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Investigation of Second-Order Nonlinear Optical Properties of Push-Pull Chromophores on a Salicylate Scaffold

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ABSTRACT

The development of photonic devices relies significantly on the creation of organic materials showing substantial second-order nonlinear optical (NLO) responses. This work investigates the salicylate scaffold, supported by an intramolecular hydrogen bond, as a highly promising yet underutilized platform for the design of high-performance chromophores. Six derivatives (AZ1–AZ6) were theoretically modeled by DFT to assess geometry, frontier molecular orbitals, dipole moments, and static first hyperpolarizability (β_tot). The results show that there is a discernible structure–property relationship: the nitro-substituted derivative (AZ3) had the strongest intramolecular charge transfer (ICT) with the largest β_tot, outperforming the standard para-nitroaniline. These results identify the salicylate framework as a promising blueprint for the design of next-generation NLO materials.

Keywords: Nonlinear Optics, Salicylate Scaffold, Push-Pull Chromophores, Hyperpolarizability, Density Functional Theory.

Introduction

Nonlinear optics (NLO) permits sophisticated photonic functionality including frequency conversion, electro-optic modulation, and high-resolution microscopy. In contrast to linear optical effects, NLO arises when the polarization response of the material is a function of light intensity, which gives rise to phenomena such as second-harmonic generation (SHG) and the Pockels effect [1–3]. Organic molecules are now viable NLO contenders as a result of their ultrafast response rates, large optical coefficients, and synthetically tunable properties relative to inorganic crystals [4–6].

One of the most commonly used design strategies is the push-pull (Donor-π-Acceptor, D-π-A) architecture in which big donor and acceptor groups are bridged together by a conjugated π-bridge that forms intramolecular charge transfer (ICT) necessary for large β values [7,8]. Although structures like azobenzene and stilbene have been thoroughly investigated, the salicylate platform is still underutilized. Its intramolecular hydrogen bond imposes planarity to maximize π-overlap and facilitate

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efficient ICT [9–11].

This research hopes to create structure–property relationships in salicylate-based push-pull systems. Six derivatives were designed with DFT using functional groups that had different electronic effects and were analyzed systematically for their nonlinear optical properties.

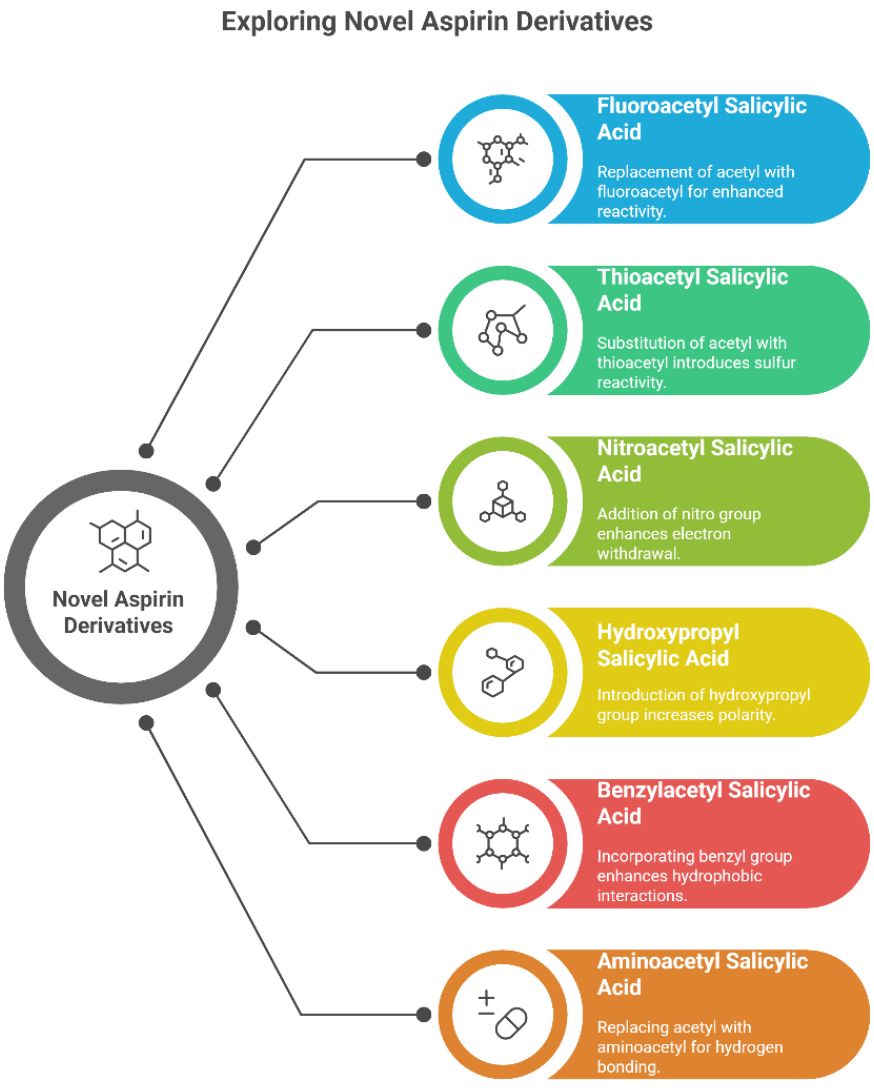


Figure 1: Schematic computer graphics of Salicylic Acid (Aspirin) Derivatives

Materials and Methods

All the calculations were carried out with Gaussian 16 applying the CAM-B3LYP functional and the 6-311+G(d,p) basis set, which were selected due to their validity in charge-transfer systems [12,13]. Geometries of molecules were optimized, and vibrational frequency analyses ensured minima. HOMO-LUMO energies, dipole moments, and β_tot were calculated with the Finite Field method [14].

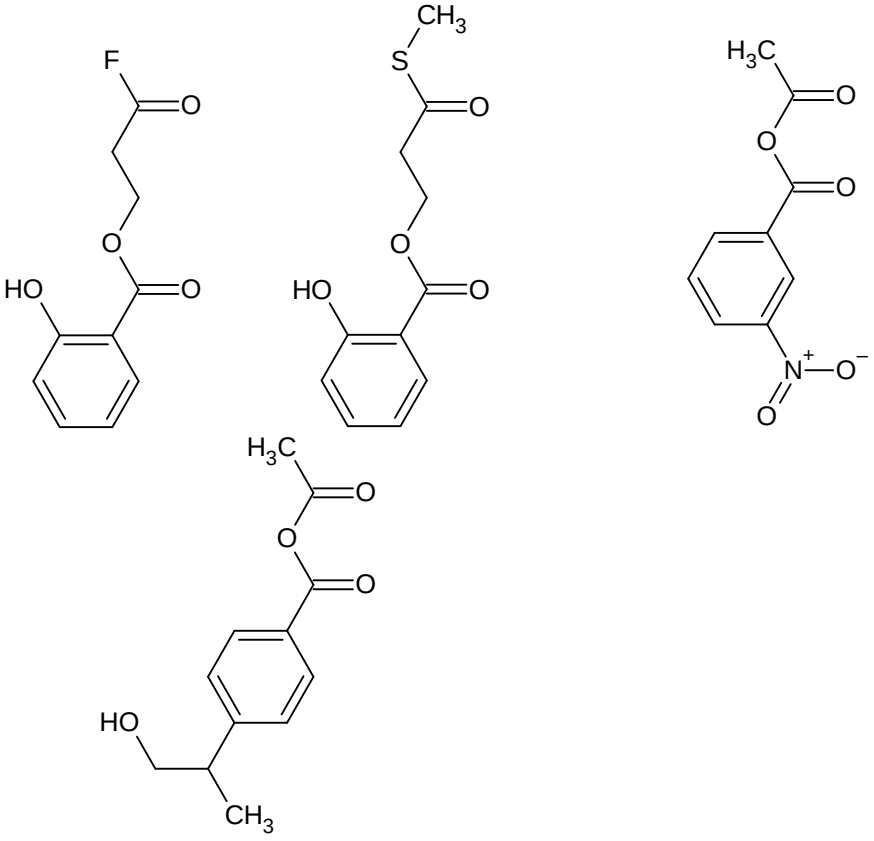
The six derivatives (AZ1–AZ6) were designed based on salicylate scaffolds with

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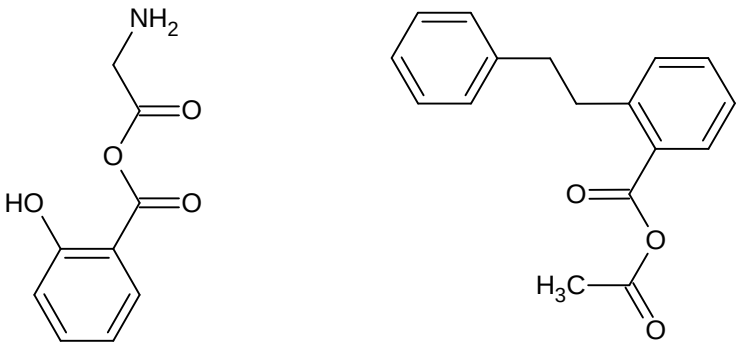
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substituents of customized design. Their rationale for design is provided in Table 1.



AZ1 AZ2 AZ3

AZ4



AZ5 AZ6

Figure 2 Designed Salicylate Derivatives (AZ1-AZ6)

Table 1 Designed salicylate derivatives (AZ1–AZ6)

Code	Chemical Name	Modification	Rationale
AZ1	Fluoroacetyl Salicylate	$–COCH_2F$	Strong inductive electron withdrawal
AZ2	Thioacetyl Salicylate	$–CSCH_3$	Polarizable sulfur atom
AZ3	Nitroacetyl Salicylate	$–NO_2$	Strong resonance

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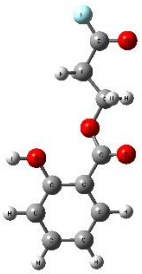
electron withdrawal

AZ4	Hydroxypropyl Salicylate	$–CH_2CH(OH)CH_3$	Polarity and steric bulk
AZ5	Aminoacetyl Salicylate	$–COCH_2NH_2$	Secondary donor group
AZ6	Benzylacetyl Salicylate	$–CH_2C_6H_5$	Bulky π-rich substituent

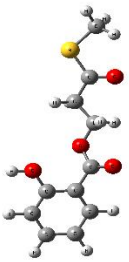
Results and Discussion

Structural Properties

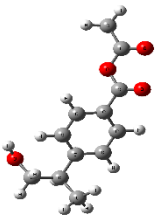
Geometry optimization ensured that the salicylate framework imposes planarity through intramolecular hydrogen bonding. Table 2 describes selected geometric parameters, and it is evident that all derivatives have near-planar conformations.



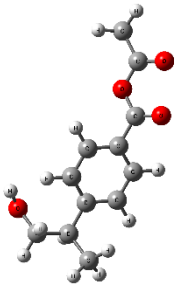
AZ1



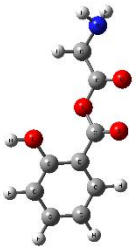
AZ2



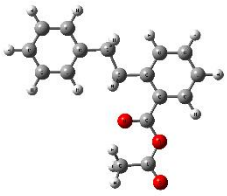
AZ3



AZ4



AZ5



AZ6

Figure3. Optimized geometrical structures of Salicylate Derivatives

Table 2. Key geometric parameters of optimized structures

Molecule	IHB Length (Å)	Planarity (°)
AZ1	1.64	179.8
AZ2	1.64	179.7
AZ3	1.63	-179.9
AZ4	1.65	-179.6
AZ5	1.64	179.5
AZ6	1.65	178.9

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The nitro-substituted AZ3 displayed the strongest resonance-assisted hydrogen bond, suggesting enhanced ICT stability.

Electronic Properties

Frontier Molecular Orbital (FMO) analysis showed donor-localized HOMOs and acceptor-localized LUMOs, in line with push-pull behavior. AZ3 had the narrowest HOMO-LUMO gap (4.74 eV), followed by AZ1 (5.43 eV), whereas AZ4 and AZ6 had the widest gaps (>5.7 eV).

Table 3. Calculated HOMO-LUMO energy gaps and dipole moments

Molecule	ΔE_H-L (eV)	Dipole Moment (Debye)
AZ1	5.43	5.88
AZ2	5.33	4.95
AZ3	4.74	7.91
AZ4	5.74	4.31
AZ5	5.65	4.65
AZ6	5.73	4.28

The very high dipole moment of AZ3 supports its better push-pull nature.

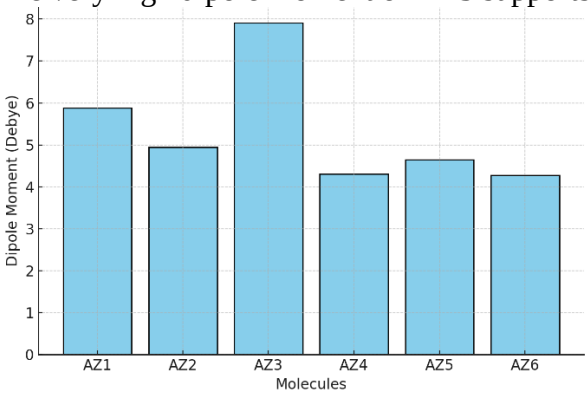


Figure4.Ground state Dipole Moments of AZ1-Az6

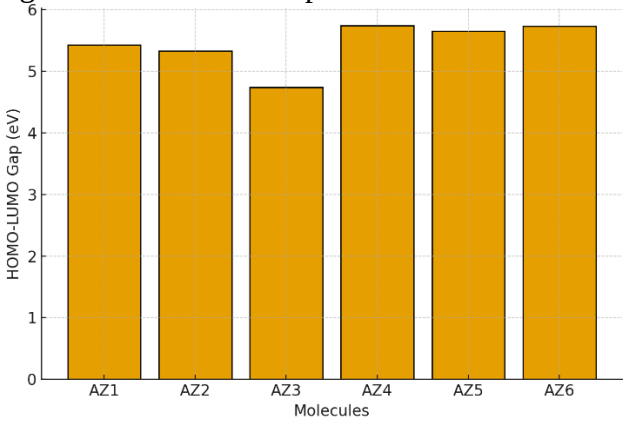


Figure 4. HOMO-LUMO Energy Gaps of AZ1-AZ6

The diagram shows that AZ3 possesses the largest dipole moment at 7.91 Debye, followed by AZ1 at 5.88 Debye. This corroborates the premise that AZ3 has the

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strongest push-pull character, as increased dipole moments are generally correlated with increased donor-acceptor character, as predicted by the Frontier Molecular Orbital (FMO) analysis.AZ4, AZ5, and AZ6 demonstrate lower dipole moments of between 4.28 and 4.65 Debye, implying weaker push-pull character than AZ1 and AZ3.AZ2 demonstrates a moderate dipole moment of 4.95 Debye, comparable to AZ4 and AZ6, meaning it may not display such strong donor-acceptor interaction as AZ1 or AZ3

AZ3, with the smallest HOMO-LUMO energy gap of 4.74 eV, also possesses the largest dipole moment (7.91 Debye). This is indicative of significant donor-acceptor interaction, which helps to enhance its push-pull character.AZ1 continues with the comparatively large HOMO-LUMO gap (5.43 eV) but possesses a comparatively high dipole moment (5.88 Debye), suggesting moderate push-pull character.AZ4 and AZ6, which have the largest HOMO-LUMO gaps (>5.7 eV), possess the lowest dipole moments, which suggests weaker push-pull characteristics and less efficient donor-acceptor interactions.

The results indicate that AZ3 shows the strongest push-pull character, both in terms of its small HOMO-LUMO gap and large dipole moment. At the other end, AZ4, AZ5, and AZ6 have weaker push-pull forces, as also seen from their larger HOMO-LUMO gaps and smaller dipole moments.

Nonlinear Optical Properties

Calculated values of β_tot showed a definite trend depending on the substituent (Table 4).

Table 4. Static first hyperpolarizability (β_tot) of AZ1–AZ6

Molecule	β_tot (a.u.)	β_tot (10^{-30} esu)
AZ1	1855	16.0
AZ2	1130	9.8
AZ3	7460	64.4
AZ4	590	5.1
AZ5	875	7.6
AZ6	582	5.0

The nitroacetyl derivative (AZ3) surpassed the standard para-nitroaniline (β_tot = 2150 a.u.) [15], establishing it as the best candidate for experimental development.

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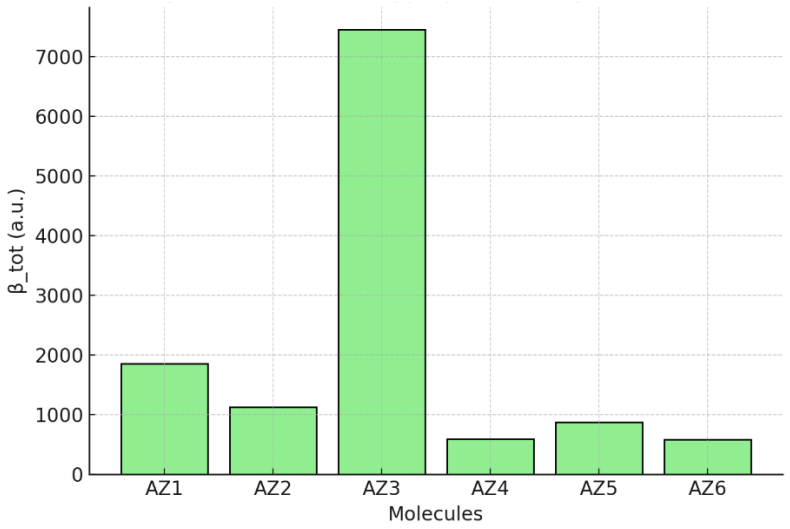


Figure 5. Static First Hyperpolarizability of AZ1-AZ6

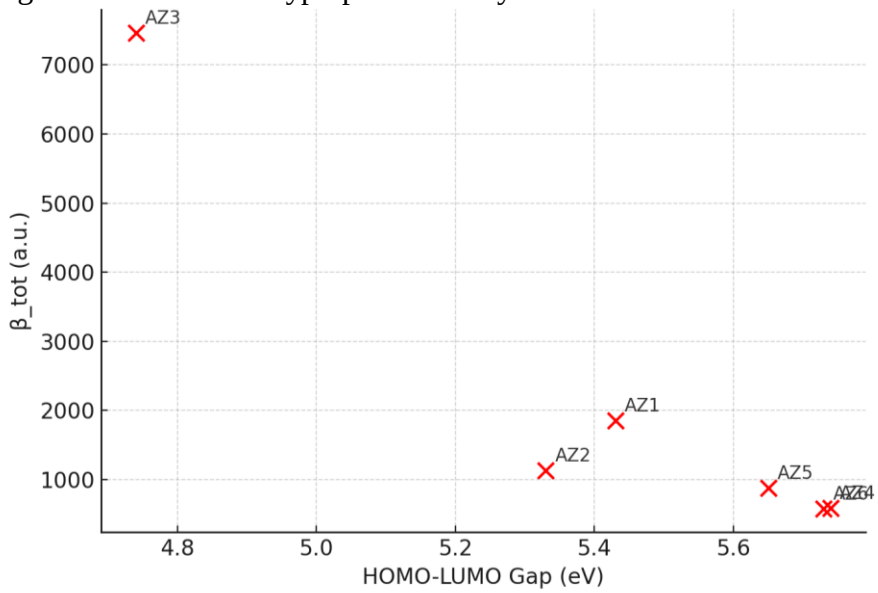


Figure 6. Correlation between the Hyperpolarizability of AZ1-AZ6

The plot in Figure 3 illustrates that AZ3 has by far the highest static first hyperpolarizability (β_tot) at 7460 a.u., higher than that of all other molecules. This is well over four times higher than the second highest, AZ1 (1855 a.u.).AZ2, AZ4, AZ5, and AZ6 contain significantly lower β_tot values, all less than 1000 a.u., corresponding to much reduced non-linear optical response in comparison with AZ3 and AZ1.

Correlation between Energy Gap and Hyperpolarizability:Figure 4 presents an evident trend with a smaller HOMO-LUMO gap corresponding to higher hyperpolarizability. AZ3, with the lowest HOMO-LUMO gap (4.74 eV), is distinguished by the highest β_tot, supporting the link between smaller energy gaps and higher non-linear optical characteristics.As the HOMO-LUMO gap gets larger, β_tot becomes smaller, particularly in the case of AZ4, AZ5, and AZ6 with the highest energy gaps and lowest hyperpolarizabilities.AZ3, which has high β_tot (7460 a.u.) and a small

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HOMO-LUMO gap, is the top contender for experimental realization, even over the reference para-nitroaniline (β_tot = 2150 a.u.).
The results indicate that lower energy gaps improve the molecule's non-linear optical abilities, suggesting that AZ3 is an optimistic material for continued exploration in optoelectronic devices or non-linear optics.

Conclusion

This work illustrates that salicylate scaffolds, stabilized by intramolecular hydrogen bonds, offer a stable platform for the engineering of high-performance push-pull chromophores. Computational data predict that substituent selection has a significant impact on NLO performance, and nitro-functionalization (AZ3) produces β_tot values almost four times higher than common benchmarks. This breakthrough opens up a predictive strategy for the design of next-generation electro-optic materials, with AZ3 being a standout candidate for synthesis and device implementation.

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