

Effect of Carbonyl Group Position on the NLO Properties of Chalcones

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Abstract: Chalcone derivatives are well known for blue-green light transmittance, second Harmonic generation and third order NLO effects. For optoelectronics and photonic applications organic molecules exhibiting high NLO properties with good thermal and chemical stability are required in the present scenario. We have designed six molecules of Donors/acceptors substituted chalcones with carbonyl group near and way from Donor/Acceptor group. The computational results clearly suggest that the molecular planarity is greatly affected by the type of the design of NLO molecules. The present study reveals the effect of Carbonyl group position on the NLO properties of chalcones. The role of Carbonyl group position and Donor/acceptor group on the molecular planarity, ICT and β_o are presented in this article. The value of β_o increases when the carbonyl group substitution is i) near the acceptor group and ii) away from donor group.

Keywords: Nonlinear optics, Chalcones, molecular First hyperpolarizability

1. Introduction

Nonlinear optics (NLO) is a new frontier of science and technology playing an important role in the upcoming area of optical communications, data storage, harmonic oscillators, frequency mixing and optical switching [1-3]. Organic NLO materials offer various advantages over the inorganic NLO materials, including high optical nonlinearities, fast response, easy molecular tailoring through precise synthetic methods, and high optical damage thresholds [4]. Even though Inorganic materials are relatively more stable than the organic materials they suffer with poor amplitudes of hyperpolarizability. Chalcone derivatives exhibit high NLO coefficients and good crystallizability [5]. The nonlinear optical response of chalcone derivatives is due to the delocalized π -electron conjugated system connecting donor and acceptor groups [6]. The molecular hyperpolarizability can be enhanced by increasing the extent of charge transfer across the molecule by placing a strong electron donor and acceptor groups at the ends of the highly polarizable conjugated bridge. With proper combination of donor / acceptor group one can easily construct molecules with D- π -A, D- π -A- π -D and D- π -A- π -A structures in chalcones. The D- π -A and D- π -A- π -A type results in asymmetric polarization of charges and is believed to enhance the NLO behavior of these molecules [7].

In order to optimize the NLO response in chalcones, we have investigated the role of carbonyl group position as well as the number of donor group effect on the NLO behavior of these materials. We describe the NLO

properties of six molecules selected for this study to elucidate structure property relation in chalcone molecules.

2. Computational Procedure

The NLO properties of six chalcones were computed using semi-empirical Quantum chemical MOPAC2016 package [8]. To optimize the molecular geometry of all the six molecules AM1 Hamiltonian with Eigen Following routine for geometry optimization is adopted. PRECISE keyword was used in all the computation to improve the accuracy. To compute static molecular First hyperpolarizability, β_o , Time Dependent Hartree-Fock (TDHF) theory was implemented. The computed results are shown in Table 1 and that of Frontiers of molecular orbitals in Figure 2.

3. Result and Discussion

The D- π -A- π -A type five push-pull structures of Chalcones namely, (2E)-1-(4-nitrophenyl)-3-phenylprop-2-en-1-one (PN1), (2E)-3-(4-nitrophenyl)-1-phenylprop-2-en-1-one (PN2), (2E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (PM1), (2E)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (PM2) and (1E, 4E)-1-(4-methoxyphenyl)-5-phenylpenta-1, 4-dien-3-one (PM3) whereas (1E, 4E)-1, 5-bis(4-methoxyphenyl)penta-1, 4-dien-3-one (PM4) has D- π -A- π -D structure were designed and the molecular structures are shown in Figure 1.

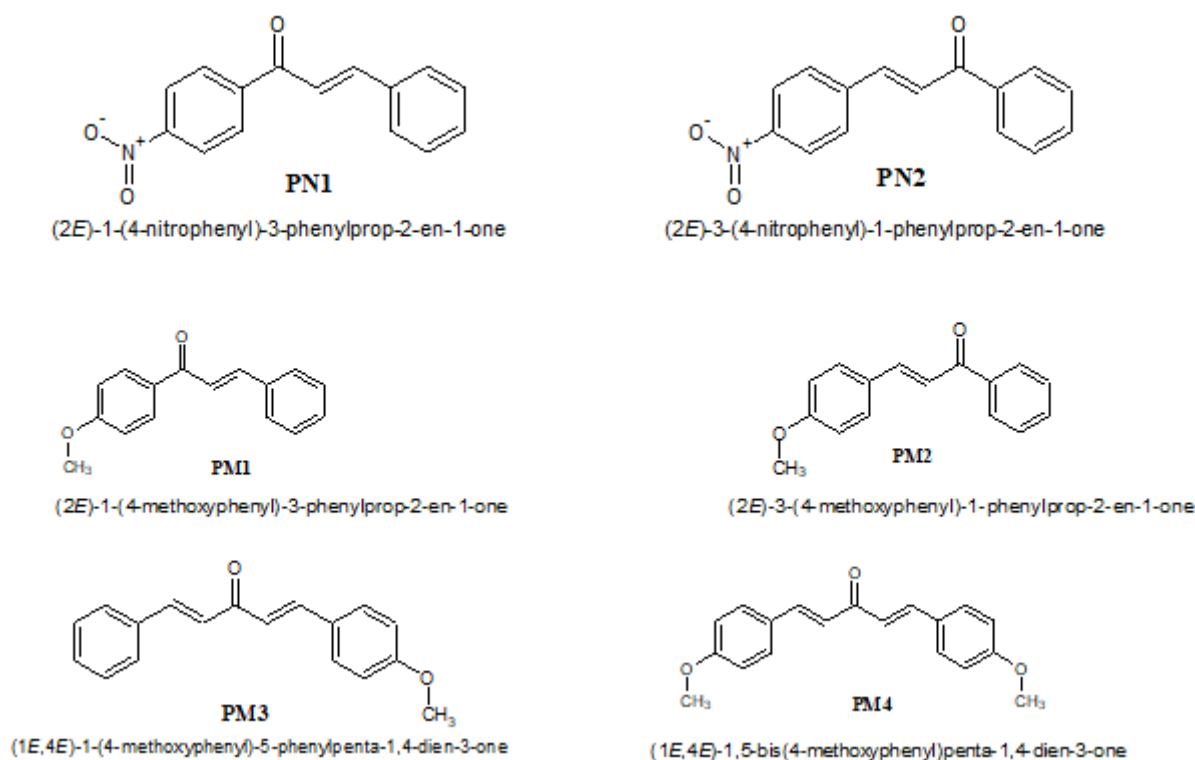


Figure 1: Molecular structures of Donor/Acceptor substituted chalcones

Six molecules of chalcone structures were carefully tailored to understand the NLO behavior. In order to optimize the Carbonyl group position suitable to enhance the NLO property in these molecules four molecules were selected. Among the four selected molecules, two molecules contain nitro group (PN1, PN2) at the para position but the carbonyl group in different position. Other two molecules (PM1, PM2) with electron donor methoxy group substitution at para position and the carbonyl group at two different location (Figure 1). The NLO properties of four molecules containing donor/acceptor group have been computed and the results are tabulated in Table 1. It is clear from β_0 values listed in Table 1 that the carbonyl group, if substituted towards the acceptor group then the chalcones has maximum β_0 values. This clearly indicates that the charge transfer is effective in the structure in which carbonyl group positioned near electron acceptor moiety (nitro phenyl). The situation is different in donor substituted chalcones and high β_0 value was observed for PM2 in which carbonyl group is substituted after the C=C (away from donor), which effectively increases the conjugation length in comparison with PM1.

Among the two acceptor group substituted chalcones (PN1 and PN2) the effectiveness of the NLO chromospheres design seems to be better in PN1 in which NO₂ group along with carbonyl group acts as an effective acceptor group. Among PM1 and PM2, PM2 design seems to be more effective as the conjugation length is more in comparison with PM1. Therefore while designing NLO chalcone one should always keep in mind that the carbonyl group should be substituted near the acceptor group and

also carbonyl group (C=O) group should be substituted away from donor group to enhance the effectiveness of charge transfer in donor substituted chalcones. Further we have computed NLO property of two more molecules PM3 and PM4. The result clearly suggests that both molecules have nearly equal β_0 magnitudes and use of one donor group in chalcone is sufficient rather than multiple group substitution to enhance NLO property. The multiple donor group substitution on chalcone does not yield larger enhancement in β_0 value. Therefore it is recommended to use one donor group instead of many.

Further from the optimized structure data it is clear that dihedral angle between the two phenyl moiety found to be larger for the molecules with acceptor/donor substituted near carbonyl group and is less for those molecules in which donor/acceptor substituted away from carbonyl group. The molecular planarity and the twist in the molecule help the molecules to exhibit good NLO property. Planar molecules show better intermolecular charge transfer than twisted molecules whereas twisted molecules helps to consolidate the noncentrosymmetric crystal structure via intermolecular C-H...O, C-H... π and π - π interactions.

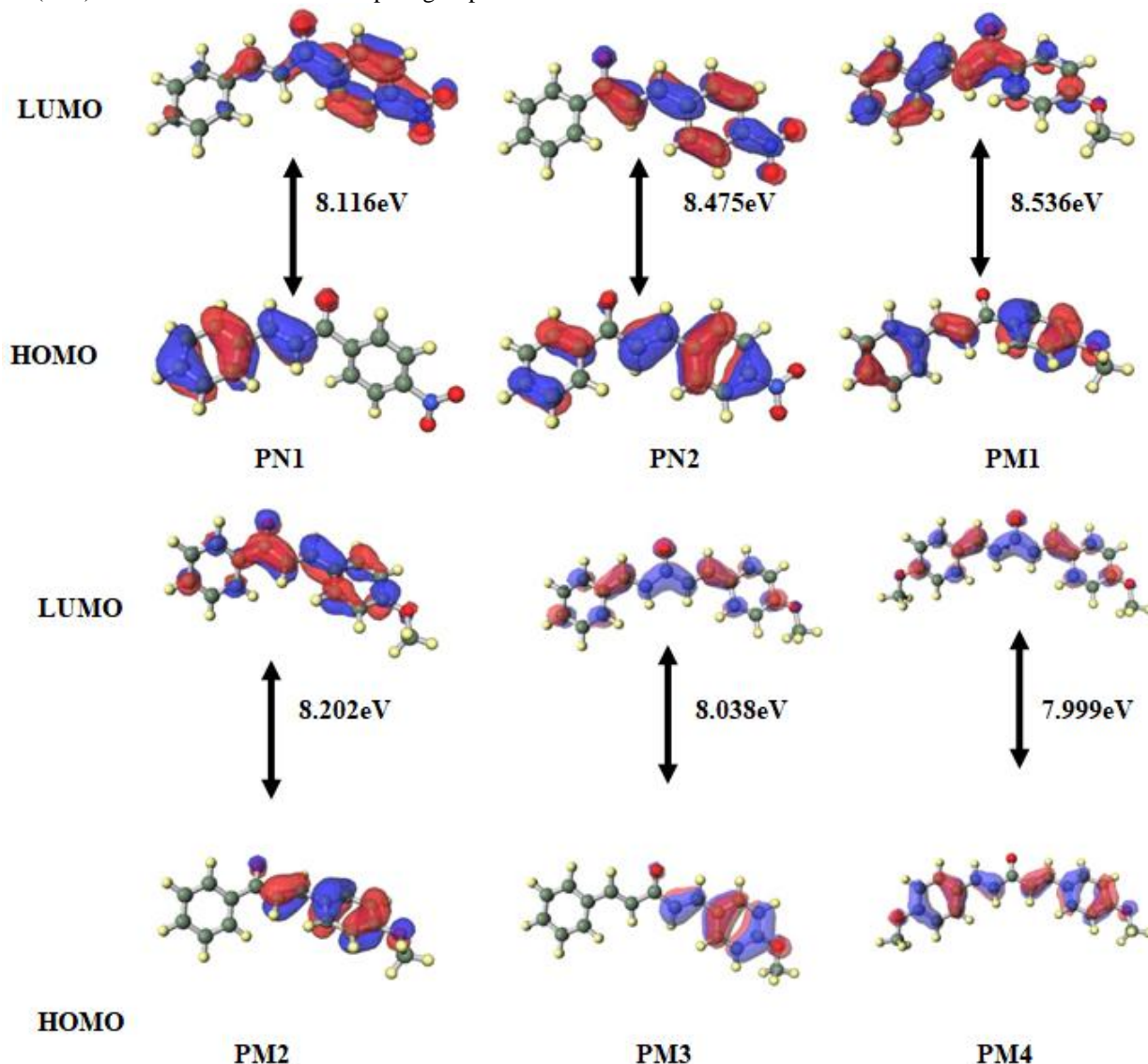
From the computed data it is clear that higher the HOMO-LUMO energy gap (E_g) less will be the value of β_0 and is in consistence with the theoretical prediction. The molecule with lesser E_g is more polarizable and hence show better NLO response.

Table 1: Semi empirical quantum chemical computational results of Donor/Acceptor substituted chalcones

Compound	μ (Debye)	β_0 ($\times 10^{-30}$) esu	HOMO(eV)	LUMO(eV)	Eg(eV)	DIHEDRAL ANGLE	C=C of substitution side (Å)
PN1	5.986	7.11	-9.602	-1.486	8.116	53.52	1.345
PN2	4.867	2.06	-10.075	-1.6	8.475	27.77	1.342
PM1	4.083	3.91	-9.209	-0.673	8.536	53.75	1.343
PM2	4.019	10.66	-8.878	-0.676	8.202	49.5	1.344
PM3	3.824	10.11	-8.825	-0.787	8.038	14.34	1.344
PM4	5.042	10.16	-8.757	-0.758	7.999	21.01	1.344

For all six designed molecules frontiers of molecular orbitals were created (HOMO-LUMO orbital) using Winmostar 8.0 computer package and are shown in Figure 2. It is clear from Figure 2 that the intermolecular charge transfer (ICT) occurs from donor to acceptor group in all

the designed molecules. The best molecule among the six in terms of ICT, β_0 , molecular planarity was found optimum in PM3.

**Figure 2:** HOMO-LUMO of Donor/Acceptor substituted chalcones

4. Conclusion

Six molecules were designed with carbonyl group at different positions in comparison with donor/acceptor group's position in Chalcone molecules and Semi empirical quantum chemical calculations have been carried out. From the results it is found that carbonyl group substitution near the acceptor and away from donor

increases the value of β_0 . To enhance the NLO response substitution of one donor group at para position is sufficient rather than many donor groups. The molecular planarity which results in effective ICT is found to be better in the molecules in which Donor group substituted away from the carbonyl group rather than near to it.

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