Investigation of The Relationship Between The Substituent and Nonlinear Optical Properties in 2- (Phenyl ((4-Vinylphenyl)Amino) Methyl)Phenol Derivative Compounds by DFT Method

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Summary: In this study, NLO properties and substituent relationship of the recently synthesized three alkylaminophenol compounds, which have electron-donating and electron-withdrawing groups were investigated. The polarizability (<α>), the anisotropy of the polarizability (<Δα>), groundstate dipole moment (μ) and the first-order hyperpolarizability (β) were studied. HF method and DFT/B3LYP, WB97XD methods with 6-311++ G(d,p) set were used for calculations. p-Nitroaniline was selected as a reference compound. Also, E_{HOMO} (the highest occupied molecular orbital energy), E_{LUMO}(the lowest unoccupied molecular orbital energy), HOMO-LUMO energy gap (ΔE), molecular surface and FMOs analysis were studied.

Keywords: NLO, DFT, Alkylaminophenol.

Introduction

2- (phenyl ((4-vinylphenyl) amino) methyl) phenol compound is one of the alkylaminophenol derivative compounds[1-4].Generally, Alkylaminophenol compoundsare used medical field[5-6]. An aromatic ring and OH group are included in their structure. The presence of the OH group causes these compounds to have antioxidant properties[. In addition, the presence of groups attached to the aromatic ring plays an important role in their chemical activity.These compounds were synthesis very high yields without catalysis with petasis reaction. Although there are many publications about synthesis, structural and electronic properties on alkylaminophenols in the literatüre[7-14], there are no studies on its optical properties.

The nonlinear optical (NLO) properties of the moleculesplay an important role in signal processing in communication technology, in the field of optoelectronics and photonics technologies, laser technology, optical memory design[15-19].Despite the need for materials with these properties, it is difficult to define a new NLO material class.The NLO properties of molecules emerge from delocalized π-electrons that move throughout the molecule. Increased conjugation and incorporation of the donör and acceptor groups in the molecule causes its NLO property to change. Quantum chemical calculations are used to describe the relationship between NLO properties and electronic structure[20-25]. In this study; NLO analysis, thermochemical and electronic properties for alkylaminophenol compounds were investigated.

Since there is no standard compound in the literature where NLO properties of alkylaminophenols can be compared, the data obtained are compared with p-Nitroaniline (pNA). pNA is one of the simplest molecules with an electron donor and acceptor system. Numerous studies have provided information on the photochemical properties of p-nitroaniline[26-28]. This is the reason why it is preferred in this study.

In this study; Gaussian 09W program, which is a very comprehensive program including molecular mechanics, semi-experimental and ab initio methods, was used. Quantum mechanical calculations; It was carried out by the HF and DFT methods. For the first time in the literature, NLO properties and thermodynamic stability of three alkylaminophenol monomers with electron acceptor and donor groups were investigated by the HF and DFT/ B3LYP and WB97XD methodswith 6-311 ++ G (d, p) set.

Experimental

Synthesis

Compounds were synthesized in the previous study[29].

Computational Method

Gaussian 09 software package[30] was used for HF and DFT calculations. Gauss-View 5.0 program[31] was used for molecular modelling.

Results and Discussion

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Optimization structure and MEP

The compounds (2-((4-methoxyphenyl)((4-vinylphenyl)amino)methyl)phenol (**4a**), 2-(phenyl((4-vinylphenyl)amino)methyl)phenol (**4b**) and (2-((4-chlorophenyl)((4-vinylphenyl)amino)methyl)phenol (**4c**) contained in the study were synthesized in the previous study. The geometrical optimization of these three monomers were done by HF,DFT / B3LYPand DFT/ WB97XD methodsusing6-311 ++ G (d, p) set.

Determination of MEP surfaces; It is important in terms of providing information about interactions and chemical behaviours within the molecule.

When looked at Total Energy ranges, ıt was seen 4a compound have a high value, especially at B3LYP calculation. ıt can be said 4a compound containing an electron-donating group is prone to chemical reactions.

Table-1: Calculated Total Energy ranges for Alkylaminophenol compounds.

Compounds	HF	B3LYP	WB97XD
4a	-7.223 e-2 and 7.223 e-2	-6.511 e-2 and 6.511 e-2	-6.942 e-2 and 6.942 e-2
4b	-7.311 e-2 and 7.311 e-2	-6.668 e^{-2} and 6.668 e^{-2}	-7.041 e-2 and 7.041 e-2
4c	-7.539 e-2 and 7.539 e-2	-6.916 e^{-2} and 6.916 e^{-2}	-7.308 e^{-2} and 7.308 e^{-2}

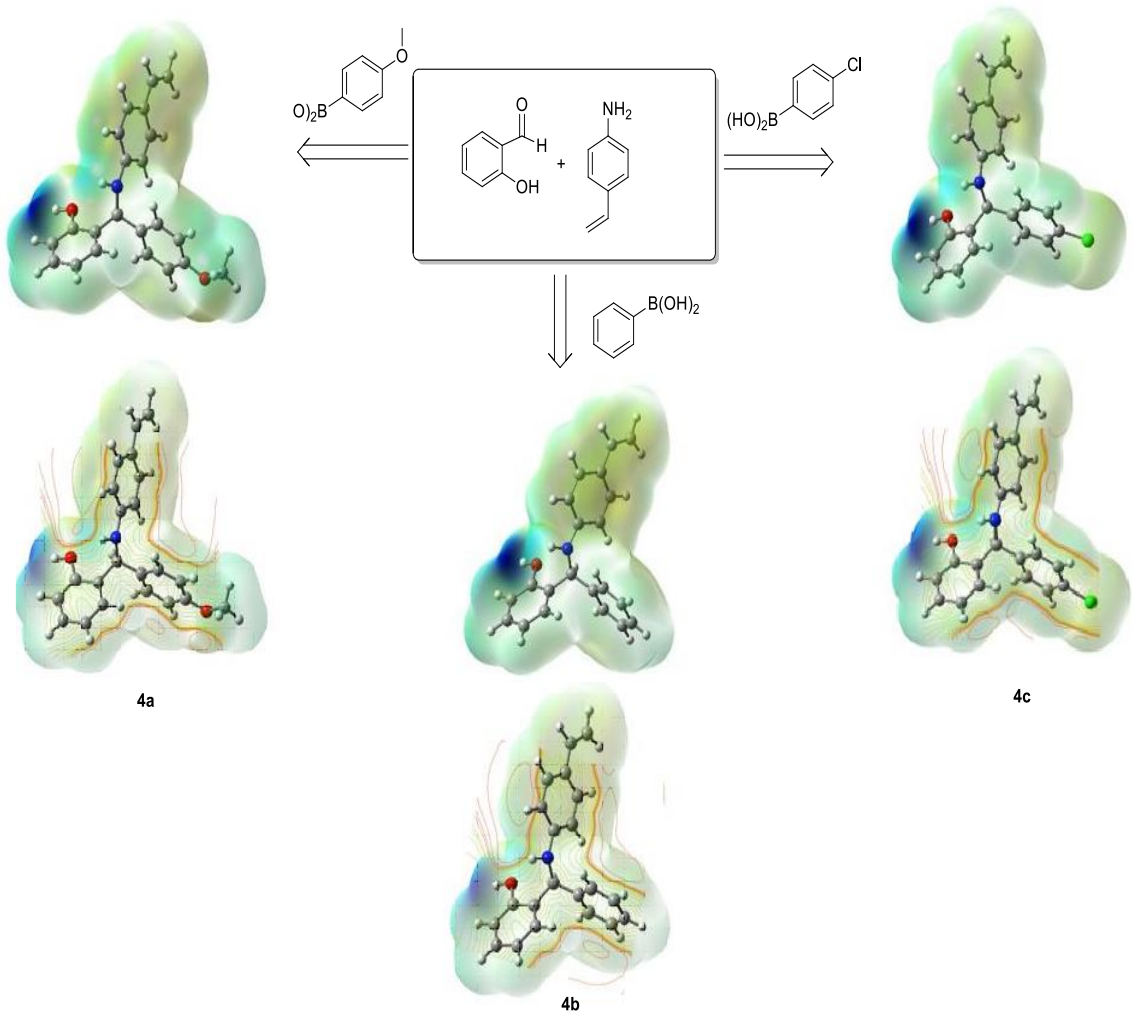


Fig. 1: Synthesis, optimization(DFT/B3LYP/6-31++G(d,p)), molecular elektrostatic surfaces and contour maps of alkylaminophenol compounds.

NLO Analysis

Nonlinear optical properties of materials (NLO) plays an important role in the design of electronic structure. NLO properties of compound are originated from π electrons. Increased conjugation or inclusion of donor groups changes NLO properties. In general, quantum chemical calculations explain the relationship between the electronic structure and NLO properties.One of the compounds used for investigation of NLO properties of molecular systems is p-nitroaniline, thus p-nitroaniline was chosen for the reference compound in this work. NLO properties of alkylaminophenol compounds have never been studied in the literature before. Isotropic linear polarizability ⟨α⟩, anisotropic linear polarizibility $\Delta\alpha$, first-order hyperpolarizability ⟨β⟩ and total dipole moment (μ) values were calculated by HF, DFT/B3LYP and DFT/WB97XD methods with 6-311++G(d,p) set.

As hyperpolarizability is difficult to measure directly, the computational calculation is an alternate choice. In the presence of an applied electric field, the energy of a system is afunction of the electric field. The first hyperpolarizability is a third ranktensor that can be described by a 3×3×3 matrix wherein the 27components of the 3D matrix can be reduced to 10 components due toKleinman symmetry [32-33]. The complete equation for calculating themagnitude of fundamental NLO parameters μ, α, Δα and β of the titlemolecule using the x, y, z components from Gaussian 09 output are asfollows.

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

where μx, μy and μz are dipole moments along x, y and z directions

$<\alpha> = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$

where μ_{xx},μ_{yy}, and $\mu_{zz}$are the diagonal components of polarizabilitytensor.

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

$<\beta> =[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2+(\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2+(\beta_{zzz} + \beta_{xxz}+ \beta_{yyz})^2]^{1/2}$

NLO data of p-NA selected as standard with alkylaminophenols containing electron acceptors, donors and neutral substituents were shown in Table 2.

Looking at the NLO data; It is seen that 4c has a higher dipole moment than 4b and 4a. However, this value is lower than the dipole moment value of p-NA selected as standard. Linear polarizability values are negative, indicating that there is a dipole in the opposite direction of the electrical field. Linear polarizability values of selected alkylaminophenols are 2.5 times of p-NA. The sequence for linear polarizability can be written as $\alpha_{Cl}>\alpha_{MeO}>\alpha_H>\alpha_{p\text{-}NA}$.In anisotropic linear polarizability, this order is $\alpha_{MeO}>\alpha_{Cl}>\alpha_H>\alpha_{p\text{-}NA}$. When the first order hyperpolarizability values are examined, it is seen that the alkylaminophenols are approximate twice the hyperpolarizability value of p-NA. Here, the order is $\beta_{Cl}>\beta_H>\beta_{MeO}>\beta_{p\text{-}NA}$.

Table-2: NLO values of alkylaminophenol compunds.

	HF				***B3LYP***				***WB97XD***			
	p-NA	***4a***	***4b***	***4c***	***p-NA***	***4a***	***4b***	***4c***	***p-NA***	***4a***	***4b***	***4c***
μ_x	**6.95**	**-1.91**	**-2.87**	**-0.92**	**-7.45**	**-2.59**	**-3.38**	**-1.55**	**7.04**	**-2.32**	**-3.23**	**-1.64**
μ_y	**0.00**	**-2.07**	**-1.95**	**-4.75**	**-0.00**	**-1.95**	**-1.84**	**-4.62**	**0.00**	**-1.88**	**-1.80**	**-4.57**
μ_z	**0.88**	**-0.83**	**0.42**	**0.47**	**0.69**	**-0.90**	**0.33**	**0.39**	**0.73**	**-0.79**	**0.36**	**0.47**
μ	**7.00**	**2.94**	**3.50**	**4.86**	**7.48**	**3.36**	**3.86**	**4.89**	**7.08**	**3.09**	**3.72**	**4.88**
α_{xx}	**-61.32**	**-152.74**	**-136.35**	**-154.37**	**-58.75**	**-155.60**	**-138.71**	**-156.33**	**-58.16**	**-151.25**	**-134.28**	**-150.50**
α_{yy}	**-52.82**	**-123.91**	**-121.69**	**-141.13**	**-53.28**	**-123.67**	**-121.96**	**-140.29**	**-52.42**	**18.07**	**-119.26**	**-137.56**
α_{zz}	**-61.00**	**-144.12**	**-132.34**	**-142.60**	**-60.62**	**-142.98**	**-131.20**	**-141.54**	**-60.32**	**-5.14**	**-131.29**	**-142.32**
$<\alpha>$	**-8.65 x10^{-24}**	**-2.08 x10^{-23}**	**-1.93 x10^{-23}**	**-2.16 x10^{-23}**	**-8.52 x10^{-24}**	**-2.08 x10^{-23}**	**-1.94 x10^{-23}**	**-2.16 x10^{-23}**	**-8.44 x10^{-24}**	**-6.83 x10^{-24}**	**-1.9 x10^{-23}**	**-2.13 x10^{-23}**
$\Delta\alpha$	**1.24 x10^{-24}**	**3.8 x10^{-24}**	**1.9 x10^{-24}**	**1.86 x10^{-24}**	**9.79 x10^{-25}**	**4.13 x10^{-24}**	**2.15 x10^{-24}**	**2.29 x10^{-24}**	**1.48 x10^{-24}**	**2.36 x10^{-23}**	**2.04 x10^{-24}**	**1.68 x10^{-24}**
β_{xxx}	**89.08**	**-22.52**	**-35.12**	**1.37**	**-99.46**	**-44.53**	**-53.34**	**-22.70**	**94.67**	**-31.22**	**-48.40**	**-19.87**
β_{xyy}	**16.16**	**-60.58**	**-46.94**	**-6.07**	**16.70**	**-63.87**	**-45.51**	**-11.43**	**16.98**	**-54.93**	**-45.06**	**-11.73**
β_{xzz}	**-13.59**	**-9.55**	**-9.59**	**-12.89**	**13.00**	**-11.51**	**-13.47**	**-15.13**	**-13.23**	**-12.37**	**-10.01**	**-13.67**
β_{yyy}	**0.00**	**-37.34**	**-32.69**	**-144.55**	**-0.00**	**-27.86**	**-28.46**	**-132.43**	**0.00**	**-24.35**	**-30.61**	**-142.62**
β_{xxy}	**-0.00**	**-7.67**	**-42.78**	**-38.60**	**-0.00**	**-9.63**	**-39.76**	**-36.70**	**0.00**	**-18.44**	**-41.11**	**-34.77**
β_{yzz}	**0.00**	**0.71**	**-5.19**	**-1.75**	**0.00**	**-3.04**	**-7.08**	**-5.19**	**-0.00**	**1.51**	**-4.238**	**2.18**
β_{zzz}	**0.73**	**12.40**	**12.03**	**12.84**	**0.50**	**11.59**	**11.10**	**11.77**	**0.56**	**10.27**	**9.88**	**9.42**
β_{xxz}	**16.38**	**-36.90**	**-6.45**	**-20.02**	**12.91**	**-34.14**	**-6.07**	**-18.42**	**13.68**	**-26.603**	**-4.96**	**-16.38**
β_{yyz}	**0.49**	**0.953**	**18.70**	**33.38**	**0.42**	**1.22**	**19.53**	**33.46**	**0.44**	**-5.29**	**16.24**	**29.30**
$<\beta>$	**8.06 x10^{-31}**	**9.1 x10^{-31}**	**1.08 x10^{-30}**	**1.62 x10^{-30}**	**8.99 x10^{-31}**	**1.09 x10^{-30}**	**1.18 x10^{-30}**	**1.58 x10^{-30}**	**8.60 x10^{-31}**	**9.42 x10^{-31}**	**1.12 x10^{-30}**	**1.58 x10^{-30}**

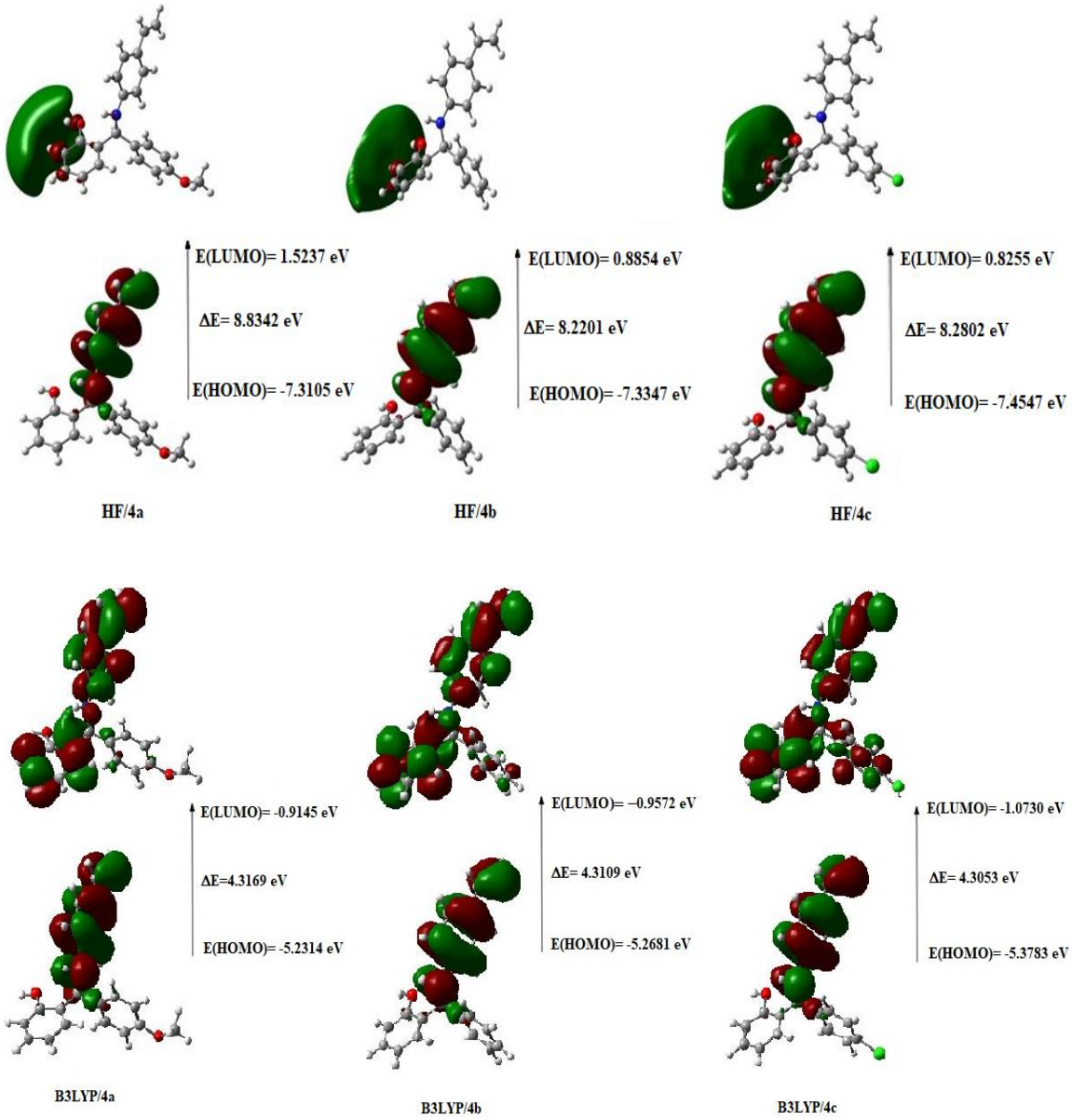
*GAUSSIAN-09W output are reported in atomic units (a.u.), the calculated values(**<α>, Δα, <β>**)havebeen converted into electrostatic units (esu) (α: 1 a.u. = 0.1482 x10-24 esu; β: 1 a.u.= 8.6393x10-33 esu)

As a result, it can be said that the NLO properties of these alkylaminophenol compounds do not have high enough values[34]. However, it can contribute to the optical field with its values that cannot be ignored.

Frontier molecular orbitals (FMOs)

The molecular reactivity (FMO) of a molecule is important in defining its optical and electrical properties, and in defining the absorption of light. According to the molecular orbital theory; all molecules have HOMO (Highest occupied molecular orbital) and LUMO (Lowest Unoccupied molecular orbital). The frontier molecular orbital (HOMO and LUMO) shapes of alkylaminophenol compounds were determined using HF and DFT/ B3LYP, WB97XD methods with 6-311++G(d,p) basis set. The HOMO and LUMO orbitals for this molecule are given in Figure 2.

Looking at Figure 2, it is seen that the alkylaminophenol containing the Meo substituent has higher energy value in all three methods. Thus, it is proved by the data that the reaction predisposition is 4a> 4b> 4c.



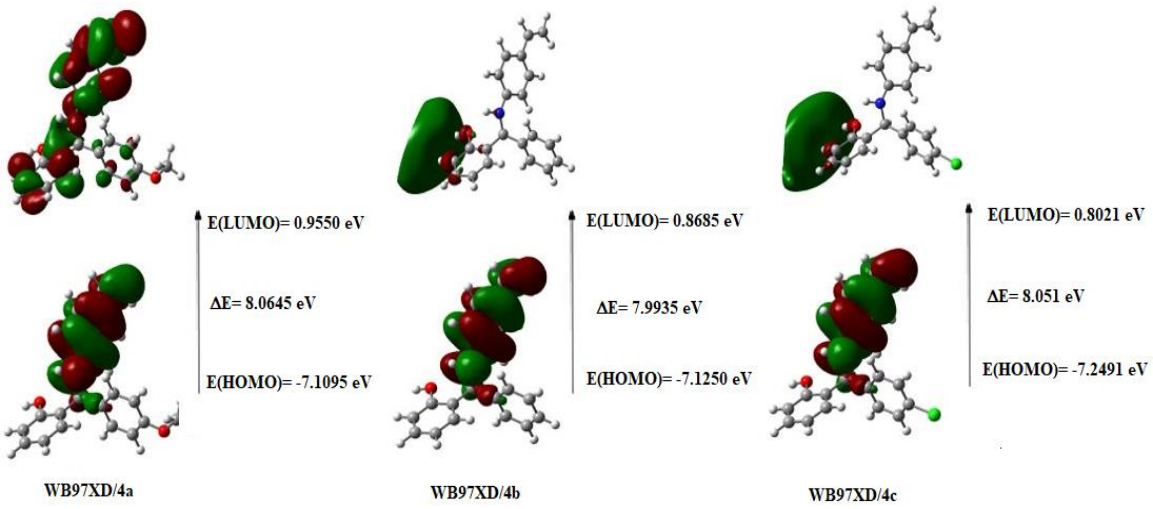


Fig. 2: HOMO and LUMO orbitals of Alkylaminophenol compunds with the energy gap (HF/B3LYP/WB97XD).

Conclusion

In this study; For the first time, non-linear optical properties of three alkylaminophenol compounds were examined depended to substituents. Compared to p-NA, it was determined that the linear polarizability value was two and a half times higher, and the hyperpolarizability values were about two times higher. It was observed that the substituents in the alkylaminophenol structure had an effect on these values. Although these values are not high enough, it suggests that NLO properties will be strengthened with different substituents. In summary, we can say that alkylaminophenol compounds have an area of use outside of medical fields.

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