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Effect of Substituents on Polarizability and Hyperpolarizability Values of Benzimidazole Metal complexes

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Abstract. In this report, the polarizability and first and second order hyperpolarizability values of bis benzimidazole Zn(II)-2R and bis benzimidazole Cd(II)-2R complexes, with different electron donating moieties R (R= Cl, Br, I, Acetate) were calculated using time dependent Hartree-Fock (TDHF) formalism embedded in MOPAC2012 package. Further the role of substituents on polarizability and hyperpolarizability values is investigated for the first time by analyzing the frontier molecular orbitals of the complexes with respect to the electronegativity of the substituents. It is found that the increase in electronegativity of the substituents correspondingly increases the energy gap of the molecules, which in turn reduces the polarizability values of both Zn and Cd benzimidazole complexes. Similarly, increase in electronegativity reduces the electric quadrupole moments of both the metal complexes, which in turn reduces the hyperpolarizability values.

Keywords: Polarizability, Semiempirical Calculations, Photon Interaction with molecules

PACS: 31.15.ap, 31.15.bu, 33.80.-b

INTRODUCTION

Organic materials with good nonlinear optical properties are widely considered for photonic applications like all optical switching, optical telecommunication and optical information processing [1]. But most of the organic materials exhibit low durability and cannot withstand at high power laser irradiations. To overcome these, often metal organic complexes (MOC) are considered as the suitable alternatives for organic materials. Generally, MOC's possess high polarizability which arises from the organic ligands and have higher thermal stability due to the presence of metal ions. Further, metal ions in the organic medium produce additional electronic transitions which also contribute to the polarization of molecules. Benzimidazole (BMZ) is one of the well known organic material investigated for variety of applications in different fields. In particular it is identified as a potential second harmonic generating (SHG) material with 4.5 times better efficiency than that of the standard KDP material. Further, the metal complexes of benzimidazole were investigated for their excellent coordination behavior and optical and magnetism related applications. Recently, we have

reported the enhanced thermal and optical properties of BMZ metal complexes compared to the parent ligand [2]. BMZ complexes can be synthesized with different halides or acetate (OAc) substituents depending on the precursor metal salt. The substituents may play a role in structure stabilization as well as on linear and nonlinear optical properties of the system. There are reports available on the role of halide substituents in different metal organic structures [3]. To the best of our knowledge, there is no systematic study available on the effects of substituents on the linear and nonlinear optical properties of metal complexes. So, in the present study, substituent dependent polarizability and hyperpolarizability calculations of benzimidazole based metal complexes, bis-benzimidazole Zn(II)-2R (Zn-R) and bis-benzimidazole Cd(II)-2R (Cd-R) (Where, R=Cl, Br, I, OAc) were calculated using semiempirical approach. The choice of metal ions is based on the fact that the d shell of Zn and Cd ions are completely filled, and therefore, it is expected that the major contribution of polarizability and hyperpolarizability arises due to the effect of substituent atoms.

COMPUTATIONAL METHODS

The molecular structures of Zn-R and Cd-R were obtained from the previous reports and sketched using ChemDraw program. If cif files are available, they were directly used as molecular inputs (MI). All the MI files are pre-optimized using UFF algorithm embedded in Avogadro software package and converted into MOPAC inputs using the same package. The geometries were optimized using PM6 algorithm with GNORM values about 0.25 and the optimized geometries were subjected to FORCE calculation to evaluate whether the geometry optimization reached the global minimum or not. If any negative vibrational frequencies were obtained, the geometrical parameters are changed and the system was reoptimized. The polarizability, first and second order hyperpolarizability of the molecules were calculated using the optimized geometries at TDHF level. Even though, TDHF method is considered as a reliable method in predicting the nonlinear optical properties of molecules, it may not exactly reproduce the experimental results. Since our intension is to identify the substituent dependent changes in linear and nonlinear optical properties of the benzimidazole metal complexes, this level of theory is adopted as enough to derive the structure dependent properties. All the POLAR calculations were done for the static frequency i.e., ($f=0.0$ eV). Further, the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) were calculated and they were used to estimate energy gap (E_g) of the molecules. GABEDIT and Molden programs were used to visualize the geometries, plot the frontier orbitals and to calculate the energy gap.

RESULTS AND DISCUSSION

Frontier Molecular Orbitals

The isosurfaces of frontier molecular orbitals for all the complexes are shown in Fig. 1. From the Fig. 1 (a-d), for HOMO, it can be seen that the major electronic cloud is distributed through metal-chloride (M-Cl) region in the case of Zn-Cl. The distribution of HOMO cloud increases with decrease in electronegativity of the substituents and a highest electronic distribution is observed in the case of Zn-I complex. But in the case of Zn-OAc complex, there is no electron contribution from acetate ions and the HOMO region is distributed over the metal ion. Similar scenario is also observed in the case of Cd complexes. Whereas for LUMO the electronic cloud is largely condensed over the ligand for all the metal

complexes and it shows the possibility of intersystem charge transfer in these molecules. The calculated frontier molecular orbitals of all the metal complexes and their energy gap values are given in Table. 1. For both Cd and Zn metal complexes, decrease in electronegativity of the halogen substituents ($\text{Cl} > \text{Br} > \text{I}$), decreases the HOMO values and increases the LUMO values which results the decrease in energy gap (E_g) values. For Zn-OAc and Cd-OAc complexes the HOMO and LUMO values are almost equal to Zn-I, Cd-I complex values, respectively.

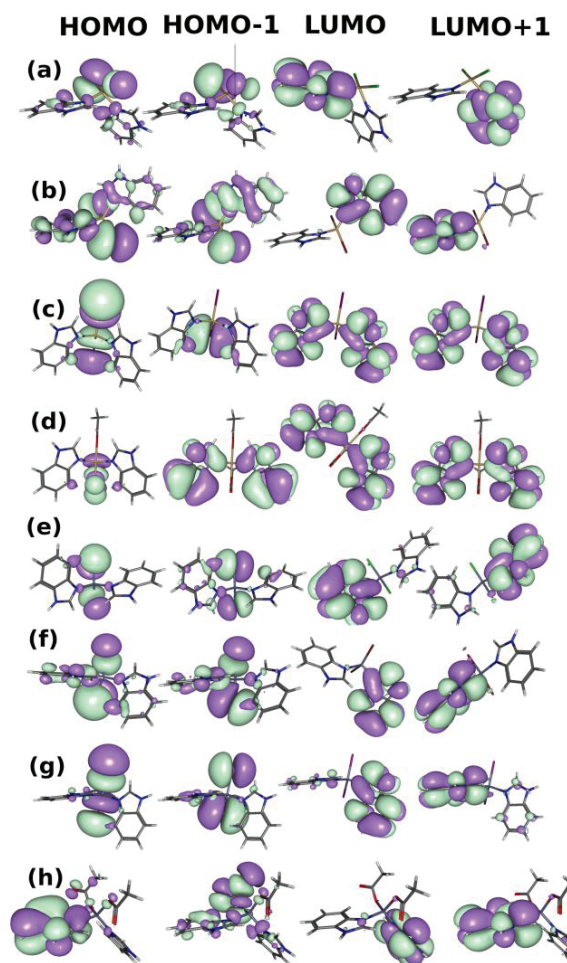


FIGURE 1. Frontier Molecular Orbitals of (a-d) Zn-R and (e-h) Cd-R (R=Cl, Br, I, OAc).

Polarizability and Hyperpolarizability

The calculated polarizability (α) and first and second order hyperpolarizability (β , γ) values of the metal complexes are given in Table. 2. The decrease in

electronegativity of the substituents increases the polarizability values of all the complexes.

TABLE 1. Energy gap values of Zn-R and Cd-R complexes (a.u.)

Metal Complex	E_g
Zn-Cl	0.31
Zn-Br	0.30
Zn-I	0.27
Zn-OAc	0.28
Cd-Cl	0.31
Cd-Br	0.29
Cd-I	0.27
Cd-OAc	0.28

In other words, polarizability increases with decrease in energy band gap. This is obvious that the decreasing E_g favors more electron cloud to get polarized and which in turn increases the polarizability values [4]. Only a small difference was observed in polarizability values of Zn and Cd complexes. The reason for observed phenomena is due to the major electronic contribution arises from the substituent atoms. Of all the complexes Metal-I complex shows better polarizability followed by Metal-OAc complexes.

TABLE 2. α and γ values of Zn-R and Cd-R Complexes

Complex	α (a.u.)	$\gamma \times 10^{-30}$ (esu)	$\gamma_{35} \times 10^{-35}$ (esu)
Zn-Cl	227.41	2.348	1.822
Zn-Br	241.06	3.546	1.838
Zn-I	274.27	6.328	2.352
Zn-OAc	260.64	1.700	1.963
Cd-Cl	218.84	2.381	1.573
Cd-Br	239.58	4.298	2.382
Cd-I	270.30	8.735	3.147
Cd-OAc	258.60	1.233	1.654

The first and second order hyperpolarizability results of Zn-R and Cd-R complexes are similar to their polarizability results and Zn-I and Cd-I complexes exhibit highest α and γ values whereas Cl complexes exhibit the lowest values. Surprisingly, for Metal-OAc complexes lowest α values are observed in contradiction to the α and γ values. It is a well known fact that the first order hyperpolarizability of the molecules are symmetry dependent and since symmetry restrictions are not imposed in the present work might be the reason for the observed variation in α values of M-OAc complexes [5]. From the results it can be seen that the γ values varying with respect to the electronegativity of the substituents. The variation in hyperpolarizability of the molecules is due to the change in electric quadrupoles induced in the complexes with respect to the electronegativity of the substituents. Anisotropic distribution of electrons in substituents causes less electron density in the z-

direction of the molecule and more electron density in the other two directions of metal complex. Due to this, the applied electric field 'feels' more positive charge on the Z-X bond direction than the other two directions. This type of interaction is called δ -hole interactions and this anisotropic electrostatic distribution around a covalently bonded substituents can induce an electric quadrupole which is purely electronic in origin [6]. The magnitude of electric quadrupoles are directly proportional to the electronegativity of the substituents and thus the variations observed in the calculated results.

CONCLUSIONS

The polarizability and hyperpolarizability of bis benzimidazole Zn(II)-2R and bis benzimidazole Cd(II)-2R complexes, were analysed using PM6 algorithm and TDHF formalism embedded in MOPAC2012 package. The calculated polarizability (α) and first and second order hyperpolarizability (γ and γ_{35}) values varies with respect to the electronegativity of the substituents. Increase in electronegativity subsequently increases the energy gap which in turn reduces the polarizability and hyperpolarizability values. Substituents with low electronegativity induces high electronic quadrupole moment in the complexes.

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