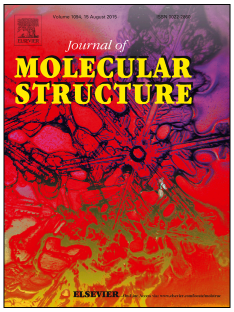

Computational study on non-linear optical property of Wittig based Schiff-Base ligands (both Z & E isomers) & Copper(II) complex

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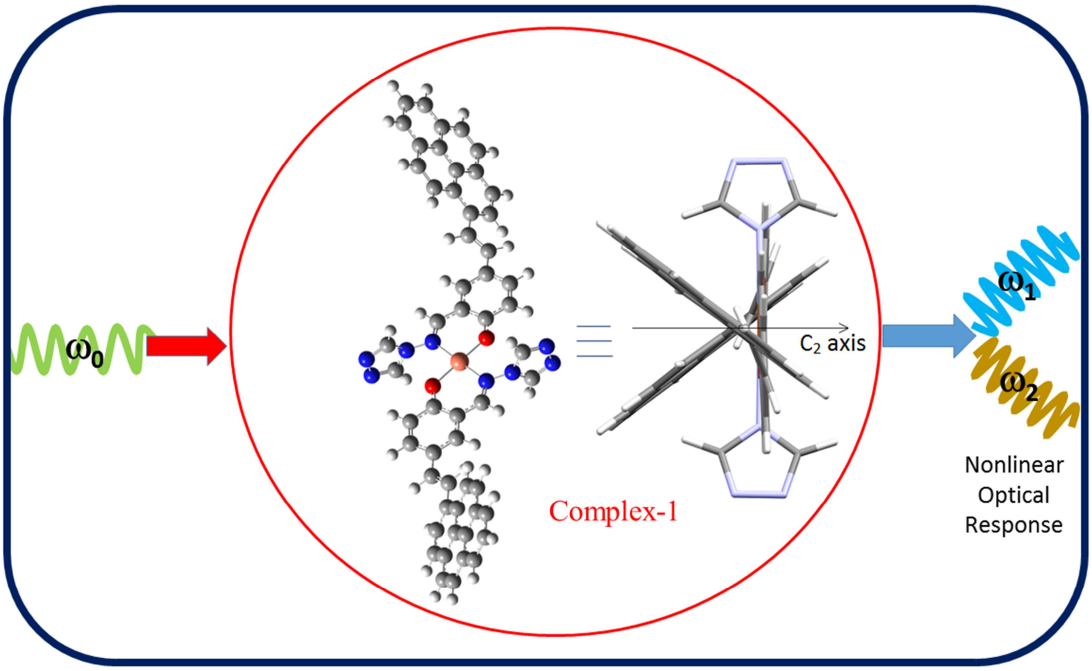
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Nonlinear Optical Response

Computational Study on Non-linear Optical property of Wittig based Schiff-Base ligands (both Z & E isomers) & Copper(II) complex

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Abstract

96 new Wittig based Schiff-Base (WSB) ligands (both E & Z conformation) containing fused aromatic rings were designed and screened for NLO property. Wittig based precursor aldehydes were synthesized and spectroscopically confirmed. WSB ligands and their copper(II) complexes were also designed, optimized and their NLO property was studied using a *GAUSSIAN09* computer program. For Optimization & Hyperpolarizability (β) calculations, DFT based B3LYP method was applied with LANL2DZ basis set for metal ion and 6-31G* basis set for C, H, N & O atoms. The study presents the Structure-Activity relationship (SAR) between WSB ligands and β. The study revealed that WSB Ligands of the category N_2, which are those derived from precursor aldehyde, (2-hydroxy-5-(2-(naphthalen-1-yl)vinyl)benzaldehyde) encoded as PA-2, showed higher β values over N_1, which are derived from, 2-hydroxy-5-(2-(naphthalen-1-yl)vinyl)benzaldehyde, encoded as PA-1. Among all ligands, Ligand-14, (E-4-(2-Pyren-1-yl-vinyl)-2-([1,2,4]triazol-4-yliminomethyl)-phenol), of N_2 category showed highest β value ($6.968\text{x}10^{-30}$ e.s.u). After complexing with Cu(II), encoded as Complex-1 ([(4-(2-Pyren-1-yl-vinyl)-2-([1,2,4]triazol-4-yliminomethyl)-phenoxy)$_2$Cu], which has C_2 symmetry, the β value ($0.310\text{x}10^{-30}$ e.s.u) unexpectedly decreased. However, it is still high as compared to that of urea ($\beta = 0.091\text{x}10^{-30}$ e.s.u). The output of TD-DFT also supports the obtained results. Different factors affecting β value especially their geometrical isomeric effect were successfully analysed.

Keywords: Nonlinear Optical Property; Hyperpolarizability; DFT & TD-DFT; Wittig based Schiff-Base ligands; Copper(II) complex.

1. Introduction

In last few decades, molecular-based NLO materials such as organic compounds, polymers and coordination complexes [1-3] which possess metal ion and organic ligand have drawn considerable focus as compared with the atomic-based materials such as $LiNbO_3$, KH_2PO_4 (KDP), gallium arsenide (GaAs), α-quartz (SiO_2) and β-barium borate (BBO) [4]. Nonlinear optical property can be defined as the interaction between electromagnetic radiation and materials which results in a change in the properties of laser beam like frequency, phase, amplitude, and polarization [5]. However, organic compounds and polymers have disadvantages like low thermal stability, mechanical weakness, volatility, etc. which is not so in the case of coordination complexes. Also, some other advantages of complexes are that they can exhibit optical bands in the Visible region on absorption of radiowave, and a metal ion which is having diversity in oxidation states as well as in redox properties can be used as a central metal ion for complexation and optimize its NLO properties by modifying the ligands [6-19].

Coordination complexes exhibit NLO property but among them also, Schiff-Base complexes seemed to be prominent chromophores showing significantly large nonlinear response

[20-36]. They have advantage of simple synthetic procedure, thermal stability, easy generation of polarizability and low energy charge transitions [37-39]. Schiff-Base coordination complexes have shown high nonlinearity than the Schiff-Base ligands alone because metal centre can act as an electron donor and/or acceptor and thereby enhancing the intramolecular charge transfer [40]. Among all Schiff-Base coordination complexes, Ni(II) (closed shell system) complexes are studied extensively [25]. De Bella et. al reported that unpaired electron system like radicals and open shell metal complexes like Cu(II), Co(II) Schiff-Base complexes have higher β (hyperpolarizability) value indicating the enhancement of nonlinearity [41-44]. Also, Copper(II) Schiff-Base complexes with extended conjugation are found to be a class of promising NLO materials [46]. Keeping all these in mind, we have designed Wittig based Schiff bases (WSB) and also have synthesized some precursors.

2. Materials and Methods

2. 1. Materials

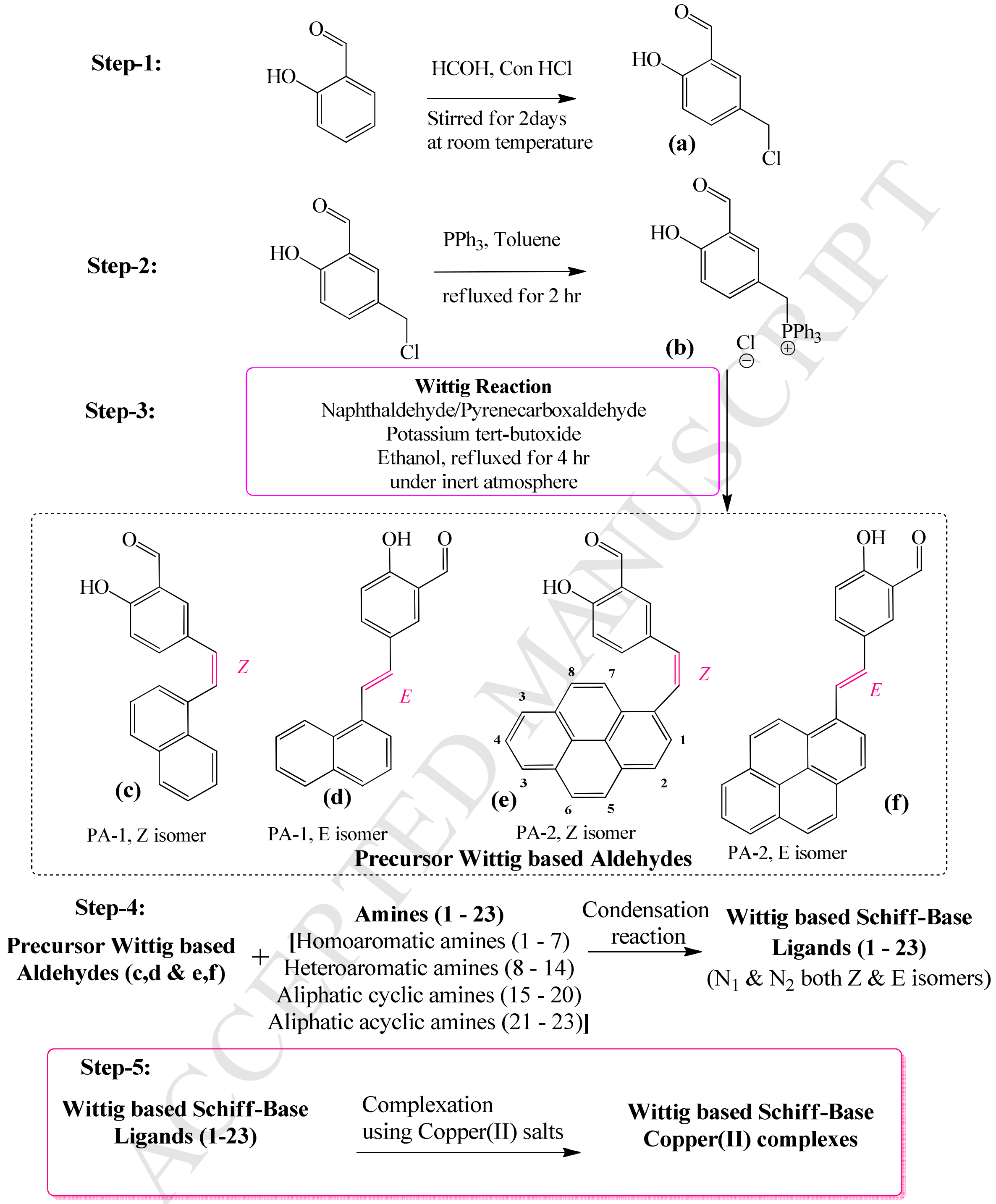
Salicylaldehyde, paraformaldehyde and diethyl ether were purchased from Loba Chemie, Hydrochloric acid from Avra, Triphenylphosphine, *potassium-tert*-butoxide from Spectrochem, 1-pyrenecarboxaldehyde from Sigma Aldrich. They were used without further purification. Ethanol, Dichloromethane and all other solvents were purified by using standard methods.

2. 2. Physical measurements

ESI-MASS spectrum measurements were carried out using 6530B AGILENT Q-TOFLC/MS analyser. Ultra-Violet (UV-Vis) spectra were measured on a Shimadzu UV-2450 PC spectrophotometer at room temperature. Infrared (IR) spectra were recorded on a Nicolet iS10 instrument using KBr pellets. The ^{1}H, ^{13}C-NMR (Nuclear Magnetic Resonance) spectra obtained from Bruker 400 MHz spectrometer and chemical shift values were reported in δ units (parts per million) relative to Me4Si as an internal standard.

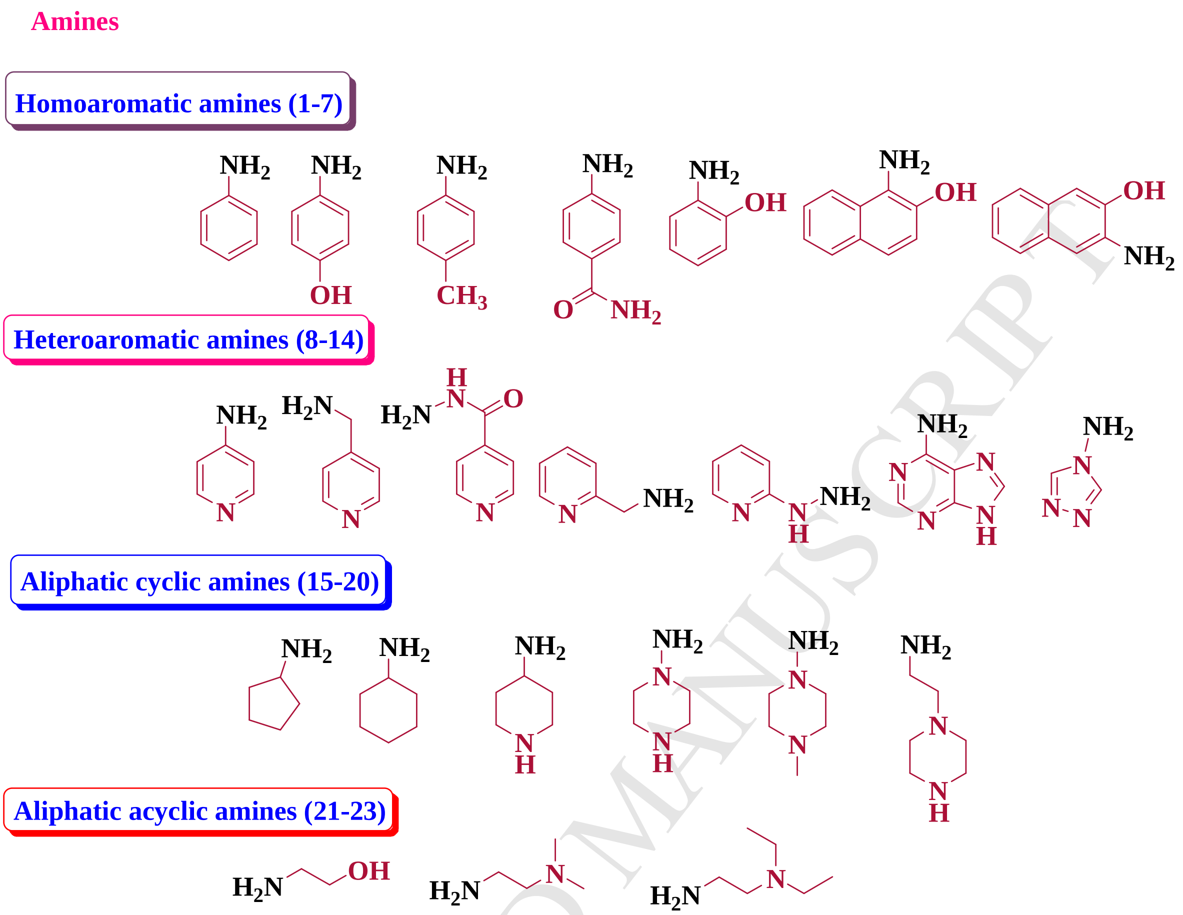
2. 3. Computational methods

Hyperpolarizability calculations of all the molecules $N_{1,\,2}$ (both E & Z) were performed using *GAUSSIAN09* [47]. For structural optimization & Hyperpolarizability calculations, DFT based B3LYP method was used and LANL2DZ basis set was used for metal ion & 6-31G* for C, H, N & O atoms. Hyperpolarizability calculations were performed for Complex-1 by giving this keyword *'# b3lyp/gen geom=connectivity gfinput pseudo=read polar=(DCSHG,Cubic) CPHF=RdFreq'* in route section and 0.1 ω frequency at bottom of XYZ coordinates. TD-DFT analysis was carried out for all ligands (see Table-S9, " S " stands for Supplementary material) using keyword [*# td=(nstates=20) b3lyp/6-31g(d) geom=connectivity*] and electronic transitions with oscillatory strength ≥ 0.05 were taken into consideration because these transitions were contributing more to the β value of the studied molecules.



Scheme-1: Schematic procedure to synthesize the Wittig based Schiff-Base Ligands (Z & E) and their Copper(II) complexes

(As a proof of principle, molecules a, b and e were synthesized & Characterized)



Note: Black color groups are interacting in the condensation reaction (Step-4) of the Scheme-1.

Figure-1. Library of Amines used in the reaction step-4 of scheme-1.

2. 4. Synthetic procedure of precursor aldehyde (PA-2), 2-Hydroxy-5-(2-pyren-1-yl-vinyl)-benzaldehyde of Z-isomer (**e**)

Step-1: Synthesis of 5-Chloromethyl-2-hydroxy-benzaldehyde **(a)**.

30g of salicylaldehyde, 13.6g of paraformaldehyde and 150 mL of concentrate hydrochloric acid were mixed and stirred for 7 hr and followed by workup with 0.5% $NaHSO_4$ solution. A pale pink color precipitate was obtained and recrystallized with diethyl ether. Yield 50 %.

Step-2: Synthesis of phosphonium chloride salt **(b)**.

10g of **(a)** dissolved in 100 mL of toluene was added to 10g of triphenylphosphine dissolved in 100 mL toluene. The mixture was refluxed for 2 hours and after removal of solvent, a white color phosphonium chloride salt (PPT) was obtained. Yield 95%.

Step-3: Synthesis of Wittig based Precursor Aldehyde **(e)**

Dissolved 4.4 mmole of ligand **(b)** in 80 mL of distilled ethanol to it added 4.5mmole of sodium methoxide directly. To this reaction mixture, 1-pyrenecarboxaldehyde dissolved in 80ml ethanol was added. It was refluxed for 11hr under an inert atmosphere, cooled to room temperature, and on addition of 370ml of 5% HCl solution, 700 ml of distilled water, yellow color precipitate was observed. This precipitate was filtered and dried in room atmosphere. Yield 55 %.

Wittig based precursor aldehyde **(e)** was synthesized according to the literature [45] and used for 2-Hydroxy-5-[2-(4-nitro-phenyl)-vinyl]-benzaldehyde preparation.

The Wittig reaction between phosphonium salt and pyrenecarboxaldehyde gave the expected product **(e)** which was confirmed by NMR, IR, UV-vis absorption, and MASS spectral analysis. FT-IR (as KBr pellet, cm^{-1}, Figure-S1) spectra: broad peak at 3433 (broad, ν(OH)), 1677 (strong, ν(C=O & alkene C=C)), 1588 & 1495 (strong, ν(aromatic C=C)), 704 (strong, ν(=C-H bending was assigned for Z conformation to the alkene C=C). ^1H, ^{13}C, and DEPT-135 analysis give the information regarding the proton, carbon skeleton structure and number of C-H, CH_2 and CH_3 groups present in the obtained product. ^1H NMR (400 MHz, $CDCl_3$, Figure-S2) δ 10.79 (s, 1H), 9.44 (d, *J* = 9.3 Hz, 1H), 8.46 (d, *J* = 7.9 Hz, 1H), 8.35 – 8.32 (m, 1H), 8.34 – 8.30 (m, 2H), 8.28 (d, *J* = 8.1 Hz, 1H), 8.24 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 3.8 Hz, 1H), 8.10 (d, *J* = 2.5 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.53 (d, *J* = 6.8 Hz, 1H), 7.45 (d, *J* = 6.5 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 1H), 5.29 (s, 1H). Chemical shifts at 7.67 δ and 7.64 δ are indicative of the compound being Z conformation, otherwise it would be close to 15 δ. ^{13}C-NMR spectra (Figure-S3) of **(e)** shows twenty peaks in the range of δ 0-220 ppm. 193 (CO), peaks from 135 to 128 were assigned for pyrenecarboxaldehyde carbons and peaks from 127 to 124 were identified as salicylaldehyde ring carbons. Alkene double bonded carbons chemical shifts appeared at 124 & 123. DEPT-135 spectra (Figure-S4) of Wittig based precursor aldehyde **(e)** showed all positive peaks. The peaks at 193 & from 132 to 127 are indications of pyrenecarboxaldehyde C-H groups, peaks from 127 to 126 were assigned for salicylaldehyde ring C-H groups and peaks at 124, 123 may be assigned to C-H groups of alkene double bond (Figure-9 & 10). UV-Visible (Dichloromethane as a solvent, λ_{max}; nm, Figure-S5): lower energy electron transitions as moderately sharp peaks at 498 nm, 394 nm, and 362 nm were identified as $n \rightarrow \pi^*$ and charge transfer from HOMO →LUMO. Another two peaks at 286 nm, 232 nm were assigned for $\pi \rightarrow \pi^*$ electron transitions. ESI MASS: 349 (M+H) (Figure-S6)

3. Results and Discussions

For convenience, the Wittig-based Schiff Base (WSB) Ligands in question are grouped in to two categories:

The first category is encoded as N_1, which are WSB Ligands derived from the precursor aldehydes, 2-hydroxy-5-(2-(naphthalen-1-yl)vinyl)benzaldehyde (encoded as PA-1) (both E & Z). To be more specific, PA-1, Z-isomer is denoted as (c) and E-isomer as (d). The second category is N_2, which are derived from the precursor aldehyde, 2-hydroxy-5-(2-(pyren-1-yl)vinyl)benzaldehyde, encoded as PA-2 (both E & Z). PA-2, Z-isomer is denoted as (e) and E-isomer as (f). WSB coordinated with Cu(II) is encoded as Complex-1. Library of Wittig based precursor aldehydes & Amines used are given in Scheme-1 & Figure-1 respectively.

3. 1. Structure-activity relationship (SAR) analysis

Table-1 & Figure-2 to 5 present change in β value with change in the structure of Wittig based Schiff-base (WSB) ligand and also the effect of HOMO-LUMO energy gap (ΔE, Kcal/mol) and electronic effects on β value. Library of Wittig based precursor aldehydes & Amines used are given in Scheme-1 & Figure-1 respectively. From this study, the key observations are noted here.

1. First hyperpolarizabilities (β_{total}) of both Z & E isomer Wittig based Schiff-Base ligands were sensitive to the HOMO-LUMO energy gap (ΔE). The general trend is that, with decrease in ΔE, the β value increases. In each case, β_{total} = β value is enhanced greatly as ΔE decreases and polarization increases. E isomer WSB ligands have shown higher β value compared to Z isomer (majority of molecules showing similar results were taken into account for convenience).

2. WSB ligands ($N_{1,\ 2}$ both Z & E isomers) derived from aromatic (homoaromatic & heteroaromatic) amines showed high β value as compared to aliphatic amines. In each case, a majority number of molecules having β >1 were taken into account for convenience. Among all, WSB ligands derived from 9H-Purin-6-ylamine and [1,2,4]triazol-4-ylamine exhibited highest β values.

3. Enhancement in β value was observed for WSB ligands (Ligands-2&4) derived from homoaromatic amines having –OH, -CO-NH_2 (in the context of resonance –OH is strong electron releasing & -CO-NH_2 is an electron withdrawing) groups at para position against –CH_3 group (Ligand-3) which is attributed to high polarization capability of the former groups. This trend is observed for $N_{1,\ 2}$ both Z & E isomers. The general trend of ΔE relationship with β (β value enhanced greatly as ΔE decreases) was observed for N_2 (both E & Z isomer) WSB ligands. However, in the case of N_1 (both Z & E isomer) WSB ligands, β value is highly influenced by the presence of ER such that the effect of ΔE was not observed.

4. It was also observed that the presence of ER and EW groups in WSB ligands (Ligand-1 to Ligand-4) were contributing to the polarization and that the contribution of EW is found to be greater than that of ER. The presence of the ER & EW groups in the molecules (Ligand-2,3 &4 form $N_{1,\ 2}$ both Z & E isomers) leads to higher β value over Ligand-1.

5. Strong ER group (–OH) at *para* positioned in WSB ligands, Ligand-2 ($N_{1,\ 2}$ both Z & E isomer; except $N_{2,}$ E isomer) showed high β values as compared to Ligand-5 (–OH group positioned at *ortho* to the imine group). Further, these results were cross-examined with ΔE

relation with β and was found that except for $N_{2,}$ E isomer, the β value of all other ligands were influenced by ER groups over ΔE.

6. Introduction of extended (fused) aromatic moiety in WSB ligands, Ligand-6 & Ligand-7 ($N_{1, 2}$ both Z & E isomer; except $N_{2,}$ E isomer) enhances the β value as compared to Ligand-5. Though, ΔE relationship with β differs in the case of N_2 (both Z & E isomers), it was observed in general that the introduction of fused aromatic rings causes a reduction in the ΔE.

7. Among Ligand-6 & Ligand-7, high β value was observed for Ligand-6 ($N_{1,2}$ Z isomer category only) which have $-NH_2$ group positioned at the 1st carbon of the naphthalene moiety whereas in the case of Ligand-7, $N_{1,2}$ where $-NH_2$ group is positioned at the 3rd carbon, only E isomer exhibited high β value as compared to Ligand-6. Further, comparison of ΔE between Ligand-6 & 7 showed that the Ligand-6 ($N_{1,2}$ both Z & E isomers) exhibited higher value.

8. In all cases, a comparative study from Ligand-1 to Ligand-7 concludes that β value was highly influenced by the amine structure. WSB ligands [Ligand-1 to 5] derived from ER group containing homoaromatic amines (Figure-1) greatly enhanced the β value as compared to fused aromatic ring containing amines [Amines-6&7] indicating that the electronic effects are dominating the β value over ΔE effect.

9. Comparative study between the WSB ligands, Ligand-1 & Ligand-8 ($N_{1,2}$ both Z & E isomers) revealed that the presence of nitrogen atom in the aromatic ring (in Ligand-8) causes enhancement of β value which may be due to the difference in the electronegativity between carbon and nitrogen and thereby causing polarization in the system at given frequency (ω=0.1 Hartrees). Polarization may also be affected by the presence of lone pair in nitrogen atom. These results are well supported by ΔE relationship with β value.

10. WSB ligands (Ligand-9 & Ligand-11) showed a positive impact for the $-R-CH_2\mathbf{N}$ (**‘N’** is part of the $-C=\mathbf{N}$ group and ‘R’ is pyridine ring) moiety position on β value. $-CH_2\mathbf{N}$ moiety placed at *para* position in Ligand-9 showed higher β value as compared to Ligand-11 in which $-R-CH_2\mathbf{N}$ moiety is placed at *ortho* position ($N_{1,2}$ both Z & E isomers). Except N_1, E isomer, all WSB ligands of these group did not follow the general trend of higher β value for lower ΔE.

11. Among all, WSB ligands derived from non-aromatic amines, Ligand-19 ($N_{1,2}$ only Z category isomers) & Ligand-20 ($N_{1,2}$ only E category isomers) showed high β value. This also must be the effect of nitrogen atom in the ring. For lower ΔE, higher β trend was observed in $N_{1,2}$ Z isomer ligands only.

12. Among WSB ligands derived from aliphatic five-membered cyclic ring containing amines, Ligand-15 (repeated trend was taken for the consideration, $N_{1,2}$ both Z & E isomers, except $N_{2,}$ Z isomers only) showed high β value as compared to six-membered cyclic ring containing amines (Ligand-16). Here, ΔE relation with β, general trend was observed in the case of $N_{1,2}$ (Z isomers

only) whereas in the case of $N_{1,2}$ E isomer ligands, it was not so. This anomaly is explained in section 3.2 together with other molecules showing similar result.

13. A gradual increment in the β value of Ligands-16 to 19 ($N_{1,2}$ both Z & E isomer) is due to increase in the number of tertiary amines in the cyclic ring. $N_{1,2}$ Z isomer WSB ligands explicitly follow the ΔE relation with β whereas in other cases this trend was not observed.

14. WSB ligands (from Ligand-21 to Ligand-23) derived from aliphatic acyclic amines, Ligand-21 ($N_{1,2}$ both Z & E isomers, except Ligand-20, N_2 E isomer) showed high β value. HOMO-LUMO trend was observed for N_1 (both Z & E isomers) category ligands only.

Table-1. ΔE and β values of WSB ligands ($N_{1,2}$ both Z & E isomers).

Ligands	N_1 [Z isomers]		N_1 [E isomers]		N_2 [Z isomers]		N_2 [E isomers]	
	ΔE (Kcal/mol)	(β)x10^{-30} e.s.u	ΔE (Kcal/mol)	(β)x10^{-30} e.s.u	ΔE (Kcal/mol)	(β x10^{-30} e.s.u	ΔE (Kcal/mol)	(β)x10^{-30} e.s.u
Pre. Ald	85.089	0.586	80.627	1.493	78.023	1.065	73.832	2.577
Ligand-1	83.947	0.807	79.623	0.752	78.644	1.005	73.863	1.130
Ligand-2	84.292	2.376	79.592	1.313	78.312	2.474	74.032	1.961
Ligand-3	83.947	1.006	79.322	1.254	78.462	1.248	74.051	1.383
Ligand-4	79.404	2.245	75.130	2.772	73.386	2.776	69.012	2.852
Ligand-5	83.846	0.556	77.659	1.124	76.411	1.070	71.811	2.035
Ligand-6	81.362	0.913	78.029	0.680	76.887	1.253	72.413	1.216
Ligand-7	80.006	0.554	75.689	1.197	74.252	1.043	71.623	1.257
Ligand-8	80.025	1.272	75.137	3.212	74.045	1.438	69.313	3.543
Ligand-9	91.094	1.661	85.792	3.251	78.964	2.176	74.748	4.191
Ligand-10	83.834	1.732	74.528	2.481	74.465	1.811	69.144	3.864
Ligand-11	89.538	1.479	86.018	1.247	77.992	1.723	74.139	1.599
Ligand-12	91.414	1.355	85.240	1.235	78.996	1.639	74.566	1.518
Ligand-13	72.087	3.713	68.115	4.664	66.471	4.424	62.354	5.611
Ligand-14	80.740	2.762	75.808	5.025	73.700	2.910	68.686	6.968
Ligand-15	91.803	0.596	86.990	0.508	78.764	0.851	74.396	0.879
Ligand-16	91.935	0.568	86.727	0.463	78.324	0.866	74.183	0.851
Ligand-17	92.224	0.361	87.022	0.870	78.488	0.322	74.302	1.121
Ligand-18	89.657	0.681	85.616	0.376	77.421	0.887	73.430	0.884
Ligand-19	89.074	1.577	87.266	0.905	77.088	1.837	74.365	1.292
Ligand-20	92.337	0.693	85.723	2.005	78.770	0.626	74.553	2.173
Ligand-21	90.868	1.085	87.335	1.353	79.140	1.759	75.036	0.745
Ligand-22	91.345	0.972	87.461	0.695	78.613	1.159	74.616	1.208
Ligand-23	91.056	0.941	87.448	0.552	78.419	1.199	74.440	0.847

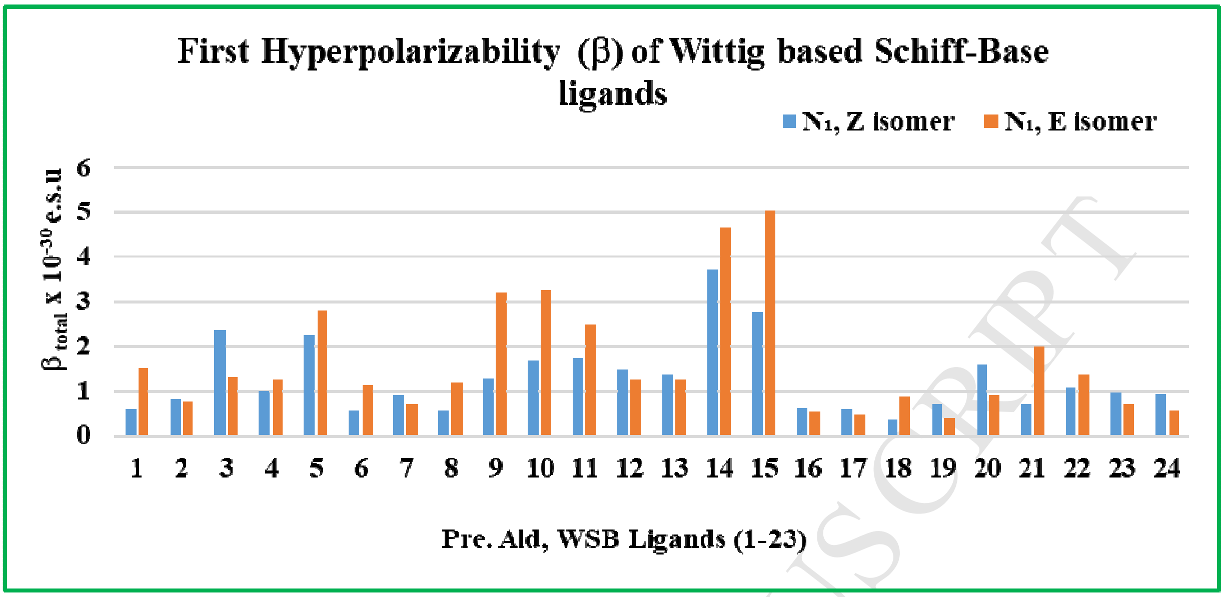


Figure-2. First Hyperpolarizability (β) of N_1, Z & E isomer Wittig based Schiff-Base ligands

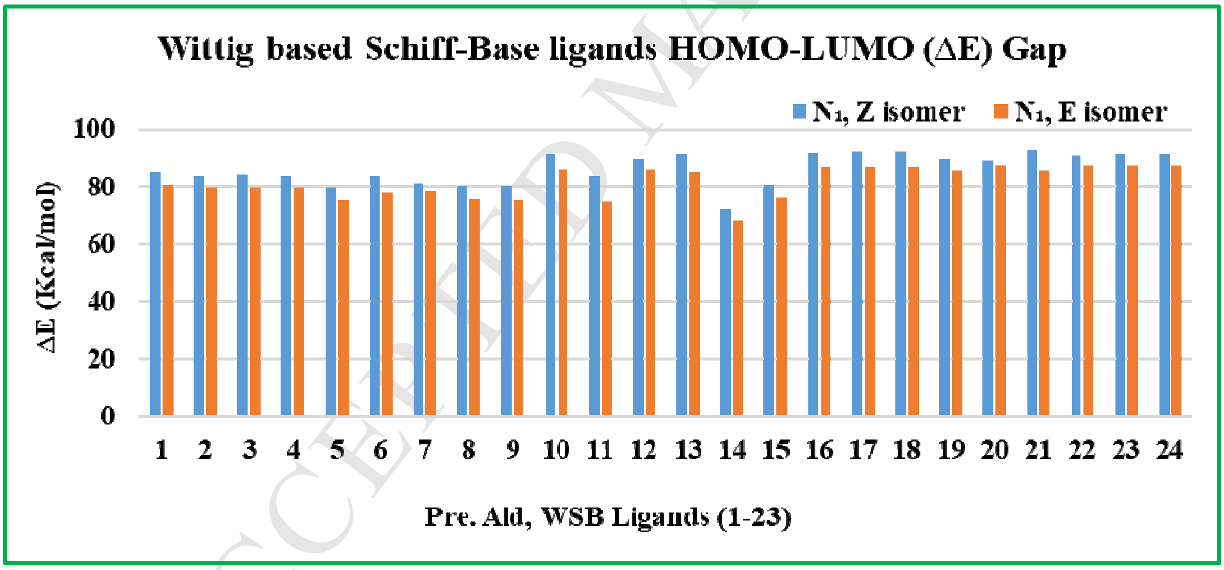


Figure-3. N_1, Z & E isomer Wittig based Schiff-Base ligands HOMO-LUMO energy gap (ΔE)

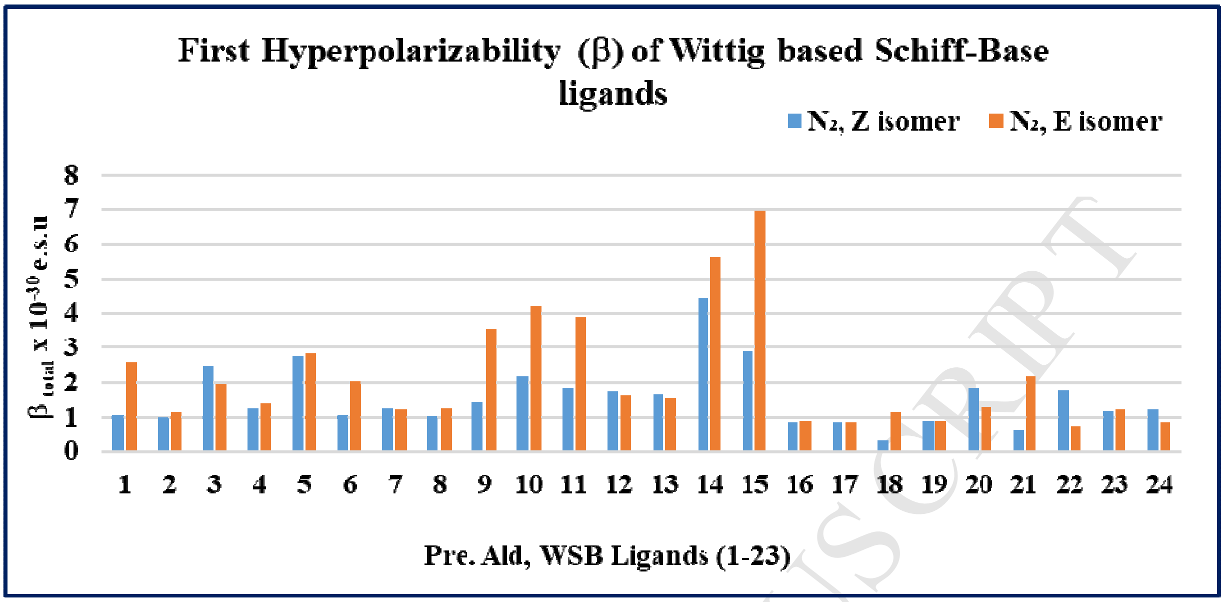


Figure-4. First Hyperpolarizability (β) of N_2, Z & E isomer Wittig based Schiff-Base ligands

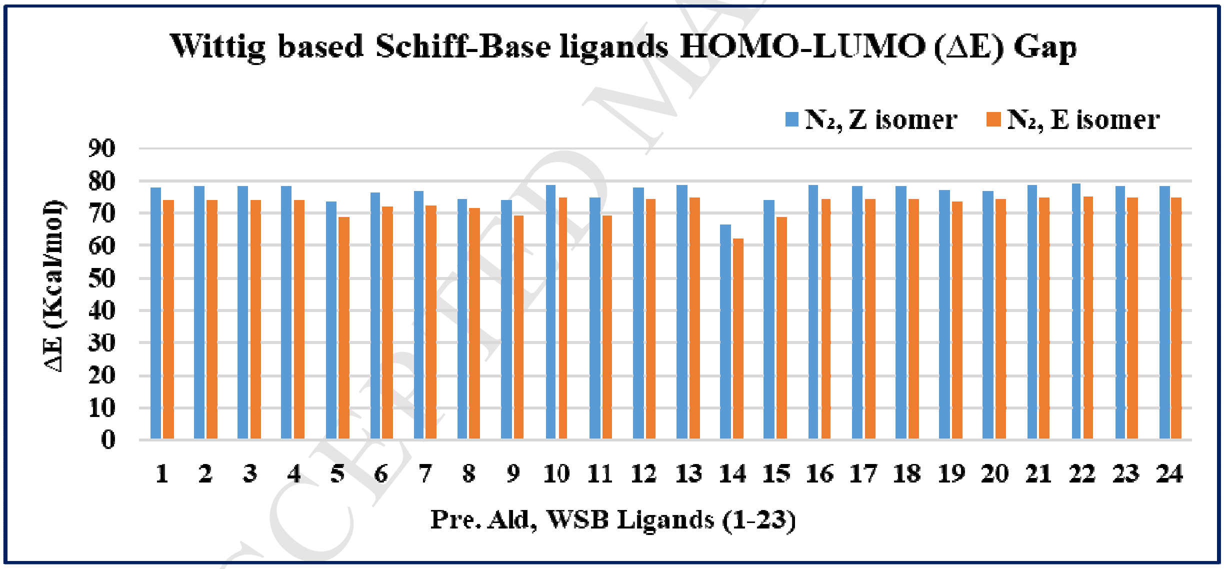


Figure-5. N_2, Z & E isomer Wittig based Schiff-Base ligands HOMO-LUMO energy gap (ΔE)

3. 2. TD-DFT Analysis of selected WSB ligands.

UV-Visible analysis supports the reason for the ligands of high ΔE to exhibit higher β value than the expectation. The analysis revealed that higher the number of electronic transitions and higher the oscillator strength (either one or both can be taken into the consideration), higher is the β value and it agrees with the reports of other researchers as well [48]. Except for few ligands highlighted in bold, this anomaly was successfully interpreted using TD-DFT study (Table-2).

Table-2. Summary view of the TD-DFT calculations for WSB ligands.

Molecule		**Number of Electronic transitions** [a]	**State**	**ΔE (eV)**	**λ (nm)**	***f***
(N_1, Z)	Ligand-2	10	Excited State 3	3.6928	335.75	0.4112
	Ligand-4	9	Excited State 2	3.5464	349.6	0.3016
	Ligand-6	7	Excited State 18	4.7856	259.08	0.3151
	Ligand-7	8	Excited State 3	3.3915	365.57	0.428
	Ligand-9	7	Excited State 18	5.1683	239.9	0.3548
	Ligand-11	7	Excited State 18	5.1949	238.67	0.504
	Ligand-22	6	Excited State 2	3.5779	346.53	0.1747
	Ligand-23	8	Excited State 8	4.4947	275.85	0.1285
(N_1, E)	Ligand-13	8	Excited State 2	3.3776	367.08	0.6557
	Ligand-14	6	Excited State 2	3.5228	351.95	0.7621
	Ligand-15	12	Excited State 2	3.4952	354.73	0.571
	Ligand-16	12	Excited State 2	3.4891	355.35	0.5612
	Ligand-18	10	Excited State 1	3.3759	367.26	0.6602
	Ligand-19	8	Excited State 2	3.4964	354.61	0.6842
	Ligand-22	9	Excited State 2	3.504	353.83	0.6254
	Ligand-23	9	Excited State 2	3.5046	353.77	0.6019
(N_2, Z)	Ligand-6	6	Excited State 3	3.1711	390.99	0.441
	Ligand-7	5	Excited State 4	3.3527	369.8	0.4518
	Ligand-9	5	Excited State 1	3.1523	393.31	0.5272
	Ligand-11	6	Excited State 1	3.1548	393	0.547
	Ligand-21	9	Excited State 1	3.1624	392.06	0.5303
	Ligand-22	8	Excited State 1	3.1269	396.5	0.5148
(N_2, E)	**Ligand-9**	6	Excited State 1	3.0368	408.28	0.8331
	Ligand-11	8	Excited State 1	3.036	408.37	0.9446
	Ligand-13	7	Excited State 8	3.8905	318.68	0.7225
	Ligand-14	6	Excited State 7	4.0524	305.95	0.3579
	Ligand-15	8	Excited State 1	3.0282	409.43	0.9922
	Ligand-16	8	Excited State 16	5.0369	246.15	0.4368
	Ligand-18	11	Excited State 1	2.9768	416.5	0.9827
	Ligand-19	6	Excited State 1	3.0302	409.17	0.9824
	Ligand-22	9	Excited State 1	3.0379	408.13	0.9711
	Ligand-23	7	Excited State 1	3.0305	409.12	0.9741

N_X, Z or E, where x = 1& 2, and Cis or Z isomer and Trans or E isomer.

[a] Number of electronic transitions with oscillator strength ≥0.05

Detailed information (TD-DFT) provided in the Table-S9.

3. 3. Comparison of Hyperpolarizabilities (β) between Z & E isomer Wittig based Schiff-Base ligands

Figure-S7 & S8, describes the geometrical isomeric effect on NLO property ($\beta=\beta_{total}$ x 10^{-30} e.s.u). From these figures, the key observations are noted here,

1. E isomer WSB ligands showed higher β value compared to Z isomers (the majority of the molecules showed this trend and thus, they alone were taken into account for convenience).

2. WSB ligands derived from aromatic (homoaromatic & heteroaromatic) amines showed higher β value as compared to aliphatic amines. Among these, WSB derived from heteroaromatic amines showed higher β values compared to homoaromatic amines.

3. N_2 (both Z & E isomers) showed higher β value than N_1. It showed that introduction of fused aromatic rings or planar aromatic moiety in the Wittig precursor aldehydes enhances the β value. With this knowledge, the present work produced synthetic procedure & structural characterization for Precursor Aldehyde (e) also (section 2. 4).

4. It was observed that the presence of strong electron releasing groups & electron rich atoms in the system leads to change in β value and that in some cases these changes do not correlate with ΔE relationship with β.

3. 4. E isomer Wittig based Schiff-Base copper(II) complex (Complex-1).

Hyperpolarizability calculations were carried out for all the molecules using GAUSSIAN09. **Complex-1** (Figure-6) was optimized using DFT based B3LYP method in which LANL2DZ basis set was used for metal ion & 6-31G* for C, H, N & O atoms. Frontier molecular orbitals of alpha and beta electrons of Complex-1 are presented in Figure-7 with HOMO-LUMO energy comparison, and selected bond lengths & angles are given in Table-3 & 4.

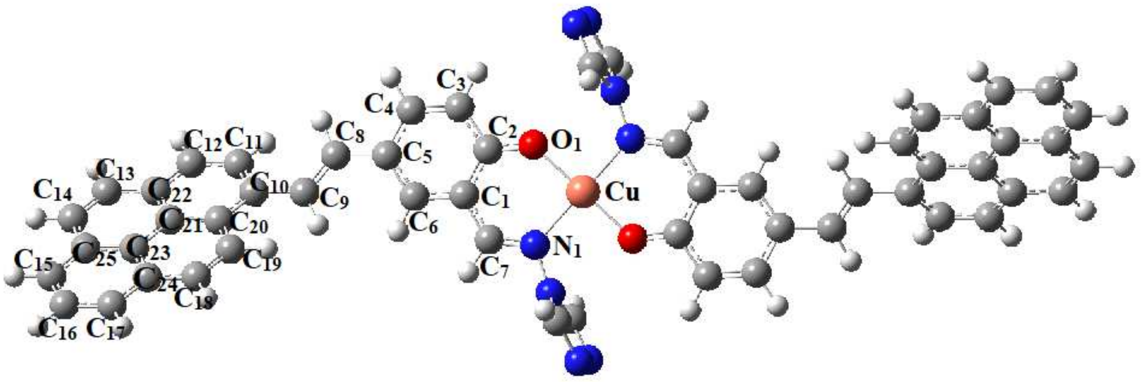


Figure-6. Optimized structure of Copper(II) Schiff-Base complex (Complex-1)

Table-3. Selected bond lengths (Å) for the Complex-1.

$N_1 – Cu= 2.0175$	$O_1 – Cu=1.9126$	$C_1 – C_7= 1.4184$	$C_7 – N_1 = 1.3147$	$C_1 – C_2 = 1.4397$
$C_2 – C_3 = 1.4239$	$C_3 – C_4 = 1.3753$	$C_4 – C_5 = 1.4269$	$C_5 – C_6 = 1.3863$	$C_6 – C_1 = 1.4206$
$C_8 – C_9 = 1.4648$	$C_9 – C_{10} =1.4663$	$C_{10} – C_{11}=1.4080$	$C_{11} – C_{12} = 1.3861$	$C_{13} – C_{14} = 1.3620$
$C_{15} – C_{16} = 1.3940$	$C_{16} – C_{17} = 1.3934$	$C_{18} – C_{19} = 1.3628$	$C_{19} – C_{20} = 1.4384$	$C_{20} – C_{10} = 1.4247$
$C_{20} – C_{21} = 1.4319$	$C_{21} – C_{22} = 1.4286$	$C_{21} – C_{23} = 1.4294$	$C_{23} – C_{24} = 1.4275$	$C_{23} – C_{25} = 1.4299$
$N_1 – N_2 = 1.3979$	$N_2 – C_{26} = 1.3709$	$C_{26} – N_3 = 1.3085$	$N_3 – N_4 = 1.3874$	$N_4 – C_{27} = 1.3085$
$C_{27} – N_2 = 1.3711$				

Table-4. Selected bond lengths (Degree) for the Complex-1.

$C_7 – N_1 – Cu = 126.0361$	$C_2 – O_1 – Cu = 131.2398$	$O_1 – N_1 – Cu = 90.2692$	$C_7 – N_1 – N_2 = 114.5957$
$C_1 – C_2 – O_1 = 124.0486$	$C_6 – C_5 – C_8 = 123.9313$	$C_5 – C_8 – C_9 = 126.6482$	$C_8 – C_9 – C_{10} = 125.2541$
$C_1 – C_7 – N_1 – N_2 = -179.6775$		$C_7 – N_1 – N_2 – C_{26} = 95.6203$	
$C_6 – C_5 – C_8 – C_9 = 19.9311$		$C_5 – C_8 – C_9 – C_{10} = -176.4652$	
$C_8 – C_9 – C_{10} – C_{11} = 29.8163$		$C_{19} – C_{20} – C_{10} – C_9 = 2.9690$	

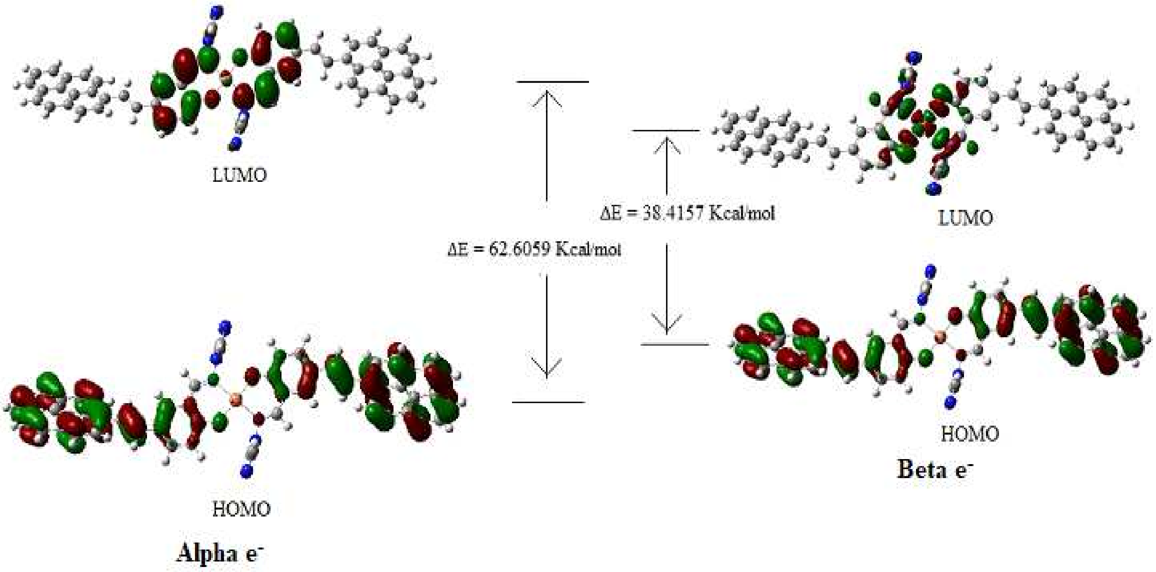


Figure-7. HOMO-LUMO energy comparison of alpha and beta electrons of Complex-1

Cartesian coordinates were used for calculating the dipole moment (μ), polarizability (α) and first static hyperpolarizability (β) by using standard equations [49-51] given below:

$$\mu = (\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2)^{1/2}$$

$$\alpha = 1/3\ (\alpha_{xx} + \alpha_{yy} + \alpha_{zx})$$

$$\beta_{total} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zyy} + \beta_{zxx})^2]^{1/2}$$

The polarizability and hyperpolarizability tensors (α_{xx}, α_{yy}, α_{zx}, β_{xxx}, β_{xyy}, β_{xzz}, β_{yyy}, β_{yzz}, β_{yxx}, β_{zzz}, β_{zyy}, β_{zxx}) were obtained from GAUSSIAN09 frequency job output file (Table-5) and atomic units (a.u.) were converted into electrostatic units (e.s.u.) (α; 1 a.u. = 0.1482 x 10^{-24} e.s.u, β; 1 a.u = 8.6393 x 10^{-30} e.s.u) and results are presented in tabular format (Table-6).

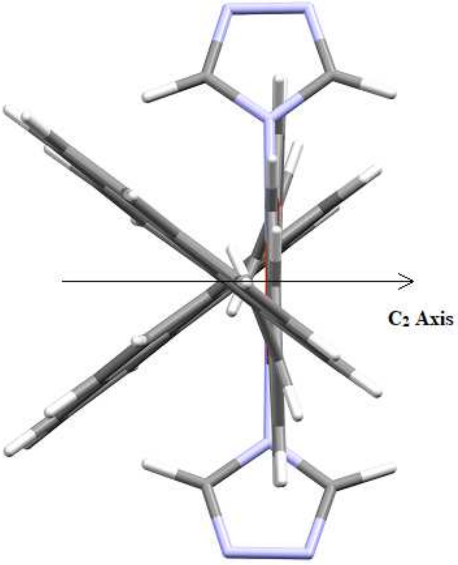


Figure-8. C_2 axis passes through the central metal

Table-5. Tensors of the Ligand-14 & its copper(II) complex

Ligand-14	**Complex-1**	**Urea** [*]
Dipole moment (μ) tensors	Dipole moment (μ) tensors	Dipole moment (μ) tensors
X = -5.2358	X = 0.0000	X = 0.0000
Y = -3.2589	Y = 0.0000	Y = 0.0000
Z = -0.4887	Z = 0.4386	Z = -3.4646
Polarizability (α) tensors	Polarizability (α) tensors	Polarizability (α) tensors
XX = -214.5895	XX = -427.8444	XX = -24.2588
YY = -185.7891	YY = -297.0102	YY = -17.6558
ZZ = -184.8137	ZZ = -356.5230	ZZ = -24.6862
Hyperpolarizbility (β) tensors	Hyperpolarizbility (β) tensors	Hyperpolarizbility (β) tensors
XXX = -563.3878	XXX = 0.0000	XXX = 0.0000
YYY = -103.8030	YYY = 0.0000	YYY = 0.0000
ZZZ = 0.0411	ZZZ = 21.6291	ZZZ = -12.2493
XYY = -183.3157	XYY = 0.0000	XYY = 0.0000
XXY = -244.8851	XXY = 0.0000	XXY = 0.0000
XXZ = -65.7905	XXZ = -18.4375	XXZ = 0.8154
XZZ = 27.2527	XZZ = 0.0000	XZZ = 0.0000
YZZ = -2.1183	YZZ = 0.0000	YZZ = 0.0000
YYZ = -34.2102	YYZ = 32.7387	YYZ = 0.7980
XYZ = -10.1595	XYZ = -211.8146	XYZ = -3.5256

[*] urea molecule was structurally optimized and hyperpolarizability calculations were carried out (see 2. 3. Computational methods) using 0.1 ω frequency.

Hyperpolarizability of copper(II) complex (Complex-1) was obtained from ‘Polar’ calculations using the GAUSSIAN09 program and presented in Table-6. Complex-1 exhibited high β value as compared to its Schiff-Base ligand (Ligand-13, N_2 & E isomer) revealing the importance of metal ion in achieving higher molecular NLO response. β value is also supported by low ΔE. In comparison with standard organic compound, urea (0.091816×10^{-30} e.s.u) [52,53], Ligand-14 & Complex-1 with C_2 symmetry showed much higher β value. However, very interestingly Ligand-14 showed higher β value than Complex-1. Generally, metal complexes show higher β value compared to the ligands [24] but in this case, it is vice versa most probably because of the symmetry of Complex-1 which is likely to be governing the β value. This infers that higher the symmetry, lower the β value. Marder & Nicoud et al also reported that molecules which are having centrosymmetry element do not exhibit high β value [54]. However, in this report, symmetry effect on β value was not studied systematically.

Table-6. μ, α, β_{total} and ΔE of Ligand-14 & Copper(II) complex (N_2, E isomer) and reference molecules

Molecules	Dipole moment (μ, Debye)	Polarizability ($\alpha \times 10^{-24}$ e.s.u)	Hyper Polarizability ($\beta_{total} \times 10^{-30}$ e.s.u)	LUMO-HOMO energy gap (ΔE; Kcal/mol)
Ligand-14	6.1865	-28.908	6.968	68.6864
Complex-1	0.4386	-53.420	0.310	62.606(Alpha) 38.416(beta)
Urea	3.4646	-3.290	0.091	189.242

4. Conclusions

We have successfully designed and screened 96 novel molecules and analyzed different factors affecting β value especially their geometrical isomeric effect.

Schiff-Base ligands derived from lone pair rich heteroaromatic amines with nitrogen as the heteroatom exhibited higher β value than other amines. Introduction of fused planar aromatic rings in precursor aldehydes enhances the β value of their Schiff-Base ligands (N_2 both Z & E isomers) as compared to others (N_1, Z & E isomers). Among the WSB of $N_{1,2}$, N_2 showed higher β value. E isomer WSB ligands showed higher β value compared to Z isomer. Schiff-Base ligands derived from homoaromatic amines containing electron withdrawing group ($-NH_2$) at *para* position showed higher β value over electron releasing group (-OH). Comparison between aliphatic five and six-membered rings, Ligand-15 & Ligand-16 respectively, revealed that five-membered ring has a higher β value over the six-membered ring. With increase in the number of tertiary amines in the cyclic ring (Ligand-16 -19), β value also increases. High β value producing molecule (e) was chosen and successfully synthesized and characterized. This study also revealed the importance of symmetry of the molecule and accordingly, experimental studies are underway.

Conflict of interest

All authors declare no conflict of interest.

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Highlights

- Designed and screened 96 Wittig based Schiff bases for hyperpolarizability (β)
- Precursor aldehydes were synthesized and spectroscopically characterized.
- Geometrical isomeric effect plays an important role in β value.
- Electron withdrawing group showed higher β value than electron releasing group
- Aliphatic five-membered ring has a higher β value than six-membered ring.