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Structural characterization and DFT studies of the highly disordered compound 2-phenyl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone

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Abstract

In this study, the crystal and molecular structure of the compound 2-phenyl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone was determined by the single-crystal X-ray diffraction method. The molecular structure of the compound consists of a N-phenyl-(aza-15-crown-5) moiety connected to the oxazol-5-one ring. A phenyl group is also linked to the oxazol-5-one fragment. Crystal structure is stabilized by C–H···O type intermolecular hydrogen bonds, C–H···O type intramolecular interaction and pi···pi interactions. Theoretical studies such as molecular geometry, frontier molecular orbitals and molecular electrostatic potential were performed using the Density Functional Theory (DFT) method B3LYP/6-311G(d,p) basis set. Geometric parameters were compared with the experimental data and the compatibility was observed.

Keywords: *Oxazole-5-one, crown ether, crystal structure, DFT, molecular orbitals.*

Yüksek disordera sahip 2-fenil-4-[4-(1,4,7,10-tetraoksa-13-azasiklopentadesil)benziliden]-5-oksazolon Bileşiğinin Yapısal Karakterizasyonu ve DFT çalışmaları

Özet

Bu çalışmada, 2-fenil-4-[4-(1,4,7,10-tetraoksa-13-azasiklopentadesil)benziliden]-5-oksazolon bileşiğinin moleküler ve kristal yapısı tek-kristal X-ışını kırınımı yöntemiyle belirlendi. Bileşiğin moleküler yapısı, bir oksazol-5-on grubuna bağlı N-fenil sübstitüe

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aza-taç eter yapıdan oluşmaktadır. Bir fenil grubu da oksazol-5-on fragmentine bağlıdır. Kristal yapı, C–H···O tipi moleküllerarası hidrojen bağları ile C–H···O tipi molekül içi zayıf etkileşmeler ve pi···pi etkileşmeleri ile kararlı haldedir. Teorik çalışmalar (moleküler geometri, frontier moleküler orbitaller ve moleküler elektrostatik potansiyel) Yoğunluk Fonsiyonu Teorisi (YFT) metodu ile ve B3LYP/6-311G(d,p) baz seti kullanılarak gerçekleştirilmiştir. Geometrik parametreler deneysel verilerle karşılaştırılarak uyumlu oldukları gözlenmiştir.

Anahtar kelimeler: *Oksazol-5-on, taç eter, kristal yapı, YFT, moleküler orbitaller.*

1. Introduction

Oxazolone derivatives make a class of five-membered heterocycles, having two oxygen and one nitrogen atom. They have very important role in the medicinal chemistry, biology and physics. They are used as intermediates for the synthesis of several biologically active molecules. They exhibit a wide spectrum of pharmacological activities such as anticancer [1], antitumor [2], antimicrobial [3], analgesic [4], anti-inflammatory [5], antidepressant [6], anti-HIV [7,8], sedative [9,10], cardiotonic activity [11], antidiabetic and antiobesity [12,13]. Oxazolones are also involved in the synthesis of several organic molecules including amino acids, amino alcohols, thiamine, peptides and polyfunctional compounds [14,15]. They are also used in semiconductor devices such as electro photographic photoreceptors and in nonlinear optical materials.

In this study, we characterized an oxazol-5-one derivative containing N-phenyl-(aza-15-crown-5) moiety. The structural analysis of the compound was performed by single-crystal X-ray diffraction method. Theoretical studies such as molecular geometry, frontier molecular orbitals and molecular electrostatic potential were carried out using the Density Functional Theory (DFT) method B3LYP/6-311G(d,p) basis set. The theoretical and experimental results were compared and discussed.

1. Material and method

1.1 Synthesis

The synthesis of the 2-phenyl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl) benzylidene]-5-oxazolone was performed by İcli et al. and described in the literature [16].

1.2 X-ray crystallography

Single-crystal X-ray diffraction data of 2-phenyl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone was collected at 293(2) K on a Rigaku-Oxford Xcalibur diffractometer with an EOS-CCD detector using graphite-monochromated MoKα radiation (λ= 0.71073 Å) with CrysAlis^{Pro} software [17]. Data reduction and analytical absorption correction was performed by CrysAlis^{Pro} program [18]. Utilizing OLEX2 [19], the structure was solved by *Intrinsic Phase* method with SHELXT [20] and refined by full-matrix least squares on F^2 in SHELXL [21]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Hydrogen atoms were placed using standard geometric models and with their thermal parameters riding on those of their parent atoms (C-H = 0.93-0.97 Å). During the initial refinement cycles, some atoms of the crown ether moiety exhibited highly anisotropic displacement ellipsoids, which were consistent with positional disorder. PART 1 and PART 2 instructions were used to separate the two positions of atoms C4A and C4B with the 40:60 (C4A:C4B) population distribution. A number of SADI/RIGU restrains and equal U_{ij} constraints (EADP) were also applied to refine some moieties of the molecular structure. The details of the crystal data and structure refinement of the title compound are given in Table 1.

1.3 Computational details

In this study, the computational studies were carried out on the basis of *Density Functional Theory* (DFT), with the Gaussian 09W and Gauss View molecular visualization program [22,23]. The molecular structure of the compound was optimized at B3LYP/6-311G(d,p) level of the theory in the ground state [24,25]. Highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and MEP have also been calculated from optimized geometry of the molecules.

Table 1. Crystallographic data and structure refinement parameters for the title compound.

Empirical formula	$C_{26}H_{27}N_2O_6$
Formula weight (g/mol)	466.52
Crystal system, space group	Orthorhombic, Pbca
a, *b*, *c* (Å)	17.7637(19), 8.9032(7), 30.280(3)
V (Å^3)	4788.9(8)
Z	8
Density$_{calc}$ (g/cm^3)	1.294
Absorption coefficient (mm^{-1})	0.092
F(000)	1984
Crystal size (mm^3)	0.684 × 0.446 × 0.215
Reflections collected / independent	12223 / 2107
Parameters	293
Goodness-of-fit on F^2	1.358
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.120, wR_2 = 0.192
R indices (all data)	R_1 = 0.336, wR_2 = 0.402

2. Result and discussion

2.1 Crystal structure determination

The molecular structure of the title compound is depicted in Fig.1 The molecule consists of a N-phenyl-(aza-15-crown-5) moiety connected to the oxazol-5-one ring bridged by the methine C17 atom and a phenyl group linked to the oxazol-5-one fragment. The crown ether group is tilted [torsion angles N11-C1-N1-C2 = -80.7(6)°, C11-N1-C10-C9 = 81.5(6)°] relative to the plane containing N-phenyl, oxazol-5-one and phenyl moieties. The rest of the complex is almost coplanar with the dihedral angles between the oxazole and N-phenyl rings of 2.5(3)°, oxazole and phenyl rings of 9.2(4)°, N-phenyl and phenyl rings of 10.2(3)°. Torsion angles, which are listed in Table 3, are also prove this planarity.

The nitrogen atom of the N-phenyl-(aza-15-crown-5) is similarly close to a trigonal planar geometry with angles of 118.3(4)° (C1-N1-C10), 121.2(4)° (C1-N11-C11) and 120.5(4)° (C10-N1-C11). C3-C4B bond length is slightly longer than the other C-C bond lengths in the crown ether due to the positional disorder. All other bond lengths, bond angles and torsion angles are within normal ranges, and are close to those observed for a very similar structures in the literature [26-29].

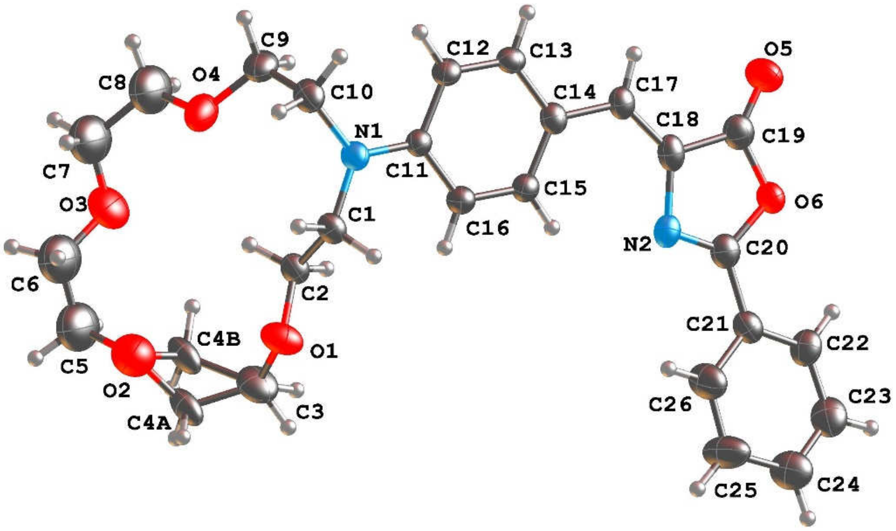

Figure 1. The molecular structure of the title compound, showing the atom labeling, Displacement ellipsoids are drawn at the 25% probability level.

Crystal structure of the compound is stabilized by an intermolecular C23-H23···O5^{i} hydrogen bond and three intramolecular interactions, which are shown in Table 2. The compound consists of a dimeric arrangement of molecules around an inversion centre formed *via* the C23-H23···O5^{i} intermolecular hydrogen bond linking the molecules. This centrosymmetric hydrogen-bonded dimers are formed with an $R_2^2(16)$ ring motif [30]. Also, there is a S(6) motif forms through the intramolecular C15-H15···N2 weak interaction. The cavity of the crown moiety does not contain any solvent or guests molecules. To get around this, the crown forms two weak C-H···O typeintramolecular hydrogen bonds, which further stabilize the conformation observed. The distances between the hydrogen and the oxygen atoms are 2.60 Å (O4) and 2.44 Å (O3), while the distances between the carbon and oxygen atoms are 3.344(8) Å and 3.064(14) Å. Comparing with the similar studies, these distances are slightly short for the expected weak hydrogen bond interactions [26]. In addition, there is a strong $\pi\cdots\pi$ interactions with 3.472(4) Å distance between the centroids Cg1···Cg1 [Cg1 = N2/C18/C19/O6/C20; Cg1···Cg1 symmetry code (ii) 1-x,1-y,1-z].

Table 2. Hydrogen-bonding interactions [Å,°] for the title compound.

D-H···A	**D-H**	**H···A**	**D···A**	**D-H···A**
C23-H23···O5^{i}	0.93	2.58	3.504(8)	176
C2-H2A···O4	0.97	2.60	3.344(8)	134
C4B-H4BA···O3	0.97	2.44	3.064(14)	122
C15-H15···N2	0.93	2.36	3.037(7)	130

symmetry code: (i) 1-x, -y, 1-z

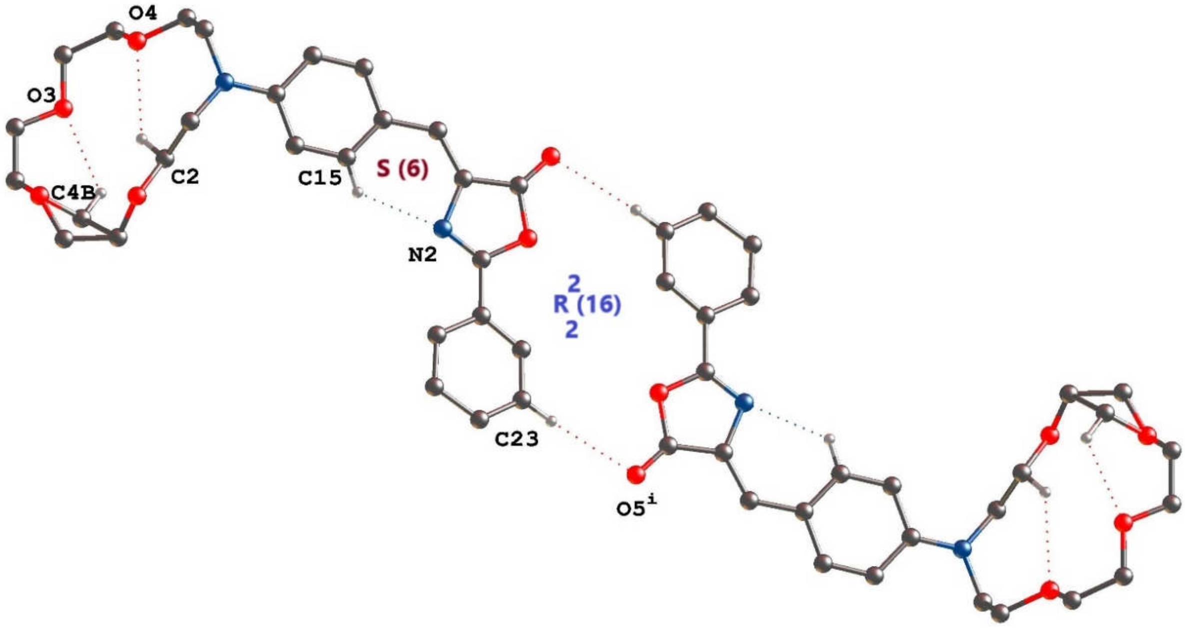

Figure 2. Centrosymmetric hydrogen-bonded dimer structure by intermolecular C-H···O hydrogen bonds around an inversion centre, and intramolecular C-H···O and C-H···N interactions. Dashed lines showed intra- and intermolecular hydrogen bonds. Hydrogen atoms not involved in the bonding, are omitted for clarity.

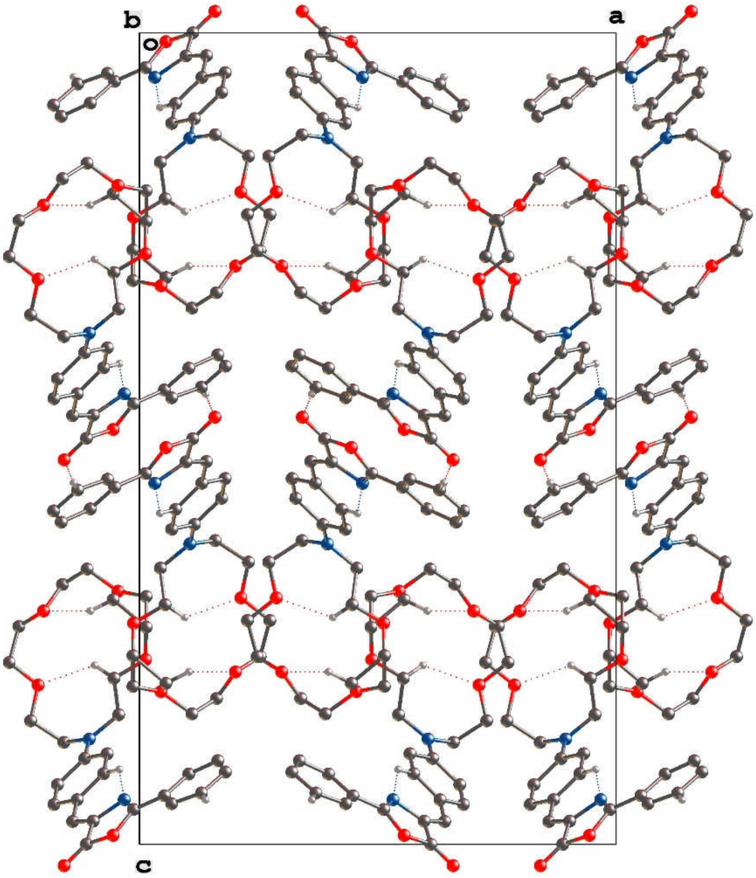

Figure 3. Part of the packing view of the title compound along the *b* axis.

2.2 DFT studies

Figure 4 shows the optimized structure of the title compound. The optimized structure parameters such as bond lengths, bond angles and torsion angles are calculated by B3LYP/6-311G(d,p), compared with those of the experimental data and are presented in Table 3. Local minimum energy was found approximately -42722.75 eV after the geometry optimization. The dipole moment is equal to 7.8822 Debye. Comparing with the experimental data, some optimized parameters are different, attributed to the fact that the theoretical calculations are performed for an isolated molecule in gaseous phase, whereas experimental results are of the molecules in solid state. The biggest difference between the experimental and calculated bond lengths is 0.072 Å at O2-C4B.

Table 3. Interatomic distances (Å), bond angles and torsion angles (°) for the title compound as observed experimentally and as calculated using DFT/B3LYP/6-311G(d,p) method.

Atoms	**Exp.**	**Calc.**	**Atoms**	**Exp.**	**Calc.**
N1-C1	1.433(7)	1.4618	N1-C10	1.454(7)	1.4595
N1-C11	1.370(6)	1.3791	O1-C2	1.373(7)	1.4263
O1-C3	1.420(8)	1.4164	O2-C4A	1.367(2)	1.4215
O2-C4B	1.350(2)	1.4215	O2-C5	1.430(2)	1.4181
O3-C6	1.374(2)	1.4201	O3-C7	1.361(2)	1.4224
O4-C8	1.370(2)	1.4199	O4-C9	1.399(8)	1.4144
N2-C18	1.438(8)	1.3957	N2-C20	1.259(8)	1.2914
O5-C19	1.174(9)	1.1964	O6-C19	1.382(8)	1.4133
O6-C20	1.363(7)	1.3731			
O5-C19-O6	123.6(6)	122.095	O5-C19-C18	132.4(6)	134.095
O6-C20-C21	117.6(5)	117.099	C1-N1-C11	121.2(4)	117.679
N2-C18-C17	128.4(5)	129.158	N2-C20-C21	125.6(6)	127.105
C10-N1-C11	120.5(4)	121.014	C13-C14-C17	119.3(5)	119.132
C14-C17-C18	127.3(5)	130.264	C15-C14-C17	124.7(5)	124.226
N2-C20-C21-C26	-10.6(10)	-0.622	O6-C20-C21-C22	-8.0(9)	-0.656
N2-C18-C17-C14	-1.3(10)	-0.185	C18-C17-C14-C15	-1.5(9)	-1.108
C18-C17-C14-C13	178.6(5)	179.269	C12-C11-N1-C1	-175.1(5)	178.892
C12-C11-N1-C10	5.6(8)	-5.980	C16-C11-N1-C10	-175.4(5)	173.520
C11-C1-N1-C2	-80.7(6)	-79.787	C11-N1-C10-C9	81.5(6)	87.373

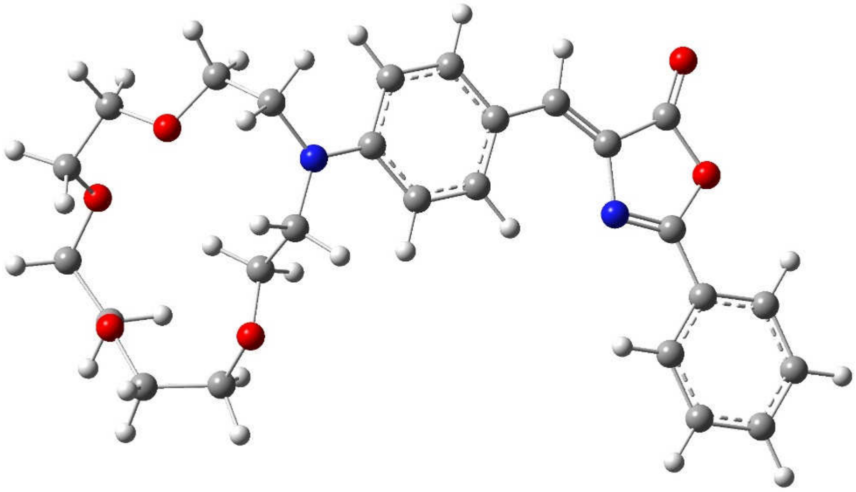

Figure 4. Optimized geometry for the B3LYP/6-311G(d,p) of the title molecule.

2.3 Frontier molecular orbitals and molecular electrostatic potential

FMO analysis is important in providing information about the electronic properties and molecular reactivity of a compound. HOMO orbitals (Highest occupied molecular orbital) act as electron donors, and LUMO (lowest unoccupied molecular orbital) orbitals are largely act as electron acceptors. In many works, the energy gap between HOMO and LUMO reflects mostly chemical reactivity of the molecule [31-33]. Frontier molecular orbital (FMO) analysis was performed at the same level of theory. In the HOMO, electrons are mainly located on the N-phenyl and oxazol-5-one fragments, whereas LUMO is distributed on the whole molecule except the crown ether moiety (Fig. 5a). The HOMO energy level is calculated at -5.25 eV, and the LUMO is calculated at -2.25 eV. The energy gaps of HOMO and LUMO could be determined about 3.00 eV which indicates the molecule becomes less stability and more reactivity.

The molecular electrostatic potential of the title compound has also been calculated. The MEP is related to the electronic density and is a very useful descriptor to have a knowledge for electrophilic attack and nucleophilic reactions [34,35]. To predict reactive sites for electrophilic attack, the electrostatic potential surface maps have been plotted for the title compounds with B3LYP/6-311G(d,p) level. In the MEP profile, the areas with major positive potential are specified by blue color, which demonstrates the strongest attraction, whereas the maximum negative potential sections have been presented red color, indicates the repulsion. As can be seen in Fig. 5b, the negative potential regions are over the electronegative O atom of the oxazole-5-one, which is responsible for the intermolecular hydrogen bonding, and the regions having the positive potential are over the part of the N-phenyl-(aza-15-crown-5) moiety. The yellow color proves the intramolecular C-H···O and C-H···N interactions.

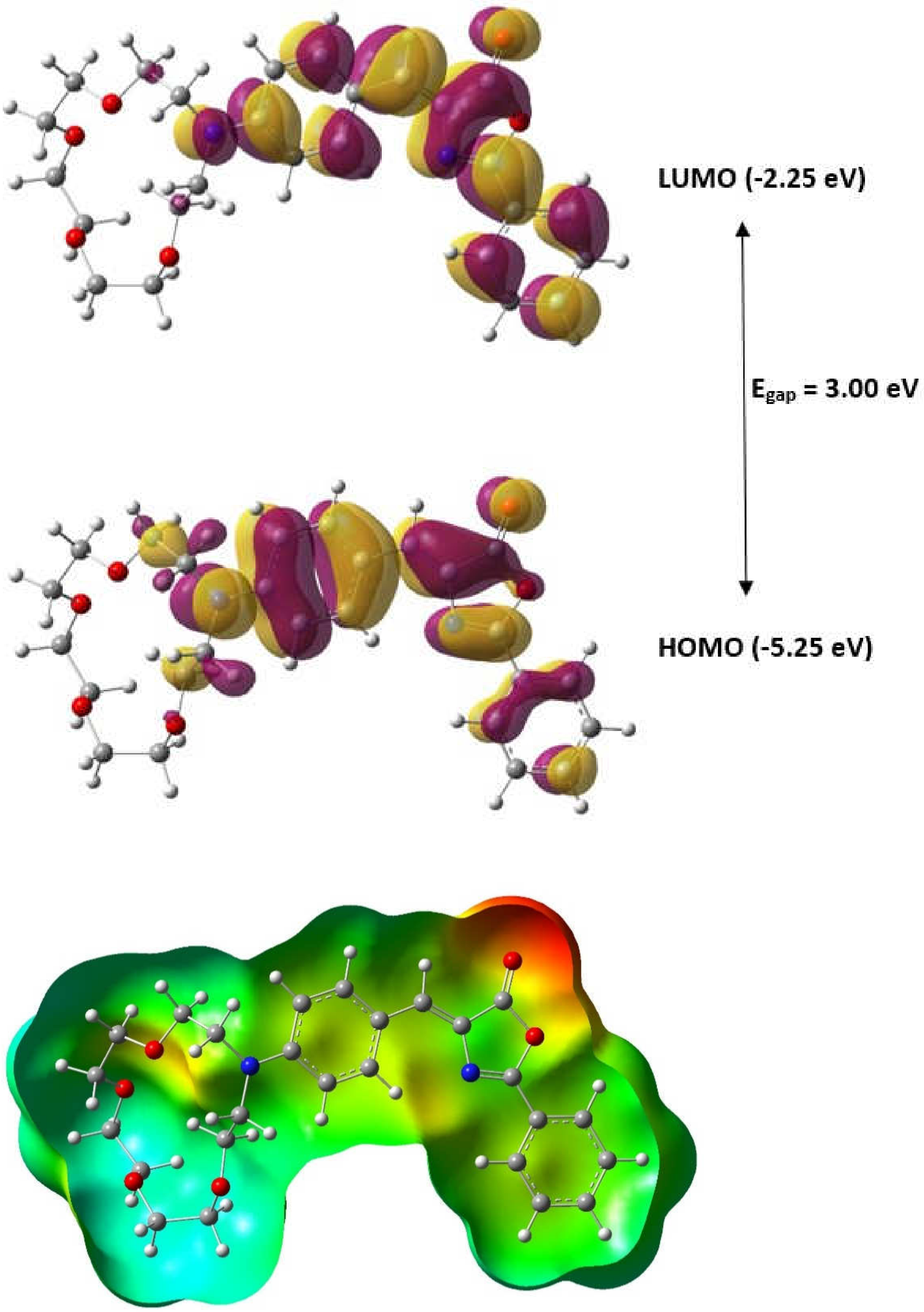

Figure 5. (a) Molecular orbital surfaces and energy levels for the HOMO and LUMO of the studied molecule at B3LYP/6-311G(d,p) (b) Molecular electrostatic potential surface (MEP) of the title compound.

3. Conclusion

Herein, the structural characterization of the 2-phenyl-4-[4-(1,4,7,10-tetraoxa-13-azacyclopentadecyl)benzylidene]-5-oxazolone compound was carried on with single crystal X-ray diffraction study. Structural study shows that the molecule consists of an oxazol-5-one ring connected to the N-phenyl-(aza-15-crown-5) moiety and a phenyl ring linked to the oxazol-5-one fragment. The crown ether is found to be tilted relative to the plane containing N-phenyl, oxazol-5-one and phenyl moieties. Crystal structure of the compound is stabilized by intermolecular C-H···Ohydrogen bond, resulting in a $R_2^2(16)$ ring motif and three intramolecular interactions. Geometry of the molecule was optimized using DFT/B3LYP/6-311G(d,p), and the calculated values were compared with the experimental data. In general, the structural parameters match well with the experimental one, with few exceptions caused due to the constraints imposed by isolated molecule model. The HOMO-LUMO patterns and molecular electrostatic potential surface analyses was also performed for the title molecule and the hydrogen bonds and other interactions were consistent with those of the experimental results.

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Supplementary

CCDC 1832558 contains the supplementary crystallographic data for the compound. Copies of the data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK. fax: (+44) 1223-336-033, email: deposit@ccdc.cam.ac.uk.

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