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Spectrophotometric and Raman studies of 2, 2, 6, 6-tetramethylpiperidine donor with different σ and π-acceptors

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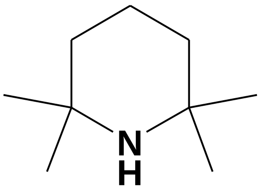
Abstract:- ***Charge-transfer (CT) complexes formed between 2,2,6,6-tetramethylpiperidine (TMP) as donor with iodine (I_2), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone(DDQ),p-chloranil (CHL) and piciric acid (PA) as acceptors have been studied spectrophotometrically. The synthesis and the molar ratio of 2,2,6,6-tetramethylpiperidine CT-complexes can be summarized as $[(Pip)_2]I^+.I_3^-$, [(Pip)(DDQ)], $[(Pip)(CHL)_2]$ and [(Pip)(PA)]. These complexes are readily prepared from the reaction of TMP with I_2, DDQ, CHL, and PA within $CHCl_3$ solvent. UV-Vis spectrophotometric, Raman laser spectra and elemental analyses (CHN) characterize the TMP charge-transfer complexes. Benesi-Hildebrand and its modification methods were applied to the determination of association constant (K), molar extinction coefficient (ε).***

Keywords: **2, 2, 6, 6-tetramethylpiperidine; spectrophotometrically; Raman spectra; σ and π-acceptors.**

I. INTRODUCTION

The theory of charge-transfer interactions or the molecular complexes produced between electron donor and electron acceptor ownership Mulliken's [1,2] this theory has been successfully applied to many interesting studies [3] amongst them is the possible role of CT-complexes in chemical reactions [4]. The charge-transfer (CT) interaction has been widely recently. Charge-transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation [5, 6]. These complexes have great attention for non-linear optical materials and electrical conductivities [7-10]. Electron donor-acceptor (EDA) interaction is also important in the field of drug-receptor binding mechanism [11], in solar energy storage [12] and in surface chemistry [13] as well as in many biological fields [14]. On the other hand, the EDA reactions of certain π- acceptors have successfully utilized in pharmaceutical analysis [15]. For these wide applications extensive studies on CT-complexes of π- acceptors have been performed [16]. 2,2,6,6-Tetramethylpiperidine (TMP; Formula I) is an organic compound with the molecular formula $C_9H_{19}N$. It is a cyclic amine with a six-member ring. It is a colorless liquid and has a "fishy", amine-like odor. This amine is used in chemistry as a hindered base (hindered amine) because it can dissolve in organic solvents unlike inorganic bases such as potassium hydroxide. The piperidine skeleton is present in numerous natural alkaloids such as piperine, the main active chemical agent in black pepper and relatives, pharmaceutical drugs such as raloxifene and minoxidil. In the literature survey [17-20] reveals that little attention has been paid to thermodynamic and electronic spectral characteristic does not contain any information on structure behavior of the CT interactions of this compound (TMP) with σ- and π-acceptors. Charge-transfer complexes of organic species are intensively studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor [21, 22]. Also, protonation of the donor from acidic acceptors are generally rout for the formation of ion pair adducts [23-25]. The solid charge-transfer complexes formed between iodine and several types of electron donors such as aromatic hydrocarbons, polycyclic amine, mixed oxygen/nitrogen cyclic bases, aromatic/aliphatic amines have been studied and categorized [26-35]. The tri-iodide ion I_3^-, penta-iodide ion I_5^-, and ennea-iodide ion I_9^- were formed through the reaction of iodine with various donors like, metal acetylacetonates [36-38], polyazacyclic [39-41], and crown ethers [42-45]. Some of charge-transfer complexes show very interesting applications in the analysis of some drugs in pure form or in pharmaceutical preparations [46, 47]. The charge-transfer (CT) in fullerene-based [48, 49] compounds is currently of great interest since these materials can be utilized as superconductors [50] and to produce non-linear optical activity [51]. This paper aimed to spectrophotometric studies of charge-transfer complexes between TMP and different acceptors (I_2, DDQ, CHL, and PA) in $CHCl_3$ solvent. Raman laser spectra of TMP charge-transfer complexes were discussed.



Formula I: Structure of 2, 2, 6, 6-tetramethylpiperidine (TMP)

II. EXPERIMENTAL

A. Materials

All chemicals used throughout this work were analar or extra pure grade. TMP was of analytical reagent grade (Merck reagent). The acceptors were purchased from Aldrich. Stock solutions of TMP or of acceptors were freshly prepared and the spectroscopic grade chloroform (Merck Co.) and chloroform (BDH) were as used as received

B. Synthesis of TMP-acceptor charge-transfer complexes

The solid charge-transfer complex of (TMP) with acceptors (iodine, DDQ, CHL and PA) were prepared by mixing 1 mmol of the donor in chloroform 10 ml with 1 mmol of the each acceptors in the same solvent with constant stirring for about 30 min. The solutions were allowed to evaporate slowly at room temperature, the solids filtered and washed several times with little amounts of solvent, and dried under vacuum over anhydrous calcium chloride. The charge-transfer complexes; $[(TMP)_2]I^+.I_3^-$ (brown), [(TMP)(DDQ)] (brown yellow), [(TMP)(CHL)] (brown) and [(TMP)(PA)] (yellow).

C. Physical measurements

Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400. The Electronic Spectra of the donors, acceptors and the resulted charge-transfer complexes were recorded in the region of (200-800 nm) by using a Jenway 6405 Spectrophotometer with quartz cells, 1.0 cm path in length. Photometric titration were performed at 25 ^oC for the reactions of TMP donor with acceptors in chloroform, as follow: the concentration of the TMP in the reaction mixtures was kept fixed at $5.0x\ 10^{-4}$ M, while the concentration of acceptors were changed over a wide range with donor: acceptor molar ratios varying from 1:0.25 to 1:3.00. IR measurements (KBr discs) of the solid donors, acceptor and CT complexes were carried out on a Bruker FT-IR spectrophotometer (400-4000 cm^{-1}). Raman laser spectra of samples were measured on the Bruker FT-Raman with laser 50 mW.

III. RESULTS AND DISCUSSION

Results of elemental analysis for all the 2,2,6,6-tetramethylpiperidine charge-transfer complexes are in agreement with the calculated ones, and the composition of the charge-transfer complexes is matched with the molar ratios presented from the photometric titration occurs between TMP and acceptors (σ- and π- acceptor). All the complexes are insoluble in cold and hot water, but easily soluble in most organic solvent. The spectra show characteristic real absorption bands which are not present in the spectra of the reactants free acceptors and TMP. These bands are assigned at 365 nm, 410 nm, 570 nm and 410 nm, due to the CT-complexes formed in the reactions of TMP with iodine, DDQ, CHL and PA in the chloroform solvent. The electronic (UV-Vis.) absorption spectra of the iodine, DDQ, CHL and PA complexes were measured in $CHCl_3$ solvent and shown in Fig. 1. In each acceptor the complex is formed by adding X ml of 5.0×10^{-4} M (acceptor) (X = 0.25, 0.50, 0.75, 1.00, 1.50, 2.00, 2.50 and 3.00 ml) to 1.00 ml of 5.0×10^{-4} M TMP donor. The volume of the mixture in each case was completed to 10 ml with the respected solvent. The concentration of TMP in the reaction mixture was kept fixed at 0.50×10^{-4} M, while the concentration of each acceptor was varied over the range of 0.125×10^{-4} M to 1.500×10^{-4} M for TMP/Acceptor systems in chloroform solvent. These concentrations produce TMP: Acceptor ratios extending along the range from 1:0.25 to 1:3.00. These photometric titration curves were obtained according to the known methods [52] by the plot of the absorbance against the X ml added of each acceptor (Fig. 2). The equivalence points shown in these curves clearly indicate that the formed CT-complex between TMP and (iodine, DDQ, CHL and PA) is 1:1. The formation of 1:1 complex was strongly supported by elemental analysis. The appearance of the two absorption bands around ≈ 360 and ≈ 290 nm are well known [53-55], to be characteristic for the formation of the tri-iodide ion Accordingly, the formed complex was formulated as $[(TMP)_2]I^+.I_3^-$. The electronic spectra of the reaction mixtures containing DDQ, CHL and PA with TMP as donor in $CHCl_3$ show absorption bands located at 410, 570 and 410 nm (Fig. 1). These definite absorption bands do not belong to any of the reactants and well known to be characteristic of the formation of new CT-complexes; [(TMP)(DDQ)], [(TMP)(CHL)] and [(TMP)(PA)]. Photometric titrations between (TMP) and mentioned acceptors; DDQ, CHL and PA systems reveals that the stoichiometry of the reactions is 1:1 (Fig. 2). This was concluded on the bases of the obtained elemental analysis data of the isolated solid CT-complexes. The equivalence points shown in this curve clearly indicate that the formed CT-complexes between TMP and each acceptor are 1:1. It was of interest to observe that the solvent has a pronounced effect on the spectral intensities of the formed charge-transfer complex. The 1:1 modified Benesi-Hildebrand equation [56] was used in the calculations.

$$\frac{C_a^o C_d^o l}{A} = \frac{1}{K\varepsilon} + \frac{C_a^o + C_d^o}{\varepsilon} \quad .... (1)$$

Where C_a^o and C_d^o are the initial concentrations of the acceptor and the TMP donor, respectively, K is a formation constant, ε is a molar extinction coefficient, and A is the absorbance of the definite band for TMP-

Acceptor system, respectively. The $C_a^o . C_d^o / A$ values are plotted against the corresponding $C_a^o + C_d^o$ values, straight lines was obtained with a slope of 1/□ and intercept of 1/k□ as shown in Fig. 3. The oscillator strength *f* was obtained from the approximate formula given in Equation (2) [57]

$f = (4.319 \times 10^{-9})\ \square_{max} . \square_{1/2}$ …. (2)

where $\square_{1/2}$ is the band-width for half-intensity in cm^{-1}. The oscillator strength value together with the corresponding dielectric constants, *D*, of the solvent used are given in Table 1. The trend of the values in this table reveals two facts:

The [(TMP)(Acceptor)] shows high values of both the equilibrium constant (*K*) and the extinction coefficient (□). This high value of *K* reflects the high stability of the TMP complex as a result of the expected high donation of the TMP consequently high value of □ which is known to have a high absorptivity values [58-60]. The transition dipole moment (μ) of the CDS complex (Table 1) have been calculated from Equation (3) [61]

$\mu = 0.0958[\square_{max}\ \square_{1/2} / \square_{max}]^{1/2}$ …. (3)

where $\nu_{1/2}$ is the bandwidth at half-maximum of absorbance, ε_{max} and ν_{max} are the extinction coefficient and wavenumber at maximum absorption peak of the CT complexes, respectively. The ionization potential (I_p) of the free TMP donor was determined from the CT energies of the CT band of its respective complex with different π–acceptors using the following Aloisi and Piganatro [62] relationships.

$I_D\ (ev) = 5.76 + 1.53 \times 10^{-4}\ \nu_{CT}$ …. (4)

Where E_{CT} is the energy of the CT of the TMP complex, the energy of the π-σ^*, n-σ^*, π-π^* or n-π^* interaction (E_{CT}) is calculated using Equation (5) [63]

$E_{CT}\ (ev) = (h\nu_{CT}) = 1243.667 / \lambda_{CT}\ (nm)$ ….(5)

where, λ_{CT} is the wavelength of the complexation band. Determination of resonance energy *(R_N)*, from Briegleb and Czekalla [64] theoretically derived the relation given in Equation (6)

$\varepsilon_{max}\ (l.mol^{-1}.cm^{-1}) = 7.7 \times 10^{-4} / [h\nu_{CT} / [R_N] - 3.5]$ …. (6)

where ε_{max} is the molar extinction coefficient of the complex at the maximum 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 obviously is a contributing factor to the stability constant of the complex (a ground state property). The value of R_N for the charge-transfer complex under study is given in Table 1. The standard free energy changes of complexation (ΔG^o) were calculated from the association constants by Equation (7) [53].

$\Delta G^o = - 2.303\ RT \log K_{CT}$ …. (7)

where ΔG^o is the free energy change of the complexes (KJ mol^{-1}), R is the gas constant (J mol^{-1} K), T is the temperature in Kelvin degrees (273 + °C), and K_{CT} is the association constant of the complexes (l mol^{-1}) in respective solvent at room temperature, the value thus calculated is represented in Table 1. The data of ΔG^o has a negative value according to the higher values of formation constant, and then the formation process of TMP charge-transfer complex is exothermic feature reactions.

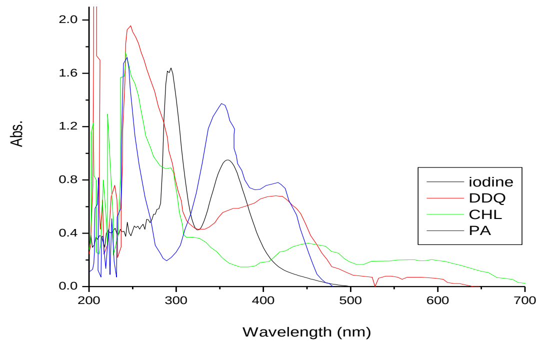


Fig. 1: Electronic absorption spectra of: TMP-I_2, TMP-DDQ, TMP-CHL and TMP-PA reaction in $CHCl_3$.

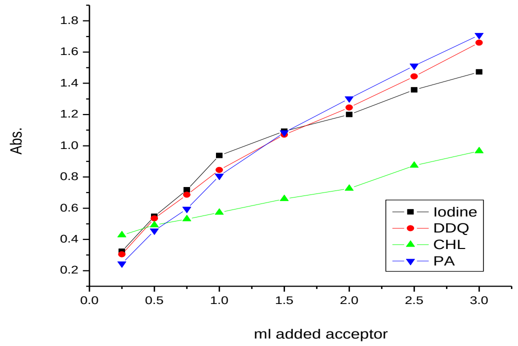


Fig. 2: Photometric titration curves of: TMP-I_2, TMP-DDQ, TMP-CHL and TMP-PA reaction in $CHCl_3$.

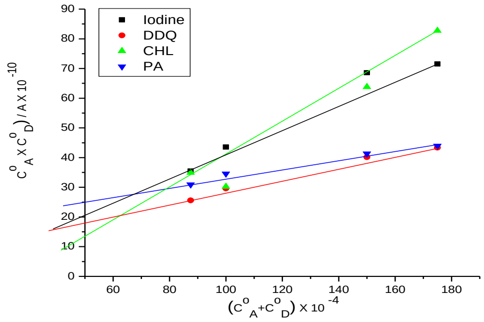


Fig. 3: The plot of $C_a^o(4C_d^o + C_a^o)$ against $C_d^o . C_a^{o2}$/A of: TMP-I_2, TMP-DDQ, TMP-CHL and TMP-PA reaction in $CHCl_3$.

Table 1: Spectrophotometric results of the TMP-I_2, TMP-DDQ, and TMP-CHL and TMP-PA reaction in $CHCl_3$

Complex	λ_{max}	E_{CT}	K	ε_{max}	f	μ	I_p	R_N	ΔG°
[(TMP)]I.I_3	365	3.41	75000	20000	8.64	26	9.95	0.464	-27816
[(TMP)(DDQ)]	410	3.03	59000	14000	6.05	23	9.49	0.337	-27222
[(TMP)(CHL)]	570	2.18	48000	13000	5.61	26	8.44	0.232	-26710
[(TMP)(PA)]	410	3.03	7686	7280	3.14	17	9.49	0.215	-27171

λ_{max}= nm, E_{CT}= eV; K= $Lmol^{-1}$, ε_{max}= $Lmol^{-1}cm^{-1}$, ΔG°(25 °C) = $kJmol^{-1}$

The Raman laser spectrum of $[(TMP)_2]I^+.I_3^-$ was recorded in the region 4000-50 cm^{-1} then interestingly, focused in the region of 50-500 cm^{-1} and given in Fig. 4. The spectrum associated with the $[(TMP)_2]I^+.I_3^-$ complex shows the characteristic bands for the triiodide ion at 222, 143 and 111 cm^{-1}. These bands can be attributed to the □$_{as}$(I-I), □$_{s}$(I-I) and □ □ □□□. These three absorptions do not exist in the spectrum of the donor, TMP. However, triiodide ion may be linear ($D_{\infty h}$) or non linear (C_{2v}). Group theoretical analysis indicates that the triiodide ion with C_{2v} symmetry displays three vibrations □$_{s}$(I-I); A_1, □$_{as}$(I-I); B_2 and □ □ □□□ □ □A_1, all are infrared active in agreement [53] with the observed three infrared bands for $[(TMP)_2]I^+.I_3^-$. Accordingly, the formed iodine complex is formulated as $[(TMP)_2]I^+.I_3^-$. The conversion of iodine molecules into polyiodide units are well known in the literature [53-55]. The Raman spectrum of the molecular complex of DDQ with TMP indicate the □ (C≡N) and □ (C-Cl) of the free acceptor are shifted to lower wave number values on complexation. Since DDQ is enhanced from any acidic centers, thus we may conclude that the molecular complexes are formed through □-□ *and/or *n*-□ * charge migration from HOMO of the donor to the LUMO of the acceptor. Also, the shift of □ (C=O) of DDQ from higher to lower value on complex formation. Raman spectrum of the molecular complex of DDQ with TMP indicate that the doublet peaks of □ (C≡N) of the free acceptor molecule which exhibited at (2250 and 2231 cm^{-1}) was shifted to a lower wave number value (2248 and 2211 cm^{-1}) while the □ (C=O) absorption band of the free DDQ at 1673 cm^{-1} was shifted to lower value (1620 cm^{-1}). Careful interpretation of Raman spectrum strongly supported that the CT-interaction in the case of TMP/DDQ complex occurs through *n*-□ * transition deprotonation of –NH group of TMO to only one of the CN groups by forming intermolecular hydrogen bonding (Fig. 5). In addition, the characteristic band concerning stretching vibration motion of –NH in TMP-DDQ was disappear, this assigned due to sharing of –NH group in the charge-transfer complexation between donor and acceptor. In the case of [(TMP)(CHL)] CT-complex, the vibration frequency of the group for TMP observed at 3393 cm^{-1} is absence in the Raman spectrum of the TMP-CHL complex. The assignment of this band is interestingly, due to the intermolecular chelation between hydrogen of –NH donor against oxygen of one of the carbonyl groups of acceptor. The stretching vibrational of □ (C=O) absorption band in the case of the free CHL is appeared at 1685 cm^{-1} but under complexation this band was shifted to lower intensity value. Doubtless, the IR spectra strongly supported that the CT-interaction in the case of TMP/CHL complex take place through *n*-□ * transition (Fig. 5). Evidently, in the spectrum of [(TMP)(CHL)] complex, the vibrations group of δ(N-H); 1608 cm^{-1}, □ (C-N); 1245 cm^{-1}, CNC; 494 cm^{-1} deformation show clearly changes compared with those of free TMP (1630, 1275 and 550 cm^{-1}). The bands associated with □ (C-Cl) vibration that appeared at 900, 750 and 700 cm^{-1} in the free CHL were shifted to lower wave numbers and decreasing in the intensities of the characteristic peaks. This result due to the increasing in the electron density around CHL moiety therefore the charge transfer interaction and deprotonation of donor upon complexation. The Raman spectrum of the formed CT complex TMP/PA is given in Fig. 4. The band assignments are appearance of a group of Raman spectral bands in the spectrum of the charge-transfer complex supports the conclusion that a deformation of the electronic environment of TMP is occurred by accepting a proton from PA. These results caused to the protonation of the ^+NH group of the donor through the proton transfer from the acidic center on the PA acceptor from –OH to the basic center on the donor ^+NH group. Such assumption is strongly supported by the appearance of an absorbance bands between 1633-1561 cm^{-1} due to $^+NH_2$ deformation, and all absorbed bands at 942 and 832 cm^{-1} which attributed to NH_2 rock. This is further supported by disappear or decrease in the stretching of OH group of PA acceptor due to intermolecular hydrogen bond forming. The shift of the Raman bands of the acceptor part to lower wave numbers and those of the donor part to higher values reflects a donor to acceptor charge transfer of π- π* interaction, $D_{HOMO} \rightarrow D_{LUMO}$ transition [65]. Accordingly, the hydrogen bonding between donor and acceptor can be formulated as Fig. 5. The [(Pip)(PA)] charge-transfer complex is particularly soluble in CH_3OH. The equivalent conductance values at $1.0x10^{-4}$ molar concentration indicated that this complex has a small limit of conductivity. The data of conductivity confirms that this complex has a positive ($^+NH_2$) and negative charge (O^- of acidic in picric acid) resulted from CT transition. The low conductivity values for the CT-complexes may be due to intermolecular hydrogen bond formation.

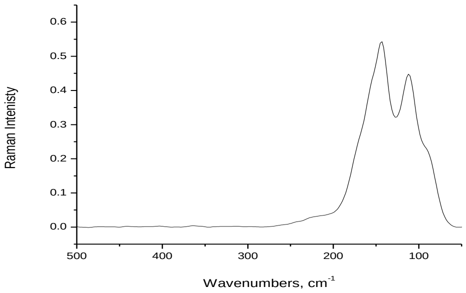


Fig. 4a: Raman spectrum of the [(TMP)]I.I$_3$ CT-complex

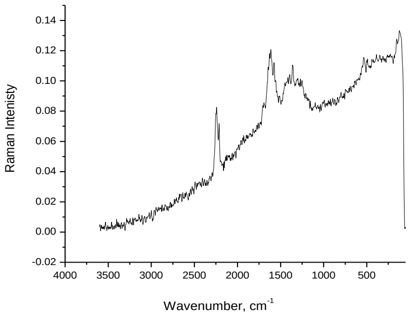


Fig. 4b: Raman spectrum of the [(TMP)(DDQ)] CT-complex

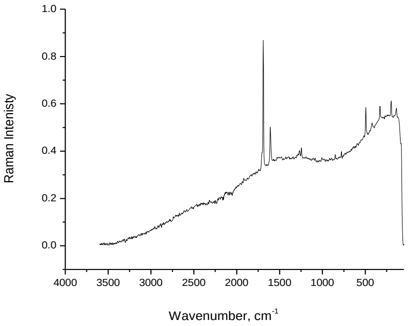


Fig. 4c: Raman spectrum of the [(TMP)(CHL)] CT-complex

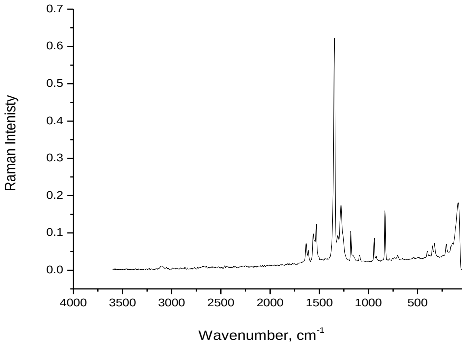


Fig. 4d: Raman spectrum of the [(TMP) (PA)] CT-complex

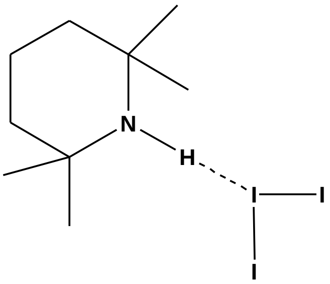


Fig. 5a: Structure of the [(TMP)]I.I$_3$ CT-complex

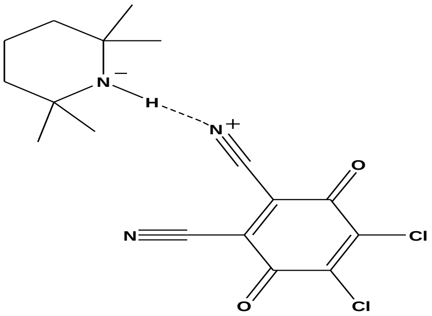


Fig. 5b: Structure of the [(TMP)(DDQ)] CT-complex

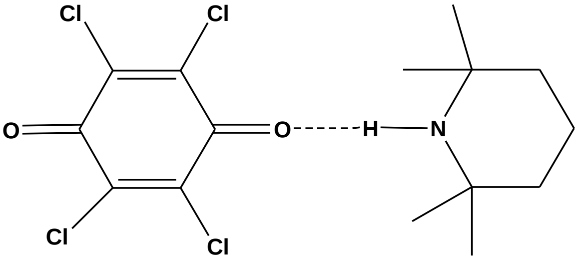


Fig. 5c: Structure of the [(TMP) (CHL)] CT-complex

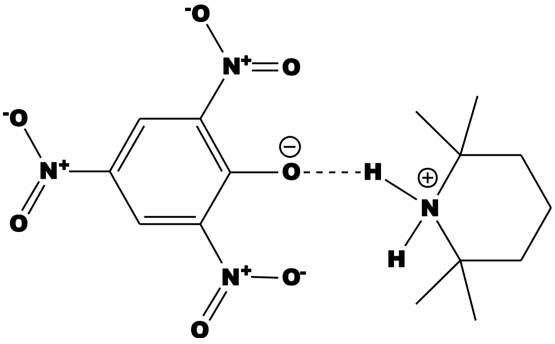


Fig. 5d: Structure of the [(TMP)(PA)] CT-complex

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