



Quantum mechanical studies on charge transfer complex of some Indolyl Schiff's bases with 1,3,5-trinitrobenzene

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ABSTRACT: The computational study on the non-covalent interactions of 1,3,5-trinitrobenzene (TNB) with some indolyl Schiff's bases having four different interaction sites have been carried out by DFT, 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.

Keywords: DFT, Indolyl diene anilinedrivatives, 1,3,5-trinitrobenzene HOMO, LUMO Binding energy.

INTRODUCTION

The study of the nature of interactions between donor and acceptor in a charge transfer complexes has attracted the attention of both theoretical[1-5] and experimental[6-10] chemists worldwide. These interactions range from hydrogen bonding, dipole-dipole interaction, π - π interaction, steric interaction, to London dispersion. The non-covalent and electrostatic interactions are most prominent in the biological systems. Study of such type of interactions is very useful in drug designing. Chemical interactions between donors and acceptors molecules to form CT-complexes have been studied theoretically[1-5] and experimentally[6-10] by many authors. These chemical reactions are also dominated by non-covalent interactions. This class of interactions spans a wide range of binding energies, and encompasses hydrogen bonding, dipole-dipole interactions, steric repulsion, and London dispersion. Molecular structure is governed by covalent, non-covalent, and electrostatic interactions, the latter two of which are the driving force in most bio-chemical processes. The three-dimensional molecular structure defines covalent bonds, however, non-covalent interactions are hidden within voids in the bonding network. Although there are several ways to view and analyze covalent and electrostatic interactions, an analogous method for non-covalent interactions is conspicuously missing. Such a method would aid understanding of the complex interactions between biomolecules, and the design of self-assembled materials and drugs, among others covalent interactions play a dominant role in many important areas of chemistry, from material design [11-14] to molecular biology[15-20]. 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 [21], 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[22-23]. 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.

Keeping in view the biological importance of the indole-nucleus we investigated the preferred site of interactions between 1,3,5-trinitrobenzene 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 the geometry of the molecular complexes and in determining the counterpoise corrected binding energies because 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 -CH=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 geometry, of the optimized CT-complexes, the counterpoise corrected binding energies of the charge transfer complexes and various other energy components of the donors, acceptor and the CT-complexes.

MATERIAL 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-BLY-3 method of theory choosing . 6-31g ^{##} basis set. The molecule was assigned net zero charge and singlet multiplicity

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 calculation of a counterpoise-corrected binding energy for a dimeric complex actually consists of seven calculations: Geometry optimization of the complex (calculation 1) Geometry optimization of each of the two molecular fragments in their own basis sets (calculations 2, 3). Single-point calculations of each of the fragments in their own basis sets at the geometries that they adopt in the complex (calculations 4, 5) Single-point counterpoise calculations on each fragment at the geometries that they adopt in the complex using the basis set of the complex (calculations 6, 7) The usual, uncorrected binding energy would be calculated as:

$$\Delta E_{bind} = E1 - (E2 + E3)$$

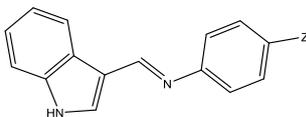
where the energy subscripts refer to the calculations listed above. The counterpoise correction to the binding energy expresses the artificial gain in energy of each molecular fragment when it can use the basis functions of the other fragment in addition to its own basis functions:

$$\Delta E_{cp} = (E4 - E6) + (E5 - E7)$$

Calculated in this way, the counterpoise correction is a positive number, and it is added to ΔE_{bind} to yield the final binding energy. Counterpoise corrections are often several kilocalories per mole in magnitude, and decrease as the size of the basis set increases.

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 this work, we present an approach to map and analyze non-covalent interactions, requiring only molecular geometry information and all the sites of interactions of the desired three donors having structure



where Z= H, OCH₃, NO₂ and acceptor TNB were used for the theoretical calculation of 1:1 charge transfer complex.

RESULTS AND DISCUSSION

The energy of HOMO and LUMO, energy gap between HOMO and LUMO and the gas phase energy of TNB (1a), (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)-1-(1H-indol-3-yl)-N-phenylmethanimine compound with 1,3,5-trinitrobenzene (3a), (E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with 1,3,5-trinitrobenzene (3b), (E)-1-(1H-indol-3-yl)-N-(4-nitro phenyl)methanimine compound with 1,3,5-trinitrobenzene (3c) 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 3(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 3(a-c) appear in Table-3. The interactions are mainly electrostatic in nature. The formation of the CT complex in ground states of donor and acceptor is favorable in the order $-\text{NO}_2 > -\text{H} > \text{OCH}_3$. In case of interaction in (3a), O44 of NO_2 of TNB situated at a distance of 3.322 Å from C16. The C31 of TNB moiety is situated closely at a distance of 3.860 Å and 4.892 Å from C17 and N11 respectively, O41 of other NO_2 group of TNB situated at a distance of 3.916 Å from C2 of pyrrole ring and 4.611 Å from N11. The benzene ring of indole moiety and one of the NO_2 of TNB molecule are out of the interaction field showing no interactions. O41 of NO_2 group of TNB is located at a close distance of 3.440 Å and also O43 of NO_2 is closely situated from C15 of aryl group at a distance of 3.871 Å. O44 of NO_2 group is closely located at a distance of 3.796 Å from C17 of the same aryl group.

In complex(3b) substituted aryl group and TNB molecule are held through π - π - interaction. They are situated at a distance of about 3.8 Å from the acceptor. O45 of NO_2 is closely situated at a distance of 3.630 and 3.587 Å from N11 and C17 of substituted aryl group on the Schiff's base respectively. The O18 of methoxy group substituted at para position of aryl group is at a close distance of 3.898 Å from O47 of NO_2 of TNB molecule. In complex (3c) the donor and the acceptor molecule align themselves to appear like V-shape complex in which NO_2 substituent of the aryl group of the donor moiety located outside of the interaction site of TNB molecule. O46 of NO_2 is situated at a distance of 3.496 Å from C7 of benzene ring of indole moiety while O43 of NO_2 is located at a closest distance of 2.999 Å from N atom of the pyrrole of the donor molecule.

Table1. 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 |
|--|------------------|------------|------------|------------|
| 1,3,5-trinitrobenzene (1a) | -23013.4646 | 8.932 3 | 3.682 7 | -5.2495 |
| (E)-1-(1H-indol-3-yl)-N-phenylmethanimine(2a) | -18730.7794 | 5.306 2 | 1.210 9 | -4.0953 |
| (E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine(2b) | -21847.1949 | 5.072 9 | 0.959 1 | -4.1138 |
| (E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine(2c) | -24295.5860 | 5.808 8 | 2.372 4 | -3.4364 |
| (E)-1-(1H-indol-3-yl)-N-phenylmethanimine compound with 1,3,5-trinitrobenzene(3a) | -41744.2037 | 5.475 4 | 3.735 0 | -1.7404 |
| (E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with 1,3,5-trinitrobenzene(3b) | -44860.5275 | 5.308 3 | 3.363 3 | -1.9450 |
| (E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine compound with 1,3,5-trinitrobenzene(3c) | -47308.9305 | 5.979 9 | 3.977 7 | -2.0022 |

Table2. The corrected binding energy(E), counterpoise (CP) for different complexes by DFT calculations.

| Complex | Counterpoise Correction (kcal/mol) | corrected Binding Energy(E) (kcal/mol) | E+CP |
|--|--|---|--------------|
| (E)-1-(1H-indol-3-yl)-N-phenylmethanimine compound with 1,3,5-trinitrobenzene(3a) | 3.054943 | -1.150882 | 1.90406 1 |
| (E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with 1,3,5-trinitrobenzene(3b) | 3.767611 | -0.58719 | 3.18042 1 |
| (E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl)methanimine compound with 1,3,5-trinitrobenzene(3c) | 2.431001 | -1.520059 | 0.91094 2 |

while that of charge transfer complexes appear in Figure(4.7). The counterpoise correction and the corrected binding energies of the Charge transfer complexes 3(e-g) appear in Table.28. 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 3(e-g) appear in Table-3.

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

| | 3a | 3b | 3c | |
|---------|-------|---------|-------|--------|
| C31-C17 | 3.860 | C35-N11 | 3.912 | O43-N1 |
| C31-N11 | 4.892 | C35-C5 | 5.620 | O42-N1 |
| | | | | 2.999 |
| | | | | 3.884 |

| | | | | | |
|------------------------|-------|--------------|-------|--------------|--------|
| C31-C3 | 5.489 | C35-C17 | 3.630 | O4O-O19 | 12.471 |
| C31-C5 | 7.743 | | | C35-N11 | 7.192 |
| | | O45-C5 | 3.555 | C34-C8 | 4.272 |
| O44-C16 | 3.322 | O45-C3 | 4.529 | C32-C6 | 4.930 |
| O44-N11 | 5.880 | O45-N11 | 3.686 | C33-C8 | 3.610 |
| | | | | | |
| O41-C2 | 3.440 | O48-C17 | 3.587 | O39-N11 | 8.402 |
| O41-N11 | 4.611 | O48-N11 | 5.140 | O42N11 | 7.062 |
| | | O48-O18 | 3.898 | | |
| <i>Dihedral angle.</i> | | | | | |
| C18C17C31C30 | 11.2 | C10N11C35C34 | 105.9 | C33C32C8C7 | 173.1 |
| N11C10C31C30 | 5.6 | C35C36C4C5 | 108.0 | C35C34C4C3 | 59.6 |
| C2C3C31C32 | 64.8 | C34C35C14C15 | 49.1 | C35C36C12N11 | 66.7 |
| C4C5C31C32 | -65.3 | C3C4C35C36 | 145.4 | C35C34C13C12 | 20.0 |

The interactions are mainly electrostatic in nature. The formation of the CT complex in ground states of donor and acceptor is favorable in the order $-\text{NO}_2 > -\text{H} > \text{OCH}_3$.

Fig1. Picture of HOMO,LUMO of multidonors and acceptor molecules calculated by DFT method in isolated state.

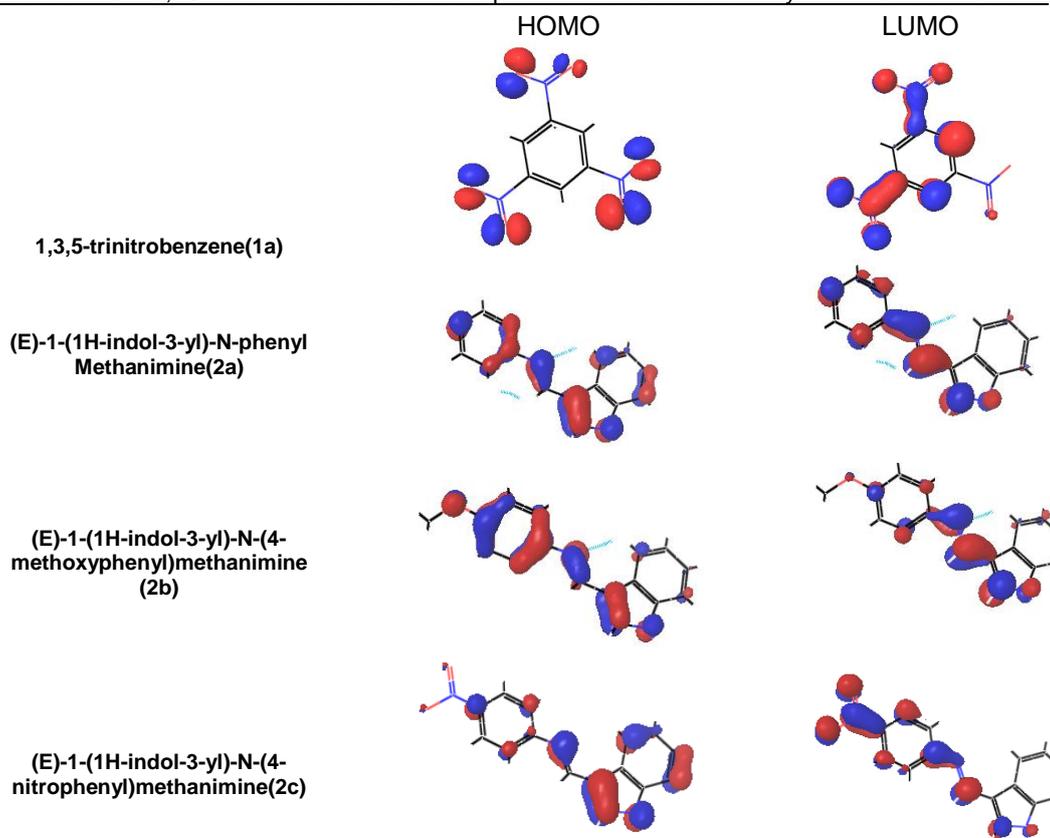
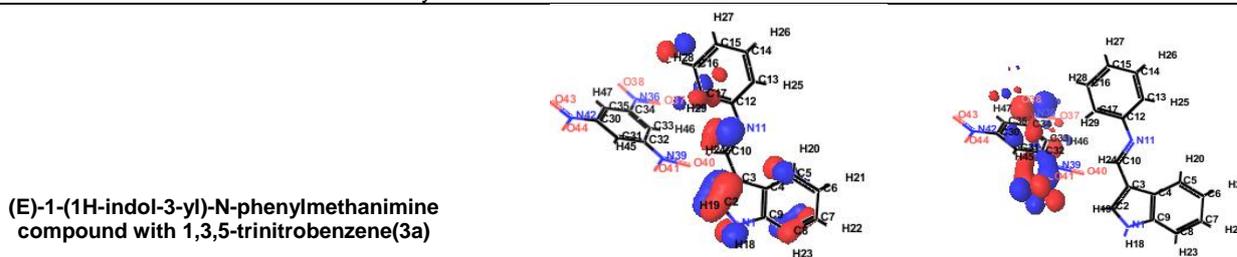
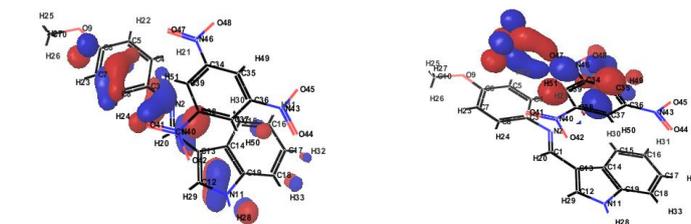


Fig 2. Picture of HOMO,LUMO of CT complexes of multidonors and acceptor molecules calculated by DFT method in isolated state.



(E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl) methanimine compound with 1,3,5-trinitrobenzene(3b)



(E)-1-(1H-indol-3-yl)-N-(4-nitrophenyl) methanimine compound with 1,3,5-trinitrobenzene(3c)

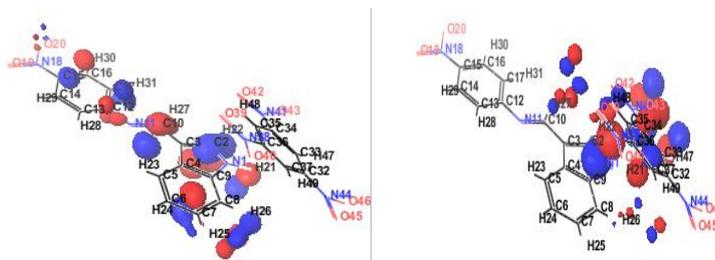
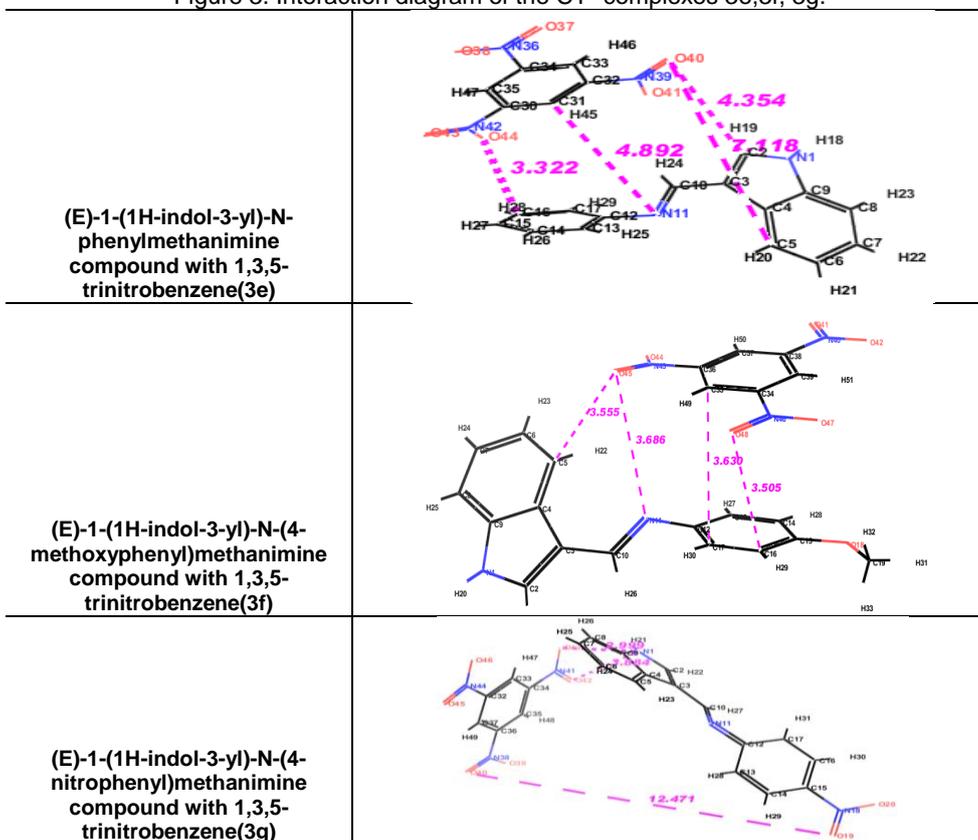


Figure 3. Interaction diagram of the CT- complexes 3e,3f, 3g.



In case of interaction in (3a), O44 of NO₂ of TNB situated at a distance of 3.322Å from C16. The C31 of TNB moiety is situated closely at a distance of 3.860Å and 4.892 from C17 and N11 respectively, O41 of other NO₂ group of TNB situated at a distance of 3.916 Å from C2 of pyrrole ring and 4.611 Å from N11. The benzene ring of indole moiety and one of the NO₂ of TNB molecule are out of the interaction field showing no interactions. O41 of NO₂ group of TNB is located at a close distance of 3.440 Å and also O43 of NO₂ is closely situated from C15 of aryl group at a distance of 3.871 Å. O44 of NO₂ group is closely located at a distance of 3.796 from C17 of the same aryl group.

Results of the complex formation between donor having four interactions sites derived from Schiff's base and neutral acceptor(TNB).

The energy of HOMO and LUMO, energy gap between HOMO and LUMO and the gas phase energy of TNB (1a), (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)-1-(1H-indol-3-yl)-N-phenylmethanimine compound with 1,3,5-trinitrobenzene (3a), (E)-1-(1H-indol-3-yl)-N-(4-methoxyphenyl)methanimine compound with 1,3,5-trinitrobenzene (3b), (E)-1-(1H-indol-3-yl)-N-(4-nitro phenyl)methanimine compound with 1,3,5-trinitrobenzene (3c) 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 Figure(4.6)

CONSLUSION

From the comparision of the counterpoise corrected binding energies of the CT-complexes it is clear that the donor indolyl Schiff's bases and the non acidic acceptor TNB molecule forms weakly non covalent interaction forming charge transfer complexes. The substitution in the aryl ring attached with the nitrogen of the Schiff's base increases and also decreases the binding .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 3a, 3b and 3c the two components are attracted through π - π interaction.

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