TD-DFT Calculations, NBO, NLO Analysis and Electronic Absorption Spectra of Some Novel Thiazolo[3,2-a]Pyridine Derivatives Bearing Anthracenyl Moiety

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Abstract: The electronic structure and spectra of the studied compounds 1–4 are investigated using TD-DFT/B3LYP/6-311G (d, p) level of theory. The results of calculations show that all the studied compounds 1–4 are non-planar, as indicated from the dihedral angles. The electronic absorption spectra of the studied compounds are recorded in the UV-VIS region, in both Acetone (as polar solvent) and Xylene (as non-polar solvent). The observed vertical electronic transitions assignments are facilitated via time-dependent density functional theory TD-DFT. Solvent dependence of the band maxima ($\lambda_{\text{max}}$) and intensities of the observed spectra are explained in terms of blue and red shifts. Electronic configurations contributing to each excited state are identified and the relevant MOs are characterized. The natural bond orbital (NBO) analysis were discussed in terms of the extent of delocalization, intermolecular charge transfer and second order perturbation interactions between donor and acceptor MOs. The Coulomb-attenuating method (CAM-B3LYP) and Corrected Linear Response Polarizable Continuum Model (CLR) PCM studied for theoretically obtaining the electronic absorption spectra in gas phase, Acetone and Xylene, respectively, indicate a good agreement with the observed spectra. The calculated nonlinear optical parameters (NLO); polarizibility ($\alpha$), anisotropy of the polarizibility ($\Delta\alpha$) and first order hyperpolarizibility ($\beta$) of the studied compounds show promising optical properties. The HOMO-LUMO energy gap helped in analyzing the chemical reactivity, hardness, softness, chemical potential and electro negativity. 3D-plots of the molecular electrostatic potential (MEP) for the studied compounds are investigated and analyzed showing the distribution of electronic density of orbital's describing the electrophilic and nucleophilic sites of the selected molecules.

Keywords: UV Spectra, TD-DFT, Solvent and Substituent Effects, NBO and NLO Analysis

1. Introduction

The novel structure may be used in designing new potent and less toxic antimicrobial agents. Nitrogen-containing heterocyclic compounds have a diverse range of biological and pharmacological properties [1–4]. Thiazolo[3,2-a]pyridines, containing two fused heterocyclic rings, also; it's found in medicinal chemistry as they have an excellent biological activity with a wide range of applications, including antimicrobial [5], antiviral [6] antihypertensive [7], antihistaminic [8], neurotropic [9], anticonvulsant [10], antidepressant, sedative, analgesic [11,12] and anti-cancer activities. Among the various of anthraquinones are identified also biologically active compounds. A lot of anthraquinone compounds are found in plants, microorganisms [13], among of them are natural antibiotics anthracyclines [14] and cidamicines [15]. Recently, anthracone derivatives actively began to gain new application areas such as biologically active agents, analytical reagents [16–18], phosphors [19], the components of liquid crystal compositions, photo materials, chemical additives for polymeric materials and they have found their application in color photography and electrophotography, laser technology, LCD and photochromic materials [20, 21].

The newly synthesized thiazolo[3,2-a]Pyridines having anthranyl moiety derivatives 1-4 are expected to have
biological potential which needs to be explored by investigating their electronic structure and spectra experimentally and theoretically. The UV spectra, NLO and NBO analysis have been used to explain charge transfer transitions, which is known as solvatochromism Corrected Linear Response Polarizable Continuum Model (CLR) PCM.

In continuation to our previous work [22-24], the objective of the present study aims to the calculations of density functional theory (DFT) and time-dependent density functional theory (TD-DFT) by using B3LYP at the 6-311G(d,p) basis set to obtain geometries, electronic structures, non liner optical properties (NLO), natural bonding orbital's (NBO), UV-Vis spectra, and molecular electrostatic potential contours of the studied compounds 1–4, these parameters characterize the forces that govern the structure of the studied compounds 1–4. The hybridization of each atom, natural charges, bonding and antibonding orbital's second order perturbation energy (E(2)), exact configurations and Lewis and non-Lewis electrons results from natural bonding orbital analysis. The present work attempts to provide a detailed experimental (UV) and theoretical electronic structure and spectra of the studied compounds 1–4 using CAM-B3LYP/6-311G (d, p). The origin of each absorption band is identified and the contributing configurations and MOs are characterized. The identify the extent of delocalization and the charge transfer of the electron density in the studied molecular systems by Natural bond orbital analysis (NBO) and also; extent of conjugative interaction between different subsystems of the studied compounds. The effect of solvent polarity on the observed spectra and hence, predicting the relative stabilities, extent of charge transfers character and assignment of the observed electronic transitions are analyzed. The effect substituent's of different electron donating groups (X= CH3 and X= OCH3) and electron withdrawing groups (X= Cl) on the electronic spectra of the studied compounds are discussed and analyzed. The molecular electrostatic potential (MEP) of the studied molecules were explored as well

2. Experimental

2.1. Compounds

The structure of the four proposed molecules 1–4 of Anthranyl Thiazolo[3,2-a]Pyridine derivatives, is shown below, where compound 1 is 5-amino-2 (anthracen-9-ylmethylene)-3-oxo-7-phenyl-2,3-dihydro-7H-thiazolo[3,2-a]pyridine-6,8-dicarbonitrile. Compound 2 is 5-amino-2-(anthracen-9-ylmethylene)-3-oxo-2,3-dihydro-7H-thiazolo[3,2-a]pyridine-6,8-dicarbonitrile. Compound 3 is 5-amino-2-(anthracen-9-ylmethylene)-7-(4-methoxyphenyl)-3-oxo-2,3-dihydro-7H-thiazolo[3,2-a]pyridine-6,8-dicarbonitrile, and compound 4 is 5-amino-2-(anthracen-9-ylmethylene)-7-(4-chlorophenyl)-3-oxo-2,3-dihydro-7H-thiazolo[3,2-a]pyridine derivatives. The structure of the four proposed molecules 1–4 of Anthranyl Thiazolo[3,2-a]Pyridine derivatives is shown in figure 1.

2.2. Solvents

Polar (acetone) and non-polar (xylene) solvents were obtained from Merck, AR- grade, and were used without further purification.

2.3. Apparatus

A Perkin Elmer lambda 4B spectrophotometer using 1.0 cm fused quartz cells were used to measured the electronic absorption spectra over the range 200-900 nm.

2.4. Computational Details

All computations were carried out using Khon-Sham’s DFT method subjected to the gradient-corrected hybrid density functional B3LYP method [25]. 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 [26]. For each structure, a full geometry optimization was performed using this function [26] and the 6-311G (d, p) bases set [27] as implemented by Gaussian 09 package [28]. All geometries were visualized either using GaussView 5.0.9 [29] or chemcraft 1.6 [30] software packages. No symmetry constrains were applied during the geometry optimization. Also, the total static dipole moment (μ), (Δα), and (β), values were calculated by using the following equations [31-33]:

\[
\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2},
\]

\[
(\alpha) = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}).
\]

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

\[
(\beta) = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2},
\]

Where

### Table 1. The structure of the four proposed molecules 1–4 of Anthranyl Thiazolo[3,2-a]Pyridine derivatives.

| Compounds | X       |
|-----------|---------|
| 1         | H       |
| 2         | CH₃     |
| 3         | OCH₃    |
| 4         | Cl      |
\[ \beta_{x} = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}, \]
\[ \beta_{y} = \beta_{yyy} + \beta_{xyy} + \beta_{yzz}, \]
\[ \beta_{z} = \beta_{zzz} + \beta_{xzz} + \beta_{yyz}. \] (2)

The electronic transition properties which include the maximum excitation wavelength \( (\lambda_{\text{max}}) \) and relative intensities (oscillator strengths, \( f \)) were obtained by the time dependant density functional theory (TD-DFT), [34] using “A new hybrid exchange-correlation-functional correlation using the Coulomb-attenuating method (CAM-B3LYP),” at the 6-311G (d, p) bases set [35]. The population analysis has also been performed by the natural bond orbital method [36] at B3LYP/6-311G (d, p) level of theory using natural bond orbital (NBO) under Gaussian 09 program package. The second-order Fock matrix was used to evaluate the donor-acceptor interactions in the NBO basis [37]. For each donor \((i)\) and acceptor \((j)\), the stabilization energy \( E_{ij} \) associated with the delocalization \( i \rightarrow j \) is estimated as

\[ E_{ij} = \Delta E_{ij} = q_{i} \left( F \left( \beta_{ij} \right) \right)^{2} / \varepsilon_{i} - \varepsilon_{j}, \] (3)

Where \( q_{i} \) is the donor orbital occupancy, \( \varepsilon_{i} \) and \( \varepsilon_{j} \) are diagonal elements and \( \beta_{ij} \) is the off-diagonal NBO Fock matrix element. For the conversion factors of hyperpolarizability \( \beta \), the atomic unit (a.u.) = 0.1482 \times 10^{–24} \text{ esu} \), and the polarizability \( \alpha \), 1 a.u. = \( 8.6393 \times 10^{–33} \text{ esu} \) for first hyperpolarizability \( \beta \), 1 a.u. = \( 27.2116 \text{ eV} \) for HOMO and LUMO energies.

3. Result and Discussion

3.1. Electronic Structure

3.1.1. Geometry Structure

Figures 2-4, presents the optimized structures of the studied compounds 1-4, numbering system, HOMO and LUMO-charge density maps and the vector of dipole moment using the B3LYB/6-311G (d, p). From “Figures 2-4, it is obvious that, the optimized structures of the studied compounds, 1-4, is non-planer with the phenyl ring at C3 and anthranyl moiety at C9 are out of the molecular plane of novel thiazolo[3,2-a]pyridines having anthranyl moiety by a dihedral angles of 111° and 128° respectively. The insertion of X= p-Cl, p-CH3, and p-OCH3 at C1-ph does not change the geometry of the studied compounds 1-4 "Figure 2". This may be attributed to that the phenyl at C3 and anthranyl moiety at C9 are out of the molecular plane.

The optimized geometric parameters (bond lengths, bond angles and dihedral angles) of the parent molecule 1 and some of its derivatives 2-4 using B3LYP/6-311G (d,p) method are listed in Tables 2 and 3. The optimized bond lengths and bond angles are compared with the available X-ray experimental data [38–40]. The observed bond lengths of C1-C2 and C2-C3 in pyridine ring are 1.371Å and 1.521Å respectively, while the theoretical values are 1.370Å and 1.518Å respectively. For C-S bonds (C9-S8 and S8-C10), the calculated values are greater than the experimental values by 0.045Å and 0.014Å respectively. There is a great agreement between the calculated bond lengths of the parent 1 and the experimental values indicating the power of the method used. For derivative 2, the calculated bond angles <C4C5S8 (124.85°) and <N6C10C9 (110.24°) are overestimated than the experimental values, whereas, the calculated bond angles <C5N6C1 (119.23°) and <N6C5S8 (111.86°) are underestimated than the experimental values (c.f. Table 2). The effect of different substituents in the derivatives 3 and 4 are listed in Table 2. There are disagreement between the calculated bond angle and the experimental values which may be attributed to that the calculation were carried out in the gas phase and the experimental measured in the solid state. All the studied compounds 2a-d are non-planer as indicating from the calculated dihedral angles (c.f. Table 3).

| Parameters | EXP [38-40] | 1 | 2 | 3 | 4 |
|------------|-------------|---|---|---|---|
| Bond lengths (Å) | | | | | |
| C1–C2      | 1.371       | 1.370 | 1.370 | 1.370 | 1.370 |
| C2–C3      | 1.521       | 1.518 | 1.518 | 1.518 | 1.517 |
| C4–C5      | 1.341       | 1.349 | 1.349 | 1.349 | 1.349 |
| C3–N9      | 1.389       | 1.402 | 1.402 | 1.402 | 1.402 |
| C1–N8      | 1.387       | 1.420 | 1.420 | 1.420 | 1.420 |
| C3–S8      | 1.722       | 1.767 | 1.767 | 1.768 | 1.766 |
| S8–C9      | 1.753       | 1.767 | 1.767 | 1.767 | 1.768 |
| C9–C10     | 1.399       | 1.481 | 1.481 | 1.482 | 1.480 |
| C10–C11    | 1.341       | 1.346 | 1.346 | 1.346 | 1.347 |
| C11–C12    | 1.451       | 1.468 | 1.468 | 1.468 | 1.467 |
| C12–N5     | 1.412       | 1.406 | 1.406 | 1.405 | 1.407 |
| C13–O23    | 1.290       | 1.217 | 1.217 | 1.217 | 1.217 |
| C1–N24     | 1.345       | 1.354 | 1.355 | 1.356 | 1.354 |
| C2–C27     | 1.389       | 1.414 | 1.414 | 1.414 | 1.414 |
| C27–N9     | 1.190       | 1.159 | 1.159 | 1.159 | 1.159 |
| C3–C13     | 1.524       | 1.533 | 1.532 | 1.531 | 1.533 |
## Table 3. Dihedral Angles (°) and Natural Charge for the studied compounds (1–4) computed at the B3LYP/6-311G(d,p) level of theory.

| Parameters | EXP.[38-40] | 1     | 2     | 3     | 4     |
|------------|-------------|-------|-------|-------|-------|
| C4 – C28   | 1.412       | 1.419 | 1.419 | 1.419 | 1.419 |
| C28 – N30  | 1.190       | 1.157 | 1.157 | 1.157 | 1.157 |
| Bond Angles (°) |       |       |       |       |       |
| <N4-C8-C2   | 120.00     | 119.31 | 119.29 | 119.31 | 119.31 |
| <C4-C2-C3   | 124.99     | 124.89 | 124.87 | 124.91 | 124.81 |
| <C4-C2-C4   | 109.31     | 109.82 | 109.75 | 109.71 | 109.82 |
| <C4-C2-C5   | 121.00     | 122.28 | 122.26 | 122.28 | 122.20 |
| <C4-C2-S8   | 123.99     | 124.85 | 124.90 | 124.93 | 124.86 |
| <C4-C2-N3   | 123.95     | 123.29 | 123.26 | 123.26 | 123.26 |
| <N1-C4-C1   | 119.80     | 119.23 | 119.22 | 119.20 | 119.25 |
| <N4-C8-S8   | 110.96     | 111.86 | 111.84 | 111.81 | 111.88 |
| <N1-C1p-C9  | 109.55     | 110.24 | 110.26 | 110.27 | 110.25 |
| <S5-C8-C10  | 110.69     | 111.39 | 111.37 | 111.36 | 111.38 |
| <C5-S5-C6   | 95.41      | 91.102 | 91.102 | 91.110 | 91.107 |
| <C11p-C7p-S8| 130.81     | 127.94 | 127.98 | 128.10 | 128.03 |
| <C9-C1p-C11 | 127.99     | 128.40 | 128.45 | 128.67 | 128.67 |
| <O9p-C9p-O2  | 124.61     | 124.82 | 124.81 | 124.79 | 124.92 |
| <O2p-C9p-N4  | 125.00     | 124.94 | 124.93 | 124.94 | 124.83 |
| <C10p-N4p-C1| 125.00     | 125.36 | 125.36 | 125.36 | 125.34 |
| <N4-C1p-N24 | 115.92     | 116.23 | 116.23 | 116.22 | 116.31 |
| <N4-C1p-C2   | 125.00     | 124.39 | 124.40 | 124.40 | 124.32 |
| <C2-C7-C27   | 116.95     | 117.11 | 117.11 | 117.06 | 117.18 |
| <C2-C27p-N24 | 177.99     | 178.15 | 178.16 | 178.10 | 178.28 |
| <C2-C7p-C13  | 113.69     | 112.10 | 112.10 | 113.18 | 113.06 |
| <C2-C7p-C13  | 113.36     | 111.25 | 111.28 | 111.30 | 111.06 |
| <C2-C7p-C28  | 117.96     | 118.27 | 118.26 | 118.27 | 118.22 |
| <C2-C7p-N30  | 177.99     | 179.17 | 179.15 | 179.14 | 179.05 |

## Parameters

| Dihedral Angles (°) | 1     | 2     | 3     | 4     |
|---------------------|-------|-------|-------|-------|
| <C4-C8-C4           | 9.324 | 10.904 | 10.031 | 10.150 |
| <C4-C8-C6           | 3.255 | 3.534 | 3.712 | 3.641 |
| <C4-C8-C11          | 6.323 | 6.669 | 6.572 | 6.640 |
| <C4-C8-N3           | 177.72 | 177.44 | 177.24 | 177.55 |
| <N4-C8-S4           | -1.474 | -1.670 | -1.834 | -1.612 |
| <S4-C8-C7           | 1.044 | 0.969 | 0.972 | 1.130 |
| <S4-C8-N4           | 1.538 | 1.511 | 1.150 | 1.058 |
| <O8-C8-N4-C1        | -5.148 | -5.266 | -5.059 | -5.225 |
| <C11-N4-C1-C26      | -7.961 | -7.518 | -7.634 | -6.924 |
| <N4-C1-C1-N3A2      | 173.43 | 173.10 | 173.11 | 173.73 |
| <C2-C2p-N3          | -9.194 | -9.633 | -7.939 | -8.454 |
| <C2-C2p-N3O2        | -54.427 | -55.646 | -57.167 | -42.223 |
| <C1-C1-C2p-C26      | -63.119 | -63.658 | -63.350 | -63.796 |
| <C1-C1-C2p-H2       | 118.034 | 118.088 | 118.095 | 118.128 |
| <C1-C2p-C2p-H2      | -175.43 | -175.40 | -175.40 | -175.41 |

### Natural Charge

| C1     | 0.4622 | 0.4615 | 0.4598 | 0.4633 |
| C2     | -0.2796 | -0.2794 | -0.2778 | -0.2838 |
| N6     | -0.4702 | -0.4701 | -0.4691 | -0.4705 |
| S8     | 0.4004 | 0.3998 | 0.3987 | 0.4024 |
| C9     | -0.2673 | -0.2668 | -0.2675 | -0.2689 |
| C10    | 0.6842 | 0.6851 | 0.6839 | 0.6851 |
| O23    | -0.6064 | -0.6077 | -0.6077 | -0.6063 |
| N24    | -0.7677 | -0.7678 | -0.7696 | -0.7661 |
| N29    | -0.3461 | -0.3436 | -0.3446 | -0.3420 |
| N30    | -0.3037 | -0.2990 | -0.3008 | -0.2960 |
| C55    | -------- | -0.5835 | -0.1977 | -------- |
| O54    | -------- | -------- | -0.5216 | -------- |
| C154   | -------- | -------- | -------- | -0.0070 |
**Figure 2.** Optimized geometry, vector of the dipole moment and numbering system, for the studied compounds 1-4 at B3LYP/6-311G (d, p).

**Figure 3.** HOMO, LUMO maps and energy gap of 1-4 at B3LYP/6-311G (d, p).
presented in Table 3. In case of our studied compounds 1-4, donates an electron. Of the molecule, these negative atoms have a tendency to distribute of partial charges on the skeletal atoms show accepting properties of novel thiazolo[3,2-a]Pyridines having accepting property (reducing power) is 2.89 eV. The order of the most negative centers are N6, O23, N24, N29, N30.

However the electron affinity, E.A., of 1 which measures the donating property (oxidation power) is 5.90 eV (c.f. Table 4). The effect of substituent's of different strengths measures the charge separation over the molecule is 6.62 D. The general trend of the dipole moment changes for the studied compounds 1-4 follow the order 4 > 3 > 1 > 2 (c.f. Table 4) and the vector of the dipole moment is presented in "Figure 2". From the computed dipole moment, it’s found that the presence of two cyano groups at C3 and C4 and anthracene group at C9 (c.f. "Figures 2 and 3") are responsible for the polarity of the compound 1 (c.f. Table 2).

### 3.1.2. Ground State Properties

The ionization energy, I.E, of compound 1 which measures the donating property (oxidation power) is 5.90 eV (c.f. Table 4). The effect of substituent's of different strengths and hence in the donating properties follows the order: 3 > 2 > 1 > 4, as shown in Table 4 and "Figures 3 and 4". However the electron affinity, E.A., of 1 which measures the accepting property (reducing power) is 2.89 eV. The order of accepting properties of novel thiazolo[3,2-a]Pyridines having

The natural population analysis [41] performed on the electronic structures of compounds 1-4 clearly describes the distribution of electrons in various sub-shells of their atomic orbits. The accumulations of charges on the individual atom presented in Table 3. In case of our studied compounds 1-4, the most negative centers are N6, O23, N24, N29, N30, O54, and CI54-atoms. According to an electrostatic point of view of the molecule, these negative atoms have a tendency to donate an electron. Whereas, the most electropositive atoms such as; S8 have a tendency to accept an electron. These distributions of partial charges on the skeletal atoms show that the electrostatic repulsion or attraction between atoms can give a significant contribution to the intra- and intermolecular interaction.

### 3.1.3. Natural Charge

Table 4. Total energy, energy of HOMO and LUMO, energy gap, dipole moment, The ionization potential (I /eV), electron affinity (A /eV), chemical hardness (η /eV²), global softness (S /eV), chemical potential (V/eV), electronegativity (χ /eV), and global electrophilicity index, (ω/eV), of the studied compounds (1-4) computed at the B3LYP/6-311G(dp).

| Compounds | 1       | 2       | 3       | 4       |
|-----------|---------|---------|---------|---------|
| E(T/au)   | -1846.7984 | -1886.1263 | -1961.3519 | -2306.4198 |
| E(HOMO)   | -5.90267  | -5.88608  | -5.88091  | -5.96224  |
| E(LUMO)   | -2.89109  | -2.86933  | -2.86688  | -2.97813  |
| E(gap)    | 3.01158   | 3.01675   | 3.01403   | 2.98411   |
| µ (Debye) | 6.6222    | 6.3840   | 7.2805   | 8.0169    |
| I (eV)    | 5.90267   | 5.88608   | 5.88091   | 5.96224   |
| A(eV)     | 2.89109   | 2.86933   | 2.86688   | 2.97813   |
| χ(eV)     | 4.39688   | 4.37770   | 4.37389   | 4.47018   |
| V(eV²)    | -4.39688  | -4.27770  | -4.73789  | -4.47018  |
| S(eV)     | 1.50579   | 1.50837   | 1.50701   | 1.49206   |
| ω(eV)     | 0.33205   | 0.33148   | 0.33178   | 0.33511   |
| Eg(eV)    | 6.49190   | 6.35261   | 6.34729   | 6.69630   |

The frontier molecular orbital (FMO) energies of the studied compounds were calculated at the same level of theory. HOMO energy characterizes the electron donating ability, while LUMO energy characterizes the electron withdrawing ability. Energy gap (Eg) between

![Figure 4. Energy of HOMO, LUMO and energy gap of the studied compounds 1-4 at B3LYP/6-311G (d, p) level of theory.](Image)
HOMO and LUMO characterizes the molecular chemical stability which is a critical parameter in determining molecular electrical transport properties because it is a measure of electron conductivity. The results in "Figure 3" and Table 4 indicate that the smaller the energy gap the easier the charge transfer and the polarization occurs within the molecule. Furthermore, the order of increasing reactivity in the studied compounds is: 4 > 1 > 3 > 2. The insignificant differences in $E_g$ of all the studied compounds except 4 is due to the non-planarity of the two ph-X and anthracene group with the thiazolo[3,2-a]pyridine moiety (c.f. Table 4). Using HOMO and LUMO energies, ionization potential and electron affinity can be expressed as $I$=−$E_{\text{HOMO}}$ and $A$=−$E_{\text{LUMO}}$ at the B3LYP/6-311G (d,p) as shown in (Table 4). The variation of electronegativity ($X$) values is supported by electrostatic potential, for any two molecules, where electron will be partially transferred from one of low $X$ to that of high $X$. The results show that the order of decreasing $X$ is: 4 < 1 < 2 < 3. The chemical hardness ($\eta$) = (I-A)/2, electronegativity ($X$) = (I+A)/2, chemical potential ($V$) = -(I+A)/2, electrophilicity ($\omega$) = $\mu^2$/2$\eta$ and global softness ($S$) = 1/2$\eta$ values are calculated and presented in Table 4. The results of small $\eta$ values for the studied compounds reflect the ability of charge transfer inside the molecule. Therefore, the order is: 4 > 1 > 3 > 2. There is a linear relationship between $\eta$ and $E_g$ as shown in (Table 4). Considering $\eta$ values, the higher the $\eta$ values, the harder the molecule and vice versa.

### Table 5. Total static dipole moment (μ), the mean polarizability (<α>), the anisotropy of the polarizability (Δα), and the mean first-order hyperpolarizability (<β>), for the studied compounds (1-4) computed at B3LYP/6-311G(d,p).

| Property | PNA | 1 | 2 | 3 | 4 |
|----------|-----|---|---|---|---|
| $\mu_\alpha$, D | -2.3970 | -2.19358 | -2.25501 | -1.96204 |
| $\mu_\beta$, D | 0.22663 | 0.53737 | 0.86366 | 0.32376 |
| $\mu_\gamma$, D | -0.98272 | -1.08832 | -1.53756 | -0.62330 |
| $\mu$, Debye | 2.60052 | 2.506992 | 2.862706 | 2.083967 |
| $\alpha_{xx}$, a.u. | 610.816 | 637.430 | 647.415 | 631.077 |
| $\alpha_{xy}$, a.u. | 38.9403 | 37.7679 | 32.4371 | 37.9918 |
| $\alpha_{yy}$, a.u. | 424.426 | 436.336 | 439.636 | 426.157 |
| $\alpha_{zz}$, a.u. | -6.62195 | -3.22879 | 3.51065 | 7.59677 |
| $\alpha_{xy}$, a.u. | -6.21531 | -0.33418 | 7.56950 | -1.12186 |
| $\alpha_{xx}$, a.u. | 246.694 | 256.239 | 261.914 | 253.320 |
| <$\alpha$> ×10$^{-24}$ esu | 63.33 | 65.70 | 66.64 | 64.74 |
| $\Delta \alpha \times 10^{-24}$ esu | 47.85 | 49.91 | 50.27 | 49.55 |
| $\beta_{xxx}$, a.u. | -311.565 | -254.708 | -278.249 | -205.497 |
| $\beta_{xxy}$, a.u. | 163.254 | 170.091 | 168.919 | 179.192 |
| $\beta_{xyy}$, a.u. | -113.614 | -126.586 | -111.257 | -106.845 |
| $\beta_{yyy}$, a.u. | 8.21341 | 42.3811 | 95.0644 | 21.8794 |
| $\beta_{xxz}$, a.u. | 70.4887 | 61.9425 | 2.81160 | 78.8312 |
| $\beta_{xyz}$, a.u. | -7.3633 | -15.2491 | -54.4635 | -6.1162 |
| $\beta_{zyz}$, a.u. | -49.3368 | -45.3843 | -53.0683 | -53.0622 |
| $\beta_{xxz}$, a.u. | 29.0944 | 33.8242 | 71.6342 | 32.3890 |
| $\beta_{xyy}$, a.u. | -28.8070 | -32.3737 | -22.8372 | -3.51065 |
| $\beta_{zxy}$, a.u. | -41.7722 | -46.8760 | -61.9453 | -46.7887 |
| <$\beta$> ×10$^{-30}$ esu | 15.5 | 27.167 | 22.672 | 25.964 |

a, b, c PNA results are taken from references [43-45].

### 3.3. Nonlinear Optical (NLO) Analysis

Non-linear optical properties are the ability of any compound to convert light of longer wave length into light of shorter wave length. Most applications of single crystals of any non linear materials are evident in the fields of semiconductors, infrared detectors, solid state lasers, photosensitive materials and crystalline thin films for microelectronics [42]. The investigation of the relationship between the electronic structure and NLO, parameters of the studied compounds 1-4 are calculated theoretically by using DFT/B3LYP/6-311G (d,p). Total static dipole moment (µ), the mean polarizability α, the anisotropy of the polarizability Δα, the mean first-order hyperpolarizability (β) of the studied compounds 1-4 are listed in Table 5. In this study, P-nitro aniline (PNA) is a standard prototype molecule used in NLO studies, its chosen as a reference as there were no experimental values of NLO properties of the studied compounds. The values of $\alpha$, β in Table 5 show that the order of increasing $\alpha$ with respect to PNA is: compounds 3 and 2 are ~ 3.5 and 3 times higher than (PNA), whereas compounds 4 and 1 are ~ 3 times higher than the standard (PNA) respectively. The calculated first order hyperpolarizability of p-nitroacetanilide (PNA) is 15.5 × 10$^{-30}$ esu as reported by T. Gnanasambandan et al [43-45]. The analysis of the β parameter show that compounds 1 and 3 are ~ 2 times higher than (PNA), while compounds 2, and 4 are ~ 1.5 times higher than the reference respectively. Therefore, the studies compounds show promising optical properties.
3.4. Molecular Electrostatic Potential (MEP)

The electrophilic and nucleophilic attack as well as hydrogen bonding interactions in any molecular system can be explained in terms of the charge transfer and natural charges on active sites of the studied molecules [46]. DFT/B3LYP/6-311G (d,p) method of calculation of studied molecules (1-4) are calculated 3D MEP and ESP from optimized molecular structure are shown in “Figures 5 and 6”. Potential increases in the following order: red < orange < yellow < green < blue [47,48]. The results show that, in case of 1 (X=Y=H) the negative region (red) is mainly over the N and O atomic sites, which is caused by the contribution of lone-pair electrons of nitrogen and oxygen atoms while the positive (blue) potential sites are around the hydrogen, sulfur and carbon atoms. A portion of the molecule that has negative electrostatic potential will be susceptible to electrophilic attack—the more negative the higher the tendency for electrophilic attack.

![Figure 5. Molecular surfaces of studied compounds 1-4 at B3LYP/6-311G (d, p).](image)

The color scheme for the MEP surface is as follows: red for electron rich, (partially negative charge); blue for electron deficient, (partially positive charge); light blue for (slightly electron deficient region); yellow for (slightly electron rich region); green for neutral (zero potential) respectively.
3.5. Electronic Absorption Spectra of Anthranyl Thiazolo[3,2-a]Pyridine Derivatives

The electronic absorption spectra of novel thiazolo[3,2-a]Pyridines having anthranyl moiety derivatives studied in this work 1-4 depend on the type and extent of interaction between different moieties. The possible types of interaction between subsystems are presented in Figure 7. For example, (i) Cross conjugation if no interaction between the fused thiazolo[3,2-a]pyridine and the terminal phenyl group Ph-X and the anthracene moiety, (ii) partial conjugation between Ph-X and Anthranyl Thiazolo[3,2-a]Pyridine, (iii) partial conjugation between anthrathene moiety and Anthranyl Thiazolo[3,2-a]Pyridine (iv) full conjugation between the three subsystems Ph-X, anthracene moiety, and thiazolo[3,2-a]pyridine.

![Figure 6. Atomic charge distribution (au) for 5-amino-2-(anthracen-9-ylmethylene)-3-oxo-7-phenyl-2,3-dihydro-7H-thiazolo[3,2-a]pyridine-6,8-dicarbonitrile at B3LYP/6-311G(d,p) basis set.](image)

![Figure 7. The types of conjugation between different moieties of Anthranyl Thiazolo[3,2-a]Pyridine.](image)
3.5.1. Electronic Absorption Spectra of Compound 1

"Figure 8", and Table 7 presents the experimental and theoretical electronic absorption spectra of 1 in xylene and acetone. The spectrum of 1 is composed of three bands in the range 270–550 nm. The spectrum in xylene shows two intense bands at 418 nm, and 318 nm. Increasing solvent polarity on going from xylene to acetone results in a blue shift with the first band is shifted to 415 nm, and the second band is shifted to 313 nm, respectively. The second observed bands are assigned as \((\pi-\pi^*)\) transitions, as indicated by the values of molar absorptive \((e=55000)\). Predicting and assigning the origin of the experimental spectrum of compound 1, one can calculate the theoretical gas phase transitions of the various subsystems a, b, and c as presented in "Figures 9-12", using CAM-B3LYP/6-311G (d, p). Five transitions are computed at 188.6, 234.6, 257.3, 312.4, and 371.8 nm for subsystem a; six transitions are computed at 129.4, 142.6, 168.5, 180.3, 218.0, and 235.9 nm for subsystem b; seven transitions are computed at 168.0, 187.7, 194.9, 232.2, 239.3, 260.6, and 283.6 nm for subsystem c; and five transitions are computed at 225.2, 251.5, 283.5, 301.7, and 403.8 nm for compound 1. The correlation of the theoretical transitions of the various subsystems show that the transition at 232.2, 260.6 and 283.6 nm of subsystem c correlates with the transition at 225.2, 251.5 and 283.5 nm of compound 1. Moreover, three transition at 234.6, 257.3, and 312.4 nm of subsystem a correlates with that at 225.2, 251.5 and 310.7 nm of compound 1. While, two transition at 218.0 and 235.9 nm of subsystem b correlates with that at 225.2 and 251.5 nm of compound 1. This indicates that the interaction of anthracene moiety and thiazolo[3,2-a]pyridine of subsystem c reproduces the partial conjugation \((ii)\), which verifies the negligible influence of the interaction of Ph-X (c.f. Figure 7).

In order to account for the experimentally observed UV Spectra of 1 in xylene and acetone, it is essential to consider the theoretically calculated vertical transitions using TD-DFT-CAM-B3LYP/6-311G (d, p) level. The experimental band at 418 nm (in xylene) is reproduced theoretically by PCM (xylene), at 414 (state I) nm, and in gas phase at 403.8 nm as shown in Table 7. The third \((\pi-\pi^*)\) state theoretically in xylene at 256 nm (state III), which involves the orbital’s \(\phi_{123}\) and \(\phi_{127}\) in the transition. The gas phase calculation gives a wavelength at 251.5 nm (state III), which also involves orbital’s \(\phi_{123}\) and \(\phi_{127}\). In acetone, this same band appears theoretically at 257 nm, (state III), as shown in Table 7. The nature of the electronic transition can be inferred from examining the electron density contours of molecular orbitals. The four orbital’s \(\phi_{123}, \phi_{125}, \phi_{126}\), and \(\phi_{127}\) respectively, involved in the theoretical transitions of 1, are shown in "Figure 13", where the first, second and third bands involving \(\phi_{125}\) and \(\phi_{126}\) & \(\phi_{123}\) and \(\phi_{127}\) show a delocalization of electron density, and Charge Transfer CT character.

The NBO analysis of the studied compounds 1-4 provides an efficient method for studying intra-and intermolecular bonding and also provides a convenient basis for investigating charge transfer or conjugative interactions in molecular systems. Table 6 presents the second order perturbation energies of most interacting NBOs of 1-4 and the most important interaction between filled (donor) Lewis type NBOs and empty (acceptor) non-Lewis NBOs. The charge density maps of HOMO and LUMO for 1-4 are presented in "Figure 13". The results of NBO analysis of compound 1 tabulated in Table 6 indicate that there is a strong hyper conjugative interactions \(\pi^*C_5-C_{11} \rightarrow \pi^*C_{31}-C_{33}\), LP (1) \(N_{24} \rightarrow \pi^*C_{1}-C_{2}\), LP (1) \(N_{6} \rightarrow \pi^*C_{6}-C_{8}\), LP (2) \(O_{31} \rightarrow \sigma^*N_{0}-C_{10}\), and \(\pi^*C_{12}-C_{13}\) for 1 is 55.78, 51.82, 33.88, 26.81, and 23.58 kcal/mol, respectively. The C–N \(\pi\) orbital in two cyano groups and amino group interacts equally well with pyridine ring. In fact, its interaction with the thiazolo ring is greater. Furthermore, the lone pair orbital of the nitrogen atom enjoys hyperconjugation with the C10–O23, and C1–C2 \(\pi^*\) orbital. The oxygen and sulfur lone pair orbital's, on the other hand, interact essentially with the C5–N6 \(\pi\) orbital of the thiazolo ring. It is surprising to notice a decrease in the population of the NBO C1–C2, C31–C33, and C10–O23 reflecting a charge transfer away from the thiazolo[3,2-a]pyridine ring. In conclusion, 1 enjoys the linear conjugation that is responsible for the observed spectrum. No specific part of the molecule manifests itself in the observed spectrum.

| Compound | Donor | Acceptor | \(E^{2(n)}\) (kcal/mol) | NBO | Population |
|----------|-------|----------|-------------------------|-----|------------|
| 1H       | \(\pi\)C1-C2 | \(\pi^*\)C27-N29 | 23.58 | C1-C2 | 1.64983 |
| \(\pi\)C9-C11 | \(\pi^*\)C10-O23 | 20.87 | C9-C11 | 1.86448 |
| \(\sigma\)C11-H12 | \(\pi^*\)S8-C9 | 10.96 | C11-H12 | 1.95503 |
| \(\pi\)C32-C34 | \(\pi^*\)C37-C41 | 25.59 | C32-C34 | 1.51731 |
| \(\pi\)C35-C39 | \(\pi^*\)C36-C40 | 23.32 | C35-C39 | 1.50209 |
| LP (1) N6 | \(\pi^*\)C4-C5 | 33.88 | LP (1) N6 | 1.61488 |
| LP (1) N6 | \(\pi^*\)C10-O23 | 50.05 | LP (2) S8 | 1.73751 |
| LP (2) S8 | \(\pi^*\)C4-C5 | 23.87 | LP (1) O23 | 1.97186 |
| LP(1) O23 | RY*C10 | 14.14 | LP(2) O23 | 1.84468 |
| LP(2) O23 | \(\sigma^*\)N6-C10 | 26.81 | LP(1) N24 | 1.74481 |
| LP(2) O23 | \(\sigma^*\)C9-C10 | 18.74 | LP(1) N29 | 1.96851 |
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### Table 7. Theoretical and Experimental UV spectra of 1, calculated at CAM-B3LYP/6-311G (d, p).

| Compound | Donor | Acceptor | $E^{2a}$ (kcal/mol) | NBO | Population |
|----------|-------|----------|---------------------|-----|------------|
| 2CH3     | π*C10-C17 | π*C1-C2 | 51.82 | C1-C2 | 0.35144 |
|          | π*C7-C10 | π*C7-C21 | 16.62 | C31-C33 | 0.42571 |
|          | π*C9-C11 | π*C9-C11 | 19.00 | C10-O23 | 0.31646 |
|          | π*C10-023 | π*C9-C11 | 47.61 |       |            |
| 3OCH3    | π*C47-C49 | π*C46-C48 | 17.10 | C47-C49 | 1.76398 |
|          | π*C10-023 | π*C46-C48 | 50.19 | C47-C49 | 1.73776 |
|          | π*C10-023 | π*C46-C48 | 23.83 |       | 1.61466 |
|          | π*C10-023 | π*C46-C48 | 26.74 |       | 1.74631 |
|          | π*C10-023 | π*C46-C48 | 51.24 |       | 1.84501 |
|          | π*C10-023 | π*C46-C48 | 18.97 |       | 0.35064 |
|          | π*C10-023 | π*C46-C48 | 56.61 |       | 0.42485 |
|          | π*C10-023 | π*C46-C48 | 47.32 |       | 0.31674 |
| 4Cl      | π*C9-C11 | π*C9-C11 | 21.20 | C9-C11 | 1.86172 |
|          | π*C46-C48 | π*C46-C48 | 17.17 | C46-C48 | 1.76289 |
|          | π*C10-023 | π*C46-C48 | 34.75 |       | 1.61550 |
|          | π*C10-023 | π*C46-C48 | 49.64 |       | 1.73641 |
|          | π*C10-023 | π*C46-C48 | 24.15 |       | 1.74175 |
|          | π*C10-023 | π*C46-C48 | 52.68 |       | 1.92713 |
|          | π*C10-023 | π*C46-C48 | 12.42 |       | 0.35469 |
|          | π*C10-023 | π*C46-C48 | 18.84 |       | 0.42716 |
|          | π*C10-023 | π*C46-C48 | 56.71 |       | 0.31575 |
|          | π*C10-023 | π*C46-C48 | 47.19 |       | 0.37962 |
|          | π*C10-023 | π*C46-C48 | 206.92 |       | 0.34433 |
|          | π*C10-023 | π*C46-C48 | 249.52 |       | 0.31072 |

* $E^{2a}$ means energy of hyperconjugative interactions (stabilization energy). LP<sup>n</sup> is a valence lone pair orbital (n) on atom.

### Table 7. Continued.

| State | TD-Theoretical | Experimental |
|-------|----------------|--------------|
|       | Gas phase      | Acetone      | Xylene       |
|       | Configuration  | Coefficient  | $f$       | $\lambda$, nm | $E_{\text{max}}$, nm | $\lambda_{\text{max}}$, nm |
| I     | 125-126        | 0.694        | 0.412      | 403.8       | 125-126       | 0.692       | 0.494       | 414 |
|       | 120-126        | -0.15        | 0.115      | 310.7       | 123-126       | -0.398      | 0.291       | 311 |
|       | 123-126        | 0.026        | 0.126      | 124-126     | 0.486        |            |            |     |
|       | 123-127        | -0.016       | 0.098      | 124-127     | 0.215        |            |            |     |
|       | 124-126        | 0.010        | 0.018      | 125-127     | 0.185        |            |            |     |
|       | 118-127        | 0.117        | 0.399      | 251.5       | 122-126       | -0.267      | 0.952       | 256 |
|       | 119-126        | -0.25        | 0.125      | 123-127     | 0.363        |            |            |     |
|       | 122-126        | -0.14        | 0.127      | 123-128     | -0.27        |            |            |     |
|       | 123-127        | 0.472        | 0.142      | 124-128     | 0.227        |            |            |     |
|       | 123-128        | 0.17         | 0.095      | 125-129     | 0.205        |            |            |     |
|       | 124-128        | -0.22        | 0.009      | 125-129     | 0.267        |            |            |     |
| II    | 125-126        | 0.692        | 0.471      | 412         | 415          | 313         | 318         |     |
|       | 123-126        | 0.448        | 0.303      | 308         | 313          | 318         | 318         |     |
| state | TD-Theoretical | Experimental |
|-------|----------------|--------------|
|       | Acetone        | Acetone      | Xylene      |
|       | Configuration  | Coefficient  | f           | λ, nm | λ_{exp} | λ_{exp} |
| III   | 119-126        | 0.331        |             | 0.542 | 257     |         |
|       | 119-127        | 0.117        |             |        |         |         |
|       | 122-126        | 0.225        |             |        |         |         |
|       | 123-127        | 0.244        |             |        |         |         |
|       | 123-128        | 0.255        |             |        |         |         |
|       | 124-128        | 0.205        |             |        |         |         |
|       | 125-128        | 0.268        |             |        |         |         |
|       | 125-129        | 0.185        |             |        |         |         |

**Figure 8.** Electronic absorption spectra of 1, (a) theoretical in gas phase, (b) theoretical in acetone, (c) theoretical in xylene, (d) experimental in acetone, (e) experimental in xylene.

**Figure 9.** Theoretical transitions at TD-DFT B3LYP/6-311G (d, p) level of theory of (a) 9-vinylanthracene.
Figure 10. Theoretical transitions at TD-DFT B3LYP/6-311G (d, p) level of theory of (b) benzene.

Figure 11. Theoretical transitions at TD-DFT B3LYP/6-311G (d, p) level of theory of (c) 5-amino-3-oxo-3,7-dihydro-2H-thiazolo[3,2-a]pyridine-6,8-dicarbonitrile.
Figure 12. Theoretical transitions at TD-DFT B3LYP/6-311G (d, p) level of theory of compound 1 5-amino-2-(anthracen-9-ylmethylene)-3-oxo-7-phenyl-2,3-dihydro-7H thiazolo[3,2-a]pyridine-6,8-dicarbonitrile.
3.5.2. Electronic Absorption Spectra of Compound 2

Compound 2 results when our insertion of CH3 group in position X of Ph-X in compound 1. "Figure 14", and Table 8 elucidate the experimental and theoretical electronic absorption spectra of compound 2 in two solvents xylene and acetone. In non-polar solvent (xylene), the experimental spectrum is composed of two bands, at 417 nm, and 315 nm. The blue shift of the two bands, results from increasing solvent polarity from xylene to acetone where the first band is shifted to 414 nm, and the second band is shifted to 313 nm, respectively. Furthermore, The two observed bands are assigned as (π–π*) transitions, based on the values of molar absorptive (ε = 50000), due to, increasing solvent polarity causes a marked increase in the intensity of both bands. CAM / B3LYP/6-311G (d, p) level used for the interpretation of the experimentally observed UV Spectra of 2 in non-polar solvent (xylene) and polar-solvent (acetone) these requires the theoretical calculations of the vertical transitions. State (I) the non-polar solvent (xylene), shows the spectrum band experimentally at 417 nm is reproduced theoretically at 414 nm (state I), as shown in Table 8, which involves orbital's φ129 and φ130, showing a good agreement between the observed wavelength with the calculated wavelength. The gas phase calculations give a wavelength at 403 nm (state I). Increasing solvent polarity results in a blue shift of λmax of this band to 414 nm. The polar solvent (acetone) appeared theoretically band at 410 nm (state I). The second band observed experimentally in xylene at 315 nm, is reproduced theoretically at 311 nm (state II), indicating that the orbital's φ128 and φ130 are involved in this transition. Theoretical gas phase calculations give a wavelength at 309 nm (state II). This same band is observed at 313 nm in acetone, where theoretical calculations in acetone reproduces this band at 307 nm (state II), which is lower than the observed wavelength, where the orbital's φ127 and φ130 are involved in this transition. The third band theoretically in xylene at 257 nm, (state III), indicating that the orbital's φ127 and φ131 are involved in this transition. The six orbital's φ123, φ127, φ128, φ129, φ130 and φ131 involved in the theoretical transitions of 2, are shown in "Figure 13". The first band which involves φ129 and φ130 has electron density delocalization, while orbital's φ123, φ127, φ128 and φ131 have a Charge Transfer CT character. The results of NBO analysis of compound 2 tabulated in Table 6 indicate that there is a strong hyper conjugative interactions π*C9-C11 → π*C31-C33, LP (1) N24 → π*C7-C2, LP (1) N6 → π*C10-O23, π*C10-O23 → π*Cp-C11, LP (2) O23 → σ*N6-C10, LP (2) S8 → π*C5-C5, and π*C7-C2 → π*C7-O23, for 2 is 56.16, 51.24, 50.19, 47.32, 26.74, 23.83 and 18.97 kcal/mol, respectively. NBO analysis of the p-CH3 derivative Table 6 indicates that it retained the extended conjugation of 1 as revealed by the interaction of C–N NBOs with those of pyridine ring. Furthermore, the interaction of the nitrogen lone orbital's with the C10–O23, and C1–C2 π* orbital is marked. The population of the NBO C1–C2, C31–C33, and C10–O23 reflecting a charge transfer away from the thiazolo[3,2-a]pyridine ring. This is also evident in the case of the population of the nitrogen lone orbital LP (1) N6.

Figure 13. Electron density contours of the studied compounds 1-4.
Table 8. Theoretical and experimental UV spectra of 2, calculated at CAM-B3LYP/6–311G (d, p).

| state | TD-Theoretical | Experimental |
|-------|----------------|--------------|
|       | Gas phase      | Acetone      | Xylene       |
|       | Configutation  | Coefficient  | $\lambda$, nm | Configutation  | Coefficient  | $\lambda$, nm |
| I     | 129-130        | 0.694        | 0.418         | 403          | 129-130        | 0.692        | 0.500         | 414          |
|       | 124-130        | -0.10        | 0.136         | 309          | 126-130        | -0.113       | 0.288         | 311          |
|       | 126-130        | 0.265        | 127-130       | -0.416       | 128-130        | 0.433        | 129-131       | 0.204        |
|       | 127-131        | 0.15-         | 128-131       | 0.199        | 129-131        | 0.199        |
| II    | 122-131        | 0.11-         | 123-130       | 0.183        | 127-131        | 0.376        | 253           | 0.976        | 257          |
|       | 123-130        | -0.34         | 125-130       | 0.282        | 126-130        | 0.131        | 127-131       | 0.314        |
|       | 125-130        | -0.14         | 126-131       | 0.105        | 127-131        | 0.140        |
|       | 126-131        | 0.131         | 127-131       | 0.314        | 128-131        | 0.193        |
|       | 127-132        | 0.410         | 127-132       | 0.257-        | 128-132        | -0.17        | 129-132       | -0.190        |
|       | 128-132        | 0.22-         | 129-132       | -0.230        | 129-133        | 0.11-         |
|       | 129-133        | 0.11-         | 129-133       | 0.263        |

Table 8. Continued.

| state | TD-Theoretical | Experimental |
|-------|----------------|--------------|
|       | Acetone      | Xylene       |
|       | Configutation  | Coefficient  | $\lambda$, nm | Configutation  | Coefficient  | $\lambda$, nm |
| I     | 129-130        | 0.692        | 0.473         | 410          | 129-133        | 0.191        |
|       | 125-130        | 0.145-        | 0.305         | 307          | 123-131        | 0.198        |
|       | 127-130        | 0.468         | 0.389-        | 313          | 129-131        | 0.226-        |
|       | 127-131        | 0.147-        | 0.389-        | 315          | 129-132        | -0.190        |
|       | 128-130        | 0.193-        | 128-131       | -0.17        | 129-132        | 0.191        |
|       | 128-132        | 0.193-        | 129-132       | 0.225        |
| II    | 123-130        | 0.401         | 123-131       | -0.136       |
|       | 123-131        | -0.136        | 126-130       | 0.225        |
|       | 126-130        | 0.225         | 127-131       | 0.198        |
|       | 127-130        | 0.226-        |
|       | 127-132        | 0.226-        |
|       | 128-132        | -0.190        |
|       | 129-132        | -0.225        |
| III   | 129-133        | 0.191         |

Figure 14. Electronic absorption spectra of 2, (a) theoretical in gas phase, (b) theoretical in acetone, (c) theoretical in xylene, (d) experimental in acetone, (e) experimental in xylene.

3.5.3. Electronic Absorption Spectra of Compound 3

To complete our investigation of substituent effect on the electronic structure and spectra of compound 1, we introduce OCH3-group in position X in Ph-X of compound 1 gives compound 3. The experimental and theoretical electronic
absorption spectra of compound 3 in xylene and acetone are shown in "Figure 15", and Table 9. The experimental spectrum in xylene is composed of two bands at 419 nm, and 316 nm. The change of solvent polarity from xylene to acetone results in a blue shift of the two bands, where the first band is shifted to 416 nm, and the second band is shifted to 313 nm, respectively. Furthermore, increasing solvent polarity causes a marked increase in the intensity of both bands. The values of molar absorptive (ε = 45000) indicates that the two observed bands have π–π* character. The theoretical vertical transitions using CAM / B3LYP / 6-311G (d, p) level is valuable for the analysis of the experimental UV Spectra of 3 in xylene and acetone, which gives values for λ_{max} of 415 nm (state I) for the first band, 311 nm (state II) for the second band, 258 nm (state III) for the third band, as shown in Table 9. Theoretical transitions in the gas phase give a vertical excitation at 404 nm (state I), which is about 15 nm lower than the experimental wavelength, where it involves the same orbitals as in xylene. Theoretical vertical excitation calculations in acetone give λ_{max} of this band at 411 nm (state I), which shows a fair agreement, implying that the orbitals involved in this transition are φ_{131} and φ_{134}. The experimental second band observed at 316 nm in xylene, is reproduced theoretically at 311 nm (state II), where the calculations in xylene indicate that the orbital’s φ_{131} and φ_{134} are involved in this transition. Gas phase calculations give λ_{max} at 311 nm (state II). Theoretical calculations in acetone show that, this band appears at 308 nm (state II), which is lower than the experimental wavelength. The third state (π–π*) is theoretically at 258 nm in xylene, (state III), where the calculations in xylene indicate that the orbitals’ φ_{127} and φ_{134} are involved in this transition. Gas phase calculations give λ_{max} at 258 nm (state III). Theoretical calculations in acetone show that, this band appears at 253 nm (state III). The four orbital’s φ_{127}, φ_{131}, φ_{133} and φ_{134} involved in the theoretical transitions of 3, are shown in "Figure 13". where the first band which involves φ_{127} and φ_{134}, show a CT character, while orbitals’ φ_{131} and φ_{134} & φ_{127} and φ_{134} involved in the second, and third bands show electron density delocalization and also a CT character. The results of NBO analysis of compound 3 tabulated in Table 6 indicate that there is a strong hyper conjugative interactions π*C_{31}→π*C_{33}, LP (1) N_{24}→π*C_{1}→C_{2}, LP (1) N_{6}→π*C_{10}→O_{23}, π*C_{10}→O_{23}→π*C_{2}→C_{5}, LP (1) N_{6}→π*C_{2}→C_{5}, LP (2) O_{34}→σ*C_{18}→C_{20} and LP (2) S_{11}→π*C_{3}→C_{5}, for 3 is 58.44, 50.97, 50.36, 47.88, 33.65, 31.04 and 23.66 kcal/mol, respectively. NBO analysis of the p-OCH3 derivative Table 6 indicates that it retained the extended conjugation of 1 as revealed by the interaction of C–N NBOs with those of pyridine ring. Furthermore, the interaction of the oxygen lone orbital’s with the C18–C20 σ*orbital is marked. The population of the NBO C1–C2, C31–C33, and C10–O23 reflecting a charge transfer away from the thiazolo[3,2-a]pyridine ring.

Table 9. Theoretical and experimental UV spectra of 3, calculated at CAM-B3LYP/6–311G (d, p).

| state | TD-Theoretical | Xylene | | | | | | |
|-------|----------------|--------|-------|-------|-------|-------|-------|-------|
|       | Config | Coefficient | f | λ, nm | Config | Coefficient | f | λ, nm |
| I     | 133-134 | 0.694 | 0.425 | 404 | 133-134 | 0.692 | 0.508 | 415 |
| II    | 130-134 | 0.407 | 0.193 | 311 | 130-134 | 0.357 | 0.284 | 311 |
|       | 131-134 | 0.473 |       |     | 131-134 | 0.504 |       |     |
|       | 133-135 | 0.145 |       |     | 133-135 | 0.175 |       |     |
|       | 127-134 | 0.222 |       |     | 127-134 | 0.223 |       |     |
|       | 130-135 | 0.313 | 0.286 | 258 | 130-135 | 0.486 | 0.568 | 258 |
| III   | 130-136 | -0.31 |       |     | 130-136 | -0.199 |       |     |
|       | 131-135 | 0.21 |       |     | 131-135 | 0.177 |       |     |
|       | 132-134 | 0.191 |       |     | 132-134 | 0.113 |       |     |
|       | 132-135 | -0.21 |       |     | 132-135 | 0.25 |       |     |
|       | 132-136 | 0.321 |       |     | 132-136 | 0.25 |       |     |
|       | 133-136 | -0.11 |       |     | 133-136 | 0.25 |       |     |

Table 9. Continue.

| state | TD-Theoretical | Experimental | | | | | |
|-------|----------------|--------------|-------|-------|-------|-------|-------|
|       | Config | Coefficient | f | λ, nm | λ_{max} | λ_{max} |
| I     | 133-134 | 0.692 | 0.480 | 411 | 416 | 419 |
| II    | 130-134 | 0.358 | 0.301 | 308 | 313 | 316 |
|       | 131-134 | 0.520 |       |     |     |     |
|       | 131-135 | 0.179 |       |     |     |     |
|       | 133-135 | 0.162 |       |     |     |     |
|       | 127-134 | -0.261 | 0.534 | 253 |     |     |
|       | 129-134 | 0.372 |       |     |     |     |
| III   | 130-139 | 0.157 |       |     |     |     |
|       | 131-139 | 0.139 |       |     |     |     |
|       | 133-137 | 0.41 |       |     |     |     |
3.5.4. Electronic Absorption Spectra of Compound 4

Compound 4 results by inserting Cl-atom in position X in Ph-X of compound 1. The experimental and theoretical electronic absorption spectra of compound 4 in xylene and acetone are shown in "Figure 16", and Table 10. The experimental spectrum in xylene is composed of two bands at 420 nm, and 314 nm. The change of solvent polarity from xylene to acetone results in a small red shift by 3 nm of the first band, and the second band red shift by 4 nm. Additionally, increasing solvent polarity causes a marked decrease in the intensity of both bands. The values of molar absorptive (ε = 45000) indicates that the two observed bands have π–π* character. The theoretical vertical transitions using CAM / B3LYP/6-311G (d, p) level is valuable for the analysis of the experimental UV Spectra of 4 in xylene and acetone, which gives values for λ_{max} of 419 nm (state I) for the first band, 311 nm (state II) for the second band, and 258 nm (state III) for the third band as shown in Table 10. The theoretical transition of the first band in xylene involves orbitals φ_{131} and φ_{134}, showing a good agreement between the observed and the calculated wavelengths. Theoretical transitions in the gas phase give a vertical excitation at 407 nm (state I), which is about 13 nm lower than the experimental wavelength, where it involves the same orbitals as in xylene. Theoretical vertical excitation calculations in acetone give λ_{max} of this band at 415 nm (state I), which shows a fair agreement, implying that the orbitals involved in this transition are φ_{131} and φ_{134}. The experimental second band observed at 314 nm in xylene, is reproduced theoretically at 311 nm (state II), where the calculations in xylene indicate that the orbital's φ_{131} and φ_{134} are involved in this transition. Gas phase calculations give λ_{max} at 311 nm (state II). Theoretical calculations in acetone show that, this band appears at 308 nm (state II), which is lower than the experimental wavelength. Theoretical gas phase wavelength is found to be lower than the observed wavelength in acetone. The third state (π–π*) which theoretically at 258 nm in xylene, (state III), where the calculations in xylene indicate that the orbital's φ_{131} and φ_{135} are involved in this transition. Gas phase calculations give λ_{max} at 253 nm (state III). Theoretical calculations in acetone show that, this band appears at 254 nm (state III). It shows that the orbitals involved in the transition are φ_{131} and φ_{135}. The five orbital's φ_{131}, φ_{133}, φ_{134}, φ_{135} and φ_{137} involved in the theoretical transitions of 4, are shown in "Figure 13", where the first band which involves φ_{133} and φ_{134}, show a CT character, while orbital's φ_{131} and φ_{135} & φ_{131} and φ_{134}& φ_{133} and φ_{137} involved in the second and third bands show electron density delocalization and also CT character. The results of NBO analysis of compound 4 tabulated in Table 6 indicate that there is a strong hyper conjugative interactions π*C_{10}–C_{19} → π*C_{15}–C_{16}, π*C_{5}–C_{11} → π*C_{30}–C_{32}, LP (1) N_{23} → π*C_{1}–C_{2}, LP (1) N_{5} → π*C_{10}–O_{22}, π*C_{10}–O_{22} → π*C_{30}–C_{31}, LP (1) N_{6} → π*C_{7}–C_{5} and LP (2) S_{8} → π*C_{4}–C_{5}, for 4 is 249.52, 56.71, 52.68, 49.64, 47.19, 34.25, and 24.15 kcal/mol, respectively. NBO analysis of the p-CI derivative Table 6 indicates that it retained the extended conjugation of 1 as revealed by the interaction of C–Cl NBOs with those of phenyl ring. Furthermore, the interaction of the chloro lone orbital's with the C30–C32 σ*orbital is marked. The population of the NBO C15–C18, C10–O22, C13–C14, C1–C2, C16–C19, and C30–C32 reflecting a charge transfer away from the thiazolo[3,2-a]pyridine ring.

![Figure 15. Electronic absorption spectra of 3, (a) theoretical in gas phase, (b) theoretical in acetone, (c) theoretical in xylene, (d) experimental in acetone, (e) experimental in xylene.](image)

Table 10. Theoretical and experimental UV spectra of 4, calculated at CAM-B3LYP/6–311G (d, p).

| Config | Coefficient | f | \( \lambda_{\text{nm}} \) | Coefficient | f | \( \lambda_{\text{nm}} \) |
|--------|-------------|---|----------------|-------------|---|----------------|
| \text{I} | \text{III} | \text{I} | \text{III} | \text{I} | \text{III} | \text{I} |
| 131-134 | 0.694 | 0.420 | 407 | 133-134 | 0.692 | 0.509 | 419 |
| 131-134 | -0.24 | 0.165 | 311 | 129-134 | 0.120 | 0.325 | 311 |
| 132-134 | 0.569 | 131-134 | 0.468 |
| 132-135 | 0.267 | 132-134 | 0.406- |
| 133-135 | 0.150 | 132-135 | 0.176- |
| 133-135 | -0.167 | 133-135 | -0.167- |

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| State | TD-Theoretical | Experimental |
|-------|----------------|--------------|
|       | Gas phase      | Acetone      | Xylene      |
|       | Configuration  | Coefficient  | f           | λ, nm | Configuration  | Coefficient  | f       | λ, nm |
| III   | 126-135        | 0.10-         | 0.521       | 253   | 130-134        | 0.227         | 0.869   | 258   |
|       | 127-134        | 0.144         |             |       |                |               |         |       |
|       | 129-134        | -0.160        |             |       |                |               |         |       |
|       | 130-135        | 0.132         |             |       |                |               |         |       |
|       | 131-135        | 0.415         |             |       |                |               |         |       |
|       | 131-136        | -0.250        |             |       |                |               |         |       |
|       | 132-136        | 0.25-          |             |       |                |               |         |       |
|       | 133-136        | 0.21-          |             |       |                |               |         |       |
|       | 133-137        | 0.126         |             |       |                |               |         |       |

Table 10. Continued.

| State | Acetone | Xylene |
|-------|---------|--------|
|       | Configuration | Coefficient | f | λ, nm | Configuration | Coefficient | f | λ, nm |
| I     | 133-134 | 0.692 | 0.483 | 415 | 423 | 420 |
|       | 129-134 | 0.103 | 0.312 | 308 |
|       | 131-134 | 0.485 |       |     |
|       | 131-135 | 0.103 |       |     |
|       | 132-134 | -0.389 |       |     |
|       | 132-135 | -0.188 |       |     |
|       | 133-135 | -0.133 |       |     |
| II    | 128-134 | 0.256- | 0.539 | 254 |
|       | 130-134 | 0.383 |       |     |
|       | 130-135 | 0.112 |       |     |
|       | 131-140 | 0.167- |       |     |
|       | 133-136 | -0.138 |       |     |
|       | 133-137 | 0.414 |       |     |

Figure 16. Electronic absorption spectra of 4, (a) theoretical in gas phase, (b) theoretical in acetone, (c) theoretical in xylene, (d) experimental in acetone, (e) experimental in xylene.

3.6. Summary and Conclusion

The optimized electronic structure of 5-amino-2-(anthracen-9-ylmethylene)-3-oxo-7-phenyl-2,3-dihydro-7H-thiazolo[3,2-a]pyridine-6,8-dicarbonitrile, compound 1 and its derivatives, 2–4, are investigated theoretically at B3LYP/6-311G (d, p). All the studied compounds are found to be non-planar. The dihedral angles results show that the phenyl at C3 and the anthranyl at C9 are out of the molecular plane of thiazolo[3,2-a]pyridines by 111° and 128° respectively, resulting in a significant impact on the electronic and structural properties of compounds 1–4. The ground state properties of 1 and its derivatives show that compound 4 has the lowest $E_{\text{HOMO}}$, $E_{\text{LUMO}}$, and Egap indicating highest reactivity. From the computed dipole moment, compound 3 is found to have the highest polarity. The HOMO-LUMO energy gap helped in analyzing the chemical reactivity, hardness, softness, chemical potential and electro negativity. The natural charge distribution of the compounds 1–4 were studied. The non-linear optical indicating from the values of calculated dipole moment and first order hyperpolarizability.
The total electron density surface with MEP confirmed the different negative and positive potential sites of the molecule. Electronic absorption spectra are investigated experimentally in non-polar solvent (xylene) and polar solvent (acetone); and theoretically in gas phase, xylene and acetone using CAM-B3LYP/6-311G (d, p). The band maxima ($\lambda_{\text{max}}$) and intensities of the spectra are found to have solvent dependence. The bands of compounds 1, 2, and 3 show blue shift, while compounds 4 show red shift. Theoretical calculations of the vertical excitations at the CAM-B3LYP/6-311G (d, p) reproduce the experimental spectra, indicating a good agreement between theory and experiment. The NBO analysis of the compounds 1–4 indicated the intermolecular charge transfer between the bonding and antibonding orbital's.

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