Sigma donor and pi acceptor characteristics of certain NN-bidentate ligands: a DFT Study

Syed Raashid Maqsood [a], Nasarul Islam [a], Shabnum Bashir [a],
Badruddin Khan [a] & Altaf Hussain Pandith [a]

[a] Department of Chemistry, University of Kashmir, Srinagar,
Jammu and Kashmir, India

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SYED RAASHID MAQSOOD, NASARUL ISLAM, SHABNUM BASHIR,
BADRUDDIN KHAN and ALTAF HUSSAIN PANDITH*

Department of Chemistry, University of Kashmir, Srinagar, Jammu and Kashmir, India

Metal ion binding affinity of three NN bidentate ligands in terms of simple parameters of the conceptual density functional theory is reported. Role of ligand framework for chelate stabilization for ethylenediamine (en) bipyridyl (bpy), and 1,10 phenanthroline (phen) is quantified on the basis of NCCN dihedral angle (φ) and N–N spatial distance. We find that the sigma (σ) donor character of three NN-bidentate ligands follow the order phen < bpy < en, which is quit opposite to their experimentally observed stability constant data. However, the overall binding affinity order is correlative with the chelate stabilization and pi back acceptance characteristics; thereby explaining the experimental stability order. We also studied the effect of some electron donating and electron withdrawing substituents on the sigma bonding affinity and pi (π) bonding behavior of the various substituted phen derivatives. The overall binding affinity of these derivatives was correlated on the basis of electrophilicity index (ω). σ donor character for the ligands was observed to vary in the order NH_2 > Ph > OH > CH_3 > H > Br > Cl > COOH > NO_2 for the substitution at 2 and 9 positions. The trend was found in synergism with their *Ortho, Para* directing efficiencies.

Keywords: DFT; Dihedral angle; Pi back acceptance character; HOMO; LUMO

Introduction

Thermodynamic stability of metal ion complexes of a ligand species is depicted in terms of binding constant value which in turn depends on various electronic and structural features of the ligand concerned [1–3]. The affinity of a ligand for a metal ion depends on the electrophilicity of its donor atoms which can be quantitatively estimated on the basis of orbital energies involved in the bonding interactions. Apart from electrophillicity of donor atoms, the stability of their complexes may also depend on the approach and orientation of the orbital overlap and, therefore, on the ligand skeletal frame work [4, 5]. The enhanced affinity of chelate type ligands for a metal ion compared to the affinity of a collection of similar nonchelating (monodentate) ligands for the same metal is attributed to both enthalpy and entropy factors. Entropic factors include the statistical probability of second binding site to link to the metal ion, once the nearby atom has linked to it [6]. The contribution from statistical factor, however, depends on the relative position of two binding sites and the variation in the framework structure of the overall ligand. Therefore, for

*Corresponding author. Email: altafpandit23@gmail.com

a series of ligands with same donor atoms, the binding affinities are, apart from other factors, determined by the ligand skeletal framework to the effect of keeping the second binding site juxtaposed at the proper coordination site on the central metal ion [7, 8].

Phenanthroline (Phen), a classic bidentate chelator ligand for transition metal, along with its derivatives, has an important role in coordination chemistry and is of considerable interest as a versatile starting material for organic, inorganic and supramolecular chemistry [9–11]. A number of metal complexes of phen derivatives find important applications in the field of genetic engineering and molecular biology due to their efficiency to cleave the DNA backbone. Recently, the role of the complex $[Cu(phen)_2]^{2+}$ in molecular biology as DNA cleaving reagent has attracted much attention [12, 13]. Its importance in DNA-based biochemical interactions, coupled with its analytical and industrial applications, has made the studies related to Phen derivatives a demanding area of research [14–16].

The understanding of structural and chemical reactivity of important coordination systems at electronic structure level using quantum chemical computations has assumed much significance. Density functional theory (DFT) has, so far, proved significantly efficient in evaluating accurately the substitution effects on various types of properties of biologically, industrially, and medicinally [17–19] important molecules. DFT was founded within the two basic theorems provided by Hohenberg and Kohn in the 1960s [20, 21]. DFT methods are, in general, capable of generating a variety of isolated Quantum mechanical descriptors, such as ionization energies, dipole moment, electrostatic potential, electron affinities, electronegativities, and hardness, etc. quite accurately that can be safely correlated with the physical and chemical properties of the system [22, 23]. In view of this, we have calculated various parameters of NN-bidentate ligands using DFT level of theory. The performance of the DFT method in the description of structural, energetic, and magnetic molecular properties is well established.

The work presented describes a comparative account of binding affinity of some NN-bidentate ligands based on the spatial arrangement of two donor atoms in the ligand and the energy of the orbitals involved in σ and π interactions. Whereas the steric aspects are discussed in light of N–C–C–N dihedral angle and spatial distance between two nitrogen atoms, electrophilicity is discussed in light of HOMO and LUMO energy which are involved in the σ and π interactions, respectively.

Computational method

All calculations were performed using the Gaussian 03 quantum chemistry package [24]. The initial geometries were optimized by DFT level of theory using Becke's three parameter hybrid functional (B3LYP) [25, 26] and the $6 - 31++G(d,p)$ basis set. Moreover, the frequency calculations were performed to verify the optimized structure to be at an energy minimum. σ donor and π acceptance for the studied ligands is discussed in light of given quantum mechanical descriptors (equations (1)–(8)).

Theoretical background

Parr and co-workers [26] have defined electrophilicity index (ω) as a measure of the decrease in energy due to the maximal transfer of electrons from donor to an acceptor molecule given as;

$$\omega = \frac{\mu^2}{2\eta} \tag{1}$$

where μ and η are chemical potential and hardness respectively.

Chemical potential [27], hardness [28], and softness [29] can be expressed in terms of ionization energy (I) and electron affinity (A) as;

$$\chi = -\mu = \left(\frac{\partial E}{\partial N}\right)_{v(r)} \approx -\frac{I+A}{2} \tag{2}$$

$$\eta = \frac{1}{2}\left(\frac{\partial E}{\partial N}\right)_{v(r)} \approx \frac{I-A}{2} \tag{3}$$

$$S = \frac{1}{2\eta} \tag{4}$$

Employing Koopmans' approximation [30], the IP and A are the eigenvalue of the HOMO and LUMO with change of sign [31]

$$I \approx -E_{\text{HOMO}} \qquad A \approx -E_{\text{LUMO}} \tag{5}$$

Two reactivity indices related to electrophilicity and nucleophilicity as well as electrofugality and nucleofugality in terms of the reactant's first ionization potential and electron affinity have been introduced by Ayers *et al.* [32]. Electrofugality ΔE_e is defined as:

$$\Delta E_e = \frac{(\mu - \eta)^2}{2\eta} \tag{6}$$

Nucleofugality ΔE_n is defined as:

$$\Delta E_n = \frac{(\mu + \eta)^2}{2\eta} \tag{7}$$

Polarizability is the measure of the change in a molecule's electron distribution in response to an applied electric field, which can also be induced by electric interactions with solvents or ionic reagents [33, 34]. It represents a second-order variable in energy; $\alpha_{a,b} = -(\partial^2 E / \partial F_a \partial F_b)$; $a, b = x, y, z$ and is calculated as follows:

$$\langle \alpha \rangle = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right) \tag{8}$$

Results and discussion

The lowest energy optimized structures of three molecules viz ethylenediamine (en), bipyridyl (bpy), and phen are shown in figure 1. The quantum chemical descriptors like LUMO/HOMO energy, ionization energy, electron affinity, chemical potential, hardness, softness, electrophilicity, polarization etc. calculated from optimized geometries using
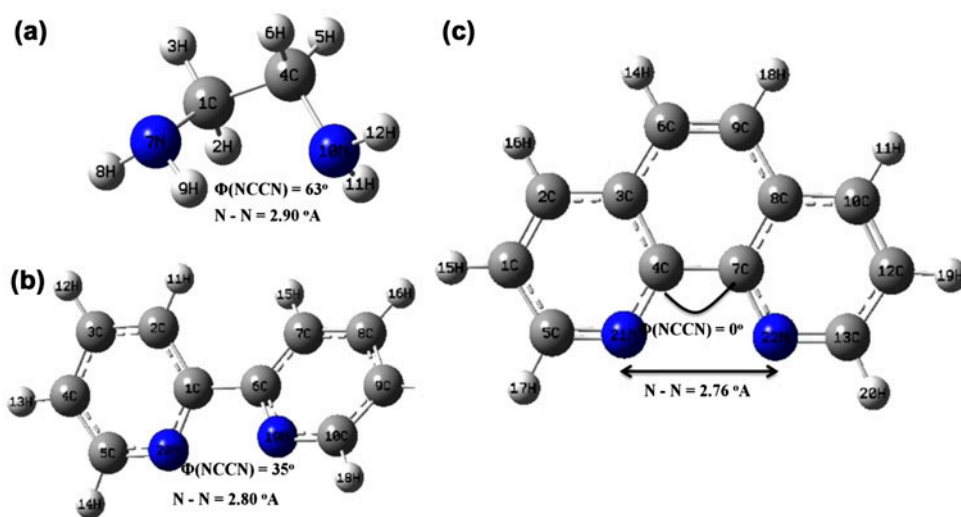
Figure 1. Spatial arrangement of atoms in optimized structures of (a) ethylenediammine, (b) bipyridyl, and (c) 1,10-phenanthroline.

equations (1)–(8), of the three NN-bidentate ligands are tabulated in tables 1, 3, and 4. A comparison of the stability constant data for the Fe(II) complexes with these three ligands follows the order phen $(21.0) >$ bpy $(17.2) >$ en (9.74) [35]. However, on the basis of calculated HOMO energies, we found that order of the σ donor strength (en (-0.217) $<$ bpy $(-0.240) <$ phen (0.250)) is opposite to that expected on the basis of experimentally reported stability constant data. The observation suggests that the metal ion binding affinity of these ligands can be explained on the basis of additional interactions like chelate stabilization and π back acceptance. The structural features of the optimized geometries reveal that the steric restriction over rotation about NC–CN bond in phen ($\varphi_{(NCCN)} = 0^\circ$) results in an entropically favored chelate binding of phen as compared to en and bpy. Moreover, the presence of low-lying LUMO orbitals and the consequent high electron affinity enables Phen to show enhanced π back acceptance characteristics as compared to the other two ligands. Favorable chelate effect and pi back acceptance character compensate for the poor σ donor characteristics of phen [36]. The overall binding affinity in terms of global electrophilicity index (ω) follows the order phen $>$ bpy $>$ en, which is in accordance with the experimentally observed stability constant data. NCCN dihedral angle (φ) and NN spatial distance (SD) of three ligands are shown in figure 1 and theoretically calculated values for the mentioned quantum mechanical descriptors are tabulated in table 1.

The trend in stability constant values was further verified by calculating free energy changes during complexation of en, bpy, and phen with Cu(I) (as bis-complexes) and Fe (II) (as tris-complexes) using B3LYP functional and LANL2MB basis set (figure S1, supporting file). The optimized coordinates of metal complexes are given in table S1 (supporting information). The polarizable continuum model was used for modeling the effect of solvent (water) on the complexation [37, 38]. Free energy change of complexation ($\Delta G_{complex}$) was calculated using the equation (9), which was correlated with log K using the equation (10).

Table 1. Calculated values of various quantum mechanical descriptors for three NN bidentate ligands, en, bpy, and phen.

Ligand	HOMO (E_H)	LUMO (E_L)	ΔE (au) (E_L–E_H)	I (eV)	A(eV)	μ(eV)	χ(eV)	η(eV)	S(eV)	ω(eV)
En	−0.217	0.079	0.296	5.913	−2.136	−1.889	1.889	4.025	0.124	0.443
Bpy	−0.240	−0.044	0.197	6.536	1.184	−3.860	3.860	2.676	0.187	2.784
Phen	−0.250	−0.052	0.198	6.803	1.426	−4.114	4.114	2.689	0.186	3.148

Table 2. Calculated Stability constant vales for complexation of en, bpy, and phen with Cu(I) and Fe(II).

Complex	$\Delta G_{complex}$ (kJ/mole)	$\log K$
$[Cu(en)_2]^{1+}$	13.72	2.41
$[Cu(bpy)_2]^{1+}$	91.44	16.03
$[Cu(phen)_2]^{1+}$	121.71	21.34
$[Fe(en)_3]^{2+}$	25.72	5.21
$[Fe(bpy)_3]^{2+}$	103.46	18.34
$[Fe(phen)_3]^{2+}$	137.31	23.01

$$\Delta G_{complex} = G_{complex} - (G_M^+ + XG_{ligand}) \tag{9}$$

where X is number of ligands

$$\log K = -\frac{\Delta G_{complex}}{2.303RT} \tag{10}$$

Theoretically calculated values of free energy change (ΔG) and stability constants (log K) for the three complexes are reported in table 2. The results indicate that the stability constant values follow the order phen > bpy > en, in quit agreement with π accepting character of ligands as mentioned above.

Molecular orbital calculations coupled with charge distribution studies revealed an excellent positioning of LUMO orbitals for a favorable pi interaction (figure 2) with a metal ion in lower oxidation state. Substitution at a particular position on the heteroaromatic ring system of phen, results in electronic redistribution and a variation in the HOMO and LUMO energies leading to a change in both sigma donor and
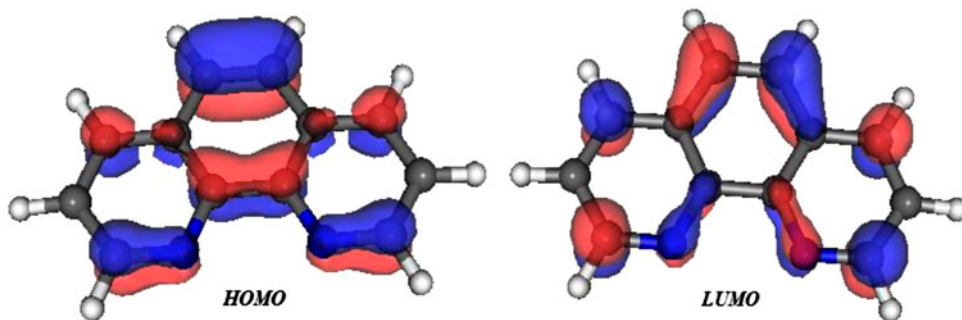

Figure 2. Distribution of HOMO and LUMO over the heteroarromatic ring system in 1,10-phenanthroline.

Table 3. Calculated values of various quantum mechanical descriptors for the studied substituted derivatives of phen.

Ligand	HOMO (E_H)	LUMO (E_L)	ΔE (au) ($E_L - E_H$)	I (eV)	A (eV)	μ(eV)	χ(eV)	η(eV)	S (eV)	ω(eV)
Phen	−0.250	−0.052	0.198	6.803	1.426	−4.114	4.114	2.689	0.186	3.148
2,methly phen	−0.228	−0.053	0.175	6.204	1.440	−3.822	3.822	2.382	0.210	3.066
2,phenylephen	−0.219	−0.062	0.157	5.951	1.690	−3.821	3.821	2.131	0.235	3.425
2,hydroxyphen	−0.219	−0.053	0.166	5.965	1.448	−3.706	3.706	2.259	0.221	3.041
2,chlorophen	−0.235	−0.062	0.174	6.400	1.679	−4.040	4.040	2.361	0.212	3.456
2,bromophen	−0.235	−0.062	0.173	6.384	1.682	−4.033	4.033	2.351	0.213	3.459
2,nitrophen	−0.243	−0.104	0.140	6.615	2.816	−4.716	4.716	1.899	0.263	5.854
2,carboxyphen	−0.237	−0.074	0.163	6.436	2.014	−4.225	4.225	2.211	0.226	4.036
2,aminophen	−0.204	−0.049	0.155	5.546	1.342	−3.444	3.444	2.102	0.238	2.821
2,9,dimethylphen	−0.220	−0.044	0.176	5.995	1.205	−3.600	3.600	2.395	0.209	2.706
2,9,diclorophen	−0.239	−0.069	0.170	6.501	1.864	−4.182	4.182	2.318	0.216	3.773
2,9, dihydroxyphen	−0.212	−0.053	0.160	5.772	1.431	−3.602	3.602	2.170	0.230	2.988
2,9,dibromophen	−0.238	−0.069	0.169	6.468	1.867	−4.167	4.167	2.301	0.217	3.774
2,9,dinitrophen	−0.257	−0.125	0.132	6.993	3.390	−5.192	5.192	1.802	0.278	7.481
2,9,diphenly phen	−0.211	−0.062	0.148	5.736	1.698	−3.717	3.717	2.019	0.248	3.422

π acceptance characters. We also quantified changes in the σ donor and pi acceptance characters of phen with different substituents at various positions. σ donor and π acceptance characters have been correlated with ionization potential and electron affinity of the substituted derivatives respectively. The overall reactivity of the substituted derivatives may be correlated on the basis of electrophillicity index (ω). Calculated values of the quantum chemical descriptors of the studied phen derivatives (see table 3) infer that substitution at ortho positions (2 and 9) to donor atoms in phen by an electron withdrawing substituents like NO_2 and COOH decreased the energy of the most loosely bound electron pair on the parent heterocyclic system, resulting in increase in the ionization potential and, therefore, its sigma donor character was observed to decrease in comparison with the parent phen. In contrast, the electron releasing substituents like NH_2 and OH increased the energy of the donor electron pair (E_{HOMO}) and, therefore, the σ donor characteristics of the derivative is higher compared to the parent phen. The decreasing order of sigma donor characteristics of substituted phen derivatives was found in the order $NH_2 > Ph > OH > CH_3 > H > Br > Cl > COOH > NO_2$. We also found that the presence of two similar substituents at two ortho positions produce cumulative effect on the σ donating to π-accepting tendency. The trend was found in good agreement with their ortho directing property. The trend was found in synergism for the substitution at position 4 and in opposition at the 3 and 5 position.
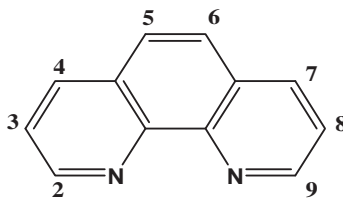

Figure 3. Substitution sites in 1,10-phenanthroline.

Table 4. Calculated values of various quantum mechanical descriptors for hydroxyl and nitro substituted derivativesat various positions on hetero aromatic ring.

Ligand	HOMO (E_H)	LUMO (E_L)	ΔE (au) $(E_L - E_H)$	I (eV)	A (eV)	μ (eV)	χ (eV)	η (eV)	S (eV)	ω(eV)
Phen	−0.250	−0.052	0.198	6.803	1.426	−4.114	4.114	2.689	0.186	3.148
2,hydroxyphen	−0.219	−0.053	0.166	5.965	1.448	−3.706	3.706	2.259	0.221	3.041
3,hydroxyphen	−0.224	−0.054	0.171	6.104	1.456	−3.780	3.780	2.324	0.215	3.074
4,hydroxyphen	−0.222	−0.053	0.170	6.047	1.431	−3.739	3.739	2.308	0.217	3.029
5,hydroxyphen	−0.214	−0.053	0.161	5.812	1.434	−3.623	3.623	2.189	0.228	2.998
2,9, dihydroxyphen	−0.212	−0.053	0.160	5.772	1.431	−3.602	3.602	2.170	0.230	2.988
3,8, dihydroxyphen	−0.212	−0.054	0.159	5.780	1.456	−3.618	3.618	2.162	0.231	3.027
4,7, dihydroxyphen	−0.216	−0.045	0.171	5.881	1.225	−3.553	3.553	2.328	0.215	2.711
2,nitrophen	−0.243	−0.104	0.140	6.615	2.816	−4.716	4.716	1.899	0.263	5.854
3,nitrophen	−0.242	−0.106	0.136	6.596	2.887	−4.742	4.742	1.854	0.270	6.062
4,nitrophen	−0.243	−0.106	0.137	6.623	2.885	−4.755	4.755	1.868	0.268	6.052
5,nitrophen	−0.243	−0.104	0.138	6.607	2.841	−4.724	4.724	1.883	0.266	5.925
2,9,dinitrophen	−0.257	−0.125	0.132	6.993	3.390	−5.192	5.192	1.802	0.278	7.481
3,8,dinitrophen	−0.253	−0.120	0.133	6.885	3.274	−5.079	5.079	1.806	0.277	7.144
4,7,dinitrophen	−0.254	−0.112	0.142	6.920	3.053	−4.987	4.987	1.933	0.259	6.431

A comparison of the electron affinities of the substituted derivatives of phen, revealed that except the amino derivative, there was an increase in the electron affinity of the ligand as compared to the un-substituted phen and, therefore, expected to show better π back acceptance character than the parent phen. The overall trend for pi back acceptance character of the studied derivatives follow the order $NO_2 > COOH > Ph > Br > Cl > OH > CH_3 > H > NH_2$, which is similar to that observed for the electrophilicity index (ω) of these substituted derivatives.

For similar substituents, the σ donor character of the ligand with an electron withdrawing substituent (NO_2) at various positions on the heteroaromatic ring of phen (figure 3) was observed to follow the trend, $2 > 4 > 3 > 5$, whereas for an electron releasing substituent (OH), the trend was reversed. In contrast to σ donor character, the pi acceptance character did not show a regular trend with that of electron releasing or electron donor tendency of the ligand. The order of decreasing π acceptance character for NO_2 was observed in the order $3 > 4 > 5 > 2$ and for OH the change in π acceptance character with respect to substitution at various positions was observed in the order $3 > 2 > 5 > 4$. For homo disubstituted derivatives, 3,8 dihydroxyphen and 4,7 dinitrophen were observed as pi acceptance enhancers compared to parent phen (table 4).

Conclusion

Metal ion binding affinity of phen is tuned by varying substitutions at various positions on the heterocyclic ring. DFT calculations reveal the energy of most loosely bound electron pair in phen is low in comparison with en and bpy, as a result of which it exhibits a poor σ donor character. However, the observations that phen forms stronger complexes in comparison to en and bpy ligands is justified on the basis of higher chelate stabilization facilitated by the proper ligand approach and enhanced π back acceptance. The energy of the orbitals actively involved in σ and pi interactions is varied as a result of substitutions on the hetrocyclic ring. Magnitude and direction of this energy change depends on the nature

and position of the substitution. Therefore, the σ binding and π acceptance character of various substituted derivatives can be understood in terms of electron donating and electron accepting character of the substituents and their position on the phen skelton.

Acknowledgments

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