A Theoretical Study of Structure and Electronic Properties of Poly (ε-Caprolactone) By Density Functional Study

Seda Hekim[1], Mustafa Ersin Pekdemir[2]*

[1]Fırat University, Faculty of Science, Department of Physics, Elazığ, Türkiye
[2]Fırat University, Faculty of Science, Department of Chemistry, Elazığ, Türkiye
*ssrchekim@gmail.com , *ersinpkdmr58@gmail.com*

Abstract

The purpose of this research is to determine the structure's electrophilic and nucleophilic character by examining at local and global chemical activity factors. The electronic behavior of Poly (ε-caprolactone) was investigated by theoretical quantum chemical computation for this purpose. Natural Bonding Orbital (NBO) analysis is a powerful technique for studying stabilization energy $E^{(2)}$, conjugated interactions, and charge transfer in quantum chemistry molecular systems. Furthermore, dipole moment, polarizability, and hyper polarizability characteristics were used to determine the structure's nonlinear optics (Nonlinear Optical, NLO) features. All the theoretical calculations of molecular structure were calculated via the Density Functional Theory (DFT) method in the B3LYP level and STO-3G basis set.

Keywords: Poly (ε-caprolactone), DFT, NLO, NBO, hardness and softness

Poli (ε-Kaprolakton)' un Yapısı ve Elektronik Özelliklerinin Yoğunluk Fonksiyonel Yöntemiyle Teorik Bir Çalışması

Öz

Bu araştırmanın amacı, lokal ve global kimyasal aktivite faktörlerini inceleyerek yapının elektrofilik ve nükleofilik karakterini belirlemektir. Poli (ε-kaprolakton)' un elektronik davranışı, bu amaçla teorik kuantum kimyasal hesaplama ile araştırıldı. Natural Bonding Orbital (NBO) analizi, kuantum kimyası moleküler sistemlerinde yük transferi, konjuge etkileşimler ve stabilizasyon enerjisini E(2), incelemek için güçlü bir tekniktir. Ayrıca yapının doğrusal olmayan optik (Doğrusal Olmayan Optik, NLO) özelliklerini belirlemek için dipol moment, polarize edilebilirlik ve hiperpolarize edilebilirlik özellikleri kullanılmıştır. Moleküler yapının tüm teorik hesaplamaları, B3LYP seviyesinde ve STO-3G baz setinde Yoğunluk Fonksiyonel Teorisi (DFT) yöntemi ile hesaplanmıştır.

Anahtar Kelimeler: Poli (ε-kaprolakton), DFT, NLO, NBO, sertlik ve yumuşaklık

INTRODUCTION

Shape memory polymers have become very interesting in recent years (Huang et al., 2005). Shape memory polymers, known as smart polymers, are polymers that can recover after being deformed by external factors such as heat, light, humidity, pH (Koerner et al., 2004; Lendlein and Kelch, 2002). The most well-known smart polymers are poly ε-caprolactone (PCL) and poly lactic acid (PLA) (Jia et al., 2008; Pekdemir, 2021). PCL is an aliphatic polyester with semi-crystalline properties (Pekdemir et al., 2021). PCL is biocompatible, biodegradable and non-toxic to living organisms, which has important applications such as drug release, tissue engineering (Jenkins et al., 1996; Peeters et al., 2005).

The computational chemistry methods establish a connection between theoretical and experimental data by using mathematical data. The physical and chemical properties of molecules are known to be connected to their geometry structure. The chemical activity of molecules can be determined using optimized structures derived from theoretical studies and electronic structure descriptors of optimized structures. In

computational chemistry investigations, ab-initio methods, which are a type of quantum mechanical method, were favored. The density function theory, which takes intramolecular electron-electron interactions into account in the ab-initio approach is one of the most preferred methods used in calculating the reactivity of molecules (Hohenberg and Kohn, 1964; Kohn, 1996).

In terms of the scope of our study, theoretical calculations were done to look at molecular and chemical characteristics of synthesized poly (ε-caprolactone) (PCL) compound that could not be achieved through experimental methods. All theoretical studies were calculated by using DFT methods with Becke's three-parameter change function, and Lee-Yang-Parr non-local correlation function (B3LYP) (Becke, 1992; Reed, 1997) combined with a standard STO-3G basis set. Natural bond orbital (NBO)analysis was used to compute the redistribution of electron density (ED) in various bonding and antibonding orbitals, as well as $E^{(2)}$ energies, to show that stabilization occurs as a result of the hyper conjugation of numerous intramolecular contacts. The frontier molecular orbitals HOMO and LUMO were used to explain information relating to ionization potential, electron affinity, energy gap, electronegativity, electrophilicity index, hardness, and softness (Orbitals, 1976; Parr and Pearson, 1983; Pearson, 1986). The non-linear optical characteristics (NLO) and some thermodynamics properties were also calculated and interpreted theoretically.

COMPUTATIONAL METHODS

All quantum chemical calculations in this study, have been performed with the Gaussian 09 (Frisch et al., 2009) package. First, the ground state and gas-phase optimization of the examined molecule was made with DFT using B3LYP and STO-3G basis set. Then, non-linear optical characteristics (NLO) such as polarizability, hyper polarizability, and thermodynamic parameters were calculated. and also Natural bond orbital (NBO) calculations involved in determining the reactive regions of the molecule were investigated. The results of the acquired calculations were determined and reported.

RESULTS AND DISCUSSION
Optimized Molecular Structure

Ground –state structure of PCL was optimized with the DFT/B3LYP/STO-3G method in gas phase. The optimized geometry is shown in Figure 1. PCL is owned by C1 point group symmetry.

Fundamental orbitals that participate in chemical reactions are called frontier molecular orbitals (HOMO and LUMO). (Martínez, 2009; Orbitals, 1976). A molecule's ability to donate electrons is called its electron-donor capacity and is described by its highest occupied molecular orbital energy (E_{HOMO}), whereas the molecule's ability to receive electrons is defined by its lowest unoccupied molecular orbital energy (E_{LUMO}). The difference between these energies (ΔE) is used to determine the chemical reactivity of the molecule. Whether the ΔE value is numerically large or small has a big impact on the reaction mechanism and reaction conditions.
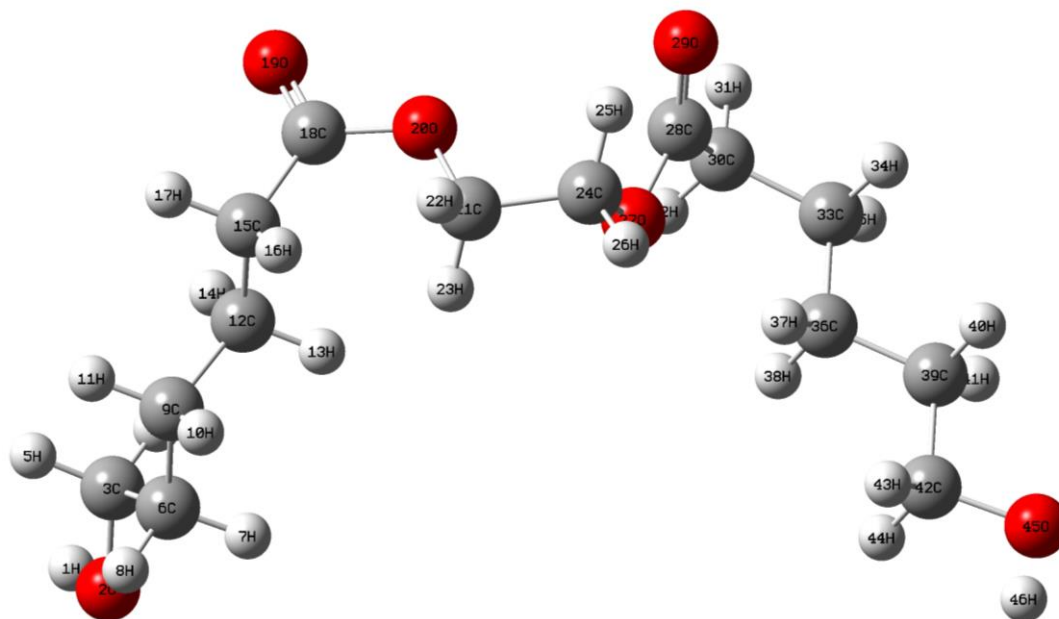
Figure 1. Optimized molecular structure and the atom numbering scheme for the PCL

E_{HOMO}=-3.379 eV E_{LUMO}=2.746 eV

ΔE (E_{LUMO}- E_{HOMO})=6.539 eV
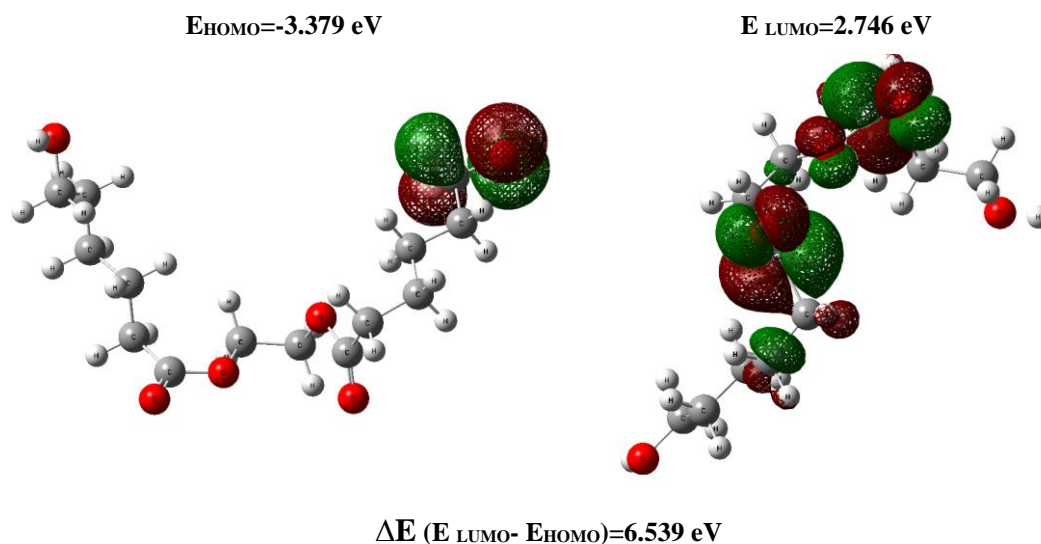
Figure 2. E_{HOMO} (eV), E_{LUMO} (eV), ΔE (eV) of PCL with B3LYP/STO-3G method in the gas phase

The E_{HOMO}, E_{LUMO}, ΔE (E_{LUMO}- E_{HOMO}) energies calculated and are shown in Figure 2. As seen in Figure 2, the PCL molecule has a large energy range (ΔE =6.539 eV). This shows that the conjugation probability of the molecule is less and it can be excited at higher energies. Moreover, the structure's high energy range indicates that it is quite stable and has limited chemical activity(Adiguzel et al., 2020; Al-khaykanee and Aboud, 2013; Babu and Kumar).

Nonlinear optical properties (NLO)

Quantum-chemical calculations have helped to clarify the electronic polarization that underpins molecular NLO activities and to develop structure-property connections (Demircioğlu et al., 2015). Nonlinear optical (NLO) features of the molecule include total static dipole moment, mean polarizability, anisotropy of polarizability, and first order hyper polarizability. The response of a system in an applied electric field is defined by its polarizabilities and hyper polarizabilities. One of the most important factors in structural chemistry is the dipole moment, which may be used as a descriptor to detect charge transport inside the molecule(Daraam et al., 2015; Evecen and Tanak, 2017; Novir, 2017). The total dipole moment can be determined using the equation below:

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \tag{1}$$

here μ_x, μ_y, μ_z are the vector components of the dipole moment. The mean polarizability (α), the anisotropy of polarizability (Δα), and the total first order hyper polarizability (β), are computed by the following formulas:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{2}$$

$$\Delta\alpha = \left[\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2}{2} \right]^{1/2} \tag{3}$$

$$\beta = \left[(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \right] \tag{4}$$

where α_{xx}, α_{yy}, α_{zz} are tensor components of polarizability, and β_{xxx}, β_{xyy}, β_{xzz}, β_{yyy}, β_{yzz}, β_{yxx}, β_{zzz}, β_{zxx}, β_{zyy} are tensor components of hyper polarizability, which can be found via a frequency calculation output in Gaussian (Novir, 2017).

To take into account the relationship between NLO characteristics, energy gap, and chemical reactivity descriptors as electronegativity, chemical hardness, softness, chemical potential, and electrophilicity index, relevant calculations were made using Koopmans's theorem (Koopmans, 1934; Parr and Pearson, 1983; Pearson, 1986) and presented in the Table 1 and Table 2. The structure has a high energy range (ΔE, in Figure 1), high hardness, and low softness characteristics, according to the results. Intramolecular charge transfer is minimal in molecules with a high chemical hardness. Moreover, the softness is correlated with polarizability and is described as the soft molecules have high polarizability and the hard molecules have low polarizability(Al-khaykanee and Aboud, 2013). As seen in the tables, the PCL molecule has low polarizability and high chemical hardness.

Thermodynamic properties

Table 3 shows the thermodynamic parameters of the PCL, which include total thermal energy (E), zero-point vibrational energy (ZPE), heat capacity (C), and entropy (S), which were calculated using frequency calculations at temperatures ranging from 100 to 500 K. Figure 3 depicts the correlation between total thermal energy, heat capacity, entropy and enthalpy changes, and temperature, as well as the quadratic formula-fitted correlation equations and the accompanying fitting factors (R^2). The results show that, with the exception of the zero-point energy, all of these thermodynamic characteristics increase as the temperature rises. Because the intensity of molecular vibrations increases as the temperature rises.(Tanış et al., 2018). However, the temperature has no effect on the zero-point vibrational energy.

Table 1. The calculated dipole moments (Debye), polarizability components (a.u.) and hyper polarizability components (a.u.).
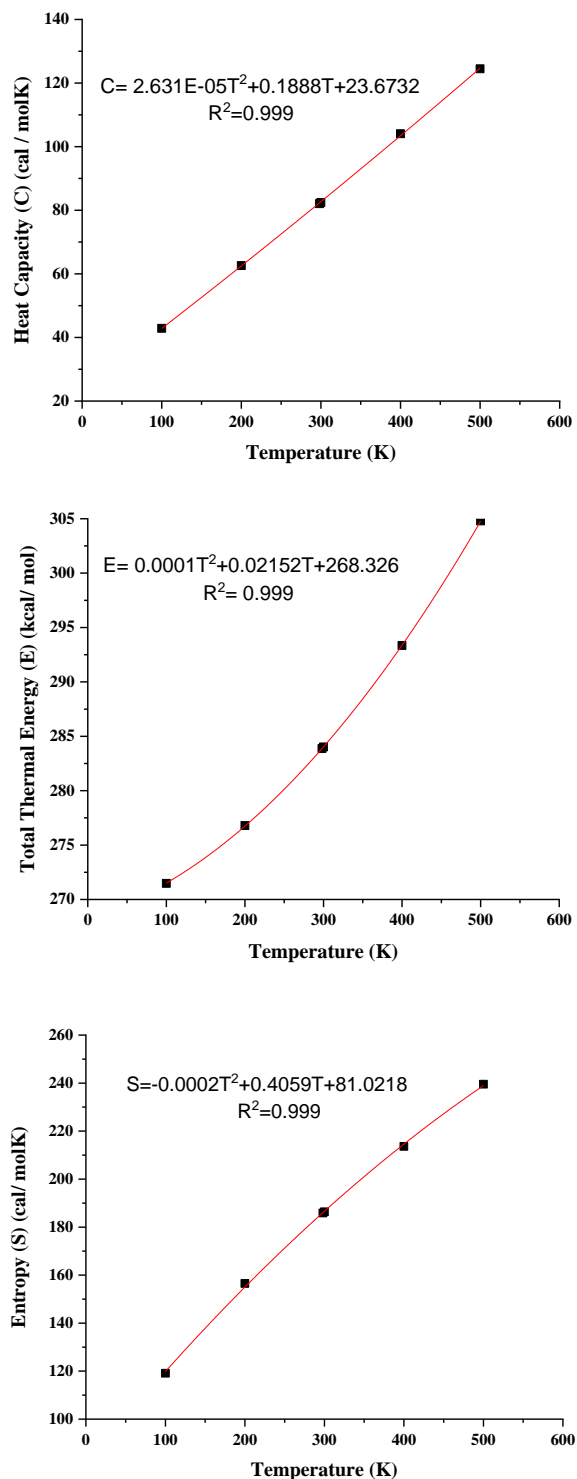
Dipole moments		Polarizability (α)		Hyperpolarizability (β)	
μ_x	-1.462 a.u.	α_{xx}	-120.273 a.u.	β_{xxx}	-160.089 a.u.
μ_y	2.258 a.u.	α_{yy}	-129.425 a.u.	β_{xyy}	51.424 a.u.
μ_z	-1.928 a.u.	α_{zz}	-102.883 a.u.	β_{xzz}	-3.197 a.u.
μ_t	**3.309 Debye**	α_t	-117,527	β_{yyy}	35.336 a.u.
		α_t	**-0.174x10^{-22} esu**	β_{yzz}	11.681 a.u.
				β_{yxx}	-21.771 a.u.
				β_{zzz}	6.497 a.u.
				β_{zxx}	24.812 a.u.
				β_{zyy}	-27.132 a.u.
				B_{tt}	114.752
				B_{tt}	**0.991x10^{-30} esu**

Table 2. Chemical Reactivity Descriptions

Parameters	eV
Chemical hardness (η)	3.269
Chemical softness (s)	0.152
Electrophilic index (w)	0.0419
Chemical potential (μ)	-0.524
Electronegativity (χ)	0.524

Table 3. Thermodynamic properties at different temperatures of PCL at the B3LYP/STO-3G level in gas phase.

Temperature (K)	Zero point energy (kcal mol^{-1})	Total thermal energy (E) (kcal mol^{-1})	Heat Capacity (C) (cal mol^{-1} K^{-1})	Entropy (S) (cal mol^{-1} K^{-1})
100	268.693	271.483	42.874	119.125
200	268.693	276.793	62.583	156.533
298.15	268.693	283.869	82.050	185.851
300	268.693	284.021	82.443	186.372
400	268.693	293.345	104.069	213.618
500	268.693	304.791	124.461	239.518

$C= 2.631E\text{-}05T^2+0.1888T+23.6732$
$R^2=0.999$

$E= 0.0001T^2+0.02152T+268.326$
$R^2= 0.999$

$S=-0.0002T^2+0.4059T+81.0218$
$R^2=0.999$

Figure 3. Correlation graphic of thermodynamic properties and temperature for PCL

Natural Bond Orbital Analysis (NBO)

Nature Bond Orbital (NBO) analysis is a useful tool for examining intermolecular bonding and interaction, as well as charge transfer and conjugative interactions in molecular systems (Weinhold and Landis, 2001). In the NBO basis, the second-order Fock-matrix was used to examine various forms of donor-acceptor interactions and their stabilization energies (Kaur et al., 2012). The stabilization energy $E^{(2)}$ obtained via second-order perturbation theory analysis of the Fock-matrix in NBO can be used to quantify the donor-acceptor interaction. The interaction between donor and acceptor orbitals rises as the stabilization energy increases.

The stabilization energy $E^{(2)}$ associated with electron delocalization between donor and acceptor is approximated for each donor NBO (i) and acceptor NBO (j) as

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F_{i,j}^2}{\varepsilon_j - \varepsilon_i} \tag{5}$$

where qi is the donor-orbital occupancy, εj and εi are diagonal elements orbital energies and F(i,j) is the Fock matrix element between the natural bonding orbitals. For the title molecule, NBO analysis was performed at the DFT/B3LYP/STO-3G level to determine the interaction between the filled (I) and unoccupied (j) orbitals with the goal of delocalization and rehybridization of intramolecular electron density. A stabilized donor-acceptor interaction is related to electron delocalization between filled Lewis-type NBO orbitals and unoccupied non-Lewis NBO orbitals. The extent of conjugation of the whole system, the possible intensive interaction values are given in Table 4.

Table 4. NBO analysis values of PCL

Donor (i)	ED /e	Acceptor (j)	ED /e	E $^{(2)}$ Kcal /mol	E(j)-E(i) a.u.	F(i,j) a.u.
σ(H1-O2)	1.98764	σ*(C3-C6)	0.02248	2.92	0.93	0.047
σ (C12-C15)	1.97597	π*(C 18-O19)	0.21069	3.69	0.56	0.043
σ(C15- C18)	1.96982	σ* (C18- O19)	0.02729	2.94	1.08	0.050
σ(C15 - C18)	1.96982	σ* (C18- O20)	0.14584	6.41	0.82	0.067
σ(C18 - O20)	1.97091	σ*(C15-C18)	0.09405	3.16	0.96	0.050
σ(C18 - O20)	1.97091	σ*(C18 - O19)	0.02729	3.44	1.17	0.057
σ(O 20 - C21)	1.97893	σ*(C18 - O19)	0.02729	2.85	1.14	0.051
σ (O20 - C21)	1.97893	σ*(C 18 - O20)	0.14584	2.04	0.89	0.039
σ (C21 - H22)	1.98569	σ*(O20 - C21)	0.03369	2.10	0.78	0.036
σ (C21 - H22)	1.98569	σ*(C24 - O27)	0.03130	2.53	0.78	0.040
σ(C21- H23)	1.98840	σ*(O20-C21)	0.03369	2.20	0.78	0.037
σ(C24 -H25)	1.98914	σ*(C24 - O27)	0.03130	2.28	0.77	0.037
σ (C24 - H26)	1.98706	σ*(O20 - C21)	0.03369	2.32	0.77	0.038
σ(C24 - O27)	1.97948	σ*(C28 - O29)	0.02637	2.94	1.13	0.052
σ(O27 - C28)	1.97500	σ*(C28 - O29)	0.02637	2.88	1.17	0.052
σ (O27 - C28)	1.97500	σ*(C28 - C30)	0.07952	3.20	0.97	0.050
σ (C28 - O29)	1.98862	σ*(O27 - C28)	0.15041	3.90	1.08	0.060
σ(C28 - C30)	1.97429	σ*(O27 - C28)	0.15041	2.87	0.83	0.045
σ (C28 - C30)	1.97429	σ*(C28 - O29)	0.02637	3.02	1.08	0.051
σ (C30 - C33)	1.97517	π*(C28 – O29)	0.22670	4.11	0.54	0.044
σ (O45 - H46)	1.98759	σ*(C39 - C42)	0.02194	2.94	0.93	0.047
σ*(C18 - O20)	0.14584	σ*(C15 - C18)	0.09405	7.07	0.04	0.041

Highest stabilization energy values were observed at transitions σ (C15 - C18) → σ* (C18- O20), σ (C30 - C33) → π*(C28 – O29), σ*(C18 - O20) → σ*(C15 - C18) and at 6.41, 4.11, and 7.07 kcal/mol values, respectively.

CONCLUSIONS

In this study, the geometry structure, electronic properties, nonlinear optical properties, thermodynamic properties, natural bond orbital analysis of the synthesized PCL compound were investigated. The frontier molecular orbital energy levels and the energy difference between these levels were determined and show that the PCL is more stable structure with a high energy difference. Due to the large HOMO-LUMO molecular energy difference, the polarizability value is also quite small. Furthermore, chemical hardness and polarizabilities values of the molecule have been found to have an inverse relationship. The thermodynamic parameters such as total thermal energy, heat capacity, and entropy of the title molecule are increasing with enhancing temperature. The NBO analysis revealed that the σ*(C18 - O20) → σ*(C15 - C18) interaction gives the strongest stabilization to the system around at 7.07 kcal/mol.

CONFLICT OF INTEREST

The Authors report no conflict of interest relevant to this article.

RESEARCH AND PUBLICATION ETHICS STATEMENT

The authors declare that this study complies with research and publication ethics.

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