stoichiometry using TCNE as a π - acceptor is 1: 1. The alkyl group (methyl group at position 1) is supposed to enhance the electron donation in AMPP but the steric hindrance is the reason for that (1:1) in comparison with the reaction stoichiometry of 2-amino-4-ethylpyridine with TCNE which was 1:2 in our previous study [20].

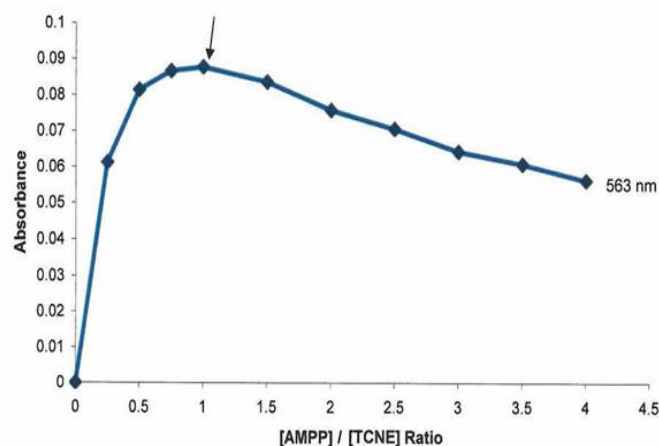


Fig 2. Photometric titration curve for AMPP – TCNE reaction in CHCl_3 measured at the 563 nm absorption.

Fig. 3 shows the electronic spectra recorded in the region 400–700 nm of the reaction of 7,7,8,8-tetracyanoquinodimethane (TCNQ) with AMPP. Similar to the reaction with the previous acceptor, strong change in color is observed upon mixing, dark blue color indicates the formation of the AMPP-TCNQ CT- complex and is associated with the electronic transitions at 515 nm.

Photometric titration measurements were performed for AMPP reaction in CHCl_3 as shown in Fig. 4. The results showed that the donor-TCNQ molar ratio was found to be 1:1. This is in good agreement with the obtained elemental analysis of the solid CT-complex, which accordingly can be formulated as $[(\text{AMPP})(\text{TCNQ})]$.

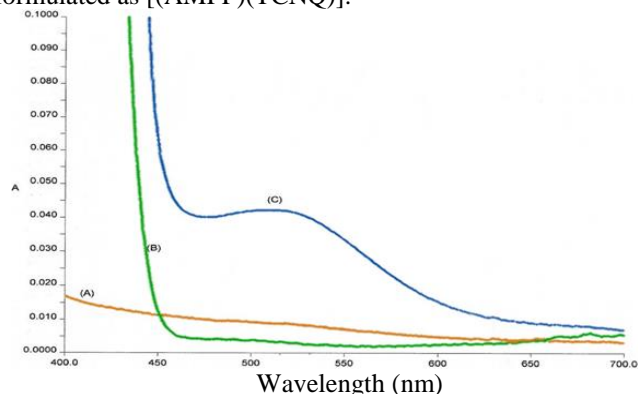


Fig 3. Electronic absorption spectra of 5-amino-1-methyl-3-phenylpyrazole - TCNQ reaction in CHCl_3 (A) $[\text{AMPP}] = 5 \times 10^{-3} \text{M}$; (B) $[\text{TCNQ}] = 5 \times 10^{-3} \text{M}$; 1:1 AMPP-DDQ mixture, $[\text{AMPP}] = 5 \times 10^{-3} \text{M}$ and $[\text{TCNQ}] = 5 \times 10^{-3} \text{M}$.

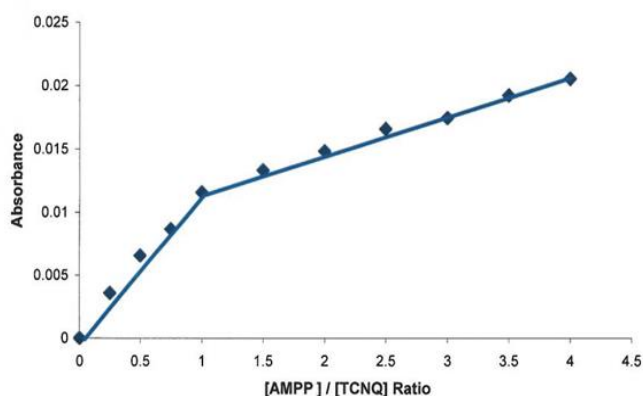


Fig 4. Photometric titration curve for 5-amino-1-methyl-3-phenylpyrazole - TCNQ reaction in CHCl_3 measured at the 515 nm absorption.

Fig. 5 shows the electronic spectra recorded in the region 250-600 nm of the reaction of iodine with AMPP. Strong change in color is observed upon mixing; dark brown color indicates the formation of the AMPP- I_2 charge-transfer complex and is associated with the electronic transitions at 360 and 264 nm.

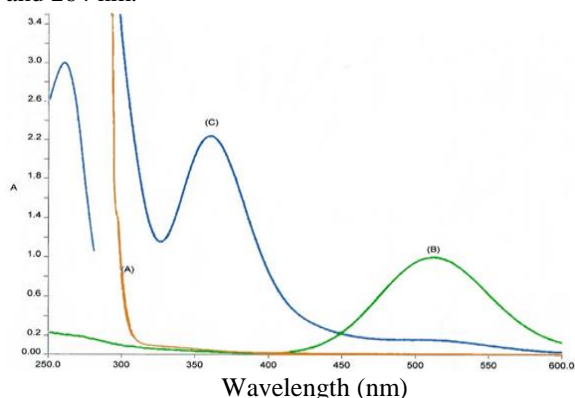
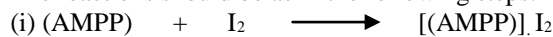


Fig 5. Electronic absorption spectra of 5-amino-1-methyl-3-phenylpyrazole I_2 reaction in CHCl_3 (A) $[\text{AMPP}] = 5 \times 10^{-3} \text{M}$; (B) $[\text{I}_2] = 1 \times 10^{-3} \text{M}$; 1:2 AMPP- I_2 mixture, $[\text{AMPP}] = 5 \times 10^{-3} \text{M}$ and $[\text{I}_2] = 1 \times 10^{-3} \text{M}$. The band assigned by arrow at 264 nm of diluted solution of AMPP/ I_2 - complex (inset).

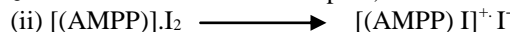
Photometric titration measurement was performed for AMPP- I_2 reaction in CHCl_3 shown in Fig. 6. The results showed that the donor- I_2 molar ratio was found to be 1:2.

The obtained elemental analysis of the solid CT-complex has matched accurately the molar ratio 1:2 and can be formulated as $[(\text{AMPP})\text{I}]^+ \text{I}_3^-$ [21].

The reactions should be as in the following steps.



• Formation of the inner complex,



• Formation of the triiodide CT-complex

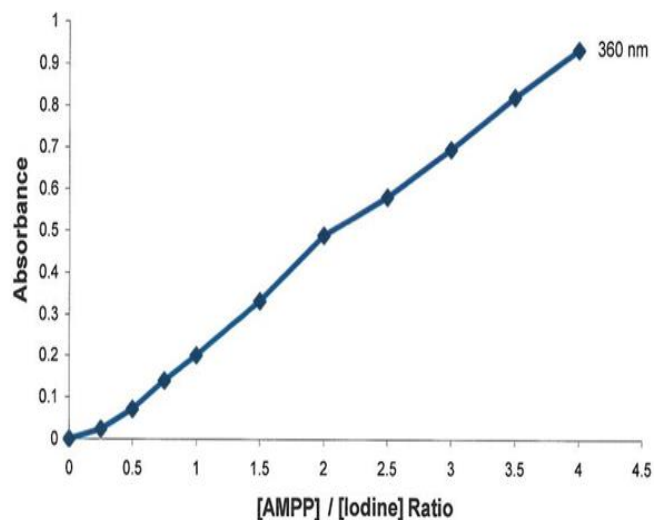
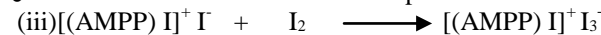


Fig 6. Photometric titration curve for AMPP - I_2 reaction in CHCl_3 measured at the 360 nm absorption.

Table 1 shows the spectroscopic data of the resulting CT-complexes. These obtained UV/Vis spectra of the CT-complexes $[(\text{AMPP})(\text{TCNE})]$, $[(\text{AMPP})(\text{TCNQ})]$ and $[(\text{AMPP})\text{I}]^+ \text{I}_3^-$ have clarified that the variation of the CT-absorptions of TCNE, TCNQ and I_2 should be related to the electron affinity of each acceptor with the donor AMPP.

These pronounced variations of CT-interaction stoichiometries are relatively complicated issue to be sorted out. It is definitely connected to many factors such as the donor molecular symmetry, the type of electron withdrawing groups or atoms Cl or $\text{C}\equiv\text{N}$ as well as the steric hindrance between reactants. All of these factors are expected to play an important role on the electron donation process from the nitrogen electron pairs of the donor AMPP and the aromatic ring of TCNQ acceptor. The four $\text{C}\equiv\text{N}$ in TCNQ has same electron accepting ability compared with that in TCNE, related to the same stoichiometric ratio obtained for both TCNQ and TCNE. This certainly, allows same electron donation from AMPP base to TCNE and TCNQ.

The formation constant (K_{CT}) and molar extinction coefficient (ϵ_{CT}) values for the formed CT-complexes of the donor 5-amino-1-methyl-3-phenylpyrazole with the π -acceptors TCNE, TCNQ and σ -acceptor iodine in CHCl_3 at 25 $^\circ\text{C}$ were calculated. The formation constant, K_{CT} (mol^{-1}), and the molar extinction coefficient ϵ_{CT} ($\text{mol}^{-1}\text{cm}^{-1}$) have been calculated for the complexes $[(\text{AMPP})(\text{TCNE})]$, and $[(\text{AMPP})(\text{TCNQ})]$ using the known [22] Eq. (1) of 1:1 complexes:

$$\frac{A_0 D_0 \ell}{A} = \frac{1}{k \epsilon} + \frac{A_0 + D_0}{\epsilon} \quad (1)$$

The corresponding spectral parameters for the complexes

$[(AMPP) I]^+ I_3^-$ was calculated using the known [23] Eq. (2) of 1:2 complexes:

$$\frac{(A_0)^2 D_0 \ell}{A} = \frac{1}{k \varepsilon} + \frac{A_0 (A_0 + 4D_0)}{\varepsilon} \quad (2)$$

Table 1. Spectroscopic data for the $CHCl_3$ solutions of solid CT- complexes of AMPP with the acceptors TCNE, TCNQ and I_2

Complex	Color	Absorption (nm)	Stoichiometry
			(Donor: acceptor)
[(AMPP)(TCNE)]	yellow	563s, 380s	1:1
[(AMPP)(TCNQ)]	Dark blue	515s	1:1
[(AMPP) I] ⁺ I ₃ ⁻	Dark brown	360s, 264s	1:2

^(a)The reactants AMPP, TCNE, TCNQ and I_2 have no measurable absorptions in the region of study with used concentrations; s, strong.

Where A_0 and D_0 are the initial concentrations of the acceptors and donors, respectively, while A is the absorbance at the mentioned CT bands and ℓ is the cell path length (1cm). The data obtained throughout this calculation are given in Table 2. Plotting the values of $A_0 D_0 \ell / A$ against $(A_0 + D_0)$ values of equation (1) and plotting values of $(A_0)^2 D_0 \ell / A$ versus $A_0 (A_0 + 4D_0)$ values of equation (2), straight lines were obtained with a slope of $1/\varepsilon_{CT}$ and intercept of $(1/K_{CT} \varepsilon_{CT})$ as shown in Figs. (7 - 9) for the CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻.

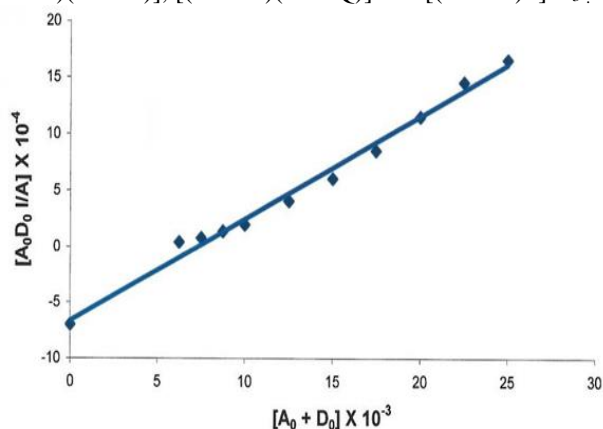


Fig 7. Spectral determination of formation constant and molar extinction coefficient of CT- complex [(AMPP)(TCNE)] at 563 nm.

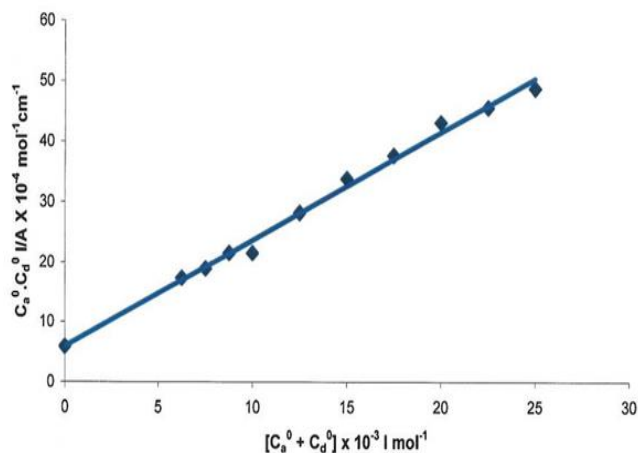


Fig 8. Spectral determination of formation constant and molar extinction coefficient of CT- complex [(AMPP)(TCNQ)] at 515 nm.

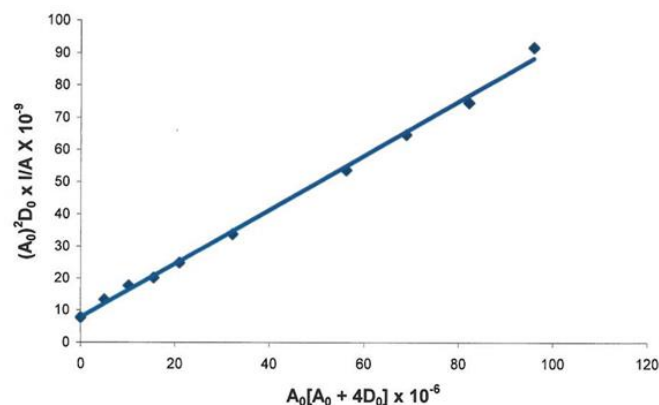


Fig. 9. Spectral determination of formation constant and molar extinction coefficient of CT- complex [(AMPP) I]⁺ I₃⁻ at 360 nm.

These complexes show high values of both the formation constant (K_{CT}) and the molar extinction coefficient (ε_{CT}). These high values of K_{CT} confirm the expected high stabilities of the formed CT- complexes because of the expected high donation of 5- amino-1-methyl-3-phenylpyrazole. The formation constants are strongly dependent on the nature of the used acceptors including the type of electron withdrawing substituent on it such as cyanide group in TCNE and TCNQ.

The free energy change ΔG^0 (cal mol⁻¹) values of the complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻ were calculated from Gibbs free energy of formation according to the Eq. (3) [24, 25]:

$$\Delta G^0 = -RT \ln K_{CT} \quad (3)$$

Where ΔG^0 is the free energy of the charge transfer complexes; R the gas constant (1.987 cal mol⁻¹ °C); T the temperature in Kelvin degrees; K_{CT} the formation constant of donor-acceptor complexes (1 mol⁻¹). The ΔG^0 values of the complexes are given in table 2.

The obtained results of ΔG^0 reveal that the CT-complexes formation process is exothermic and spontaneous. The results of ΔG^0 are generally more negative as the formation constants of the CT- complexes increase. As the bond between the components becomes stronger and thus the components are subjected to strain that is more physical or loss of freedom, the values of ΔG^0 become more negative. The more negative the value for ΔG^0 , the farther to the right the reaction will proceed in order to achieve equilibrium. The charge transfer energy E_{CT} of the formed solid CT-complexes is calculated using the following Eq. (4) [26, 27]:

$$E_{CT} (nm) = \frac{1243.667}{\lambda_{CT}} \quad (4)$$

Where λ_{CT} is the wavelength of the band of the studied CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻. The E_{CT} values calculated from equation (4) are listed in Table 2. These results in table 2 (K_{CT} , ε_{CT} , ΔG^0 and E_{CT}) are clarifying that the obtained solid CT- complexes formed in the reaction of the donor AMPP with the π -acceptors TCNE, TCNQ and σ -acceptor I_2 have high CT energy and formation constants K_{CT} . These high values confirm the expected high stabilities of the formed CT-complexes because of the expected high donation of AMPP.

The ionization potential of the free donor was determined from the CT energies of the CT band of its complexes. In case of the acceptors TCNE, TCNQ and I_2 the relationship becomes the following Eq. (5) [28]:

$$E_{CT} = I_p - 5.2 + \frac{1.5}{I_p - 5.2} \quad (5)$$

Table 2. Values of K_{CT} , ΔG^0 , E_{CT} and ϵ_{CT} of CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻ in CHCl₃.

Complex	K_{CT}/mol^{-1}	$-\Delta G^0/\text{cal mol}^{-1}$	E_{CT}/eV	$\lambda_{\text{max}}/\text{nm}$	$\epsilon_{CT}/\text{mol}^{-1}\text{cm}^{-1}$
[(AMPP)(TCNE)]	0.013×10^4	2.9×10^3	2.21	380	0.0011×10^4
[(AMPP)(TCNQ)]	0.030×10^4	1.5×10^3	2.42	515	0.056×10^4
[(AMPP) I] ⁺ I ₃ ⁻	0.001×10^4	9.6×10^3	3.45	360	0.012×10^4

Table 3. Infrared wavenumbers (cm^{-1}) and tentative band assignments for 5-amino-1-methyl-3-phenylpyrazole (AMPP), [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻

AMPP	[(AMPP)(TCNE)]	[(MPP)(TCNQ)]	[(AMPP) I] ⁺ I ₃ ⁻	Assignments
3424ms	3436m	3411s	3417ms	ν (H ₂ O); KBr
3270ms,3151ms	3161ms 3121w	3368m 3225w	3312m 3206m	ν (NH); AMPP
2937w	2958m	3148w	3132w	ν (C-H); AMPP
2873w	2854m	3087w	3071w	
	2214s,2193s,	2181s		ν (C \equiv N); TCNE
		2168s		and TCNQ
		1646s		ν (C=O); TCNQ,
1558s	1539s	1599w	1632s	ν (C=C); TCNE,
1512s	1584w	1573s	1544w	TCNQ, AMPP
1378s	1383m	1382w	1339w	Free and complexed AMPP
1306w	1325w	1363w	1314w	
1286ms	1213s	1345ms	1293m	
1203w	1205w	1207w	1215w	ν (C-N); AMPP
1156w	1196w	1171ms	1188w	
1105w	1149w	1094s	1089w	ν (C-C); AMPP
1082w	1096w	1079w	1026w	
961ms	991w	988w	986w	δ (CH)deformation,
912ms	849w	919m	912w	AMPP
827w	837w	823w	834w	δ (CH);out of plan
				Wag; AMPP
448s	493w	481ms	487ms	δ (CH);out of plane
448s	493w	481ms	487ms	bending; AMPP

s, strong; w, weak; br, broad; ν , stretching; m, medium;

Where I_p is the ionization potential and E_{CT} is the charge transfer energy of the formed solid CT- complexes. The obtained values of I_p are 6.35, 6.48 and 6.15 eV for the CT-complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻, respectively. It has been reported that the ionization potential of the electron donor may be correlated with the charge transfer transition energy of the complex [28].

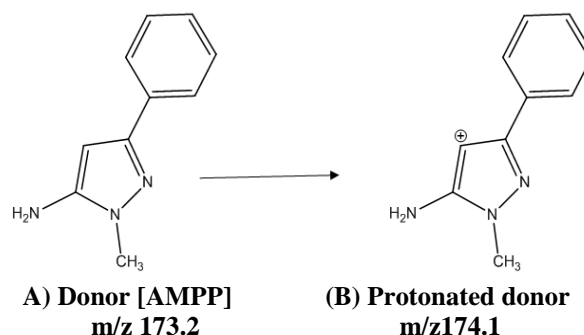
These results in table 2 (K_{CT} , ϵ_{CT} , ΔG^0 and E_{CT}) are clarifying that the obtained solid CT-complexes formed in the reaction of the donor AMPP with the π -acceptors TCNE and TCNQ and σ - acceptor iodine have high CT energy and formation constants K_{CT} . These high values confirm the expected high stabilities of the formed CT- complexes because of the expected high donation of AMPP.

3.2. Mass Spectral studies

LC MS/ MS has been used for confirming the molecular weight of the obtained CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻. Fig.10a (A) shows the mass spectrum of [(AMPP)(TCNE)] in the region $m/z = 100 - 310$. The molecular ion M^+ is observed as a short peak at $m/z = 301.1$ in good agreement with the calculated value for the molecular weight of the CT- complex of 301.29 g. The found difference of about 0.19 between the observed and calculated molecular weight value is acceptable within the allowed experimental errors. The mass spectrum also shows a number of other peaks; the peak at $m/z = 174.2$ is for protonated donor (A) (m/z 173.2 calculated), the peak at m/z 202.1 is for the mass of the donor plus one cyanide group and

H₂ (201.2 calculated). The peak at m/z 282.9 is for the donor plus 3 CN and O₂ (m/z 283.2 calculated). Fig.10b (B) shows the mass spectrum of the complex [(AMPP)(TCNQ)] in the region $m/z = 100- 480$ which is showing the molecular ion M^+ as a short peak at $m/z = 378.1$ very close to the calculated value of the molecular weight of that complex (377.39 g). The peak at $m/z = 199$ is for the donor plus one cyanide group (m/z 199.2 calculated) and the peak at m/z 282.9 is for donor plus 3 CN groups and O₂ (m/z 283.2 calculated). The mass spectrum in Fig.10c (C) for the complex [(AMPP) I]⁺ I₃⁻ in the region $m/z = 100 - 710$ is showing the molecular ion M^+ as a short peak at $m/z = 679.8$ in a good agreement with the calculated value for the molecular weight of that complex of 680.8 g.

The peak at 174.1 is for protonated donor (A) (m/z 173.2 calculated), the peak at 300 is for donor plus iodine atom very close to the calculated value (m/z 300 calculated).

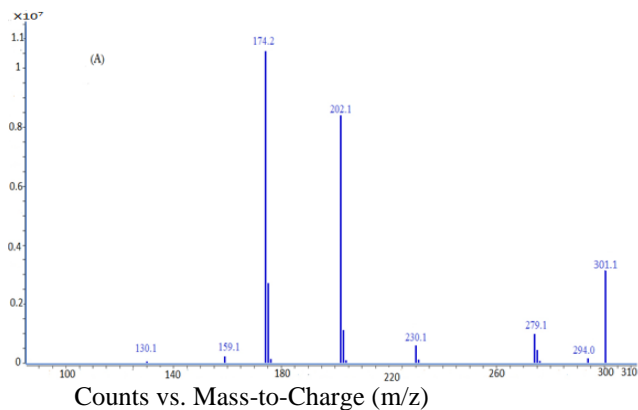


3.3. FTIR spectral studies

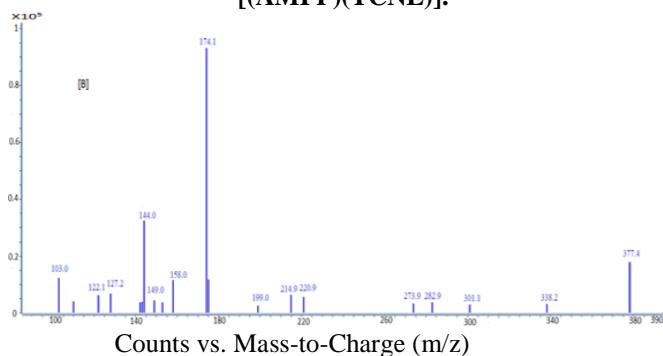
The infrared absorption spectra of the donor 5-amino-1-methyl-3-phenylpyrazol, [(AMPP) (TCNE)], [(AMPP) (TCNQ)] and [(AMPP) I]⁺ I₃⁻ are shown in Fig.11. The infrared band assignments are given in Table 3. These assignments are based on the comparison of the spectra of the formed products with the spectra of the free reactants, the donor 5-amino-1-methyl-3-phenylpyrazole (AMPP) and the acceptors TCNE, TCNQ and I₂. Interestingly, the spectra of the reaction products contain the main infrared bands for both the reactants in each case.

This strongly supports the formation of the donor-acceptor CT- complexes. However, the absorptions of AMPP and acceptors in the formed products show same changes in band intensities and in some cases small shifts in the frequency wavenumber values. These changes could be understood based on the expected symmetry and electronic structure modifications in both donor and acceptor units in the formed products compared with those of the free molecules. For example, the $\nu(\text{N-H})$ vibrations of the free 2-amino-6-methylpyridine in [(AMPP)₂(TCNE)] has medium absorption at 3161 and 3121 cm⁻¹ while in the [(AMPP)(TCNQ)], two medium absorptions are observed at 3363 and 3225 cm⁻¹ and in [(AMPP)I]⁺ I₃⁻, two medium absorptions are observed at 3312 and 3206 cm⁻¹.

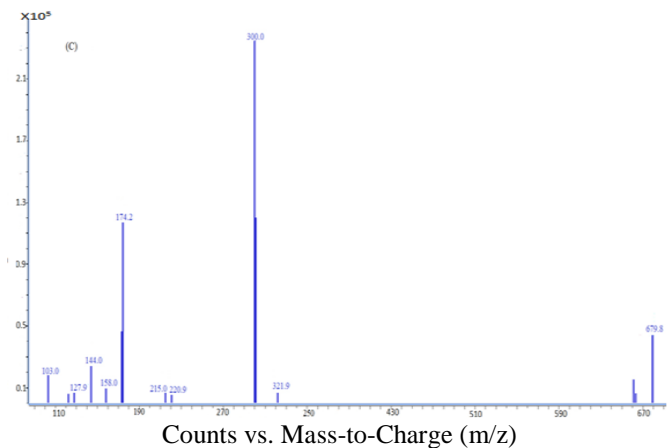
The outlined changes in $\nu(\text{N-H})$ upon complexation clearly support the involvement of the nitrogen atoms of the donor A in the CT – interaction process. It might also to indicate here that $\nu(\text{C}\equiv\text{N})$ vibrations of the acceptors TCNE and TCNQ show some changes particularly in terms of band wavenumber values upon complexation. The $\nu(\text{C}\equiv\text{N})$ vibrations for free TCNE are observed as a doublet at 2196 and 2182 cm⁻¹ and for free TCNQ at 2203 cm⁻¹. These vibrations occur at 2214 and 2193 cm⁻¹ in the spectrum of [(AMPP)(TCNE)] and at 2181 and 2168 cm⁻¹ in the spectrum of complex [(AMPP)(TCNQ)].



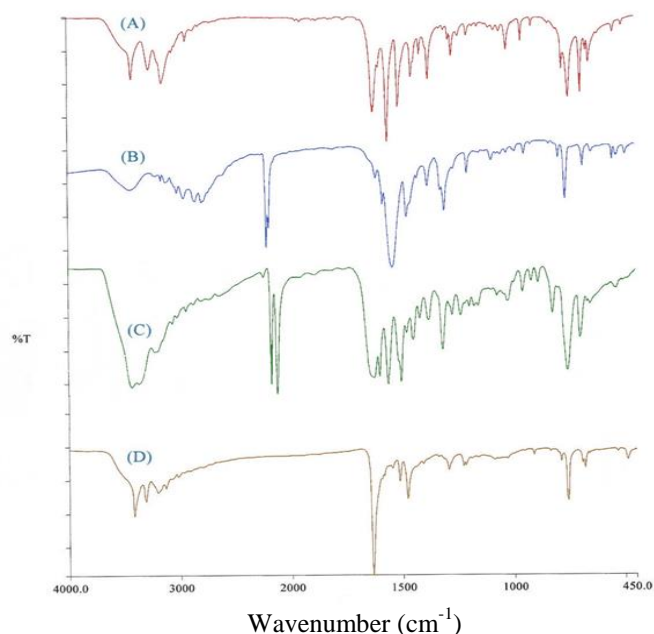
Counts vs. Mass-to-Charge (m/z)
Fig 10a. Mass spectra of CT- complexes: (A) [(AMPP)(TCNE)].



Counts vs. Mass-to-Charge (m/z)
Fig 10b. Mass spectra of CT- complexes: (B) [(AMPP)(TCNQ)].



Counts vs. Mass-to-Charge (m/z)
Fig 10c. Mass spectrum of CT- complex [(AMPP) I]⁺



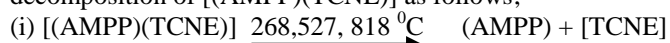
Wavenumber (cm⁻¹)
Fig 11. Infrared absorption spectra of: (A) 5-amino-1-methyl-3-phenylpyrazole (AMPP); (B) [(AMPP)(TCNE)]; (C) [(AMPP)(TCNQ)] and (D) [(AMPP) I]⁺ I₃⁻

3.4. Thermal analysis measurements

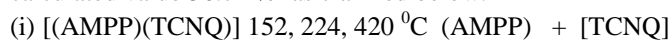
Thermal analysis (TG and DTG) were carried out under a nitrogen gas flow (20 ml min⁻¹) within a temperature range 30 – 900 °C and heating rate 10 °C ml⁻¹ to confirm the proposed formula and structure for the obtained CT- complexes. Fig. 12 (A), (B) and (C) show the thermograms of [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]⁺ I₃⁻ respectively. The thermogravimetric data for these complexes are shown in Table 4. The obtained data support the calculated formulas and structures of the formed CT-complexes. The degradations steps and their associated temperatures vary from one complex to another depending on the type of constituents as well as on the stoichiometry in each case. Obviously, these two factors have pronounced effects on the type of bonding, relative complex stabilities and geometries.

For the CT- complex [(AMPP)(TCNE)] shown in Fig.12 (A) the donor AMPP decomposed in three steps at temperatures 268, 527 and 818 °C with total mass 56.72 % (57.49 % calculated) corresponds to the decomposition of the donor [AMPP] with a mass loss of 56.72 % very close to the calculated value of 57.49 %. These steps are followed by another degradation step starting at 850 °C with mass loss 20.94 % and remaining weight 22.34 % both together

correspond to the loss of [TCNE] with total weight loss 43.28 % very close to the calculated value 42.52 % Table 4. Accordingly, a proposed mechanism for the thermal decomposition of [(AMPP)(TCNE)] as follows;



The second product [(AMPP)(TCNQ)] is shown in Fig.12 (B); at 152, 224 and 420^oC correspond to the loss of [AMPP] with total mass loss of 43.88 % (45.89 % calculated). These steps are followed by another degradation step starting at 450^oC with mass loss 52.72 % and remaining weight 3.45 % both together correspond to the loss of [TCNQ] with total weight loss 56.12 % very close to the calculated value 56.72 % as clarified below:



The third complex [(AMPP) I₃⁺ I₃⁻] is shown in Figure 12 (C); at 209^oC corresponds to the loss of the [AMPP] with a mass loss of 23.91 % close to the calculated value of 25.44 %. The 2[I₂] acceptor decomposed at 260, 280 and 396^oC with mass loss of 71.95 % and remaining residual weight 2.61 % both together correspond to the loss of 2[I₂] with total weight loss 74.56 % same like the calculated value 74.56 % ; a proposed mechanism for the thermal decomposition of [(AMPP) I₃⁺ I₃⁻] is as follows:

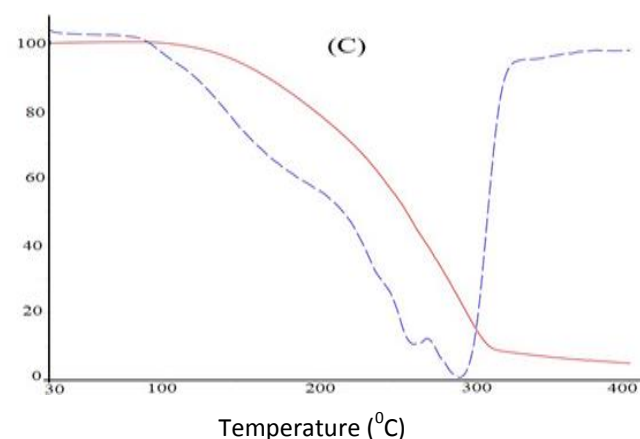
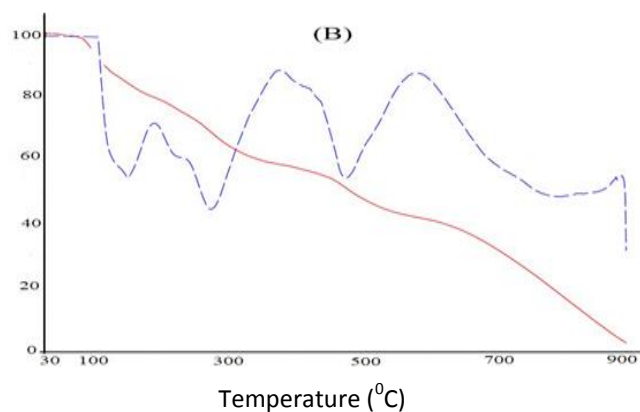
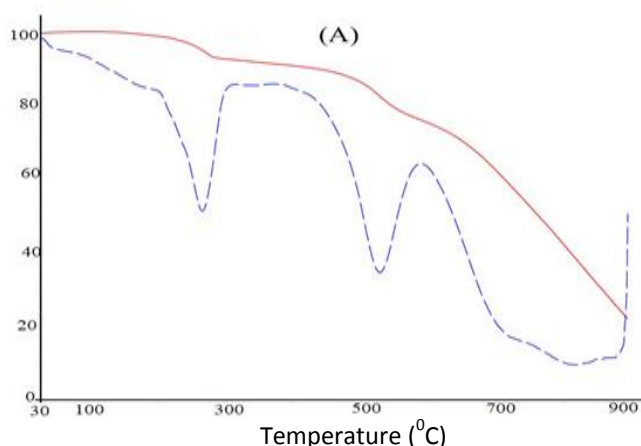
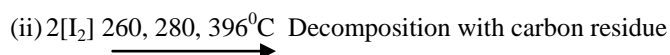
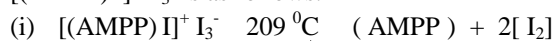


Fig 12. TG – DTG curves of: (A) [(AMPP)(TCNE)], (B)[(AMPP)(TCNQ)] and [(AMPP) I₃⁺ I₃⁻].

4. Conclusion

Charge–transfer interactions between the donor 5-amino-1-methyl-3-phenylpyrazole and the π - acceptors TCNE, TCNQ and σ -acceptor I₂ were studied in CHCl₃ at 25^oC. We were able to show that the reaction stoichiometry is the same for π -acceptors, TCNE, TCNQ; the obtained charge – transfer (CT) complexes were shown to have the formulas: [(AMPP)(TCNE)] and [(AMPP)(TCNQ)] and for σ - acceptor iodine was shown to have the formula [(AMPP) I₃⁺ I₃⁻]. Our obtained results indicate that the nitrogen atom (>NH) of the donor is involved in the complexation with acceptors. The measurements show the donor – acceptor molar ratio are 1:1 for the acceptors TCNE, DDQ and 1:2 for I₂. Next studies will focus on using different donors with different substituent groups attached to the nitrogen atoms to further investigate the nature of such complexation.

Table 4. Thermal decomposition data^a for the [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I₃⁺ I₃⁻] CT- complexes.

Complex	Reaction stoichiometry	DTG max. (°C)	TG% mass loss found / calc.	Lost species
[(AMPP)(TCNE)]	1: 1	268, 527, 818	56.72 / 57.49	AMPP
		850	20.94 / 42.52	TCNE
			22.34	Residue
[(AMPP)(TCNQ)]	1: 1	152, 224, 420	43.88 / 45.89	AMPP
		450	52.67 / 56.72	TCNQ
			3.45	Residue
			23.91 / 25.44	AMPP
[(AMPP) I ₃ ⁺ I ₃ ⁻]	1:2	209	71.95 / 74.56	2 [I ₂]
		260, 280, 396	2.61	Residue

^aThermal measurements were carried out under N₂ flow rate at 20 ml.min⁻¹.

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