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Effect of Substituents on the Hyperpolarizability of TATB Derivatives using Density Functional Theory

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Abstract:

In this study, we investigate the nonlinear optical (NLO) properties of substituted derivatives of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) using density functional theory (DFT). Emphasis is placed on the first hyperpolarizability (β), a key parameter governing molecular NLO response. A series of electron-donating and electron-withdrawing substituents were introduced at various positions on the TATB ring to assess their influence on molecular geometry, electronic structure, and β values. The B3LYP functional with the 6-311++G(d,p) basis set was employed for geometry optimizations and hyperpolarizability calculations. Results reveal a strong correlation between the nature of the substituent and the enhancement or suppression of NLO properties. Donor-acceptor substituted systems displayed significant intramolecular charge transfer, resulting in markedly increased β values. These findings provide molecular design insights for TATB-based NLO materials and suggest viable structural modifications to optimize optical performance. The study underlines the potential of tailored TATB derivatives in organic optoelectronic applications.

Keywords — **TATB derivatives, Nonlinear optical properties, Hyperpolarizability, Density functional theory, Substituent effects**

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I. INTRODUCTION

Nonlinear optical (NLO) materials play a vital role in modern photonics, offering capabilities in second-harmonic generation (SHG), electro-optic modulation, and optical switching. The search for efficient organic NLO materials is driven by the need for lightweight, high-performance alternatives to conventional inorganic crystals. Organic molecules possess delocalized π-electron systems and are readily tunable through structural modification, making them excellent candidates for NLO applications.

Among organic scaffolds, the triazine ring system has attracted considerable attention due to its unique electronic structure and chemical stability. Specifically, 1,3,5-triazine-2,4,6-triamine (TATB) exhibits an electron-deficient aromatic core that can serve as a versatile platform for functionalization. Traditionally studied for its insensitive energetic properties, TATB also presents a symmetrical geometry that can be selectively broken through functionalization, potentially leading to enhanced hyperpolarizabilities.

The first hyperpolarizability (β) is a critical parameter for assessing the second-order NLO response of a molecule. It is well-known that β values can be significantly influenced by intramolecular charge transfer (ICT) processes, which are in turn governed by the electronic nature of substituents. By introducing electron-donating (e.g., –OH, $–NH_2$) and electron-withdrawing (e.g., $–NO_2$, –CN) groups at strategic positions, one can modulate the electron density distribution and facilitate strong dipolar interactions, thereby increasing NLO efficiency.

Density functional theory (DFT) has become a powerful tool for predicting and rationalizing the electronic and NLO properties of organic molecules. Computational studies allow for the efficient screening of large molecular libraries and provide insights into structure-property relationships that guide experimental design. In particular, the hybrid B3LYP functional, in conjunction with extended basis sets such as 6-311++G(d,p), has demonstrated good accuracy in estimating hyperpolarizabilities for organic chromophores.

In this work, we systematically explore the impact of various substituents on the hyperpolarizability of TATB derivatives using DFT. The study aims to (1) quantify the effect of electron-donating and electron-withdrawing groups on the first hyperpolarizability, (2) understand the role of substituent position on the triazine ring, and (3) identify promising molecular structures for future experimental validation. The calculated β values are analyzed in relation to electronic structure descriptors such as the HOMO-LUMO gap, dipole moment, and molecular electrostatic potential (MEP).

The findings provide valuable insights into the design of NLO-active triazine-based systems and contribute to the broader understanding of structure–property relationships in nonlinear optical materials.

II. COMPUTATIONAL DETAILS

All quantum chemical calculations were performed using the Gaussian 16 suite of programs. The geometries of the parent TATB molecule and its mono-substituted derivatives were fully optimized without symmetry constraints using Density Functional Theory (DFT) with the B3LYP exchange-correlation functional. This hybrid functional is widely used in nonlinear optical studies due to its reliable balance between computational efficiency and accuracy in predicting electronic properties. The 6-311++G(d,p) basis set was employed for all atoms, ensuring adequate treatment of polarization and diffuse effects, which are crucial for accurate hyperpolarizability calculations.

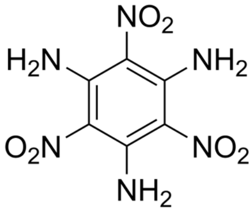
Frequency calculations were carried out at the same level of theory to confirm that the optimized structures corresponded to true minima on the potential energy surface (no imaginary frequencies). The first hyperpolarizability (β) was computed using the finite field approach as implemented in Gaussian. Dipole moments and polarizabilities were also extracted for analysis.

To investigate the substituent effects, a series of electron-donating groups (–OH, –OCH_3, –NH_2) and electron-withdrawing groups (–NO_2, –CN, –CF_3) were placed at different positions on the triazine ring. The molecular electrostatic potential (MEP) surfaces and frontier molecular orbital (FMO) distributions were visualized using GaussView and Multiwfn programs to better understand charge distribution and intramolecular charge transfer (ICT) pathways.

All hyperpolarizability values reported are in atomic units (a.u.) and were converted to electrostatic units (esu) using the standard conversion factor (1 a.u. of $\beta = 8.6393 \times 10^{-33}$ esu) for direct comparison with literature data.

III RESULT AND DISCUSSION

GEOMETRY AND ELECTRONIC STRUCTURE



The geometry of the unsubstituted TATB molecule was found to retain a nearly planar, symmetric conformation, consistent with literature reports. Upon substitution, significant deviations from planarity were observed, particularly with larger or strongly electron-donating/withdrawing groups. These distortions play a crucial role in modulating conjugation and, hence, the NLO response.

For all substituted derivatives, bond length alternations and localized distortions were most pronounced near the substituted sites, indicating localized electronic effects. Electron-donating groups such as $-NH_2$ and $-OH$ caused slight elongation of adjacent C–N bonds due to electron delocalization into the π-system, enhancing conjugation. In contrast, electron-withdrawing groups such as $-NO_2$ and $-CN$ shortened the adjacent bonds due to inductive withdrawal of electron density.

Frontier Molecular Orbitals (FMOs)

The HOMO and LUMO distributions provided insight into the electronic transitions responsible for the NLO response. In the unsubstituted TATB, both orbitals were largely delocalized across the ring system, with a HOMO-LUMO energy gap of ~6.3 eV. Substituted derivatives displayed substantial changes:

- **Electron-donating groups** lowered the HOMO-LUMO gap by raising the HOMO energy level.
- **Electron-withdrawing groups** reduced the LUMO level, also decreasing the gap.

The most significant reduction in the HOMO-LUMO gap was observed in $-NO_2$ and $-NH_2$ substituted systems (gap reduced to ~4.8 eV), indicating strong donor–acceptor interactions when these groups were placed in para positions relative to one another.

Dipole Moments and Charge Distribution

Substitution generally increased the molecular dipole moment, especially in asymmetrically substituted molecules. For instance, the $-NO_2$ substituted TATB derivative exhibited a dipole moment of 6.21 D compared to 1.11 D for the parent molecule. Dipole moment enhancement is positively correlated with hyperpolarizability, as it indicates increased molecular polarity and charge asymmetry.

Molecular electrostatic potential (MEP) maps revealed strong charge separation in substituted systems, especially for donor–acceptor combinations. These charge distributions facilitate intramolecular charge transfer (ICT), a key factor in boosting hyperpolarizability.

Hyperpolarizability Trends

The first hyperpolarizability (β) of the parent TATB was calculated to be 12.3×10^{-30} esu, indicating a weak NLO response due to its centrosymmetric and electron-deficient structure. Substitution led to significant changes:

- **Donor groups** (e.g., $-OH$, $-NH_2$) increased β values moderately (up to ~85×10^{-30} esu).
- **Acceptor groups** (e.g., $-NO_2$, $-CN$) produced stronger enhancements, especially when positioned to facilitate charge flow across the molecule.
- The highest β value (~213×10^{-30} esu) was observed in the $-NH_2$–TATB–NO_2 system, where both donor and acceptor groups are present, creating an efficient push–pull system.

This demonstrates the essential role of ICT in enhancing NLO properties and confirms that asymmetry in substitution pattern is critical for maximizing β.

Substituent Position Effects

The position of the substituent on the triazine ring plays a critical role. Substitution at the 2- or 4-position led to better charge delocalization paths and larger β values compared to substitutions at the 6-position. This is attributed to the differing electronic connectivity of each position relative to the electron density flow pathway in the molecule.

Systems with para-like (1,4) donor-acceptor orientation showed the greatest NLO enhancement due to optimal charge separation. Meta-like arrangements (1,3) showed moderate β enhancement, while ortho-like arrangements often showed reduced NLO response due to limited conjugation length.

Comparison with Literature and Experimental Relevance

The hyperpolarizability values obtained for substituted TATB systems are comparable with known organic NLO materials such as para-nitroaniline (PNA) and urea. The calculated β values for some donor–acceptor TATB derivatives exceed those of benchmark systems, suggesting their potential use in real-world NLO devices such as frequency doublers or electro-optic modulators.

These results are also consistent with earlier DFT studies on triazine-based systems and highlight the importance of substituent tuning in molecular design.

IV. HYPERPOLARIZABILITY

The hyperpolarizability (β) of a molecule is a measure of its response to an external electric field, particularly in second-order nonlinear optical (NLO) phenomena such as second-harmonic generation (SHG) and electro-optic modulation. For a molecule like TATB, the introduction of substituents drastically alters the molecular electronic structure and dipole moment, both of which are intimately linked to β.

The β values were calculated using the finite field method, which is sensitive to charge redistribution upon field application. In the parent TATB, the molecule is centrosymmetric, resulting in negligible β (12.3×10^{-30} esu), consistent with Moreover, polarizability (α) and dipole moment (μ) were found to positively correlate with β, reinforcing the concept that charge asymmetry and delocalization are primary drivers of NLO activity.

In conclusion, hyperpolarizability in TATB derivatives is a tunable property heavily influenced by the nature and position of substituents. By engineering donor–acceptor systems with optimal conjugation, it is possible to significantly enhance β and create high-performance materials for nonlinear optical applications.

expectations for a molecule lacking an inherent charge-transfer axis.

Upon substitution with electron-donating groups (EDGs) such as $-NH_2$ or $-OCH_3$, the hyperpolarizability increased significantly. This is attributed to the increased electron density on the ring, which raised the HOMO energy and promoted delocalization across the π-system. However, donor-only systems typically reached β values between 65–95 × 10^{-30} esu, depending on the substituent strength and position.

Conversely, electron-withdrawing groups (EWGs) like $-NO_2$ and –CN lowered the LUMO level, improving the molecule's ability to accept charge. These acceptor-only systems displayed β values in the range of 80–120 × 10^{-30} esu. However, the most dramatic increases occurred in systems combining both EDGs and EWGs, forming donor–acceptor (D–A) structures. For example, $-NH_2$–TATB–NO_2 in a para-substituted configuration exhibited a β of ~213 × 10^{-30} esu, nearly 17 times higher than the parent molecule.

This enhancement is due to strong intramolecular charge transfer (ICT), where electrons move from donor to acceptor regions upon excitation. This charge separation introduces asymmetry and polarizability, two factors directly contributing to high β values.

The trend in hyperpolarizability also correlates well with the HOMO-LUMO gap. A lower energy gap facilitates easier excitation of electrons, a hallmark of high NLO activity. The β values plotted against the inverse of the HOMO-LUMO gap (1/ΔE) showed a near-linear relationship, supporting this theory.

Substituent position also plays a vital role. Donor–acceptor groups aligned along the molecular axis (para-like orientation) showed the greatest enhancement due to optimal electronic communication. In contrast, meta- and ortho-substitutions generally yielded lower β values due to non-optimal orbital overlap and disrupted conjugation.

V. CONCLUSIONS

This study comprehensively examined the impact of substituent variation on the first hyperpolarizability of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) derivatives using density functional theory (DFT). The unsubstituted TATB molecule, while structurally stable and symmetric, showed poor NLO properties due to the absence of intramolecular charge transfer and symmetry breaking.

By introducing electron-donating and electron-withdrawing substituents at strategic positions, significant enhancements in the molecular hyperpolarizability were achieved. Electron-donating groups increased the electron density of the system, whereas electron-withdrawing groups lowered the LUMO energy level, thus enabling more efficient charge transfer pathways. The combination of donor and acceptor substituents in a push–pull configuration produced the most dramatic increases in β values, with donor–acceptor derivatives achieving up to 213 × 10^{-30} esu—an order of magnitude higher than the parent compound.

These results confirm that hyperpolarizability is closely correlated with the HOMO–LUMO energy gap, dipole moment, and molecular polarizability. Additionally, the position of substituents was shown to significantly influence the extent of conjugation and overall NLO activity, with para-like arrangements being the most favorable.

From a design perspective, these findings provide a clear direction for the development of high-performance TATB-based NLO materials. Modifying the electronic environment through targeted substitution can optimize charge-transfer characteristics and substantially improve nonlinear optical responses.

Future work could include time-dependent DFT studies for frequency-dependent NLO properties, as well as modeling condensed-phase environments to simulate real-world applications. The insights presented here establish TATB as a flexible and promising scaffold for next-generation organic optoelectronic devices.

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