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Computational investigation and assessment on photo-electron diffraction and Production of inter-molecular charge transfer complex (ICT complex) in organic heterocyclic system by the influence of electronegative species substitution

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ABSTRACT

The production of intermolecular charge transfer complex (ICT) in the molecular composite is very significant process for preparing functional materials for many applications. The spontaneous construction and manipulation of CT complex by injection of halogen atoms and electronegative groups were described in detail using computational tool. The respective physical and chemical properties modification of chemical compound (pyridine) were studied by monitoring HOMO-LUMO interactive lobe formation and band gap adaptation. The internal energy band gap variation is addressed by adding of halogens, amino, nitro, COOH and CONH groups. By screening the parametric values, influence of substitutions on the change of base compound property was determined. In the calculation, 3-excited electronic energy levels are assigned in order to find the CT complex absorption peaks and the respective electronic signals were determined. Irrespective of all compounds, UV-Visible spectrum showed the similar active region; Quartz UV and the identified UV band is K-Band. Among all compounds, the highest peak shift of 85.3 nm and highest energy band gap shift of 1.64 eV was found for nitro pyridine. The E_{CT} transfer of all compounds is determined as almost same and finely showed the energy transfer from ligand to base compound. The MEP for all compounds showed the arrangement of static electric multipole moment and it ensures the enabling of photo-electron scattering and photo-electron diffraction.

Key words: charge transfer complex; pyridine; Quartz UV; photo-electron scattering; photo-electron diffraction.

INTRODUCTION

The ultraviolet spectrum resulted from the change of transitions between the electronic energy levels associated with vibrational and rotational energy levels of the organic system. Each and every base molecular system has its own electronic finger print spectrum which represents the known and unknown characteristics of the respective molecule [1]. The electronic transitional regions are usually assigned for the restoring energies in the molecular system which can be addressed the vibrational and rotational energy changes. The energy absorption in the region of ultraviolet and visible region by the organic molecular species leads electronic excitation among the various existed energy states. The electronic transitions under Frank-Condon Principle, usually taking place between lone pair orbitals and an unoccupied non bonding called anti-bonding orbitals. For that, the electronic transitions only occur from electron rich molecular part to electron deficient molecular part of the total molecular system in which the intermolecular interaction taking place and inter-molecular charge transfer come in to order. They are also represented as chromophores operated Charge Transfer (CT) donor and CT acceptors. In molecular donor, the electron is having restricted kinetic potential in electronic energy region is ready to transfer the energy to molecular acceptor unit of molecular system and here the electronic energy is pushed from higher energy state and pulled by the acceptor level. Thus the push-pull process in donor and acceptor, induced in the electronic energy levels by the assigned internal energy of the molecular system [2]

Whenever, the substitutions added with base molecule, and thereby systematically, the electron acceptor and donor parts in the molecular composite is changed with respect to the change of kinetic potential. So, the donor and acceptor are identified to be different from base compound and it can be ensured from the strong dipole moment. The core of the donor and acceptor is known as CT complex source and it causes the fundamental property of the organic system [3]. Usually, in molecular species, the influence and potential alternation by the substitutions generates the first and foremost excited energy states and refurbished ground states. This effect on electronic energy states makes standard polarization domains in the molecular entities and thereby it manipulates the location of CT complex. Simultaneously, due to the energy assignment on the electronic energy states, the physical and chemical properties automatically altered. The cause of alternation of the CT complex is to be identified in order to

investigate the alternation of the properties of the compound by the substitutions. There are so many bases for operating particular property and substitutions are available to enhance, tune and customize the desired property [4] in the computational tool and in this work, the base compound is chosen to be pyridine. The pyridine is a heterocyclic base and naturally it has electro-chemical, photo sensitive properties, and non linear refractive behaviour. Initially, for developing its NLO behaviour, addition of small ligand groups added in trial and error process. Such that, diminutive ligand groups like halogens (Cl, Fl and Br), NO_2, NH_2, COOH, and CONH are added with pyridine base. The physical properties, energy gap and NLO characteristics are studied and for that the transform of CT complex is recognized and addressed using computational calculations.

COMPUTATIONAL METHODS

The GAUSSIAN program was carried out for generating energy calculations and CT complex UV-Visible absorption spectral data using B3LYP/6-311++G(d,p) methods. As per the literature reports [5], such type of basis set provides accurate energy values and it is able to synchronize with the experimental data. Here, in the calculations, no symmetry restriction was forced during the molecular structure optimization. The electronic energy excitations were carried out using TDDFT methods on internal molecular structures [6,7] The molecular structure in ground state was constructed using major calculative method of HF and DFT and all the computations were performed by Gaussian 16 in IMAC computer.

RESULTS AND DISCUSSIONS

CT complex examination

The pyridine is a heterocyclic chemical species which has an orthorhombic crystal system with space group $Pna2_1$ when it is crystallized. It is occurred as crystal in two phases with space group was assigned to be P_{na21} [8] and it has geometry is very close to mmC_{2V} symmetry. As the crystal system of pyridine was orthorhombic, its dielectric constant so high and its calculated energy gap is 8.421 eV. So, the crystal is highly NLO active and is rather transparent crystal which is active in all the visible wavelengths. Due to the 90º inclined planes in different coordinates ($x \neq y \neq z$), the non linear light propagation is observed in different axis of the crystal. The energy gap is variable one and it can be operated by the addition of

substitutional groups such as halogens, nitro, amino and acid groups. By the substitution of suitable functional groups, the energy gap can be controlled and customized. Proportionately, the electronic energy is changed with respect to the electron withdrawing and electron donating groups by changing location of donor and acceptor group. Concurrently, the ionization potential and electron affinity is also can be forced to be driven according to the requirement. By changing the energy gap and excitation energy levels of the compound, the functional materials can be fabricated for technological applications.

Compound	λ (nm)	E (eV)	(*f*)	Transition levels	Major contribution	Assignment	Region	Bands
Pyridine $\varepsilon = 7500$ L mol^{-1} cm^{-1}	213.7	5.79	0.005	H→L1 (98%)	C=N	π→π*	Quartz UV	K-Band
	212.6	5.83	0.100	H1→L (97%)				
	178.3	6.95	0.003	H→L1 (87%)				
3-Chloropyridine	219.1	5.65	0.150	H→L (88%)	C=N	π→π*	Quartz UV	
	211.3	5.86	0.080	H→L (87%)				
	204.5	6.06	0.005	H→L (69%)				
3-Fluoropyridine	216.9	5.71	0.140	H→L (78%)	C=N	π→π*	Quartz UV	
	200.7	6.17	0.004	H→L (77%)				
	197.2	6.28	0.005	H→L (67%)				
3-Bromopyridine	220.8	5.61	0.230	H→L (92%)	C=N	π→π*	Quartz UV	
	213.6	5.80	0.090	H→L (90%)				
	196.0	5.61	0.230	H→L (67%)				
3-Nitropyridine	298.4	4.15	0.001	H→L (88%)	N=O	n→π*	Quartz UV	
	264.4	5.84	0.001	H→L (89%)				
	212.1	5.84	0.220	H→L (68%)				
3-Aminopyridine	241.0	5.14	0.150	H→L (88%)	C=N	π→π*	Quartz UV	
	218.4	5.67	0.080	H→L (77%)				
	213.0	5.81	0.004	H→L (63%)				
3-Methylpyridine	220.8	5.61	0.130	H→L (71%)	C=N	π→π*	Quartz UV	
	209.2	5.92	0.030	H→L (80%)				
	205.1	6.04	0.006	H→L (76%)				
3-pyridinecarboxylic acid	220.2	5.62	0.230	H→L (86%)	C=O	n→π*	Quartz UV	
	213.8	5.79	0.002	H→L (69%)				
	211.4	5.86	0.004	H→L (60%)				
Formamide-pyridine	221.0	5.60	0.030	H→L (98%)	C=O	n→π*	Quartz UV	
	218.8	5.66	0.180	H→L (87%)				
	212.0	5.84	0.004	H→L (73%)				

Table 1: Electronic spectral data

In other hand, the charge transfer complex (CT complex) is the energy domain which is produced in each and every chemical product and is produced by blending organic base and organic and inorganic ligand groups. The CT complex has specific electronic excitation band

known as collection of vibrational bands, which can be identified from the UV-Visible absorption spectrum [9].

Inter molecular CT complex is a dipole bond which possessed the source of energy and is able to produce particular property for the product compound. The shift of electronic excitation band (ICT) as change of wavelength in hypsochromic (Blue shift) and Bathochromic (red shift) with respect to the substitutional group is shown in Figure 1. In this case, first part of figure shows the electronic absorption spectrum of pyridine compound and consecutive figures showed spectrum of Cl, Fl, and Bromo pyridine compounds and followed by amino, methyl, nitro, and carboxylic acid pyridine compounds.

As per the Table 1, for pyridine, the band was observed at 212 nm with the energy band gap of 5.83 eV at oscillator strength of 0.005. The band was assigned to H→L1 (87%) orbital levels as $\pi \rightarrow \pi^*$ transition. Simultaneously, the band was assigned in Quartz UV region of spectrum and identified CT complex is C=N. When the addition of halogen compounds with pyridine, the energy band is located manipulated in different region.

Such that, the band observed at 211 nm with energy gap of 5.86 for Cl-P, the band at 200 nm with band gap of 6.17 eV for Fl-P and the band at 213 nm with band gap of 5.80 eV for Br-P. All the bands are invariably assigned to be $\pi \rightarrow \pi^*$ transition and Quartz UV region band is addressed by K-Band. Such band contributed by C=N species as a CT complex. In the case of Nitro group addition with the Pyridine, the band is shifted to 264 nm with energy gap of 5.84 eV at oscillator strength 0.001. According to the pyridine, the band was found to be shifted up to +52 nm and the energy is almost same.

But the CT complex was located at N=O bond. Whereas, for amino pyridine, the band is recognized at 218 nm with 5.67 eV energy gap and the CT complex is found to be C=N. Here, the electronic band is shifted up to +6 nm and the change of internal energy is – 0.16 eV and it is not very high. In methyl substitution, the band is found at 209 nm with energy gap of 5.92 eV and the CT band is C=N. The energy gap and shifting of band is not very high and the substitution of methyl group making not huge energy change in pyridine compound. In the case of carboxylic acid group substitution with pyridine, the absorption band is located at 213 nm with energy gap of 5.79 eV and the CT complex is C=O for $n \rightarrow \pi^*$ transition. For Formamide-pyridine, the energy band is observed at 218 nm and its absorption energy is 5.66 eV and it is

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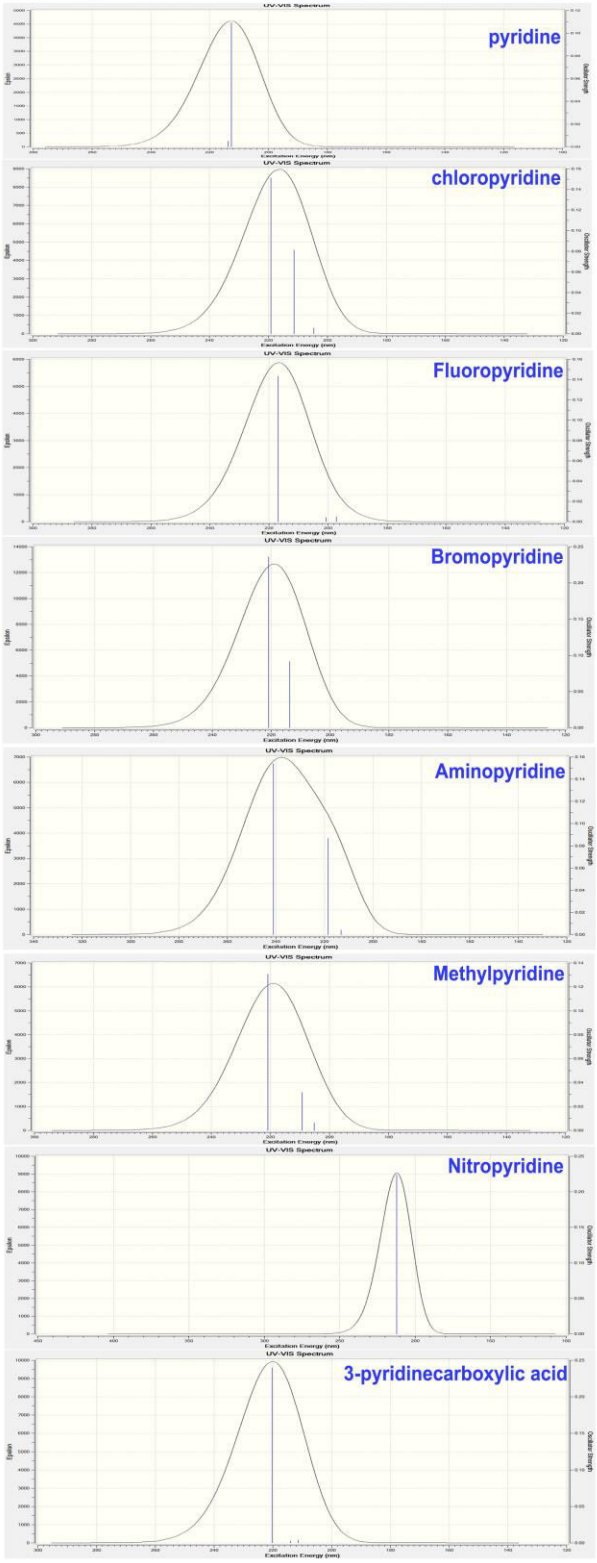
consistent with 0.180. The band of CT complex; C=O is due to the transition of n→π* which is located in the quartz UV region.



212 nm 5.83 eV

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200 nm 5.86 eV

213 nm 5.80 eV

264 nm 5.84 eV

218 nm 5.67 eV

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213 nm 5.79 eV

Figure 1

The halogenated pyridine compounds are usually having little bit impact halogens injection and particularly, the bominated pyridine is showed maximum bathochromic shift known as red shift and fluorinated pyridine has minimum impact which is shifted towards blue known as hypsochromic shift.

But for all the halogenated compounds, the CT complex is found to be C=N. Whereas in the case of nitro group, acid and Formamide substituted compounds, the CT complex is changed to be respective dominant bonds such as N=O and C=O. In the case of amino and methyl ligand addition, the main CT complex; C=N is retained. By this work, it is clear that Small ligand groups are not taking effect to modify the CT complex of the product compound instead of that, the massive ligand groups strongly influence the production of CT complex and forcefully modified on par with the ligand groups.

Table 2: Electronic energy band shift observation

Compound	λ (nm)	E (eV)	Peak shift (nm)	Energy gap shift (eV)
Pyridine	213.1	5.79	-	-
3-Chloropyridine	219.1	5.65	6.0	-0.14
3-Fluoropyridine	216.9	5.71	3.8	-0.08
3-Bromopyridine	220.8	5.61	7.7	0.18
3-Nitropyridine	298.4	4.15	85.3	-1.64
3-Aminopyridine	241.0	5.14	28.0	0.65
3-Methylpyridine	220.8	5.61	7.7	0.18
3-pyridinecarboxylic acid	220.2	5.62	7.1	-0.17
Formamide-pyridine	221.0	5.60	7.9	-0.19

The band gap is modified according to the ligand group and it is observed ligand group vice andit is depicted in Table 2. The band gap is decreased by 0.14 and 0.08 eV for pyridine compound when it is substituted by Cl and Fl respectively. Whereas the band gap is 0.18 eV increased on pyridine compound when Br substituted. Similarly, for nitro, carboxylic acid and formamide addition, the band gap is reduced by 1.64, 0.17 and 0.19 respectively. But, by the

addition of methyl and amino group, the band gap is increased by 0.65 and 0.18 eV respectively. So, the band gap can be controlled in organic and inorganic species by such ligand groups.

Table 3: Physico-chemical parameters

Compound	HOMO	LUMO	$\Delta E_{HOMO-LUMO\ gap}$ (eV)	Chemical hardness	Chemical Softness	Electron egativity (χ)	Electrophilicity index	E_{CT} transfer
Pyridine	9.523	1.213	8.310	4.155	0.120	5.368	3.457	1.291
3-Chloropyridine	9.605	1.206	8.421	4.210	0.118	5.394	3.433	1.281
3-Fluoropyridine	9.823	1.229	8.593	4.296	0.116	5.526	3.542	1.286
3-Bromopyridine	9.442	1.284	8.174	4.087	0.122	5.375	3.524	1.315
3-Nitropyridine	8.435	1.208	7.227	3.613	0.138	4.821	3.207	1.334
3-Aminopyridine	10.503	0.849	9.651	4.825	0.103	5.676	3.318	1.176
3-Methylpyridine	9.197	1.115	8.081	4.040	0.123	5.156	3.269	1.276
3-pyridinecarboxylic acid	10.013	1.121	8.892	4.446	0.112	5.567	3.471	1.252
Formamide-pyridine	9.959	1.134	8.832	4.416	0.113	5.551	3.481	1.257

The calculated physico-chemical parameters are presented in Table 3 in which molecular parameters for all the compounds were detailed. As per the Table 3, the measured values of HOMO and LUMO for all cases are displayed according which the chemical hardness, softness, electronegativity, and electrophilicity index are calculated. The electrical band gap is calculated and it is ranged from 8.17 eV to 9.651 eV for all the cases under study. The first order energy gap for halogenated compounds is ranged from 8.174 to 8.593 eV when the band gap of base compound; pyridine is 8.310 eV. In the case of Br, the gap is found to be decreased whereas the band gap is increased for rest of others. In the case of nitro pyridine, the band gap is 0.083 eV decreased when compared with pyridine. The band gap of amino pyridine is 1.341 eV increased when compared with base compound. When Br, Nitro, and methyl groups substituted, the band gap is lesser than base compound whereas when Cl, Fl, Amino, carboxylic acid, and formamide groups substituted, the band gap is increased than base compound. From the band gap analysis, it is confirmed that the main frame of compound is possessed high degree of dielectric property and thereby the compound is having enhanced NLO property. By adding suitable ligand groups, the band gap can be controlled and manipulated as it needs. The electrophilicity index for all compounds is rather similar (3.207-3.542 eV) for all substitutions taken in this work. Similarly, irrespective of all the ligand groups, the electronegativity is same for all compounds and it is ranged between 5.1 eV and 5.5 ev. The electrophilicity transfer among base and ligand group is also found for all compounds which explicit the charge transfer donor and acceptor of the compounds. For all compounds, the E_{CT} is found to be +ve and it confirms that the potential is

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transferred from ligand to base compound supportively; the chemical properties are modified on par with the ligand groups.

FMO observation

The organized HOMO-LUMO set of orbital lobes are simulated and displayed in Figure 2. As a result of assembling of molecule, all the atoms and their related conduction and valence band electrons are assembled separately to form HOMO and LUMO levels. In such constructive orbital clouds, the HOMO is capable of having electrons and able to transfer to the available empty electronic energy states known as LUMO.

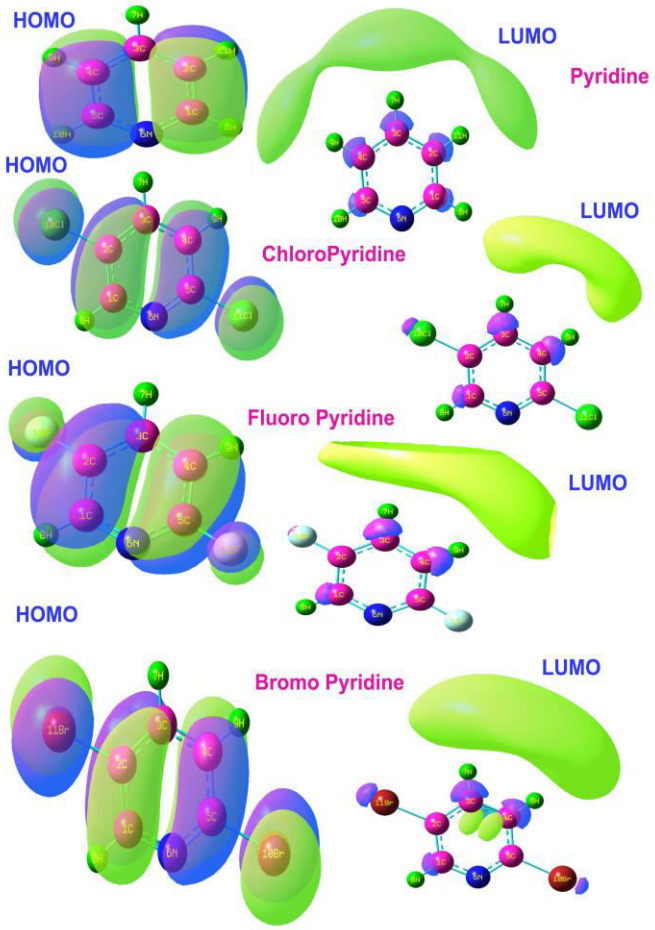

Figure 2

According to the selection rule, the transitions are permitted other than HOMO and LUMO to furnish physical and chemical properties. As per the hybridization of orbital

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overlapping, the possible p-p, s-p, sp^2, sp^3 orbitals of base and ligand groups are inter-related and interactive 3D lobes are formed.

By the application of degenerate orbitals in both HOMO and LUMO, the individual 3D orbitals are interlinked with one another and making σ, π, and δ orbital segmentation. Such type of orbital formation in the compound used to study the property modification of compounds from their base compound. The figure 2 shows the HOMO-LUMO modification by the injection of substitutional (Halogen) groups. The first part of the figure shows the HOMO-LUMO set up of pure pyridine compound and here, in HOMO, π-orbital interaction is taking place and the orbital segmentation covers semi circle of CC on base frame along with hydrogen orbitals whereas in LUMO, the σ-orbital segmentation id formed as a umbrella pattern and it covers all H orbitals. Here the space orbital interaction is created commonly for all σ-hydrogen bonds. In second part,

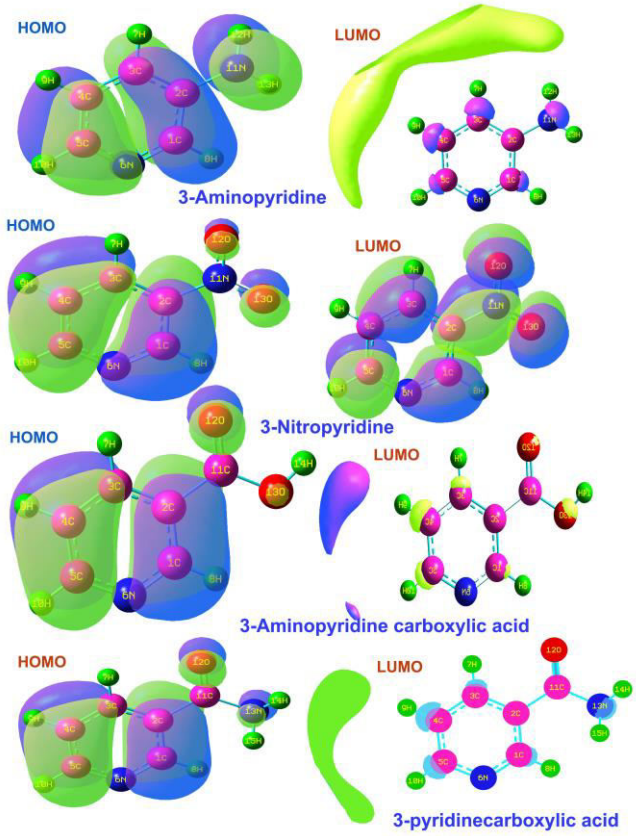

Figure 3

Chloropyridine, δ-interactive modelled orbital segment is observed on CCN and CCC symmetrically on left and right moieties of the frame. The σ-overlapping taking place on Cl separately. In LUMO, space σ-interaction is found over two hydrogen and new 3D space orbital domain is created. Only partial electron receiving voids found on core CC (LUMO) and there is no empty orbital availability in Cl, N and H. For Fl and Br adopted pyridine, similar perception is found whereas 3D space orbital system is broken by the di-Cl, Di-Fl and Di-Br groups. The HOMO is observed on CCN and CCC symmetrically as a δ-interaction and making charge displacement known as dipole moment which is main cause for stretching of pyridine ring in crystal plane. By the application of lattice equipotential force of attraction and the molecular orbital lobe repulsion, the chain of pyridine rings in one coordinate is twisted with respect to other coordinates. This implies that the non linear refraction taking place within the pyridine crystal material and it is different in different axis.

The frontier molecular interactive overlapping orbitals for amino, nitro, carboxylic and methyl substituted pyridine compounds are shown in Figure 3. Dissimilarly, δ-interactive overlapping of orbitals is found on HCCNH of left moiety of pyridine ring whereas π-interactive lobes found on CCC of right moiety. The NH_2 is covered by σ-interaction lobe and not at all H. In all above orbitals; the enriched electron domain is present blended property could be expected. In LUMO, the bifurcated σ-interactive lobes are appeared between core C and H bonds. Similarly, the HOMO segments are appeared to be same and all the substitutional groups are left behind the lobes. In LUMO, other than Nitro pyridine, for all compounds like amino, carboxyl and formamide pyridine, 3D space orbital lobe system is found and spread over the H bonds.

From the above discussion on HOMO-LUMO interaction in the molecular entities within the molecular structure, it is greatly inferred that the halogenated pyridine compounds are having δ-interactive orbital system and is isolated only in main frame of the molecule whereas in the case of rest of others, δ-interactive lobes appeared not only on main frame and also allied CH bonds. This means that, the chemical property of halogenated compounds is reserved only on core frame. But, for others the chemical properties are reserved not only on main core and also involved in substitutional groups.

MEP observation

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The MEP usually describes ground and excited state molecular electronic structure activity, crude electronic densities of the molecular configuration structure activity relationship and photo-electron diffraction and photo-electron scattering [10]. The multipole expansion is generally generated by mulliken charge distribution or partial atomic charges. The partial charges of the atoms in molecular site making dipole moment of each bond and thereby all bonds are summed up known as multipole moments. Usually, the molecular configuration is fulfilled by the heteronuclear and homonuclear bonds and the dipole moment is effective only on heteronuclear bonds.

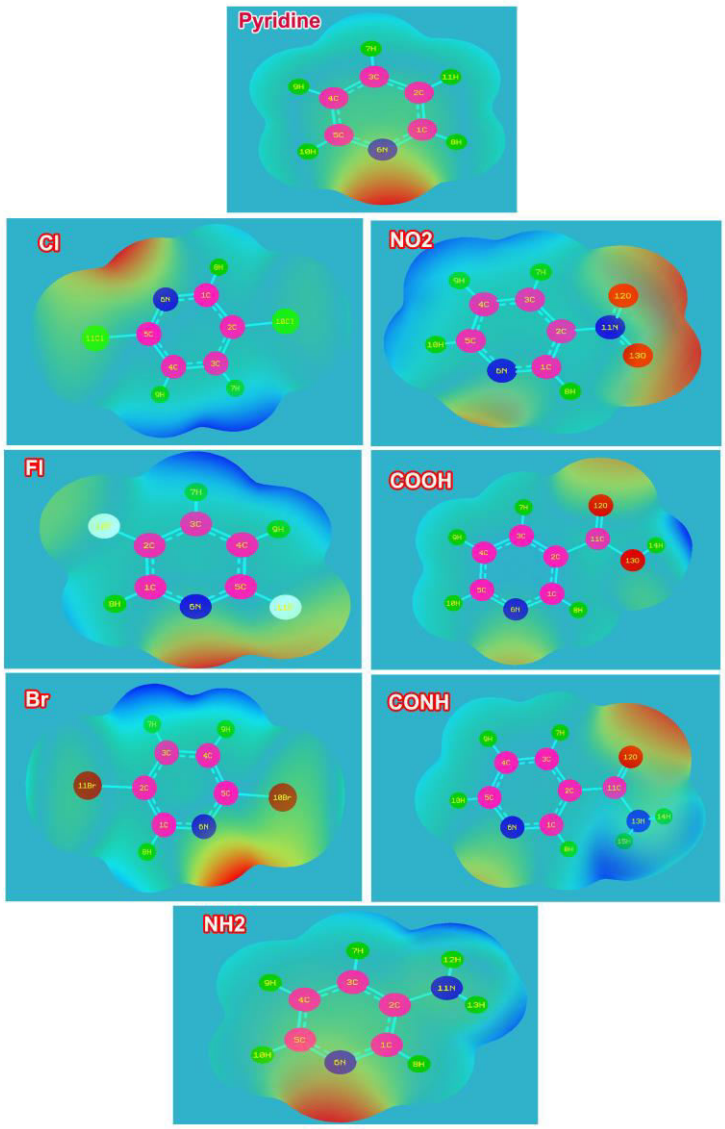

Figure 4

The present compound is having number of dipole bonds and the molecule as whole possessed multipole moments. As a result, the accumulative atomic multipole moments known as dipole moment of molecule [11]. The MEP colour gradient is ordered from blue to red with respect to the formulation of +ve and –ve charge displacement. The blue shows the proto-positive content of charges and red shows electronegative content charges. According to the mulliken charge distribution, the colour gradient is appeared in the molecular surface.

In this case the colour gradient map of molecular electrostatic potential of all the cases is presented in the Figure 4. The saddle points of electrostatic potential is shown in Figure in which two opposite charges 3D space regions pointed out by the critical points. The saddle points for pyridine compound for negative gradient is located around nitrogen atom where electrophilic attack (electronic content) is largely appeared. Usually, the nucleophilic is to be appeared at other than nitrogen region. But in this case, no intensive nucleophilic content is addressed. Whereas in Cl, Fl, and Br substituted pyridine, as usual, electrophilic attack is observed at nitrogen region and associated electronic content is displaced towards the N of the ring. Therefore, the strong electrostatic regions are located on the plane of molecule and thus different multipole moments are created in the crystal that generates photo-electron scattering zones. As in the figure, the nitro pyridine has intensive electrophilic attack zone around NO_2 than nitrogen atom of the ring. In COOH and CONH injected pyridine compounds, the electrophilic zones located at N of ring and O of acid group. By the application of heterogeneous electrostatic rigid bonds enable photo-electron diffraction in the crystal. In the case of amino ligand adopted pyridine, electrophilic region administrated on N of ring instead of N of amino group. At NH_2, the electron content is diluted by the H atoms and the nucleophilic zones are surrounded H of amino group instead of H of ring.

CONCLUSION

The study of inter molecular charge complex is very much useful for finding the appropriate property and thus the application of chemical species. In this work, the creation and modification of CT complex on the organic chemical species by the addition of different massive atoms and groups is detail studied. The chemical energy manipulation of all the molecular system is investigated and the respective energy bands are assigned in radical characteristics regions. The allowed energy gap variation on the fusion of the substitutions in the heterocyclic

base compound is analyzed. The manipulation of ground state energy of the basic organic system is keenly addressed and the energy variation is scaled in order to calculate the energy of unknown substituted compounds. The operating condition of band gap of the organic compounds has been studied and parametric control of such band gap for obtaining desired molecular property is found. The frontier molecular lobe formation confinement on par with the substitutional instrument is mapped and their movement for operating the band gap is described. The electrostatic critical points assignment to generate MEP 3D space regions for producing saddle zones is identified from which the electrophilic and nucleophilic parting to induce photo-electron scattering and diffraction was quantified.

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