

# Role of substituents on the reactivity and electron density profile of diimine ligands: A density functional theory based study

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**Abstract.** In this paper, we study the reactivity of diimines like 2, 2'-bipyridine, 1, 10-phenanthroline and 1, 2, 4-triazines using density-based reactivity descriptors. We discuss the enhancement or diminution in the reactivity of these ligands as a function of two substituent groups, namely methyl ( $-\text{CH}_3$ ) group and phenyl ( $-\text{C}_6\text{H}_5$ ) group. The global reactivity descriptors explain the global affinity and philicity of these ligands, whereas the local softness depicts the particular site selectivity. The inter-molecular reactivity trends for the same systems are analysed through the philicity and group philicity indices. The  $\sigma$ -donor character of these ligands is quantified with the help of electron density profile. In addition, the possible strength of interaction of these ligands with metal ions is supported with actual reaction energies of Ru-L complexes.

**Keywords.** Reactivity descriptors; DFT; diimine; 2,2'-bipyridine; substituent effects; Ru-ligand interaction.

## 1. Introduction

Aromatic nitrogen heterocycles represent an important class of ligands in coordination chemistry.<sup>1</sup> Among them monodentate ligands, such as pyridine, chelating ligands, such as 2,2'-bipyridine and its analogues, 1,10-phenanthroline readily form stable complexes with most of the transition metal ions and have been extensively used in both analytical and preparative coordination chemistry.<sup>2-6</sup> The particular reasons for this property include (i) the versatile coordination behaviour due to the good  $\sigma$ -donor and  $\pi$ -acceptor characteristics and the flexibility of the  $\alpha$ -diimine molecule, and (ii) the apparently facile activation of the metal coordinated  $\alpha$ -diimine for a whole range of both stoichiometric and catalytic reactions.<sup>7-14</sup> Such compounds are also used to model important bio-inorganic systems such as some metalloproteins and are finding applications as photosensitizers which are used in dye-sensitized solar cells. The charge-transfer properties of photosensitizers can be tuned by substituting the different functional groups. The ability of  $\alpha$ -diimines to form ionic and neutral guest compounds makes them useful precursors in supra-molecular chemistry.<sup>15-19</sup> Six-membered aromatic nitrogen heterocycles have relatively low energy

$\pi^*$  orbitals which act as good acceptors of metal d-orbital electron density in metal-ligand back bonding. Thus metal-ligand interactions are governed by the specific metal and ligand involved.<sup>20,21</sup> Such complexes can exhibit interactions, such as electron transfer, magnetic coupling and inter-valence transfer.<sup>21</sup> The interaction between the metal centre and ligand takes place via the  $\pi$  system.

These kinds of metal-ligand interactions can be tuned by conjugation between the coordination sites. The measure of some important electronic properties such as ionization energy, electron affinity, etc., through the introduction of electron donating (ED) or electron withdrawing (EW) substitutions follows a long established method in bio-chemical and molecular electronics engineering.<sup>22-26</sup> ED or EW substituents can increase or decrease the energies of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) relative to that of bare molecule, allowing a significant modification of the molecular electronic properties. Therefore, fine tuning of the ligand using different functional groups can help in designing various metal-ligand reactions which can be used in various chemical and biochemical process as mentioned earlier.

Theoretical descriptors using conceptual density functional theory have been used extensively in recent years to calculate chemical properties.<sup>27</sup> Recent studies describe the utility of these concepts in both qualitative and quantitative terms in the field of molecular

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structure, chemical bonding, reactivity and selectivity of molecules.<sup>28–35</sup> Among these, density based descriptors such as, global reactivity descriptors, local reactivity descriptors and local hard–soft, acid–base principle, principle of maximum hardness are extensively used to understand the chemical systems and its reactivity.<sup>36–40</sup> The global reactivity descriptors chemical potential ( $\mu$ ), electronegativity ( $\chi$ ), hardness ( $\eta$ ) and philicity ( $w$ )<sup>41,42</sup> have systematized the study of overall stability of the chemical species in this area.

Concerning the local descriptors specifically the Fukui function (FF),  $f(r)$ , the local softness  $s(r)$  and the local philicity  $w(r)$  have attracted recent attention. The atom condensed versions of these descriptors are frequently used to study site selectivity and intra-molecular reactivity of various systems probing accurate electrophilic and nucleophilic attacks.<sup>43a</sup> There are many other local reactivity descriptors used for site reactivity and selectivity namely multiphilic descriptors, local ionization energy, reactivity-selectivity descriptor, etc.<sup>43</sup> Although these indices were successful in generating the experimentally observed intra-molecular reactivity trends in several cases, Roy *et al.*<sup>44</sup> showed that relative electrophilicity and relative nucleophilicity, based on the ratio of electrophilic and nucleophilic FFs (or local softness) and its inverse, are more reliable descriptors to generate improved intra-molecular reactivity trends compared to those obtained from condensed FF indices. Further, the description of the inter-molecular reactivity has been analysed by Krishnamurthy and Pal using the concept of group softness where the group consists of the reacting atoms and the atoms that are directly connected to the reacting atoms.<sup>45</sup> In addition, a specific quantity, philicity  $w(r)$ , defined by Parr *et al.*<sup>46a</sup> and its condensed version are rigorously used in explaining reactivity. Recently, Tanwar *et al.*<sup>47</sup> proposed two reactivity descriptors, viz. Normalized Fukui Function (NFF) and Bond Deformation Kernel (BDK) 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,<sup>48</sup> and pursued by Pal and co-workers,<sup>49</sup> as well as, Geerlings and co-workers<sup>50</sup> to a variety of chemical situations, is suited to semi-quantitative description of interaction energy.

In this paper, we study the role of substituents towards the enhancement and/or diminution of the reactivity of 2, 2' bipyridine and its analogues with Ruthenium metal using these descriptors. For this purpose, we consider various substituted diimines. The effect of methyl and phenyl groups on the reactivity of these diimines will be studied within the framework of Frozen Core Approximation (FCA). The reliability

of FCA has been already discussed by Kulkarni *et al.* in analysing the ligand characteristics.<sup>27d</sup>

The present paper has been organized as follows. In section 2, we describe theoretical background leading to definitions of various global and local reactivity descriptors. Section 3 provides the computational details and the methodology used for the calculations. In section 4 we focus on the results and discussion of the various calculations for the systems under consideration.

## 2. Theoretical background

### 2.1 Density based descriptors of reactivity

The chemical potential ( $\mu$ ), global hardness  $\eta$  and philicity ( $w$ ) are global descriptors which indicate overall stability of the system.<sup>21–24</sup> The global descriptor of a molecule is just the square of the electronegativity divided by its chemical hardness

$$\frac{\mu^2}{2\eta} \quad (1)$$

$$\mu = \left( \frac{\partial E}{\partial N} \right)_{v(r)}, \quad (2)$$

where  $v(r)$  is defined as the external potential

$$\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \quad \text{or} \quad \eta = \frac{1}{2} \left( \frac{\partial \mu}{\partial N} \right)_{v(r)}. \quad (3)$$

Under the FCA and finite difference approximation, the working equation of chemical potential and hardness turns out as follows,

$$\mu = \frac{E_{HOMO} + E_{LUMO}}{2} \quad (4)$$

$$\eta = \frac{E_{LUMO} - E_{HOMO}}{2}. \quad (5)$$

Higher the chemical hardness of an ensemble of the system with constant chemical potential, more stable is the system.

The global softness (S) is the half inverse of the hardness and is related to the overall reactivity of the system. A more powerful global reactive index defined as philicity as follows.<sup>46</sup>

$$W = \frac{\mu^2}{2\eta}. \quad (6)$$

The response of the electron density at each point in space to the variation in the number of electrons is defined as Fukui Function (FF) by Parr and Yang.<sup>17</sup>

Fukui functions have been used widely to measure the reactivity parameters.<sup>45</sup>

$$\left(\frac{\partial^2 E}{\partial N \partial v(r)}\right) = \left(\frac{\partial \rho(r)}{\partial N}\right)_{v(r)} = f(r). \quad (7)$$

A related local property, called local softness is defined as

$$s(r) = \left(\frac{\partial \rho(r)}{\partial \mu}\right)_{v(r)}, \quad (8)$$

so that we obtain

$$\int s(r) dr = S, \quad (9)$$

from equation 8 and 10, it is seen that

$$s(r) = f(r) S. \quad (10)$$

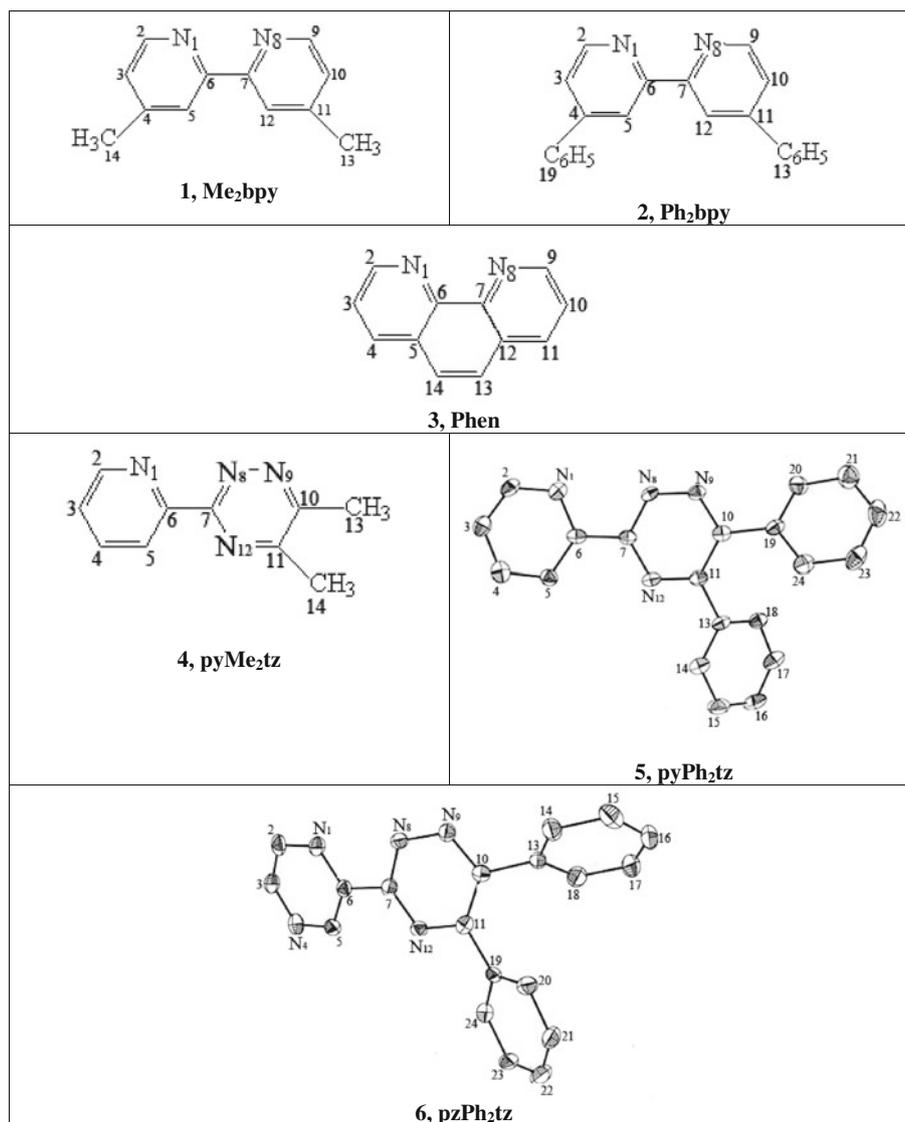
Using left and right derivatives with respect to number of particles, electrophilic and nucleophilic Fukui functions and corresponding local softness and local philicity index is written as,

$$f^+(r) = \rho_{N+1}(r) - \rho_N(r),$$

$$s^+(r) = f^+(r) S, w^+(r) = f^+(r) w \quad (11)$$

$$f^-(r) = \rho_N(r) - \rho_{N-1}(r),$$

$$s^-(r) = f^-(r) S, w^-(r) = f^-(r) w, \quad (12)$$



**Figure 1.** Structural representations of various substituted analogues of diimines considered as ligands in the present work. Note: Depending upon the number of nitrogen atoms present in the systems, it is further categorized as substitution at (i) 2,2'-bipyridine (**1**, **2**), (ii) 3-(2-pyridinyl)-1,2,4-triazine (**4**, **5**) and (iii) 3-(2-pyrazinyl)-1,2,4-triazine (**6**). Along with these systems an extremely important and widely used  $\alpha$ -diimine 1,10-phenanthroline (**3**) is also studied.

$\rho_N$  in the above expression represents the electron density on atom  $k$  for  $N$ -electron system. Similarly,  $\rho_{N+1}$  and  $\rho_{N-1}$  are the electron densities of the  $(N+1)$  and  $(N-1)$  electronic systems calculated at the geometry of the  $N$ -electron system, respectively. To describe the reactivity of atom  $k$  in a molecule, Yang and Mortier<sup>46</sup> defined the condensed quantities as follows,

The condensed electrophilic FF and local softness:

$$f_k^+ = q_k(N+1) - q_k(N), s_k^+ = f_k^+ S \quad (13)$$

and the condensed nucleophilic FF and local softness;

$$f_k^- = q_k(N) - q_k(N-1), s_k^- = f_k^- S, \quad (14)$$

where  $q_k(N)$ ,  $q_k(N-1)$  and  $q_k(N+1)$  are the electronic population of the  $k$ th atom in the  $N$ ,  $(N-1)$  and  $(N+1)$  electronic systems, respectively. Under FCA the atom-condensed Fukui functions will be nothing but the respective atomic population of HOMO or LUMO orbitals. These condensed FFs and local softness has been used as a reliable descriptor of reactivity and site selectivity to predict the intra-molecular reactivity.

Earlier Krishnamurty *et al.*<sup>39a</sup> proposed 'group softness' to describe inter-molecular reactivity trends in carbonyl compounds and organic acids. They defined group softness as

$$s_g = \sum_{k=1}^n s_k, \quad (15)$$

where  $n$  is the number of atoms bonded to the reactive atom,  $s_k$  is the atom-condensed softness of the atom  $k$ , and  $s_g$  is the group softness. Roy *et al.*<sup>44</sup> defined the relative electrophilicity and relative nucleophilicity as  $(f^+/f^-)$  and  $(f^-/f^+)$ , respectively and further it is used to predict the intra-molecular reactivity trend.

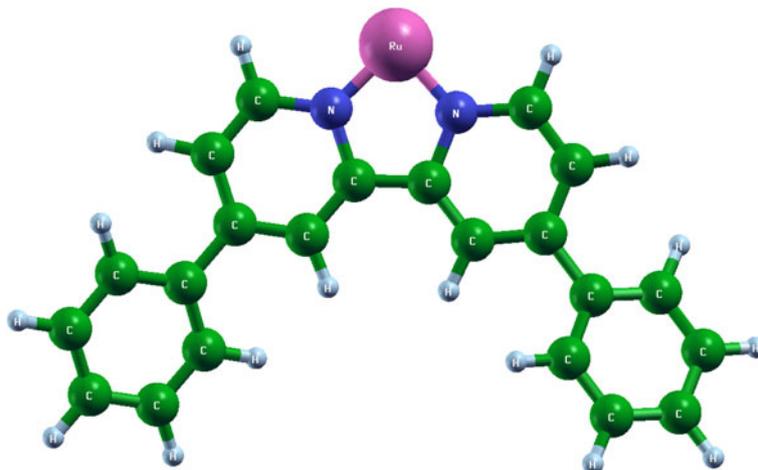
Similarly the local atom-condensed philicity,  $w_A^\alpha$  in the definition is given by,<sup>46c</sup>

$$w_A^\alpha = W f_A^\alpha, \forall \alpha = +, -, 0. \quad (16)$$

The corresponding intermolecular electrophilicity and nucleophilicity condensed to the atom can be calculated using equation 16. This quantity is found to be useful in predicting the extent of partial electron transfer that contributes to the lowering of the total binding energy by maximum flow of electrons.<sup>46,51</sup>

### 3. Computational details

In our previous study, we explained the donor-acceptor character of the 2, 2'-bipyridine and its important analogues viz; 3-(2-pyridinyl)-1,2,4-triazine and 3-(2-pyrazinyl)-1,2,4-triazine, where  $-\text{CH}$  group were substituted by N atoms in basic bipyridine ring.<sup>27d</sup> In the present paper, we further substitute here with methyl and phenyl groups in the concerned ligands. The figure 1 presents all these systems. Along with these systems, an extremely important and widely used  $\alpha$ -diimine 1,10-phenanthroline (3) is also studied. Substituents considered here are mainly the methyl group ( $-\text{CH}_3$ ) and the phenyl group ( $-\text{C}_6\text{H}_5$ ). Thus the systems studied are: (i) 1,Me<sub>2</sub>bpy, (ii) 2,Ph<sub>2</sub>bpy, (iii) 3,Phen, (iv) 4,pyMe<sub>2</sub>tz, (v) 5,pyPh<sub>2</sub>tz, (vi) 6,pzPh<sub>2</sub>tz. The nature of the substituent i.e., methyl and phenyl groups are analysed and have been used to predict the trends in global and local reactivity. The optimization of all these systems is carried out with DFT using the restricted Hartree Fock (RHF) procedure as employed in GAMESS.<sup>52a</sup> The functional used is hybrid functional B3LYP. The basis set used for the geometry optimization and property analysis is 6-31G (d, p). For the



**Figure 2.** The Ru-ligand complex where ligand is 2,2'-bipyridine substituted with the phenyl group.

computation of the corresponding cations and anions of these systems, restricted open shell Hartree-Fock (ROHF) procedure is used under the FCA. The electronic population on the atoms for these neutral, anionic and cationic systems is obtained from Löwdin population analysis.<sup>53</sup> The ionization energy, electron affinity and all other related properties reported here are calculated under FCA. These properties along with condensed version of local softness and the local philicity are computed and are used to explain the substituent effect describing the reactivity of the diimines.

The Ru–ligand interaction energy and all other thermochemical analysis have been computed using the GAUSSIAN.<sup>52b</sup> Considering the heavy nature of metal atom effective core potential (ECP) LANL2<sup>54</sup> have been used for calculating interaction energy. Further, we ensure the complete optimization of all individual ligands and their complexes with non-negative frequency analysis. The pictorial representation of one of the Ru–ligand complex studied in the present study has been shown in figure 2.

#### 4. Results and discussion

The substituent  $-\text{CH}_3$  exerts electron donating (+I) and hyperconjugative effect, whereas  $-\text{C}_6\text{H}_5$  exerts electron withdrawing (–I) effect and depending on the system to which it is attached and the manner in which it is attached determine the structural parameters and the change in the atomic charge redistribution and properties like ionization energies and electron affinities, etc. It may be noted however that we have observed that the substituents of diimine do not change the structural parameters, but only affect other properties and the consequent reactivities.

##### 4.1 Global reactivity

The calculated ionization energy and the electron affinity values of these diimines along with global reactivity descriptors are summarized in table 1. The ionization

energy and electron affinity are among the primary energy considerations used in quantifying chemical systems. In general, the electron affinity increases as more number of  $-\text{CH}$  groups are substituted by nitrogen atoms in the diimine ring as shown in our previous study.<sup>27d</sup> These additional N atoms holds partial negative charge more effectively compared to C atoms at the same position, ultimately increasing its overall affinity. Therefore, one may expect the phenyl ring to affect the affinity of 5,pyPh<sub>2</sub>tz and 6,pzPh<sub>2</sub>tz. However, the bulky phenyl substitution at adjacent carbon atoms causes steric hindrance and loses the planarity with the triazine ring of the system. The lower affinity values of 2,2'-bipyridine substituents viz; structure 1, 2 and 3 highlights the step-up  $\pi$ -acceptance of the diimines containing more number of N atoms in structure 4, 5 and 6. In addition, the affinity comparison between the 1, Me<sub>2</sub>bpy and 2,Ph<sub>2</sub>bpy systems clearly highlights the significance of hyperconjugative effect of methyl group in stabilizing the 1, Me<sub>2</sub>bpy like systems.

The ionization energy physically signifies a measure of the reluctance of a molecule to surrender an electron. The overall trend observed for ionization energies among the 6 diimines is: 4, pyMe<sub>2</sub>tz < 5, pyPh<sub>2</sub>tz < 6, pzPh<sub>2</sub>tz < 1, Me<sub>2</sub>bpy < 3, Phen < 2, Ph<sub>2</sub>bpy. Following the trend one can conclude that the ionization energy decreases with the increase of N atoms. Further, the methyl substituents show lower ionization energy than the phenyl substituents, when compared between the molecules containing the same number of N atoms. This suggests that the systems with methyl substituents contribute more towards electron donating character. The above results demonstrate the strongest influence of the type and position of the substitution on the electronic properties of the diimines.

Similar conclusion can be drawn from the chemical potential and hardness parameters reported in table 1. Based on the 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

**Table 1.** Global properties of the systems: Chemical potential, hardness, softness and philicity (values in atomic units).

System	Electron affinity	Ionization energy	Hardness	Chemical potential	Softness	Philicity
1, Me <sub>2</sub> bpy	0.0419	0.2261	0.0921	–0.1340	5.4288	0.0974
3, Phen	0.0491	0.2265	0.0887	–0.1378	5.6369	0.1070
2, Ph <sub>2</sub> bpy	0.0556	0.2285	0.0864	–0.1420	5.7836	0.1166
4, pyMe <sub>2</sub> tz	0.0628	0.2160	0.0766	–0.1394	6.5274	0.1268
5, pyPh <sub>2</sub> tz	0.0676	0.2185	0.0754	–0.1430	6.6269	0.1355
6, pzPh <sub>2</sub> tz	0.0770	0.2240	0.0737	–0.1507	6.7842	0.1540

system has maximum chemical hardness value. Hence, MHP is a qualitative tool to study the stability of the system. In the present investigation, the chemical hardness values decrease straightly from 0.0921 to 0.0737 for 1,Me<sub>2</sub>bpy and 6,pzPh<sub>2</sub>tz, respectively. The substituents with -R effect and -I effect (phenyl group) destabilizes the diimines than that containing the substituent with +I (methyl group) effect. However, the global softness increases with the N substitution and the phenyl substitution, predicting higher polarizability, hence reactivity of the systems. To analyse the change in electrophilic power of the diimines system upon ED and EW substitution, the molecular electrophilic power has been calculated. In general, the substituted N atoms enhance the electrophilic power of the diimines irrespective of the nature and position of the methyl and the phenyl substitution. In addition, the EW phenyl group contributes more to the increment of overall electrophilic power as shown in table 1.

Thus, the overall global reactivity of diimines are increasing as the number of N atoms in the ring increases as depicted by the softness values of table 1. In comparing reactivity of systems containing same number of N atoms in the ring, the ED methyl group stabilizes and hence makes it less reactive system where as phenyl group increases its reactivity. The phenyl groups when substituted on the adjacent C atoms of the ring (5 and 6) suffer from steric hindrance and lose its planarity with diimine rings. Therefore, tuning of the substitution either with ED or EW functional groups allows these systems to be more reactive and can be shown to be more interactive with metals.

#### 4.2 Intra and inter-molecular reactivity trend

Although the global reactivity descriptors explain the reactivity of these systems, it is very important to understand the individual atom activity to design new materials. Hence, in this section, we analyse the electrophilic and nucleophilic nature of functional ring atoms with the help of atom condensed local softness descriptors, namely, electrophilic,  $s_k^+$  and nucleophilic,  $s_k^-$ . Similarly, philicity descriptors are used to discuss the inter-molecular reactivity trend among these molecules. The electrophilic and nucleophilic local softness descriptors calculated under FCA are presented in tables 2 and 3 for that of 2,2'-bipyridine substituents and -1,2,4-triazine substituents, respectively.

In our previous study, we have shown that the 2, 2'-bipyridine exerts  $\sigma$ -donor character through the N atoms and  $\pi$ -acceptor character through C atoms.<sup>27d</sup> As we consider various substituents to this ligand, the individual atom of the ring shows diverse reactivity. In case of methyl substituent, 1,Me<sub>2</sub>bpy, the nucleophilicity of both N atoms and electrophilicity of C<sub>3</sub>-C<sub>10</sub>, C<sub>6</sub>-C<sub>7</sub> enhances. The reason for this reactivity enhancement can be attributed to the +I effect and hyper-conjugative effect of -CH<sub>3</sub> group. On the contrary, in phenyl group substitution, 2,Ph<sub>2</sub>bpy, these N atoms are no longer nucleophile, instead, their  $s_k^+$  values predict them to be competent electrophile. The EW nature i.e., -R effect of phenyl group increases electron density at C<sub>3</sub>-C<sub>10</sub>, thus transferring nitrogen atom's nucleophilic nature to them. In general, the other atoms present in the 2,Ph<sub>2</sub>bpy shows higher  $s_k^+$  values over their respective

**Table 2.** Atom condensed local softness descriptors of the systems.

Atom number	1,Me <sub>2</sub> bpy		2,Ph <sub>2</sub> bpy		3,Phen	
	$s_k^+$	$s_k^-$	$s_k^+$	$s_k^-$	$s_k^+$	$s_k^-$
1	<b>0.5180</b>	<b>1.9314</b>	<b>0.6037</b>	<b>0.3823</b>	<b>0.2595</b>	<b>0.2352</b>
2	0.0638	0.1811	0.0642	0.1774	0.6513	0.5127
3	0.7659	0.1527	0.5339	0.9824	0.0375	0.0143
4	0.2761	0.0113	0.4483	0.1287	0.5748	0.3955
5	0.2739	0.0994	0.0236	0.1443	0.2272	0.1976
6	0.7330	0.1789	0.3383	0.3919	0.1708	0.3999
7	0.7330	0.1789	0.3382	0.3919	0.1708	0.3999
8	<b>0.5180</b>	<b>1.9314</b>	<b>0.6036</b>	<b>0.3823</b>	<b>0.2595</b>	<b>0.2352</b>
9	0.0638	0.1811	0.0642	0.1774	0.6513	0.5127
10	0.7659	0.1527	0.5339	0.9824	0.0375	0.0143
11	0.2761	0.0113	0.4483	0.1287	0.5748	0.3955
12	0.2739	0.0994	0.0236	0.1443	0.2272	0.1976
13	0.0141	0.0124	0.1801	0.1726	0.8584	1.0428
14	0.0141	0.0124	0.2001	0.1382	0.8584	1.0428

Note: Figures in bold indicate descriptor values of N atom, where as other indicate C atom's descriptor values

**Table 3.** Atom condensed local softness descriptors of the systems.

Atom number	4,pyMe <sub>2</sub> tz		5,pyPh <sub>2</sub> tz		6,pzPh <sub>2</sub> tz	
	$s_k^+$	$s_k^-$	$s_k^+$	$s_k^-$	$s_k^+$	$s_k^-$
1	<b>0.1301</b>	<b>0.4105</b>	<b>0.3209</b>	<b>0.4212</b>	<b>0.6794</b>	<b>0.4440</b>
2	0.0572	0.0437	0.0232	0.0496	0.0492	0.0758
3	0.2851	0.0330	0.3716	0.0415	0.7188	0.0723
4	0.0243	0.0051	0.1590	0.0053	<b>0.3090</b>	<b>0.2321</b>
5	0.2352	0.0581	0.1435	0.0650	0.1377	0.0935
6	0.2220	0.0446	0.2572	0.0466	0.5095	0.0739
7	0.5652	0.4289	0.6917	0.4368	0.8672	0.431
8	<b>0.2619</b>	<b>2.0863</b>	<b>1.0409</b>	<b>2.0756</b>	<b>0.6804</b>	<b>1.9093</b>
9	<b>1.5048</b>	<b>1.7866</b>	<b>0.1420</b>	<b>1.7567</b>	<b>0.1125</b>	<b>1.7015</b>
10	0.7579	0.4169	0.6602	0.4102	0.8681	0.3920
11	0.5788	0.2000	0.9719	0.2134	0.4712	0.2114
12	<b>1.6349</b>	<b>0.8020</b>	<b>0.1152</b>	<b>0.7377</b>	<b>0.1571</b>	<b>0.7274</b>
13	0.0246	0.1129	0.1769	0.1006	0.0704	0.0982
14	0.0292	0.0258	0.2074	0.0222	0.0918	0.0230

Note: Figures in bold indicate descriptor values of N atom, where as other indicate C atom's descriptor values

$s_k^-$  values, making this system strong  $\pi$ -acceptor rather than  $\sigma$ -donor. In continuation to this, nitrogen atoms of 1, 10 phenanthroline (3,Phen) are found to be weak nucleophile. Also their electrophilic descriptors,  $s_k^+$ , are as good as their respective nucleophilic descriptors,  $s_k^-$ . Hence, here, N atoms are not even strong electrophile. Similarly, the ring C atoms, C<sub>2</sub>–C<sub>9</sub>, C<sub>4</sub>–C<sub>11</sub> and C<sub>13</sub>–C<sub>14</sub> exert equally prominent  $s_k^+$  values as their respective  $s_k^-$  values, which make this system average  $\sigma$ -donor and  $\pi$ -acceptor. On the other hand, the substituted 1, 2, 4-triazine ligands (structure 4, 5, 6) (see table 3) showing the major donation at N<sub>8</sub> and N<sub>9</sub> whereas N<sub>12</sub> partially contributes. No significant donation is observed through N<sub>1</sub> and/or N<sub>4</sub> of pyridine ring. However, in case

of 4,pyMe<sub>2</sub>tz when we look at the  $s_k^+$  value (1.6349) of N<sub>12</sub>, it is almost double that of its  $s_k^-$  value (0.8020) thereby proving it to be potential nucleophile attacking site in addition to C<sub>7</sub>, C<sub>10</sub> and C<sub>11</sub> as nucleophile attacking sites. Similarly, in case of 5,pyPh<sub>2</sub>tz and 6,pzPh<sub>2</sub>tz, C<sub>3</sub>, C<sub>7</sub>, C<sub>10</sub> and C<sub>11</sub> of triazine ring affirm electrophilicity. In addition, the N<sub>1</sub> and/or N<sub>4</sub> of the pyridine ring confirm nucleophile attack from their adequate  $s_k^+$  values. Therefore, the –R effect of phenyl group affects the reactivity if and only if the phenyl ring is planar with diimine ring; else it has no role in strengthening the reactivity of ligand.

Tables 4 and 5 focus on the atom-condensed philicity and group philicity of bipyridine substituents and

**Table 4.** Atom condensed philicity and group philicity of the systems.

Atom number	1,Me <sub>2</sub> bpy		2,Ph <sub>2</sub> bpy		3,Phen	
	$w_k^+$	$w_k^-$	$w_k^+$	$w_k^-$	$w_k^+$	$w_k^-$
1	<b>0.0093</b>	<b>0.0346</b>	<b>0.0121</b>	<b>0.0077</b>	<b>0.0044</b>	<b>0.0040</b>
2	0.0011	0.0032	0.0012	0.0035	0.0112	0.0088
3	0.0137	0.0027	0.0107	0.0198	0.0006	0.0002
4	0.0049	0.0002	0.0090	0.0025	0.0099	0.0068
5	0.0049	0.0017	0.0004	0.0029	0.0039	0.0034
6	0.0131	0.0032	0.0068	0.0079	0.0029	0.0069
$\Sigma$	0.047	0.0456	0.0402	0.0443	0.0329	0.0301
7	0.0131	0.0032	0.0068	0.0079	0.0029	0.0069
8	<b>0.0093</b>	<b>0.0346</b>	<b>0.0121</b>	<b>0.0077</b>	<b>0.0044</b>	<b>0.0040</b>
9	0.0011	0.0032	0.0012	0.0035	0.0112	0.0088
10	0.0137	0.0027	0.0107	0.0198	0.0006	0.0002
11	0.0049	0.0002	0.0090	0.0025	0.0099	0.0068
12	0.0049	0.0017	0.0004	0.0029	0.0039	0.0034
$\Sigma$	0.0474	0.046	0.0402	0.0443	0.0329	0.0301

Note: Figures in bold indicate descriptor values of N atom, where as other indicate C atom's descriptor values

**Table 5.** Atom condensed philicity and group philicity of the systems.

Atom number	4,pyMe <sub>2</sub> tz		5,pyPh <sub>2</sub> tz		6,pzPh <sub>2</sub> tz	
	$w_k^+$	$w_k^-$	$w_k^+$	$w_k^-$	$w_k^+$	$w_k^-$
1	<b>0.0025</b>	<b>0.0079</b>	<b>0.0065</b>	<b>0.0086</b>	<b>0.0154</b>	<b>0.0100</b>
2	0.0011	0.0008	0.0004	0.0010	0.0011	0.0017
3	0.0055	0.0006	0.0076	0.0008	<b>0.0163</b>	<b>0.0016</b>
4	0.0004	9.9E-05	0.0032	0.0001	0.0070	0.0052
5	0.0045	0.0011	0.0029	0.0013	0.0031	0.0021
6	0.0043	0.0008	0.0052	0.0009	0.0115	0.0016
$\Sigma$	<i>0.0183</i>	<i>0.0112</i>	<i>0.0258</i>	<i>0.0127</i>	<i>0.0544</i>	<i>0.0222</i>
7	0.0109	0.0083	0.0141	0.0089	0.0196	0.0097
8	<b>0.0050</b>	<b>0.0405</b>	<b>0.0212</b>	<b>0.0424</b>	<b>0.0154</b>	<b>0.0433</b>
9	<b>0.0292</b>	<b>0.0347</b>	<b>0.0029</b>	<b>0.0359</b>	<b>0.0025</b>	<b>0.0386</b>
10	0.0147	0.0080	0.0135	0.0083	0.0197	0.0088
11	0.0112	0.0038	0.0198	0.0043	0.0106	0.0048
12	<b>0.0317</b>	<b>0.0155</b>	<b>0.0023</b>	<b>0.0150</b>	<b>0.0035</b>	<b>0.0165</b>
$\Sigma$	<i>0.1027</i>	<i>0.1108</i>	<i>0.0738</i>	<i>0.1148</i>	<i>0.0713</i>	<i>0.1217</i>

Note: Figures in bold indicate descriptor values of N atom, where as other indicate C atom's descriptor values

-1,2,4-triazine substituents, respectively. The philicity index is used to compare the inter-molecular reactivity trends among these substituted ligands. In case of bipyridine substituents, both the pyridine rings show similar probability of electrophilic or nucleophilic attack. The 1,Me<sub>2</sub>bpy molecule shows equal extent of nucleophilicity and electrophilicity, hence results in  $\sigma$ -donor and  $\pi$ -acceptor type of ligand. However, 2,Ph<sub>2</sub>bpy shows higher nucleophilicity than the electrophilicity, hence it is better  $\pi$ -acceptor ligand. The 3,phen ligand, on the contrary, shows stronger electrophilicity compared to its nucleophilicity, hence concluded to be better  $\sigma$ -donor ligand. This is consistent with the local softness descriptor analysis. In case of -1,2,4-triazine substituents, the group philicity index of triazine ring is more than the adjacent pyridinyl or pyrazinyl rings of 4,pyMe<sub>2</sub>tz to 6,pzPh<sub>2</sub>tz. This predicts that the overall reactivity of triazine ring is higher than the adjacent ring as well as than that of the bipyridine substituents. The -CH<sub>3</sub> group substituted ligand (4,pyMe<sub>2</sub>tz) do not show large difference in the  $w_k^+$  and  $w_k^-$  values. Nonetheless, this difference is noteworthy when -C<sub>6</sub>H<sub>5</sub> group is substituted to these ligands. In general, the nucleophilicity of triazine ring is higher than

the respective electrophilicity value, indicating their enhanced  $\pi$ -acceptance.

#### 4.3 Electron density analysis

Table 6 presents the electron density values calculated at different distances (experimentally observed for metal approach) for the bipyridine substituents and triazine substituents. It may, however, be noted that experiments have been carried out in solution phase where as our calculations are done on the gas phase molecules. As our main interest here is to count the  $\sigma$ -donation character of these molecules, we focus on the  $\rho(r)$  numbers. The electron density value for 3,Phen ligand is maximum among the 6 ligands. This outcome is in agreement with the previous reactivity analysis where 3,Phen was found to be good  $\sigma$ -donor ligand. The reason of such strong interaction can be attributed to the specific geometrical features of 3,Phen. 3,Phen having two N donor atoms, separated by two carbon atoms, form a five-member ring, a chelate ring. The diimine part of the 3,Phen delocalizes the electrons in the chelate ring as well as in three aromatic rings, eventually increasing the electron density of ligand. Such

**Table 6.** Comparative density values of 2,2'-bipyridine substituents and triazine substituents.

Distance from N atoms		Density* 10 <sup>-4</sup> (a. u.)					
N(1)	N(8)	1,Me <sub>2</sub> bpy	2,Ph <sub>2</sub> bpy	3,Phen	4,pyMe <sub>2</sub> tz	5,pyPh <sub>2</sub> tz	6,pzPh <sub>2</sub> tz
2.257	2.139	3.83	0	165.65	3.93	4.1	68.91
2.262	2.104	4.18	0	184.98	4.43	4.66	68.94
2.296	2.124	3.74	0	165.65	3.85	4.06	63.12

chelation is no longer effective for phenyl substituted ligands (2, 5) as their  $-R$  effect fails to delocalize electron density cloud through resonance thus reducing it at diimine nitrogen. Conversely, electron density value for phenyl substituted pyridinyl triazine ligand (6) is significantly higher. In case of 5,pyPh<sub>2</sub>tz only one phenyl ring is out of diimine ring plane whereas second phenyl ring, which is planar with diimine ring, pertains  $-R$  effect, finally reducing electron density at the chelating N atoms. However, in case of 6,pzPh<sub>2</sub>tz both phenyl rings are non-planar to diimine ring, which assists to resonate charge in the chelating ring. Surprisingly, electron density of methyl substituted ligand is less. This suggests that enhancement of  $\sigma$ -donation cannot be increased sufficiently by substitution of merely  $-CH_3$  group, instead, a group with stronger  $+I$  effect is needed to improve the  $\sigma$ -donor character of these ligands.

#### 4.4 Reaction energies for Ru–ligand interaction

Relevance of calculations presented in the previous section can be verified by actually evaluating the reaction energies for Ru–ligand interaction. Hence, we have calculated the interaction energy, enthalpy and free energy of complex formation for the considered ligands when complexes with Ru metal atom. These quantities are tabulated in tables 7 and 8 for basic ligands and substituted ligands, respectively. The actual interaction energies have been calculated using the following conventional formula.

$$E_{ABint} = [E_{ABcomplex} - (E_A + E_B)].$$

We have already discussed the reactivity of 2,2'-bipyridine and its important analogues 3-(2-pyridinyl)-

1,2,4-triazine and 3-(2-pyrazinyl)-1,2,4-triazine, which are generated by substitution of  $-CH$  group by N-atoms in the bipyridine ring in our previous publication.<sup>27d</sup> In the present study, we briefly recall this, which is necessary for understanding the possible influence of substituents on the strength of their interaction with metal ions. The previous study concluded that 2,2'-bipyridine is a better  $\sigma$ -donor and its analogues are better  $\pi$ -acceptors. In line with this, our reaction energy values (as shown in table 7) show complex formation of Ru metal atom more favourable for both triazines compared to bipyridine. Although, reaction with the Ru metal is exothermic for all these three basic ligands, these values are increasing with the number of N atoms. While making the complex formation with Ru metal the pyridinyl triazine interaction energy is 14 kcal/mol and pyrazinyl triazine is 17 kcal/mol relative to the bipyridine ligand. This stability is also reflected while measuring the metal ligand bonding distances. In case of bipyridine complex, Ru metal is optimized at 1.76 Å from both nitrogen donor atoms. However, in triazine complexes the Ru metal gets closer to triazine ring nitrogen atom N(8) and is stable at 1.72 Å bond distance. We explain this extra stability of latter complexes from the charges built on the Ru metal atom in the respective complexes. The Natural Population Analysis (NPA) depicts that the positive charge on Ru is higher in triazine complexes (0.515 and 0.549 a.u. in pyridinyl and pyrazinyl, respectively) than that in bipyridine complex (0.447 a.u.). In addition, we also calculate the gross orbital population. It has been shown in the earlier studies that the Ruthenium metal undergoes *sd* hybridization of 5s and 4d orbitals while making the complex with the ligands.<sup>55–58</sup> In our analysis, the corresponding *sd*-population in bipyridine complex is 7.36 a.u and

**Table 7.** Comparative reaction energies for Ru complexes of 2,2'-bipyridine and triazine.

Properties	Relative reaction energies (kcal/mol)		
	(2,2'-bipyridine)-Ru	(3-(2-pyridinyl)-1,2,4-triazine)-Ru	(3-(2-pyrazinyl)-1,2,4-triazine)-Ru
Interaction energy( $\Delta E$ )	0.0	13.8	17.0
Enthalpy( $\Delta H$ )	0.0	13.9	17.2
Free energy( $\Delta G$ )	0.0	12.7	15.6

**Table 8.** Comparative reaction energies for 2,2'-bipyridine substituents and triazine substituents complexes with Ru.

Properties	Relative reaction energies (kcal/mol)					
	(1,Me <sub>2</sub> bpy)-Ru	(2,Ph <sub>2</sub> bpy)-Ru	(3,Phen)-Ru	(4,pyMe <sub>2</sub> tz)-Ru	(5,pyPh <sub>2</sub> tz)-Ru	(6,pzPh <sub>2</sub> tz)-Ru
Interaction energy( $\Delta E$ )	3.1	7.1	0.0	15.7	17.3	19.8
Enthalpy( $\Delta H$ )	3.1	7.0	0.0	15.8	17.0	19.9
Free energy( $\Delta G$ )	1.4	6.4	0.0	14.3	15.9	18.7

triazine complex is 7.22 a.u. This indicates that Ru metal loses its electrons mostly from hybridized sd-orbitals. Thus, the reason for this extra stability can be attributed to the better  $\pi$ -acceptor character of the triazine rings which eventually help back bonding between metal sd-orbitals and ligand  $\pi^*$ -orbitals.

Further, the +I effect of methyl substituted bipyridine (1) shows  $\sim 3$  kcal/mol increase in reaction energies, whereas the -R effect of phenyl ring (2) increases these quantities by  $\sim 7$  kcal/mol (see table 8). Consequently, the methyl substitution at pyridinyl triazine (4) ligand and the phenyl substitutions (which are non-planar with reactive rings) at triazine (5, 6) ligands do not impart any effect and the corresponding reaction energies are same as those for the corresponding parent ligand (table 7). Briefly, we can conclude that the methyl substituents by their +I effect reduce the  $\pi$ -acceptor character of ligand and on the other hand, phenyl substituents which are planar with active ring by their -R effect enhance the  $\pi$ -acceptor character of ligand. Moreover, all the reaction energies for 3,Phen ligand are less than bipyridine. In actual complex formation, LUMO ( $\pi^*$ -orbital is much higher in energy (0.0213 a.u.) than the metal bonding d-orbitals (-0.0430 a. u.)) of this ligand fails to accept the electron density from HOMO of metal. This fact can be verified by the NPA charges, where the positive charge on Ru (i.e., 0.316 a.u) is less in this complex compared to any other complex. Thereby, 3,Phen can be considered as prominent  $\sigma$ -donor but poor  $\pi$ -acceptor than 2,2'-bipyridine.

## 5. Conclusion

The effect of substituents on the reactivity and electron density profile of diimines like 2, 2'-bipyridine, 1, 10-phenanthroline and 1, 2, 4-triazines has been illustrated with the help of global and local reactivity descriptors. The global reactivity descriptors such as electron affinity, chemical potential, softness, etc. predict that the values of parameters increase with the ligands having more number of N atoms as depicted in our previous study.<sup>27d</sup> Further, substituting phenyl group in our present study shows higher polarizability and hence higher reactivity of the ligands as concluded from our results of calculation of ionization energy, hardness and other parameters depicted in table 1. Consequently, the ionization potential and hardness parameters suggest that the methyl substitution increases the stability of ligands and hence make it less reactive towards the Ruthenium metal as shown from our present study.

The intra-molecular reactivity of these systems is studied with the local softness. The methyl substitution enhances nucleophilic and electrophilic nature of the ring N and C atoms, respectively. The phenyl substitution enhances overall electrophilic nature of the ring atoms. Conversely, local softness descriptor could not express clearly local reactivity of ring atoms in 3,Phen. The inter-molecular reactivity descriptors, philicity and group philicity, suggest that the group electrophilicity of -1,2,4-triazine ligands and phenyl substituted ligands is higher than that of bipyridine ligand and methyl substituted ligands. Hence, these systems can be used for complexation where back bonding with metal is involved. This outcome is also supported with actual reaction energies of Ru-L complexes as shown in table 8. The Ru-L complexes are formed by s-d hybridization.

The electron density profile of these ligands quantifies the  $\sigma$ -donor character of these ligands. The +I effect of -CH<sub>3</sub> group does not show exceptional density at diimine nitrogen as it does not help chelation. Similarly, the -C<sub>6</sub>H<sub>5</sub> group which is planar (in case of ligands 2 and 5) to diimine ring does not help to increase density due to its -R effect. However, when these groups lose their planarity with diimine ring (as in case of ligand 6) due to steric hindrance, it helps to enhance the density to a substantial value due to +R effect. Among all these ligands, 3,Phen shows extraordinary electron density at the diimine N atoms, which is ascribed to its specific geometrical features.

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