EXPERIMENTAL AND THEORETICAL INVESTIGATIONS (FTIR, UV-VIS SPECTROSCOPY, HOMO-LUMO, NLO AND MEP ANALYSIS) OF AMINOTHIOPHENOL ISOMERS

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ABSTRACT: In this research, theoretical and experimental investigation was performed on the structural and spectral data of aminothiophenol isomers. The theoretical electronic structure analyses were performed by density functional theory at the B3LYP level with the LanL2DZ basis set in the gas phase of the isolated compounds at the ground state. Potential energy distribution analysis was performed to determine the assignments of the vibration bands. Experimental and theoretical spectroscopic data were compared. Energy gap, ionization potential, electron affinity, and electronegativity were obtained through frontier molecular orbitals.

KEY WORDS: Aminothiophenols, Density functional theory, Polarizability, Vibrational assignments, Molecular electrostatic potential surface

INTRODUCTION

Aminothiophenol (ATP) isomers (mercaptoamelines, aminobenzenthiols) are organic compounds with a ring structure to which a-SH and a-NH₂ functional groups are attached to the benzene ring. Aromatic thiols have interesting properties with ortho, meta and para positions and they have been the subject of many studies for years [1–6]. Batz et al. investigated a study on the electrochemical properties of ATP isomers adsorbed on gold and mentioned that most of the functionalized thionophenol isomers can be used for surface modification by undergoing electrochemical transformations [7]. In the literature search, it has been seen that ATP derivatives are frequently used in corrosion prevention processes because they contain single electron pairs such as thiol and amine groups in the benzene ring [8, 9]. In the paper of Li et al., they used molecular dynamics simulation to investigate the inhibitory adsorption of four thiophenol derivatives on the surface of Fe (001) in 0.1 M hydrochloric acid solution. They wrote that the corrosion inhibition performance mainly depends on the interaction between polar groups and metal surface [10]. Kabel et al. investigated the inhibition efficiency for corrosion due to its 2-ATP adsorbing property [1].

Similar studies have been reported by Karthik et al. and Anto Maria Jeraldin et al. [11, 12]. The synthesis and antibacterial properties of poly (ATPs) were reported by Anto Maria et al. and Sorasaenee et al. in other studies [13, 14].

There have been studies showing significant changes in the relative SERS (surface-enhanced Raman spectroscopy) intensities when ATP isomers were used as a probe molecule and adsorbed on some metals [15–17]. Sun et al. used the 4-ATP + Ag complex to visualize the chemical mechanism between the 4-ATP and metal complexes [18]. Jiang et al. reported photo-induced surface catalytic binding reactions of ATPs by SERS and density functional theory (DFT) methods [19]. In the literature, adsorption of 4-ATP on Au was performed and geometric and electronic structure was investigated by using DFT [6, 20].

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As it can be seen from the research in the literature, while several experimental and theoretical studies for ATPs have been ascertained, no study has been searched examining the structural change of the isomer and its effect on the characterization of the compounds in detail. In this study, it was aimed to investigate structural differences in the molecule caused by the position of the amine and thiol group in the phenyl ring by experimental and theoretical spectroscopic analyses.

DFT is a powerful method for revealing the geometric differences of isomers precisely and allows an estimate to be made before designing new experiments. In this study, molecular geometry, vibration spectra and assignments, HOMO-LUMO energies, Mulliken charges and polarizability were determined, and experimental results were compared with theoretical results. We anticipate that the identification of the characteristic structural differences of isomers will make an important contribution to the literature.

EXPERIMENTAL

ATPs were obtained commercially, from Aldrich (2-ATP and 3-ATP) and Merck (4-ATP) company. They are all analytical grade purity. The spectroscopic measurements were recorded at room temperature. FTIR spectroscopic analyses were carried out by Perkin Elmer Spectrum BX model. UV-Vis analyses were performed by Shimadzu 1280 Spectrophotometer.

Quantum chemical calculations were performed by using the DFT method with the B3LYP function and LanL2DZ basis set. Gaussian 09 [21] software package was used for the theoretical calculations. The geometry optimizations were followed by frequency calculations using the same basis set. Time-dependent DFT (TD-DFT) method was used to obtain UV-Vis Spectra and electronic properties. The results were visualized using the Gauss View and Chemcraft 1.8 program [22]. Potential energy distribution, corresponding to the observed frequencies, was calculated using VEDA program [23].

RESULTS AND DISCUSSION

Molecular geometry

The molecular crystal structures of the title compounds are shown in Figure 1a, b, c. The numerical values of the bond lengths are written on Figure 1. The calculated bond angles of all molecules are summarized in Table 1.

The bond length of the C1 atom with the C2 and C6 atoms is the same in all isomers and its value is 1.42 Å. Again, in ATPs, the bond length of the C1 atom with the N1 atom is the same and its value is 1.39 Å. When all bond lengths are examined, the highest bond length is detected where the carbon atom is attached to the sulfur atom.

In Figure 1, these conjunction points are C2-S1, C3-S1 and C4-S1, they have the value of 1.86, 1.85 and 1.86 Å, respectively. The shortest bond length is observed between the nitrogen atom and the hydrogen atom with the value of 1.01 Å for each isomer.

When the bond angles are examined, it is determined that the smallest bond angle is between C-S-H atoms with a value of around 97° among all isomers in Table 1. The bond angle between C2-C1-C6 is important in terms of showing the place where NH2 is attached to the ring from the C1 atom. By investigating this bond, it is observed that there is a slight decrease in bond angle for 2-ATP, 3-ATP, and 4-ATP, respectively. The fact that the SH group gradually moves away from the NH2 group may be the reason for this decrease in the bond angle.
Figure 1. Geometric structure of (a) 2-ATP, (b) 3-ATP and (c) 4-ATP.

Table 1. Optimized parameters for 2-ATP, 3-ATP and 4-ATP (bond angles [°]: degree).

| Atoms | 2-ATP bond angles [°] | 3-ATP bond angles [°] | 4-ATP bond angles [°] |
|-------|----------------------|---------------------|---------------------|
| C2-C1-C6 | 119.3                | C2-C1-C6 | 119.1                | C2-C1-C6 | 118.6           |
| C2-C1-N1 | 121.5                | C2-C1-N1 | 120.3                | C2-C1-N1 | 120.7           |
| C6-C1-N1 | 120.5                | C6-C1-N1 | 120.6                | C6-C1-N1 | 120.7           |
| C1-C2-C3 | 120.6                | C1-C2-C3 | 120.1                | C1-C2-C3 | 120.5           |
| C1-C2-S1 | 120.0                | C1-C2-S1 | 119.5                | C1-C2-S1 | 119.8           |
| C3-C2-S1 | 122.6                | C3-C2-S1 | 120.3                | C3-C2-S1 | 119.8           |
| C2-C3-H1 | 119.3                | C2-C3-H1 | 121.0                | C2-C3-H1 | 120.7           |
| C2-C3-C4 | 119.0                | C2-C3-C4 | 116.8                | C2-C3-C4 | 119.7           |
| C4-C3-H1 | 120.3                | C4-C3-H1 | 122.2                | C4-C3-H1 | 119.6           |
| C4-C4-C5 | 118.9                | C4-C4-C5 | 118.5                | C4-C4-C5 | 119.9           |
| C3-C4-H2 | 120.3                | C3-C4-H2 | 121.8                | C3-C4-H2 | 120.4           |
| C5-C4-H2 | 120.8                | C5-C4-H2 | 120.2                | C5-C4-H2 | 120.4           |
| C4-C5-C6 | 120.8                | C4-C5-C6 | 121.4                | C4-C5-C6 | 120.6           |
| C4-C5-H3 | 119.9                | C4-C5-H3 | 119.2                | C4-C5-H3 | 119.6           |
| C6-C5-H3 | 119.3                | C6-C5-H3 | 119.4                | C6-C5-H3 | 119.8           |
| C1-C6-C5 | 120.9                | C1-C6-C5 | 119.8                | C1-C6-C5 | 120.5           |
| C1-C6-H4 | 119.0                | C1-C6-H4 | 119.9                | C1-C6-H4 | 119.8           |
| C5-C6-H4 | 120.1                | C5-C6-H4 | 120.3                | C5-C6-H4 | 119.8           |
| C1-N1-H6 | 119.6                | C1-N1-H6 | 121.0                | C1-N1-H6 | 120.9           |
| C1-N1-H5 | 120.6                | C1-N1-H5 | 120.8                | C1-N1-H5 | 120.9           |
| H5-N1-H6 | 119.2                | H5-N1-H6 | 118.2                | H5-N1-H6 | 118.2           |
| C2-S1-H7 | 97.6                 | C3-S1-H7 | 97.1                 | C4-S1-H7 | 97.7            |

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**IR spectroscopic analysis**

ATR device is used for ATP isomers with the range between 4000-600 cm⁻¹. Experimental and Theoretical IR spectra for 2-ATP, 3-ATP and 4-ATP are shown in Figure 2 and Figure 3, respectively. The IR and Raman bands positions calculated with the method B3LYP/ LanL2DZ and their assignments are reported in Table 2. The main objective of this study is to investigate the results of intermolecular interactions occurring in ATP isomers. Isomer effects have been studied through some vibrational bands. For this purpose, characteristic vibration bands were examined in detail and the compatibility of experimental and theoretical results was observed.

The band characteristics of the NH groups are usually observed around 3500-3300 cm⁻¹ [1, 2]. While the N-H bands for 2-ATP were experimentally observed at 3438 and 3349 cm⁻¹ in the IR spectrum they were calculated as 3617 and 3473 cm⁻¹ theoretically [24]. Similarly, these bands for 3-ATP were observed at 3427 and 3348 cm⁻¹, while they were calculated at 3632 and 3497 cm⁻¹. For 4-ATP, it was observed at 3427 and 3348 cm⁻¹ and calculated at 3630 and 3496 cm⁻¹.

In the FT-IR spectrum, the S-H stretching vibration band is observed around 2530 cm⁻¹ [2, 25, 26]. This band was calculated for 2-ATP, 3-ATP, and 4-ATP at 2363, 2427, 2364 cm⁻¹, respectively, and it was observed experimentally at 2522, 2553 and 2545 cm⁻¹, respectively. Correspondingly, in the Raman spectroscopic resources, these vibrations appear at 2532 cm⁻¹ for 2-ATP and 2544 cm⁻¹ for 4-ATP cm⁻¹ [5, 27].

For aromatic and heteroatomic structures, C-H stretching vibrations usually appear in the range of 3200-3000 cm⁻¹ [5, 19, 28]. These modes are not affected by subgroups and are therefore pure vibration modes. Asymmetric and symmetrical C-H stretching vibrations are observed in the FT-IR spectrum of the 2-ATP, at 3061 and 3016 cm⁻¹ [24]. The corresponding bands are observed in the range 3075 and 3057 cm⁻¹ in the calculated form. In the FT-IR spectrum of 3-ATP, asymmetric C-H stretching vibration is observed at 3048 cm⁻¹ [24] and this band is calculated at 3065 cm⁻¹. Symmetrical C-H stretching vibration is observed at 3024 cm⁻¹ for 4-ATP. The corresponding bands are calculated in near 3060 cm⁻¹ [2, 19, 24]. The 900-675 cm⁻¹ range is the region with the most informative bands in the spectra of aromatic compounds [29] and this region is inside in the 1500-600 cm⁻¹ range known as fingerprints [30]. The C-H in-plane bending vibrations appear at 1480 cm⁻¹, 1327 cm⁻¹, 1275 cm⁻¹ and 1144 cm⁻¹ for 2-ATP and 1483 cm⁻¹, 1328 cm⁻¹, 1275 cm⁻¹ and 1144 cm⁻¹ for 3-ATP and 4-ATP.

![Figure 2. The experimental infrared spectra of ATP isomers (a) 2-ATP, (b) 3-ATP and (c) 4-ATP.](image-url)
Figure 3. The theoretical infrared spectra of ATP isomers (a) 2-ATP, (b) 3-ATP and (c) 4-ATP.

Table 2. Detailed assignments of experimental and theoretical wavenumbers (cm⁻¹) of 2-ATP, 3-ATP and 4-ATP, along with potential energy distribution (PED).

| Theoretical | Experimental | Assignment (%PED) | Theoretical | Experimental | Assignment (%PED) | Theoretical | Experimental | Assignment (%PED) |
|-------------|--------------|------------------|-------------|--------------|------------------|-------------|--------------|------------------|
| 2-ATP       | Scaled       | IR               | Raman       | 3-ATP        | Scaled           | IR          | Raman        | 4-ATP            |
| 3768        | 3617         | 3438 vs          | ν₅₅ (98)    | 3783         | 3632             | 3427 vs     | ν₅₅ (100)    | 3781             | 3630             | 3427 vs          | ν₅₅ (100)    |
| 3618        | 3473         | 3349 vs          | ν₅₅ (98)    | 3643         | 3497             | 3348 vs     | ν₅₅ (100)    | 3642             | 3496             | 3348 vs          | ν₅₅ (100)    |
| 3214        | 3160         | ν₇₈ (94)          | 3223        | 3094         | 3210 m          | ν₇₈ (96)    | 3223         | 3096             | 3207 m          | ν₇₈ (99)        |
| 3203        | 3075         | ν₉₇ (97)          | 3203        | 3075         | 3081 s          | ν₉₇ (90)    | 3220         | 3091             | ν₉₇ (99)        |
| 3184        | 3057         | 3061 m, 3068 vs  | ν₉₇ (100)   | 3193         | 3065             | 3048 vs     | ν₉₇ (99)    | 3190             | 3063             | 3046 vs          | ν₉₇ (99)    |
| 2461        | 2363         | 2522 m, 2532 s   | ν₉₇ (100)   | 2528         | 2427             | 2533 m      | ν₉₇ (100)   | 2462             | 2364             | 2545 m          | ν₉₇ (100)    |
| 1673        | 1673         | δ₉₉₅ (78)         | 1688        | 1688         | 1701 m          | δ₉₉₅ (95)   | 1688         | 1688             | δ₉₉₅ (94)        |
| 1645        | 1645         | 1603 b, 1610 m   | ν₁₅ (46)+δ₉₉₅ (14)+δₑₑₑ (13) | 1656       | 1656             | 1630 m      | ν₁₅ (53)+δₑₑₑ (10) | 1655     | 1655             | 1614 b          | ν₁₅ (44)+δₑₑₑ (16) |
| 1613        | 1613         | 1573 sh          | ν₁₅ (59)+δₑₑₑ (1) | 1619       | 1619             | 1599 b      | ν₁₅ (64)+δₑₑₑ (28) | 1615     | 1615             | 1595 b          | ν₁₅ (59)+δₑₑₑ (26) |
| 1520        | 1520         | 1477 w           | ν₁₅ (16)+δₑₑₑ (37)+δₑₑₑ (18) | 1522       | 1522             | 1520 w      | ν₁₅ (10)+ν₁₅ (14)+δₑₑₑ (32)+δₑₑₑ (11) | 1531     | 1531             | 1491 b          | δₑₑₑ (48)+ν₁₅ (16)+ν₁₅ (11)+δₑₑₑ (10) |
| 1480        | 1480         | 1445 s           | νₑₑₑ (23)+δₑₑₑ (45) | 1483       | 1483             | 1477 w      | νₑₑₑ (26)+δₑₑₑ (21) | 1456     | 1456             | 1446 m          | νₑₑₑ (45)+δₑₑₑ (35) |
| Wave Number | ν_{CC} (82) | ν_{CC} (73) + δ_{CCC} (13) | δ_{CC} (48) + ν_{CC (25)} + ν_{CC (25)} | ν_{CC (27)} + δ_{CCC (45)} | ν_{CC (27)} + δ_{CCC (45)} |
|-------------|-------------|----------------------------|---------------------------------|--------------------------|--------------------------|
| 1376        | 1348        | 1381                       | 1334                            | 1334                     | 1334                     |
| 1354        | 1327        | 1355                       | 1334                            | 1334                     | 1334                     |
| 1301        | 1275        | 1325                       | 1333                            | 1333                     | 1333                     |
| 1204        | 1180        | 1213                       | 1218                            | 1218                     | 1218                     |
| 1167        | 1144        | 1144                       | 1154                            | 1154                     | 1154                     |
| 1072        | 1051        | 1051                       | 1041                            | 1041                     | 1041                     |
| 1025        | 1005        | 1003                       | 1020                            | 1020                     | 1020                     |
| 1019        | 999         | 993                        | 998                             | 998                      | 998                      |
| 987         | 967         | 918                        | 991                             | 991                      | 991                      |
| 904         | 886         | 897                        | 907                             | 907                      | 907                      |
| 876         | 858         | 889                        | 848                             | 848                      | 848                      |
| 847         | 830         | 871                        | 815                             | 815                      | 815                      |
| 786         | 770         | 799                        | 833                             | 833                      | 833                      |
| 743         | 728         | 707                        | 730                             | 730                      | 730                      |
| 677         | 663         | 688                        | 653                             | 653                      | 653                      |
| 565         | 554         | 541                        | 526                             | 526                      | 526                      |
| 562         | 551         | 455                        | 431                             | 431                      | 431                      |
| 510         | 500         | 446                        | 422                             | 422                      | 422                      |
| 460         | 451         | 412                        | 399                             | 399                      | 399                      |

(ν = stretching; δ = deformation bending; τ = torsion; γ = in plane bending; vs = very strong; s = strong; m = medium; w = weak; vw = very weak; b = broad; sh = shoulder).
1328, 1299 and 1121 cm\(^{-1}\) for 3-ATP. On the other hand, the C-H in-plane bending vibrations appear at 1456, 1307, 1306 and 1131 cm\(^{-1}\) for 4-ATP. In addition to, the C-H out-of-plane bending vibrations appear at 999, 967 and 770 cm\(^{-1}\) for 2-ATP; 982, 879, 871 and 783 cm\(^{-1}\) for 3-ATP; 971, 889, 831, 715 cm\(^{-1}\) for 4-ATP. These results line up with the experimental ones [31, 32].

According to the PED results, these in-plane and out-of-plane bending vibrations are mixed modes mostly combined with other bending and stretching modes.

Vibration bands observed in the range of 1650–1430 cm\(^{-1}\) are attributed to aromatic C-C vibrations [24, 34, 35]. While these bands were observed experimentally in the range of 1603-1477 cm\(^{-1}\), they were calculated in the range of 1645-1348 cm\(^{-1}\) for 2-ATP. In addition, the band observed in the experimental spectra at 1630 cm\(^{-1}\) was assigned as the C-C vibrational band in the range of 1656-1353 cm\(^{-1}\) in the spectrum calculated for 3-ATP. In experimental data, bands at 1614 cm\(^{-1}\) and 1595 cm\(^{-1}\) are assigned as C-C vibrations calculated in the range of 1655-1347 cm\(^{-1}\) for 4-ATP [2, 5, 19]. These vibration modes are highly mixed modes with an additive range of 82-44% and are often combined with HNC, HCC and HNH vibrations as well as some bending vibrations. For ATP isomers, these differences can be said to be caused by both the change in where the amine group is attached to the phenyl ring and the distance between the amine and thiol group.

Figure 4. Molecular electrostatic potential map of (a) 2-ATP, (b) 3-ATP and (c) 4-ATP.

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The molecular electrostatic potential surface (MEP) maps present the charge distribution of the molecules and enable us to observe a variable charge region. Figure 4 shows the MEP surfaces of the ATP isomers ranging from darkest red to deepest blue. The blue color indicates nucleophilicity, the red color indicates electrophilicity and the green color indicates the neutral, zero electrostatic potential region, which refers to hydrogen-bond interactions [36, 37]. The surface maps of MEP show that regions with negative potential are on sulfur, nitrogen and carbon atoms, and regions with positive potential are on hydrogen atoms attached to the amine group. When the MEP surface maps are examined, it is observed that the negative and positive charge densities of 4-ATP are concentrated at the opposite ends of the molecule. Therefore, we can say that the 4-ATP molecule has bigger polarizability than others and the results of NLO analysis also support this idea.

**HOMO and LUMO analyses and chemical activity**

In frontier molecular orbitals, HOMO denotes a wide variety of donor orbitals, while LUMO denotes acceptor orbitals. HOMO is the highest occupied energy orbital that can function as an electron donor. The LUMO is the lowest unoccupied energy orbital, which has enough space to accept electrons and can act as an electron acceptor [38]. HOMO-LUMO values give information about the polarization, electronegativity, hardness, reactivity, and kinetic stability of the molecule. [39, 40]. Surface images are shown in Figure 5, the most likely spectral parameters corresponding to wavelengths and electronic transitions are presented Table 3, and chemical reactivity indices are presented in Table 4.

![Figure 5. HOMO and LUMO plot of (a) 2-ATP, (b) 3-ATP and (c) 4-ATP.](image)

The data obtained from the results show that ATPs have high hardness and low softness parameters due to their high energy gaps. These indicate that these molecules have low chemical activity, high kinetic stability, and it can therefore be concluded that they are highly stable. The results of chemical reactivity descriptors indicate higher hardness and lower softness values, lower intermolecular charge transfer and thus lower polarity.
Experimental and theoretical investigations of aminothiophenol isomers

Table 3. The experimental and calculated UV-Vis excitation energies and oscillator strength (f) for 2-ATP, 3-ATP, 4-ATP.

| Molecule | C1 expansion coefficient | Excitation energy [eV] | \(\lambda_{exp}\) [nm] | \(\lambda_{cal}\) [nm] | f Oscillator strengths | Major contributions |
|----------|--------------------------|------------------------|------------------------|------------------------|------------------------|---------------------|
| 2-ATP    | 0.68249                  | 4.4479                 | 265                    | 278.75                 | 0.0848                 | HOMO\(\rightarrow\)LUMO (93%) |
|          | 0.63603                  | 5.4350                 | 228                    | 238.75                 | 0.1463                 | HOMO\(\rightarrow\)LUMO+1 (80%) |
|          | 0.45314                  | 5.5556                 | 210                    | 223                    | 0.0189                 | HOMO\(\rightarrow\)LUMO (41%) |
| 3-ATP    | 0.57269                  | 4.5201                 | 260                    | 274.29                 | 0.0642                 | HOMO\(\rightarrow\)LUMO (88%) |
|          | 0.66489                  | 5.3407                 | 220                    | 232.15                 | 0.0002                 | HOMO\(\rightarrow\)LUMO+2 (92%) |
|          | 0.67925                  | 5.3651                 | 231.10                 | 243.29                 | 0.0434                 | HOMO\(\rightarrow\)LUMO (53%) |
| 4-ATP    | 0.70611                  | 4.5377                 | 250                    | 273.23                 | 0.0490                 | HOMO\(\rightarrow\)LUMO (99%) |
|          | 0.67838                  | 5.2655                 | 227                    | 235.46                 | 0.3899                 | HOMO\(\rightarrow\)LUMO (92%) |
|          | 0.67960                  | 5.5955                 | 221.58                 | 233.75                 | 0.0004                 | HOMO\(\rightarrow\)LUMO+1 (92%) |

(nm: nanometer, Cal.: Calculated, Exp.: Experimental, eV: electron Volt, \(\lambda\): Absorption wavelengths).

Table 4. Global chemical reactivity indices for the 2-ATP, 3-ATP and 4-ATP.

| Parameters                      | 2ATP [eV] | 3ATP [eV] | 4ATP [eV] |
|--------------------------------|-----------|-----------|-----------|
| \(E_{\text{HOMO}}\)            | -5.679    | -5.697    | -5.689    |
| \(E_{\text{LUMO}}\)            | -0.576    | -0.379    | -0.460    |
| \(\Delta E\)                   | 5.121     | 5.243     | 5.229     |
| Ionization potential (I = - \(E_{\text{HOMO}}\)) | 5.679     | 5.697     | 5.589     |
| Electron affinity (A = - \(E_{\text{LUMO}}\)) | 0.576     | 0.379     | 0.460     |
| Electronegativity (\(\chi = (I+A)/2\)) | 3.128     | 3.038     | 3.075     |
| Chemical potential (\(\mu = (I+\chi)/2\)) | -3.128    | -3.038    | -3.075    |
| Chemical hardness (\(\eta = (I-\chi)/2\)) | 2.552     | 2.659     | 2.615     |
| Chemical softness (\(s = 1/2\eta\)) | 0.196     | 0.188     | 0.191     |
| Electrophilic index (\(w = \mu^2/s\)) | 1.917     | 1.735     | 1.808     |
| Maximum load transfer parameter (\(\Delta N_{max} = (I+\chi)/(I-A)\)) | 1.378     | 1.142     | 1.176     |

HOMO energies are calculated as -5.697, -5.622, and -5.689 eV for 2-ATP, 3-ATP, 4-ATP, respectively. LUMO energies are calculated as -0.576, -0.379, and -0.460 eV, respectively. Also, the energy gap between the HOMO and LUMO orbital is determined as 5.121, 5.243, and 5.229 eV for 2-ATP, 3-ATP, 4-ATP, respectively. In the literature review, it was observed that when the HOMO-LUMO energy gap is greater than 4.5 eV, the molecule is interpreted as being chemically stable [41, 42]. The relatively high HOMO-LUMO energy gap value indicates that the investigated isomers have high chemical stability and low reactivity. In this study, it is observed that 3-ATP is the most stable isomer among the ATPs. This idea has been supported by searching the literature; the publication numbers about the adsorption of 3-ATP is the least among other adsorption of ATPs.
In molecules, electrons flow from high chemical potential to low chemical potential. In our molecules, χ values are defined as 3.128, 3.038 and 3.075 eV for 2-ATP, 3-ATP and 4-ATP, respectively. From the HOMO and LUMO energies, the η values are defined as 2.552, 2.659, and 2.615 eV for 2-ATP, 3-ATP, and 4-ATP, respectively. When the electronegativity of the isomers was examined, it was calculated as 3.128, 3.038, 3.075 eV for 2-ATP, 3-ATP and 4-ATP, respectively.

**NLO analysis**

The first and second hyperpolarization values for molecular systems depend on the efficiency of electronic communication between donor and withdrawing groups, which play an important role in intramolecular charge transfer. For the ATPs molecules, the dipole moment (μ), the polarizabilities (α) and the first-order hyperpolarizabilities (β) at the static state were computed by using keyword polar=enonly with the B3LYP/LanL2DZ level. The quantities of µ, α and β in terms of x, y, and z components are listed in Table 5. The µ_{total}, <α> and β_{total} quantities were obtained via the following equations [43]:

$$\mu_{total} = \left( \mu_x^2 + \mu_y^2 + \mu_z^2 \right)^{\frac{1}{2}}$$

$$\alpha_{total} = \frac{1}{3} \left( \alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right)$$

$$\beta_{total} = \left( \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \right)^2 + \left( \beta_{yxy} + \beta_{yyz} + \beta_{yzz} \right)^2 + \left( \beta_{zxx} + \beta_{zxy} + \beta_{zzz} \right)^2$$

| Components | 2-ATP       | 3-ATP       | 4-ATP       |
|------------|-------------|-------------|-------------|
| µx         | -0.210      | -0.915      | 2.201       |
| µy         | 0.736       | 0.034       | 0.00009     |
| µz         | 0.346       | 0.0002      | 0.450       |
| µ_{total}  | 0.841       | 0.979       | 2.247       |
| α_{xx}     | 112.698     | 123.246     | 156.832     |
| α_{yy}     | 92.185      | 94.483      | 80.447      |
| α_{zz}     | 42.769      | 32.033      | 45.710      |
| <α>        | 82.551      | 83.254      | 94.330      |
| β_{xxx}    | 12.234×10^{-24} | 12.338×10^{-24} | 13.980×10^{-24} |
| β_{xyy}    | -54.18      | -227.04     | -669.76     |
| β_{xzz}    | -89.24      | 259.02      | 0.053       |
| β_{yxy}    | -157.73     | 14.08       | 184.70      |
| β_{yzz}    | -80.71      | 69.76       | 0.63        |
| β_{zxx}    | 15.73       | 0.25        | 21.01       |
| β_{zxz}    | -6.83       | -0.12       | 13.16       |
| β_{zxy}    | -5.79       | -31.86      | 5.47        |
| β_{zyy}    | -3.63       | 17.03       | 0.10        |
| β_{zyz}    | 32.51       | 0.13        | 31.16       |
| β_{zzz}    | 281.49      | 390.37      | 484.02      |
| β_{total}  | 2.429×10^{-20} | 3.369×10^{-20} | 4.178×10^{-20} |

(µ = dipole moment at x direction, µ = dipole moment at y direction, µ = dipole moment at z direction, α = dipole polarizability, <α> = static average dipole polarizability, β = further extended first hyperpolarizabilities a.u. = atomic unit, for α, 1 a.u. = 0.1482×10^{-24} esu, for β, 1 a.u. = 0.008629×10^{-30} esu.)
The static $\mu_{\text{total}}, \langle \alpha \rangle$, and $\beta_{\text{total}}$ values of the 2-ATP were calculated as 0.841 Debye, 12.234 x 10^{-24} esu, and 2.429 x 10^{-30} esu, respectively. Similarly, for 3-APT, these values were calculated as 0.979 Debye, 12.338 x 10^{-24} esu, 3.369 x 10^{-30} esu, and for 4-ATP, these values were determined as 2.247 Debye, 13.980 x 10^{-24} esu, 4.178 x 10^{-30} esu, $\mu_{\text{total}}, \langle \alpha \rangle$, and $\beta_{\text{total}}$, respectively. For 4-ATP, the dipole moment value in the x axes is higher than the other axes, and at this value it is 2.247 Debye. The hyperpolarizability value of urea is used as a reference in compounds with nonlinear optical properties [44, 45]. When we survey the literature, the dipole moment ($\mu$) and first-order hyperpolarizabilities values ($\beta$) of urea calculated by the B3LYP/LanL2DZ method are 1.3732D and 0.3782 x 10^{-30} esu, respectively. [44]. When the hyperpolarizability value of ATPs are compared with urea, the hyper polarizable values of ATP isomers appear to be higher than that of urea. Since ATP isomers have a higher intramolecular charge transfer than urea, these isomers are very good candidates for nonlinear optical materials.

CONCLUSION

The vibrational frequencies of an organic molecule have got a unique spectrum for each organic compound. In this point of view, IR spectroscopy has a feature for the identification of chosen isomer set. It is explained how the geometrical differences in molecular dimensions of isomers with the same chemical formula and molecular weight affect the properties of the molecule such as characteristic wavenumbers, polarizability, electronegativity, HOMO-LUMO energies.

It was observed that vibration frequencies increased around 1200 cm\(^{-1}\) as the amine group moved away from the ring-bound S-H group in ATPs. NH\(_2\) is attached to the ring on the C1 atom in all three isomers. However, the angle between C6-C1-C2 carbon atoms, which are in the same order in all isomers, differs in each isomer. For ATPs, it can be said that these differences are due to both the change in the place where the thiol group is attached to the phenyl ring and the distance between the amine and thiol group.

In Figure 4c, it is seen that the negative and positive charge densities are concentrated at the opposite ends of the molecule. The yellow pole with the thiol group is seen as the region where more electrons are collected, while the blue pole with the amine group shows the electron-poor region. The most striking feature of 4-ATP is the distribution of charges on a straight line and this caused the 4 ATP to look like a dipole. In Figure 5, it is sighted viewed that the images of the HOMO-LUMO energies of 4-ATP are quite symmetrical. The property of 4 ATP shows that the charge distributions are symmetrical as in a dipole. This feature indicates that the adsorption properties of 4-ATP are higher than other isomers [46]. When the study of Batz et al. was examined, it was observed that 4-ATP was the most concentrated in the monolayer among the other isomers.

In the literature study, it was realized that 4-ATP was used more frequently in adsorption studies than other isomers. As a result of the experimental and theoretical examination in our study, it is estimated that the symmetry, spatial positioning, and electrical charge distribution of the 4-ATPs may cause this. The information that the dipole moment is effective in facilitating the adsorption of ATPs was given in a study. There is also a study showing that 4-ATP has a high adsorption capacity in studies on corrosion[10, 47].

The relatively high HOMO-LUMO energy gap value indicates that the investigated isomers have high chemical stability and low reactivity. It means they do not show affinity to give in a chemical reaction in room condition. In this study, it is seen that 3-ATP is the most stable isomers among others. Among the isomers, the largest $\mu$ value belongs to 4-ATP and its value is 2.241 D, also dipole moment ($\mu_{\text{total}}$), polarizability ($\langle \alpha \rangle$) and hyper polarizability ($\beta_{\text{total}}$) has the biggest value for 4-ATP as can be seen in Table 5. The hyperpolarizability values of ATPs shows that ATP molecules are very good candidates for nonlinear optical materials.
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