Structural and solvent dependence on the molecular and nonlinear optical properties of 10-octyl thiophene-based phenothiazine and substituted derivatives – a theoretical approach

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ABSTRACT

This work presents an investigation on the structural and solvent dependence on the molecular, electronic and nonlinear optical properties of some conjugated organic molecules based on phenothiazine units using quantum chemical calculations with pure BLYP and hybrid B3LYP correlation with a high polar basis set, 6–31G\(^*\) in the gas-phase and in solutions towards understanding their structure–property relationship. The ground state molecular properties like the frontier orbitals (FMOs) energies, dipole moments (\(\mu\)), polarizabilities (\(\alpha\)), molecular first hyperpolarizabilities (\(\beta\)) were obtained. The results showed that the insertion of substituents enhanced molecular properties like the optical limiting abilities. It was also observed that the energy band gap (\(E_g\)), derived from the FMOs were reduced while \(\mu\), \(\alpha\) and \(\beta\) increased. The \(\lambda_{\text{max}}\) of the substituted derivatives are higher than the unsubstituted 10-octyl thiophene-based phenothiazine and results obtained are in good agreement with available experimental findings. The substituted derivatives proved to possess better optical responses than the unsubstituted derivative on the basis of the properties analysed.

1. Introduction

Conjugated organic molecules with a donor part on a side and an acceptor part on the other side (D–A) configuration have been studied intensively owing to their important applications in photovoltaic and optoelectronic applications such as batteries and inverters [1], electroluminescence applications like in light-emitting diodes [2,3], optical limiting applications like nonlinear optical (NLO) devices [4–6]. Their optical limiting potentials are important as they serve as a protective shield to sensors and the human eyes from intense laser beams [7,8]. Many researchers have reported conjugated organic materials for their NLO functions through processes like two- or multi-photon absorption, 2PA/mPA [9,10], reverse saturable absorption, RSA [11], nonlinear scattering, NLS [12] and so on. Materials could exhibit one or more of these processes. Usually, these compounds exhibit large dipole moments (\(\mu\)) [13], polarizabilities (\(\alpha\)) and molecular first hyperpolarizabilities (\(\beta\)) [14]. The search for excellent NLO materials requires the full understanding of NLO processes as a function of electronic and geometrical structures. Some changes (brought about by the effect of substituents and/or solvents) in the molecular structure can lead to variations in the electronic and molecular properties such as the energy band gap (\(E_g\)); which is derived from the energies of the frontier molecular orbitals, \(\mu\), \(\alpha\), \(\beta\) and so on [15–17].

The molecular beam methods [18,19], collision-induced scattering of light [20–22], Kerr-effect experiments [23,24], third-harmonic generation techniques, THG [25–27] and electric field-induced second harmonic generation experiments, EFISHG [28–30] have been used to determine molecular polarizabilities and hyperpolarizabilities. Molecular properties have been studied by means of quantum chemical methods. Different methods have been used to predict the impact of these properties in certain chemical phenomena like optical limiting technology. Determining polarizabilities and hyperpolarizabilities of molecules is very important in explaining their NLO properties, theoretically and usually in the gas phase. Density functional theory (DFT) programs have been employed in calculating molecular polarizabilities and hyperpolarizabilities [19,31–33], either with the finite field approach or with Kohn–Sham method [19,32,33]. The B3LYP exchange correlation, in past and recent times, has been reported to predict and investigate the electronic properties of \(\pi\)-conjugated organic molecules [15,16,34]. Nonetheless, the pure BLYP, although least
explored, has been considered as a comparative option to predict molecular behaviours. Hence, both were chosen in order to validate which of them is broadly consistent with available experimental results. In this study, the structural and solvent dependence on the molecular, electronic and NLO properties of some π-conjugated organic molecules based on phenothiazine units were investigated using quantum chemical DFT calculations with pure BLYP and hybrid B3LYP correlation with a high polar basis set, 6-31G* in vacuum, acetone and tetrahydrofuran (THF) towards understanding their structure–property relationship.

2. Computational details

Quantum mechanical investigations were carried out on 10-OTBP (Figure 1) and its substituted analogues with computational chemistry software on intel® Core (TM) i5-3317U CPU @1.70 GHz 1.70 Hz computer with the ab initio restricted pure BLYP and hybrid DFT and the time-dependent DFT [32,33], B3LYP exchange-correlation method with 6-31G* basis set, all implemented on Spartan 14 software package [35]. The DFT calculations were carried out in vacuum and in different solvent media like acetone (ε = 20.7) and Tetrahydrofuran, THF (ε = 7.58). Structural optimization was done without any constraints. Some experimental data for unsubstituted 10-OTBP and –CN substituted analogue are available and were compared with theoretical values. It was observed that the theoretical methods employed correlated well with experimental observations. Such method(s) were employed in understanding structure–property relationships of other molecules.

The energy band gaps (Eg) were all obtained from the $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ values (the difference between $E_{\text{LUMO}}$ and $E_{\text{HOMO}}$) while the chemical hardness ($\eta$) is half of $E_g$ value and softness is the inverse of $\eta$ [15,16]. Molecular parameters like the polarizabilities and hyperpolarizabilities were calculated. The polarizability of a molecule is related to its dipole moment by:

$$\mu = \alpha \varepsilon,$$

where $\alpha$ is the polarizability, $\mu$ is the dipole moment and $\varepsilon$ is the electric field strength. $\mu$ and $\alpha$ usually increase with a decrease in $E_g$ values [15,16,36]. The dipole moment is necessary in order to understand the intermolecular interactions and is found to increase with a decrease in the $E_g$ values of molecular systems [15,16].

The molecular first hyperpolarizability ($\beta$) is a third-rank tensor that is described by a $3 \times 3 \times 3$ matrix from a reduced 27 components of the 3D matrix which becomes 10 components owing to Kleimann symmetry [37] and is given by:

$$\beta_{\text{eff}} = \left[ (\beta_{xxx} + \beta_{xyy} + \beta_{xzz} )^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx} )^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy} )^2 \right]^{1/2}. $$

The second-order susceptibility of an NLO material, $\chi^2$ strongly depends on $\beta_{\text{eff}}$ value. $\beta_{\text{eff}}$ value increases with reduced $E_g$ values and increased $\alpha$ values [34].

The molecules were optimized using these two functionals, the BLYP functional is based purely on DFT approximations while the B3LYP is a hybrid of the HF (20%) and DFT methods.

The control of the band gap of π-conjugated systems is important for synthetic chemists in the area of organic conductors. The bond length alternation (BLA) parameter was used to characterize the alternation of single or double carbon–carbon bonds within the ring moieties [38,39]. It is the difference between the average length of single and double bond, $\delta r$. The relaxation of BLA is always accompanied with reduction in band gap of molecules [40]. It has been used as a structural parameter that can be manipulated for better NLO responses as it directly quantifies the ground state polarization [41].

$$\text{BLA} = \sum \frac{|d_i - d_j|}{N}.$$  

3. Results and discussion

3.1. Geometric parameters

The geometric and electronic structure of 10-OTBP is used as a reference while the properties of other substituted analogues were compared with its properties (Figure 2). For all molecules, molecular geometries were obtained after total optimization with BLYP and B3LYP/6-31G*.
The reference molecule (R=H) has C12–C8 as 1.401 Å, C8–C11 as 1.406 Å, C8–C14 as 1.466 Å, C14–C15 as 1.377 Å, C15–C16 as 1.425 Å, C16–C17 as 1.367 Å, C17–S2 as 1.735 Å and C17–H18 as 1.082 Å. These bonds were selected because it is from the area of substitution. The bonds are the same from other thiophene side; hence there is no need to repeat the bonds since they are of the same values and are recorded with their BLA values. Optimized NLO responses of a given molecule can be achieved by distorting (which is usually controlled by adjusting the strength of the donor and acceptor substituents and solvent polarity) the conjugation bridge from a polyenic-like structure towards a partially ionic cyanine-like structure that is fully delocalized. It has been established that solvents have a great influence on the structure and electronic properties of organic materials with extended π-conjugation [15,16]. The BLA in equation 1.03, is the average distance in length between adjacent bonds in the conjugation pathway. In order to account for the medium effects on the molecular geometry and optical properties, the molecules were subjected to DFT calculations in acetone (ε = 20.7) and THF (ε = 7.58). The BLA of the substituted analogues were minimized as compared to the standard molecule. This is an indication that the substituted analogues might possess promising NLO properties than the standard, subject to further findings. Other results like the polarizability, dihedral angles, hyperpolarizability, UV-vis absorption, band gap, will establish fully if these materials are better than the unsubstituted 10-OTBP. This is in line with what some researchers observed in their work.

The type of donor and acceptor substituents affect the extent and efficiency of nonlinearity as seen in Tables 1 and 2 and Figure 2(a,b), the substituted derivatives minimized the BLA. This definitely will have great effect on the molecular linear and NLO behaviours. This is what is also observed in acetone and THF. The existence of strong intramolecular charge transfer excitations in a non-centrosymmetric molecule is paramount in explaining their NLO responses [31]. It has been established from literature that the polarizabilities and hyperpolarizabilities of molecules, together with their dipole moments increase as the HOMO–LUMO band gaps decrease [15,16,34].

$E_g$ decreases with increasing angle twists; this observation is seen in the dihedral angles (supplementary materials), all molecules are planar i.e. their angles are close to either 0 or 180° (0 ± 10 is cis-planar while 180 ± 10 is trans-planar), however, all substituted molecules are twisted from their positions when compared to their unsubstituted analogues, a phenomenon also observed in solvents, that

### Table 1. Selected bond lengths and BLA in (Å) of 10-OTBP and substituted analogues with B3LYP/6-31G* in vacuum, acetone (ε = 20.7) and THF (ε = 7.58).

| Molecules   | C12–C8 | C8–C11 | C8–C14 | C14–C15 | C15–C16 | C16–C17 | C17–S2 | C17–H18 | BLA(Å) |
|-------------|--------|--------|--------|---------|---------|---------|--------|---------|--------|
| **Vacuum**  |        |        |        |         |         |         |        |         |        |
| R=H         | 1.401  | 1.406  | 1.466  | 1.377   | 1.425   | 1.367   | 1.735  | 1.082   | 0.269  |
| 2-NO₂       | 1.402  | 1.407  | 1.462  | 1.386   | 1.412   | 1.373   | 1.737  | 1.429   | 0.199  |
| 2-CN        | 1.401  | 1.406  | 1.464  | 1.382   | 1.414   | 1.380   | 1.752  | 1.414   | 0.209  |
| 2-CHO       | 1.401  | 1.406  | 1.463  | 1.386   | 1.411   | 1.380   | 1.750  | 1.460   | 0.201  |
| 2-CH=C(CN)COOH | 1.402 | 1.407 | 1.460 | 1.389 | 1.405 | 1.392 | 1.769 | 1.429 | 0.210 |
| **Acetone** |        |        |        |         |         |         |        |         |        |
| R=H         | 1.402  | 1.407  | 1.466  | 1.377   | 1.425   | 1.367   | 1.735  | 1.082   | 0.269  |
| 2-NO₂       | 1.403  | 1.408  | 1.460  | 1.390   | 1.410   | 1.378   | 1.740  | 1.415   | 0.209  |
| 2-CN        | 1.401  | 1.406  | 1.464  | 1.384   | 1.410   | 1.383   | 1.753  | 1.406   | 0.210  |
| 2-CHO       | 1.401  | 1.406  | 1.464  | 1.387   | 1.408   | 1.382   | 1.750  | 1.452   | 0.201  |
| 2-CH=C(CN)COOH | 1.403 | 1.408 | 1.459 | 1.393 | 1.400 | 1.396 | 1.763 | 1.418 | 0.208 |
| **THF**     |        |        |        |         |         |         |        |         |        |
| R=H         | 1.403  | 1.407  | 1.467  | 1.376   | 1.424   | 1.366   | 1.736  | 1.082   | 0.269  |
| 2-NO₂       | 1.404  | 1.408  | 1.461  | 1.389   | 1.407   | 1.377   | 1.740  | 1.415   | 0.200  |
| 2-CN        | 1.403  | 1.407  | 1.463  | 1.383   | 1.411   | 1.381   | 1.753  | 1.407   | 0.209  |
| 2-CHO       | 1.403  | 1.407  | 1.464  | 1.387   | 1.408   | 1.381   | 1.751  | 1.453   | 0.201  |
| 2-CH=C(CN)COOH | 1.404 | 1.409 | 1.459 | 1.392 | 1.401 | 1.395 | 1.763 | 1.420 | 0.208 |

Figure 2. (a) The BLA of 10-OTBP with B3LYP/6-31G*. (b) The BLA of 10-OTBP with BLYP/6-31G*. 

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is, the molecules have better degree for internal rotation in solutions. That is to say that substituents and solvents can affect the internal rotation of molecules. $E_g$ is therefore, expected to be altered with substitution and in solutions. This may be due to the increased steric and inductive effects as hyper-conjugation is always affected by the insertion of different substituent group(s). Consequently, the substituted derivatives are expected to possess higher dipole moments ($\mu$), polarizabilities ($\alpha$) and hyperpolarizabilities ($\beta$). In nonlinear materials, the systems consist of net permanent dipole moment, that is, they are non-centrosymmetric.

### 3.2. Frontier orbital energies

Apart from the results obtained earlier, that is, the BLA and dihedral angles, it is important to investigate the electronic properties. Theoretical analysis began with optimization using the electron correlation of the pure BLYP and hybrid B3LYP at the 6-31G* basis set for all systems under investigation. To compare the NLO properties of a series of similar molecules, $E_g$ must differ, to ascertain a difference in their intra-molecular charge transfer (ICT). Molecules that possess lower $E_g$ values might exhibit large second harmonic generation (SHG) efficiency because charge transfer tends to be easier to be confirmed by $\beta$ values. The two molecular orbitals must overlap in the middle region of the electron density, for efficient charge transfer, that is, $E_g$ values determine level of charge transfer and also possess large $\mu$, $\alpha$ and $\beta$ values.

Both methods used afford a comparison between the results obtained and see if they also follow the same trend and which is closer to experimental data. From Tables 3 and 4 and Figure 3(a,b), the experimental $E_g$ for $R=H$ (unsubstituted 10-OTBP) was found to be 2.89 eV in vacuum and 2.86 eV in THF solution [42]. Its B3LYP $E_g$ value is 3.65 eV in vacuum and 3.54 eV in THF, respectively.

#### Table 2. Selected bond lengths and BLA in (Å) of 10-OTBP and substituted analogues with BLYP/6-31G* in vacuum, acetone ($\varepsilon = 20.7$) and THF ($\varepsilon = 7.58$).

| Molecules | $C_{12}$$-$$C_8$ | $C_8$$-$$C_{11}$ | $C_8$$-$$C_{14}$ | $C_{14}$$-$$C_{15}$ | $C_{15}$$-$$C_{16}$ | $C_{16}$$-$$C_{17}$ | $C_{17}$$-$$S_2$ | $C_{17}$$-$$H_{18}$ | BLA (Å) |
|-----------|------------------|------------------|------------------|------------------|------------------|------------------|----------------|----------------|---------|
| $R=H$     | 1.413            | 1.419            | 1.470            | 1.390            | 1.431            | 1.379            | 1.753           | 1.089          | 0.267   |
| 2-NO$_2$  | 1.414            | 1.420            | 1.467            | 1.401            | 1.418            | 1.386            | 1.755           | 1.439          | 0.199   |
| 2-CN      | 1.413            | 1.421            | 1.469            | 1.394            | 1.420            | 1.393            | 1.774           | 1.416          | 0.212   |
| 2-CHO     | 1.415            | 1.420            | 1.468            | 1.400            | 1.416            | 1.393            | 1.773           | 1.466          | 0.203   |
| 2-CH=$=$C(CN)COOH | 1.416 | 1.421         | 1.465            | 1.403            | 1.411            | 1.405            | 1.785           | 1.430          | 0.212   |
| $R=H$     | 1.414            | 1.420            | 1.471            | 1.389            | 1.431            | 1.378            | 1.754           | 1.089          | 0.269   |
| 2-NO$_2$  | 1.415            | 1.421            | 1.462            | 1.404            | 1.411            | 1.389            | 1.76            | 1.422          | 0.199   |
| 2-CN      | 1.417            | 1.42            | 1.467            | 1.397            | 1.415            | 1.395            | 1.776           | 1.407          | 0.213   |
| 2-CHO     | 1.416            | 1.420            | 1.466            | 1.402            | 1.412            | 1.394            | 1.773           | 1.456          | 0.204   |
| 2-CH=$=$C(CN)COOH | 1.417 | 1.422        | 1.461            | 1.408            | 1.404            | 1.406            | 1.786           | 1.421          | 0.213   |
| $R=H$     | 1.414            | 1.42            | 1.471            | 1.389            | 1.431            | 1.378            | 1.754           | 1.089          | 0.269   |
| 2-NO$_2$  | 1.416            | 1.421            | 1.463            | 1.403            | 1.412            | 1.391            | 1.76            | 1.424          | 0.200   |
| 2-CN      | 1.415            | 1.42            | 1.467            | 1.396            | 1.416            | 1.396            | 1.776           | 1.408          | 0.213   |
| 2-CHO     | 1.416            | 1.42            | 1.467            | 1.401            | 1.413            | 1.396            | 1.774           | 1.457          | 0.204   |
| 2-CH=$=$C(CN)COOH | 1.416 | 1.421       | 1.465            | 1.403            | 1.411            | 1.405            | 1.785           | 1.43           | 0.212   |

#### Table 3. Electronic properties of 10-OTBP and substituted analogues with B3LYP/6-31G* in vacuum, acetone ($\varepsilon = 20.7$) and THF ($\varepsilon = 7.58$).

| Molecules | $\varepsilon_{\text{LUMO}}$ (eV) | $\varepsilon_{\text{KMO}}$ (eV) | $\theta$ (eV) | $A$ (eV) | $E_g$ (eV) | $\eta$ (eV) | $S$ (eV$^{-1}$) |
|-----------|-------------------------------|-------------------------------|-------------|---------|-----------|-----------|-------------|
| $R=H$     | −1.17                         | −4.82                         | 4.82        | 1.17    | 3.65 (2.89) | 1.83      | 0.55        |
| 2-NO$_2$  | −2.80                         | −5.54                         | 5.54        | 2.80    | 2.64      | 1.32      | 0.75        |
| 2-CN      | −2.15                         | −5.39                         | 5.39        | 2.15    | 3.24      | 1.62      | 0.62        |
| 2-CHO     | −2.21                         | −5.27                         | 5.27        | 2.21    | 3.06 (2.48) | 1.53      | 0.65        |
| 2-CH=$=$C(CN)COOH | −2.84  | −5.41         | 5.41        | 2.84    | 2.57      | 1.29      | 0.78        |
| $R=H$     | −1.23                         | −4.80                         | 4.80        | 1.23    | 3.57      | 1.79      | 0.56        |
| 2-NO$_2$  | −2.73                         | −5.04                         | 5.04        | 2.00    | 3.04      | 1.52      | 0.66        |
| 2-CN      | −2.11                         | −4.95                         | 4.95        | 2.11    | 2.84      | 1.42      | 0.70        |
| 2-CHO     | −2.73                         | −4.89                         | 4.89        | 2.73    | 2.16      | 1.08      | 0.93        |
| 2-CH=$=$C(CN)COOH | −2.73  | −4.94         | 4.94        | 2.73    | 2.21      | 1.11      | 0.90        |

Note: Experimental results in brackets [42].
Table 4. Electronic properties of 10-OTBP and substituted analogues with BLYP/6-31G* in vacuum, acetone ($\varepsilon = 20.7$) and THF ($\varepsilon = 7.58$).

| Molecules          | $E_{\text{LUMO}}$ (eV) | $E_{\text{HOMO}}$ (eV) | $I$ (eV) | $A$ (eV) | $E_g$ (eV) | $\eta$ (eV) | $S$ (eV$^{-1}$) |
|--------------------|------------------------|------------------------|---------|---------|-----------|------------|---------------|
| VACUUM             |                        |                        |         |         |           |            |               |
| R=H                | -1.65                  | -3.94                  | 3.94    | 1.65    | 2.29 (2.89) | 1.15       | 0.87          |
| 2-NO$_2$           | -3.22                  | -4.70                  | 4.70    | 3.22    | 1.48      | 0.74       | 1.35          |
| 2-CN               | -2.59                  | -4.53                  | 4.53    | 2.59    | 1.94      | 0.97       | 1.03          |
| 2-CHO              | -2.68                  | -4.44                  | 4.44    | 2.68    | 1.76 (2.48) | 0.88       | 1.14          |
| 2-CH=C(CN)COOH     | -3.22                  | -4.60                  | 4.60    | 3.22    | 1.38      | 0.69       | 1.45          |
| ACETONE            |                        |                        |         |         |           |            |               |
| R=H                | -1.68                  | -3.92                  | 3.92    | 1.68    | 2.24      | 1.12       | 0.89          |
| 2-NO$_2$           | -3.10                  | -4.30                  | 4.30    | 3.10    | 1.20      | 0.60       | 1.60          |
| 2-CN               | -2.39                  | -4.10                  | 4.10    | 2.39    | 1.71      | 0.86       | 1.17          |
| 2-CHO              | -2.55                  | -4.09                  | 4.09    | 2.55    | 1.54      | 0.77       | 1.29          |
| 2-CH=C(CN)COOH     | -3.10                  | -4.23                  | 4.23    | 3.10    | 1.13      | 0.57       | 1.77          |
| THF                |                        |                        |         |         |           |            |               |
| R=H                | -1.66                  | -4.08                  | 4.08    | 1.66    | 2.42 (2.86) | 1.21       | 0.83          |
| 2-NO$_2$           | -3.09                  | -4.34                  | 4.34    | 3.09    | 1.25      | 0.63       | 1.59          |
| 2-CN               | -2.41                  | -4.22                  | 4.22    | 2.41    | 1.81      | 0.91       | 1.10          |
| 2-CHO              | -2.55                  | -4.14                  | 4.14    | 2.55    | 1.59 (2.46) | 0.79       | 1.28          |
| 2-CH=C(CN)COOH     | -3.09                  | -4.29                  | 4.29    | 3.09    | 1.20      | 0.60       | 1.60          |

Note: Experimental results in brackets [42].

Figure 3. (a) The band gaps of 10-OTBP with B3LYP/6-31G*. (b) The band gaps of 10-OTBP with BLYP/6-31G*.

While its BLYP value is 2.29 eV in vacuum and 2.42 eV in THF, this result is consistent with the observation of some researchers that the hybrid B3LYP overestimates $E_g$ values while the pure BLYP underestimates it, though closer [34]. It is expected that the substituted derivative will have a lower $E_g$ value than unsubstituted 10-OTBP, -CHO substituted derivative of 10-OTBP has an experimental $E_g$ value of 2.48 eV in vacuum and 2.46 eV in THF (Xebiao et al., 2015), the same was seen in its theoretical result, its B3LYP result is 3.06 eV in vacuum and 2.89 eV in THF, an expected overestimation while its BLYP $E_g$ value is 1.76 eV in vacuum and 1.59 eV in THF, an underestimation. One could use the theoretical methods and their results to explain chemical observations because the results obtained follow similar patterns. –NO$_2$, –CN, –CHO and –CH=C(CN)COOH derivatives reduced $E_g$ value because the take part in the conjugation as electron donating units. The effect of $E_g$ value reduction is felt more on acetone than in THF, this might be due to the higher dielectric constant of acetone than THF. The same trend was observed in BLYP except for the underestimation of $E_g$ values. –CH=C(CN)COOH substituted derivative has the lowest value of 2.57 eV, followed by –NO$_2$, with a value of 2.64 eV.

The BLYP results for $E_g$ of 10-OTBP are within the range of 1.38–2.29 eV with –CH=C(CN)COOH substituted analogue having the lowest value of 1.38 eV, followed by –NO$_2$, with a value of 1.48 eV. $E_g$ values also decreased slightly in acetone and THF. That is to say the presence of solvents affects the $E_g$ values owing to a distortion in the structure of molecules in solutions. $E_g$ values decreased as different substituents were added, this may be due to the larger molecular weight of the substituted derivatives, it may also be due to mesomeric effects and conjugation length. –CH=C(CN)COOH and –NO$_2$ derivatives have better properties than others because –NO$_2$ is a stronger electron withdrawing group than the others, that is there is an increase in mesomeric effect of the NO$_2$ acceptor group while –CH=C(CN)COOH has the longest $\pi$-conjugation length.

$\eta$ is expected to follow similar trend like the band gap when comparing it with the experimental results and in different solvent media since it is directly calculated from the band gap value as seen on Tables 5 and 6 and Figure 4(a,b). $S$ is expected to follow a reverse trend since it is the inverse of $\eta$ as seen in Tables 5 and 6 and Figure 5(a,b). –CH=C(CN)COOH is the softest of all the molecules under investigation followed by –NO$_2$ substituted derivative. It will be easier for
Table 5. The dipole moments (μ), polarizabilities (α), hyperpolarizabilities (β), \( \lambda_{\text{max}} \), oscillator strengths (f) and excitation energies of 10-OTBP and substituted analogues with B3LYP/6-31G* in vacuum, acetone (ε = 20.7) and THF (ε = 7.58).

| Molecules          | μ (D) | α (cm²V⁻¹) | β (×10⁻³⁰ esu) | \( \lambda_{\text{max}} \) (nm) | f   | \( E_{\text{ex}} \) (eV) |
|--------------------|-------|------------|----------------|---------------------------------|-----|---------------------|
| VACUUM             |       |            |                |                                 |     |                     |
| R=H                | 2.15  | 80.37      | 1.09           | 293 (294)                       | 0.94| 4.22                |
| 2-NO₂              | 6.58  | 84.07      | 4.67           | 360                             | 0.42| 3.44                |
| 2-CN               | 5.94  | 83.65      | 3.88           | 317                             | 0.75| 3.91                |
| 2-CHO              | 6.42  | 83.91      | 3.68           | 328 (328)                       | 0.39| 3.77                |
| 2-CH= C(CN)COOH    | 9.87  | 89.90      | 5.13           | 378                             | 1.53| 3.22                |
| ACETONE            |       |            |                |                                 |     |                     |
| R=H                | 3.01  | 80.41      | 1.12           | 294                             | 0.62| 4.22                |
| 2-NO₂              | 8.94  | 84.10      | 5.56           | 364                             | 0.63| 3.42                |
| 2-CN               | 8.76  | 83.67      | 4.59           | 348                             | 0.62| 3.79                |
| 2-CHO              | 7.90  | 83.95      | 4.23           | 380                             | 0.34| 3.67                |
| 2-CH= C(CN)COOH    | 12.97 | 90.01      | 7.58           | 395                             | 1.01| 3.12                |
| THF                |       |            |                |                                 |     |                     |
| R=H                | 2.97  | 80.41      | 1.11           | 295 (292)                       | 0.65| 4.35                |
| 2-NO₂              | 8.34  | 84.11      | 5.36           | 361                             | 0.61| 3.48                |
| 2-CN               | 7.65  | 83.68      | 4.39           | 340                             | 0.64| 3.84                |
| 2-CHO              | 7.22  | 83.88      | 4.12           | 325 (324)                       | 0.33| 3.71                |
| 2-CH= C(CN)COOH    | 11.67 | 90.00      | 7.29           | 380                             | 1.11| 3.15                |

Note: Experimental results in brackets [42].

electrons to move from the HOMO to LUMO orbitals in –CH= C(CN)COOH and –NO₂ derivatives than others, that is, better intramolecular charge transfer. This is an indication that they might possess the tendencies to form instantaneous dipoles than others.

3.3. Dipole moments and polarizabilities

All molecules increased α values of 10-OTBP for both BLYP and B3LYP methods on Tables 5 and 6, ranging from 80.37–89.90 cm²V⁻¹ to 81.08–94.45 cm²V⁻¹, respectively, while it is 89.90 cm²V⁻¹ for 2-CH= C(CN)COOH in vacuum, 2-NO₂ has a value of 84.07 cm²V⁻¹, with B3LYP method and 94.45 cm²V⁻¹ for 2-CH= C(CN)COOH in vacuum, with 2-NO₂ having the next highest value of 84.82 cm²V⁻¹ with BLYP method. These values are increased as different solvent media were considered, though slightly in both solvents. Targema and co-workers studied some aniline derivatives and concluded that diethylaniline (DEA) would be the best among the studied compounds for electro-optic response on the basis that it has the highest polarizability value of 55.15, 55.17 and 55.18 cm²V⁻¹ in vacuum, ethanol and THF, respectively [16]. The polarizabilities of 10-OTBP and its substituted derivatives are far greater than DEA, with unsubstituted 10-OTBP having a value of 80.37 cm²V⁻¹ with B3LYP in vacuum (Table 7) while it is 81.08 cm²V⁻¹ with BLYP (Table 6).

Table 6. The dipole moments (μ), polarizabilities (α), hyperpolarizabilities (β), \( \lambda_{\text{max}} \), oscillator strengths (f) and excitation energies of 10-OTBP and substituted analogues with BLYP/6-31G* in vacuum, acetone (ε = 20.7) and THF (ε = 7.58).

| Molecules          | μ (D) | α (cm²V⁻¹) | β (×10⁻³⁰ esu) | \( \lambda_{\text{max}} \) (nm) | f   | \( E_{\text{ex}} \) (eV) |
|--------------------|-------|------------|----------------|---------------------------------|-----|---------------------|
| VACUUM             |       |            |                |                                 |     |                     |
| R=H                | 2.17  | 81.08      | 1.04           | 362 (294)                       | 0.26| 3.42                |
| 2-NO₂              | 6.76  | 84.82      | 4.36           | 429                             | 0.28| 2.89                |
| 2-CN               | 6.04  | 84.37      | 3.87           | 419                             | 0.11| 2.96                |
| 2-CHO              | 6.53  | 84.64      | 3.01           | 444 (328)                       | 0.66| 2.79                |
| 2-CH= C(CN)COOH    | 10.79 | 94.45      | 5.76           | 470                             | 0.80| 2.66                |
| ACETONE            |       |            |                |                                 |     |                     |
| R=H                | 3.01  | 81.12      | 1.07           | 368                             | 0.33| 3.40                |
| 2-NO₂              | 8.86  | 84.92      | 5.48           | 460                             | 0.28| 2.77                |
| 2-CN               | 8.04  | 84.42      | 4.81           | 439                             | 0.19| 2.79                |
| 2-CHO              | 8.33  | 84.66      | 4.33           | 442                             | 0.65| 2.67                |
| 2-CH= C(CN)COOH    | 13.99 | 94.55      | 7.48           | 498                             | 0.81| 2.55                |
| THF                |       |            |                |                                 |     |                     |
| R=H                | 3.27  | 81.11      | 1.07           | 368 (292)                       | 0.34| 3.40                |
| 2-NO₂              | 8.71  | 84.90      | 5.31           | 457                             | 0.26| 2.75                |
| 2-CN               | 7.88  | 84.41      | 4.36           | 423                             | 0.21| 2.78                |
| 2-CHO              | 8.04  | 84.65      | 4.15           | 413 (324)                       | 0.66| 2.64                |
| 2-CH= C(CN)COOH    | 13.01 | 94.53      | 6.91           | 492                             | 0.83| 2.53                |

Note: Experimental results in brackets [42].
Figure 4. (a) Chemical hardness for 10-OTBP with B3LYP/6-31G*. (b) Chemical hardness for 10-OTBP with BLYP/6-31G*.

for 2-CH=\text{C(CN)COOH} in vacuum, with 2-NO\textsubscript{2} having the next highest value of 6.76 D with BLYP method. These values are increased as different solvent media were considered, more significantly in both solvents, with an increase in the dielectric constants of the solvents (Figure 7).

3.4. Molecular first hyperpolarizabilities

The $\beta$ values obtained for 10-OTBP with B3LYP/6-31G* are in Table 5 range from 1.09–5.13 $\times 10^{-30}$ esu. 2-\text{CH=\text{C(CN)COOH}} has the highest value of 5.13 $\times 10^{-30}$ esu while 2-\text{NO\textsubscript{2}} has a value of 4.67 $\times 10^{-30}$ esu. These values increased in solvents, with an increase in dielectric constant of the solvents. A similar trend was observed with BLYP/6-31G* calculations (Table 6). However, all the studied molecules have higher $\beta$ values than urea, with unsubstituted 10-OTBP (1.09), 1.7 times than of urea’s 0.65 $\times 10^{-30}$ esu [34] while the substituted derivatives are much higher with

Table 7. The dipole moments ($\mu$), polarizabilities ($\alpha$), hyperpolarizabilities ($\beta$), $\lambda$ max, oscillator strengths ($f$) and excitation energies 10-OTBP and substituted analogues with B3LYP/6-31G* in vacuum, acetone ($\varepsilon = 20.7$) and THF ($\varepsilon = 7.58$).

| Molecules       | $\mu$ (D) | $\alpha$ (cm$^2$/V$^{-1}$) | $\beta$ ($\times 10^{-30}$ esu) | $\lambda$ max (nm) | $f$ | $E_{ex}$ (eV) |
|-----------------|---------|--------------------------|-----------------|-----------------|----|-------------|
| VACUUM          |         |                          |                  |                 |    |             |
| R=H             | 2.15    | 80.37                    | 1.09             | 293 (294)       | 0.94 | 4.22        |
| 2-NO\textsubscript{2} | 6.58    | 84.07                    | 4.67             | 360             | 0.42 | 3.44        |
| 2-CN            | 5.94    | 83.65                    | 3.88             | 317             | 0.75 | 3.91        |
| 2-CHO           | 6.42    | 83.91                    | 3.68             | 328 (328)       | 0.39 | 3.77        |
| 2-\text{CH=\text{C(CN)COOH}} | 9.87    | 89.9                     | 5.13             | 378             | 1.53 | 3.22        |
| ACETONE         |         |                          |                  |                 |    |             |
| R=H             | 3.01    | 80.41                    | 1.12             | 294             | 0.62 | 422         |
| 2-NO\textsubscript{2} | 8.94    | 84.1                     | 5.56             | 364             | 0.63 | 3.42        |
| 2-CN            | 8.76    | 83.67                    | 4.59             | 348             | 0.62 | 3.79        |
| 2-CHO           | 7.90    | 83.95                    | 4.23             | 380             | 0.34 | 3.67        |
| 2-\text{CH=\text{C(CN)COOH}} | 12.97   | 90.01                    | 7.58             | 395             | 1.01 | 3.12        |
| THF             |         |                          |                  |                 |    |             |
| R=H             | 2.97    | 80.41                    | 1.11             | 295 (292)       | 0.65 | 4.35        |
| 2-NO\textsubscript{2} | 8.34    | 84.11                    | 5.36             | 361             | 0.61 | 3.48        |
| 2-CN            | 7.65    | 83.68                    | 4.39             | 340             | 0.64 | 3.94        |
| 2-CHO           | 7.22    | 83.88                    | 4.12             | 325 (324)       | 0.33 | 3.71        |
| 2-\text{CH=\text{C(CN)COOH}} | 11.67   | 90.00                    | 7.29             | 380             | 1.11 | 3.15        |

Figure 5. (a) Chemical softness of 10-OTBP with B3LYP/6-31G*. (b) Chemical softness of 10-OTBP with BLYP/6-31G*.
Table 8. The dipole moments ($\mu$), polarizabilities ($\alpha$), hyperpolarizabilities ($\beta$), $\lambda_{\text{max}}$, oscillator strengths ($f$) and excitation energies ($E_{\text{ex}}$) of 10-OTBP and substituted analogues with BLYP/6-31G* in vacuum, acetone ($\varepsilon = 20.7$) and THF ($\varepsilon = 7.58$).

| Molecules       | $\mu$ (D) | $\alpha$ ($\text{cm}^2\text{V}^{-1}$) | $\beta$ ($\times 10^{-30}$ esu) | $\lambda_{\text{max}}$ (nm) | $f$ | $E_{\text{ex}}$ (eV) |
|-----------------|-----------|----------------------------------------|----------------------------------|-------------------------------|-----|----------------------|
| VACUUM          |           |                                        |                                  |                               |     |                      |
| R=H             | 2.17      | 81.08                                  | 1.04                             | 362 (294)                     | 0.26| 3.42                 |
| 2-NO$_2$        | 6.76      | 84.82                                  | 4.36                             | 429                           | 0.28| 2.89                 |
| 2-CN            | 6.04      | 84.37                                  | 3.87                             | 419                           | 0.11| 2.96                 |
| 2-CHO           | 6.53      | 84.64                                  | 3.01                             | 444 (328)                     | 0.66| 2.79                 |
| 2-CH=\text{C(CN)COOH} | 10.79    | 94.45                                  | 5.76                             | 470                           | 0.80| 2.66                 |
| ACETONE         |           |                                        |                                  |                               |     |                      |
| R=H             | 3.01      | 81.12                                  | 1.07                             | 368                           | 0.33| 3.40                 |
| 2-NO$_2$        | 8.86      | 84.92                                  | 5.48                             | 460                           | 0.28| 2.77                 |
| 2-CN            | 8.04      | 84.42                                  | 4.81                             | 439                           | 0.19| 2.79                 |
| 2-CHO           | 8.33      | 84.66                                  | 4.33                             | 442                           | 0.65| 2.67                 |
| 2-CH=\text{C(CN)COOH} | 13.99    | 94.55                                  | 7.48                             | 498                           | 0.81| 2.55                 |
| THF             |           |                                        |                                  |                               |     |                      |
| R=H             | 3.27      | 81.11                                  | 1.07                             | 368 (292)                     | 0.34| 3.40                 |
| 2-NO$_2$        | 8.71      | 84.90                                  | 5.31                             | 457                           | 0.26| 2.75                 |
| 2-CN            | 7.88      | 84.41                                  | 4.36                             | 423                           | 0.21| 2.78                 |
| 2-CHO           | 8.04      | 84.65                                  | 4.15                             | 413 (324)                     | 0.66| 2.64                 |
| 2-CH=\text{C(CN)COOH} | 13.01    | 94.53                                  | 6.91                             | 492                           | 0.83| 2.53                 |

Figure 6. (a) Polarizability of 10-OTBP with B3LYP/6-31G*. (b) Polarizability of 10-OTBP with BLYP/6-31G*.

Figure 7. (a) Dipole moments of 10-OTBP with B3LYP/6-31G*. (b) Dipole moments of 10-OTBP with BLYP/6-31G*.

2-CH=\text{C(CN)COOH} (5.13), 7.9 times that of urea, the highest (Figure 8).

These substituted analogues have reduced the BLA, they have lower $E_g$ values, higher $\alpha$ values, higher $\mu$ values, lower $\eta$ values, higher $S$ values, an indication that these substituted analogues may exhibit better NLO behaviours than the unsubstituted analogue. In order to confirm this, the $\beta$ values were investigated and it has also shown that they all have higher $\beta$ values, indicating that these compounds have better second-order susceptibilities ($\chi^2$) than the unsubstituted analogue.

3.5. UV absorptions

The extent of absorption of a compound can tell the type of transition(s) present in the molecule. The TD-DFT methods were used in calculating the excitation energies ($E_{\text{ex}}$), absorption ($\lambda_{\text{max}}$), oscillator strength ($f$) and the various transitions associated with them were indicated, all due to $\pi-\pi^*$ transitions. The $\lambda_{\text{max}}$ of the
compounds is the one corresponding to the transition with the highest oscillation strength (intensity) as seen in Tables 5 and 6.

The unsubstituted molecule (R=H) absorbed at 294 nm in vacuum, exactly as the experimental value of 294 nm [42], 294 nm in acetone and 295 nm (close to the experimental value of 292 nm [42]) in THF, with oscillator strengths of 0.94, 0.62 and 0.65, respectively, and also with excitation energies of 4.22 in vacuum and in both solvents for B3LYP/6-31G* calculation. Upon substitution with –NO2, absorption took place at 360 nm in vacuum, 364 nm in acetone and 361 nm in THF. –CN absorbed at 317 nm in vacuum, 348 nm in acetone and 340 nm in THF. –CHO absorbed at 328 nm in vacuum, exactly as the experimental value [42], 380 nm in acetone and 325 nm in THF (exp. 324 nm, [42]). –CH=–C(CN)COOH absorbed at 378 nm in vacuum, 395 nm in acetone and 380 nm in THF. The unsubstituted molecule (R=H) absorbed at higher values than the experimental values as seen in Table 8 for BLYP. The B3LYP results agree with the available experimental results very closely. One could suggest the use of the hybrid B3LYP methods in predicting the absorption properties of this kind of π-conjugated organic molecules.

From the results obtained, it shows clearly that the substituted derivatives shift the λmax bathochromically (increase the λmax) as compared to the unsubstituted analogues. The substituted derivatives can be synthesized and investigated for light emitting and NLO applications as they have higher α, μ, β values than their unsubstituted analogues, they also have lower Eg values.

4. Conclusions

Material scientists are saddled with the responsibility of designing/creating materials that meet certain applications and also improve on those materials. Theoretical chemistry affords the opportunity to study the properties of existing molecules and find methods that agree with experimental findings, such methods can then be used to predict the properties of hypothetical molecules with the aim of using them for some applications. Modifying the structures of existing molecules could help improving the second-order susceptibility via the molecular first hyperpolarizability (β), polarizability (α), the band gap (Eg) and other properties. Some organic molecules based on phenothiazine units and some of their substituted analogues have been synthesized and studied for light emitting applications [42]. However, the second-order responses, the geometric parameters, structural and solvent dependence on molecular polarizability and hyperpolarizability of these compounds were not studied. Therefore, this research was designed using computational approach to study the molecular and electronic properties and the structural and solvent dependence on the molecular properties of phenothiazine-based organic molecules and some of their substituted analogues.

The molecular properties investigated are the energies of the Lowest Unoccupied Molecular Orbital (E_LUMO), Highest Occupied Molecular Orbital (E_HOMO), energy gap (E_g), dipole moment (μ), polarizability (α), first hyperpolarizability (β), UV absorptions (λ_abs), BLA and dihedral angles were obtained using restricted hybrid DFT with pure BLYP and hybrid Becke three, Lee Yang and Parr correlation (B3LYP) with the large polar 6-31G* basis set. Chemical hardness (η) and Softness (S) were all calculated from E_LUMO and E_HOMO.

It was discovered that the NLO properties of these compounds can be modelled in vacuum/gas phase and in solutions. The inclusion of solvent was found to alter α and β, with the effect felt more on β than α. The multipolar decomposition (dipolar and octapolar) of α and β-tensor components was developed by the Kleinmann’s symmetry model with the TD-DFT calculations. All calculations were carried out using quantum mechanical software.

These substituted analogues have reduced the BLA, and shown to be planar, they have lower E_g values, higher α values, higher μ values, lower η values, higher S values. All these are pointers that these analogues may exhibit good NLO behaviours, but was confirmed by investigating β properties (a measure of second-order susceptibilities, χ^2) of these compounds with 2-CH=C(CN)COOH and 2-NO₂ having the best NLO properties than others.
4.1. Recommendations

The addition of different substituent groups alters the frontier orbital energies and as a result altered the energy gaps leading to the enhancement of the reactivities and the ability to form dipoles of the molecules; the polarizabilities and first hyperpolarizabilities are also enhanced by these substitutions. This work also used a solvent model in predicting the NLO properties of the investigated organic molecules. These molecules can be synthesized by synthetic chemists for the practical purpose of studying them for light emitting and NLO applications.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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