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Effect of a pyramidine ring formation at the Linker part on the non linear optical property of a D–π–A type chalcone: An In silico study

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Abstract

Theoretical calculations of energies, geometries polarizability, hyperpolarizabilities of (2*E*)–3–(4–aminophenyl)–1–(4–nitrophenyl)prop–2–en–1–one(ANC) and 6–(4–aminophenyl)–4–(4–nitrophenyl)–1,6–dihydropyrimidin–2–ol(ANCU) were studied based on density functional theory(DFT) using hybrid functional B3LYP with basis set 6–311G(d,p) and UV–Visible spectral analysis using time–dependent (TD–DFT) with same basis set. Calculated HOMO and LUMO energies represent the stability of the molecule. Stabilization energies of strong interactions are obtained from NBO analysis. The hyperpolarizability values of ANC and ANCU are thousand times than that of standard NLO material urea. The MESP analysis show variation in activity site thus the whole chemistry of the molecules changed with the condensation of chalcone with urea.

Keywords: Chalcone, Pyramidine, Hyperpolarizability, Intramolecular charge transfer

1. INTRODUCTION

Chalcones are the important class of organic compounds which possess non linear optical properties which varies with the substituent's present in the chalcone skeleton [1.2]. In chalcones two phenyl rings are connected through enone system, commonly benzoyl ring is designed as ring A and phenylene ring as ring B (Figure 1). Carbonyl group attached to the ring A can have a polar nature C^{+}–O^{-} which will be enhanced by electron donation from the skeleton and thus act as acceptor end, especially when electron donating substituent are attached to ring B in ortho and para position. The presence of donor acceptor entities with a conjugated linker is a characteristic feature shown by compounds with intramolecular charge transfer (ICT) and show non linear optical properties (NLO).

Compounds with chalcone skeletons have different pharmacological activities such as anticancer, antileishmanial, antiinflammatory, anti TB, antimicrobial, antifungal, antioxidant, cytotoxic, antitumour activities [3–8]. In the present study (2*E*)–3–(4–aminophenyl)–1–(4–nitrophenyl)prop–2–en–1–one(ANC) is selected in such a way the donor property of ring B is enhanced by p–amino substitution and the acceptor property was enhanced by p–nitro substitution. The effect of linker chain is altered by the condensation urea at the enone moiety which resulted in a heterocyclic pyramidine ring formation (Ring C) in 6–(4–aminophenyl)–4–(4–nitrophenyl)–1,6–dihydropyrimidin–2–ol(ANCU). The ring can effectively change the NLO properties of chalcone derivative. A detailed investigation was done based on the geometry optimization, NBO analysis, HOMO–LUMO and their energies and band gap, MESP analysis on the difference in first order hyperpolarizability of ANC and ANCU.

2. EXPERIMENTAL

2.1. Computational details

The computation of ground state geometries, electronic structures, fundamental frequencies, polarizability, hyperpolarpolarizabilities, electronic absorption, natural charge and natural bond orbital analysis for the title compounds was done using DFT with Gaussian '09 package [9]. The Becke's three parameter exchange–corrected exchange potential and the Lee–Yang–Parr gradient corrected correlation potential(B3LYP) along with double zeta split valence basis set 6–311G(d,p) was used to perform geometry optimization [10]. The electron absorption spectra require excitation and oscillator strengths, these calculations were done using TD–DFT [11] with the same basis set. Graphical representation of MESP, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) data in structure optimized files were made using the Gaussview visualization program [12].

3. RESULTS AND DISCUSSIONS

3.1. Geometry Optimization

The important optimized geometry parameters of ANC and ANCU obtained from Gaussian 09 and were shown in Table 1. The optimized geometries visualized from Gaussview program and the numbering scheme for ANC and ANCU are in given in Figure 1.

Table 1: Selected geometrical parameters of ANC and ANCU

Theoretical bonds	(Å)	
	ANC	**ANCU**
$C_6 – C_7$	1.512	1.486
$C_7 – C_8$	1.472	1.348
$C_8 – C_9$	1.351	1.508
$C_9 – C_{10}$	1.449	1.523
$C_{13} – N_1$	1.379	1.389
$C_3 – N_2$	1.481	1.474
$C_7 – O_1$	1.224	–
Theoretical dihedral angles (º)		
$C_5 – C_6 – C_7 – C_8$	–18.1	–15.3
$C_6 – C_7 – C_8 – C_9$	176.8	179.4
$C_7 – C_8 – C_9 – C_{10}$	179.0	–123.8
$C_8 – C_9 – C_{10} – C_{11}$	–1.3	–124.5
$C_5 – C_6 – C_7 – O_1$	162.7	–
$C_5 – C_6 – C_7 – N_3$	–	166.4

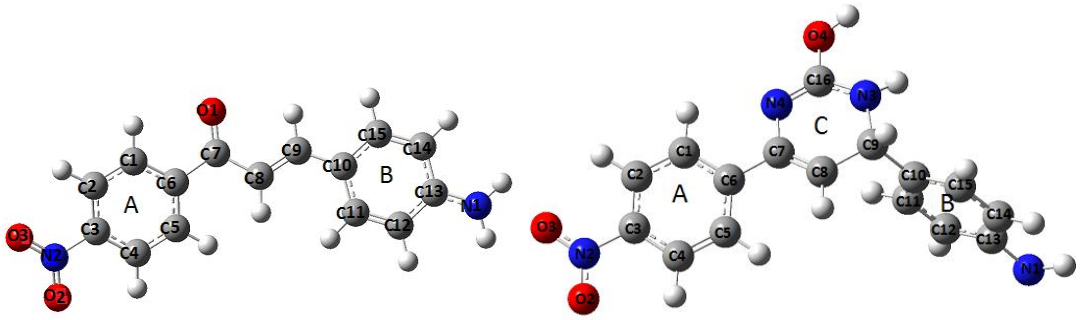

Fig. 1: Optimized geometries

The pyramidine ring formation at enone moiety not only alters the bond lengths in alkene skeleton but also in the substituent's as shown by C_3–N_2 and C_{13}–N_1. The bond length of C_6–C_7 is decreased and C_9–C_{10} was increased. The single and double bond characters C_6–C_7 and C_7–C_8 were reversed by ring formation. Increase of bond length of C_9–C_{10} from 1.449 to 1.523Å in illustrates the lesser conjugation of donor end ANCU however enhanced conjugation is observed in acceptor end (The C_6 – C_7 bond length shortened from 1.512Å to 1.486Å). The pyramidine ring formation alters the overall geometry of the compounds, the ring B flipped away however ring A become more planar to the newly formed ring C as indicated by the dihedral angle C_7–C_8–C_9– C_{10} and C_8–C_9–C_{10}–C_{11} which support the view that the conjugation in ring A increased and ring B reduced.

3.2. Non-linear Optical Properties

The inter related properties, dipole moment(μ), polarizability(α_0), average polarizability (Δα), first order polarizability(β_0) of the investigated molecules are calculated with B3LYP/6-311G(d,p) basis set, using finite-field approach. All these properties depend on the presence of applied electric field and the molecular structure of a system. The total dipole moment defines as

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

The mean polarizability and anisotropy of polarizability are defined as

$$\alpha_0 = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2]^{1/2}$$

The components of the first hyperpolarizability can be calculated using following equation,

$$\beta_i = \beta_{iii} + 1/3\sum(\beta_{ijj} + \beta_{jij} + \beta_{jji}), (i \neq j)$$

Using the x,y,z components, the magnitude of the first hyperpolarizability tensor was calculated by

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The values of hyperpolarizability in a.u have been converted to esu by conversion β: 1 a.u. = 0.008639×10^{-30}esu

The dipole moment of the title compounds ANC, ANCU is 9.61D and 12.11D respectively and hyperpolarizability (β) components of ANC, ANCU calculated using DFT/B3LYP 6–311G(d,p) method are listed in Table 2. The static first order hyperpolarizability of ANC (86.95×10^{-30} esu) is reduced to 40.12×10^{-30} esu by the ring formation in ANCU. Both molecules have same donor and acceptor groups(amino and nitro respectively), The pyramidine ring formation in eneone skeleton at

the middle of the compound decrease the effective π electron conjugation from donor to the acceptor end which reduces the NLO activity of urea condensed product ANCU to half of the ANC. However both the molecules have higher NLO activity than the standard NLO material urea (0.13×10^{-30} esu) [13]. The NLO activity of ANC and ANCU were 67,000 and 31,000 times than that of urea.

Table 2: Hyperpolarizability components of ANC and ANCU

Components	ANC	ANCU
	10^{-30} esu	
β_{xxx}	84.11	14.7
β_{xxy}	13.84	1.75
β_{xyy}	2.01	0.15
β_{yyy}	0.27	0.58
β_{xxz}	–3.82	12.97
β_{xyz}	–0.42	1.57
β_{yyz}	0.02	1.05
β_{xzz}	–0.36	12.25
β_{yzz}	–0.15	4.95
β_{zzz}	0.31	14.59
β_{tot}	**86.95**	**40.12**

3.3. Frontier Molecular Orbitals and excitation spectra

Chemical reactivity of a molecule is highly dependent on the orbital properties and energy of frontier molecular orbitals [14], highest occupied molecular orbital(HOMO) and lowest unoccupied molecular orbital(LUMO). Lower HOMO–LUMO energy difference that is small band gap enhances effective overlapping of these orbitals which resulted in easy ICT. Ionization potential of a molecule depends on the ability of donating electron and is associated with HOMO and the characteristics of LUMO are associated with electron affinity [15].

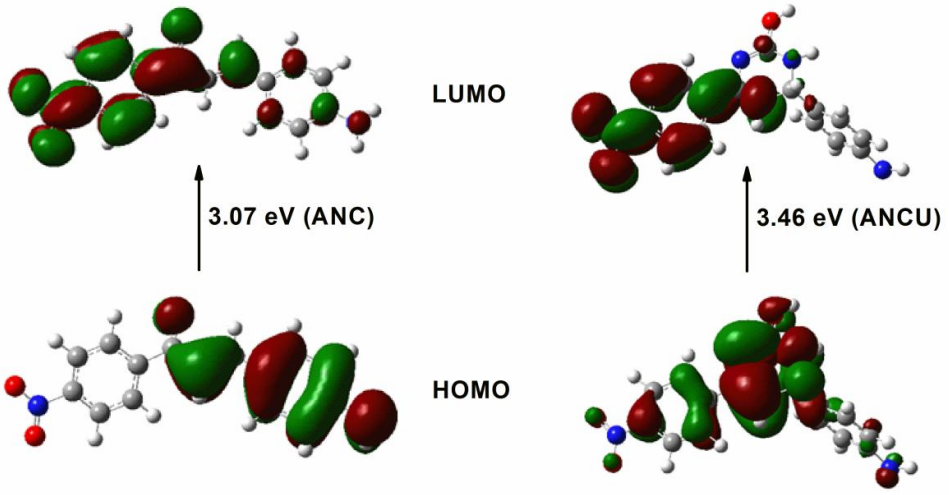

Fig. 2: Frontier molecular orbitals of ANC and ANCU

The Figure 2 represents the FMO's of ANC, ANCU. In ANC the energies of HOMO and LUMO are –5.95 and –2.89 eV respectively. HOMO localized over ring B (donor end), ethylenic bond and carbonyl group, LUMO delocalized over phenyl ring A (acceptor end). The band gap is 3.07eV. In ANCU HOMO energy is –5.81eV and mainly localized on the pyramidine ring at the middle region of the molecule this indicates the less conjugation of lone pair of electrons from amino group to the

pyramidine ring which is observed by the flipping of ring B. The lowest unoccupied molecular orbital lies at –2.35 eV delocalized on the electron withdrawing nitro substituted phenyl ring A, and the band gap is 3.46eV. This demonstrates intramolecular charge transfer in both cases but in different part of the molecule, the extent of ICT reduces in ANCU thus the NLO property. More easily charge excitation takes place in case of ANC due to the lower band gap it helps to develop enhance hyperpolarizability. The electronic translational behaviour of ANC and ANCU have been studied using time-dependent density functional theory with B3LYP/6-311G(d,p) basis set in gas phase. The calculated UV-Vis spectrum of ANC consists a maximum absorption peak at 446nm corresponds to the π→π*(homo to lumo) transition (98%), the λ_{max} value of ANCU at 403nm also attribute to π→π*(H to L) excitation (95%).

3.4. Molecular Electrostatic Potential

Molecular electrostatic potential (MESP) plot specifies the net electrostatic effect produced at a point by the total charge distribution over the molecule [16]. MESP surface helps to assess the nucleophilic and electrophilic binding sites in order to assign biological recognition and H–bonding interactions [17]. The different electrostatic potentials are represented by different colours. More electron dense region is represented by red colour and more positive region as blue colour. Green represents the neutral potential. Fig. 3 depicts the MESP map of ANC, ANCU. In ANC, the partial negative potential(orange colour) are mainly situated over nitro group and the highest negative potential on carbonyl oxygen atom, positive potential are localized over hydrogen atoms of amino group. In ANCU no change is observed for the electrophilic attacking centre, however the carbonyl centre has reduced nature due to more conjugation with the ring A as suggested by the geometry parameters. The shift in nucleophilic attack centre is observed, the highest at the ring C with a lowering nature in amino groups of ring B indicating a total variation in the chemistry of molecule by the condensation with urea.

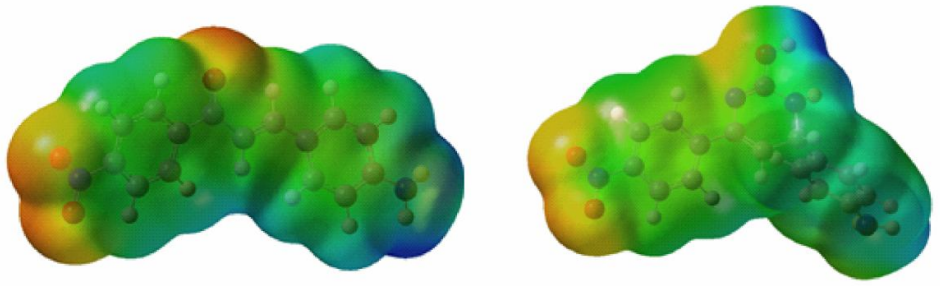

Fig. 3: MESP plots of tile compounds

3.5. Natural Charge Analysis

The charge on each atoms were determined on the basis of natural charge analysis calculated using NBO method at B3LYP/6–311G(d,p) basis set in vacuum. The atomic charges of selected atoms are tabulated in Table 3. The graphical representation of charge analysis of equivalent atoms (C_1–C_{15}) of ANC, ANCU are given in Figure 4. All hydrogen atoms in both cases are positively charged. More positively charged carbon atom among C_1–C_{15} are C_7 due to the presence of electronegative oxygen atom. Alternative higher and lower electronic charges represent the electron conjugation in both cases. In ANCU, two nitrogen and hydroxyl oxygen atom of the pyramidine ring possess negative charge and the carbon atom in between nitrogen atoms have positive charge (0.5029e).

Table 3: The natural atomic charges

Atoms	ANC	ANCU
C_3	0.1274	0.1259
C_6	–0.1283	–0.110
C_7	0.2565	0.1613
C_8	–0.1002	–0.0462
C_9	0.1064	0.2145
C_{10}	–0.0843	–0.1417
C_{13}	0.1316	0.1105
N_1	–0.0312	–0.0469
N_2	0.1720	0.1678

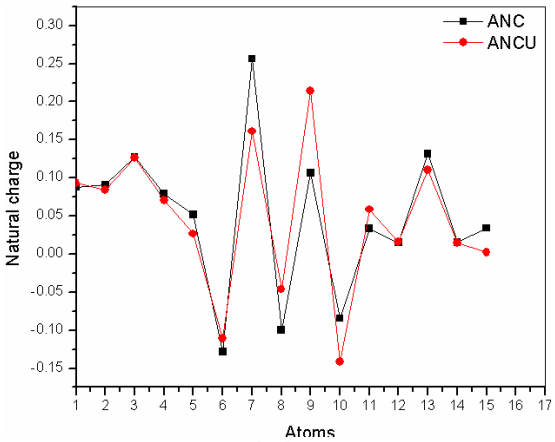

Fig. 4: Natural charge Diagram

3.6. Natural Bond Orbital Analysis

The Natural Bond Orbital(NBO) study using NBO program [18] executed in Gaussian '09 characterize all the intra–, inter molecular interactions and corresponding stabilization energies($E^{(2)}$). Stabilization energy depends on the strength of donor-acceptor interface. Tabulation of intensive intramolecular interactions of ANC, ANCU are in Table 4.

From the table 4 it is clear that π to π* interactions within the phenyl rings are of comparable stabilization energies. Maximum stabilization energy is reported in case of interaction within the nitro group. In the donor end, amino group interact with the phenyl ring B with stabilization energies 137.90, 123.05kJmol^{-1} described in case of ANC and ANCU respectively. It illustrate that in ANC the donor interaction is better, when it condensed with urea that donor interaction decreases and the intra molecular charge transfer (ICT) within the molecule reduced. The significant condition for a molecule to be NLO active is it must possess an ICT from donor end to acceptor end, as distance between donor to acceptor end increases the NLO activity also increases. In case of ANCU it weakens due to the presence of pyramidine ring, stabilization energy of 4.98 kJmol^{-1} shows that weak σ to σ* interaction of that ring with the acceptor end, the presence of ring C decreases the p–electron delocalization. As a result the first order hyperpolarizability value of ANC is 2 times that of ANCU.

Table 4: Second-order perturbation theory analysis of Fock matrix in NBO basis corresponding to the intramolecular interactions of ANC and ANCU computed at B3LYP/6–311G (d,p) level

ANC			ANCU		
Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ ($kJmol^{-1}$)	Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ ($kJmol^{-1}$)
$\pi C_5 - C_6$	$\pi^* C_3 - C_4$	96.36	$\pi C_1 - C_6$	$\pi^* C_2 - C_3$	103.30
$\pi C_1 - C_2$	$\pi^* C_7 - O_1$	62.43	$\pi C_1 - C_6$	$\pi^* C_7 - C_8$	56.15
$\pi C_1 - C_2$	$\pi^* C_3 - C_4$	92.93	$\pi C_2 - C_3$	$\pi^* N_2 - O_2$	105.65
$\pi C_1 - C_2$	$\pi^* C_5 - C_6$	87.95	$\pi C_7 - C_8$	$\pi^* C_1 - C_6$	47.74
$\pi C_3 - C_4$	$\pi^* N_2 - O_2$	110.21	$\sigma C_7 - N_3$	$\sigma^* C_6 - C_7$	4.98
$\pi C_8 - C_9$	$\pi^* C_7 - O_1$	97.99	n(2) O_4	π^* N_3–C_7	129.87
$\pi C_{10} - C_{15}$	$\pi^* C_8 - C_9$	86.36	n(2) N_4	π^* N_3–C_{17}	216.52
n(1) N_1	$\pi^* C_{13}$ –C_{14}	137.90	n(1) N_1	π^* C_{13}–C_{14}	123.05
n(2) O_1	σ^* C_6–C_7	81.84	n(3) O_3	π^* N_2–O_2	683.62
n(3) O_3	$\pi^* N_2$ –O_2	691.99			

$E^{(2)}$ means energy of hyperconjugative interactions (stabilization energy).

4. CONCLUSIONS

Using density functional theory with hybrid functional B3LYP, the geometries, electronic structures, dipole moment, hyperpolarizability, natural charge and natural bond orbital analysis, frontier molecular orbital analysis, corresponding energies, band gap and electrostatic potential map of two potential nonlinear optical materials, (2*E*)–3–(4–aminophenyl)–1–(4–nitrophenyl)prop–2–en–1–one(ANC) and 6–(4–aminophenyl)–4–(4–nitrophenyl)–1,6–dihydropyrimidin–2–ol(ANCU)were performed using Gaussian software. The optimized geometries shows that ANC is almost planar and ANCU is non planar in nature. The hyperpolarizability calculations reveals that both molecules are thousands of times more NLO active than standard urea, among them ANC is more active. This is due to the strong ICT in ANC. ANC and ANCU posses a band gap of 3.07eV and 3.46 eV respectively. FMO plots illustrate a charge transfer within the molecules for both cases. Both molecules are polar in nature. NBO analysis confirms a prominent intramolecular interaction on nitro group. Natural charge analysis shows all hydrogen atoms are positively charged and presence of two electronegative nitrogen atoms adjacent to carbon atom in ring C of ANCU have maximum positive charge(0.5029e).

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Conflict of Interest

The authors confirm that there are no known conflicts of interest associated with this publication. It is also certify that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

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