



TD-DFT quantum mechanical (QM) calculations, electronic spectroscopy (ES), Bond Orbital (NBO) and nonlinear optical (NLO) properties of 4-(2-(4-nitrophenyl) ethylidene) amino-hippurate (NEAH) in solutions

Esam A. Gomaa¹, Shimaa Abdel Halim², Hamed M. Abu El Nader¹, Ehab Abdel Lateef¹, Ahmed Fakri¹, Shymaa E Rashed¹

¹Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt.

²Department of Chemistry Faculty of Education, Ain Shams University, Roxy 11711, Cairo, Egypt

Abstract A new Schiff base compound (4-(2-(4-nitrophenyl)ethylidene)amino-hippurate) (NEAH) was experimentally measured and theoretically quantum mechanically (QM) calculated with molecular vibration and electronic spectroscopy (ES). The (NEAH) molecule was also tested for antimicrobial activity (AB) against human pathogenic Gram-positive (GP), Gram-negative (GN) bacteria and fungi (F). Among the tested micro-organisms (MOr), pseudomonas aeruginosa (PA) was most sensitive effect. The electronic spectroscopy (ES) of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) was measured in polar (ethanol, ETOH) as well as non-polar N,N-dimethylformamide (DMF) solvents. The geometry (G) was adjusted quantum mechanically (QM) and optimized using B3LYP 6-311G (p,d) theoretical method. The most stable geometry of the studied compound is the adjusted nonlinear structure as indicated from the values of the dihedral angles (DA). The compound (NEAH) was measured spectro-photometrically (Pho) in experimental UV and visible region (VS) of spectrum in ethanol (ETOH).

Keywords DFT, electronic structure (ES), absorption spectra, bonding, nonlinear optical characteristics

Introduction

Schiff bases (SB) have a large number of uses in organic chemistry and medical application. Several complexes exhibit exceptional biological activities (BA). Additionally, new Schiff base (SB) complexes can be formed show great antibacterial activity (AA).

The NLO properties depend on the extent of the charge transfer (CT) interaction across the conjugative paths and the electron transfer (ET) of aromatic ring and on its ionization potential (IP) and electron affinity (EA) [1-2]. Polarizability ($\Delta\alpha$) and hyperpolarizability (β) are need for adjusted optimized materials for photonic systems such as electro optical modulators and all optical switches [3-4]. In this study our contribution here is to shed more light on the ground state properties of 4-(2-(4-nitrophenyl) ethylidene) amino-hippurate (NEAH) using Density Functional Theory (DFT-B3LYP) and basis set 6-311G (d,p), and nonlinear optical (NLO) analysis quantum mechanically (QM), which are performed to identify and characterize the forces that govern the adjusted structure of the title (NEAH) molecule. In addition to investigate the effect of solvent polarity (SP) on the observed spectra and



hence, predicting the stabilities, charge transfer character and assignment of the observed electronic transitions bands, delocalized and/or of charge transfer (CT) has been facilitated by Density Functional Theory (DFT) and time-dependent density functional theory (TD-DFT) calculations. The electronic structure of molecules usually shows itself in the electronic absorption (ES) and emission spectra (EmS). This spectra enables the detailed understanding of the forces that govern the electronic structure of the studied compound 4-(2-(4-nitrophenyl) ethylidene) amino-hippurate (NEAH).

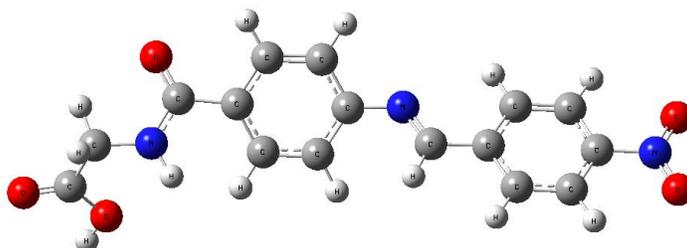


Figure 1: The optimized structure of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) at B3LYP/6/311G (p,d)

Experimental

Computational calculations have been performed by the use KhonSham's Density Functional Theory (DFT) method quantum mechanically (QM) subjected to the gradient-corrected hybrid density functional B3LYP method [5]. This function is a combination of the Becke's three parameters non-local exchange potential with the non-local correlation functional of Lee et al [6]. For each structure, the full optimization for the structure was performed using this function [6] and the 6-311G (p,d) basis set [7] as implemented by quantum mechanics (QM) Gaussian 09 package [8]. All geometries were visualized either using quantum mechanics (QM) Gaussian View 5.0.9 [9] or chemcraft 1.6 software packages. No symmetry constrains or conditions were applied during the adjusted geometry optimization. Also, the total static dipole moment (μ), and ($\Delta\alpha$), (β) values were calculated by using the following equations [10-12]: $\mu = (\mu_{2x} + \mu_{2y} + \mu_{2z}) / 2$, $(\alpha) = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$, $\Delta\alpha = ((\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2)^{1/2}$, $(\beta) = (\beta_{2x} + \beta_{2y} + \beta_{2z}) / 2$, (1) Where $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$, $\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$. (2) By using HOMO and LUMO energy values for a molecule, electronegativity, and chemical hardness can be calculated as follows: $\chi = (I + A) / 2$ (electronegativity), $\eta = (I - A) / 2$ (chemical hardness), $S = 1/2\eta$ (chemical softness) where I and A are ionization potential and electron affinity, and $I = -EHOMO$ and $A = -ELUMO$, respectively [13,14]. The conversions for α , β , γ , and HOMO and LUMO energies in atomic and cgs units: 1 atomic unit (a.u.) = 0.1482×10^{-24} electrostatic unit (esu) for polarizability; 1 a.u. = 8.6393×10^{-33} esu for first hyperpolarizability; 1 a.u. = 27.2116 eV (electron volt) for HOMO and LUMO available energies, respectively.

Solvents: Ethanol (ETOH) used was from Al-Nasr Co., 98%, and was used without further purification.

Results and Discussion

Ground state properties

The total energy (ET), energy of highest occupied molecular orbital (EHOMO), energy of lowest unoccupied molecular orbital (ELUMO), energy gap (Eg) and dipole moment (μ) for the studied compound are shown in Table (1). The adjusted optimized structure of the title molecule is obtained using the B3LYB/6311G (p,d) level, numbering system, net charge, vector of dipole moment (μ) and the charge density maps of HOMO and LUMO are presented in Fig. 2 explained (optimized geometry, numbering system, vector dipole moment (a), net charge (b) HOMO and LUMO (c) for 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) using B3LYP/6-311G (d, p)). From Table (1) and Fig. 2 one can reveal the following: The ionization energy (IE) of compound 4-(2-(4-nitrophenyl) ethylidene) amino-hippurate (NEAH) which measures the donating property, DP (oxidation power) is -



6.835 eV (c.f. Table 1). Also the electron affinity (E.A) which measures the accepting property (reducing power) is -3.179 eV. So the calculated energy gaps, (E_g), which measure the chemical activity, of compound 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) is 3.656 eV. Finally, the theoretically quantum mechanically (QM) computed dipole moment (μ), which tests the polarity or charge separation over the title molecule, is 4.4437 D.

Table 1: Total energy, energy of HOMO and LUMO, energy gap and dipole moment of 4-(2-(4-nitrophenyl)ethylidene) amino-hippurate (NEAH) (1), and the studied compound computed at the B3LYP/6-311G(p,d) level of

Compounds	theory				
	E_T (au)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	μ (Debye)
1	-1158.14	-6.835	-3.179	3.656	4.4437

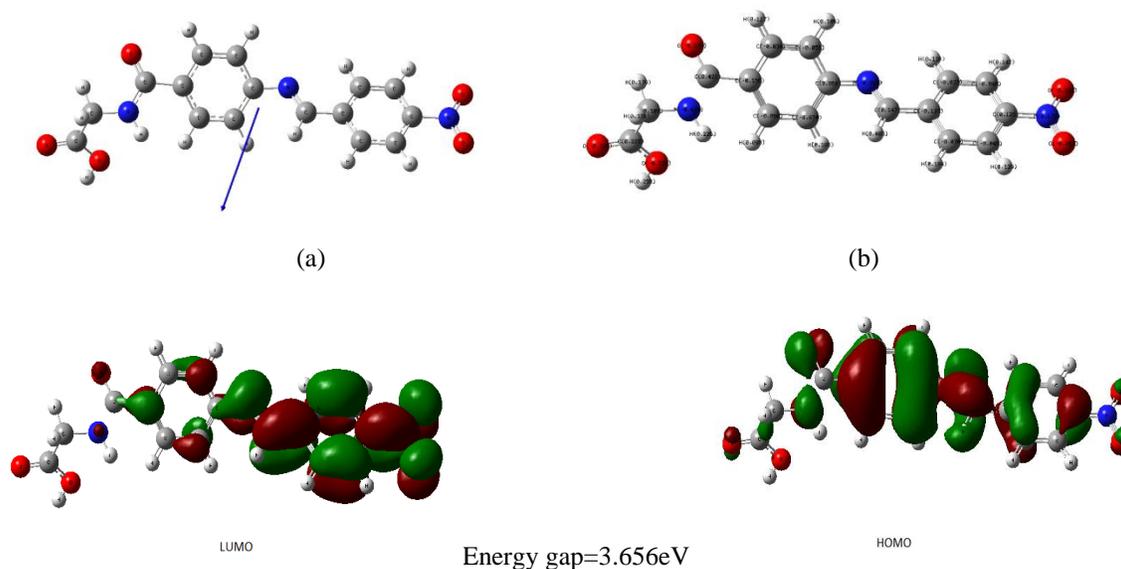


Figure 2: Optimized geometry, numbering system, vector dipole moment (a), net charge (b) HOMO and LUMO (c) for 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) using B3LYP/6-311G (d, p) by QM.

Global reactivity descriptors

The frontier molecular orbital (FMO) energies of the title molecule were calculated quantum mechanically (QM) using B3LYP/6-311G (d, p). HOMO energy characterizes electron giving ability, while LUMO energy characterizes electron withdrawing ability. The Energy gap between the available HOMO and LUMO characterizes the molecular stability and it is a critical parameter in determining molecular electrical transport properties which facilitate the electron conductivity. From Fig. 2 (Optimized geometry, numbering system, vector dipole moment (a), net charge (b) HOMO and LUMO (c) for 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) using B3LYP/6-311G (d, p), and Table (2), (The ionization potential (I / eV), electron affinity (A / eV), chemical hardness (η / eV), softness (S / eV⁻¹), chemical potential (μ) and electronegativity (χ / eV), of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) using B3LYP/6-311G (d, P)). HOMO available energy is calculated as -6.835eV and LUMO energy is calculated as -3.179 eV by using B3LYP/6-311G (d, p) level. The small energy gap between HOMO and LUMO indicated that charge transfer occurs by the title molecule and the molecule can be polarized [13,14]. By the use of HOMO and LUMO energies, ionization potential and electron affinity can be explicated as $IP \approx -EHOMO$, $EA \approx -ELUMO$. The variation of electro negativity (χ) values is supported by the electrostatic potential (EIP). For any two molecules, electron will be partially transferred from one of low χ to that of high χ (electron flow from high chemical potential to low chemical potential). The chemical hardness (η) = $(IP - EA)/2$, electro negativity (χ) = $(IP + EA)/2$, chemical potential (μ) = $-(IP + EA)/2$, and chemical softness (S) = $1/2\eta$, values were calculated as 5.2455, 8.4245, -8.4245 and 2.62275 respectively. Obtained small η value means that the charge transfer occurs in the molecule. Considering the η values, large HOMO – LUMO gap means a hard molecule and small HOMO – LUMO



gap means a soft molecule. Additionally, it can be said that the small HOMO–LUMO available energy gap represents more reactive molecule [15-17].

Table 2: The ionisation potential (I /eV), electron affinity (A /eV), chemical hardness (η /eV), softness (S/ eV⁻¹), chemical potential (μ) and electronegativity (χ /eV), of 4-(2-(4-nitrophenyl) ethylidene)amino-hippurate (NEAH) using B3LYP/6-311G (d, P).

Compounds	I(eV)	A(eV)	X(eV)	μ (eV)	η (eV)	S (eV ⁻¹)
1	6.835	3.179	8.4245	-8.4245	5.2455	2.62275

Nonlinear optical (NLO) properties

P-nitroaniline (PNA) is one of the prototypical molecules used in the study of the nonlinear optical NLO properties of molecular systems. In this study, the typical, the nonlinear optical properties (NLO) material, PNA, paranitroaniline was chosen as a reference molecule; because there were no experimental data about the title compound 4-(2-(4-nitrophenyl) ethylidene)amino-hippurate (NEAH) in the literature. The relatively, nonlinear optical properties NLO of the 4-(2-(4-nitrophenyl) ethylidene)amino-hippurate (NEAH) molecule compared to PNA, paranitroaniline indicate their promising applications in, nonlinear optical(NLO) materials. It was used as threshold value for comparative purposes and still continues to be a used as prototype of organic nonlinear optical NLO chromophores. Its hyperpolarizability was studied theoretically in different solvents and at different frequencies [15-18]. Polarizabilities and hyperpolarizabilities characterize the response of a system in any applied electric field [19]. The power of molecular interactions beside the cross-sections of different scattering and collision processes, also the non-linear optical (NLO) properties of the system can be studied [19-23]. In order to investigate the relationships among photo-current generation, molecular structures and NLO, the polarizabilities and hyperpolarizabilities of 4-(2-(4-nitrophenyl) ethylidene)amino-hippurate (NEAH) was calculated using B3LYP method, 6-311G (d, p) basis set, based on the finite-field approach. The mean first order hyperpolarizability (β), total static dipole moment (μ), the mean polarizability ($\langle\alpha\rangle$), and the anisotropy of the polarizability ($\Delta\alpha$), of title molecule are presented in Table (3) describes (total static dipole moment (μ), the mean Polarizability ($\langle\alpha\rangle$), the anisotropy of the Polarizability ($\Delta\alpha$), and the mean first-order Hyperpolarizability ($\langle\beta\rangle$) for 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) using B3LYP/6-311G (d, P). The calculated value of dipole moment was found to be 3.3035 D at B3LYP/6-311G (d, p). The calculated mean polarizability ($\langle\alpha\rangle$) is -23.633×10^{-24} esu i.e. are two times smaller than PNA molecule. In addition, the calculated mean hyperpolarizability (β), of the title molecule is 1.789×10^{-30} esu i.e. smaller than PNA molecule [24,25]. This result indicates the non linearity of the title molecule and promising out to be used as NLO materials.

Table 3: Total static dipole moment (μ), the mean polarizability ($\langle\alpha\rangle$), the anisotropy of the polarizability ($\Delta\alpha$), and the mean first-order Hyperpolarizability ($\langle\beta\rangle$) for 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) using the quantum mechanics sets B3LYP/6-311G (d, P).

Property	PNA	B3LYP/6-311G(d,P)
μ_x		0.4129 Debye
μ_y		-2.8361 Debye
μ_z		-1.6430 Debye
μ	2.44 Debye ^a	3.3035 Debye
α_{xx}		-212.7343 a.u.
α_{xy}		-14.8829 a.u.
α_{yy}		-131.9828 a.u.
α_{zz}		-133.6897 a.u.
α_{yz}		7.6998 a.u.
α_{xz}		-5.6046 a.u.
$\langle\alpha\rangle$	22×10^{-24} cm ^{3b}	-23.633×10^{-24} esu
$\Delta\alpha$		12.6817×10^{-24} esu



β_{xxx}	-170.3114 a.u.
β_{xxy}	89.9663 a.u.
β_{xyy}	17.3054 a.u.
β_{yyy}	-5.3473 a.u.
β_{xxz}	-73.1141 a.u.
β_{xyz}	-57.5847 a.u.
β_{yyz}	1.3507 a.u.
β_{xzz}	20.4211 a.u.
β_{yzz}	5.0125 a.u.
β_{zzz}	15.4463 a.u.
$\langle\beta\rangle$	15.5×10^{-30} esu ^c 1.789×10^{-30} esu

^{a, b, c} PNA results are taken from references [24,25]

Electronic absorption spectroscopy (ES) of the used compound 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH).

The electronic spectroscopy (ES) of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) in ethanol (ETOH) and DMF solvents and the assignment of spectra are given in Figs. (3 and 4) describe the electronic absorption spectra (ES) of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH), theoretical and experimental and Table (4) describes (Theoretical and experimental UV spectra (UV) of 4-(2-(4-nitrophenyl) ethylidene)amino-hippurate (NEAH), calculated at TD-B3LYP/6-311G (d, p). The spectrum in ethanol (ETOH) and water is composed of three bands centered at 170, 173 nm, 160, 162 nm, 147, 149 nm, and 139, 141 nm. Increasing solvent polarity causes small changes in band positions indicating that the polarity of the excited and ground state which are of the same values, that is, solvent independent. All bands are assigned to (π - π^*) transitions as shown in intensities (0-35000).

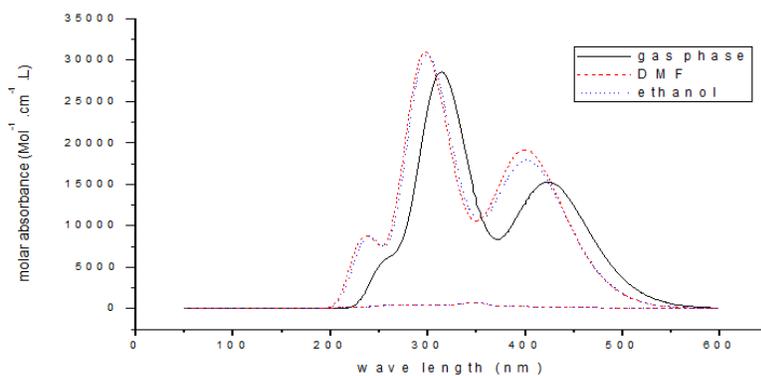


Figure 3: Electronic absorption spectra (ES) of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH), theoretically

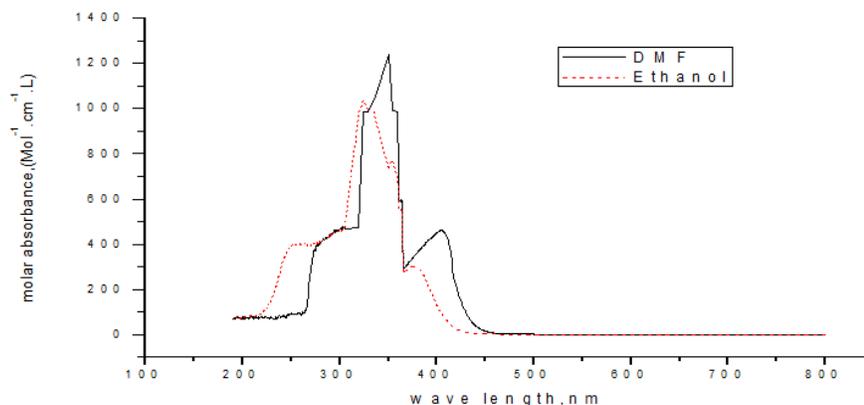


Figure 4: Electronic absorption spectra (ES) of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH), experimentally



Table 4: Theoretical and experimental UV spectra (UV) of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH), calculated at TD-B3LYP/6-311G (d, p).

State	Configuration	Theoretical			Experimental		
		Gas phase			Ethanol (ETOH)	DMF	
		Coefficient	F	λ , nm	type	λ , nm	λ , nm
1	81->86	0.13064	0.3746	390.18	π - π^*	379	401
	85->86	0.26223					
2	76->86	-0.1045	0.2886	301.87	π - π^*	323	326
	77->86	-0.18658					
	78->86	0.13379					
	81->86	0.56699					
	83->86	0.20827					
	85->86	-0.14192					
	85->87	-0.14321					
3	77->86	0.12109	0.4320	282.29	π - π^*	282	288
	81->86	0.25076					
	85->87	0.62644					

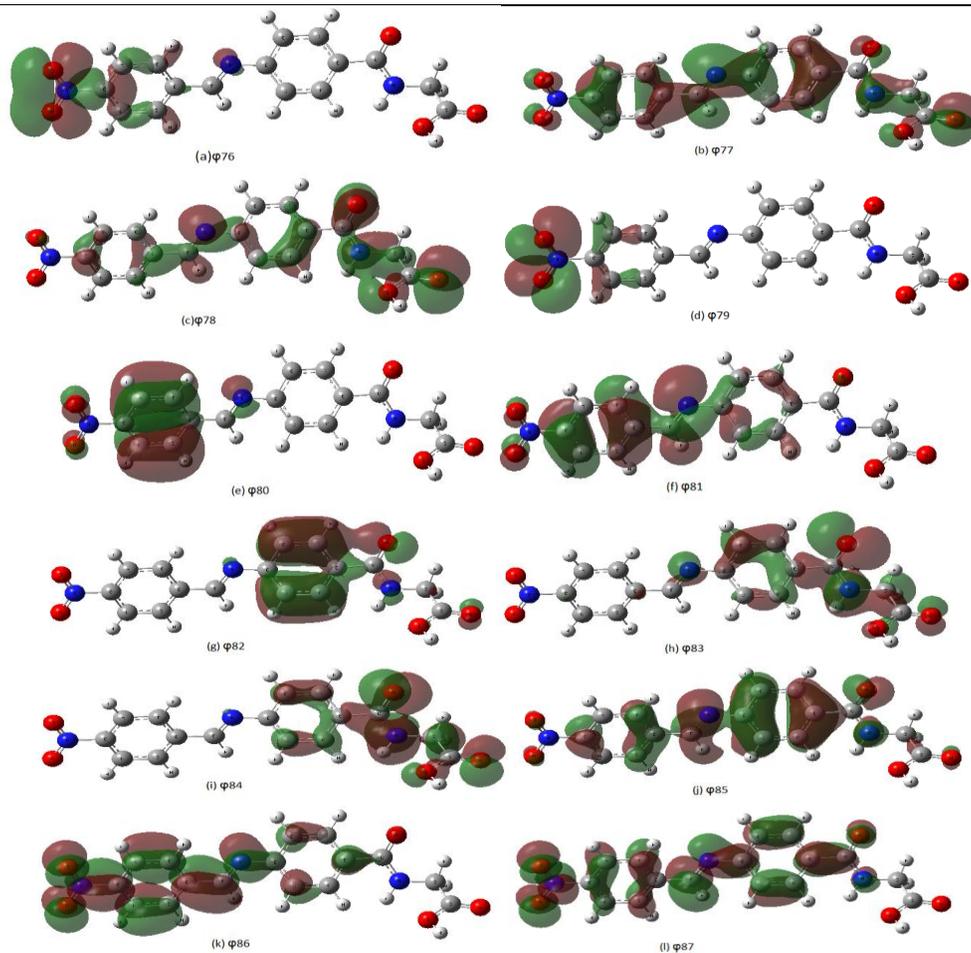


Figure 5: The charge density maps of the occupied (a - j) and unoccupied (k,l) of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH)

The excited configurations in 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) are those which results from electron excitation of 10 highest quantum mechanically occupied molecular orbital's ($\varphi_{76}^{-1}\varphi_{85}$) and the lowest two vacant molecular orbital's ($\varphi_{86}^{-1}\varphi_{87}$). The correspondence between the theoretically computed and the experimentally observed transitions are necessary. The first ($\pi-\pi^*$)¹ state is centered at 379, 401 nm in ethanol and DMF this band is predicted theoretically at 390.18 nm, in very good agreement with the experiment, and is composed of a mixture of seven configurations, (c.f. Table 4) and assigned as CT, localized and delocalized configurations may be expected. This state is composed of a mixture of two configurations, namely, ($\varphi_{81}^{-1}\varphi_{86}$) and ($\varphi_{85}^{-1}\varphi_{86}$). The second ($\pi-\pi^*$)¹ state is observed at 323, 3126 nm in ethanol and DMF is predicted theoretically at 301.87 nm. This state is composed of a mixture of seven configurations, ($\varphi_{76}^{-1}\varphi_{86}$), ($\varphi_{77}^{-1}\varphi_{86}$), ($\varphi_{78}^{-1}\varphi_{86}$), ($\varphi_{81}^{-1}\varphi_{86}$), ($\varphi_{83}^{-1}\varphi_{86}$), ($\varphi_{85}^{-1}\varphi_{86}$) and ($\varphi_{85}^{-1}\varphi_{87}$), that is, delocalized configurations and CT character may be expected (Fig. 5). The third ($\pi-\pi^*$)¹ state is observed at 282, 288 nm in ethanol and DMF and predicted theoretically at 282.29 nm. This band is composed of a mixture of three configurations, (Table 4), ($\varphi_{77}^{-1}\varphi_{86}$), ($\varphi_{81}^{-1}\varphi_{86}$) and ($\varphi_{85}^{-1}\varphi_{87}$) which is of CT character may be expected (Fig. 5). Studying solvent effect is important in theoretical and experimental further studies [26-50].

Conclusion

The molecular geometry of 4-(2-(4-nitrophenyl)ethylidene)amino-hippurate (NEAH) in the ground state has been calculated quantum mechanically by the use of density function theory (DFTB3LYP/6-311G (d,p) levels of theory. The quantum mechanics optimized molecule is nonplanar as indicated from the dihedral angles. The HOMO-LUMO energy gap helped in explaining the chemical reactivity, hardness, softness, chemical potential and electronegativity. The calculated dipole moment and hyperpolarizability results indicate that the molecule 4-(2-(4-nitrophenyl)ethylidene)aminohippurate (NEAH) has good polar and reactive behavior. All the observed bands in the UV spectra can be assigned to ($\pi-\pi^*$) transitions as reflected from their intensities. The correspondence between the theoretically computed and the experimentally observed transitions are satisfactory. The solvent dependence of the observed bands can be attributed to the change in the transition dipole moments of the ground and excited states

Conflict of Interest

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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