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Studies on the nature of molecular interaction in o-phenanthroline picrate

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ABSTRACT

Spectroscopic and computational studies on the CT complex of 1,10-phenanthroline and picric acid have been studied with a view to know the type and nature of interaction between them. The FTIR data revealed that the complex in the solid state is a mixture of two complexes viz. components in ionic states and non-ionic states. Quantum mechanical calculations have been carried out to investigate the nature and type of interactions between them using high level DFT-theory. The binding energy of complex involving ionic states of the components is approximately 21 times higher than that of the complex formed by components in unionized states.

Keywords: Picric acid, o-phenanthroline, CT-complex, DFT, Counterpoise.

INTRODUCTION

Many molecular complexes of picric acid are known from along time[1-11]. Mulliken[1] suggested that the formation of molecular complexes from two molecules can arise from a π- molecular orbital of a Lewis base to a vacant π- molecular orbital of a Lewis acid with resonance between the dative structure and no bond structure stabilizing the complex. He also suggested the possibility of a complex formation through donating of an electron from a non- bonding molecular orbital in a Lewis base to a vacant π-orbital of an acceptor (n- π) interaction with resonance stabilization of the combination.

Kross and Fassel [3] studies the regularities in the i.r spectra of forty picric acid molecular complexes. They noted that the nitro-asymmetric stretching and the out of plane C-H bending vibrations of the picric acid components are sensitive to complex formation. They suggested that the frequencies of these vibrations can be correlated with the type of complex formed i,e π– π or n- π- type charge transfer. They observed a noteworthy behavior of o-phenanthroline-picrate, which showed behavior different from other lone pair containing nitrogenous aromatic compounds. On the basis of i.r spectra of the complex recorded in nujol mulls with a Perkin Elmer model 13 infrared spectrophotometer using sodium chloride optics they inferred the nature of this complex as π– πcontrary to the expected n- π; this observation was based on the basis of a single nitro asymmetric stretching vibrations as against two vibrations shown by similar basic compounds. They thought that the steric factor may be the reason behind the π– π complex formation.The observation pertaining to peculiar behavior and the explanation led the present authors to reinvestigate the nature of interaction in view of the availability of more sophisticated FTIR instrument and availability of computational facility for determining the visual molecular structure. Therefore, this paper reports the results of the FTIR spectra of o-phenanthroline-picrate in KBr pellet and visual molecular structure arrived at on the basis of DFT calculations.

MATERIALS AND METHODS

The IR spectra were recorded on Perkin Elmer spectrometer.

The computational work was carried out on Jaguar panel of the Schrodinger 2012 software on quad core processor-3770K, liquid cooling system Corsair H70, 8 GB RAM, 4.5 GHz Bio-setting computer. The drawing of the relevant structures were done with Chem-Draw ultra 8.0 software and optimized on Chem3D ultra 8.0.The quantum mechanical calculations were carried out using DFT-BPLY-3 method of theory choosing . 6-31g $^{\#\#}$ basis set. The molecule was assigned net zero charge and singlet multiplicity.

2..1Synthesis of Charge transfer complex

Picric acid (0.01m) and o-phenanthroline mono-hydrate (0.01m) were dissolved separately in minimum volume of THF. The two solutions were mixed together and heated under reflux on a water bath. The canary yellow crystals, which separated, were collected by filtration. The crystals were washed with hot THF, dried in an air oven at 110°C and then kept overnight in a vacuum desiccators.

2.2 Computational details:

The drawing of the structure of the donors and acceptors were carried out on the Chem-Draw ultra 8.0 software and the structures were transported to Chem3D ultra 8.0 software for optimization. The optimized structures of required donor and acceptor were exported to the Maestro-9.3 panel of the Schrodinger 2012software. The interaction geometry between the donor and acceptor, the actual non covalent interaction site, the counterpoise corrected binding energies of each of the charge transfer complexes were implemented on the Jaguar panel using its counterpoise platform. The calculations were done using defaults as prescribed in the manual of the Schrodinger software 2012. The structures of the charge transfer complexes were visualized on the monitor by navigating on the workflow menu of the Maestro 9.3 as a result of which manage surface dialog appears through which structures were imported and visualized. The measurement of the distances between different atoms and the dihedral angles between the two components were measured using the prescribed procedure in the manual.

2.3 Computational methods

The initial structure of donor, acceptor and the CT-complexes were built with Chem-Draw ultra8.0 and the structure was optimized on Chem3D ultra 8.0. The structure was exported to Maestro 9.3 of Schrodinger 2012 version. The optimization of the structure was done on the Jaguar panel of the Maestro 9. The DFT-BPLY-3 method of theory was chosen. 6-31g $^{\#\#}$ basis set was selected and 255 basis functions were created for calculation. The molecule was assigned net zero charge and singlet multiplicity. In the solvent menu of the jaguar panel PBF solver was used for optimization of the structure in both the gaseous. The optimization the gaseous state and in the different solutions were done in ground state of the molecule. The counterpoise calculations were performed on the plate form of Jaguar panel of the Schrodinger software.

RESULTS AND DISCUSSION

A) Interpretation of IR spectra

The IR spectra of the charge transfer complex appears in the fig1 , and the IR spectra data of picric acid, 1,10-phenanthroline-picrate and the assignment of bands appear in the Table1.

a) Interpretation of IR spectra data of picric acid

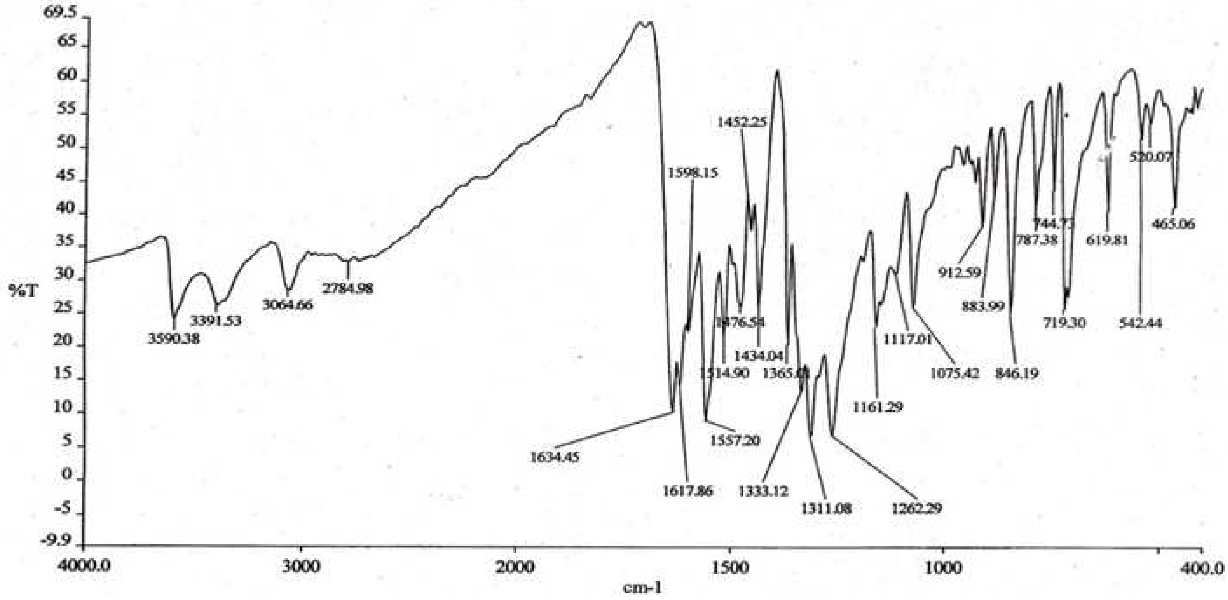
Picric acid contains three nitro groups where stretching frequencies are not expected to equivalent. One nitro group ortho to phenolic-OH involved in the hydrogen bond with that group. As a result of this interaction, the asymmetrical stretching frequency of nitro group is rotated out of the plane of the ring because of steric- effect of –OH group. The para nitro group is coplanar with the ring as is one of the ortho nitro group but it is not involved in the intra-molecular H-Bonding. The three nitro group asymmetrical stretching frequencies are not resolved and appears as one broad band with maximum at 1529cm^{-1}.

b) Interpretation of IR spectral data of o-phenanthroline-picrate.

The heterocyclic nitrogen atoms in o-phenanthroline should lead to the formation of an n - π complex but the appearance of only a single nitro asymmetric stretching vibrations indicates π-π *complex is formed. In this compound steric factor may be inhibiting the formation of n - π complex in favour of π-π complex .The appearance of a group of FTIR spectral band in the spectra of CT-complex supports the conclusion that a deformation of the electronic environment of ortho phenanthroline has occurred by accepting a proton from Picric acid. The shift of FTIR bands of the acceptor to lower wave no.s reflects a donor to acceptor charge transfer of π-π* interaction i,e

$D_{HOMO} \text{-----------------}> A_{LUMO}$ transition

Fig.1. FTIR spectra of CTC of 1,10-phenanthroline-picrate



The FTIR spectrum of the complex of picric acid and o-phenanthroline shows the presence of of characteristics absorption bands due to the varied force constant in the donor and acceptor species on account of the prevalent charge transfer mechanism .This makes the crystals of the type more ionic than other organic crystals. In the FTIR spectra of the complex the O-H and N-H streatching vibrations are observed at 3590.38 cm-1 and 3391.63 cm-1 respectively . The band at 3064cm^{-1} is due to aromatic C-H stretching vibration. The NHdeformation mode is observed by the absorption at 1634.45 cm^{-1} . This band overlaps with the aromatic C=C stretching vibrations The asymmetric and symmetric stretching vibration of NO_2 groups are observed at 1557.20 cm^{-1} and 1333.12 cm^{-1} respectively .Normally the asymmetrical stretching vibration of NO_2 group is sensitive to polar influences and the electronic state of the species .Therefore it has been realized that the shift to the lower frequency of $\nu_{asy}(NO_2)$ vibration (1557 cm^{-1}) in the spectrum of the complex compared with the picric acid (1606 cm^{-1}) is due to increase electron density on the picric acid moeity owing to charge transfer complex. The absorption at 1634.45 cm^{-1} 1617.86 and 1598 cm^{-1} are due to aromatic C=C absorption stretching vibrations . The absorption at 1311.08 cm^{-1} is due to the C-N stretching vibration .The C-O stretching vibration is observed as a band of medium intensity at 1117.01 cm^{-1} .The C-H out of the plane bending is shown by the presence of a band at 787.38 cm^{-1} .The C-NO_2 stretching is observed at 912.59 cm^{-1} . The NO_2 wagging vibrations are observed at 744.73 cm^{-1} and 719.3 cm^{-1}

Table1. The assignment of the various absorptions frequencies of the compounds are given below

Picric acid	1,10-phennathroline	Complex	Assignment
3108 s, br		3590.38	ν_{O-H}
-		3391.53	ν_{N-H}
-		3064.66	ν_{C-H}
2875 w		-	$\nu_{s(C-H)}$
		2784.98	ν_{N-H}bending
	1646		$\nu_{C =N}$
1630 vs		1634.45	ν_{N-H}def
	1617		$\nu_{C=C}$
1529 br			
1606 ms			$\nu_{C=C}$Ar
-	1591	1617.86	$\nu_{C=C}$Ar
-		1557.2	$\nu_{asy(NO2)}$
-	1505	1434.04	ν_{C-H}def
1437 ms			
-			
1341 vs		1365	$\nu_{s(NO2)}$
1275 vs		1311.08	ν_{C-N}
1154 ms	1137	1262.29	ν_{C-O}
1083 ms	1092	1161.29	ν_{C-H} in plane bending
916 ms 830 w	856	1075.42	ν_{C-H} in plane bending
779 sharp	783	912.59	ν_{C-NO2}-str
vms		846.19	N_{C-C}
703 ms	704	787.38	ν_{C-H}out of plane bending
663 w		719.3	ν_{NO2}wagging

s, strong, w, weak ; m, medium; sh, shoulder, v, very ; vs, very strong ; br, broad n stretching vs symmetrical stretching ν_{asy} *asymmetry*

FTIR spectra of CT-complex formed between 1,10-phenanthroline(D) and picric acid (A) revealed that the nature of interactions between the D and A are of two types. The presence of absorption band at 3590.38 cm^{-1} due to O-H stretching in the complex indicates that picric acid is in the neutral state while the appearance of a new absorption band at 3391.53 cm^{-1} is due to $^{+}$N-H stretching showing the another complex formed which is in ionic state.

c) comparison of the IR spectra of the complex with the results of Kross and Fassal:
Krauss and Fassel had reported appearance of only one band at 1545 cm^{-1}due to NO2 stretching; this led them conclude the π–π nature of the complex. We, on the other hand, have observed two nitro asymmetric stretching vibration- one stronger at 1557 and other weaker at 1514.9 cm^{-1}.We have observed the C-H out of plane bending vibrations at 787.38, 774.73 and 719.3cm-1 indicating both the n–π and π–π nature of the complex, while, Krauss and Fassel had reported appearance of C-H out of plane bending at 784.9 cm-1. The presence of absorption band at 3590.38 cm^{-1} is due to –OH stretching in the complex. This indicates that picric acid in the complex is in unionized state. The appearance of a new absorption band at 3391.53 cm-1 is due to –N^{+}-H stretching, The appearance of the band is possible only if the donor and acceptor are in their ionized states. Thus it appears that the complex is a mixture of π–π complex and ionic compound.

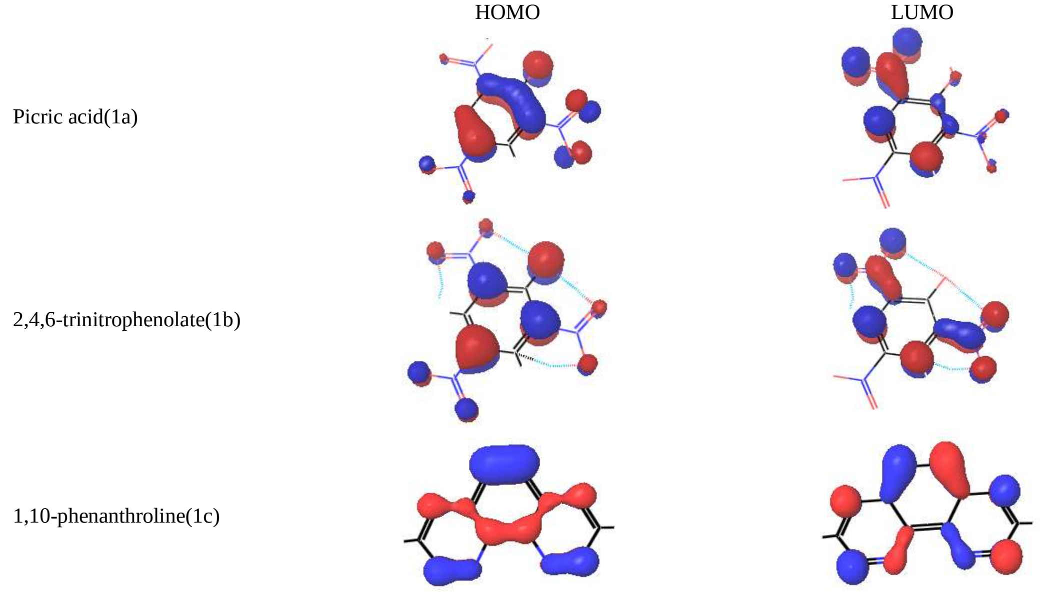
B) Interpretation of computational studies:
The DFT calculation of the two kinds of complexes i.e containing donor and acceptor in unionized states and the donor and acceptor in ionized states gives us the energy of HOMO, LUMO, energy gap of HOMO-LUMO and the gas phase energy of Picric acid(1a), 2,4,6-trinitrophenolate(1b) 1,10-phenanthroline(1c), 1,10-phenanthrolin-1-ium(1d), 1,10-phennathroline picrate(1e), 1,10-phenanthrolin-1-ium-2,4,6-trinitrophenolate(1f) in eV calculated by DFT method appear in Table-21.

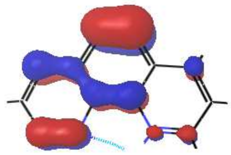
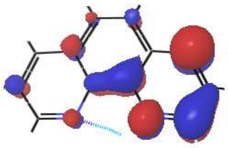
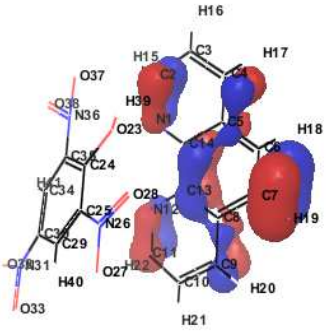
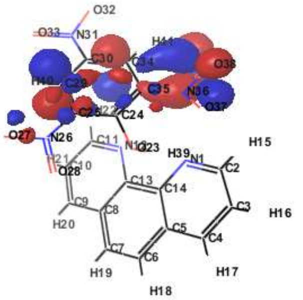
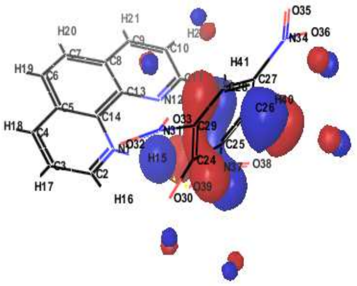
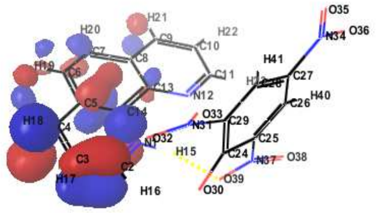
Table 2: Energy of HOMO, LUMO, Energy gap and gas phase energy of donors acceptors, and CT-complexes in eV calculated form DFT

compounds	Gas Phase Energy	HOMO	LUMO	Energy gap
Picric acid(1a)	-25060.7062	-8.2233	-3.9076	-4.3157
2,4,6-trinitrophenolate(1b)	-25046.7848	-2.9334	0.6585	-3.5919
1,10-phenanthroline(1c)	-15554.6349	-6.2586	-1.4150	-4.8436
1,10-phenanthrolin-1-ium(1d)	-15565.6283	-10.5852	-6.5035	-4.0817
1,10-phenanthroline-picrate(1e)	-40615.7084	-6.6124	-3.3742	-3.2382
1,10-phenanthrolin-1-ium-2,4,6-trinitro-phenolate(1f)	-40615.6268	-5.9049	-3.3742	-2.5307

The surfaces of HOMO's and LUMO's of the acceptors and donors and CT-complex appear in the fig.2 .

Fig2. Picture of HOMO, LUMO of donors , acceptor, and CT complexes (in neutral and ionic states) calculated by DFT method



1,10-phenanthrolin-1-ium(1d)		
1,10-phenanthroline-picrate(1e)		
1,10-phenanthrolin-1-ium-2,4,6-trinitro-phenolate (1f)		

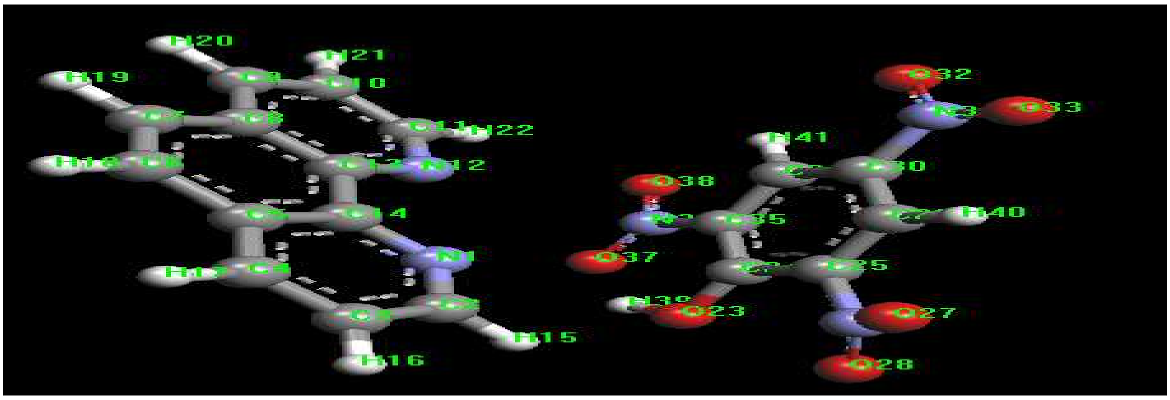
The corrected binding energy (E), counterpoise (CP) for two types of complexes appear in Table3.

Table3. The corrected binding energy (E), counterpoise (CP) for different complexes by DFT calculations

compounds	Counterpoise Correction (kcal/mol)	Binding Energy (kcal/mol)	E+CP
1,10-phenanthroline-picrate(1e)	3.50	-3.44	0.06
1,10-phenanthrolin-1-ium-2,4,6-trinitro-phenolate (1f)	4.49	-73.04	-68.55

The complex (1f) has binding energy approximately 21 times higher than the complex (1e) so in the mixture of (1e) and (1f), (1f) predominates.

Fig. 3. Interaction diagram of optimized structures of 1,10-phenanthroline and picric acid in neutral states using DFT



The shape of the complex comprising unionized donor and acceptor

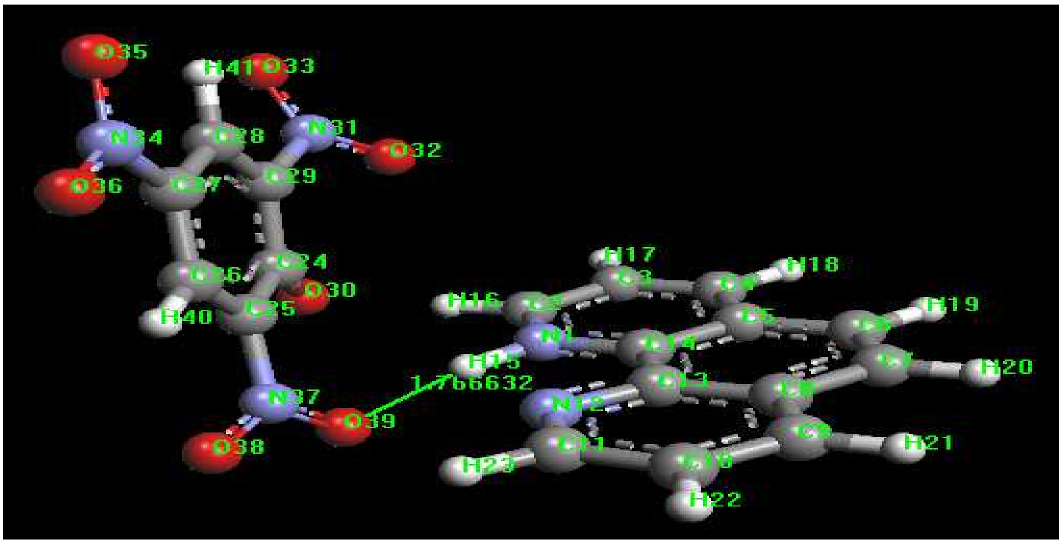
From the computational studies the visual picture of the complex is like that shown in fig 4.1. i) The donor and acceptor align in such a way to form a V shaped complex. O 33 of p- nitro group is situated far away from C4 of the D molecule at a distance of 7.600A$^{o.}$

H39 attached with O23 of picric acid is intra-molecular H-bonded with O-37 of ortho nitro-group ii) N1 and N12 of the donor molecule is located at a distance of 3.226A^{o} and 4.088 respectively from H39.)

The shape of the complex comprisingionized donor and acceptor

The DFT calculations show that picric acid is perpendicular to the molecular plane of 1,10-phenanthroline as shown in the fig. 5

Fig.4 Interaction diagram of optimized structures of 1,10-phenanthroline and picric acid in ionic states using DFT



i. O39 of ortho nitro-group is hydrogen bonded with H15 of D.
ii. O30 of phenolate is located at a distance of 2.579 A^{o} .
iii. N34 of p- nitro of phenolate is situated faraway from C10 of the D.

CONCLUSION

From the comparison of the counterpoise corrected binding energies of the two CTs complexes, it was found that the CT-complex formed in ionic state is much strongly (approximately 21 times) than in neutral state. The higher binding energy in ionic state is due to intermolecular H- bonding between protonated H of the D and oxygen atom of one of the o-nitro-group of 2,4,6-trinitrophenolate ion.

IR and the computational work led us to conclude that the charge transfer complex is actually is a mixture of $\pi-\pi$ and n-π type complexes and not simple $\pi-\pi$ complex as concluded by Kross and Fassal

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