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Molecular structure, vibrational, electronic, NBO and NLO analyses of 2, 6diphenyl-4H-pyran-4-one by DFT calculations

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ABSTRACT

The optimized molecular geometry, normal mode wavenumbers, infrared intensities, corresponding vibrational assignments and atomic charges were investigated with the help of DFT/B3LYP method using 6-311++ G(d,p) basis set. The FT-IR spectrum of 2, 6-diphenyl-4H-pyran-4-one (DPO) has been recorded in the region 4000-400 cm⁻¹. For the comparison between calculated and experimental results, assignments of fundamental modes were examined. The stability and charge delocalization of the molecule were studied by natural bond orbital (NBO) analysis. In addition, a molecular electrostatic potential map (MEP) of the title compound was studied to predict the reactive sites. The reactivity of the compound of interest was described by HOMO - LUMO energies and global descriptors. The electronic properties were also studied and the transition corresponds to $\pi \rightarrow \pi^*$. The title compound exhibited good nonlinear optical activity and ten times greater than that of urea.

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Introduction

The pyran series of compounds are useful as fungicides, herbicides and in the treatment of hypersensitivity conditions, such as asthma and allergies [1-2]. These compounds and its derivatives have been the subject of intensive research because of their importance in various applications and their widespread biological significance. Presence of 4H-pyran derivatives in organic molecules imparts them with the extensive range of biological and pharmacological properties, such as spamolytic, diuretic, anti-coagulant, anti-cancer and anti-anaphylactic activities. They are also helpful for the treatment of neurodegenerative disorders, including Alzheimer's disease, amyotropic lateral sclerosis, Huntington's disease and Parkinson's disease [3]. Moreover, these compounds are also useful as photoactive materials [4] and occur in various natural products [5] such as avermectines, aplysiatoxins, oscillatoxins, latrunculins, talaromycins and acutiphycins and are also a part of the backbone of several important carbohydrates, polyether antibiotics and marine macrolides [6]. Therefore, it is important to analyze the characterization of the title compound for future studies. Moreover, researchers are interested in theoretical to support the experimental evidences studies since computational methods are reliable to characterize the molecule because of their efficiency and accuracy with regard to the evaluation of a number of molecular properties [7]. A suitable quantum chemical study is helpful to predict compound properties economically and to clarify some experiment phenomena insightfully [8]. Therefore, theoretical studies are either reliable or useful to identify the compound. In this respect, the computational researches on the compound properties tend to increase [9].

In this study, the vibrational wavenumbers were calculated using B3LYP with 6-311++ G (d, p) basis set and compared with the experimental data. It was found that the computations are in good agreement with experimental values. Furthermore, the optimized molecular structure, atomic charges were also investigated to provide the information about dipole moment resulting from non-uniform distribution of charges on the various atoms in the structures. In addition, electronic, natural bond orbital (NBO), molecular electrostatic potential (MEP) and reactivity analyses were explained. The aim of this study is to clarify the characterization and show the way to future researches and applications in physics, chemistry, biology and industry of this molecule.

Experimental Details

The compound under investigation namely 2, 6- diphenyl-4H- pyran- 4-one (DPO) was purchased from Sigma Aldrich Chemical Company, USA and used for the spectral measurements as such without any further purification. The FT-IR spectrum of the title compound was recorded in the region 4000-400cm⁻¹ using KBr pellet on BRUKER IFS 66V model instrument.

Computational Details

The molecular structure optimization of the title compound and corresponding vibrational harmonic wavenumbers were calculated using B3LYP exchange correlation functional [10, 11] which consist of the Lee-Yang-Parr correlation functional in conjunction with a hybrid exchange functional first proposed by Becke. Gaussian 03 program package was used without any constraint on the geometry with the triple split valence basis set along with the diffuse and polarization functions; 6-311++ G (d, p). Furthermore, IR intensity, atomic charges, non linear optical parameters were calculated using the Gaussian 03 package [12]. By combining the results of the GAUSSVIEW [13] program with symmetry considerations, vibrational assignments were made with a high degree of accuracy and the vibrations match quite well with the motions observed. The observed slight disagreement between theory and experiment could be the consequence of the anharmonicity and the general tendency of the quantum mechanical methods to overestimate the force constants at the exact equilibrium geometry. Therefore, in order to improve the calculated values in agreement with the experimental ones, it is necessary to scale down the calculated harmonic wavenumbers. The theoretical harmonic wavenumbers are scaled by 0.962 at B3LYP/6-311++ G (d, p) level as predicted in the earlier references [14]. To investigate the reactive sites of the title compound, the molecular electrostatic potentials for the 0.002 a.u. isosurfaces of electron density was evaluated using the B3LYP/6-311 ++ G (d,p)method.

The natural bonding orbital (NBO) calculations [15] were performed using NBO 3.1 program as implemented in the Gaussian 03W package at the DFT/B3LYP level. The second order Fock matrix was carried out to evaluate the donor–acceptor interactions in the NBO basis [16]. For each donor (i) and acceptor (j), the stabilization energy E(2) associated with the delocalization $i \rightarrow j$ is estimated as

The electronic properties of the molecules are calculated from the total energies (TE) and the Koopmans' theorem (KE). The ionization potential is determined from the energy difference between the energy of the compound derived from electron-transfer (radical cation) and the respective neutral compound; $IP_{TE} = E_{cation} - E_n$; $IP_{KE} = -E_{HOMO}$ while the electron affinity is computed from the energy difference between the neutral molecule and the anion molecule: $EA_{TE} = E_n - E_{anion}$; $EA_{KE} = -E_{LUMO}$ respectively. The other important quantities such as electronegativity (χ), hardness (η), softness (ζ), and electrophilicity index (ψ) were deduced from ionization potential and electron affinity values [17–19]. Electronegativity (χ): --- (2)

$$\mu \approx -\chi = -\frac{IP + EA}{2} \qquad (2)$$

Chemical hardness $(\eta) \approx \frac{IP - EA}{2}$ (3)

Softness
$$(\zeta) = \frac{1}{2\eta}$$
 (4)

Electrophilicity index $(\psi) = \frac{\mu^2}{2\eta}$ (5) Results And Discussion Molecular geometry



Fig. 1- The optimized molecular structure of 2,6-diphenyl-4H-pyran-4-one

The molecular structure along with numbering of atoms of DPO is obtained from Gaussian 03 and GAUSSVIEW programs and is as shown in Figure 1. The title molecule belongs to C_1 point group symmetry. The optimized structural parameters

calculated by DFT/B3LYP with 6-311++ G (d, p) basis set are represented in Table 1 and compared with the crystallographic data [20, 21]. Most of the optimized bond lengths and bond angles are slightly greater than the experimental values, due to the fact that the theoretical calculations belong to the isolated molecule in the gas phase.

The C-C bonds in DPO are not of the same length in accordance with the valence band model of bonding. So, in line with the above said theory, the bonds C2-C3, C4-C5, C2-C14 are about 1.35 Å, 1.46 Å, 1.47 Å respectively and C8-C9, C8-C13, C14-C15, C14-C19 are about 1.40 Å, whereas other C-C bonds are about ≈ 1.39 Å. The experimental value of C=O bond length 1.213 Å was reported earlier[22]. In the title compound the bond length of C4=O7 is 1.226 Å using DFT method. This increasing bond length is due to the inductive effect of the carbonyl group with pyran ring. The order of the optimized bond length of heterocyclic ring of DPO as C2- C3 =C5-C6 < O1-C2 = O1-C6 < C3-C4 = C4 - C5. The bond length of O1-C2 and O1-C6 are reduced in size compare with C3-C4 and C4 - C5 because of symmetrical substitution of phenyl groups in heterocyclic ring. The bond lengths of C2-C14, C6- C8 are about 1.474 Å, this increasing bond lengths is also the substitution of phenyl groups in heterocyclic ring. The bond angle C9-C8-C13 ≈118.8 is less when comparing other bond angles C8-C9-C10, C9-C10-C11, C10-C11-C12, C11-C12-C13, C8-C13-C12 (\approx 120°). It may be due to the phenyl ring is attached at the position C6 of pyran ring. Similar trend has been observed in the second phenyl ring.

Vibrational assignments

The maximum number of potentially active observable fundamentals of a non-linear molecule, which contains N atoms, is equal to (3N - 6) vibrations [23, 24]. Hence, the DPO molecule has 31 atoms with 87 normal modes of vibrations and considered under C₁ point group symmetry. The experimental and theoretical FT-IR spectra of DPO are shown in figure 2. The observed and calculated vibrational wavenumbers along with their relative intensities and proposed assignments are presented in Table 2.



Figure 2: Comparision of the experimental and calculated FT -IR spectra of DPO

C-H vibrations

The aromatic C-H stretching vibrations give rise to multiple bands in the region 3100-3000 cm⁻¹ [25, 26]. Earlier researchers [27, 28] have reported IR bands occurring in the range 3100-2900 cm⁻¹ is due to C-H stretching in their study on six membered heterocyclic molecules. In this case, the C-H stretching vibration in FT-IR spectrum observed at 3055cm^{-1} . In substituted benzene ring compounds the C-H out of plane bending vibrations give rise to bands in the region $1000-700 \text{ cm}^{-1}$ [22]. The C-H in plane bending is found in the region $1600-1000 \text{ cm}^{-1}$ [29]. In disubstituted DPO gives the strong peaks at 1388 cm^{-1} , medium peaks at 1492, 1448, 1293, 1237, 1182, 1077 cm^{-1} and weak band at 1021 cm^{-1} in FT-IR which exhibits the DPO has the C-H in plane bending in above wavenumbers. The DPO shows that the C-H out of plane bending strongly at 768 and 680 cm⁻¹ and medium bands at 940, 896, 850 cm⁻¹ and 573 cm⁻¹ is weak band which agrees well in the literature values [30].

C=O Vibrations

The C=O absorption occurs in the range of 1680-1630 cm⁻¹. The stretching vibration of wavenumber of a carbonyl group decrease with increasing number of alkyl groups attached to it. This is due to +I effect of alkyl groups and lengthens the C=O double bond [22]. We have assigned the bond occurring at 1649 cm⁻¹ in IR spectrum to carbonyl stretching vibrations of the title compound.

C-C and ring vibrations

The bands between 1400 and 1650 cm⁻¹ in aromatic and heteroaromatic compounds are assigned to C-C stretching vibrations [31-33]. Therefore, the FT-IR band found at 1492 cm⁻¹ has been assigned to C-C stretching vibrations [34]. Also, the ring modes are affected by the substitutions in the heterocyclic ring of the title compound. Accordingly in the present study, the band observed at 1388 cm⁻¹ in FT-IR spectrum has been designated to ring in plane bending modes. The out of plane bending mode is observed at 457 cm⁻¹ in FT-IR spectrum. The ring stretching vibrations of the title compound are observed at 634 cm⁻¹ in IR spectrum.

Atomic Charges

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. The Mulliken and NPA atomic charges of DPO were calculated by DFT/B3LYP method using 6-311++ G (d, p) basis set are illustrated in Table 3. The magnitudes of the atomic charges of carbon for the compound were found to be both positive and negative. The atomic charges of oxygen for the compound were computed to be negative. So, the carbon atoms connected to oxygen atoms appear as positive. These results also support intramolecular charge transfer (ICT) taking place within molecule [35]. Additionally, the atomic charges of hydrogen atoms were noted to be only positive values, indicating the charge transfer from hydrogen to carbon atom because of all hydrogen atoms in the molecules lost electrons.

Molecular electrostatic potential

In the present study, 3D plots of molecular electrostatic potential (MEP) of DPO are illustrated in Figure 3. The MEP which is a plot of electrostatic potential mapped onto the constant electron density surface. The MEP is a useful property to study reactivity given that an approaching electrophile will be attracted to negative regions (where the electron distribution effect is dominant). In the majority of the MEPs, while the maximum negative region which preferred site for electrophilic attack indications as red colour, the maximum positive region which preferred site for nucleophilic attack as blue colour. The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of colour grading (Figure 3) and is very useful in research of molecular structure with its physiochemical property relationship [36-38]. The

resulting surface simultaneously displays molecular size and shape and electrostatic potential value. The different values of the electrostatic potential at the surface are represented by different colours. Potential increases in the order red < orange < vellow < green < blue. The colour code of these maps is in the range between -0.0647 a.u. (deepest red) to +0.0647 a.u. (deepest blue) in compound, where blue indicates the strongest attraction and red indicates the strongest repulsion regions of negative V(r) are usually associated with the lone pair of electronegative atoms. As can be seen from the MEP map of the title molecule, while regions having the negative potential are over the electronegative atom (Oxygen atoms), the regions having the positive potential are over the hydrogen atoms. The predominance of green region in the MEP surfaces corresponds to a potential halfway between the two extremes red and dark blue colour.



Figure 3: Molecular electrostatic potential (MEP) of 2, 6diphenyl -4H - pyran 4-one

NBO analysis

Natural bond orbital analysis provides an efficient method for studying intra- and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems [39]. The larger the E(2) value, the more intensive is the interaction between electron donors and electron acceptors, i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the title molecule (DPO) at the B3LYP/6-311++G (d, p) level in order to elucidate the delocalization of electron density within the molecule. The intramolecular interaction are formed by the orbital overlap between bonding n (LP₂O₆), n (LP₂O₇) and antibond π^* (C₂- C₃) orbital which results in intramolecular charge transfer (ICT) causing stabilization of the system. The second-order perturbation theory of Fock matrix in the NBO analysis shows strong intramolecular hyperconjugative interactions, and the results are presented in Table 4. The most important interaction energies of n (LP₂O₆) $\rightarrow \pi$ * (C₂- C₃) and n (LP₂O₇) $\rightarrow \pi$ *(C₂-C₃) are 127.61 and 94.14 kJ/mol, respectively. This larger energy provides the stabilization to the molecular structure and will also enhances the bioactivity of the molecule (DPO).

Electronic properties

Electronic absorption wavelength calculated by the TD (DFT)/B3LYP/ 6-311++ G(d,p) level and the excitation energy, oscillator strength and composition of the most significant singlet states are listed in Table 5.

Tuble II op	perimized and experimental geometrical parameters i				
Parameters	B3LYP/ 6-311G++(d.p)	Exp. [18,19]	Parameters	B3LYP/ 6-311G++(d.p)	Exp.[18,19]
Bond lengths(Å)	0 0 1 1 0 1 1 (u,p)		Bond Angels(°)	(u,p)	
01 - C2	1.368	1.355	01 - C2 - C3	121.1	121.9
01 - C6	1.368	1.376	$C_3 - C_2 - C_{14}$	126.6	127.7
C2 –C3	1.351	1.356	01 - C2 - C14	112.2	-
C2 - C14	1.474	1.467	$C_2 - C_3 - C_4$	121.9	118.4
C3 – C4	1.463	1.417	$C_2 - C_3 - H_{20}$	120.5	-
C3 – H20	1.082	-	C4 - C3 - H20	117.5	-
C4 – C5	1.463	1.382	C3 –C4 –C5	113.3	119.7
C4 – O7	1.226	1.213	C3 –C4 –O7	123.3	122.3
C5 – C6	1.351	1.374	C5 –C4 –O7	123.3	124.1
C5-H21	1.082	-	C4 – C5 – C6	121.9	120.5
C6 – C8	1.474	1.439	C4 – C5 – H21	117.5	-
C8 – C9	1.402	1.378	C6 – C5 – H21	120.5	-
C8-C13	1.403	1.374	O1 C6 C5	121.1	-
C9-C10	1.390	1.349	C5 –C6 –C8	126.6	129.6
C9-H22	1.084	-	O1 C6 C8	112.2	-
C10-C11	1.394	1.368	C2 O1 C6	120.5	118.8
C10-H23	1.085	-	C6 – C8 – C9	120.6	122.3
C11 –C12	1.393	1.379	C6-C8-C13	120.5	118.9
C11-H24	1.085	-	C9-C8-C13	118.8	118.8
C12-C13	1.391	1.379	C8-C9-C10	120.5	119.4
C12 – H25	1.085	-	C8 – C9 – H22	119.9	-
C13-H26	1.083	-	C10-C9-H22	119.5	-
C14 –C15	1.403	1.370	C9-C10-C11	120.2	122.1
C14-C19	1.402	1.404	C9-C10-H23	119.6	-
C15-C16	1.391	1.381	C11-C10-H23	120.1	-
C15-H27	1.083	-	C10-C11-C12	119.6	118.7
C16-C17	1.393	1.380	C10-C11-H24	120.1	-
C16-H28	1.085	-	C12-C11-H24	120.1	-
C17 –C18	1.394	1.364	C11 -C12 -C13	120.3	120.6
C17 –H29	1.085	-	C11 -C12 -H25	120.0	-
C18-C19	1.390	1.379	C13-C12-H25	119.6	-
C18-H31	1.085	-	C8 C13 C12	120.4	120.3
C19-H31	1.084	-	C8-C13-H26	119.5	-
			C12-C13-H26	120.0	-
			C2 C14 C15	120.5	121.0
			C2 C14 C19	120.6	119.7
			C15-C14-C19	118.8	119.3
			C14-C15-C16	120.4	120.3
			C14 C15 H27	119.5	-
			C16-C15-H27	120.0	-
			C15-C16-C17	120.3	120.5
			C15-C16-H28	119.6	-
			C17 C16 H28	120.0	-
			C16-C17-C18	119.6	119.4
			С16-С17-Н29	120.1	-
			С18 –С17 –Н29	120.1	-
			C17C18C19	120.2	121.2
			С17 –С18 –Н30	120.1	-
			C19 -C18 -H30	119.6	-
			C14 –C19 –C18	120.5	119.3
			C14C19H31	119.9	-
	1		C18 –C19 –H31	119.5	-

Table 1. Optimized and experimental geometrical parameters for DPO in the ground state

Table 2. Comparision of the experimental and calculated vibrational wavenumbers (cm⁻¹) of DPO

Modes	Б	B3LYP/6-311G++(d,p)		Vibrational Assignments
	Exp.	Scaled (cm ⁻¹)	I_{IR} (km mol ⁻¹)	
1	-	3114	0.35	v _{CH}
2	-	3113	6.62	v _{CH}
3	-	3102	8.47	ν _{CH}
4	-	3100	2.82	v _{CH}
5	-	3091	0.39	v _{CH}
6	-	3090	36.19	ν _{CH}
7	-	3083	35.59	v _{CH}
8	-	3082	22.24	v _{CH}

_				
9	-	3072	8.41	$\nu_{\rm CH}$
10	-	3071	12.46	V CH
11		20(2	0.42	V CH
11	-	3062	0.43	ν_{CH}
12	3055m	3061	0.27	V CH
12	1640c	1667	649.12	· ch
15	10498	1007	040.15	$\nu CO + \delta CCC + \delta CCH$
14	-	1620	20.13	$v_{CC+\delta CCH}$
15	_	1597	1 15	V cousory
15		1507	1.15	V CC+oCCH
16	-	1596	0.99	$\nu_{CC+\delta CCH}$
17	-	1578	20.65	HCC SCCH
10		15(0	11 70	VCC+OCCH
18	-	1308	11./8	νCC+δCCH
19	-	1562	32.70	νCC+δCCH
20	1492m	1484	10.85	
20	1472111	1404	10.05	vCC +8CCH
21	-	1481	18.25	δCCH
22	1448m	1437	1.67	SCCU
22	1.1.0111	1426	45.00	оссн
25	-	1450	43.22	δCCH
24	1388s	1339	408.03	$\delta CCC + \delta CCH$
25	_	1324	0.17	0000 V 00011
25	_	1324	0.17	бССН
26	-	1318	17.21	δCCH
27	-	1316	2.46	SCOU
20	1202	1002	20.74	оссн
28	1295m	1285	39.74	δCCH
29	-	1274	1082	åCCH
30	1237m	1236	7 81	been
50	123/111	1250	/.04	δCCH
31	-	1214	14.03	δССН
32	_	1206	0.38	2007
32	1102	1200	1.47	дссн
33	1182m	11/4	1.47	δCCH
34	_	1170	10.41	2001
25		1151	0.01	OCCH
35	-	1151	0.01	δCCH
36	-	1150	0.47	åCCH
27	1077m	1075	8 12	ocen
57	1077111	1075	0.42	δCCH
38	-	1073	6.65	δCCH
30		1052	10.58	
57	1001	1032	17.56	бССН
40	1021w	1024	0.14	δCCH
41	-	1017	15.87	SOCI
10		1017	10.07	OCCH
42	-	1000	12.75	δCCH
43	-	985	0.09	Vcc
4.4		094	1.04	
44	-	984	1.04	V _{CC}
45	-	965	0.28	Уссен
46		964	0.36	/
40		704	0.50	/CCCH
47	940m	941	0.59	Усссн
48	-	939	0.99	Veccu
40		005	0.77	ЛСССН
49	-	925	31.84	$\delta CCO + \delta CCH+, \gamma CCCH$
50	-	903	10.73	SCCIL VCCCII
51	906m	002	2.07	occh+/ccch
51	890m	902	2.87	$\delta CCH + \gamma CCCH$
52	-	877	16.53	$\gamma_{\rm CCCH} + \tau_{\rm CCCH}$
52	850m	962	19 19	Vecchi Vecchi
55	05011	805	40.40	/ CCCH
54	-	845	0.04	үсссн
55	-	824	0.11	Veccu
50		021	1.71	ЛСССН
56	-	823	1./1	үсссн
57	-	818	0.18	$\delta CCH + VCC$
58	768.	761	52.02	
50	1008	701	52.02	/ CCCH
59	-	755	9.67	үсссн
60	-	706	0.01	VCCCH
<i>E</i> 1		201	5 50	/tttn
01	-	004	5.59	үсссн
62	680s	682	87.66	үсссн
63	_	659	3 04	
0.5		657	5.07	occh +occc
64	634W	634	16.88	$\gamma_{CCCH +} \nu_{CC}$
65	-	628	1.35	VCCCH VCC
66		621	0 20	, , , , , , , , , , , , , , , , , , , ,
00	-	021	0.39	үсссн
67	-	614	0.68	үсссн
68	_	613	0.01	Vacan
60			0.01	/ CCCH
69	5/3W	562	3.83	$\gamma_{CCCH} + \tau_{CCCH}$
70	-	502	0.86	SCCH V CC
71		450	0.00	
/1	-	439	0.01	YCCCH+YCCCC
72	457w	456	10.85	$\gamma_{\rm CCCH} + \tau_{\rm CCCH}$
73	_	401	0.03	V
	-	401	0.05	ľсссн
74	-	400	0.50	үсссн
75	_	390	5 54	VCCCILLSCCOLSCCIL
75		246	0.46	ACCCH + OCCO+OCCH
/6	-	546	0.46	$\delta CCH + \tau_{CCCH}$
77	-	273	1.65	800H +8000
70		266	0.10	
/ð	-	200	0.18	δCCH
79	-	230	0.72	үсссн

80 81 82 83	- - -	219 159 141	0.01 4.82 1.68 0.09	Υсссн Υсссн + V сс δссн +δссо
84 85	-	70 63	0.11 0.18	үсссн үсссо + үсссн әссн
86 87	-	40 36	0.01 0.27	үсссн үсссн

w-weak; m- medium; s- strong; v-stretching; δ - in plane bending; γ -out of plane bending; τ - torsion.

Table 3. Atomic charges for optimized geometry of DPO

	B3LYP/6-31	1G++(d,p)	Atom	B3LYP/6-311G++(d,p)		
Atom	Mulliken's charges	Natural charges		Mulliken's charges	Natural charges	
01	-0.328	-0.475	H20	0.217	0.254	
C2	0.250	0.360	H21	0.214	0.254	
C3	-0.347	-0.350	H22	0.216	0.240	
C4	0.334	0.477	H23	0.204	0.239	
C5	-0.348	-0.350	H24	0.199	0.237	
C6	0.253	0.360	H25	0.196	0.238	
O7	-0.353	-0.575	H26	0.211	0.246	
C8	-0.056	-0.098	H27	0.218	0.246	
C9	-0.185	-0.204	H28	0.203	0.238	
C10	-0.198	-0.226	H29	0.200	0.237	
C11	-0.177	-0.221	H30	0.197	0.239	
C12	-0.196	-0.226	H31	0.207	0.240	
C13	-0.161	-0.205				
C14	-0.054	-0.098				
C15	-0.160	-0.205				
C16	-0.196	-0.226				
C17	-0.177	-0.221				
C18	-0.190	-0.226				
C19	-0.185	-0.204				

Table 4. Second order perturbation theory analysis of Fo	ock matrix in NBO basis.
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Donor (i)		Accorton (i)	ED(a)	E(2) ^a	$E(j)-E(i)^{b}$	F (i , j) ^c
Donor (I)	ED(e)	Acceptor (j)	ED(e)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(kJ mol ⁻¹)
$\sigma (C_2 - C_{14})$	1.9706	$\sigma^{*} (C_{3} - C_{4})$	0.0637	10.42	3019.33	126.02
$\sigma (C_2 - C_{14})$	1.9706	σ^* (C ₁₅ – C ₁₆)	0.0154	8.45	3308.13	118.15
$\sigma (C_4 - C_5)$	1.9711	$\sigma^* (C_6 - C_8)$	0.0350	21.46	2914.31	178.53
$\pi (C_4 - O_7)$	1.9678	π^* (C ₅ – C ₆)	0.1909	23.93	1023.95	115.52
$\pi (C_5 - C_6)$	1.8340	$\sigma^{*} (C_{6} - C_{8})$	0.0350	17.20	3203.11	168.03
$\pi (C_5 - C_6)$	1.8340	$\pi^* (C_4 - O_7)$	0.2705	82.13	866.42	194.29
$\sigma (C_6 - O_1)$	1.9881	$\sigma^* (C_2 - C_{14})$	0.0350	8.16	3675.70	123.4
$\sigma (C_6 - C_8)$	1.9706	$\sigma^* (C_2 - O_6)$	0.0350	13.72	2730.52	136.53
$\pi (C_8 - C_{13})$	1.6402	π^* (C ₅ – C ₆)	0.1909	51.38	761.4	147.03
$\pi (C_8 - C_{13})$	1.6402	π^* (C ₉ – C ₁₀)	0.3137	84.98	761.4	181.16
$\pi (C_8 - C_{13})$	1.6402	π^* (C ₁₁ – C ₁₂)	0.3269	83.09	761.4	178.53
$\pi (C_9 - C_{10})$	1.6654	π^* (C ₁₁ – C ₁₂)	0.3269	86.53	761.4	181.16
$\pi (C_{11} - C_{12})$	1.6504	π^* (C ₉ – C ₁₀)	0.3137	84.06	761.4	178.53
$\pi (C_{14} - C_{15})$	1.6402	π^* (C ₂ – C ₃)	0.1909	51.34	761.4	147.03
$\pi (C_{14} - C_{15})$	1.6402	π^* (C ₁₈ – C ₁₉)	0.3137	84.98	761.4	181.16
$\pi (C_{16} - C_{17})$	1.6504	π^* (C ₁₄ – C ₁₅)	0.3731	90.12	761.4	183.79
$\pi (C_{18} - C_{19})$	1.6654	π^* (C ₁₆ – C ₁₇)	0.3269	86.53	761.4	181.16
$n (LP_1O_6)$	1.9591	$\sigma^* (C_2 - C_{14})$	0.0350	5.15	2625.5	84.02
$n (LP_2O_6)$	1.7402	π^* (C ₂ – C ₃)	0.1909	127.61	1023.95	259.93
$n (LP_2O_7)$	1.8824	π^* (C ₂ – C ₃)	0.1909	94.14	1864.11	299.31

^a E(2) means energy of hyperconjugative interactions; cf. Eq. (1). ^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.

	excited states for DrO at the BSL 11/0-511++G(d,p) level of theory							
		TD/DFT method			Symmetry	MOs		
	Transition	λ (nm)	Excitation	Oscillating				
			energy,E (eV)	strength, f				
ĺ	Ι	299	4.14	0.0034	А	$79\%(H-2\rightarrow L)+4\%(H-2\rightarrow L+5)+11\%(H-1\rightarrow L)$		
	П	284	4.36	0.4800	А	93%(H→L)		
	III	267	4.61	0.0567	А	8%(H-2→L) +56%(H-1→L) +30%(H→L+1)		

Table 5. Wavelength λ (nm), excitation energies (eV), oscillator strength (f) and composition of the most significant singlet excited states for DPO at the B3LYP/6-311++G(d,p) level of theory

Table 6. The calculated energy values of DPO in their ground state at B3LYP/6-311G++ (d, p) level of theory

Quantity	Value (a.u)
E _{HOMO}	-0.228
E _{LUMO}	-0.050
$ \Delta E_{HOMO-LUMO} $	0.178
Electronegativity (χ)	0.139
Chemical hardness (η)	0.089
Softness (ζ)	5.618
Electrophilicity index (ψ)	0.1086

Table 7. The first hyperpolarizability β_{ijk} and β_{tot} (x10⁻³¹ cm⁵/esu) values for DPO

Parameters	Values
β _{xxx}	3.308
β_{xxy}	0.353
β_{xxz}	-0.189
β_{vvv}	-0.177
β_{yyz}	28.457
β_{yyx}	0.266
β_{xyz}	-5.079
β_{xzz}	-3.065
β_{zzz}	-0.160
β_{yzz}	21.991
β_{tot}	35.583

Table 8. Theoretically computed energies (a.u.), zero-point vibrational energy (kcal mol⁻¹), rotational constants (GHz), entropies (cal mol⁻¹ K⁻¹), heat capacities (cal mol⁻¹ K⁻¹), thermal energies (kcal mol⁻¹) and dipole moment (Debye) of DPO

Parameters	Values
Total energy	-805.47518929
Zero-point vibrational energy	152.387
-	0.588
Rotational constants	0.236.
	0.172
Entropy	123.599
Heat capacity	57.939
Thermal energy	161.515
Dipole moment	5.234

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. HOMO, which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand, LUMO can be thought the innermost orbital containing free places to accept electrons [37]. Owing to the interaction between HOMO and LUMO orbital of a structure, transition of $\pi - \pi^*$ type is observed with regard to the molecular orbital theory [40]. Therefore, the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. The energy difference between HOMO and LUMO orbitals is called as energy gap that is an important property called stability for structures [41] and the global descriptors such as electronegativity (χ), chemical hardness (η), softness (ζ) and electrophilicity index (ψ) were calculated and are presented in Table 6. The energy levels of the HOMO and LUMO orbitals computed at the B3LYP/ 6-311++G (d,p) level for the title compound is shown in Figure 4.



Figure 4: The frontier molecular orbitals of DPO (HOMO-LUMO)

According to B3LYP/6-311G++ (d, p) level of theory, the energy band gaps $|\Delta E_{HOMO-LUMO}|$, was found to be about 0.178 a.u. for the title compound. The HOMO and LUMO calculated energies explain the charge transfer occurs within the molecule. However, the dark red and green blobs of compound were found indicating the more delocalized electrons promoted during the absorption of light. From the molecular orbital analysis the highest occupied level is 65 this locates over the C-C and C-H groups and the 66 is the excited frontier orbital, this orbital located over the C=O and carbon atoms in heterocyclic and phenyl rings. Furthermore, it is well known that the band gap energy value helps to identify the chemical reactivity and kinetic stability of a molecule [42]. A molecule obtaining a small band gap energy is more polarizable and the small gap is generally related to a high chemical reactivity and low kinetic stability (soft molecule) [43]. Based on the results, the title compound was found to be most reactive and least stable.

Non-linear optical effects

NLO is at the forefront of current research because it provides the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing, and optical interconnections [44, 45]. In discussing nonlinear optical properties, the polarization of the molecule by an external radiation field is often approximated as the creation of an induced dipole moment by an external electric field. The first hyperpolarizability (β_0) of this molecular system is calculated using B3LYP/6-311++G (d,p) method, based on the finite field approach. The calculated hyperpolarizability values of DPO are given in Table 7. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems and frequently used as a threshold value for comparative purposes. The computed first hyperpolarizability, β_{tot} of MDPO molecule is 35.583 x10⁻³¹ cm⁵/esu and is ten times more than that of urea (β of urea is 3.7289 x10⁻³¹ cm⁵/esu). Thus, this molecule might serve as a prospective building block for nonlinear optical materials.

Other molecular properties

Several molecular parameters were performed by B3LYP with 6-311++G (d,p) level of theory are given in Table 8. As seen from table, total energy and total entropy were obtained to be about -805.47518929 a.u. and 123.599 cal mol⁻¹ K⁻¹ for DPO, respectively. Moreover, it was found that the title molecule has the greatest zero-point vibrational and thermal energy (152.387 and 161.515 kcal mol⁻¹, respectively). On the other hand, it was noted that DPO have the least heat capacity (57.939 cal mol⁻¹K⁻ ¹). Additionally, the dipole moment, which is an important quantity explaining the electronic property of a molecule, stems from non-uniform distribution of charges on the various atoms in the molecule. The dipole moment was computed to be about 5.234 Debye indicating that the DPO molecule was polar (nonuniform distribution of charges on various atoms). This result was also supported by the evidences of other parts in this investigation.

Conclusion

Vibrational, electronic, reactivity and structural aspects of 2,6-diphenyl-4H-pyran-4-one (DPO) were studied in detail using DFT method and the harmonic wavenumbers were also compared with the experimental values. In addition, Mulliken and NPA atomic charges were also calculated. MEP predicts the electronegative oxygen of carbonyl group and hydrogen atoms to be the most reactive site for electrophilic and nucleophilic attacks. The NBO analysis reveals that intramolecular charge transfer (ICT) takes place within the molecule. The frontier molecular orbital energy gap and global descriptors illustrate the less reactivity of the title compound. The title compound exhibits good NLO activity. These observations may promote further development of research groups to explore more about the utility of such reactions in the synthesis of novel heterocycles and natural products.

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