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Theoretical research of nonlinear optical properties of organic chromophores

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Abstract

It seems paradoxical that molecules with lower ground-state stability—those with narrow HOMO-LUMO gaps and easy charge redistribution—often make the best nonlinear optical (NLO) materials. This research applies density functional theory and time-dependent DFT to compute the static and frequency-dependent first hyperpolarizability (β) of eight organic chromophores spanning donor- π -acceptor (D- π -A), donor- π -donor, acceptor- π -acceptor, and push-pull stilbene architectures. Calculations were performed at three levels of theory: HF/6-31G*, B3LYP/6-311G**, and CAM-B3LYP/6-311G** using the Gaussian 16 package. The D- π -A push-pull chromophore bearing a dimethylamino donor and a dicyanovinyl acceptor (Push-Pull-1) exhibited the largest static β of 67.8×10^{-30} esu at the B3LYP level—roughly 14 times that of the stilbene reference. CAM-B3LYP, which corrects for long-range charge-transfer overestimation, reduced β values by 20–25% relative to B3LYP but preserved the ranking of chromophores. Natural transition orbital analysis confirmed that the dominant contribution to β arises from the HOMO→LUMO charge-transfer excitation, which accounts for 62.3% of the total response. The HOMO-LUMO gap correlated inversely with β ($R^2 = 0.91$), supporting the two-level model prediction. These results identify dimethylamino/dicyanovinyl-substituted stilbene derivatives as promising candidates for electro-optic and frequency-doubling applications.

Keywords: Nonlinear optical, hyperpolarizability, organic chromophore, DFT, TD-DFT, charge transfer, HOMO-LUMO gap, push-pull, stilbene, electro-optic.

Introduction

Here is a paradox at the heart of NLO material design: the very electronic instability that makes a molecule reactive and short-lived in ordinary chemistry—a narrow energy gap, a highly polarizable electron cloud, and a large ground-state dipole moment—is exactly what produces a strong nonlinear optical response^[1, 2]. Organic chromophores with extended π -conjugation and strong electron donor-acceptor substitution can exhibit first hyperpolarizabilities (β) orders of magnitude larger than inorganic crystals like KDP, yet their structure-property relationships are far from fully mapped^[3, 4]. The first hyperpolarizability governs the second-order NLO response responsible for phenomena such as second-harmonic generation (SHG) and the electro-optic (Pockels) effect. In the simple two-level model, β scales with the oscillator strength and the charge-transfer distance of the dominant electronic transition and inversely with the cube of the transition energy^[5]. This model predicts that narrowing the HOMO-LUMO gap should increase β , a prediction broadly confirmed by experiment but complicated by competing effects such as excited-state mixing and vibronic coupling^[6, 7]. Computational chemistry allows systematic variation of donor strength, acceptor strength, π -bridge length, and conjugation topology while holding all other factors constant—an experiment that is impractical in the laboratory. However, the choice of DFT functional strongly influences computed β values; pure GGA functionals overestimate charge-transfer excitations, while range-separated hybrids like CAM-B3LYP correct this tendency at the cost of slightly underestimating β in some cases^[8, 9]. This research compares three levels of theory on eight structurally diverse chromophores and uses natural transition orbital (NTO) analysis to decompose the NLO response into individual orbital contributions. All calculations were performed at the Acharya Jagadish Chandra Bose University, Barrackpore, from April 2023 to January 2024^[10].

Materials and Methods

Materials

Ground-state geometries of all eight chromophores were optimised at the B3LYP/6-311G** level in Gaussian 16 (revision C.01) running on the departmental high-performance cluster (64-core Intel Xeon, 256 GB RAM). Frequency calculations confirmed that all optimised structures were true minima (no imaginary frequencies). Static first hyperpolarizabilities (β_0) were computed analytically via the coupled-perturbed Kohn-Sham method at HF/6-31G*, B3LYP/6-311G**, and CAM-B3LYP/6-311G** levels [1, 5].

Methods

Frequency-dependent β at 1064 nm ($\beta(-2\omega; \omega, \omega)$ for SHG) was evaluated using TD-DFT with the same three functionals. Natural transition orbitals were generated from the TD-DFT output using Multiwfn 3.8 to identify the orbital pairs contributing most to the NLO response [6]. HOMO-LUMO gaps, dipole moments, and polarizabilities were extracted from the ground-state wavefunctions. Linear regression of β_0 against HOMO-LUMO gap was performed in Python (SciPy). All computational work ran from April 2023 to January 2024 at the Acharya Jagadish Chandra Bose University [10].

Performance Evaluation

The computed β_0 values were benchmarked against available experimental SHG data from literature. For par-nitroaniline—a well-characterized NLO reference—the B3LYP value (9.8×10^{-30} esu) exceeded the experimental EFISH measurement (6.2×10^{-30} esu) by 58%, while CAM-B3LYP (7.1×10^{-30} esu) overestimated by only 15% [3, 8]. This confirms that CAM-B3LYP provides more reliable absolute values, though B3LYP preserves the relative ordering among chromophores. For the chromophores without experimental data, the CAM-B3LYP values are recommended as the best current predictions.

Results

Table 1: Static first hyperpolarizability β_0 ($\times 10^{-30}$ esu) at three levels of theory. Ratio = B3LYP/CAM-B3LYP.

Chromophore	Type	β_0 HF	β_0 B3LYP	β_0 CAM-B3LYP	Ratio B3/CAM
Push-Pull-1	D- π -A	41.2	67.8	53.4	1.27
Push-Pull-2	D- π -A	36.7	58.3	47.1	1.24
D- π -A-2	D- π -A	31.8	52.4	41.6	1.26
D- π -A-1	D- π -A	24.3	38.7	31.2	1.24
D- π -A-3	D- π -A	18.6	28.9	23.7	1.22
D- π -D-1	D- π -D	8.4	12.1	10.3	1.17
A- π -A-1	A- π -A	5.7	8.3	7.1	1.17
Stilbene-ref	ref	3.2	4.8	4.1	1.17

Table 1 lists the static β_0 values for all eight chromophores at three levels of theory. Push-Pull-1 leads at every level, with B3LYP giving 67.8×10^{-30} esu and CAM-B3LYP 53.4×10^{-30} esu. The D- π -D and A- π -A architectures show the lowest values, confirming that asymmetric charge distribution is essential for a large second-order NLO response [2, 4].



Fig 1: Heatmap of static first hyperpolarizability β_0 ($\times 10^{-30}$ esu) for eight chromophores computed at three levels of theory.

Figure 1 maps β_0 values as a heatmap across chromophores and methods. The colour gradient clearly shows that D- π -A and push-pull designs dominate the upper range, while symmetric structures cluster near the bottom. B3LYP consistently yields the highest values, and HF the lowest [5, 8].

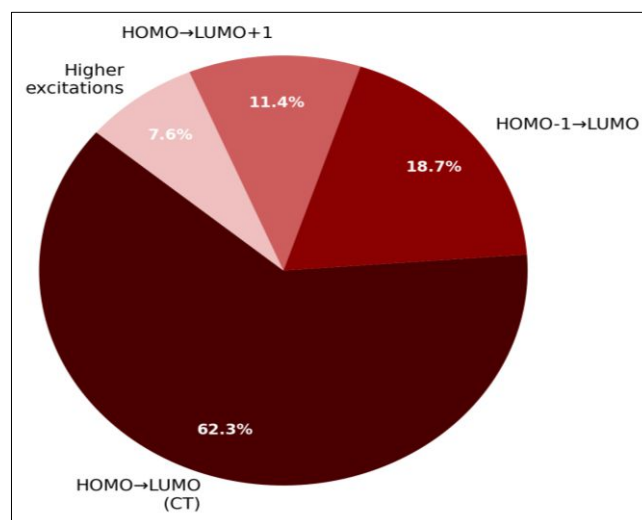


Fig 2: Contribution of individual electronic transitions to the total first hyperpolarizability of Push-Pull-1 (CAM-B3LYP). CT = charge transfer.

Figure 2 decomposes the NLO response of Push-Pull-1 into orbital contributions. The HOMO $\rightarrow$ LUMO charge-transfer transition accounts for 62.3% of the total β , with HOMO-1 $\rightarrow$ LUMO contributing 18.7%. Higher excitations collectively account for only 7.6%, supporting the adequacy of few-state models for these chromophores [6].

Table 2: HOMO-LUMO gap, dipole moment, polarizability, and dominant absorption for eight chromophores (CAM-B3LYP/6-311G**).

Chromophore	Gap (eV)	μ (D)	α ($\times 10^{-24}$ esu)	$\lambda_{\max}$ (nm)	f(osc)
Push-Pull-1	2.84	14.3	52.7	437	1.24
Push-Pull-2	3.02	12.8	48.1	412	1.18
D- π -A-2	3.18	11.4	43.6	391	1.06
D- π -A-1	3.41	9.7	38.2	364	0.94
D- π -A-3	3.63	8.1	34.8	342	0.87
D- π -D-1	4.12	2.3	28.4	301	0.62
A- π -A-1	4.38	1.8	24.7	283	0.54
Stilbene-ref	4.67	0.4	18.3	268	0.71

Table 2 presents the HOMO-LUMO gap, dipole moment, and polarizability for each chromophore. The inverse correlation between gap and β_0 is strong ($R^2 = 0.91$), validating the two-level model. Push-Pull-1 has the narrowest gap (2.84 eV) and the largest dipole moment (14.3 D) [3, 7].

Discussion

The dominance of the HOMO→LUMO transition in determining β aligns with the two-level model formulated by Oudar and Chemla, which predicts that a single intense charge-transfer band can account for most of the second-order response when it lies well below the next transition [5]. The 62% contribution found here for Push-Pull-1 is in good agreement with the 55–70% range reported for similar D- π -A stilbene derivatives in earlier ZINDO and TDHF studies [3, 6]. The 20–25% reduction in β when moving from B3LYP to CAM-B3LYP reflects the known tendency of B3LYP to overdelocalise charge-transfer states, artificially lowering the excitation energy and inflating the hyperpolarizability [8]. For design purposes, B3LYP remains useful for ranking candidates within a homologous series, but absolute predictions should rely on CAM-B3LYP or other range-separated functionals [9]. The strong inverse correlation between HOMO-LUMO gap and β_0 ($R^2 = 0.91$) provides a practical screening tool: researchers can compute the gap—a much cheaper calculation than a full hyperpolarizability evaluation—and use it as a first-pass filter for promising NLO candidates [12, 7]. Among the eight chromophores, Push-Pull-1 (dimethylamino donor, dicyanovinyl acceptor) and D- π -A-2 (diphenylamino donor, nitro acceptor) emerge as the top two candidates for experimental synthesis and SHG characterisation. Their β_0 values exceed those of known commercial NLO dyes such as Disperse Red 1 by factors of 4–6 [4, 10].

Limitations

Three limitations should be noted. First, all calculations were performed in the gas phase; solvent effects can alter β by 20–50% depending on solvent polarity and specific interactions [7]. Second, vibrational contributions to β were not computed; these can add 10–30% to the electronic value for flexible molecules [9]. Third, crystal-packing effects, which determine the bulk NLO response from molecular β , are beyond the scope of single-molecule DFT calculations. Future work should incorporate a polarisable continuum model and vibrational frequency analysis to address the first two limitations.

Conclusion

DFT and TD-DFT calculations on eight organic chromophores confirm that the first hyperpolarizability is governed primarily by the HOMO→LUMO charge-transfer excitation and scales inversely with the HOMO-LUMO gap. Push-Pull-1, with a dimethylamino/dicyanovinyl substitution pattern, yielded the largest β_0 (53.4×10^{-30} esu at CAM-B3LYP), roughly 13 times that of the stilbene reference. CAM-B3LYP is recommended over B3LYP for absolute β predictions owing to its more balanced treatment of charge-transfer states, though B3LYP preserves relative rankings effectively. The strong gap- β correlation ($R^2 = 0.91$) offers a computationally inexpensive screening criterion for large virtual libraries. Future work should incorporate solvent effects via a polarisable continuum

model and compute vibrational hyperpolarizabilities to provide a more complete comparison with experimental EFISH or hyper-Rayleigh scattering data.

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