



Scholars Research Library

Archives of Applied Science Research, 2014, 6 (2): 67-75
(<http://scholarsresearchlibrary.com/archive.html>)



Theoretical investigation on the interactions between some indolyl schiffs bases and picric acid in CT-complexes

K. K. Srivastava^a, Shubha Srivastava^b, Md. Tanweer Alam^a and Rituraj^a

^aDepartment of Chemistry, Vinoba Bhave University, Hazaribagh

^bDepartment of Chemistry, KBW College, Hazaribagh

ABSTRACT

The computational study on the interactions of picric acid with some indolyl Schiff's bases having four different interaction sites have been carried out by DFT method both in neutral and ionic states, The geometry of the resulting charge transfer complex, the actual site of interaction, nature of interactions and counterpoise corrected binding energies, etc. have been determined. The interaction in the ionic state was found to be much stronger than the corresponding molecules in the neutral states.

Keyword: DFT, Indolyldiethylaniline derivatives, Picric acid, HOMO, LUMO Binding energy

INTRODUCTION

Non covalent interactions play a dominant role in many important areas of chemistry, from material design[1-4] to molecular biology[5-10]. A detailed understanding of the physical origin and scope of such interactions include hydrogen bonds, ion pairs, the hydrophobic interactions, the π - π interactions, cation- π - interactions [11], etc.

High-level theoretical studies have provided an excellent method for investigating non-covalent interactions. Semi empirical methods, eg. AM1 ab- initio calculation, and DFT methods with extended basis set such as 6-31G^{##} have been used by several authors[12-15]. In many cases the theoretical predictions have been experimentally found correct and in many other cases the work has been complemented by the computational work.

Given the relevance of non-covalent interactions to a number of biological structures there is a special interest in the simple aromatics that models amino acid side chains. These are benzene (phe), phenol (Tyr), indole(Trp) and imidazole (His). Of these, indole is clearly stronger cation- π -binder suggesting that Trp may be especially important in cation- π bindingsuggesting that Trp may be especially important in cation- π - binding[11]. It is interesting that electrostatic maps [16,17] and quantitative calculations[18] indicate that the benzene ring is the preferred cation- π -bonding site over the 5-membered pyrrole type ring. Levitt and Perutz[19-21] concluded from their study of haemoglobin-drug interactions that aromatic rings can serve as general hydrogen bond acceptors Mitchell[22-23] showed that amino acids containing sp² hybridized nitrogen the stacked geometry is favoured over perpendicular hydrogen bonding geometry by a 2.5:1 ratio (fig-1)

The stacked arrangement seems especially interesting because of a possible hydrophobic contribution. Although gas phase calculations indicate that the perpendicular, hydrogen bonding arrangement of guanidium /benzene pair is more energetically favourable than the stacking interaction, this preference is completely reversed in aqueous simulations. A large part of the reversal is done to the better hydrogen bonding to water by the guanidium in the stacked geometry.

Keeping in view the biological importance of the indole nucleus we investigated the preferred site of interactions between picric acid and some Schiff's bases derived from indole derivatives in 1:1 molecular complex and determined the geometry of the complex in the gaseous state. Our interest was in determining whether the two components form molecular complex in their neutral state or in ionic state. The donor has four sites for interaction with the acceptor i) the six membered benzene ring of the indole moiety ii) the five membered pyrrole ring of the indole moiety. iii) the $-\text{CH}=\text{NH}-$ group and iv) the aryl group attached to nitrogen. Therefore, in this paper we report the actual site of non-covalent interaction between the donor and acceptor, the optimization geometry, and the counterpoise corrected binding energies of the charge transfer complexes.

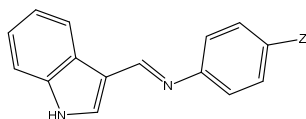
MATERIALS AND METHODS

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-B3LYP method of theory choosing 6-31g^{##} basis set. The molecule was assigned net zero charge and singlet multiplicity

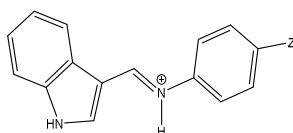
1.1. Computational details:

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 2012 software. 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.

In the present study three donors having structure



where Z= H, OCH₃, NO₂ and acceptor picric acid were used for the theoretical calculation of 1:1 charge transfer complex similarly the protonated form of the above three donors were used to study their interactions with the phenolate ion derived from picric acid.



RESULTS AND DISCUSSION

The energy of HOMO and LUMO, energy gap between HOMO and LUMO and the gas phase energy of Picric acid(1a), 2,4,6-trinitrophenolate(1b), (E)-1-(1H-indol-3-yl)-N-phenylmethanimine(2a), (E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine (2b), (E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine(2c), (E)-N-((1H-indol-3-

yl)methylene)benzenaminium (3a), (E)-N-((1H-indol-3-yl)methylene)-4-methoxybenzenaminium(3b), (E)-N-((1H-indol-3-yl)methylene)-4-nitrobenzenaminium(3c), (E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with picric acid(4b), (E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine compound with picric acid(4c), (E)-N-((1H-indol-3-yl)methylene)benzenaminium 2,4,6-trinitrophenolate(5a), (E)-N-((1H-indol-3-yl)methylene)-4-methoxybenzenaminium 2,4,6-trinitrophenolate(5b), (E)-N-((1H-indol-3-yl)methylene)-4-nitrobenzenaminium 2,4,6-trinitrophenolate(5c) in eV calculated by DFT method appear in Table-1. The surfaces of HOMO's and LUMO's of the acceptors and donors appear in the Figure2 while that of charge transfer complexes appear in Figure.3. The counterpoise correction and the corrected binding energies of the Charge transfer complexes 4(a-c) and 5(a-c) appear in Table.2. The structural parameters namely the atomic distances and the dihedral angles between the two components of the charge transfer complexes formed between donor and acceptor in the neutral state 4(a-c) and the donor and acceptor in ionic states 5(a-c) appear in Table-3 and Table-4 respectively. The interactions are mainly electrostatic in nature, except 5b where hydrogen bond was also found to be present. From the perusal of the Table-2 it appears that the charge transfer complex formed in ionic states are 62.39 times strongly bonded than the CT complex formed in the neutral states of the donor and acceptor in which the donor aryl group is unsubstituted. If the donor aryl group is substituted by OCH₃ or NO₂ group then the counterpoise corrected binding energies of the CT complexes formed in ionic states are 64.14 and 86.16 times higher than the corresponding CT complexes formed in the neutral states. So, the formation of the CT complex in the ionic states of donor and acceptor is favorable in the order -NO₂ > -OCH₃ > -H. But, if viewed in isolation the binding energies of the CT complexes in 4(a-c) is in the order -H > -OCH₃ > -NO₂. Similar order is also observed in case of the CT complexes 5(a-c) formed between ionic states of the donors and acceptors.

In case of interaction in (4a), Schiff's base the O40 of the NO₂ group located at the para position is attracted to the π-electron of the pyrrole ring of the indole moiety. The two molecules are almost perpendicular to each other and the O34 of the other nitro group is attracted to the phenyl ring of the Schiff's base. The visualization of the surface of the complex (4b) revealed that the picric acid molecule is perpendicular to the indole moiety. O41 is attracted to N2 of Schiff's base, C3 of methoxy substituted aryl group, C11 of pyrrole ring and C13 of six membered ring of indole and situated at a distances of 2.671, 3.307, 4.030 and 3.109 Å respectively. In (4c), the complex O32 of OH of picric acid is closest to N2 of C=N of Schiff's base. The distance between O32 and N2 is 3.50 Å and O41 of p-nitro of picric acid is situated at a distance of 3.60 Å from C15 of six membered ring of Indole moiety. While aryl group attached with Schiff's base is located outside showing no interaction. The indole moiety is looking like π-stacking with picric acid moiety. The C14 of indole molecule and C43 of picric acid is situated at a distance of 3.651 Å.

In (5a) the O37 of the acceptor is located at a distance of 2.342 Å from H20 of donor. The O37 is also attracted to the un-substituted ring and also to the aryl ring of the indole moiety; the distance being 3.094 and 3.123 Å respectively. In the complex (5b), point of inter molecular attraction is similar, but H18 and O41 are hydrogen bonded. In (5c) The pattern of interaction is reversed; the O⁻ ion is now on opposite side and the donor is attracted towards the acceptor through the oxygen atom of the nitro group located at the para carbon of the phenolate ion.

The site of interactions:

In 4a the O35 of the nitro group is located at a distance of 3.305 Å from C6 of the aryl ring attached to nitrogen of the donor, the O40 of the p-nitro group is located at a distance of 3.648 Å from C10 of the pyrrole ring of the indole moiety. C36 is separated from C8 at a distance of 3.913 Å. The third nitro group does not experience any attraction with the donor. The donor and acceptor form a V-shaped CT complex. So, the point of interactions are varying, but the interaction of the ortho nitro group with the isolated aryl ring is maximum.

The complex(4b) picric acid and six membered ring of indole moiety are held through π-π interaction. They are situated at a distance of about 3.8 Å from the acceptor. The p-methoxy phenyl group is situated far away from the

acceptor. The O43 of NO₂ group is closer to N9 of pyrrole ring of indole moiety of the Schiff's base; the distance being 3.29 Å while one of the o-nitro group of picric acid is nearer to C=N of the Schiff's base. The distance between N48 of the o-nitro group of picric acid and N of C=N is 3.692 Å. Thus complex formed in this case has binding energy of -1.10 kcal/mol is mainly of a π-π complex between a six membered benzene ring of indole moiety and picric acid moiety.

The binding energy of the complex 4c is lowest (-0.69 kcal/mol). In this complex O32 of OH of picric acid is nearer to N2 of C=N of Schiff's base. The distance between O32 and N2 is 3.50 Å and O41 of p-nitro group of picric acid is situated at a distance of 3.60 Å from C15 of benzene ring of Indole moiety while the p-nitro phenyl group attached with Schiff's base is located outside showing no interaction. The indole moiety is appears like π-stacked with picric acid moiety. The C14 of indole molecule and C43 of picric acid are situated at a distance of 3.651 Å.

Thus picric acid is mainly attracted to benzene ring of indole moiety and C=N of Schiff's base through π-π interaction.

Among the three ionic complex (5a) has the showing highest corrected binding energy (i.e. 71.96 kcal/mol) the pattern of binding and interaction sites are different from the corresponding complex 4a in neutral states. The CT complex has almost T-shaped appearance. The O37 of phenolate ion is highly attracted to NH⁺ group of Schiff's base. The distance between H18 and O37 is found to be 1.622 Å. The other nitro groups are also closer to N2. The O40 and O45 of ortho nitro group are at a distance of 2.787 Å and 4.634 Å while p-NO₂ group shows no interactions/influence on the interaction sites of the donor moiety.

Among all studied complexes, (5b) shows second highest binding energy. It has intermolecular H-bonding between O41 and H18 also. The visualization of the surfaces of the complex indicates that the picric acid moiety is almost perpendicular to the imine group of the donor molecule. The geometrical details appear in Table 4.

The complex 5c has binding energy of -59.31 kcal/mol but the pattern of binding is reversed as the O39 is now situated on the opposite side. The acceptor is attracted through oxygen atom (O44) with C10 of the pyrrole ring of the indole moiety. The two rings are slanting to each other. The other geometrical details appear in Table 4.

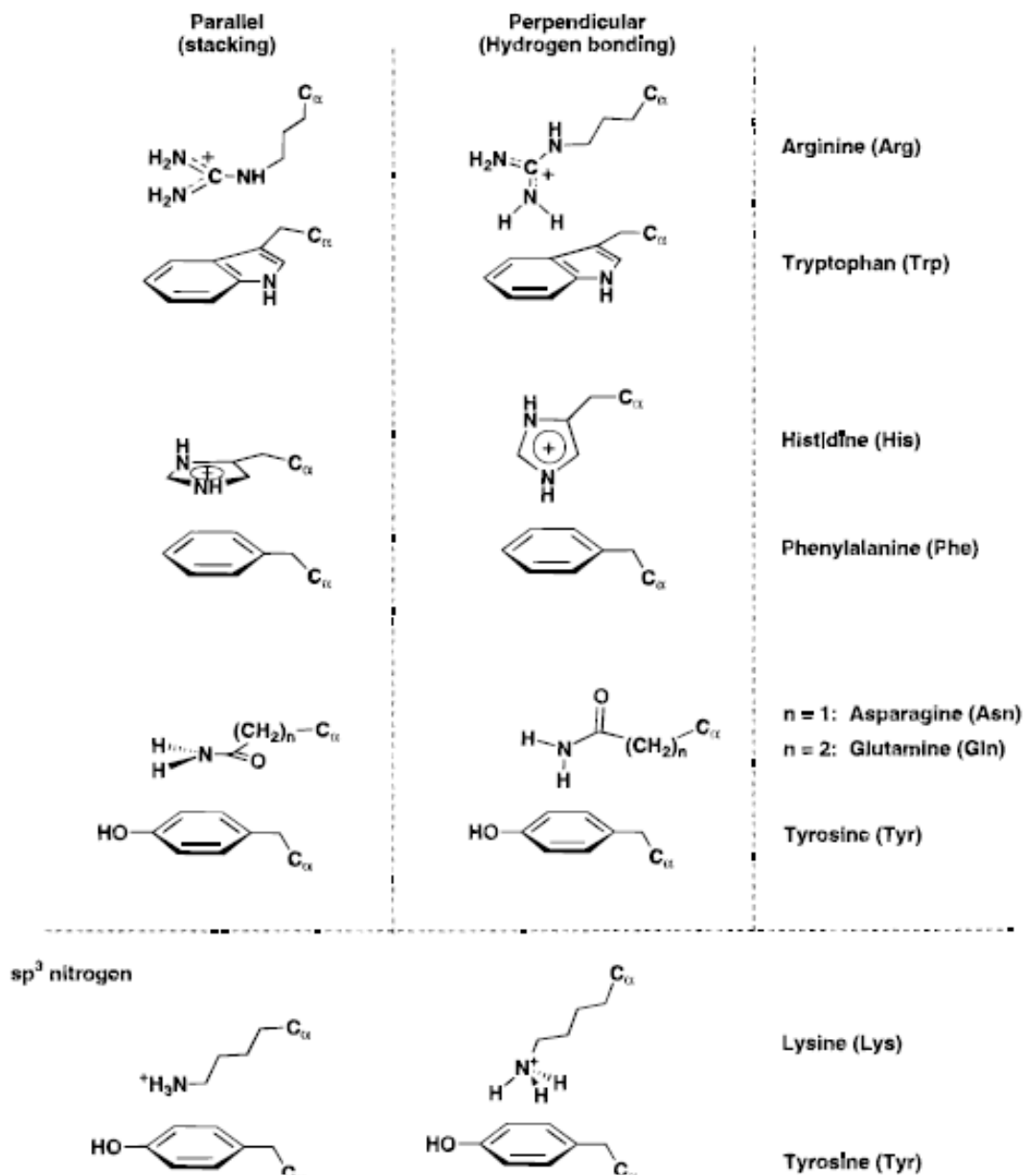
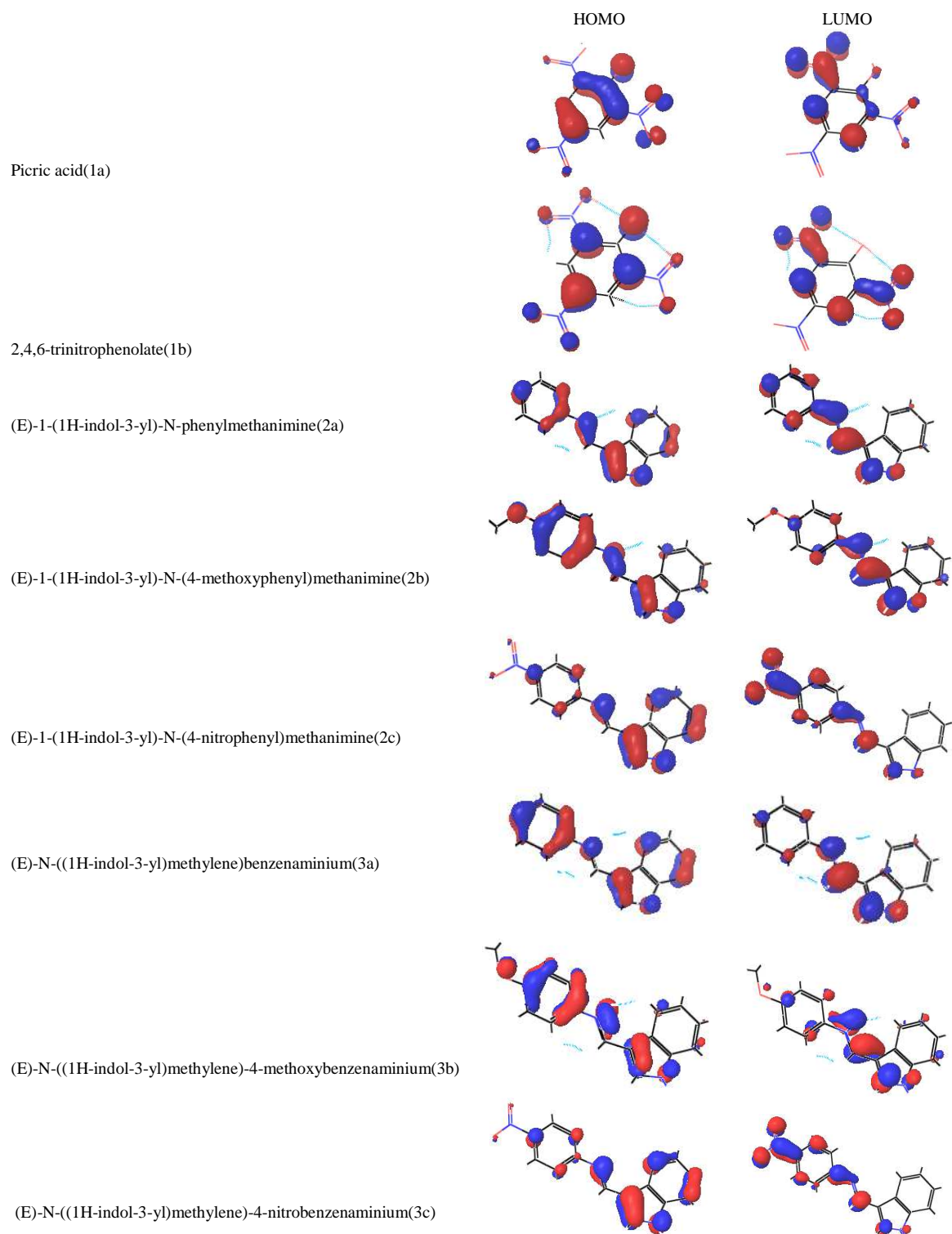
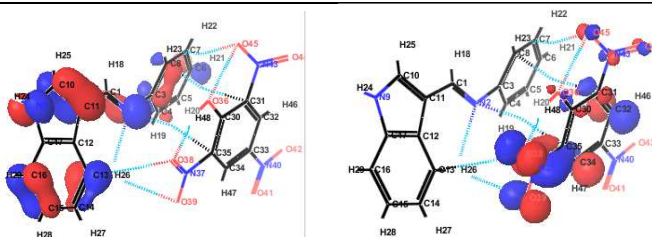


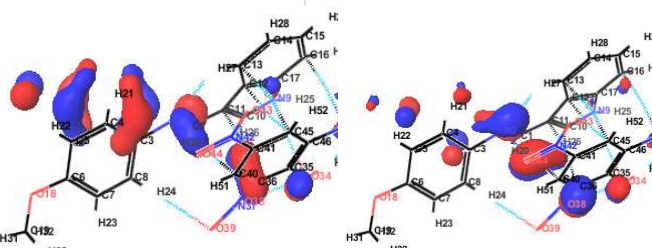
Figure1. Side-chain structures for amino acids involved in amino-aromatic interactions. Prototypical, limiting geometries are shown. Structures are illustrative only, and are not intended to indicate preferences for particular geometries or combinations of amino acids.

**Figure 2.** Picture of HOMO,LUMO of multidonors and acceptor molecules calculated by DFT method

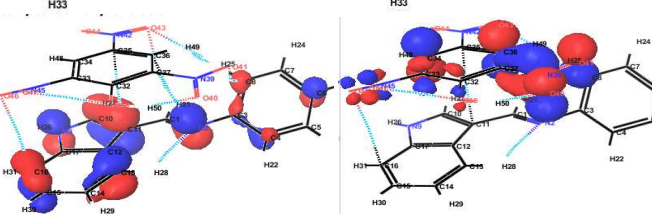
(E)-1-(1H-indol-3-yl)-N-phenylmethanimine compound with picric acid(4a)



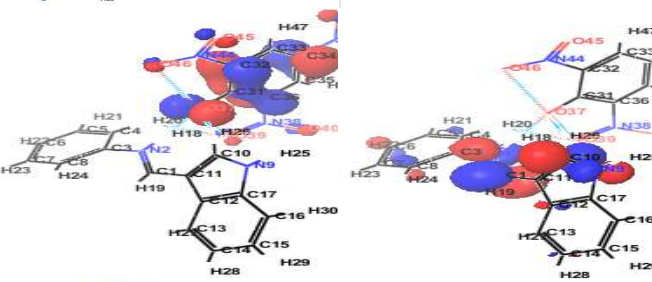
(E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with picric acid(4b)



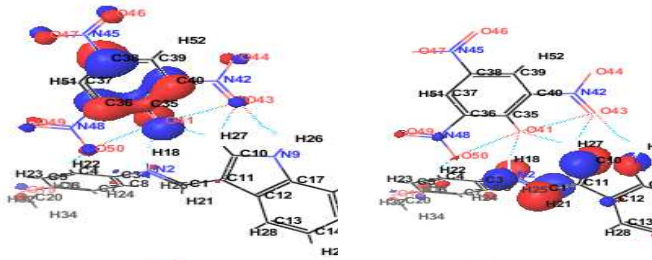
(E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine compound with picric acid(4c)



(E)-N-((1H-indol-3-yl)methylene)benzenaminium 2,4,6-trinitrophenolate(5a)



(E)-N-((1H-indol-3-yl)methylene)-4-methoxybenzenaminium 2,4,6-trinitrophenolate(5b)



(E)-N-((1H-indol-3-yl)methylene)-4-nitrobenzenaminium 2,4,6-trinitrophenolate(5c)

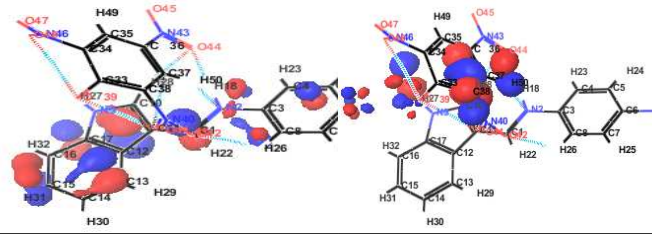


Figure3. Picture of HOMO,LUMO of CT-complexes in neutral and ionic states calculated by DFT method

Table 1. Energy of HOMO, LUMO, energy gap and gas phase energy of Donors, acceptors and CT-complexes in eV calculated from DFT method

Title	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
(E)-1-(1H-indol-3-yl)-N-phenylmethanimine(2a)	-18730.7794	-5.3062	-1.2109	-4.0953
(E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine(2b)	-21847.1949	-5.0729	-0.9591	-4.1138
(E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine(2c)	-24295.5860	-5.8088	-2.3724	-3.4364
(E)-N-((1H-indol-3-yl)methylene)benzenaminium (3a)	-18741.8109	-9.4886	-5.9647	-3.5239
(E)-N-((1H-indol-3-yl)methylene)-4-methoxybenzenaminium(3b)	-21858.3081	-8.8410	-5.7144	-3.1266
(E)-N-((1H-indol-3-yl)methylene)-4-nitrobenzenaminium(3c)	-24306.1966	-9.9267	-6.4246	-3.5021
(E)-1-(1H-indol-3-yl)-N-phenylmethanimine compound with picric acid(4a)	-43791.7468	-5.4042	-3.8477	-1.5565
(E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with picric acid(4b)	-46908.1107	-5.2681	-3.5647	-1.7034
(E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine compound with picric acid(4c)	-49356.5679	-6.1661	-3.7252	-2.4409
(E)-N-((1H-indol-3-yl)methylene)benzenaminium 2,4,6-trinitrophenolate(5a)	-43791.9863	-6.1334	-2.7647	-3.3688
(E)-N-((1H-indol-3-yl)methylene)-4-methoxybenzenaminium 2,4,6-trinitrophenolate(5b)	-46908.4290	-6.0790	-2.6313	-3.4477
(E)-N-((1H-indol-3-yl)methylene)-4-nitrobenzenaminium 2,4,6-trinitrophenolate(5c)	-49355.8033	-5.7661	-3.8314	-1.9347

Table 2. The corrected binding energy(E), counterpoise (CP) for different complexes by DFT calculations

	Counterpoise Correction (kcal/mol)	corrected Binding Energy(E) (kcal/mol)	E+CP
(E)-1-(1H-indol-3-yl)-N-phenylmethanimine compound with picric acid(4a)	3.673344	-1.153324	2.52002
(E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with picric acid(4b)	4.403097	-1.096568	3.306529
(E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine compound with picric acid(4c)	4.172418	-0.688337	3.484081
(E)-N-((1H-indol-3-yl)methylene)benzenaminium 2,4,6-trinitrophenolate(5a)	5.584145	-71.958473	-66.374328
(E)-N-((1H-indol-3-yl)methylene)-4-methoxybenzenaminium 2,4,6-trinitrophenolate(5b)	5.700354	-70.337203	-64.636849
(E)-N-((1H-indol-3-yl)methylene)-4-nitrobenzenaminium 2,4,6-trinitrophenolate(5c)	5.042796	-59.307258	-54.264462

Table 3. Intramolecular geometrical parameters of the CT-Complexes in neutral states calculated by DFT method

	4a	4b		4c	
N2-O30	7.073	N2-O34	4.410	N2-O32	3.505
N2-H46	7.610	N2-H50	4.029	N2-H48	-3.419
N2-N38	4.686	N2-N37	6.108	N2-N35	4.847
N2-N33	5.798	N2-N47	3.613	N2-N40	6.368
N2-N43	7.271	N2-N42	6.279	N2-N45	3.789
C32-C7	4.256	C35-C13	3.853	C38-C14	5.056
C37-C8	4.689	C35-C11	4.348	C14-C11	3.947
C32-C11	6.470	C35-C3	5.109	C3-C8	4.139
O30-C5	5.485	O34-C3	4.925	O32-C8	3.256
O30-C11	8.252	O34-C11	5.064	O32-C10	5.308
O30-C13	9.705	O34-C13	4.293	O32-C13	5.146
Dihedral angle.					
C32C36C3N2	136.9	C35C46C17N2	172.2	C38C34N2C1	73.1
C8C33C6C37	134.9	C35C46N2C3	-101.8	C38C34C8C7	120
C10C11C36C37	44.5	C35C46C16C15	-16.8	C38C34C14C15	27.9
C15C14C36C37	29.5	C35C46C3C8	-137.7	C38C34C12C11	137

Table 4. Intramolecular geometrical parameters of the CT-Complexes in ionic states calculated by DFT method

	5a	5b		5c	
O37-N2	2.649	O41-N2	2.671	O39-N2	7.833
O37-H18	1.622	O41-H18	1.1647	O39-H18	8.535
N2-N38	3.862	N2-N48	5.260	N2-N40	5.910
N2-N44	5.241	N2-N42	3.911	N2-N43	4.685
N2-N41	7.8	N2-N45	7.944	N2-N46	8.086
C36-C14	4.017	C40-C1	4.9945	C33-C7	6.172
C36-C1	5.030	C40-C3	5.064	C33-C1	6.522
C36-C3	4.909	C40-C11	5.001	C33-C10	7.228
O37-C3	3.295	O41-C4	3.050	O39-C1	7.628
O37-C13	3.123	O41-C13	3.109	O39-C4	7.948
O37-C11	4.052	O41-C11	4.030	O39-C10	8.422
Dihedral angle					
C31C37N2C1	46.6	C35O41N2C1	84.0	O39C33C1N2	8.3
C31O37C3C4	80.8	C35O41C4C3	121.3	O39C33C8C7	22.4
C31O37C15C14	39.1	C35O41C11C12	64.2	O39C33N9C17	43.1
C31O37C12C17	16.6	C35O41C13C14	37.4	O39C33C13C14	-80.5

CONCLUSION

From the comparison of the counterpoise corrected binding energies of the CT-complexes it is clear that the donorindolyl Schiff's bases and the acidic acceptor picric acid forms charge transfer complexes in their ionic states much strongly than in their neutral states. The substitution in the aryl ring attached with the nitrogen of the Schiff's base lowers the binding energy irrespective of the fact that the complexation occurs in the neutral states or in the ionic states. The two rings in the charge transfer complexes are in different planes in all the cases. The interaction sites between the donors and the acceptors are also structural dependent. In 4a, 4b and 4c the two components are attracted through π - π interaction. In 5a, 5b and 5c both π - π interaction and electrostatic attraction are experienced; only in 5b intermolecular hydrogen bonding also occurs.

Acknowledgment

We are thankful to Will Richard, Raghu Rangaswamy, Vinod Dewarjee for providing Shrodinger 2012 software.

REFERENCES

- [1]Sastry, G. N., &Mahadevi, A. S. *Chemical Reviews*, 113, (2013) 2100
- [2]H. P. Cheng et al., cf. *J. Phys. Chem.* 113,(2009) 20713–20718;
- [3]Moore et al., cf. *JACS* 130(32), (2008)10466.
- [4] Art D. Bochevarov, etal, *International journal of Quantum Chemistry*, 13,(2013)2110-2142
- [5] Šponer J, Gabb HA, Leszczynski J, Hobza P. *Biophys. J.*;73:(1997)76-87.
- [6] Zirbel CL, Sponer JE, Sponer J, Stombaugh J, Leontis NB. *Nucleic Acids Res.*;37 (2009)4898-4918.
- [7]Cockroft, Scott L.; Hunter, Christopher A.. *Chemical Society Reviews* 36 (2)(2007) 172.
- [8]Sponer J, Mladek A, Sponer JE, Svozil D, Zgarbova M, Banas P, Jurecka P,Otyepka M. *Phys.Chem.*14(2012) 15257-15277.
- [9] Krepl M, Otyepka M, Banas P, Sponer J., *J. Phys. Chem. B* 117 (2013)1872-1879.
- [10]Šponer J, Leszczynski J, Hobza P . *Biopolymers* ;61(2001)3-31
- [11]Jennifer C. Ma and Dennis A. Dougherty *Chem. Rev.*, 97(1997) 1303-1324
- [12] Benjamin J. Lynch, Yan Zhao, and Donald G. Truhlar *J. Phys. Chem. A*, 107(2003)1384-1388
- [13]Steven E Wheeler and KN Houk *J Am Chem Soc* 131 (9) (2009) 3126-3127
- [14] Erin R-Johnson *J Am Chem Soc*132 (18) (2010)6498-6506
- [15]Jia Deng, Andrew T. B. Gilbert, and Peter M. W. Gilla *The journal of Chemical Physics* 135, (2011)081105
- [16](1) Dougherty, D. A. *Science*, 271, 1996 163-168.
- [17] (21) Mecozzi, S.; West, A. P., Jr.; Dougherty, D. A. *Proc. Natl. Acad. Sci. USA*, 93 (1996) 10566-10571.
- [18] Mecozzi, S.; West, A. P., Jr.; Dougherty, D. A. *J. Am. Chem. Soc.*, 118, (1996)2307-2308.
- [19] Perutz, M. F.; Fermi, G.; Abraham, D. J.; Poyart, C.; Bursaux,E. *J. Am. Chem. Soc.* 108, (1986),1064-1078.
- [20] Levitt, M.; Perutz, M. F. *J. Mol. Biol.*, 201,(1988)751-754.
- [21] Perutz, M. F. *Phil. Trans. R. Soc. A*, 345,(1993) 105-112.
- [22]Mitchell, J. B. O.; Nandi, C. L.; Ali, S.; McDonald, I. K.; Thornton,J. M.; Price, S. L.; Singh, J. *Nature*, 366, (1993)413.
- [23] Mitchell, J. B. O.; Nandi, C. L.; McDonald, I. K.;J. M.; Price, S. L.; Singh, J. *Nature*, 366,(1993)413.