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Quantum Chemical Investigation of Molecular Structure, Thermal, Electronic Properties and Reactivity of propargyl 2-bromoisobutyrate

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Abstract: To predict reactivity and reactive sites on the propargyl 2-bromoisobutyrate molecule, several global and local reactivity descriptors have been computed. All calculations have been made through a computational study based on density functional theory (DFT/B3LYP) using a basis set LanL2DZ. The stability of the molecule has been investigated using the natural bond orbital (NBO) analysis. The highest occupied molecular orbital (HOMO) energies, the lowest unoccupied molecular orbital (LUMO) energies have been calculated and the electronic properties depending on HOMO-LUMO energies were determined. Also, the thermodynamic properties of the title compound were studied. The electron density-based local reactivity descriptors such as the Fukui functions have been calculated to explain the chemical selectivity or reactivity site in the molecule.

Keywords: Propargyl 2-bromoisobutyrate, DFT, NBO, B3LYP, LanL2DZ basis set, HOMO and LUMO orbital energies

Propargil 2-bromoizobütiratın Moleküler Yapısının, Termal, Elektronik Özelliklerinin ve Reaktivitesinin Kuantum Kimyasal İncelenmesi

Öz: Propargil 2 bromoizobutirat molekülü üzerindeki reaktiviteyi ve reaktif bölgeleri tahmin etmek için bir dizi global ve lokal reaktivite tanımlayıcısı hesaplanmıştır. Tüm hesaplamalar, LanL2DZ temel seti kullanılarak yoğunluk fonksiyonel teorisine (DFT/B3LYP) dayalı hesaplamalı çalışma yoluyla yapılmıştır. Molekülün stabilitesi, doğal bağ orbitali (NBO) analizi kullanılarak araştırılmıştır. En yüksek dolu moleküler orbital (HOMO) enerjileri, en düşük boş moleküler orbital (LUMO) enerjileri hesaplanmış ve HOMO-LUMO enerjilerine bağlı elektronik özellikler belirlenmiştir. Ayrıca başlıktaki bileşiğin termodinamik özellikleri incelenmiştir. Fukui fonksiyonları gibi elektron yoğunluğuna dayalı lokal reaktivite tanımlayıcıları, moleküldeki kimyasal seçiciliği veya reaktivite bölgesini açıklamak için hesaplanmıştır.

Anahtar Kelimeler: Propargil 2-izobutirat, DFT, NBO, B3LYP, LanL2DZ baz seti, HOMO ve LUMO orbital enerjileri

1. Introduction

The synthesis of polymers, whose chemical structure is well defined and whose functional groups can be arbitrarily controlled, continues to attract the attention of researcher’ s day by day. This situation, which allows the polymer chains to grow in a controlled manner, can be achieved with living polymers and the best example of this is ATRP [1-3]. Alkyl halides containing active

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substituents such as aryl carbonyl or alkyl groups at the α-carbon are potential initiator species frequently used in ATRP. Propargyl 2-bromoisobutyrate is one of the most widely used initiators in ATRP polymerization and click chemistry [4].

The properties of the molecules have been determined without the need for experiments thanks to recent theoretical methods. These equations can be conveniently applied to synthetic or non-synthetic compounds that do not occur in nature to produce the desired results. In this way, the behavior of the molecules can be predicted without any experiments. Density functional theory (DFT) [5] is a very commonly used method used in calculating the energy, dipole moment, geometric parameters, hardness and softness parameter, and chemical activity of molecules. In the DFT model, knowing the full wave functions begins with a Hamiltonian that fits ideally in a multi-electron system. The solution is found by optimizing the molecular system to be closest to the real system. The most stable state of the building is achieved with optimization. As a result of the optimization, the suitability of the used method and the base set is determined by the harmony of the geometric parameters obtained by experimental measurements with the theoretical data.

In this study, quantum calculations of the synthesized propargyl 2-bromoisobutyrate molecule were computed using the B3LYP and LanL2DZ base set, which is the correlation energy 3-parameter Becke hybrid model of DFT [5-7]. After determining the structure's most stable condition, local and global chemical activity calculations were obtained to evaluate the properties derived from energy, electrophilic and nucleophilic existence. While global chemical activity data were obtained with hardness and softness parameters calculated using HOMO and LUMO energies, which are the frontier molecular orbitals, local chemical activity data were obtained with Fukui function analysis, Mulliken population, and natural population net charge values, and molecular electrostatic potential map analysis.

2. Computational Details

Molecular modeling of the propargyl 2-bromoisobutyrate molecule and all the theoretical analysis on the structure were made using Gaussian 09W [8] and Gaussview 5.0 [9] molecular imaging programs. Optimized geometry, electronic, reactivity, and thermodynamic properties of the relevant molecule were investigated using the DFT B3LYP/LanL2DZ basis set.

The ionization energy (I) and electron affinity (A) given by Koopmans' theorem[10] are approximated using the frontier molecular orbitals in quantum chemical characteristics calculations. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are types of molecular orbitals and are called frontier molecular orbitals. The gap between HOMO and LUMO energy values is defined as the chemical stability of the molecule. [11-14] The smaller this energy, the easier the interaction will be. The ionization energy is defined as $I=-E_{HOMO}$, which is the minimum energy necessary to remove an electron from a molecule in the gas phase, and the electron affinity is defined as $A=-E_{LUMO}$, which is the amount of energy that increases when an electron is added to a molecule in the gas phase. The hardness value, which is a measure of the inhibition of charge transfer within the molecule, is given by $\eta=(I-A)/2$, and the softness parameter is represented by $S=1/(2\eta)$ [15]. The Mulliken electronegativity parameter is defined as $(I+A)/2$, which represents the ability of an atom in a molecule to attract electrons. In addition, the electrophilic index is calculated with $w=\mu2/(2\eta)$, the chemical potential $\mu=-(I+A)/2$ and the maximum charge transfer parameter $\Delta N_{max}=(I+A)/2(I-A)$.

The Fukui functions of the studied structure have been calculated using Natural population analysis (NPA) net charges. The electrophilic and nucleophilic regions of a structure are determined by the local Fukui function values of the atoms in a molecule using Fukui function analysis. The $f_k^+(r)$

defined susceptibility to nucleophilic attack $f_k^-(r)$ determines electrophilic attack and $f_k^0(r)$ determines free radical attack. Equations for these functions are given below;

$$f_k^+(r) = q_k(N+1) - q_k(N) \tag{1}$$

$$f_k^-(r) = q_k(N) - q_k(N-1) \tag{2}$$

$$f_k^0(r) = \frac{q_k(N+1) - q_k(N-1)}{2} \tag{3}$$

The above equations q_k represents atomic charges, (N) neutral, (N + 1) anionic, (N-1) kth atomic charges belonging to the cationic chemical region.

Natural bond orbital (NBO) analysis is the most effective method that examines intermolecular bonds, charge transfers, and conjugated interactions between them. A good donor-acceptor interaction can be achieved by delocalizing the electron density between Lewis-type filled NBO orbitals and non-Lewis empty orbitals. In the NBO method, the stabilization energy value indicates the intense interaction between the acceptor electron and the donor electron. The stabilization energy value $E^{(2)}$ depends on a variable acceptor orbital occupancy, the donor-acceptor orbital energy, and the NBO Fock-Matrix element. The stabilization energy value $E^{(2)}$ given by

$$E^{(2)} = q_i \frac{F^2(i,j)}{E_i - E_j} \tag{4}$$

Where E_i, E_j are diagonal elements (orbital energies), q_i is the donor orbital occupancy, *F (i,j)* are non-diagonal Fock matrix elements [15-20].

3. Results And Discussion

3.1. Geometric Optimization

In Figure 1, the theoretical geometric structure of propargyl 2-bromoisobutyrate is given together with the atom numbering scheme.

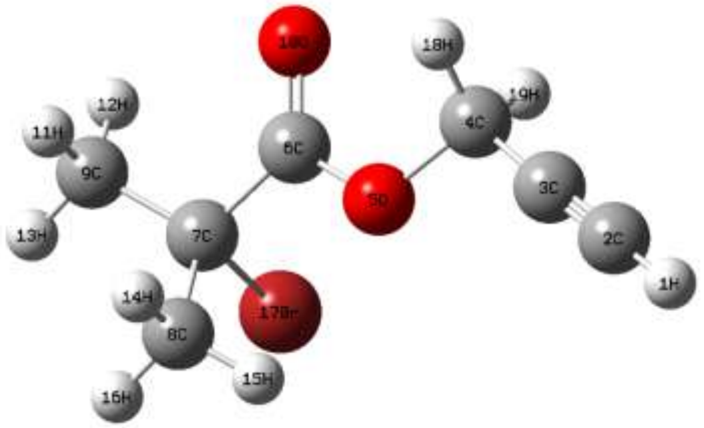

Figure 1. The theoretical geometric structure of the propargyl 2-bromoisobutyrate (with B3LYP/ LanL2DZ level)

3.2. Local Chemical Activity Calculations: Molecular Electrostatic Potential (MEP)

Electrophilic nature, nucleophilic reactions, and hydrogen bond interactions can all be explained using molecular electrostatic potential, which is related to electron density. It is known that molecular electrostatic potential surfaces are defined by color codes. The most negative regions are represented in red and these regions describe electrophilic reactions, while blue and green are predicted to represent the most positive regions and nucleophilic dominant regions [21-23]. The total electron density surface and the surface of the contour in the form of two-dimensional surface curves of the propargyl 2-bromoisobutyrate is given in Figure 2, which has color codes from red to blue, represents a potential distribution in the range of -0.048 a.u. to 0.048 a.u. The optimum electrophilic reaction zones are localized on O5, O10 atoms, as shown in Figure 2. Maximum positive regions defining nucleophilic reactions are concentrated on hydrogen atoms in the methyl group. The results in the MEP map showed that there is a positive potential region around the hydrogen and hydrogen atoms, while there is a negative potential region on the electronegative atoms. It is these locations that allow us to receive information between regions of the molecule where it has non-covalent interactions.

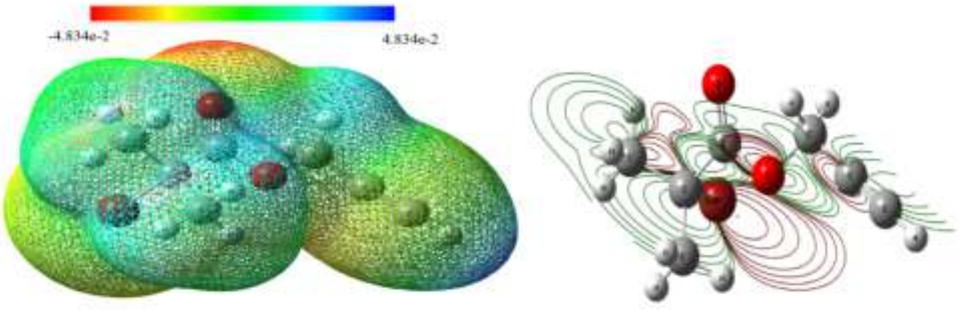

Figure 2. The total electron density surface and the surface of the contour in the form of two-dimensional surface curves of the propargyl 2-bromoisobutyrate

3.3. Local Chemical Activity Calculations: Net Charges (MPA and NPA)

Natural population (NPA) load analysis and Mulliken population analysis (MPA) [24] are frequently used in net load analysis calculation. Mulliken population method, one of the oldest and most widely used methods, is based on the principle of obtaining molecular orbitals as a result of a linear combination of atomic orbitals. It is predicted in the literature that it gives sufficient results in determining the charges of atoms and using them in understanding the electrophilic and nucleophilic nature. Natural population charge analysis is also a theoretical calculation method similar to Mulliken. Natural population charges are calculated as a result of natural bond orbital (NBO) analysis. In Table 1, the net charges of both methods are given comparatively for each atom of the optimized structure. The net charge values obtained in both methods have a very good agreement with each other. It is seen in Table 2 that the most positive charges are on C2, C3, C6, and all hydrogen atoms, While the most negative charges are localized on C4, C7, C8, C9, O10, and Br17 atoms. The most positive and negative regions discovered by the net charge analysis were found in the direction of the MEP map.

3.4. Local Chemical Activity Calculations: Fukui Function Analysis

Fukui Function analysis helps to understand chemical reactions by determining the molecule's local region activity. The Fukui function's calculated values are qualitative descriptors of the activity of various atoms in the molecule. $\Delta f_k(r)$ is a parameter that determines the electrophilic and nucleophilic character of the structure's atoms (r) and is determined by. $\Delta f_k(r) = (f_k^+(r) - f_k^-(r))$. If $\Delta f_k(r) > 0$ nucleophilic susceptibility is dominant if $\Delta f_k(r) < 0$ electrophilic susceptibility is dominant. As shown in Table 2, nucleophilic dominant regions are concentrated on the H1, C2, C3, H11, H14, Br17, H18, and H19 atoms, whereas electrophilic dominant regions are concentrated on the C4, O5, C6, C7, C8, C9, O10, H12, H13, H15, and H16 atoms,

Table 1. Mulliken population and natural population charge analysis data

Atom	Mulliken Charges	NPA
H1	0.280	0.2338
C2	0.432	-0.1907
C3	0.167	-0.0399
C4	-0.278	-0.1368
O5	-0.293	-0.5696
C6	0.379	0.8108
C7	-0.177	-0.0827
C8	-0.598	-0.6600
C9	-0.596	-0.6597
O10	-0.258	-0.6048
H11	0.202	0.2325
H12	0.251	0.2518
H13	0.220	0.2354
H14	0.199	0.2309
H15	0.258	0.2548
H16	0.219	0.2309
Br17	-0.043	-0.0280
H18	0.249	0.2436
H19	0.249	0.2432

Table 2: Fukui function analysis values obtained from NPA net charge

Atom No	$q_k(N)$	$q_k(N+1))$	$q_k(N-1)$	$f_k^-(r)$	$f_k^+(r)$	$\Delta f_k(r)$
H1	0.2338	0.2626	0.2167	0.0171	0.0288	0.0117
C2	-0.1907	-0.0025	-0.2752	0.0845	0.1882	0.1037
C3	-0.0399	0.0600	0.0052	-0.0451	0.0999	0.145
C4	-0.1368	-0.1528	-0.1480	0.0112	-0.016	-0.0272
O5	-0.5696	-0.5387	-0.6139	0.0443	0.0309	-0.0134
C6	0.8108	0.7962	0.6989	0.1119	-0.0146	-0.1265
C7	-0.0827	-0.0820	-0.1561	0.0734	-0.0007	-0.0741
C8	-0.6600	-0.6651	-0.6628	0.0028	-0.0051	-0.0079
C9	-0.6597	-0.6657	-0.6630	0.0033	-0.006	-0.0093
O10	-0.6048	-0.5396	-0.7558	0.1510	0.0652	-0.0858
H11	0.2325	0.2702	0.1977	0.0348	0.0377	0.0029
H12	0.2518	0.2622	0.2361	0.0157	0.0104	-0.0053
H13	0.2354	0.2533	0.2035	0.0319	0.0179	-0.014
H14	0.2309	0.2647	0.1977	0.0332	0.0338	0.006
H15	0.2548	0.2569	0.2368	0.0180	0.0021	-0.0159
H16	0.2309	0.2555	0.2023	0,0286	0.0246	-0.004
Br17	-0.0280	0.3868	-0.3794	0,3514	0.4148	0.0634
H18	0.2436	0.2913	0.2301	0,0135	0.0477	0.0342
H19	0.2432	0.2864	0.2308	0,0124	0.0432	0.0308

3.5. Natural Bond Orbital Analysis (NBO)

Intermolecular charge transfer is enabled through intermolecular hyper conjugative interactions, which stabilize the molecular system through overlapping orbitals between bonding and antibonding orbitals. To understand the delocalization of the intermolecular electron density of the propargyl α-bromoisobutyrate molecule on the DFT/B3LYP/LanL2DZ base set, the electron donor, electron acceptor, and stabilization energy of the molecule was obtained by using the NBO 3.1 program together with Gaussian 09 W. As a result of the NBO analysis, the total Lewis interaction of the structure was 99.153% and the total non-Lewis interaction was 98.471%. Natural bond orbital analysis data of optimized structure is given the Table 3. These interactions, lead to increased electron density in the antibonding orbitals, was observed as σ (C2-C3) → σ* (C3-C4) 2.68 kcal/mol, σ (C3-C4) → σ* (C2-C3) 5.28 kcal/mol. As seen in Table 3, the strongest interaction was found as 15.74 kcal/mol with the transition σ* (O6-C6) → σ* (C4-O5). Intense interactions between the donor electron and the acceptor electron made by the atoms that make intermolecular hydrogen bonds of the structure σ (H1-C2) →σ* (C2-C3), σ (H1-C2)→σ* (C3-C4), σ (C2-C3)→σ* (H1-C2), σ (C8- H14)→σ* (C7-Br17), σ (C8- H16) → σ* (C6-C7), σ (C9-H11) → σ* (C7-Br17) were observed the 6.50 kcal/mol, 7.06 kcal/mol, 2.51 kcal/mol, 5.61 kcal/mol, 4.78 kcal/mol, 5.62 kcal/mol, respectively.

Table 3. Natural bond orbital analysis data of optimized structure

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-C2)	1.98908	σ* (C2-C3)	0.01287	6.50	1.64	0.092
		σ* (C3-C4)	0.01930	7.06	0.93	0.072
σ (C2-C3)	1.99166	σ* (H1-C2)	0.00544	2.51	1.38	0.053
		σ* (C3-C4)	0.01930	2.68	1.21	0.051
σ (C3-C4)	1.98577	σ* (H1-C2)	0.00544	3.16	1.15	0.054
		σ* (C2-C3)	0.01287	5.28	1.70	0.084
		σ* (O5-C6)	0.11129	3.41	0.86	0.049
σ (C4-O5)	1.98000	σ* (C6-C7)	0.08274	3.24	1.14	0.055
σ (C4-H18)	1.97756	σ* (C2-C3)	0.01287	3.08	1.59	0.063
		π* (C2 –C3)	0.02295	3.81	0.66	0.045
σ (C4-H19)	1.97789	σ* (C2-C3)	0.01287	3.01	1.60	0.062
		π* (C2 –C3)	0.02295	3.40	0.67	0.043
σ (O5-C6)	1.98292	σ* (C3-C4)	0.01930	2.57	1.19	0.049
σ (C6-C7)	1.97257	σ* (C4-O5)	0.02990	2.66	0.91	0.044
		σ* (C8-H16)	0.00776	2.28	1.19	0.047
		σ* (C9-H13)	0.00724	2.17	1.19	0.046
π (C6-O10)	0.19808	σ* (C7-Br17)	0.05878	3.20	0.48	0.035
σ (C7-C8)	1.97639	σ* (C6-O10)	0.02155	3.15	1.07	0.052
		σ* (O5-C6)	0.11129	2.34	1.15	0.046
σ (C7-C9)	1.97266	σ* (O5-C6)	0.11129	4.33	0.84	0.055
		σ* (C8-H15)	0.00731	2.30	1.15	0.046
σ (C7-Br17)	1.95658	π* (C6-O10)	0.19808	5.79	0.53	0.052
		σ* (C8-H14)	0.01039	2.93	1.08	0.051
		σ* (C9-H11)	0.01019	2.89	1.08	0.050
σ (C8- H14)	1.97655	σ* (C7-Br17)	0.05878	5.61	0.59	0.052
σ (C8- H15)	1.98563	σ* (C7-C9)	0.03012	4.45	0.83	0.054
σ (C8- H16)	1.98465	σ* (C6-C7)	0.08274	4.78	0.82	0.057
σ (C9-H11)	1.97714	σ* (C7-Br17)	0.05878	5.62	0.59	0.052
σ (C9-H12)	1.98591	σ* (C7-C8)	0.03193	4.45	0.83	0.054
σ (C9-H13)	1.98298	σ* (C6-C7)	0.08274	5.15	0.82	0.059
σ* (O6-C6)	0.11129	σ* (C4-O5)	0.02990	15.74	0.02	0.058
π* (C6-O10)	0.19808	σ* (C7-Br17)	0.05878	2.59	0.13	0.045

3.6. Frontier Molecular Orbitals and Global Chemical Activity Parameters

Frontier molecular orbitals (FMOs) are used to define molecular reactivity, light absorption, optical and electrical properties of molecules. HOMO is the Highest Occupied Molecular Orbital by electrons, and it serves as an electron donor; LUMO is the Lowest Unoccupied Molecular Orbital, and it serves as an electron acceptor; both are known as frontier molecular orbitals. The chemical stability of a molecule is determined by the energy difference between HOMO and LUMO orbitals. As illustrated in Figure 3, the Gauss-Sum 3.0 Program was used to determine the group contributions to the molecular orbitals and prepare the density of state (DOS). The DOS spectra were obtained by combining molecular orbital information with unit height GAUSSIAN cures [25]. The energy gap between HOMOs and LUMOs is an important parameter used to calculate the electrical transport properties of the molecule, which is used to calculate electron conductivity. The HOMO, LUMO orbital energy, and energy range of the optimized molecule were calculated as -7.584 eV, -1.979 eV, and 5.604 eV, respectively. Moreover, the electronic properties of the title molecule obtained depending on the HOMO and LUMO orbitals are shown in Table 4. The structure has a very high hardness of 2.8025 eV and a very low softness of 0.1784 (eV) -1 due to the high-energy range. As a result, the molecule is demonstrated to be extremely stable, with low chemical activity and great kinetic stability.

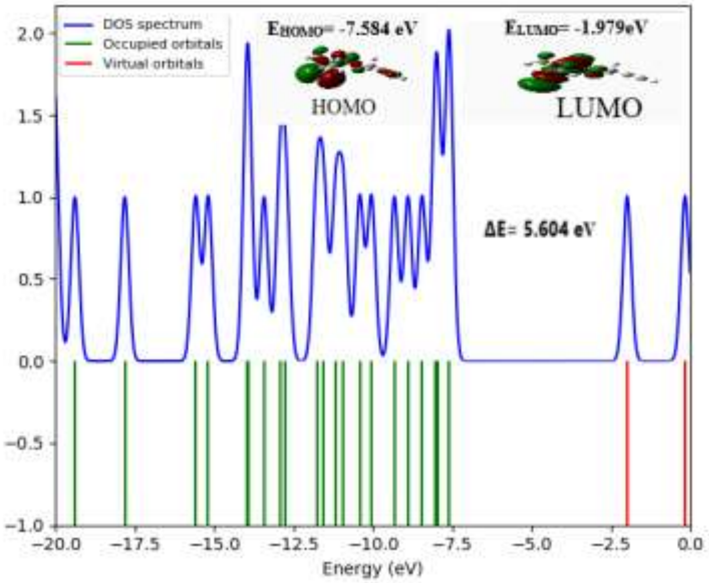

Figure 3. DOS spectrum of the propargyl 2-bromoisobutyrate

Table 4. Calculated global chemical activity, hardness, and softness parameter values

B3LYP/ LanL2DZ	
Parameters	**eV**
E_{HOMO}	-7.584
E_{LUMO}	-1.979
Ionization energy (I)	7.584
Electron affinity(A)	1.979
Energy gap (ΔE)	5.604
Electronegativity (χ)	4.7815
Chemical potential (μ)	-4.7815
Chemical hardness (η)	2.8025
Chemical softness (s)	0.1784
Electrophilic index (w)	4.0789
Maximum charge transfer (ΔN_{max})	0.8530

3.7. Thermodynamics Properties

Thermochemical characteristics of the systems are also acquired throughout the optimization process. Due to the difficulties of understanding heat effects, quantum chemical computations have become increasingly important. Thermodynamic quantum chemical data is frequently utilized to study organic compound reaction processes. Thermal energy, heat capacity, entropy, zero-point vibration energy (ZPVE), rotation constants, and rotational temperatures thermodynamic parameters can be calculated quantum chemical. In Table 5, thermal data of propargy 2-bromoisobutyrate were calculated using the DFT method.

Table 5. Calculated thermodynamics parameters

Parameters	
Zero-point vibrational energy (kcal/mol)	91.361
Thermal energy (kcal/mol)	98.814
Specific heat capacity (cal/mol K)	41.349
Entropy (cal /molK)	110.612
Rotational Constants (GHz)	1.456 0.493 0.446
Rotational temperatures (Kelvin)	0.0069 0.0236 0.0214

4. Conclusion

All theoretical calculations of the studied molecule were made using DFT/B3LYP/LanL2DZ. Theoretical calculations are an effective method used to determine the hardness and softness parameters that cannot be obtained experimentally. In this study, electrophilic and nucleophilic nature, local and global chemical activity parameters of the structure were calculated. The molecular electrostatic potential map predicted that the electrophilic regions are located on the oxygen atoms and that these regions are active in chemical binding and activation. The structure was more susceptible to electrophilic attack, according to net charge analysis and Fukui function analysis. It revealed that the molecule is in a very stable state, with high hardness, low softness, and a large energy band gap, as well as low chemical activity and good kinetic stability.

Authors’ contributions

Seda HEKİM performed the theoretical calculations of the experimentally synthesized molecule. Mustafa Ersin PEKDEMİR synthesized the organic molecule and characterized it experimentally. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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