Journal of Neonatal Surgery
ISSN(Online): 2226-0439
Vol. 14, Issue 21s (2025)
https://www.jneonatalsurg.com

OPEN ACCESS

Investigation The Non Linear optical Properties and Spectroscopy Properties of Polyimide Using DFT

Zainab A. Ahmed *[1], Qasim Hassan Ubaid[1], M. A. Al-Kaabi[1]

[1]College of Health and Medical Technology, AL-Zahraa University for Women, Karbala, Iraq
***Correspondence Author**
Zainab A. Ahmed
College of Health and Medical Technology, AL-Zahraa University for Women, Karbala, Iraq
Email ID*zainab.adil.ahmed@alzahraa.edu.iq*

Cite this paper as: Zainab A. Ahmed , Qasim Hassan Ubaid, and M. A. Al-Kaabi, (2025). Investigation The Non Linear optical Properties and Spectroscopy Properties of Polyimide Using DFT. *Journal of Neonatal Surgery*, 14 (21s), 128-135.

ABSTRACT

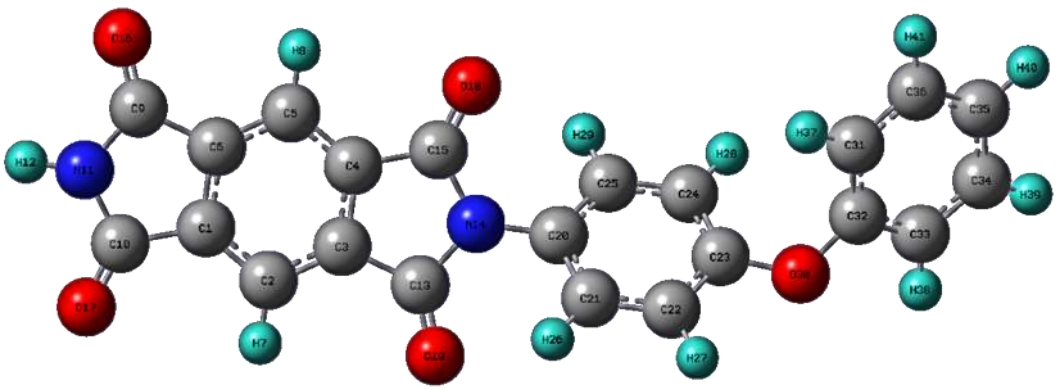
In the current work, nonlinear optical(NLO) properties of polyimide (PI) including polarizability (α), dipole moment (μ), first order hyperpolarizability (β), and susceptibility (χ), have been calculated by using (DFT)\B3LYP method with a 6-311G(d,p) basis set. The results show that the anisotropy of polarizability and first hyperpolarizability is found to have significant values of 259.1x 10-24 esu and 160.4518 x10-33 esu for DFT method. These very small values reflect that the polyimide compound is a good insulator. Moreover, Spectroscopy properties like infrared (IR) absorption spectroscopy, and ultraviolet (UV) Spectroscopy have been calculated by using the DFT method.

Keyword: *Spectroscopy Properties, Polyimide, DFT*

1. INTRODUCTION

Polyimide (PI; C22H10O5N2) is widely used in various fields [1]. In 1908, Marston Bogert produced the first aromatic polyimides [2]. A two-step process is used to produce aromatic PI: first, polyamic acid (PAA) is synthesized from dianhydride and diamine monomers, next, PAA is solvent eliminated [3]. Because of their high electrical resistivity, low dielectric constant, low thermal and chemical durability, and relative ease of use in coating and film production, polyimides have garnered increased attention. With the increasing use of polymers in the microelectronic industry, the significance of comprehending the mechanism causing adhesion between metals and polymers at the microscopic level has increased. The low dielectric constant, high electrical resistivity, thermal and chemical durability, and relative ease of production of coatings and films make polyimides, a class of polymers perfect for microelectronic applications, more appealing [4]. Additionally, PIs are a great option for the production of flexible sensors due to their exceptional thermal and chemical stability[5-9]. In these applications, PI films are used as a matrix, substrate, or electrical insulator. Nevertheless, this material is chemically inert and has a smooth surface. Therefore, specific surface treatments are required in order to maximize their adhesion to other materials [10-12].

In this paper purposes to understand some nonlinear optical properties and spectroscopy of PI to bring insight into the molecular structure



.

2. METHOD OF CALCULATION

DFT has been used for estimate some nonlinear optical properties such as dipole moment (μ), polarizability (α), Hyperpolarizability (β), and Susceptibility (χ) of the monomer of PI using the Becke 3-parameter Lee-Yang-Parr (B3LYP) at the 6-311G(d,p) basis set. In addition, the calculations also including the Spectroscopy Properties like infrared (IR) absorption spectroscopy, and ultraviolet (UV) Spectroscopy. The IR spectroscopy properties were achieved using the same B3LYP method. While UV absorption properties were using the TD-B3LYP method. All calculations are finished and get results using Gaussian 09 software and gaussView6 programs [13].

3. RESULTS AND DISCUSSION

POLARIZABILITY, SUSCEPTIBILITY, AND FIRST ORDER HYPERPOLARIZABILITY CALCULATIONS

To determine the relationship between molecular structure and NLO, it is essential to investigate the dipole moment (μ), polarizability (α), first-order hyperpolarizability (β), and optical susceptibility of the PI molecule [14]. These properties were calculated using the B3LYP method and the 6-311G(d,p) basis set. The next equation can be used to estimate the full dipole moment in terms of its constituent parts [14]:

$$\mu_{tot} = \left(\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2\right)^{1/2} \qquad (1)$$

The mean polarizability and anisotropy of the polarizability ( ) can be found using the following formulas [15]

$$\bar{\alpha} = \frac{1}{3}\left(a_{xx} + a_{yy} + a_{zz}\right) \qquad (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xz}^2 + 6\alpha_{xy}^2 + 6\alpha_{yz}^2\right]^{\frac{1}{2}} \qquad (3$$

The rate value of the first hyperpolarizability can be taken by [16]:

$$\langle\beta\rangle = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{\frac{1}{2}}$$

The DFT method was used to determine the total dipole moment, anisotropy of polarizability, and average hyperpolarizability, which were displayed in Table 1. 160.4518×10-33 esu, 259.1×10-24 esu, and 1.5253 Debye are the respective values. Based on polarizability, the susceptibility was calculated theoretically and compared to experimental values [18]. Table.2 shows the values of the susceptibility. The average of the susceptibility can be given by [17] :

$$\chi = \frac{N\acute{\alpha}}{1 - \frac{4\pi N\acute{\alpha}}{3}} \qquad (5)$$

Table 1: The polyimide's dipole moments, polarizability, and first hyperpolarizability.

The parameter	B3LYP	[17] Experimental amount
The dipole moment		
μ_x	1.1480	
μ_y	0.9840	
μ_z	-0.2069	
μ(Debye)	1.5249	
In esu, polarizability (x 10^{-24}).		
a_{xx}	-148.7201	
a_{xy}	4.2150	

a_{yy}	-179.1570	
a_{xz}	-4.9319	
a_{yz}	-3.3320	
a_{zz}	-159.5559	
$\bar{a}$	-162.470	
Δα	259.2	268.3
	In esu, hyperpolarizability (x 10^{-33}).	
β_{xxx}	64.8454	
β_{xxy}	76.8193	
β_{xyy}	89.5280	
β_{yyy}	-7.8728	
β_{xxz}	-49.3284	
β_{xyz}	18.3787	
β_{yyz}	10.0175	
β_{xzz}	-14.1011	
β_{yzz}	-3.3353	
β_{zzz}	-2.6843	
$\langle\beta\rangle$	160.4518	

Table 2: Polyimide susceptibility

Parameter	PI
α'	$2.5x10^{-24}$
Density	1.40
N	$2.20x\ 10^{27}$
MW	382
χ	0.24
χ (Experimental) [17]	0.13

where χ stands for susceptibility, MW for molar mass, N for molecular number density, and α' for polarizability volume.

More active NLO characteristics are known to be associated with higher dipole moments, polarizability, and first-order hyperpolarizability values, therefore, it is important to take into account the molecular hyperpolarizability of the NLO system

4. SPECTROSCOPY PROPERTIES

It is commonly known that additional information regarding molecular vibrations can be obtained through infrared (IR) absorption spectroscopy. The number of vibrational transitions for nonlinear particles is 3N-6 [18]. Our molecule has 117 vibrational frequencies because it is composed of 41 atoms. The PI's modes of vibration were determined by applying the DFT method with B3LYP and a 6-311G (d, p) basis set. The experimental frequencies and the obtained results have been compared. The PI IR spectrum is shown during the [500–4000] cm^{-1} region in shape 2. The experimental values for the IR technique are also displayed in figure 3.

C-H Vibrations

Multiple weak bands are often seen in the 3100–3000 cm-1 region of aromatic compounds due to their aromatic C–H [19]. The typical range of C-H in-plane bending vibrations is between 1300 cm-1 and 1000 cm-1 [20]. The theoretical and experimental infrared spectra of the PI molecular system are shown in Figures 2 and 3. The benzene ring's C-H stretching vibrations are located in the area (3065.5-3115.6) cm-1, according to figures that show nine C-H stretching vibrations that were assigned in the existing study. The infrared spectrum shows the low band for these stretching vibrations. These are modes of extension. They show good compliance with the specified empirical spectrum range of 2900–3100 cm^{-1} [21].

Aromatic Ring Vibrations

Because the double bond is in conjugation with the ring in the vibrational spectra of benzene and its derivatives, the ring-stretching vibrations are very prominent [22]. Generally speaking, bands that show up in the (1400–1650) cm-1 range are thought to be responsible for the benzene ring vibrations [23]. The range of (1436.8–1593.4) cm-1 is where the C=C stretching vibrations on benzene were detected. The measured experimental values for this mode in infrared were (1500–1520) cm-1.

C=O and C-O-C Vibrations

A double bond forms between carbon and oxygen due to their differing electronegativity. This vibration usually shows very strong peaks in the (1750–1600) cm-1 expected region of the carbonyl C=O stretching mode [24]. The stretching band of the C=O was found at 1779.4 cm-1 and 1793.3 cm-1. These numbers are consistent with 1770 cm-1 and 1780 cm-1. The DFT calculation agrees well with the IR experimental measurements.

C-N and N-H vibration

The C-N stretching vibration typically oscillates between 1200 and 1400 cm-1 [25]. The observations in this study indicate that there is a strong correlation between the theoretically computed value at 1341.7 cm-1 and the experimental values at (1360–1380) cm-1. The stretching N-H mode for the B3LYP can be seen at 3511.6 cm-1. The values of the Fourier Transform Infrared Spectroscopy experiment were 3400 cm-1 [21].

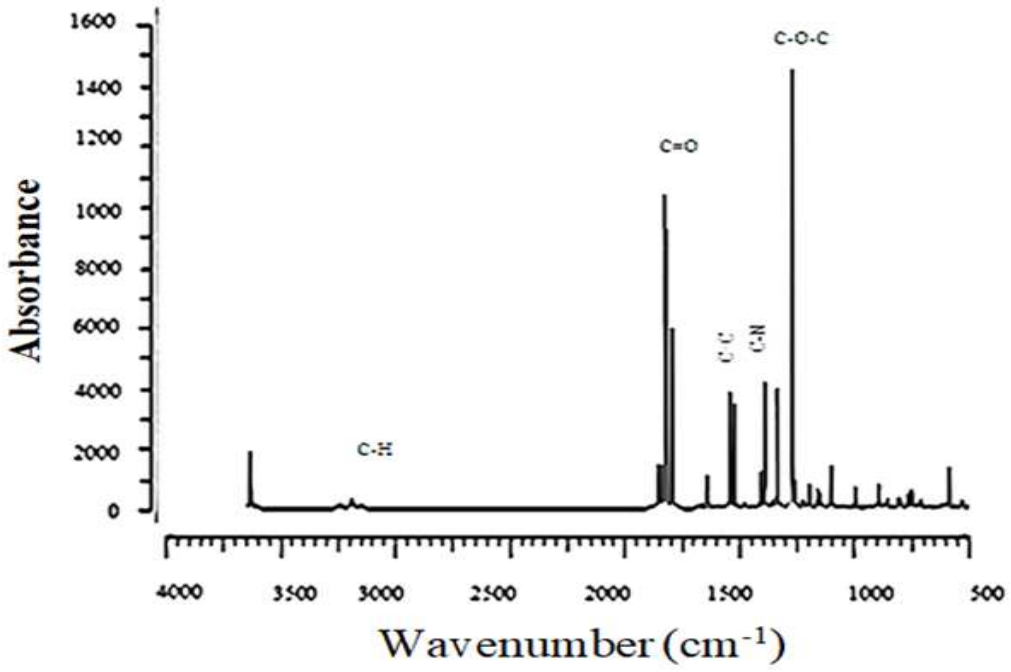


Figure 2: Polyimide's theoretical infrared spectra.

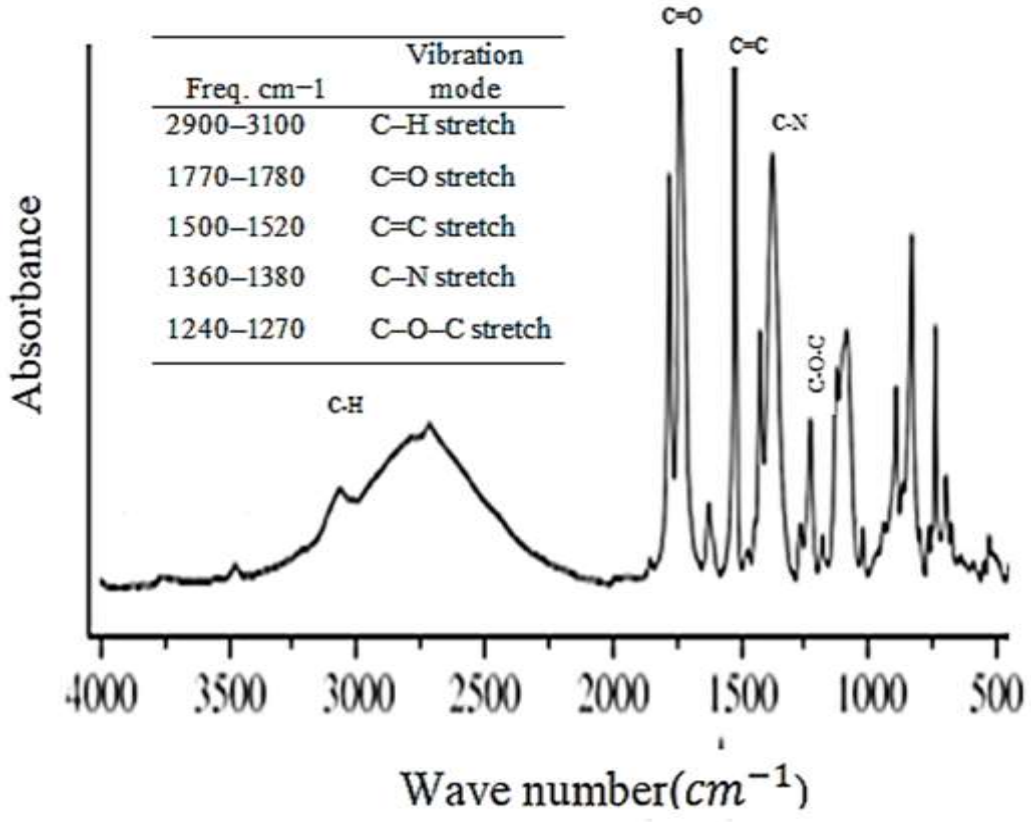


Figure 3: Polyimide's experimental infrared spectra [21].

5. ULTRAVIOLET (UV) SPECTROSCOPY

Aromatic compounds (PIs) are generally believed to absorb UV light by forming a charge-transfer complex (CTC) between the dianhydride and the diamine. Utilizing the TD/B3LYP method and a 6-311G (d, p) basis set, the optimized ground-state geometric monomer of the theoretical absorption spectra of the PI has been examined. Figure 5 display the wavelength obtained using UV technology, which is measured in the range of 300–1100 nm. The maximum wavelength is 510 nm, as shown in Figure 4 and Table 3. It was found that these results are consistent with the experimental value [26] .

Table 3: The maximum wavelength for polyimide, both theoretically and experimentally

experimentally.

Theoretically λ_{max}(nm)		**Experimentally λ_{max} (nm) [26]**
TD-B3LYP	510	500

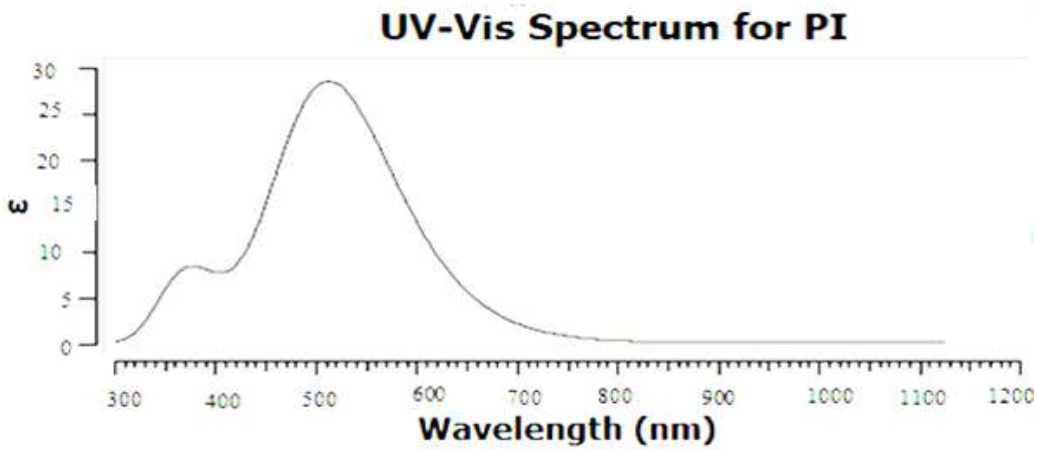


Figure 4: Polyimide's theoretical ultraviolet spectrum.

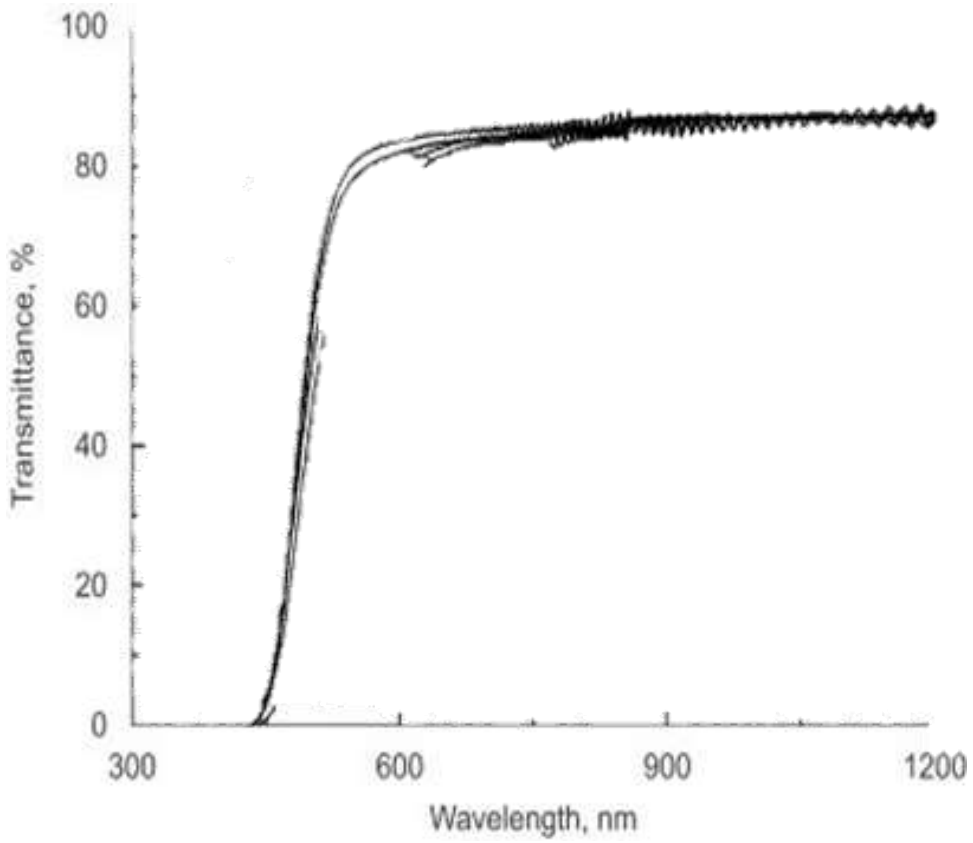


Figure 5: Polyimide's experimental ultraviolet spectrum [26].

ANALYZATION

To understand the polyimide's chemical analysis and the movement of its electrons within the atom and molecular level, the nonlinear optical properties included and spectroscopy properties. The polyimide is a good insulator because the susceptibility value of 0.2 indicates that the electron's mobility was constrained. We conclude the polyimide compound does not exhibit nonlinear optical properties, as demonstrated by the very low values we found for dipole moment, polarizability, and first order hyperpolarization, as well as optical susceptibility. We employed 6-311G(d,p) basis set using a DFT/B3LYP. Furthermore, the longest wavelength of 510 nm that we obtained with ultraviolet spectroscopy using the TD-B3LYP method with a 6-311G(d, p) basis set suggests that long wavelength UV radiation is not regarded as ionizing radiation due to the low

energy of the photon. The calculations were done in order to provide theoretical information for upcoming monomer PI research.

REFERENCES

[1] .Ismail, A., D. Nasrallah, and E. El-Metwally, Modulation of the optoelectronic properties of polyimide (Kapton-H) films by gamma irradiation for laser attenuation and flexible space structures. Radiation Physics and Chemistry, 2022. 194: p. 110026.

[2] Ohya, H., V. Kudryavsev, and S.I. Semenova, Polyimide membranes: applications, fabrications and properties. 1997: CRC Press.

[3] Sezer Hicyilmaz, A. and A. Celik Bedeloglu, Applications of polyimide coatings: A review. SN Applied Sciences, 2021. 3: p. 1-22.

[4] Feger, C., Advances in polyimide: science and technology. 1993: CRC Press.

[5] Cen-Puc, M., et al., An assessment of surface treatments for adhesion of polyimide thin films. Polymers, 2021. 13(12): p. 1955.

[6] Boll, D., et al., Miniaturized flexible interdigital sensor for in situ dielectric cure monitoring of composite materials. IEEE sensors journal, 2014. 14(7): p. 2193-2197.

[7] Yang, T., et al., Fabrication of silver interdigitated electrodes on polyimide films via surface modification and ion-exchange technique and its flexible humidity sensor application. Sensors and Actuators B: Chemical, 2015. 208: p. 327-333.

[8] Hübner, M., et al., Online monitoring of moisture diffusion in carbon fiber composites using miniaturized flexible material integrated sensors. Sensors, 2019. 19(8): p. 1748.

[9] Engel, J., J. Chen, and C. Liu, Development of polyimide flexible tactile sensor skin. Journal of micromechanics and microengineering, 2003. 13(3): p. 359.

[10] Lin, F., et al., High-performance polyimide filaments and composites improved by O2 plasma treatment. Polymers, 2018. 10(7): p. 695.

[11] Qu, H., Z. Wang, and D. Cang, Flexible bandpass filter fabricated on polyimide substrate by surface modification and in situ self-metallization technique. Polymers, 2019. 11(12): p. 2068.

[12] Park, Y.J., et al., Surface modification of polyimide films by an ethylenediamine treatment for a flexible copper clad laminate. Macromolecular Research, 2012. 20: p. 168-173.

[13] M. J. Frisch, G.W.T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[14] Ramalingam, S., et al., Spectroscopic (infrared, Raman, UV and NMR) analysis, Gaussian hybrid computational investigation (MEP maps/HOMO and LUMO) on cyclohexanone oxime. 2012. 96: p. 207-220.

[15] Asghari-Khiavi, M., P. Hojati-Talemi, and F.J.J.o.M.S.T. Safinejad, Polarizability and first-order hyperpolarizability of cyclic imides. 2009. 910(1-3): p. 56-60.

[16] Kosar, B. and C. Albayrak, Spectroscopic investigations and quantum chemical computational study of (E)-4-methoxy-2-[(p-tolylimino) methyl] phenol. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2011. 78(1): p. 160-167.

[17] Lei, H., et al., DFT and molecular dynamic simulation for the dielectric property analysis of polyimides. Chemical Physics Letters, 2022. 786: p. 139131.

[18] Raja, M., et al., Synthesis, spectroscopic (FT-IR, FT-Raman, NMR, UV–Visible), NLO, NBO, HOMO-LUMO, Fukui function and molecular docking study of (E)-1-(5-bromo-2-hydroxybenzylidene) semicarbazide. Journal of Molecular Structure, 2017. 1141: p. 284-298.

[19] Cairns, T., et al., Modern methods of chemical analysis. Pecsok. 1976: John Wiley & Sons.

[20] Altun, A., K. Gölcük, and M. Kumru, Structure and vibrational spectra of p-methylaniline: Hartree-Fock, MP2 and density functional theory studies. Journal of Molecular Structure: THEOCHEM, 2003. 637(1-3): p. 155-169.

[21] Diaham, S., et al., Thermal imidization optimization of polyimide thin films using Fourier transform infrared spectroscopy and electrical measurements. Thin solid films, 2011. 519(6): p. 1851-1856.

[22] Varsányi, G., Vibrational spectra of benzene derivatives. 2012: Elsevier.

[23] Amul, B., et al., Spectral, DFT and molecular docking investigations on Etodolac. Journal of Molecular Structure, 2019. 1195: p. 747-761.

[24] Barbet, F., et al., Comparative Raman spectroscopy studies of photosensitive polymers. Materials chemistry and physics, 1998. 55(3): p. 202-208.

[25] Boopathi, M., et al., ISSN 0975-413X CODEN (USA): PCHHAX.

[26] Ando, S., et al., Effective reduction of volumetric thermal expansion of aromatic polyimide films by incorporating interchain crosslinking. Polymers, 2018. 10(7): p. 761.

..