Reactivity descriptors and electron density analysis for ligand chemistry: A case study of 2,2′-bipyridine and its analogues

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Abstract.   In this paper, we study the reactivity of diimines like 2,2′-bipyridine and its analogues using reactivity descriptors. We discuss evaluation of local descriptors using relaxed as well as frozen approximation and characterize the σ/π acceptance/donor characteristics of the above ligands. The intermolecular reactivity sequence for the same systems is examined by the global and local philicity index. In addition, electron density analysis has been carried out to highlight the possible strengths of interaction of the bipyridine and its analogues with metal ions.

Keywords.   2,2′-Bipyridine; reactivity descriptors; DFT.

1.   Introduction

The prediction of changes in reactivity and selectivity at particular atom centers is an important concept related to the activation (de-activation) at that site. Site activation (de-activation) may be promoted in several ways, including solvation effects, substitution of a particular functional group, the presence of a reagent or a catalyst or in general by any external source of perturbation. Such prediction has been one of the objectives of chemical reactivity indices.

In recent years, density functional theory (DFT) has emerged as a powerful tool through which chemical concepts such as reactivity, selectivity, and reaction path of a system have been studied.[1–5] The concepts of chemical potential (μ), electronegativity, and hardness (η),[6–8] collectively known as global reactivity descriptors, have systematized the study in this area. The principle of maximum hardness(PMH),[9] relating the relative stability of a system to a larger value of hardness, has been tested using semi-empirical as well as *ab initio* quantum chemical techniques.[10] Local reactivity descriptors, such as Fukui function (FF) and local softness, relating changes in electron density to the number of electrons and chemical potential, respectively, have been used to determine the site-

reactivity of a system.[11] Electrophilic and nucleophilic FFs have been used as indicators of reactivity to nucleophilic and electrophilic reagents, respectively.[12] Roy *et al*[13] proposed that relative electrophilicity and relative nucleophilicity, based on the ratio of electrophilic and nucleophilic FFs and its inverse, are more reliable descriptors to locate the preferable sites for electrophilic and nucleophilic attack respectively within a molecule. Parr and co-workers have defined a new concept of global philicity[14a] using which Chattaraj and co-workers have defined local philicity indices.[14b] The importance of charges and different frontier-controlled descriptors in description of electrostatic interactions in ligand chemistry has been highlighted in the past.[14c] Recently, Tanwar *et al* proposed two reactivity descriptors viz. normalized Fukui function (NFF) and bond deformation kernel (BDK)[14d] for comparative studies on the systems with varying number of atoms. A local version of the hard-soft-acid-base (HSAB) principle, proposed by Gazquez and Mendez,[15] and pursued by Pal and co-workers[16], as well as, Geerlings and co-workers[17] to a variety of chemical situations, is suited to semi-quantitative description of interaction energy.

In this report, we present a study of the reactivity descriptors in explaining the donor–acceptor character of the 2,2′-bipyridine and its important analogues 3-(2-pyridinyl)-1, 2, 4-triazine and 3-(2-

pyrazinyl)-1,2,4-triazine, generated by substitution of –CH group by N-atoms in the bipyridine ring. We observe that this class of systems presents an example where cation is to be exercised in the calculation of condensed FF. We discuss two different schemes of calculations of the Fukui functions and related descriptors, one using 'relaxed orbital' and the other 'frozen orbital' approach. Depending on the symmetry of the orbitals involved during complexation, the ligands are generally classified as σ-donor, π-donor and π-acceptor ligands.[18] 2,2′-bipyridine is both a σ-donor and π-acceptor ligand.[19] We have also used electron density to highlight the possible strengths of interaction of the bipyridine and its analogues with metal ions. There has been significant interest in bipyridine and polypyridine complexes of heavy metal ions due to their inherently interesting and unusual excited state properties and the potential utility of this class of compounds in solar energy conversion schemes.[20–26] The ability of bipyridines to form ionic and neutral guest compounds makes them useful precursors in supra-molecular chemistry.[19,27] Moreover, self-organization of bipyridine structures and metal cation often leads to the formation of helicates, which are supra-molecular complexes formed between pre-organized receptors and metal ions.[28-30] In addition to the areas mentioned above, bipyridine units are also significant in catalytic studies.[31,32] Polypyridine complexes constitute an important class of redox mediators in biosensors.[33] Studies in this area focus on design and control for the selective preparation of complicated organized chemical structures. Simple concepts based on density descriptors can facilitate controlled selective preparation of the above complexes by identification of reactivity of the different sites of the systems.

The paper has been organized as follows. In §2, we describe theoretical background leading to definitions of Fukui functions, philicity, local philicity indices, relative electrophilicity and nucleophilicity. Section 3 provides the computational details and the methodology used for calculations. In §4, we focus the results and discussion of the various calculations for the model systems.

2. Theoretical background

According to Hohenberg–Kohn (HK) theorem, the ground state energy of atom or molecule is written as a function of electron density (ρ):[34a]

$$E[\rho] = \int \rho(r)v(r)dr + F_{HK}[\rho], \tag{1}$$

with

$$F_{HK}[\rho] = T[\rho] + V_{ee}[\rho], \tag{2}$$

where $v(r)$, defined in the (1), is the external potential and F_{HK} is the universal Hohenberg–Kohn functional, which comprises of electronic kinetic energy functional ($T[\rho]$) and electron-electron interaction functional ($V_{ee}[\rho]$).

The first and second partial derivatives of $E[\rho]$, with respect to the number of electrons N under the constant external potential $v(r)$, are defined as the chemical potential (μ) and the global hardness η of the system, respectively.[6–8] The global softness (S) is the half inverse of the hardness. The global descriptor of hardness has been known as an indicator of the overall stability of the system.[9]

It has been customary to use finite difference approximation for the computation of μ and η:[3a]

$$\mu = -\frac{(I + A)}{2} \tag{3}$$

$$\eta = \frac{1}{2}(I - A), \tag{4}$$

where I and A are the first vertical ionization energy and electron affinity of chemical species respectively. Under the Koopmanns' approximation,[34b] working equations of chemical potential and hardness turn out as follows,

$$\mu = \frac{\varepsilon_{HOMO} + \varepsilon_{LUMO}}{2} \tag{5}$$

$$\eta = \frac{\varepsilon_{HOMO} - \varepsilon_{LUMO}}{2} \tag{6}$$

where ε_{HOMO} and ε_{LUMO} are the orbital energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the N electron system respectively.

The site-selectivity of a chemical system, cannot, however, be studied using the global descriptors of reactivity. For this, appropriate local descriptors need to be defined. An appropriate definition of local softness $s(r)$ is given by[11]

$$s(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} \left(\frac{\partial N}{\partial \mu}\right)_{v(r)} = f(r)S \qquad (7)$$

Such that,

$$\int s(r)d(r) = S \qquad (8)$$

where $f(r)$ is defined as the Fukui function.[11] It is obvious that local softness contains the same information as the Fukui function,[35] in addition, information to the softness of the whole molecule. FF can be interpreted either as the change of the electron density $\rho(r)$ at each point r when the total number of electrons is changed or as the sensitivity of a system chemical potential to an external perturbation at a particular point r.

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = \left(\frac{\partial \mu}{\partial v(r)}\right)_N. \qquad (9)$$

The latter point of view, by far the most prominent in the literature, faces the N-discontinuity problem of atoms and molecules,[36] leading to the introduction[11a] of both right- and left-hand-side derivatives, both to be considered at a given number of electrons, $N = N_0$:

$$f^+(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^+_{v(r)}. \qquad (10)$$

The above equation (10) describes nucleophilic attack provoking increase of an electron in the system. Similarly,

$$f^-(r) = \left(\frac{\partial \rho(r)}{\partial N}\right)^-_{v(r)}, \qquad (11)$$

describes electrophilic attack provoking decrease of an electron in the system.

Although, in principle, the electron density of neutral or N_0-electron system contains all information needed for the evaluation of the Fukui function, most studies in the literature have been carried out using the finite difference method, approximating,

$$f^+(r) \approx \rho_{N_0+1}(r) - \rho_{N_0}(r), \qquad (12)$$

and

$$f^-(r) \approx \rho_{N_0}(r) - \rho_{N_0-1}(r). \qquad (13)$$

A third function describing radical attack, $f^0(r)$, is then obtained as the arithmetic average of $f^+(r)$ and $f^-(r)$.

Since the derivative of (9) is not known exactly, there are various different strategies to calculate, in an approximate way, the Fukui function. Two different finite-difference approaches can be followed. Separate calculations of $(N_0 + 1)$ and $(N_0 - 1)$ electrons imply relaxation of orbitals from the neutral system. This approach has been known as the 're-laxed orbital' approach. The practical difficulty of the FF, especially of $f^+(r)$, using this approach suffers the technical difficulties of computing the density of anionic system at the same level of accuracy as the neutral system. At this stage it is difficult to get the correlation effect. A manner of taking into account, in an approximate way, the orbital relaxation effects doing a single point calculation on the neutral system and avoiding the complexity of the anionic species has been presented and implemented in the literature including the work of present authors. On the contrary, assuming that the shape of molecular orbitals does not change when a small amount of charge is added or subtracted, Yang *et al* calculated the derivative of (9) as, governing electrophilic attack,

$$f^-(\vec{r}) \approx \rho_{\text{HOMO}}(\vec{r}), \qquad (14)$$

governing nucleophilic attack,

$$f^+(\vec{r}) \approx \rho_{\text{LUMO}}(\vec{r}), \qquad (15)$$

and governing radical attack,

$$f^0(\vec{r}) \approx \frac{1}{2}\left[\rho_{\text{HOMO}}(\vec{r}) + \rho_{\text{LUMO}}(\vec{r})\right], \qquad (16)$$

Known as the 'frozen orbital' approximation, where $d\rho$ is same as $d\rho_{\text{valance}}$.[11a] However, limitations of the frozen orbital approximation has been analysed, within the conceptual DFT framework.[11c] Apart from these two approximations completely different route for the evaluation of the FF can also be pursued. However, approximations other than 'relaxed orbital' and 'frozen orbital' indirectly involve the quality of functionals entering in *F*, and hence are less reliable.

For determining site-selectivity or site reactivity one usually calculates what are called atom-condensed Fukui functions, first introduced by Yang *et al* based on idea of integrating the Fukui function over atomic regions,[12] similar to the procedure followed

in population analysis technique.[37] Combined with finite difference approximation, this yields working equations of the type,

$$f_A^+ = q_{A,N_0+1} - q_{A,N_0}, \tag{17}$$

$$f_A^- = q_{A,N_0} - q_{A,N_{0-1}}, \tag{18}$$

where, q_{A,N_0} denotes the electronic population of atom A of reference system. In *ab initio* calculations these numbers are obtained mostly by a Mulliken and Lowdin population[38] analysis. Under frozen orbital approximation atom-condensed Fukui functions will be nothing but the respective atomic population of HOMO or LUMO orbitals.

In addition to the FF, other reactivity descriptors based on FF have also been used. For example, relative electrophilicity and relative nucleophilicity, defined as (f^+/f^-) and (f^-/f^+) respectively,[28a] are greatly used to explain intra and inter molecular reactivity. Parr *et al*[14a] proposed a global philicity (W) as $\mu^2/2\eta$. Using this, Chattaraj *et al*[14b] proposed the existence of local philicity index $w(r)$ as $Wf(r)$ such that $w(r)$ integrates to global W. The atom-condensed philicity, w_A^a in the definition is given by

$$w_A^a = W f_A^a, \forall a = +, -, 0. \tag{19}$$

Earlier Krishnamurty *et al*[39a] proposed 'group softness' to describe intermolecular reactivity trends in carbonyl compounds and organic acids. They defined group softness as the sum of softness of atoms present in an appropriately defined group. Based on this concept, Chattaraj and co-workers[39c] proposed the 'group philicity' as the summed condensed-philicity of atoms present in the group.

$$w_g = \sum_{k=1}^{n} w_k, \tag{20}$$

where n is the number of atoms bonded to the reactive atom, w_k is the atom-condensed philicity of the atom k, and w_g is the group philicity.

These reactivity descriptors have been used extensively for the study of site selectivity of atoms in a molecule.[13,39–42] In this paper these quantities will be computed and its validity is tested in predicting the intramolecular and intermolecular reactivity trends.

3. Computational details and methodology

DFT calculations were performed to test the validity of the different approaches (frozen orbital versus relaxed orbital approach) using the GAMESS[43] system of programs. The ground state geometries of 2,2′-bipyridine ligand and its substituted analogues namely 3-(2-pyridinyl)-1,2,4-triazine and 3-(2-pyrazinyl)-1,2,4-triazine were completely optimized with split valence basis set 6-31G(*d, p*) along with B3LYP hybrid functional. The electronic populations on the atoms for these systems were obtained from Lowdin population analysis.

4. Results and discussion

Figure 1 presents the optimized structures of 2,2′-bipyridine, 3-(2-pyridinyl)-1,2,4-triazine and 3-(2-pyrazinyl)-1,2,4-triazine. The interaction at a molecular level depends on both electron donating and accepting character of the system, which in turn is dependent on the substitution.

4.1 *Global reactivity*

Table 1 presents the ionization energies, electron affinities and global reactivity of the ligands. The substitution of –CH groups by N atoms at bipyridine ring do not change the structural parameters widely. However, due to re-distribution of atomic charges within the molecule, there is a significant change in the magnitude of global properties. With the increase of *N* atoms in the ring, electron affinities increases linearly, however, the change in ionization potential is not prominent. Similar conclusion can be drawn from the chemical potential and hardness parameters reported in table 1. Based on principle of maximum hardness (MHP), the molecular stability has been extensively studied employing chemical potential and chemical hardness. According to this principle the minimum energy system has maximum chemical hardness value. Hence, MHP is a qualitative tool to study the stability of the system. The stability decreases as more number of –CH groups are substituted with *N* atoms. However, the global softness increases with the *N* substitution, predicting higher polarizability, hence reactivity of the systems. To analyse the change in electrophilic power of the systems, the molecular electrophilic power has been calculated. In general, the substituted *N* atoms enhance the electrophilic power irrespective

Table 1. Ionization energies, electron affinities and global reactivity.

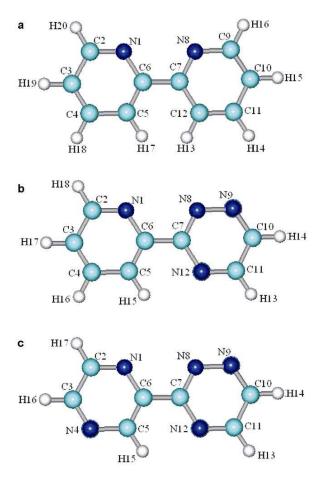| Properties (a.u.)	2,2′-Bipyridine	Pyridinyltriazine	Pyrazinyltriazine
Ionization energy	0·2321	0·2259	0·2337
Electron affinity	0·0543	0·0713	0·0808
Chemical potential	−0·1432	−0·1486	−0·1572
Chemical hardness	0·0889	0·0773	0·0764
Softness	5·6242	6·4683	6·5445
Philicity	0·1153	0·1428	0·1616

Figure 1. (**a**) 2,2′-Bipyridine (**b**) 3-(2-pyridinyl)-1,2,4-triazine (**c**) 3-(2-pyrazinyl)-1,2,4-triazine. Expected metal binding sites are N(1) and N(8), metal approach in the plane of molecule.

of the nature and position of the substitution. For pyridinyl triazine this substitution is only at one pyridine ring, whereas for pyrazinyl triazine it is at both rings. As we go from bipyridine to triazines, the values of these properties are increased.

4.2 *Local reactivity: Relaxed versus Frozen approximation*

2,2′-bipyridine is one of the critical case studied here for understanding the prediction of observed experimental results. This is a typical case where relaxed orbitals could not predict the correct acceptance/donor character. Table 2 highlights the failure of the atom-condensed Fukui functions in explaining electrophilic and nucleophilic attacks using relaxed orbitals. The Nitrogen atoms, carrying lone pair of electrons are expected to be prominent σ-donors, which, is not observed by looking at the f^- values on N atoms. However, it instead predicts the electron deficient ring carbon atoms to be a competent nucleophile. On the contrary, the same ring carbon atoms along with nitrogen atoms are shown to be equally good electrophile, which goes against the expected reactivity. Here this discrepancy lies with calculation of nucleophilic Fukui functions. The HOMOs of $N_0 - 1$ and N_0 state of 2,2′-bipyridine are shown in figure 2a and 2b respectively. This should be noted that the HOMO of neutral 2,2′-bipyridine is of σ-type while that of the cationic 2,2′-bipyridine is π type. As can be seen from the (9), the definition of Fukui function involves derivative of $\rho(r)$ with respect to infinitesimally small number of electrons (δN). This addition or deletion of δN number does not allow the relaxation of orbitals. Table 3 presents the orbital energies of HOMO and LUMO of both σ and π type orbitals. HOMO of π-type and σ type are nearly degenerate in case of 2,2′-bipyridine. The removal of one electron from neutral 2,2′-bipyridine causes too much relaxation and the symmetry of (HOMO-1) orbital and HOMO orbital of the ion changes with respect to the neutral system. As a result of this, it appears that the electron is removed from HOMO-1 (π-type) instead of the HOMO (σ-type). Hence, it is more prudent to calculate FF us-

Table 2. Atom condensed Fukui functions of the systems using relaxed orbitals.

Atom number	2,2′-Bipyridine		Pyridinyltriazine		Pyrazinyltriazine	
	f^+	f^-	f^+	f^-	f^+	f^-
1	**0·0538**	**0·0485**	**0·0468**	**0·0959**	**0·0763**	**0·0846**
2	0·0096	0·0346	0·0322	0·0432	0·0298	0·0488
3	0·0585	0·0543	0·0992	0·0518	0·1134	0·0555
4	0·0345	0·0296	0·0379	0·0438	**0·0617**	**0·0950**
5	0·0005	0·0318	0·0453	0·0368	0·0372	0·0407
6	0·0211	0·0137	0·0332	0·0057	0·0470	0·0150
7	0·0211	0·0137	0·0832	0·0563	0·0811	0·0494
8	**0·0538**	**0·0485**	**0·0336**	**0·1121**	**0·0383**	**0·0971**
9	0·0096	0·0346	**0·1088**	**0·1233**	**0·0832**	**0·1151**
10	0·0585	0·0543	0·1176	0·0663	0·1219	0·0639
11	0·0345	0·0296	0·0359	0·0645	0·0333	0·0598
12	0·0005	0·0318	**0·1144**	**0·0827**	**0·0881**	**0·0733**

Figures in bold letters indicates N atom's FF values where as others indicate C atom's FF values
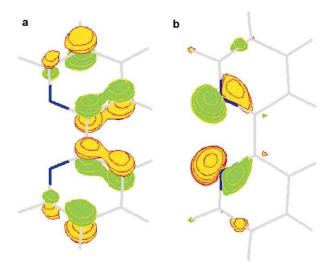

Figure 2. HOMO density plots (**a**) $N_0 - 1$ state of 2,2′-bipyridine (**b**) N_0 state of 2,2'-bipyridine.

ing addition or deletion of one electron, but using orbitals which are frozen (frozen orbital approximation). On removal and addition of an electron to the ground state of a molecular system, only the frontier molecular orbitals (FMO) will undergo the changes. The frozen orbital approach is thus more reliable as it avoids undue relaxation and will be used for further calculations.

4.3 *Intra and intermolecular reactivity sequence*

The electrophilic and nucleophilic FFs calculated under frozen orbital approximation are presented in table 4. Though, the analogues of 2,2′-bipyridine, considered here using relaxed orbitals (see table 2) were indeed predicting the σ-donation from nitrogen and π-acceptance from ring carbon atoms for pyridinyl triazine and pyrazinyl triazine, these effects were only moderate, as indicated by the small values. Electrophilicity or nucleophilicity is highlighted more with the use of frozen orbitals. All the three molecules show the highest nucleophillic FF at N_8. 2,2′-bipyridine shows highest and equal nucleophillic FFs for N_1 and N_8 where as electrophilic FFs for C_3–C_{10}, C_6–C_7. The results obtained so reflects symmetry of 2,2′-bipyridine confirming the equal probability for σ-donation and π-acceptance. In Pyridinyl triazine, C_9–H_{16} and C_{12}–H_{13} of 2,2′-bipyridine are substituted by electron withdrawing N atoms. With these additional N atoms not only symmetrical geometry is lost but also reactivity is affected. The major donation is seen at N_8 and N_9 whereas N_{12} partially contributes. No donation is observed through N_1 in pyridine ring. In this system, when we look at the f^+ values of N_9 and N_{12}, it is higher than f^- values thereby proving to be better π-acceptor sites within the molecule. In addition, C_{10} and C_{11} of the triazine ring affirm nucleophilic attack. Similarly, for pyrazinyl triazine, the lone pair donation is through N_8 and N_9. The C_7 and C_{10} have higher electrophilic FFs, but N_9 and N_{12} of pyrazinyl ring do not depict as strong π-acceptance character as pyridinyl triazine. The additional N atom substituted for C_4–H_{18} of the 2,2′-bipyridine increases the acceptance at C_3 and C_6 of the pyrazinyl ring.

Table 3. Orbital energies (a.u.).

Orbital symmetry	HOMO		LUMO	
	σ	π	σ	π
2,2′-Bipyridine	−0·2317	−0·2324	0·0882	−0·0459
Pyridinyltriazine	−0·2259	−0·2545	0·0985	−0·0713
Pyrazinyltriazine	−0·2337	−0·2675	0·1036	−0·0808

Table 4. Atom condensed Fukui functions of the systems using frozen orbital approximation.

	2,2′-Bipyridine		Pyridinyltriazine		Pyrazinyltriazine	
Atom number	f^{+}	f^{-}	f^{+}	f^{-}	f^{+}	f^{-}
1	**0·1039**	**0·2572**	**0·0160**	**0·0956**	**0·0689**	**0·0986**
2	0·0049	0·0495	0·0081	0·0100	0·0072	0·0164
3	0·1482	0·0523	0·0366	0·0076	0·0984	0·0154
4	0·0530	0·0092	0·0024	0·0010	**0·0219**	**0·0551**
5	0·0463	0·0185	0·0332	0·0108	0·0381	0·0186
6	0·1383	0·0533	0·0264	0·0091	0·0734	0·0156
7	0·1383	0·0533	0·0822	0·0636	0·1339	0·0599
8	**0·1039**	**0·2571**	**0·0505**	**0·3157**	**0·0099**	**0·2648**
9	0·0049	0·0495	**0·2575**	**0·2546**	**0·1529**	**0·2319**
10	0·1482	0·0523	0·1132	0·0592	0·1568	0·0524
11	0·0531	0·0092	0·1009	0·0276	0·0689	0·0986
12	0·0463	0·0185	**0·2673**	**0·1202**	**0·0072**	**0·0164**

Figures in bold letters indicates N atom's FF values where as others indicate C atom's FF values

Table 5 focuses on the atom-condensed philicity and group philicity values of bipyridine and its analogues. The philicity index is used to compare the 3 molecules. In case of 2,2′-bipyridine, N_1 and N_8 shows similar probability for the electrophilic attack whereas in the analogues only triazine ring is active with highest nuclephilic FF at N_8 and no contribution from N_1 of the adjacent ring. This suggests the loss of chelation in the two analogues. The experimentally observed metal approach distances (see table 6) supports these site selectivity calculations, where metal is closer to the N_8 of the triazine rings. Also from the local philicity, we observe that N_8 of pyridinyl triazine shows higher probability for electrophillic attack where as N_9, N_{12} shows higher probability for nucleophillic attack compared to 2,2′-bipyridine and pyrazinyl triazine. The global philicity for 2,2′-bipyridine is 0·1153 and increases to 0·1428 and 0·1616 for pyridinyl triazine to pyrazinyl triazine respectively. We have also calculated the group philicity (both donation and acceptance

character) of atoms in the triazine ring (atoms numbering 7 to 12) of pyridinyl triazine and pyrazinyl triazine and observe that the reactivity of this ring is lower in pyrazinyl triazine, although overall reactivity of pyrazinyl triazine is higher. This is due to the substitution of one CH group by N atom in the adjacent ring in the pyrazinyl compound. This shows higher donation and acceptance at triazine ring of pyridinyl triazine than the pyrazinyl triazine.

In order to discuss the electrophilicity or nucleophilicity of the systems from the perspective of the type of orbital involved for the attack, Geerlings and co-workers[44] separated the σ and π molecular orbitals to calculate the Fukui functions. The idea of separating the σ and π molecular orbitals is extremely important to study the supra-molecular formation involving such class of systems. However, within the framework of frozen orbital approximation, $\sigma-\pi$ separation is more trivial and the following relations will hold:

Table 5. Atom condensed philicity and group philicity of the systems using frozen orbital approximation.

Atom number	2,2′-Bipyridine		Pyridinyltriazine		Pyrazinyltriazine	
	w^+	w^-	w^+	w^-	w^+	w^-
1	**0·0119**	**0·0296**	**0·0022**	**0·0136**	**0·0111**	**0·0159**
2	0·0005	0·0057	0·0011	0·0014	0·0011	0·0026
3	0·0170	0·0060	0·0052	0·0010	0·0159	0·0024
4	0·0061	0·0010	0·0003	0·0001	**0·0035**	**0·0089**
5	0·0053	0·0021	0·0047	0·0015	0·0061	0·0030
6	0·0159	0·0061	0·0037	0·0012	0·0118	0·0025
Σ	0·0570	0·0507	0·0175	0·0191	0·0497	0·0355
7	0·0159	0·0061	0·0117	0·0090	0·0216	0·0096
8	**0·0119**	**0·0296**	**0·0072**	**0·0450**	**0·0016**	**0·0427**
9	0·0005	0·0057	**0·0367**	**0·0363**	**0·0247**	**0·0374**
10	0·0170	0·0063	0·0161	0·0084	0·0253	0·0084
11	0·0061	0·0010	0·0144	0·0039	0·0111	0·0159
12	0·0053	0·0021	**0·0381**	**0·0171**	**0·0011**	**0·0026**
Σ	0·0570	0·0507	0·1244	0·1200	0·0855	0·1169

Figures in bold letters indicates N atom's philicity values where as others indicate C atom's philicity values.

Table 6. Comparative density values of 2,2′-bipyridine, pyridinyl triazine, pyrazinyl triazine.

Distance from N atoms		Density$*10^{-4}$ (a.u.)		
$N(1)$	$N(8)$	2,2′-Bipyridine	Pyridinyltriazine	Pyrazinyltriazine
2·257	2·139	49·70	32·83	27·55
2·262	2·104	54·82	38·14	31·99
2·296	2·124	51·78	35·58	29·70

$$f^- \approx f_x^- \quad \forall\{HOMO \in x \mid x = \sigma, \pi\}$$
$$f^+ \approx f_x^+ \quad \forall\{LUMO \in x \mid x = \sigma, \pi\}$$
(21)

hence values presented in table 4 for f^- and f^+ are nothing but f_σ^- and f_π^+, respectively. The high value of f_σ^- on N atoms using HOMO indicates high reactivity for an electrophilic attack in the molecular plane of ring, hence proving σ-donation through N atom. Similarly, f_π^+ obtain through LUMO indicates that it is very likely for a nucleophile to attack in the plane perpendicular to molecular plane of the ring. The stereographs of HOMO and LUMO of all three ligands are shown in figure 3. The density plots show that HOMO is of σ-symmetry and LUMO is of π-symmetry for each system. As observed from the plots, HOMO contribution mainly comes from the σ-orbitals centered on the nitrogen atoms and LUMO contributions from the P_z orbitals of C atoms in case of 2,2′-bipyridine whereas additional triazine

N atoms also contributes in case of its analogues. All the three ligands are therefore of the same class i.e. σ-donor and π-acceptor.

4.4 *Electron density analysis*

Table 6 presents the electron density values calculated at different distances (experimentally observed for metal approach) for the bipyridine and its analogues. It may, however, be noted that experiments have been carried out in solution phase where as our calculations are done on the gas phase. As our main interest here is to count the σ-donation character of three molecules, we focus on the $\rho(r)$ numbers. The electron density values for bipyridine analogues are lower than the bipyridine. This drop is primarily due to the substitution of –CH groups by N atoms. 2,2′-bipyridine being both σ-donor and π-acceptor, the lone pair on nitrogen atom forms a σ-bond with the central metal atom while the aromatic system takes

part in back bonding. 2,2′-bipyridine having two *N* donor atoms, separated by two carbon atoms, form a five member ring, which is the most stable structu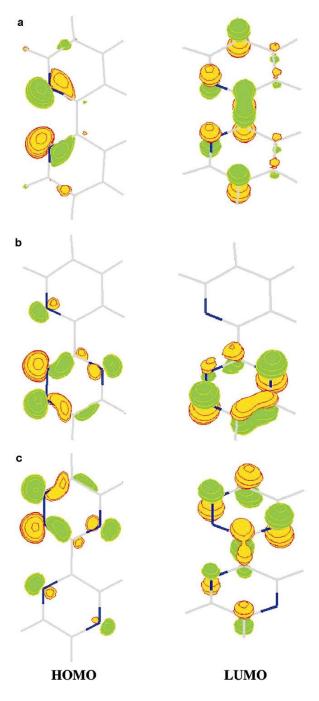re. The diimine part of the bipyridine delocalizes the electrons in the chelate ring.[19] This chelation is no longer effective for pyridinyl triazine and pyrazinyl triazine as additional *N* atoms act as electron withdrawing agent and thus reducing electron density at diimine nitrogen.

5. Conclusion

Two approximations to calculate Fukui functions have been discussed. The significance of frozen orbital approximation compared to relaxed orbital approximation is highlighted with the illustrative example. Atom-condensed Fukui functions within the FOA, clearly predicts the intra-molecular reactivity, electron rich *N* atoms being dominant nucleophile where as electron deficient C atoms as electrophiles. Further, the inter-molecular reactivity index 'philicity' interprets that as the more number of –CH groups are substituted by *N* atoms, only triazine ring gets activated with the highest donor character at N_8 atom, where as N_1 has no contribution, there by reducing the chelation at diimine nitrogen atoms. This is also supported by our electron density calculations. Electron density analysis shows that the electron density around the bonding distances of N-atoms are higher in bipyridine ring, compared to the density of the corresponding atoms in pyridinyl triazine and pyrazinyl triazine. The calculation of group philicity of triazine ring shows lower donation or acceptance character of the ring in pyrazinyl compound than the pyridinyl compound, though latter has overall lower reactivity. The idea of calculating descriptors using σ and π molecular orbital separation is impelling to explain the formation of supra-molecular assemblies through sigma-pi complexation. All the three molecules are of σ-donor and π-acceptor type. 2,2′-bipyridine being stronger σ-donor and its analogues being better π-acceptor.

Figure 3. HOMO and LUMO density plots (**a**) 2,2′-bipyridine (**b**) 3-(2-pyridinyl)-1,2,4-triazine (**c**) 3-(2-pyrazinyl)-1,2,4-triazine.

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