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Quantum Chemical Modeling of *N*-(2-benzoylphenyl) oxalamate: Geometry Optimization, NMR, FMO, MEP and NBO Analysis Based on DFT Calculations

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ABSTRACT

In the present work, the quantum theoretical calculations of the molecular structure of the (*N*-(2-benzoylphenyl) oxalamate has been investigated and are evaluated using Density Functional Theory (DFT). The geometry of the title compound was optimized by B3LYP method with 6-311+G(d) basis set. The theoretical ^{1}H and ^{13}C NMR chemical shift (GIAO method) values of the title compound are calculated and compared with the experimental results. The computed data of the chemical shift are in good agreement with the experimental data. Frontier molecular orbitals (FMOs) such as HOMO orbital, LUMO orbital and energy gap between HOMO and LUMO, molecular electrostatic potential (MEP), electronic properties such as ionization potential (I), electron affinity (A), global hardness, global hardness (η), electronegativity (χ), electronic chemical potential (μ), electrophilicity (ω) and chemical softness (S) of the title compounds were investigated discussed by theoretical calculations. The FMO analysis suggests that charge transfer is taking place within the molecule. Also the electronic structure of the title compound was studied by using Natural Bond Orbital (NBO) analysis in order to understand hyper conjugative interactions and charge delocalization.

Keywords: *N*-(2-benzoylphenyl)oxalamate; DFT; natural charge; NBO analysis; electronic properties

INTRODUCTION

Oxamide derivatives are used as a model to study bonds in biomolecules, particularly intermolecular and intramolecular hydrogen bonding [1]. The hydrogen bond is a weak chemical bond between an electronegative atom, such as fluorine, oxygen or nitrogen and a hydrogen atom bound to another electronegative atom. Hydrogen bonds are responsible of water and many biological molecules [2-4]. These hydrogen-bond attractions can occur between molecules (intermolecular) or within different parts of a single molecule (intramolecular) [5]. A three-center intramolecular hydrogen bonding interaction can be seen in all oxamides. Three-center intramolecular hydrogen bonding is bifurcated hydrogen bonding. There are two types of bifurcated hydrogen bonding in biological systems, organic compounds, that can be as intermolecular, intramolecular or both. One is three

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centered hydrogen bond where an electronegative atom participate as acceptor group and two hydrogen atoms as donor in two different hydrogen bonds, and the other kind is where two same electronegative atoms participate as acceptor groups and hydrogen as acceptor atom [6].

In recent years, computational chemistry has become an important tool for chemists and a well-accepted partner for experimental chemistry [7-10]. Density functional theory (DFT) method has become a major tool in the methodological arsenal of computational organic chemists [11]. Isabel Rozas and et al. investigated bifurcated or three-centered hydrogen bonds (HB) using DFT (B3LYP/6-31G(d)) on different families of compounds such as monomers with intramolecular three-centered HB, dimers with a HB donor (HBD) and a molecule with two HB acceptor (HBA) groups, and trimers with one HBD and two HBAs [12]. A. Lakshmipriya et al. studied existence of three-centered C=O…H(N)…X-C hydrogen bond in diphenyloxamide derivatives involving halogens using NMR spectroscopy and quantum theoretical studies [13]. Martinez-Martinez reported synthesis of *N*-(2-benzoyl-phenyl)oxalyl derivatives [14]. Three crystal structures *N*-(2-benzoylphenyl)acetamide, *N*-(2-benzoylphenyl)oxalamate and *N1*,*N2*-bis(2-benzoylphenyl)oxalamide is reported by Carlos Z. Gomez-Castro et al [15]. They studied the formation of three-center hydrogen bonds in three oxalyl derivatives was by the X-ray diffraction analysis. In the present work, we investigate the energetic and structural properties of crystal structures (*N*-(2-benzoylphenyl)oxalamate using DFT calculations. The optimized geometry, frontier molecular orbitals (FMO), detail of quantum molecular descriptors, molecular electrostatic potential (MEP), chemical tensors, natural charge and NBO analysis of the title compound were calculated.

COMPUTATIONAL METHODS

In this work, we have carried out quantum theoretical calculations and have optimized structure of the title compound using DFT (B3LYP) [16] methods with 6-311+G(d) basis set by the Gaussian 09W program package [17] and calculate its properties. The electronic properties such as dipole moment (μ_D), point group, E_{HOMO}, E_{LUMO}, HOMO-LUMO energy gap (ΔE), natural charges and electronic properties were detected [18]. The optimized molecular structure, HOMO and LUMO surfaces were visualized using GaussView 05 program [19]. Also we calculated NMR parameters such as chemical shift isotropic (CS^I) and chemical shift anisotropic (CS^A) [20] for the title structures using B3LYP/6-311+G(d) level of energy. The electronic structure title compound were studied by using Natural Bond Orbital (NBO) analysis [21] using B3LYP/6-311+G(d) level of energy in order to understand hyperconjugative interactions and charge delocalization.

RESULTS AND DISCUSSION

Optimized geometry

The optimized geometry of *N*-(2-benzoylphenyl) oxalamate is performed by DFT/B3LYP methods with 6-311+G(d) basis set (see Fig. 1(b)). The selected experimental and calculated geometrical parameters of the title compound such as bond lengths (Å), bond angles (°) and torsion angels (°) have been obtained by B3LYP/6-311+G(d) level are listed in Table 1. As can be seen from Table 1, the calculated parameters show good approximation and can be used as a foundation to calculate the other parameters for the title compound. According to Table 1, the average differences of the theoretical parameters from the experimental for bond lengths of the title compound were found to be about 0.01Å (O_{17}-C_{16}), 0.001Å (O_8-C_7), 0.003Å (N_{15}-C_3), 0.02Å (N_{15}-C_{16}), 0.008Å (C_3-C_2), 0.006Å (C_2-C_7), 0.012Å (C_{16}-C_{18}), 0.004Å (C_7-C_9). The bond length of N_{15}-C_3 bond in the X-ray and optimized structure of the title compound is 1.399 and 1.402Å respectively, whereas experimental and theoretical value for the bond length of N_{15}-C_{16} bond is 1.346Å and 1.366Å, respectively. It shown the bond length of N_{15}-C_{16} bond is shorter than N_{15}-C_3 bond due to the fact that lone pair of N_{15} conjugated with the C_{16} (carbonyl group). We found that most of the calculated bond lengths are slightly longer than X-ray values that it is due to the fact that experimental result corresponds to interacting molecules in the crystal lattice, whereas computational method deals with an isolated molecule in gaseous phase [22]. The bond angel of N15-C3-C2 in the X-ray and optimized structure is 119.08 and 119.410° respectively, which they are close to the typical hexagonal angle of 120°.

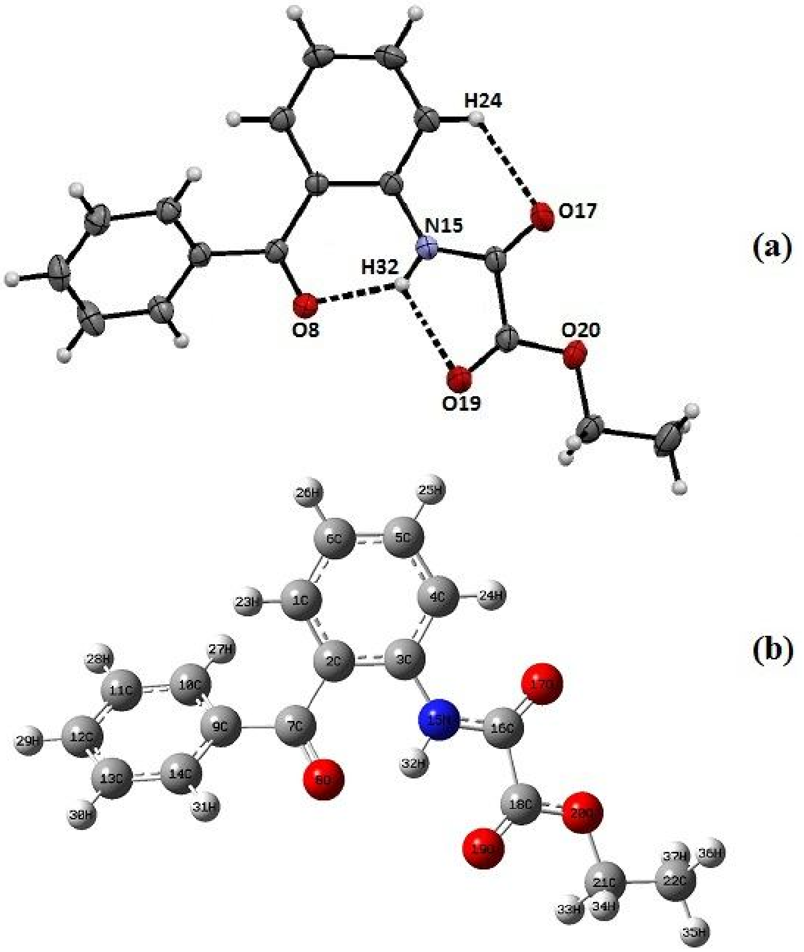

Fig. 1. (a) X-Ray crystal structure of the title compound (b) The theoretical geometric structure of the title compound (optimized using the B3LYP/6-311+G(d) level).

In addition, the hydrogen bonds length values of experimental [15] and theoretical of *N*-(2-benzoylphenyl) oxalamate is summarized in Table 2. X-ray diffraction analysis of the title compound shows that the structure is stabilized by intramolecular hydrogen bonding. According to experimental results is obtained by Carlos Z. Gómez-Castro [15], it revealed that the title compound has three intramolecular hydrogen bondings (see Fig. 1 (a)). By knowing the bond length, the strength of the hydrogen bond can be determined as very strong (below 2.5Å), strong (2.5-2.7Å), normal (2.7-2.9Å) and weak (above 2.9Å). The first intramolecular hydrogen bonding [N15-H32…O19] of the title compound, the experimental and theoretical values of bond length H32…O19 are 2.25 and 2.23Å respectively, that suggesting the existence of very strong intramolecular hydrogen bond. For second intramolecular hydrogen bonding [N15-H32…O8] of the title compound, the experimental bond length H32…O8 is 1.97Å and calculated value is 1.90Å. This suggesting the intramolecular N15-H32…O8 hydrogen bond is very strong. The experimental and theoretical values of H24…O17 hydrogen bond [C4-H24…O17] is 2.29 and 2.18Å respectively.

Natural charges and NMR parameters

The atomic charges play an important role on molecular polarizability, dipole moment, electronic structure and lot of related properties of molecular systems. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transferring the molecule. We calculated the charge distributions for equilibrium geometry of molecule by NBO method

Table 1. Selected optimized geometrical parameters of the title compound

Parameter	Exp. [a]	Cal. [b]	Parameter	Exp. [a]	Cal. [b]
Bond lengths(Å)			Bond angles (°)		
C2-C3	1.416(3)	1.425	C3-N15-C16	129.61(16)	127.872
C2-C7	1.486(2)	1.492	N15-C3-C2	119.08(16)	119.410
C3-N15	1.399(2)	1.402			
C7-O8	1.227(2)	1.228	Torsion angels (°)		
C7-C9	1.496(2)	1.500	C2-C3-N15-C16	-171.96(18)	168.112
N15-C16	1.346(2)	1.366	O17-C16-N15-C3	-5.8(3)	-0.553
C16-O17	1.204(3)	1.214	O8-C7-C9-C10	151.65(18)	-142.555
C16-C18	1.538(3)	1.550	C3-C2-C7-O8	25.4(3)	25.261

[a] Taken from Ref. [15].

[b] Calculated using the DFT method (B3LYP/6-311+G(d))

Table 2. Hydrogen-Bond Geometry (Å) (Exp.[a] and Cal.[b]) of the title compound

D-H…A	D-H (Å)		H…A(Å)		D…A(Å)	
	Exp.	Cal.	Exp.	Cal.	Exp.	Cal.
N15-H32…O19	0.86	1.02	2.25	2.23	2.666(2)	2.702
N15-H32…O8	0.86	1.02	1.97	1.90	2.662(2)	2.703
C4-H24…O17	0.93	1.08	2.29	2.18	2.908(3)	2.889

[a] Taken from Ref. [15].

[b] Calculated using DFT method (B3LYP/6-311+G(d))

(natural charge) [23] using B3LYP/6-311+G(d) level of energy. The results of Natural Bond Orbital (NBO) are listed in Table 3 (Atoms labeling is according to Fig. 1). The total charge of the investigated molecules is equal to zero. Also Fig. 2 shows results of natural charge in graphical form. The natural charge (NBO) analysis of the title compound shows that carbon atoms have both positive and negative charges magnitudes. The C atoms attached to the O and N atoms have positive charge due to the electron-withdrawing nature of the O and N atoms. The C3, C7, C16 and C18 atoms have the positive charge (0.204, 0.548, 0.591 and 0.734e, respectively) therefore they are more acidic. The C18 has the highest positive charge (0.734e) due to attachment to two O atoms. Other C atoms of the title compound have negative charge. The charges of O atoms are negative. The highest negative charge is observed for N15 atom (-0.607e). Natural charges also show that all hydrogen atoms have the positive charge and H32 atom has the highest positive charge (0.454e) compared with other hydrogen atoms due to attachment to N15 atom and also participate in forming three-centered intramolecular hydrogen bonding (O8…H32…O19).

In the present study, we calculated the ^{13}C, ^{15}N, ^{17}O and ^{1}H shielding tensors of the title compound. The shielding tensors calculations were carried out at the B3LYP method using 6-311+G(d) basis set. The isotropic chemical shift (CS^{I}) and anisotropic chemical shift (CS^{A}) for the title compound are summarized in Table 3. The C7 atom is deshielde compared with other C atoms (CS^{I} = -22.371 ppm). The C_{21} (CH_2 group) and C_{22} (CH_3 group) atoms have the highest CS^{I} value compared with other carbon atoms (116.798 and 168.778 ppm, respectively), therefore they are shielder than other C atoms. The H32 atom in N-H group has the lowest CS^{I} (20.416 ppm) and the highest CS^{A} (10.774 ppm) values compared with hydrogen atoms, therefore it is deshielder than other hydrogen atoms that it is as a result of forming three-centered intramolecular O8…H32…O19 hydrogen bond.

Table 3. Natural Charges (NBO charges, e) and NMR parameters (ppm) such as chemical shift isotropic (CS^{I}) and chemical shift anisotropic (CS^{A}) of the title compound using the B3LYP/311+G(d) level

atoms	Natural charge	CS^{I} (ppm)	CS^{A} (ppm)
C_1	-0.157	44.787	184.483
C_2	-0.169	54.297	158.975
C_3	0.204	34.439	155.239
C_4	-0.225	57.688	179.918
C_5	-0.155	44.239	191.420
C_6	-0.221	57.835	173.629
C_7	0.548	-22.371	157.173
O_8	-0.580	-276.578	921.097
C_9	-0.139	37.075	174.589
C_{10}	-0.175	47.760	184.963
C_{11}	-0.203	52.157	180.895
C_{12}	-0.178	46.356	190.185
C_{13}	-0.199	49.497	184.382
C_{14}	-0.151	46.648	192.702

atoms	Natural charge	CS^{I} (ppm)	CS^{A} (ppm)
N_{15}	-0.607	110.860	152.232
C_{16}	0.591	24.480	78.626
O_{17}	-0.577	-93.434	669.744
C_{18}	0.734	16.445	75.482
O_{19}	-0.588	-72.104	586.068
O_{20}	-0.524	103.128	154.793
C_{21}	-0.037	116.798	62.806
C_{22}	-0.585	168.778	22.803
H_{23}	0.218	24.666	9.738
H_{24}	0.249	23.031	10.071
H_{25}	0.208	24.533	4.845
H_{26}	0.209	25.136	4.803
H_{27}	0.216	24.685	9.765
H_{28}	0.208	24.815	5.377
H_{29}	0.206	24.567	4.589
H_{30}	0.208	24.541	4.919
H_{31}	0.224	23.920	7.387
H_{32}	0.454	20.416	10.774
H_{33}	0.186	28.102	5.122
H_{34}	0.187	28.072	5.220
H_{35}	0.205	31.056	9.299
H_{36}	0.207	30.632	7.642
H_{37}	0.207	30.641	7.642

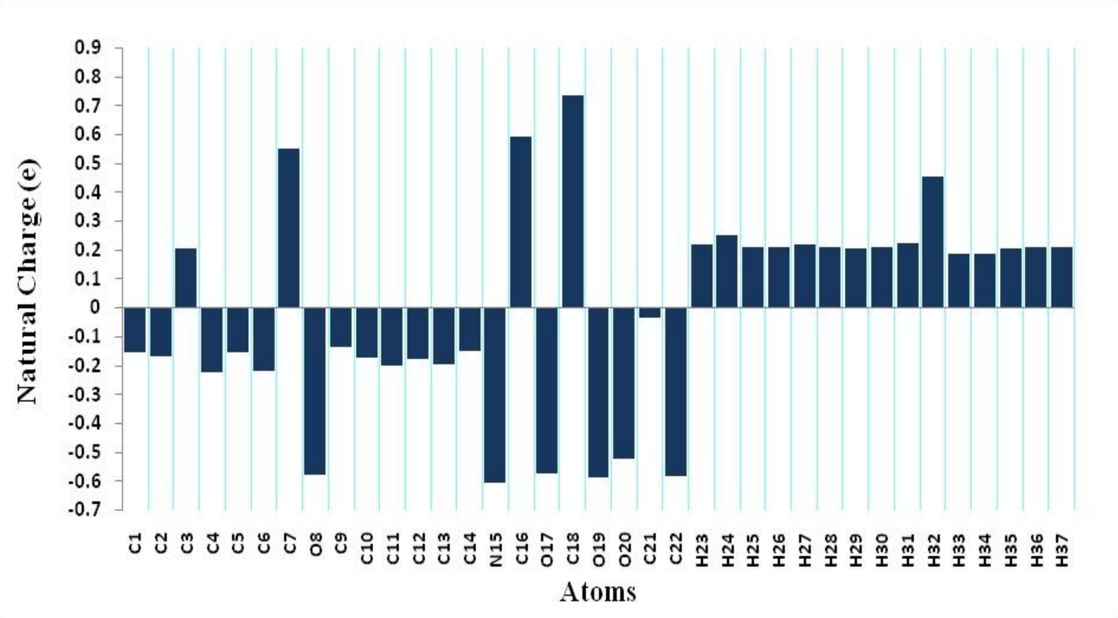

Fig. 2. Natural charge distribution of the title compound.

Electronic properties

Quantum chemical methods are important for obtaining information about molecular structure and electrochemical behavior. A Frontier Molecular Orbitals (FMO) analysis [24] was done for the compound using B3LYP/6-311+G(d) level of theory. The energies of two important molecular orbitals of compound in gas phase such as E_{HOMO}, E_{LUMO} and the HOMO-LUMO energy gap (ΔE) of title compound were calculated as shown in the Table 4 and Fig. 3. The values of energy of the highest occupied molecular orbital (E_{HOMO}) can act as an electron donor and the lowest unoccupied molecular orbital (E_{LUMO}) can act as the electron acceptor [25]. The energy of HOMO (-6.64 eV) is directly related to the ionization potential, while the energy of LUMO (-2.4 eV) is related to the electron affinity. The title compound contains 78 occupied molecular orbital and 449 unoccupied virtual molecular orbital. As shown in Fig. 3, the positive and negative phase is represented in green and red color respectively. According to Fig. 3, charge transfer is taking place within molecule. The graphic pictures of orbitals show HOMO orbital of molecule is localized mainly on amide group and one of phenyl ring, whereas LUMO orbital of molecule is localized mainly on two phenyl rings and carbonyl of ketone group. The HOMO-LUMO energy gap (ΔE) explains the eventual charge transfer interaction taking within the molecule. As seen in Table 4, the HOMO-LUMO energy gap (ΔE) of compound is 4.24 eV that reflect the chemical activity of the molecule. Also the calculated energy gap clearly is shown in DOS plot (see Fig. 3) [26].

A detail of quantum molecular descriptors of title compound such as ionization potential (I=- E_{HOMO}), electron affinity (A=- E_{LUMO}), global hardness (η=I – A/2), electronegativity (χ=I + A/2), electronic chemical potential (μ=-(I + A)/2) and electrophilicity ($\omega=\mu^2/2\eta$), chemical softness ($S=1/\eta$) [24] are calculated and are listed in Table 4. The global hardness (η) corresponds to the HOMO-LUMO energy gap. A molecule with a small energy gap has high chemical reactivity, low kinetic stability and is a soft molecule, while a hard molecule has a large energy gap [24]. The ionization potential value (6.64 eV) obtained by DFT method also support the stability of the title molecule. Electronegativity (χ) is a measure of the power of an atom or a group of atoms to attract electrons [27] and the chemical softness (S) describes the capacity of an atom or a group of atoms to receive electrons [24]. Dipole moment (μ_D) is a good measure for the asymmetric nature of a structure [28]. The size of the dipole moment depends on the composition and dimensionality of the 3D structures. The calculated dipole moment value shows that the molecule is highly polar in nature. As shown in Table 4, dipole moment and point group of title structure is 2.5406 Debye.

Table 4. Electronic properties of the title compound calculated by B3LYP method with 6-311+G(d) basis sets

Property	**B3LYP/6-311+G(d)**
E_{HOMO} (eV)	-6.64
E_{LUMO} (eV)	-2.4
Energy gap (eV)	4.24
Ionisation potential I (eV)	6.64
Electron affinity A (eV)	2.4
Electronegativity (χ)	4.52
Global hardness (η)	2.12
Chemical potential (μ)	-4.52
Global electrophilicity (ω)	4.82
Chemical softness S (eV^{-1})	0.47
Dipole moment (Debye)	2.5406

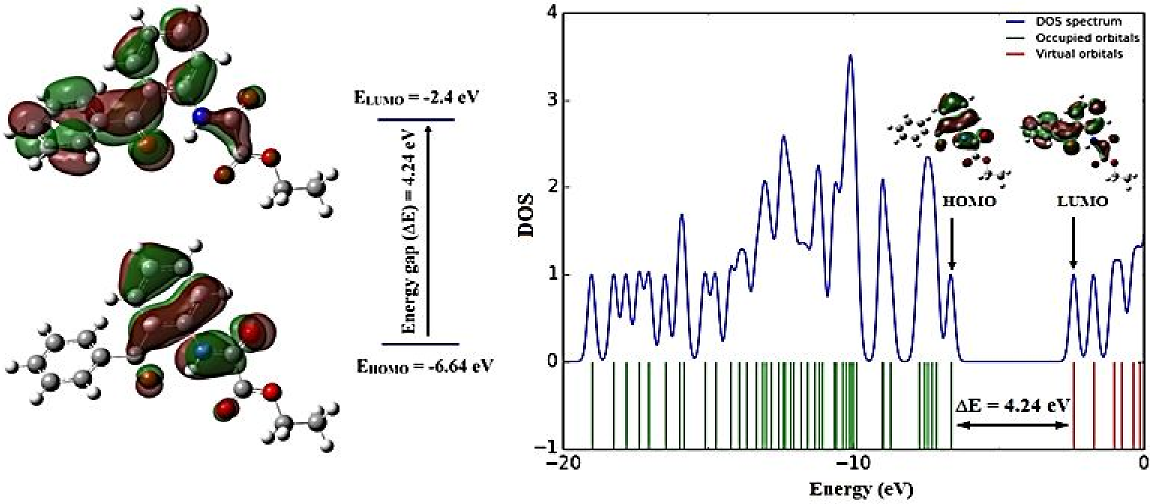

Fig. 3. Calculated Frontier molecular orbitals and DOS plots of the title compound (using the B3LYP/6-311+G(d)).

Molecular electrostatic potential (MEP)

The molecular electrostatic potential (MEP) [24] was checked out by theoretical calculations using B3LYP/6-311+G(d) level. Molecular electrostatic potential shows the electronic density and is useful in recognition sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions. The different values of the electrostatic potential at the surface are represented by different colors. The negative areas (red, orange and yellow color) of MEP were related to electrophilic reactivity, the positive areas (blue color) ones to nucleophilic reactivity and green color is neutral regions. According to the MEP map in Fig. 4, negative region of compound is mainly focused on oxygen atoms of carbonyl group (O8, O17 and O19 atoms) with the highest red color intensity which is caused by the contribution of lone-pair electrons of oxygen atom. Therefore they are suitable sites for electrophilic attack. The parts of the title compounds with pale red or yellow color are sites with weak interaction that including phenyl rings and oxygen atom in C-O bond (ester group). The positive potential sites (blue color) are around the hydrogen atoms.

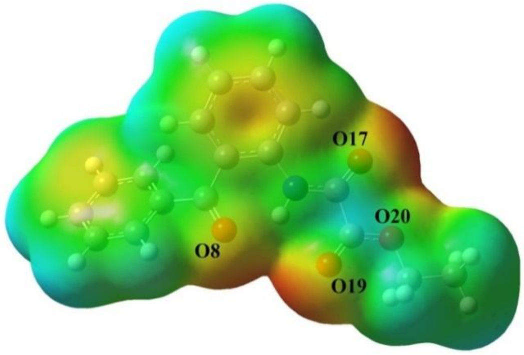

Fig. 4. Molecular electrostatic potential (MEP) map of the title compound calculated using the B3LYP/6-311+G(d) level.

NBO analysis

Natural bond orbital (NBO) analysis is important method for studying intra- and inter-molecular bonding and interaction between bonds [29, 30]. The results of NBO analysis such as the occupation numbers with their energies for the interacting NBOs [interaction between natural bond orbital A and natural bond orbital B (A-B)] and the polarization coefficient amounts of atoms in title compound are presented using the B3LYP/6-311+G(d) level is summarized in Table 5 (Atoms labeling is according to Fig. 1). The size of polarization coefficients shows the importance of the two hybrids in the formation of the bond. The differences in electronegativity of the atoms involved in the bond formation are reflected in the larger differences in the polarization coefficients of the atoms (C-O, C-N, N-H and C-H bonds). The calculated bonding orbital for the σ(C7-O8) bond is the $\sigma=0.5898sp^{2.36}+0.8076sp^{1.41}$ with high occupancy 1.99252a.u. and low energy -1.07311a.u.. The polarization coefficients of C7= 0.5898 and O8= 0.8076 shows importance of O8 in forming C7-O8 bond compared with C7 atom. Also the calculated bonding orbital for the π(C16-O17) is $\sigma=0.5591sp^{1.00}+0.8291sp^{1.00}$ with high occupancy 1.97729a.u. and energy -0.38878a.u.. The polarization coefficients of C16 and O17 atoms show importance of O17 in forming C16-O17 bond compared with C16 atom. According to the calculated bonding orbital of π(N15-H32) [$\sigma=0.8601sp^{2.52}+0.5102s$], the polarization coefficients of N15 and H32 are 0.8601 and 0.5102 respectively, therefore N15 atom has more importance in forming N15-H32 bond compared with H32 atom. The low difference in the polarization coefficients is observed when similar atoms are founded in bond (C-C bonds). As shown in Table 6, the calculated bonding orbital for the σ(C5-C6) bond is $\sigma=0.7066sp^{1.78}+0.7076sp^{1.82}$ with energy -0.71192a.u. and high occupancy 1.97981a.u.. The polarization coefficients of C5= 0.7066 and C6= 0.7076 shows low difference in polarization coefficients C5 and C6 atoms in C5-C6 bond and importance of two atoms in forming bond.

Table 5. Calculated natural bond orbitals (NBO) and the polarization coefficient for each hybrid in selected bonds of the title compound using the B3LYP/6-311+G(d) level

Occupancy (a.u.)	Bond (A-B)[a]	Energy (a.u.)	ED_A(%)	ED_B(%)	NBO
1.97093	σ(C1-C2)	-0.70964	48.56	51.44	0.6969 ($sp^{1.85}$) + 0.7172 ($sp^{1.84}$)
1.97858	σ(C1-C6)	-0.71731	50.40	49.60	0.7100 ($sp^{1.74}$) + 0.7042 ($sp^{1.80}$)
1.66495	π(C1-C6)	-0.26676	48.01	51.99	0.6929 ($sp^{1.00}$) + 0.7210 ($sp^{1.00}$)
1.98629	σ(C3-N15)	-0.81789	38.45	61.55	0.6201 ($sp^{2.67}$) + 0.7845 ($sp^{1.75}$)
1.97755	σ(C4-C5)	-0.71281	50.35	49.65	0.7095 ($sp^{1.76}$) + 0.7047 ($sp^{1.79}$)
1.97981	σ(C5-C6)	-0.71192	49.93	50.07	0.7066 ($sp^{1.78}$) + 0.7076 ($sp^{1.82}$)
1.99252	σ (C7-O8)	-1.07311	34.78	65.22	0.5898 ($sp^{2.36}$) + 0.8076 ($sp^{1.41}$)
1.97858	σ(C10-C11)	-0.71468	50.29	49.71	0.7091 ($sp^{1.78}$) + 0.7051 ($sp^{1.79}$)
1.97995	σ(C11-C12)	-0.71379	50.10	49.90	0.7078 ($sp^{1.79}$) + 0.7064 ($sp^{1.79}$)
1.65017	π(C11-C12)	-0.26503	50.98	49.02	0.7140 ($sp^{1.00}$) + 0.7001 ($sp^{1.00}$)
1.99399	σ(C16-O17)	-1.08506	59.84	80.12	0.5984 ($sp^{1.89}$) + 0.8012 ($sp^{1.46}$)
1.97729	π (C16-O17)	-0.38878	31.26	68.74	0.5591 ($sp^{1.00}$) + 0.8291 ($sp^{1.00}$)
1.97172	σ(C16-C18)	-0.65820	49.83	50.17	0.7059 ($sp^{2.11}$) + 0.7083 ($sp^{1.84}$)
1.99601	σ(C18-O19)	-1.10569	35.15	64.85	0.5929 ($sp^{1.84}$) + 0.8053 ($sp^{1.48}$)
1.98383	π (C18-O19)	-0.40562	30.32	69.68	0.5506 ($sp^{1.00}$) + 0.8348 ($sp^{1.00}$)
1.99225	σ(C18-O20)	-0.95932	31.74	68.26	0.5634 ($sp^{2.36}$) + 0.8262 ($sp^{2.03}$)
1.98725	σ(O20-C21)	-0.81877	69.83	30.17	0.8356 ($sp^{2.56}$) + 0.5493 ($sp^{4.20}$)
1.99177	σ(C21-C22)	-1.64558	50.87	49.13	0.7132 ($sp^{2.19}$) + 0.7009 ($sp^{2.45}$)
1.97668	σ(C1-H23)	-0.53332	60.91	39.09	0.7804 ($sp^{2.52}$) + 0.6253 (s)
1.98033	σ(C12-H29)	-0.53256	60.37	39.63	0.7770 ($sp^{2.52}$) + 0.6295 (s)
1.97857	σ(C14-H31)	-0.52442	61.28	38.72	0.7828 ($sp^{2.48}$) + 0.6222 (s)
1.97961	σ(N15-H32)	-0.66226	73.97	26.03	0.8601 ($sp^{2.52}$) + 0.5102 (s)
1.98470	σ(C21-H33)	-0.52928	59.68	40.32	0.7725 ($sp^{3.02}$) + 0.6350 (s)
1.98473	σ(C21-H34)	-0.52929	59.70	40.30	0.7727 ($sp^{3.01}$) + 0.6348 (s)
1.98105	σ(C22-H35)	-0.51196	60.05	39.95	0.7749 ($sp^{3.31}$) + 0.6320 (s)
1.98779	σ(C22-H37)	-0.51002	60.41	39.59	0.7772 ($sp^{3.17}$) + 0.6292 (s)

[a] A-B is the bond between atom A and atom B. (A: natural bond orbital and the polarization coefficient of atom; A-B: natural bond orbital and the polarization coefficient of atom B).

Electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro disturbance theory are reported in Table 6. The electron delocalization from filled NBOs (donors) to the empty NBOs (acceptors) describes a conjugative electron transfer process between them [31]. For each donor (*i*) and acceptor (*j*), the stabilization energy $E^{(2)}$ associated with the delocalization $i \rightarrow j$ is estimated:

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

where qi is the donor orbital occupancy, ε_j and ε_i are diagonal elements and F(i,j) is the off diagonal NBO Fock matrix element. The resonance energy ($E^{(2)}$) detected the quantity of participation of electrons in the resonance between atoms. The larger $E^{(2)}$ value, the more intensive is the interaction between electron donors and acceptor, i.e. the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system [9]. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydgberg) non Lewis NBO orbitals correspond to a stabilization donor–acceptor interaction. NBO analysis has been performed for title compound at the B3LYP/6-311+G(d) level in order to elucidate the intramolecular, rehybridization and delocalization of electron density within the molecule. The strong, moderate and weak intramolecular hyperconjugative interactions of the title compound are presented in Table 6. According to results of the NBO analysis, the intramolecular hyperconjugative interactions of the π→π* transitions in phenyl ring that lead to a strong delocalization are such as C1-C6→C2-C3, C1-C6→C4-C5, C2-C3→C1-C6, C2-C3→C7-O8, C9-C10→C11-C12 and C9-C10→C13-C14 with resonance energies (E(2)) 17.48, 21.59, 21.59, 16.88, 18.84 and 19.72 kcal/mol, respectively. The intramolecular hyperconjugative interactions of the π*→π* transitions in title compound such as C2–C3→C1–C6 and C2–C3→C4–C5 leads to strong stabilization energies of 247.89 and 202.39 kcal/mol, respectively. These resonance energies ($E^{(2)}$) are the highest energies compared with other interactions of the title compound and lead to stability of molecule. According to Table 6, the n1(O8)→σ*(N15-H32), n2(O8)→σ*(N15-H32) and n2(O19)→σ*(N15-H32) interactions with stabilization energy of 2.58, 5.83 and 1.41 kcal/mol show the existence of three-centered intramolecular O8…H32…O19 hydrogen bond in the title compound. Another important intramolecular hyperconjugative interaction including n2(O20)→π*(C18-O19) orbital that show the strong stabilization energy of 53.18 kcal/mol. The n1(O17)→σ*(C4-H24) and n2(O17)→σ*(C4-H24) interactions with stabilization energy of 2.58, 0.61 and 1.22 kcal/mol show the existence of intramolecular O17…H24-C4 hydrogen bond in the title compound.

Table 6. Significant donor–acceptor interactions and second order perturbation energies of the title compound calculated using the B3LYP/6-311+G(d) level

Donor (i)	Occupancy	Acceptor (j)	Occupancy	E(2)^a kcal/mol	E(j)-E(i)^b a.u.	F(i , j)^c a.u.
π(C1-C6)	1.66495	π*(C2-C3)	0.44616	17.48	0.27	0.063
π(C1-C6)	1.66495	π*(C4-C5)	0.30750	21.59	0.29	0.071
π(C2-C3)	1.60237	π*(C1-C6)	0.31876	21.95	0.29	0.072
π(C2-C3)	1.60237	σ*(C7-O8)	0.01246	0.81	0.83	0.026

Donor (i)	Occupancy	Acceptor (j)	Occupancy	E(2)[a] kcal/mol	E(j)-E(i)[b] a.u.	F(i , j)[c] a.u.
π(C2-C3)	1.60237	π*(C7-O8)	0.18610	16.88	0.27	0.063
π(C9-C10)	1.64395	σ*(C2-C7)	0.05846	0.78	0.69	0.022
π(C9-C10)	1.64395	σ*(C7-O8)	0.01246	1.20	0.83	0.031
π(C9-C10)	1.64395	π*(C7-O8)	0.18610	13.90	0.27	0.057
π(C9-C10)	1.64395	π*(C11-C12)	0.32130	18.84	0.28	0.066
π(C9-C10)	1.64395	π*(C13-C14)	0.29312	19.72	0.29	0.068
π*(C2-C3)	0.44616	π*(C1-C6)	0.31876	247.89	0.01	0.080
π*(C2-C3)	0.44616	π*(C4-C5)	0.30750	202.39	0.02	0.083
n1(O8)	1.97327	σ*(N15-H32)	0.03814	2.58	1.11	0.048
n2(O8)	1.88784	σ*(C7-C9)	0.06195	18.69	0.70	0.104
n2(O8)	1.88784	σ*(N15-H32)	0.03814	5.83	0.69	0.058
n1(N15)	1.61271	π*(C2-C3)	0.44616	37.94	0.28	0.093
n1(N15)	1.61271	π*(C16-O17)	0.28903	62.57	0.27	0.119
n1(O17)	1.98053	σ*(C4-H24)	0.01543	0.61	1.15	0.024
n2(O17)	1.85735	σ*(C4-H24)	0.01543	1.22	0.72	0.027
n2(O17)	1.85735	σ*(N15-C16)	0.07369	24.81	0.71	0.121
n2(O17)	1.85735	σ*(C16-C18)	0.12674	24.74	0.58	0.108
n2(O19)	1.84698	σ*(N15-H32)	0.03814	1.41	0.69	0.029
n2(O19)	1.84698	σ*(C16-C18)	0.12674	21.10	0.60	0.101
n2(O19)	1.84698	σ*(C18-O20)	0.08709	29.58	0.67	0.128
n2(O19)	1.84698	σ*(C21-C22)	0.00665	0.58	0.67	0.018
n2(O20)	1.76341	π*(C18-O19)	0.23708	53.18	0.33	0.118
n2(O20)	1.76341	σ*(C21-H33)	0.02021	4.31	0.71	0.052
n2(O20)	1.76341	σ*(C21-H34)	0.02018	5.25	0.71	0.052

[a] E(2) means energy of hyperconjucative interactions.

[b] Energy difference between donor and acceptor i and j NBO orbitals.

[c] F(i, j) is the Fock matrix element between i and j NBO orbitals

CONCLUSIONS

In the present study, the electronic structure of *N*-(2-benzoylphenyl)oxalamate has been analyzed using the DFT calculations (B3LYP/6-311+G(d) level). From the theoretical and experimental geometric parameters values, it can be seen experimental values are in good agreement with the theoretical values. The natural charge (NBO) analysis of the title compound shows that the highest negative and positive charges are observed for N15 and C18 atoms, respectively. According to calculated shielding tensors, the H32 atom (N15-H32) has the lowest CS^{I} and the highest CS^{A} values compared with hydrogen atoms, therefore it is deshielder than other hydrogen atoms that it is as a result of forming three-centered intramolecular O8…H32…O19 hydrogen bond. The FMO analysis suggests that charge transfer is taking place within the molecule. From the MEP map, it can be seen negative region of the title compound is mainly focused on oxygen atoms of carbonyl group (O8, O17 and O19 atoms), therefore they are suitable site for electrophilic attack. According to the results of NBO analysis, the n1(O8)→σ*(N15-H32), n2(O8)→σ*(N15-H32) and n2(O19)→σ*(N15-H32) interactions show the existence of three-centered intramolecular O8…H32…O19 hydrogen bond in the title compound.

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