Pyrazoles are a class of compounds that have the ring $C_3N_2$ 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 $\pi$- and $\sigma$-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 $\pi$- and $\sigma$-electron acceptors.

The $\pi$-acceptors are tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) and the $\sigma$-electron acceptor is iodine.

All reactions were carried out in CHCl$_3$ as a solvent. The obtained results enabled us to investigate the stoichiometries and structure inherent in these formed new CT-complexes.

**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 $\pi$-acceptors tetracyanoethylene (TCNE) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) and $\sigma$-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$^+ I^- 3$] in full agreement with the known reaction stoichiometry in solution as well as the elemental measurements. The formation constant $k_{CT}$, molar extinction coefficient $\varepsilon_{CT}$, free energy change $\Delta G^0$ and ECT energy have been calculated for the CT-complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I$^+ I^- 3$].

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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 CHCl₃ 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⁺ I⁻] 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 CHCl₃ 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 CHCl₃ 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 P₂O₅. 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⁺ I⁻] 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 CHCl₃](image)

**Fig. 1.** Electronic absorption spectra of 5-amino-1-methyl-3-phenylpyrazole-TCNE reaction in CHCl₃. (A) [AMPP] = 5 x10⁻³ M; (B) [AMPP] = 5 x10⁻² M; (C) [TCNE] = 5 x10⁻³ M; 1:1 AMPP-TCNE mixture, [AMPP] = [TCNE] = 5 x10⁻³ M.

Photometric titration measurements based on these absorptions were performed in order to determine the reaction stoichiometry in CHCl₃ (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 CHCl₃ measured at the 563 nm absorption](image)

Fig. 3 shows the electronic spectra recorded in the region 400–700 nm of the reaction of 7,7,8,8-tetra cyanoquinodimethane (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 CHCl₃ as shown in Fig. 4. The results showed that the donor–TCNE 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 [(AMPP)(TCNE)].

Photometric titration measurement was performed for AMPP–I₂ reaction in CHCl₃ shown in Fig. 6. The results showed that the donor–I₂ 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 [(AMPP)I]⁺ I⁻ [21].

The reactions should be as in the following steps.

(i) (AMPP)⁺ + I₂ → [(AMPP)I]⁺

(ii) [(AMPP)I]⁺ + I⁻ → [(AMPP)I]⁺I⁻

(iii) [(AMPP)I]⁺I⁻ + I₂ → [(AMPP)I]⁺I⁻I₂

Fig. 3. Electronic absorption spectra of 5-amino-1-methyl-3-phenylpyrazole - TCNQ reaction in CHCl₃ (A) [AMPP] = 5 x 10⁻³ M; (B) [TCNQ] = 5 x 10⁻³ M; 1:1 AMPP-DDQ mixture, [AMPP] = 5 x 10⁻³ M and [TCNQ] = 5 x 10⁻³ M.

Fig. 4. Photometric titration curve for 5-amino-1-methyl-3-phenylpyrazole - TCNQ reaction in CHCl₃ 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-I₂ charge-transfer complex and is associated with the electronic transitions at 360 and 264 nm.

Table 1 shows the spectroscopic data of the resulting CT-complexes. These obtained UV/Vis spectra of the CT-complexes [(AMPP)(TCNQ)], [(AMPP)(TCNE)] and [(AMPP)I]⁺I⁻ have clarified that the variation of the CT-absorptions of TCNQ, TCNE and I₂ 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 C≡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 C≡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 (Kᵣ) and molar extinction coefficient (εᵣ) 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 CHCl₃ at 25 °C were calculated. The formation constant, Kᵣ (lmol⁻¹), and the molar extinction coefficient εᵣ (lmol⁻¹cm⁻¹) have been calculated for the complexes [AMPP](TCNQ), and [(AMPP)(TCNE)] using the known [22] Eq. (1) of 1:1 complexes:

$$\frac{A_1D_1\lambda}{A} = \frac{1}{k\varepsilon} + \frac{A_2\lambda}{\varepsilon}$$  (1)

The corresponding spectral parameters for the complexes...
[(AMPP) I]+ I[ used the known [23] Eq. (2) of 1:2 complexes:

\[
\frac{(A)_{\text{c}} + D_{\text{c}} \cdot \varepsilon}{A} = \frac{1}{k \varepsilon} + A \cdot \frac{(A)_{\text{c}} + 4D_{\text{c}}}{\varepsilon}
\]  

(2)

Table 1. Spectroscopic data for the CHCl₃ solutions of solid CT- complexes of AMPP with the acceptors TCNE, TCNQ and I₂

<table>
<thead>
<tr>
<th>Complex</th>
<th>Color</th>
<th>Absorptions (nm)</th>
<th>Stoichiometry (Donor: acceptor)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(AMPP)(TCNE)]</td>
<td>yellow</td>
<td>563s, 380s</td>
<td>1:1</td>
</tr>
<tr>
<td>[(AMPP)(TCNQ)]</td>
<td>Dark blue</td>
<td>515s</td>
<td>1:1</td>
</tr>
<tr>
<td>[(AMPP) I]+ I₂</td>
<td>Dark brown</td>
<td>360s, 264s</td>
<td>1:2</td>
</tr>
</tbody>
</table>

The reagents AMPP, TCNE, TCNQ and I₂ have no measurable absorptions in the region of study with used concentrations; s, strong.

Where Ao and Do are the initial concentrations of the acceptors and donors, respectively, while A is the absorbance at the mentioned CT bands and \( \ell \) is the cell path length (1cm). The data obtained throughout this calculation are given in Table 2. Plotting the values of \( \frac{A_0 D_0}{A} \) against \( (A_0 + D_0) \) values of equation (1) and plotting values of \( (A_0)D_0 \ell/A \) versus \( A_0 \) (Ao + 4Do) values of equation (2), straight lines were obtained with a slope of 1/ \( \varepsilon \text{CT} \) and intercept of (1/ \( K_{\text{CT}} \text{ect} \)) as shown in Figs. (7-9) for the CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]+ I₂.

The reactants AMPP, TCNE, TCNQ and I₂ have no measurable absorptions in the region of study with used concentrations; s, strong.

Where Ao and Do are the initial concentrations of the acceptors and donors, respectively, while A is the absorbance at the mentioned CT bands and \( \ell \) is the cell path length (1cm). The data obtained throughout this calculation are given in Table 2. Plotting the values of \( \frac{A_0 D_0}{A} \) against \( (A_0 + D_0) \) values of equation (1) and plotting values of \( (A_0)D_0 \ell/A \) versus \( A_0 \) (Ao + 4Do) values of equation (2), straight lines were obtained with a slope of 1/ \( \varepsilon \text{CT} \) and intercept of (1/ \( K_{\text{CT}} \text{ect} \)) as shown in Figs. (7-9) for the CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]+ I₂.

The more negative the value for \( \Delta G \) the closer to the right the reaction will proceed in order to achieve equilibrium. The charge transfer energy \( \Delta G^0 \) of the formed solid CT- complexes is calculated using the following Eq. (4) [26, 27]:

\[
E_{\text{CT}}(nm) = \frac{1243.667}{\lambda_{\text{CT}}}
\]  

(4)

Where \( \lambda_{\text{CT}} \) is the wavelength of the band of the studied CT- complexes [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP) I]+ I₂. The \( E_{\text{CT}} \) values calculated from equation (4) are listed in Table 2. These results in table 2 ( \( K_{\text{CT, ect}}, \Delta G^0 \) and ECT) are clarifying that the obtained solid CT- complexes formed in the reaction of the donor AMPP with the \( \pi \)-acceptors TCNE, TCNQ and \( \sigma \)-acceptor I₂ have high CT energy and formation constants \( K_{\text{CT}} \). 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 I₂ the relationship becomes the following Eq. (5) [28]:

\[
E_{\text{CT}} = Ip - 5.2 + \frac{1.5}{Ip - 5.2}
\]  

(5)

These complexes show high values of both the formation constant (\( K_{\text{CT}} \)) and the molar extinction coefficient (\( \varepsilon \text{CT} \)). These high values of \( K_{\text{CT}} \) 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.
Table 2. Values of $k_{CT}$, $\Delta G^0$, $E_{CT}$ and $\varepsilon_{CT}$ of CT- complexes [[AMPP](TCNE)], [[AMPP](TCNQ)] and [[AMPP] $I^+$ I$^-$. in CHCl$_3$.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$k_{CT}$/mol$^{-1}$</th>
<th>$\Delta G^0$/cal mol$^{-1}$</th>
<th>$E_{CT}$/eV</th>
<th>$\lambda_{max}$/nm</th>
<th>$\varepsilon_{CT}$/l mol$^{-1}$cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[<a href="TCNE">AMPP</a>]</td>
<td>0.013 x 10$^4$</td>
<td>2.9 x 10$^4$</td>
<td>2.21</td>
<td>380</td>
<td>0.0011 x 10$^4$</td>
</tr>
<tr>
<td>[<a href="TCNQ">AMPP</a>]</td>
<td>0.030 x 10$^4$</td>
<td>1.5 x 10$^4$</td>
<td>2.42</td>
<td>515</td>
<td>0.056 x 10$^4$</td>
</tr>
<tr>
<td>[[AMPP] $I^+$ I$^-$.]</td>
<td>0.001 x 10$^4$</td>
<td>9.6 x 10$^4$</td>
<td>3.45</td>
<td>360</td>
<td>0.012 x 10$^4$</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>AMPP</th>
<th>[<a href="TCNE">AMPP</a>]</th>
<th>[<a href="TCNQ">AMPP</a>]</th>
<th>[[AMPP] $I^+$ I$^-$.]</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3424ms</td>
<td>3436m</td>
<td>3411s</td>
<td>3417ms</td>
<td>$V$ (H$_2$O); KBr</td>
</tr>
<tr>
<td>3270ms, 3151ms</td>
<td>3161ms</td>
<td>3168m</td>
<td>3132m</td>
<td>$V$ (C-H); AMPP</td>
</tr>
<tr>
<td>2937w</td>
<td>2958m</td>
<td>3148w</td>
<td>3071w</td>
<td>$V$ (C≡N); TCNE</td>
</tr>
<tr>
<td>2873w</td>
<td>2854m</td>
<td>3108w</td>
<td>2168s</td>
<td>and TCNQ</td>
</tr>
<tr>
<td>1558s</td>
<td>1539s</td>
<td>1599w</td>
<td>1632s</td>
<td>$V$ (C≡C); TCNQ, TCNQ, AMPP</td>
</tr>
<tr>
<td>1512s</td>
<td>1584w</td>
<td>1573s</td>
<td>1544w</td>
<td>Free and complexed AMPP</td>
</tr>
<tr>
<td>1378s</td>
<td>1383m</td>
<td>1382w</td>
<td>1339w</td>
<td>$V$ (C-N); AMPP</td>
</tr>
<tr>
<td>1306w</td>
<td>1325w</td>
<td>1363w</td>
<td>1314w</td>
<td>$V$ (C-C); AMPP</td>
</tr>
<tr>
<td>1286ms</td>
<td>1213s</td>
<td>1345ms</td>
<td>1293m</td>
<td>$\delta$ (CH) deformation,</td>
</tr>
<tr>
<td>1203w</td>
<td>1205w</td>
<td>1207w</td>
<td>1215w</td>
<td>$\delta$ (CH) out of plane</td>
</tr>
<tr>
<td>1156w</td>
<td>1196w</td>
<td>1171ms</td>
<td>1188w</td>
<td>$\delta$ (CH) out of plane</td>
</tr>
<tr>
<td>1105w</td>
<td>1149w</td>
<td>1094s</td>
<td>1089w</td>
<td>$\delta$ (CH) out of plane</td>
</tr>
<tr>
<td>1082w</td>
<td>1096w</td>
<td>1079w</td>
<td>1026w</td>
<td>$\delta$ (CH) bending; AMPP</td>
</tr>
<tr>
<td>961ms</td>
<td>991w</td>
<td>988w</td>
<td>986w</td>
<td>$\delta$ (CH) out of plane</td>
</tr>
<tr>
<td>912ms</td>
<td>849w</td>
<td>919m</td>
<td>912w</td>
<td>AMPP</td>
</tr>
<tr>
<td>827w</td>
<td>837w</td>
<td>823w</td>
<td>834w</td>
<td>$\delta$ (CH) out of plane</td>
</tr>
<tr>
<td>448s</td>
<td>493w</td>
<td>481ms</td>
<td>487ms</td>
<td>$\delta$ (CH) out of plane</td>
</tr>
<tr>
<td>448s</td>
<td>493w</td>
<td>481ms</td>
<td>487ms</td>
<td>$\delta$ (CH) out of plane</td>
</tr>
</tbody>
</table>

s, strong; w, weak; br, broad; $V$, 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] $I^+$ I$^-$.]. 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 ($K_{CT}$, $\varepsilon_{CT}$, $\Delta G^0$ and $E_{CT}$) are clarifying that the obtained solid CT-complexes formed in the reaction of the donor AMPP with the $\pi$-acceptors TCNE and TCNQ and $\sigma$- 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 solid CT- complexes [[AMPP](TCNE)], [[AMPP](TCNQ)] and [[AMPP] $I^+$ I$^-$.]. Fig.10a (A) shows the mass spectrum of [[AMPP](TCNE)] and Fig.10b (B) shows the mass spectrum of the complex [[AMPP] $I^+$ I$^-$.]. 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] $I^+$ I$^-$.]. 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).

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These results in table 2 ($K_{CT}$, $\varepsilon_{CT}$, $\Delta G^0$ and $E_{CT}$ ) are clarifying that the obtained solid CT-complexes formed in the reaction of the donor AMPP with the $\pi$-acceptors TCNE and TCNQ and $\sigma$- 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 solid CT- complexes [[AMPP](TCNE)], [[AMPP](TCNQ)] and [[AMPP] $I^+$ I$^-$.]. 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] $I^+$ I$^-$.]. 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-phenylpyrazole [(AMPP) (TCNE)], [(AMPP) (TCNQ)] and [(AMPP) I⁺ I⁻] 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 ν(N–H) vibrations of the free 2-amino-6-methylpyridine in [(AMPP)(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⁺ I⁻], two medium absorptions are observed at 3312 and 3206 cm⁻¹.

The outlined changes in ν(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 ν(C≡N) vibrations of the acceptor TCNE and TCNQ show some changes particularly in terms of band wavenumber values upon complexation. The ν(C≡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)].

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⁺ I⁻], 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 degradation 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;

(i) [(AMPP)(TCNE)] \(268,527,818 \ ^{0}\text{C}\) (AMPP) + [TCNE] \\
(ii) [TCNE] \(850^{0}\text{C}\) Decomposition with carbon residue

The second product [(AMPP)(TCNQ)] is shown in Fig.12 (B); at 152, 224 and 420\(^{0}\text{C}\) 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 \(^{0}\text{C}\) with mass loss 52.67 % and remaining weight 2.61 % 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:

(i) [(AMPP)(TCNQ)] \(152, 224, 420 \ ^{0}\text{C}\) (AMPP) + [TCNQ] \\
(ii) [TCNQ] \(450^{0}\text{C}\) Decomposition with carbon residue

The third complex [(AMPP)\(^{+}\)I\(^{3-}\)] is shown in Figure 12 (C); at 209 \(^{0}\text{C}\) corresponds to the loss of the [AMPP] with a mass loss of 23.91 % close to the calculated value of 25.44 %. The 2[I\(^{2-}\)] acceptor decomposed at 260, 280 and 396 \(^{0}\text{C}\) with mass loss of 71.95 % and remaining residual weight 2.61 % both together correspond to the loss of 2[I\(^{2-}\)] with total weight loss 74.56 % same like the calculated value 74.56 %; a proposed mechanism for the thermal decomposition of [(AMPP)\(^{+}\)I\(^{3-}\)] is as follows:

(i) [(AMPP)\(^{+}\)I\(^{3-}\)] \(209^{0}\text{C}\) (AMPP) + 2[I\(^{2-}\)] \\
(ii) 2[I\(^{2-}\)] \(260, 280, 396^{0}\text{C}\) Decomposition with carbon residue

Table 4. Thermal decomposition data* for the [(AMPP)(TCNE)], [(AMPP)(TCNQ)] and [(AMPP)\(^{+}\)I\(^{3-}\)] CT- complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Reaction stoichiometry</th>
<th>DTG max. (°C)</th>
<th>TG % mass loss found / calc.</th>
<th>Lost species</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(AMPP)(TCNE)]</td>
<td>1:1</td>
<td>268,527,818</td>
<td>56.72 / 57.49</td>
<td>AMPP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>208,850</td>
<td></td>
<td>TCNE</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.94 / 42.52</td>
<td></td>
<td>Residue</td>
</tr>
<tr>
<td>[(AMPP)(TCNQ)]</td>
<td>1:1</td>
<td>152,224,420</td>
<td>43.88 / 45.89</td>
<td>AMPP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>450</td>
<td>52.67 / 56.72</td>
<td>TCNQ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.45</td>
<td></td>
<td>Residue</td>
</tr>
<tr>
<td>[(AMPP)(^{+})I(^{3-})]</td>
<td>1:2</td>
<td>209</td>
<td>71.95 / 74.56</td>
<td>2[I(^{2-})]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>260,280,396</td>
<td>2.61</td>
<td>Residue</td>
</tr>
</tbody>
</table>

*Thermal measurements were carried out under N\(_2\) flow rate at 20 ml.min\(^{-1}\).
References