Turkish Computational and Theoretical Chemistry

Turkish Comp Theo Chem (TC&TC)

Volume(Issue): 3(2) – Year: 2019 – Pages: 47-58

e-ISSN: 2602-3237

https://doi.org/10.33435/tcandtc.457453

Received: 05.09.2018 ***Accepted:*** 22.02.2019 *Research Article*

Structural Characterization, Theoretical Investigation and Hirshfeld Surface Analysis of 2,6-(E,E)-bis((thiophene-2-yl)methylene)cyclohexanone

Gül YAKALI[1,a,b], Abdullah BİÇER[c], Günseli Turgut CİN[1,c]

[a] Akdeniz University, Serik Gülsün Süleyman Sural Vocational School of Higher Education, Department of Opticianry Program, 07058 Antalya/TURKEY

[b] Central Research Laboratory, İzmir Katip Çelebi University, 35620-İzmir, Turkey

[c] Akdeniz University, Faculty of Science, Department of Chemistry, 07058 Antalya/TURKEY

Abstract: The title bis(chalcone) compound has been synthesized and characterized by FTIR, 1H-NMR, 13C-NMR techniques, X-ray structure analysis. The optimized molecular structure of the studied compound is calculated using DFT/B3LYP with 6-31G (d,p) level. The calculated geometrical parameters are in compatible with the experimental data obtained from X-ray structure analysis. The calculated IR fundamental bands, 1H and 13C-NMR chemical shifts of the compound were assigned and compared with the experimental data. Additionally, frontier molecular orbital energies (HOMO, LUMO), their energy gap (ΔE), molecular electrostatic potential analysis of the compound have been calculated by the same method. The charge distribution of the molecule is obtained with molecular electrostatic potential (MEP). In addition, the intercontacts in the crystal structure are analyzed using Hirshfeld surfaces computational method. The title compound (C16H14OS2) crystallizes in the monoclinic chiral space group P21/c with a=15.0492(10)Å, b=12.0085(9)Å, c=7.6283(6) Å, β=95.883(7)o, V=1371.31(17)Å3, Dcalc=1.387g/cm3. The central cyclohexanone ring has a chair conformation and the the fragments at the vinyl group of the compound exhibit a trans conformation, and the two thiophene rings adopt a syn conformation and are located on the both side of the cyclohexanone. The asymmetric unit of the title compound, C16H14OS2, contains one-half of a molecule. The other half of the molecule is generated with (x,y,-z) symmetry operator. In the molecule there are two weak C-H…S and C-H…O intramolecular and only C-H…O intermolecular hydrogen bonds. In addition, π…π interactions are found in the crystal structure between the thiophene rings.

Keywords: *Bis(chalcone), X-ray crystallography, DFT, Hirshfeld Surface Analysis*

1. Introduction

Chalcones, also known as α,β-unsaturated ketones, are not only important precursors for synthetic manipulations but also form a major component of the natural products. Chalcones as well as their synthetic analogues display enormous number of biological activities [1]. The presence of double bond in conjugation with carbonyl functionality is believed to be responsible for the biological activities of chalcones, as removal of this functionality make them inactive [2,3]. These are also found useful in the field of material sciences; few chalcones due to their good SHG (second-harmonic generation) conversion efficiencies [4] have been found useful in nonlinear optical [5] and electro-active fluorescent materials such as fluorescent dyes [6] and light-emitting diodes, LEDs [7]. Claisen-Schmidt reaction is the one of

[1] Corresponding Authors

e-mail: gulyakali@akdeniz.edu.tr (Gül YAKALI) and gturgut@akdeniz.edu.tr (Günseli Turgut CİN)

the most important reaction for the synthesis of donor-acceptor conjugated dienes, known as chalcones [8]. Although studies on the Claisen-Schmidt reaction have been focused on α-alkylidene- and α-arylidene-carbonyl compounds, interest in α,α'-bisalkylidene- and α,α'-bisarylidene-carbonyl compounds is still increasing.

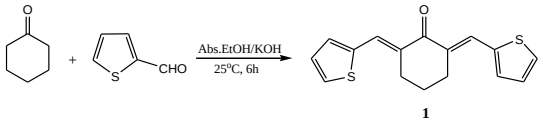
Diarylidenecyclohexanones with donor-(π-spacer)–acceptor-(π-spacer)–donor (D-π–A-π–D) molecular configuration are closely related to the class of organic chromophores known as 'bis-chalcones' [9]. The double condensation reaction of a cycloalkanone that possesses two active α,α'-sites with two equivalents of aldehyde yields a bis-chalcone derivative. In general, such reactions proceed in a straightforward manner and the resulting product, which is normally isolated without difficulty, can be electronically tuned to produce a variety of colors through control of the extant π-conjugation. In recent years, bis-chalcone derivatives have been extensively used in numerous applications ranging from anti-cancer [10,11], radio-protective and anti-viral activities [12], synthons for heterocycles [13], chemoprotective agents, phase 2 enzyme inducers, radical scavengers [14], catalysis [15,16] and nonlinear optics [17].

Control of the polymorphic properties displayed by medicinally active D-π–A-π–D bis(chalcones) is important to the pharmaceutical industry [18,19]. A thorough understanding of the stability and relative energies of different polymorphic forms of a compound is best achieved through a combined experimental and computational approach. Herein we report our results on the structural and computational analysis of the bis(chalcone) compound 2,6-(E,E)-bis((thiophene-2-yl)methylene)cyclohexanone. DFT calculations on the compound confirm the solid-state structure as the preferred ground-state minimum and the geometrical parameters, the mechanism for the cis/trans isomerism of the thiophene moieties and IR vibrational bands of carbonyl group is discussed. Additionaly, the GIAO (gauge-independent atomic orbital) ^{1}H and ^{13}C-NMR chemical shifts are determined theoretically. The presence of weak H-bonds of the compound in a noncovalent manner is verified by Hirshfeld surface analysis.

2. Experimental

2.1. Materials and Equipments

The bis(chalcone) compound was synthesized according to previous studies (Scheme 1) [20]. FTIR spectra were recorded on Bruker Tensor27 FTIR spectrometer calibrated with polystyrene film using the KBr disc. Nuclear magnetic resonance (^{1}H and ^{13}C) spectra were taken on BRUKER Spectrospin Avance DPX400 Ultrashield (400 MHz) spectrometer, reference tetramethylsilane as internal standard.



1

Scheme 1. Synthesis procedure for title compound

Bis-chalcones (**1-3**) were synthesized following literature procedures by the condensation of cyclohexanone and cyclopentanone with aromatic aldehydes, respectively. [26-27]. Synthesis and spectroscopic details of the compounds are given in these literatures [26-27].

2.2. X-ray Crystallographic Data

Good-quality single-crystal of dimensions 0.493 × 0.137 × 0.118 mm was selected for the X-ray diffraction experiment at T = 293(2) K. Diffraction data was collected on an Oxford Diffraction X-Calibur equipped with an Eos-CCD detector, operated at 50 kV and 40 mA with graphite monochromated Mo-Kα (λ = 0.71073 Å) radiation for the compound. The absorption corrections of the collected data was done using the program CrysAlis Pro [21]. The structure was solved with the SHELXS structure solution program using the Direct Methods and refined with the SHELXL using least squares minimization [22], using Olex2 [23]. All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms on their respective parent carbon atoms were generated geometrically C–H = 0.93 A° and Uiso(H) = 1.2Ueq(C) for thiophene rings H atoms, C–H = 0.97 A° and Uiso(H) = 1.5Ueq(C) for cyclohexanone ring H atoms, C–H = 0.93 A° and Uiso(H) = 1.2Ueq(C) for methlene vinyl H atoms and assigned isotropic displacement parameters before the final cycle of least-squares refinement. A summary of crystallographic data, experimental

details, and refinement results for the compound are given in Table 1.

Table 1. Crystal data and structural refinement parameters for the title compound.

Crystal Data	
Empirical Formula	$C_{16}H_{14}OS_2$
Formula Weight (g/mol)	286.39
Cell setting / Space group	monoclinic/ $P2_1/c$
Unit cell dimensions (Å)	a= 15.0492(10)
	b= 12.0085(9)
	c= 7.6283(6)
Unit cell volume (Å^3)	1371.31(17)
Temperature (K)	293 (2)
Absorption coefficient (mm^{-1})	0.376
Z / Density [g/cm^3]	4/ 1.387
F(000)	600
Crystal size (mm^3)	0.493 × 0.137 × 0.118
θ range (°)	2.18-25.68
h range	−18 → 15
k range	−7 → 14
l range	−4 → 9
Reflections collected / unique	4304/2590
Completeness to θ_{max}	99.99%
Goodness-of-fit on F^2	1.037
Final R indices [I > 2σ(I)]	R_1 = 0.0633
	wR_2 = 0.1593
R indicesall data	R_1 = 0.1045
	wR_2 = 0.1862
Large diff. peak and hole	0.48/-0.37

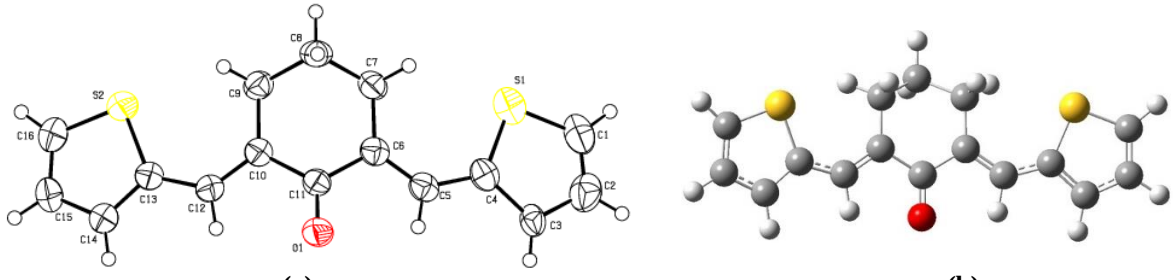
2.3. Theoretical Studies

All the quantum chemical calculations of the compound were performed by DFT method with the B3LYP functional and 6–31G(d,p) basis set [24-25] using Gaussian 09 software [26]. The geometrical parameters, frontier molecular orbital energies, Molecular Electrostatic Potential (MEP) analysis, frequency (FT-IR) and NMR calculations were obtained from the optimized structures. GaussView 5.0 [27] program has been used to draw the structure of the optimized geometry and to visualize the MEP, HOMO, and LUMO pictures. Frequency calculations at the optimized geometry were done to confirm the optimized structure to be at an energy minimum. The true energy minimum at the optimized geometry of the studied compound was confirmed by the absence of any imaginary frequency modes [27]. The 1H and 13C chemical shifts referenced to the TMS calculations were carried out at the same level of theory.

3. Results and discussion

3.1. X-ray Structure Analysis and Computational Studies

The ortep diagram and the optimized geometries at the optiumum conformation of the title compound is shown in Fig. 1. The asymmetric unit of the title compound, $C_{16}H_{14}OS_2$, has one-half-molecule and it is completed with a twofold symmetry axis [symmetry code:x, y, -z]. The molecular structure of the compound, $C_{16}H_{14}OS_2$, has an E-configuration so that the substituents at the vinyl group of the compound [(C5=C6, C10=C12)] indicate a trans conformation, and the two thiophene rings adopt a syn orientation and are located on both side of the cyclohexanone.



(a) **(b)**

Fig. 1 (a) The ortep diagram and **(b)** the optimized structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

Table 2. Experimental and optimized geometrical parameters of the title compound.

Parameter	Experimental	Calculated
Bond length (Å)		
S1-C1	1.686(5)	1.730(2)
O1-C11	1.223(4)	1.234(2)
S1-C4	1.726(4)	1.763(2)
S2-C13	1.733(4)	1.763(2)
S2-C16	1.698(5)	1.730(2)
C5-C6	1.346(5)	1.358(2)
C10-C12	1.345(5)	1.358(2)
C4-C5	1.442(5)	1.440(2)
C12-C13	1.446(4)	1.440(2)
Bond Angle (^{0})		
S1-C4-C5	125.7	126.538(2)
S2-C13-C12	126.0(3)	126.540(2)
O1-C11-C10	121.8(3)	120.762(2)
O1-C11-C6	121.1(3)	120.766(2)
C13-S2-C16	92.6(2)	91.942(2)
C4-S1-C1	92.2(2)	91.941(2)
C13-C12-C10	131.0(3)	131.864(2)
C4-C5-C6	131.2(3)	131.865(2)
Torsion Angle (^{0})		
S1-C4-C5-C6	-0.2(6)	5.91(2)
C5-C6-C11-O1	18.2(5)	-5.11(2)
C12-C10-C11-O1	-20.6(6)	5.10(2)
C10-C12-C13-S2	-1.0(6)	-5.94(2)
C11-C10-C12-C13	-172.9(4)	-177.23(2)
C4-C5-C6-C11	173.4(4)	177.23(2)
C9-C10-C12-C13	2.9(7)	1.87(2)
C4-C5-C6-C7	-2.1(7)	1.87(2)

The title compound has three earthly diastreoisomers which are ZZ, ZE, EE forms depending on the sterochemical configurasyon of the thiophenes and carbonyl moieties. The (EE) diastereomer that thiophene groups are located trans to the central carbonyl fragment is more stable than others.

The two independent thiophene ring systems are essentially identical and the central cyclohexanone ring is not planar with these rings with the dihedral angles of 19.09 (2)0 (include S1 ring) and 19.73(2)0 (include S2 ring). So thiophene rings are tipped out of the plane. The tipping of each these moiety provides to short contacts between the C7-H7B/S1 and C9-H9B/S2. The carbonyl group and its conjugated double bonds show to be synperiplanar (O1-C11-C6-C5= -5.11(2), C12-C10-C11-O1= -5.10(2))

The two thiophene rings are nonplanar where the cyclohexanone bridge is out of the molecular plane of thiophene core and are twisted with respect to each other by angle is 36.5(2)0 with a maximum deviation from the plane of 0.012(1)Å for S1, 0.001(1)Å for S2, respectively. The cyclohexanone ring is parallel to the molecule plane with the dihedral angle of 1,35(5)0. From this result support that pure sample of the compound could be isolated as in chalcone[28].

In the molecular structure, the central cyclohexanone ring display a chair conformation with the C8 atom lying 0.385(4)Å above the plane C7-C9 atoms. The exocyclic alkenyl moieties defined by the C5=C6, C10=C12 vectors reveal bond distances of 1,345(5)Å and 1,346(5)Å, respectively consistent with their double bond character [29]. The C12-C13, C4-C5 bond lengths of 1.442(5)Å, 1.446(4)Å respectively, are intermediate between the double and single bonds. The C-C bond length of the cyclohexanone moiety (1.499(5)Å to 1.533(5)Å) are normal single bonds. Similarly, the bond lengths within thiophene rings which include S1 atom are between 1.341 (8)Å and 1.726 (4)Å, which include S2 atom are between 1.378 (6)Å and 1.733(4)Å which exhibit that the rings have the aromatic character [30].

In Table 2, theoretical studies indicated that the shorting of the C=C double bonds (C5=C6, C10=C12) showing the partial double bond character of the C=C bands which are influenced by adjacent conjugated double bonds. Also, the conformation of these molecules is the result of the interaction between the electronic pair of oxygen in the carbonyl group [30].

The optimized C=O bond length obtained by B3LYP/6-31G is slightly longer than the experimental value of 1.223 Å [31]. The experimetal bond angles are very close calculationed values but the torsion angles are slightly differ experimental values. These discrepancies showed that the calculations assume an isolated molecule, where the intermolecular coulombic interactions with the neighboring molecules are absent and inplane deformation of the =C-H bond.

In the molecule, there are two C-H…S and C-H…O intramolecular, only C-H…O intermolecular hydrogen bonds (Table 3 and Fig. 2). In addition to this, there are two very weak π…π interactions found in the crystal structure between the thiophene rings with 5.149(2)Å distance between the centroids Cg1 Cg1 (Cg 1: C1/C6; symetry code: 1/2-x, 1/2-y,-1/2 + z)

Table 3. Hydrogen-bond interactions geometry(Å, °) for the compound.

Bond	D – H	H…A	D…A	D – H…A
C5-H5…O1	0.929(5)	2.340(4)	2.751(4)	106.4(3)
C7-H7A…S1	0.969(5)	2.675(3)	3.164(3)	111.7(3)
C9-H9A…S2	0.969(5)	2.711(4)	3.142(3)	107.5(3)
C12-H12…O1	0.930(5)	2.376(4)	2.774(4)	105.5(3)
C16-H16…O1^{i}	0.930(7)	2.451(5)	3.329(5)	157.5(5)

Symetry code: (i) 1-x,1/2+y,1/2-z

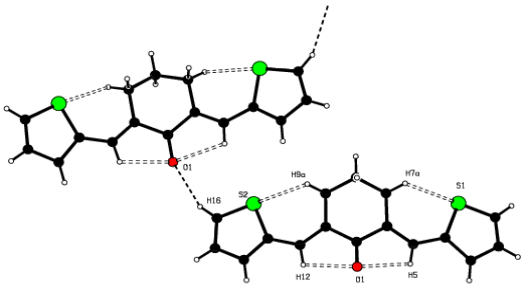


Fig. 2 Intramolecular and intermolecular C-H…O and intramolecular C-H…S hydrogen bonding of the title compound.

The result of these interactions leads to 1D supramolecular network along the *(010)* plane (Fig. 3). A packing diagram of the molecule is formed by intermolecular C-H…O, π…π these interactions along the *(010)* plane (Fig. 4). The 1D supramolecular network and the packing diagram indicate chain structure with hydrogen bonds and interactions. A weak aromatic stacking interactions stabilised the crystal structure.

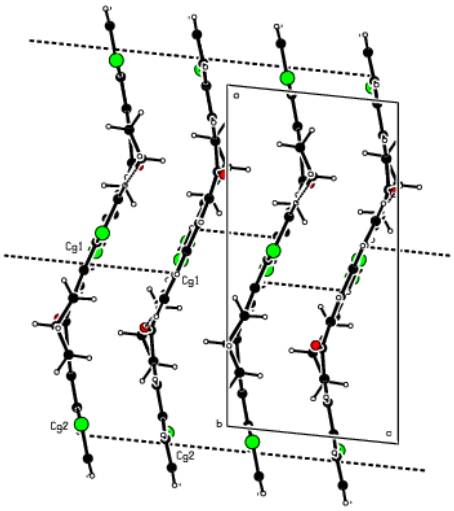


Fig. 3 Packing structure of the title compound by intermolecular $\pi \ldots \pi$ and C-H ... O interactions along the *b* axis.

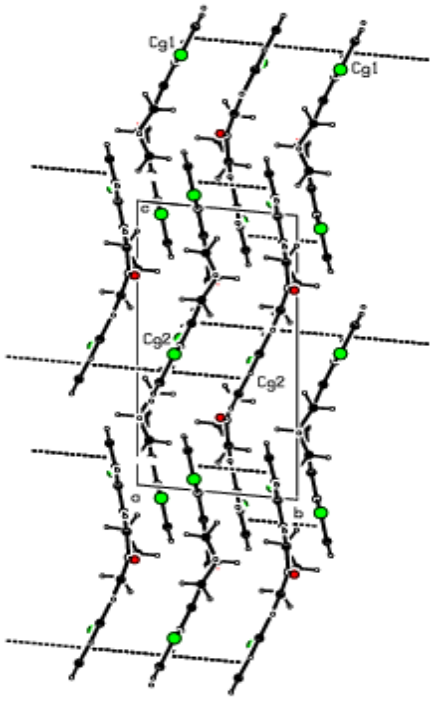
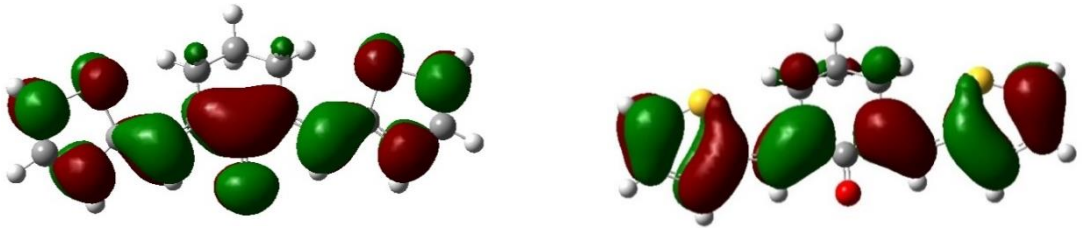


Fig. 4 Showing the 1D supramolecular network of the molecule along the *(010)* plane in the crystal structure by intermolecular $\pi \ldots \pi$ interactions.

3.2. Frontier Molecular Orbitals

The electron densities of the frontier molecular orbitals (FMOs) were used for estimating the most reactive position in π–electron systems and to explaine several types of reactions in the conjugated system [30]. The energy values of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) and their energy gap (ΔE) reflect the chemical reactivity of the molecule. This also forecasted that the region of electrophiles and nucleophiles of atom where the HOMO and LUMO are stronger [32].



LUMO ***HOMO***

Fig. 5 Frontier molecular orbital surfaces for the HOMO and LUMO of the compound computed at B3LYP/6-311 G(d,p) level.

The energy gap of the compound was calculated using B3LYP/6-31G (d,p) level. In this title compound, highest electronic energy which exhibited at 76th is calculated about -5.74 eV. The lowest electronic, which exhibited at 75$^{\mathbf{th}}$ virtual orbital and measured as LUMO value -2.18 eV. The energy gap of HOMO and LUMO could be calculated about -7.92 eV, which leads the molecule becomes more stability and less reactivity. Also, The HOMO–LUMO energy gap (ΔE) represents the lowest energy electronic transition which mainly belongs to π–π* excitation [33]. HOMO–LUMO band gap increases linearly with increasing aromaticity [34]. Thiophene ring is more aromatic structure. Corresponding frontier molecular orbitals are shown in Fig 5.

Chemical hardness is approximated using equation $\eta = (E_{LUMO} - E_{HOMO})/2$, electronegativity is determined using equation $\chi = -(E_{HOMO} + E_{LUMO})/2$, electronic chemical potential determined using equation $\mu = (E_{HOMO} + E_{LUMO})/2$, electronic chemical potential determined using equation $\mu = (E_{HOMO} + E_{LUMO})/2$ and global electrophilicity index (ω), introduced by Parr, is calculated using the electronic chemical potential and chemical hardness as shown in equation $\omega = \mu^2/2\eta$ are calculated using DFT (Table 4) [35].

Table 4. Calculated energies, dipole moments (D), frontier orbital energies and chemical reactivity descriptors of the compound.

Basis Set	B3LYP/6-31 G(d,p)
E_{total} (Hartree)	-1489.718
E_{HOMO} (eV)	-5.74
E_{LUMO} (eV)	-2.18
E_{HOMO} - E_{LUMO} *(energy* gap) (eV)	-3.56
Chemical hardness (η)	1.78
Chemical potential (μ)	-3.96
Electronegativity (χ)	3.96
Electrophilicity index (ω)	4.40
D (debye)	1.9003

3.3. Molecular Electrostatic Potential

The molecular electrostatic potential (MEP) display earthly region for the electrophilic and nucleophilic attacks and hydrogen bonding interaction of organic molecules. So as to forecast bulunmakthe reactive site of the electrophilic and nucleophilic attack the MEP of the title compound was also calculated from B3LYP/6-31G (d, p) optimized geometry. The negative region (red) of MEP which exist nearby the O1 atom of cyclohexanone ring were related to electrophilic reactivity that is responsible intramolecular hydrogen bonding and positive region (blue) which exist nearby the thiophene rings correspond to nucleophilic reactivity that is responsible intermolecular hydrogen bonds (Fig. 6).

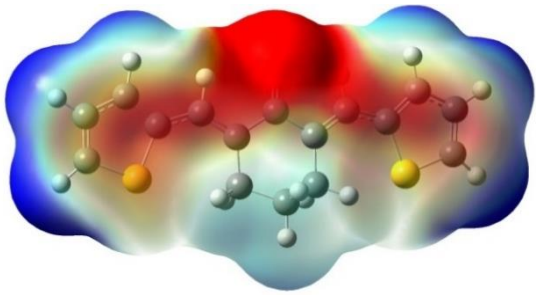


Fig. 6 Molecular electrostatic potential diagram of the title compound

3.4. NMR Spectra

The ^{1}H and ^{13}C chemical shifts (δcalc) of the title compound were calculated and the results are compared to the experimental NMR data (δexp). The details of NMR values are given in Table 5. According to these results, the calculated chemical shifts are in harmony with the experimental results.

The ^{1}H-NMR spectrum of the double bonds of chalcone were calculated at 9.1686(5) ppm. The high frequency resonances of these protons are due to the intramolecular hydrogen bond formed with the carbonyl group. In addition, this result indicates cis configuration of the molecule conformation. ^{13}C-NMR spectrum of the compound the carbonyl carbon atom was calculated at 185.780(5) ppm. The carbon atoms of the double bonds (C5, C6, C10, C12) give characteristic signals at 136.657(5), 136.924(5), 136.922(5), 136.659(5) ppm. These values are good aggrement with reported values [28].

Table 5. Experimental and theoretical ^{13}C and ^{1}H chemical shifts (ppm) for the compound

Atom		Experimental (ppm)		Calculated (ppm)	
C1	C8	130.171	21.875	139.016(15)	32.087(5)
C2	C9	129.982	28.342	128.546(5)	37.829(5)
C3	C10	127.849	136.441	136.460(5)	136.922(5)
C4	C11	133.412	189.912	151.529(5)	185.780(5)
C5	C12	133.268	133.268	136.657(5)	136.659(5)
C6	C13	136.441	133.412	136.924(5)	151.526(5)
C7	C14	28.342	127.849	37.830(5)	136.464(5)
C15	C16	129.982	130.171	128.547(5)	139.012(5)
H1	H8B	7.378	1.973	8.2673(5)	2.5596(5)
H2	H9A	7.151	2.941	7.9977(5)	3.3255(5)
H3	H9B	7.536	2.941	8.1942(5)	3.7647(5)
H5	H12	7.985	7.985	9.1686(5)	9.1688(5)
H7A	H14	2.941	7.536	3.3256(5)	8.1943(5)
H7B	H15	2.941	7.151	3.7642(5)	7.9978(5)
H8A	H16	1.973	7.378	2.6994(5)	8.2670(5)

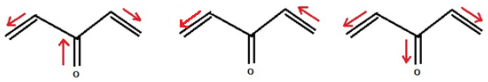
3.5. Analysis of the Vibrational Spectra

Selected calculated and experimental vibrational frequencies of the compound and their assignments are showed in Table 6. A correlation graph between these frequencies values is indicated in Fig. 7. As shown in figure 7, high correlation coefficient (R^2 = 0.9996) exhibit a good correlation between the calculated and the experimental vibrational frequencies.

In the IR spectra of chalcones ontained from optimized structure symetric and asymmetric streching vibrations of the thiophene C-H bonds 3264.40 and 3217.40 cm^{-1}, respectively. C-H streching band of the =C-H group (C5, C12) is observed at 3166 cm^{-1} (symetric) and 3165 cm^{-1} (asymmetric). The carbonyl stretching vibrations (C=O) can be found at 1733.28 cm^{-1}. The C=O strecthing mode of trans-conformer is observed at the lower frequency, whereas the C=O stretching mode of cis-conformer is observed at the higher frequency [28]. On the other hand, the IR spectrum of the compound exhibited an absorption band at 746.23 cm^{-1} corresponding to the C-S-C stretching frequency. These values are good aggrement with reported values.

The IR spectrum for the compound demonstrates three bands which are expected for the carbonyl at 1619.60 cm^{-1}, 1647.81 cm^{-1} and 1733.28 cm^{-1} in which are obtained from DFT analysis. Of these three bands, the strongest band at 1733.28 cm^{-1} was carbonyl stretching band of the bis(chalcone) fragment. The other two IR bands are best explaned as antisymmetric and symmetric stretching modes of the vibrationally coupled

alkene and carbonyl groups of the bis(chalcone) moiety [36]. The dipole changes of these vibrations are shown in Fig. 7.



1733.28 cm^{-1} 1647.81 cm^{-1} 1619.60 cm^{-1}

Fig. 7 Carbonyl group IR frequencies of the compound in DFT.

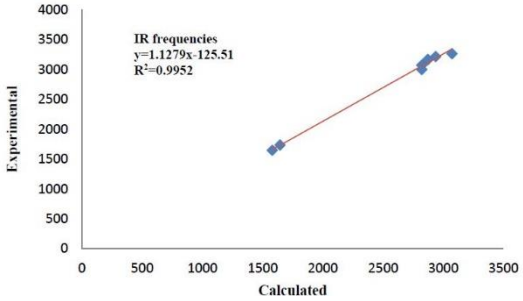


Fig. 8 Correlation graph of calculated and experimental frequencies of the title compound (R: correlation coefficient)

Table 6. Details of IR frequence values for the compound

Experimental frequency	Calculated frequency	Assignment
3074	3264.40	ν_{sym}(C-H) Thiophene rings
2939	3217.40	ν_{asym} (C-H) Thiophene rings
2885	3166.00	ν_{sym}(C-H) C5, C12
2873	3165.00	ν_{asym}(C-H) C5, C12
2822	3072.47	ν_{sym}(C-H) CH_2
2822	2999.61	ν_{asym}(C-H) CH_2
1646	1733.28	ν_{asym}(C=O)
1582-1549	1647.81	ν_{asym}(C=C) C5=C6,C10=C12
1411	1619.60	ν_{sym}(C-C)C4-C5, C12-C13, (C=O)
1371	1371.66	β(C-H) whole molecule
1263	1256.33	β(C5=C6,C10=C12)
700	746.23	ν(C-S-C)

Vibration mode: ν; stretching, β; bending, sym; symmetric, asym; asymmetric.

3.6. *Hirshfeld Surface Analysis*

Hirshfeld surface analysis is a quite practical technique for indicating intermolecular contacts in a crystal structure. Hirshfeld surfaces are based on the ratio representing a weight function between the electron distribution of a sum of spherical atoms for a molecule and the same sum for the whole crystal [37]. It is important to specify a normalized contact distance, given by Eq.(1), in terms of d_e, d_i and the van der Waals radii of the atoms. As the intermolecular contacts closer than the sum of their van der Waals radii of related atoms, d_{norm} is negative and these contacts are stressed in red on the d_{norm} surface. Longer contacts are blue (d_{norm} is positive), and contacts nearby the sum of van der Waals radii are white on the d_{norm} surface [38].

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} - \frac{d_e - r_e^{vdw}}{r_e^{vdw}} \quad (1)$$

The Hirshfeld surfaces and the associated 2D fingerprint plots for the title compound were calculated using CrystalExplorer 3.0 [39].

The 2D-fingerprint plots of various intermolecular interactions is formed by Hirshfeld surface of the compound are given in Fig 9. 2D-fingerprint plots of the Hirshfeld surface showed intermolecular interactions of the molecule.

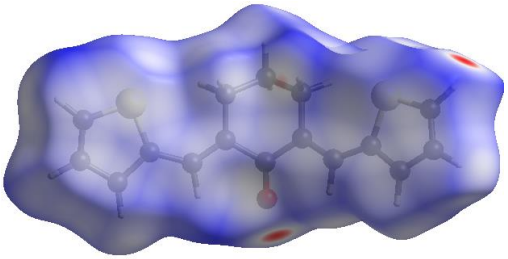


Fig. 9 Hirshfeld Surface mapped with d_{norm} for the compound.

The chart indicates that the contribution of inter contacts to the Hirshfeld surfaces, H...H (51.5%),

S...H (12.9%), O...H (9.3%), H…C (indicate C-H…π) (13%). Fig. 11 showed that the percentage of these intermolecular contacts which is obtained Hirshfeld Surface analysis. These inter molecular interactions are highlighted by clasicl mapping of d_{norm} on molecular Hirshfeld surfaces are shown in Fig. 10. In Fig. 9, the d_{norm} is showed C16-H16…O1 intermolecular interaction.

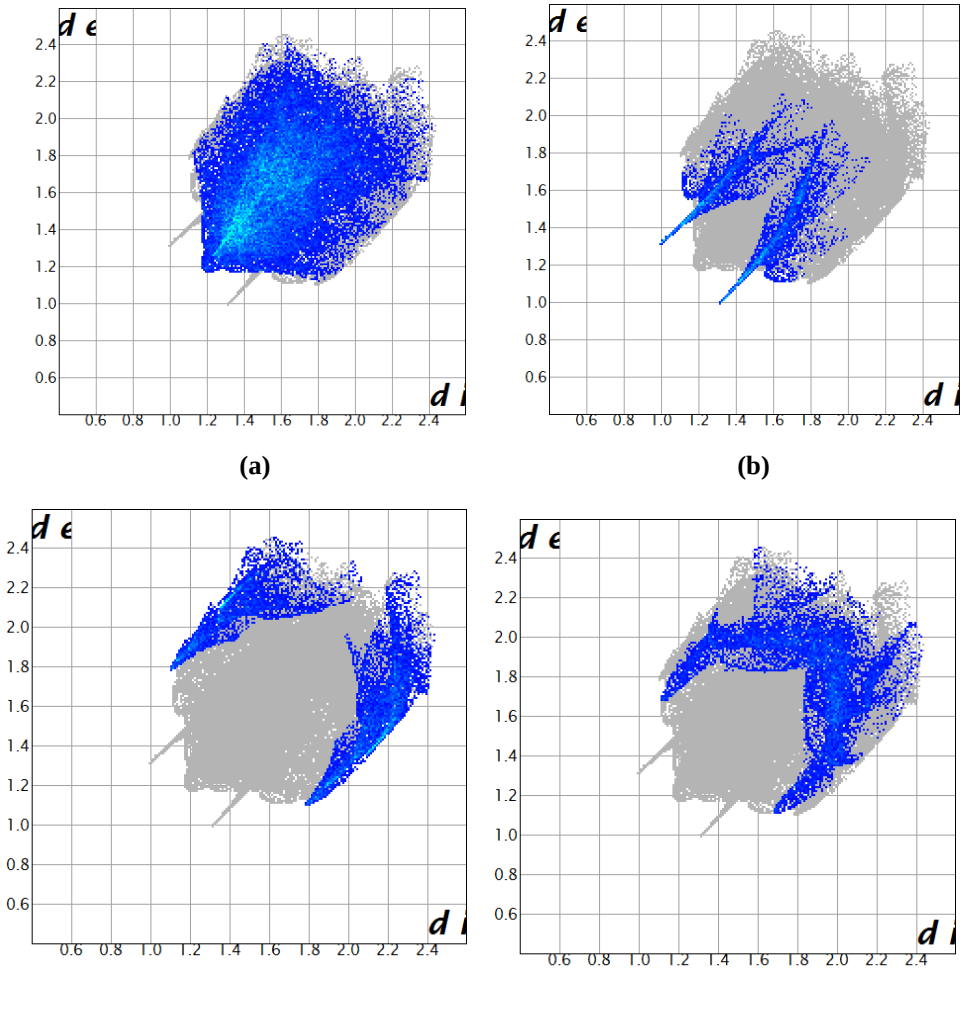


Fig. 10. Fingerprint plots of the compound: **(a)** H…H contacts, **(b)** Reciprocal O…H/H…O contacts, **(c)** Reciprocal H…S/ S…H contacts, **(d)** Reciprocal H…C/C…H contacts, mainly indicating C-H…π interactions.

The fingerprint plot at de ≈di < 1.2 A (van der Waals radius of Hatom), whereas hydrogen bonds characteristically display spikethemselves as spikes [35]. H...H intercontacts, (Figure 10(a)) indicated large surfaces .H…C/C…H also known as C-H…π interactions show up as a pair of ‘‘wings’’ in Fig. 9d. H…O/O…H (Figure 10(b)) interactions and H…S/S…H interactions appearing as distinct spikes in fingerprint Plot.

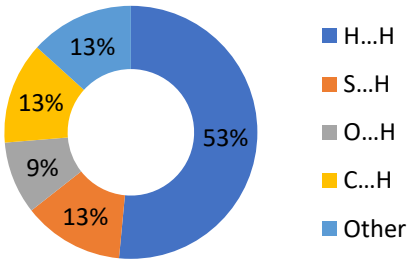


Fig. 11 The result of Hirshfeld surface Analysis.

4. Conclusion

The structural characterization of the title compound is reported. The molecular structure of that has been optimized using the DFT/B3LYP method and 6-31G (d,p) basis set. The theoretical bond distances and bond angles harmony with with X-ray crystal structure analysis. The MEP results demonstrated that the carbonyl oxygen (O1) is the most electronegative and the H atoms of thiophene rings are the most electropositive sites. According to the HOMO-LUMO energy gap (ΔE), the molecule is taken into account as a better aromatic character. The GIAO ^{1}H- and ^{13}C-NMR chemical shift values correlated well with the experimental data. The IR vibrational frequencies are calculated and the basis bands were assigned and compared with the experimental data (R^2 = 0.9996). Utilising Hirshfeld surfaces computational method the intercontacts in the crystal structure are determined. The result of analyzed intercontacts in the crystal structure are good aggreement DFT calculations.

Acknowledgements

This work has been completed at Dokuz Eylül University, Akdeniz University and Atatürk University. The authors acknowledge Dokuz Eylül University for the use of the Agilent Xcalibur Eos diffractometer (purchased under University Research Grant No: 2010.KB.FEN.13), Akdeniz University Research Fund (grand number: FDK-2016-1541) for their financial support and Faculty of Sciences and Atatürk University, for the use of BRUKER Spectrospin Avance DPX400 Ultrashield (400 MHz) Spectrometer.

References

[1] G. D. Carlo, N. Mascolo, A. A. Izzo, F. Capasso, Flavonoids: old and new aspects of a class of natural therapeutic drugs. Life Sci. 65 (1999) 337-353.

[2] G. Romanelli, G. Pasquale, A. Sathicq, H. Thomas, J. Autino, P. Vazquez, Synthesis of chalcones catalyzed by aminopropylated silica sol–gel under solvent-free conditions. J. Mol. Catal A Chem. 340 (2011) 24-32.

[3] S. Eddarir, N. Cotelle, Y. Bakkour, C. Rolando, An efficient synthesis of chalcones based on the Suzuki reaction. Tetrahedron Letters 44 (2003) 5359-5363.

[4] S. Shettigar, K. Chandrasekharan, G. Umesh, B. K. Sarojini, B. Narayana, Studies on nonlinear optical parameters of bis-chalcone derivatives doped polymer. Polymer 47 (2006) 3565-3567.

[5] P. S. Patil, S. M. Dharmaprakash, H. K. Fun, M. S. Karthikeyan, Synthesis, growth and characterization of 4-OCH3-4'-Nitrochalcone single crystal: A potential NLO material, J. Cryst. Growth. 297 (2006) 111-116.

[6] T.A. Fayed, M.K. Awad, Dual Emission of Chalcone-Analogue Dyes Emitting in the Red Region, Chemical Physics 303 (2004) 317-326.

[7] R. Sens, K. H. Drexhage, Fluorescence quantum yield of oxazine and carbazine laser dyes. Journal of Luminescence 24 (1981) 709-712.

[8] A. M. Asiri, S. A. Khan, Synthesis, Characterization, and In Vitro Antibacterial Activities of Macromolecules Derived from Bis-Chalcone. Journal of Heterocyclic Chemistry 49 (2012) 1434-1438

[9] N. S. K. Reddy, R. Badama, R. Sattibabub, M. Mollib, V. S. Muthukumarb, S. S. S. Sai, G. N. Rao, Synthesis, characterization and nonlinear optical properties of symmetrically substituted dibenzylideneacetone derivatives. Chemical Physics Letters 616 (2014) 142-147.

[10] A. Modzelewska, C. Pettit, G. Achanta, N. E. Davidson, P. Huang, S. R. Khan, Anticancer activities of novel chalcone and bis-chalcone derivatives. Bioorg. Med. Chem. 14 (2006) 3491-3495.

[11] M. Bazzaro , R. K. Anchoori , M. K. Mudiam , O. Issaenko, S. Kumar, B. Karanam , Z. Lin, V. R. Isaksson, R. Gavioli, F. Destro, V. Ferretti, R. B. Roden, S. R. Khan, α,β-Unsaturated carbonyl system of chalcone-based derivatives is responsible for broad inhibition of proteasomal activity and preferential killing of human papilloma

virus (HPV) positive cervical cancer cells. J. Med. Chem. 54 (2011) 449-456.

[12] C. G. D. Raj, B. K. Sarojini, V. Bhanuprakash, R. Yogisharadhya, B. E. K. Swamy, R. Raghavendra, Studies on radioprotective and antiviral activities of some bischalcone derivatives. Med. Chem. Res. 21 (2012) 2671-2679.

[13] B. V. Padmavathi, B. J. M. Reddy, D. R. C. V. Subbaiah, Bischalcones-synthons for a new class of bis (heterocycles). New Journal of Chemistry 28 (2004) 1479-1483.

[14] A. T. Dinkova-Kostova, C. Abeygunawardana, P. Talalay, Chemoprotective Properties of Phenylpropenoids, Bis(benzylidene)cycloalkanones, and Related Michael Reaction Acceptors: Correlation of Potencies as Phase 2 Enzyme Inducers and Radical Scavengers. J. Med. Chem. 41 (1998) 5287-5896.

[15] E. D. D'silva, D. N. Rao, R. Philip, R. J. Butcher, R. Rajnikant, S.M. Harmaprakash, Synthesis, growth and characterization of novel second harmonic nonlinear chalcone crystal. J. Phys. Chem. Solids 72 (2011) 824-830.

[16] A. M. Asiri, S. A. Khan, Synthesis, characterization and optical properties of mono- and bis-chalcone. Mater. Lett. 65 (2011) 1749-1752.

[17] B. Zhao, Y. Wu, Z. H. Zhou, W. Q. Lu, C. Y. Chen, Theoretical study on the organic molecular second-order hyperpolarizability. Appl. Phys. B 70 (2000) 601-605.

[18] J. R. Dimmock, V. K. Arora, M. Chen, T. M. Allen, G. K. Kao, Cytotoxic evaluation of some N-acyl and N-acyloxy analogues of 3,5-bis(arylidene)-4-piperidones. Drug Des. Discovery 12 (1994) 19-28.

[19] J. R. Dimmock, V. K. Arora, M. J. Duffy, R. S. Reid, T. M. Allen, G. Y. Kao, Evaluation of some N-acyl analogues of 3,5-bis(arylidene)-4-piperidones for cytotoxic activity. Drug Des. Discovery 8 (1992) 291-299.

[20] M. A. Hussein, H. M. Marwani, K. A. Alamry, A. M. Asiri, S. A. El-Daly, Surface selectivity competition of newly synthesized polyarylidene(keto amine) polymers toward different metal ions. J. Appl. Poly. Sci. 131 (2014) 40873-40883.

[21] Agilent Technologies, Data Collection and Processing Software for Agilent X-ray Diffractometers, CrysAlis PRO and CrysAlis RED, Yarnton, Oxfordshire England, 2002.

[22] G. M. Sheldrick, A short history of SHELX. Acta Cryst A 64 (2008) 112-122.

[23] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program. J. Appl. Cryst. 42 (2009) B339-B341.

[24] P. Hohenberg, W. Kohn, Inhomogeneous Electron Gas. Phys. Rev. 136 (1964) 846-871.

[25] W. Kohn, L. J. Sham, Self-Consistent Equations Including Exchange and Correlation Effects. Phys. Rev. 140 (1965) A1133-A1138.

[26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, J. T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, G. J. M. C. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, R. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. V. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, Revision E. 01,

Gaussian Inc., Pittsburgh, PA, 2003.

[27] A. Frisch, R. D. Dennington, T. A. Keith, J. Milliam, A. B. Nielsen, A. J. Holder, J. Hiscocks, GaussView Reference, Version 4.0., Gaussian Inc., Pittsburgh, 2007.

[28] B. E. Aksöz, R. Ertan,Spectral Properties of Chalcones II. J. Pharm. Sci. 37 (2012) 205-216.

[29] Y. Zhang, K. L. Pan, F. He, L. F. Chen, Z. G. Liu, G. Liang, Crystal structure of (2E,6E)-2,6-bis[2-(trifluoromethyl)benzylidene]cyclohexanone, C22H16F6O. Z. Kristallogr. NCS 230 (2015) 271-272.

[30] D. Contreras, Y. Moreno, C. Soto, M. Saavedra, F. Brovellı, R. Baggıo, Synthesis and Structural Determination of a New Chalcone 1,5-Bis(3-Methyl-2-Thienyl)penta-1,4-dien-3-one, $C_{15}H_{14}OS_2$. J. Chil. Chem. Soc. 54 (2009) 470-472.

[31] C. Jiang, Z. Feng, B. Song, X. Lib, X. Lia, (2E,6E)-2,6-Bis(2,5-difluorobenzyl-idene)cyclohexanone. Acta Cryst. E66 (2010) o1009.

[32] L. Padmaja, C. Ravikumar, D. Sajan, I. H. Joe, V. S. Jayakumar, G. S. Pettit, Density functional study on the structural conformations and intramolecular charge transfer from the vibrational spectra of the anticancer drug combretastatin-A2. J. Raman Spectros. 40 (2009) 419-428.

[33] A. Barakat, A. M. Al-Majid, S. M. Soliman, Y. N. Mabkhot, M. Ali, H. A. Ghabbour, H. K. Fun, A. Wadood Structural and spectral investigations of the recently synthesized chalcone (E)-3-mesityl-1-(naphthalen-2-yl)prop-2-en-1-one, a potential chemotherapeutic agent. Chemistry Central Journal 9 (2015) 2-15.

[34] H. Karabıyık, R. Sevincek, H. Karabıyık, Effects of pnictogen and chalcogen bonds on the aromaticities of carbazole-like and dibenzofuran-like molecular skeletons: Cambridge Crystallographic Data Centre (CCDC) Study. J. Phys. Org. Chem. 28 (2015) 490-496.

[35] S. Murugavel, N. Manıkandan, D. Lakshmanan, K. Naveen, P. T. Perumal, Synthesis, Crystal Structure, DFT and Antibacterial Activity Studies of (E)-2-Benzyl-3-(furan-3-il)-6,7-dimethoxy-4-(2-phenyl-1H-ınden-1-ylidene)-1,2,3,4-Tetrahydroisoquinoline. J. Chil. Chem. Soc. 60 (2015) 3015-3020.

[36] V. V. Nesterov, V. N. Nesterov, M. G. Richmond, Structural characterization of cis-2,6-(E,E)-bis(ferrocenylidene)-N-methyl-4-piperidone and DFT evaluation of alternative polymorphic modifications via ferrocene rotation. Polyhedron, 35 (2012) 124-129.

[37] N. R. Babu, S. Subashchandrabose, M. S. A. Padusha, H. Saleem, Y. Erdoğdu, Synthesis and spectral characterization of hydrazone derivative of furfural using experimental and DFT methods. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 120 (2014) 314-322.

[38] M. A. Spackman, J. J. McKinnon, Fingerprinting intermolecular interactions in molecular crystals. Cryst. Eng. Comm. 4 (2002) 378-392.

[39] S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, CrystalExplorer (Version 3.0), University of Western Australia, 2012.