Study of spectral and NLO properties of (2E)-1-(2, 4-dihydroxyphenyl)-3- (4-hydroxyphenyl) prop-2-en-1-one by DFT

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Theoretical calculations of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one have been performed using Gaussian 09 software package. The geometry optimization and vibrational frequency determinations of the molecule have been developed using DFT/B3LYP/6-31G (d, p). Substituents at aliphatic double bond are Trans to each other. The standard thermodynamic functions: heat capacity (CV), entropy (S), and enthalpy (E) were obtained at B3LYP/6-31G (d, p) level. DFT has been used to calculate the total dipole moment (μ), the mean linear polarizability (α), the anisotropic polarizability ($\Delta\alpha$), the first-order hyperpolarizability (β) and the second-order hyperpolarizability (γ) in terms of x, y, z components. Simultaneously UV-Vis absorption spectra, electronic transitions, vertical excitation energies and oscillator strengths of the same molecule were computed with the Time Dependent DFT (TD-DFT) method using the same basis sets. FMO, ESP study were also carried out using the same basis set.

Keywords: DFT, TD-DFT, Mulliken atomic charge, FMO, ECD, ESP

1 Introduction

Chalcones or 1, 3-diaryl-2-propen-1-ones, are natural compounds that are largely distributed in plants, fruits, and vegetables and belong to the flavonoid family. Chemically they consist two aromatic rings (A & B) joined by a three-carbon α, β-unsaturated carbonyl system with various substituents on the two aromatic rings. General Structure of Chalcones is shown in Fig. 1.

Due to the extended conjugation, the complete delocalisation of π-electrons on both the benzene rings makes it good for wide range of applications in the fields of biology such as antitumor[1,2], anti-inflammatory[3-5], and antimalarial[6] agents. Literature survey reveals that chalcones have been used as Langmuir film[7] nonlinear optical material[8,9], electrochemical sensing[10], optical limiting material[11], etc. The chemistry of chalcone has been recognized as a significant field of study. The phenomenal growth of publications in this area reflects interest in this field throughout the world. These findings motivated us to carry out computational study of chalcone molecule.

2 Material and Methods

All theoretical calculations of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-

(Fig. 2) have been performed using Gaussian 09 software package[12]. The molecule under consideration was explored at Density Functional Theory (DFT), and the Becke three-parameter exchange functions in combination with the LYP correlation function of the Lee, Yang and Parr (B3LYP) method. The geometry optimization and vibrational frequency determinations of the molecule have been developed using DFT/B3LYP/6-31G (d,p). Simulated UV–Vis absorption spectra, electronic transitions, vertical excitation energies and oscillator strengths of the
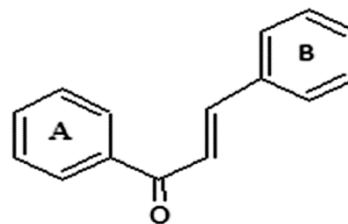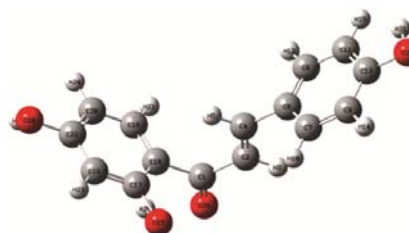

Fig. 1 – General Structure of Chalcones.

Fig. 2 – (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one.

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same molecule were computed with the Time Dependent DFT (TD-DFT) method using the same basis sets.

3 Results and Discussion

3.1 Geometrical analysis

The molecular structure of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-oneemempherical formula $C_{15}H_{12}O_4$,Molecular mass: 256.07356 amu is an asymmetric top type molecule with 87 degrees of freedom.The optimised molecular structure of the title chalcone is obtained from Gaussian 09 and Gauss view programme with the atom numbering scheme as shown in Fig. 3. The optimised geometrical parameters (bond length,bond angle and dihedral angle) calculated by B3LYP/ 6-31G(d.p) level basis set are listed in Table 1.

In the present study, the molecule consists of two rings (Ring A and Ring B) which are planar, with dihedral angles D(4, 6, 8, 11) =179.8304 and D(177.8693). At the aliphatic double bond substituents are trans to each other with dihedral angles D(3,2,4,5) = -173.6553,D(3,2,4,6) = 4.146,D (1,2,4,5)=-4.4914,D(1,2,4,6)=173.3099˚. As oxygen is more electronegative than carbon, the electrons in the C=O bond are drawn towards the oxygen. This means that carbonyl compounds are polar and have substantial dipole moments. The C=O bond has bond length of 1.2523 Å.

3.2 Vibrational assignment

The fundamental vibration of a non-linear molecule which contains N atoms is equal to (3N-6), apart from three translational and three rotational degrees of freedom[13,14]. The studied molecule belongs to
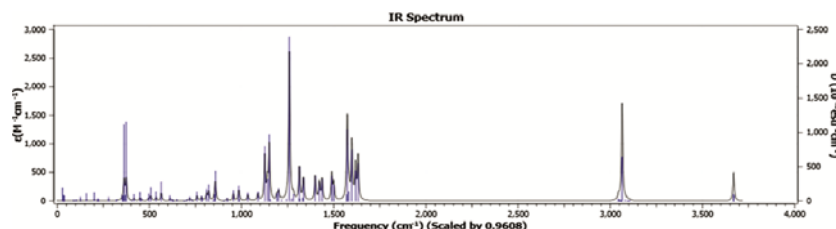

Fig. 3 – Optimised Geometry.

asymmetric top group symmetry and has 31 atoms; hence 87 normal modes of vibrations are possible. As mentioned above, IR vibrational properties of the studied molecule has been done using B3LYP by DFT at 6-31G (d, p) Basis level set shown in fig. 4 and the frequencies, intensities and their corresponding assignments for the theoretical spectra are tabulated in Table 2. The vibrational assignments were made by visual inspection of modes animated by using the Gauss view program standard values reported[13].

3.3 Aromatic hydrocarbon-

The most prominent and most informative bands in the spectra of aromatic hydrocarbon occur in the low frequency range between 900 and 675 cm^{-1}. These strong absorption bands results from the out-of-plane bending of the ring C-H bonds. In-plane bending bands appear in the 1300-1000 cm^{-1} region. Skeletal vibrations, involving carbon-carbon stretching with in the ring absorb in the 1600-1585 and 1500-14000 cm^{-1} region. The skeletal band vibrations frequently appear as doublets, depending on the nature of the ring substituents. Aromatic C-H stretching bands occur between 3100 and 3000 cm^{-1}. In-phase out-of-plane bending of ring hydrogen atom appear at 900 to 675 cm^{-1} and are frequently intense. The absorption band that frequently appears in the spectra of substituted benzene near 600 to 420 cm^{-1} is attributed to out-of-plane ring bonding.

3.4 Phenol

The non-hydrogen bonded -OH group of phenol absorbs strongly in the 3700 to 3584 cm^{-1} region and this is due to O-H stretching vibrations. A strong band in 1260 to 1000cm^{-1} region of the spectrum is due to C-O stretching vibration in phenol. The O-H in-plane bending vibration occurs in the general region 1420-1330 cm^{-1}.

3.5 Ketone

Ketones show a strong absorption band in the region 1870-1540 cm^{-1} due to C=O stretching vibration. Here C=O group is in conjugation with

Fig. 4 – Theoretical IR spectra of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2- en-1-one.

Table 1 – Optimized geometrical Parameters of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one as calculated at B3LYP by DFT at 6-31G (d, p) Basis level set

S.No.	Bonds between Atoms	Bond Length (A^0)	Bond Angle between Atoms	Bond Angle $(^0)$	Dihedral Angle between Atoms	Dihedral Angle $(^0)$
1	R(1,2)	1.4787	A(2,1,16)	123.0748	D(16,1,2,3)	-153.0918
2	R(1,16)	1.4682	A(2,1,25)	116.4433	D(16,1,2,4)	36.9664
3	R(1,25)	1.2523	A(16,1,25)	120.4781	D(25,1,2,3)	27.6095
4	R(2,3)	1.087	A(1,2,3)	112.4649	D(25,1,2,4)	-142.3324
5	R(2,4)	1.3496	A(1,2,4)	125.9104	D(2,1,16,17)	-166.6372
6	R(4,5)	1.0878	A(3,2,4)	120.8539	D(2,1,16,18)	15.5718
7	R(4,6)	1.4621	A(2,4,5)	118.1196	D(25,1,16,17)	12.6342
8	R(6,7)	1.4088	A(2,4,6)	127.2746	D(25,1,16,18)	-165.1568
9	R(6,8)	1.4076	A(5,4,6)	114.5733	D(1,2,4,5)	-4.4914
10	R(7,9)	1.3881	A(4,6,7)	118.991	D(1,2,4,6)	173.3099
11	R(7,10)	1.0869	A(4,6,8)	123.5084	D(3,2,4,5)	-173.6553
12	R(8,11)	1.3882	A(7,6,8)	117.4998	D(3,2,4,6)	4.146
13	R(8,12)	1.0851	A(6,7,9)	121.8752	D(2,4,6,7)	-175.0038
14	R(9,13)	1.3992	A(6,7,10)	119.0294	D(2,4,6,8)	5.3192
15	R(9,14)	1.0846	A(9,7,10)	119.0951	D(5,4,6,7)	2.8639
16	R(11,13)	1.4023	A(6,8,11)	121.2492	D(5,4,6,8)	-176.8131
17	R(11,15)	1.0879	A(6,8,12)	120.0275	D(4,6,7,9)	-179.8996
18	R(13,26)	1.3617	A(11,8,12)	118.7228	D(4,6,7,10)	0.2988
19	R(16,17)	1.4321	A(7,9,13)	119.5379	D(8,6,7,9)	-0.2032
20	R(16,18)	1.4102	A(7,9,14)	121.4524	D(8,6,7,10)	179.9952
21	R(17,19)	1.3989	A(13,9,14)	119.0096	D(4,6,8,11)	179.8304
22	R(17,27)	1.3363	A(8,11,13)	120.1087	D(4,6,8,12)	0.0701
23	R(17,29)	1.8727	A(8,11,15)	119.9964	D(7,6,8,11)	0.1489
24	R(18,20)	1.3831	A(13,11,15)	119.8948	D(7,6,8,12)	-179.6114
25	R(18,21)	1.0834	A(9,13,11)	119.7288	D(6,7,9,13)	0.1093
26	R(19,22)	1.3906	A(9,13,26)	117.5563	D(6,7,9,14)	-179.8896
27	R(19,23)	1.0833	A(11,13,26)	122.7148	D(10,7,9,13)	179.9108
28	R(20,22)	1.4088	A(1,16,17)	118.7538	D(10,7,9,14)	-0.0881
29	R(20,24)	1.0869	A(1,16,18)	123.5405	D(6,8,11,13)	-0.0032
30	R(22,28)	1.3599	A(17,16,18)	117.6705	D(6,8,11,15)	-179.9213
31	R(26,31)	0.9665	A(16,17,19)	120.2833	D(12,8,11,13)	179.7601
32	R(28,30)	0.9665	A(16,17,27)	121.7205	D(12,8,11,15)	-0.158
33			A(16,17,29)	90.9812	D(7,9,13,11)	0.0438
34			A(19,17,27)	117.9952	D(7,9,13,26)	179.9192
35			A(19,17,29)	148.6429	D(14,9,13,11)	-179.9573
36			A(27,17,29)	30.86	D(14,9,13,26)	-0.0818
37			A(16,18,20)	122.017	D(8,11,13,9)	-0.096
38			A(16,18,21)	118.9506	D(8,11,13,26)	-179.9648
39			A(20,18,21)	119.0037	D(15,11,13,9)	179.8222
40			A(17,19,22)	119.9834	D(15,11,13,26)	-0.0466
41			A(17,19,23)	119.5457	D(9,13,26,31)	179.8251
42			A(22,19,23)	120.4527	D(11,13,26,31)	-0.3034
43			A(18,20,22)	119.132	D(1,16,17,19)	177.8693
44			A(18,20,24)	120.6026	D(1,16,17,27)	-1.7711
45			A(22,20,24)	120.2586	D(1,16,17,29)	-4.6576
46			A(19,22,20)	120.7881	D(18,16,17,19)	-4.2096
47			A(19,22,28)	117.3132	D(18,16,17,27)	176.15
48			A(20,22,28)	121.8902	D(18,16,17,29)	173.2634
49			A(13,26,31)	109.4213	D(1,16,18,20)	-179.2293
50			A(22,28,30)	109.2283	D(1,16,18,21)	2.7375

(*Contd.*)

Table 1 – Optimized geometrical Parameters of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one as calculated at B3LYP by DFT at 6-31G (d, p) Basis level set (*Contd.*)

S.No.	Bonds between Atoms	Bond Length (A^0)	Bond Angle between Atoms	Bond Angle (^{0})	Dihedral Angle between Atoms	Dihedral Angle (^{0})
51					D(17,16,18,20)	2.9574
52					D(17,16,18,21)	-175.0758
53					D(16,17,19,22)	2.6192
54					D(16,17,19,23)	-178.9274
55					D(27,17,19,22)	-177.7272
56					D(27,17,19,23)	0.7262
57					D(29,17,19,22)	-172.5212
58					D(29,17,19,23)	5.9322
59					D(16,18,20,22)	-0.0835
60					D(16,18,20,24)	-179.1309
61					D(21,18,20,22)	177.9486
62					D(21,18,20,24)	-1.0987
63					D(17,19,22,20)	0.3652
64					D(17,19,22,28)	179.3258
65					D(23,19,22,20)	-178.074
66					D(23,19,22,28)	0.8866
67					D(18,20,22,19)	-1.6514
68					D(18,20,22,28)	179.4363
69					D(24,20,22,19)	177.3993
70					D(24,20,22,28)	-1.513
71					D(19,22,28,30)	-179.3024
72					D(20,22,28,30)	-0.354

Table 2 – The frequencies, intensities and their corresponding assignments for the theoretical spectra of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2- en-1-one

Mode	Frequency Unscaled cm^{-1}	Frequency Scaled cm^{-1}	Intensity Epsilon M^{-1} cm^{-1}	Vibrational assignment
1	29.54	28.38	1.3860	
2	37.51	36.04	0.7091	
3	39.03	37.50	0.7059	
4	92.42	88.80	0.2845	
5	107.05	102.85	0.4913	
6	131.52	126.36	1.8365	
7	165.26	158.78	4.4761	
8	208.93	200.74	6.3758	
9	228.19	219.25	1.3892	
10	232.33	223.23	1.4779	
11	290.31	278.93	3.9325	
12	335.25	322.11	1.5400	
13	368.02	353.60	7.0895	
14	371.81	357.24	5.7341	
15	377.27	362.48	105.7920	Out-of plane bending of C-H bond of aromatic ring
16	385.71	370.59	7.2711	
17	389.55	374.28	111.7392	Out-of plane bending of C-H bond of aromatic ring
18	420.56	404.08	0.4134	
19	432.82	415.86	10.2220	
20	467.17	448.86	14.9304	Out-of-plane ring bending vibration of substituted benzene ring
21	475.52	456.88	4.0219	
22	516.68	496.43	13.0554	

(*Contd.*)

Table 2 – The frequencies, intensities and their corresponding assignments for the theoretical spectra of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2- en-1-one (*Contd.*)

Mode	Frequency Unscaled cm^{-1}	Frequency Scaled cm^{-1}	Intensity Epsilon M^{-1} cm^{-1}	Vibrational assignment
23	528.53	507.81	25.4134	Out-of-plane ring bending vibration of substituted benzene ring
24	558.19	536.31	18.9210	
25	587.29	564.27	41.0176	Out-of-plane ring bending vibration of substituted benzene ring
26	636.61	611.65	11.9590	
27	648.62	623.19	3.1518	
28	655.87	630.16	0.8523	
29	675.31	648.84	3.8371	
30	716.95	688.85	0.5718	
31	731.94	703.25	3.6550	
32	748.31	718.98	10.6344	
33	762.12	732.25	2.0148	
34	788.88	757.96	25.8478	
35	814.57	782.64	14.4255	
36	818.01	785.94	7.8554	
37	843.37	810.31	35.4076	
38	855.47	821.94	49.6615	In-phase , out-of-plane bending of a ring hydrogen atom
39	879.88	845.38	2.9047	
40	888.18	853.36	19.8983	
41	893.06	858.06	96.5447	In-phase , out-of-plane bending of a ring hydrogen atom
42	941.88	904.96	0.5342	
43	959.15	921.55	10.2389	
44	962.23	924.51	0.4686	
45	994.68	955.69	38.5984	In-phase , out-of-plane bending of a ring hydrogen atom
46	1025.05	984.87	54.9055	
47	1027.17	986.91	5.0073	
48	1076.08	1033.90	30.9316	
49	1133.60	1089.16	37.8440	
50	1172.22	1126.27	232.6049	In-plane bending of C-H bond of aromatic ring
51	1187.08	1140.55	93.0280	In-plane bending of C-H bond of aromatic ring
52	1197.27	1150.33	289.8834	In-plane bending of C-H bond of aromatic ring
53	1204.17	1156.96	5.6499	
54	1240.32	1191.70	30.4504	
55	1249.89	1200.89	51.1934	C-C-C stretching vibration of ketone group
56	1266.71	1217.06	5.3461	
57	1294.98	1244.22	8.6729	
58	1310.39	1259.02	784.7052	C-O stretching vibration of phenolic group
59	1323.38	1271.51	9.9876	
60	1334.02	1281.73	31.0644	C-C-C stretching vibration ofketone group
61	1367.31	1313.71	167.2422	C-C-(=O)-C bending in C-C-C bond of ketone group
62	1368.16	1314.53	9.6803	
63	1385.56	1331.25	14.1204	
64	1390.42	1335.92	113.9770	O-H in-plane bending vibration of phenolic group
65	1456.41	1399.32	129.6489	O-H in-plane bending vibration of phenolic group
66	1479.79	1421.78	100.4396	O-H in-plane bending vibration of phenolic group
67	1495.69	1437.06	115.2457	Skeletal vibration C-C stretching with in aromatic ring
68	1550.28	1489.51	141.8309	Skeletal vibration C-C stretching with in aromatic ring
69	1561.40	1500.19	89.9468	
70	1633.06	1569.04	35.7136	Skeletal vibration C-C stretching with in aromatic ring
71	1637.63	1573.44	423.8790	Skeletal vibration C-C stretching with in aromatic ring
72	1647.25	1582.67	55.8561	>C=O stretching vibration of ketone group

(*Contd.*)

Table 2 – The frequencies, intensities and their corresponding assignments for the theoretical spectra of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-
(4-hydroxyphenyl)prop-2- en-1-one (*Contd.*)

Mode	Frequency Unscaled cm^{-1}	Frequency Scaled cm^{-1}	Intensity Epsilon M^{-1} cm^{-1}	Vibrational assignment
73	1663.43	1598.22	309.5252	>C=O stretching vibration of ketone group
74	1684.49	1618.46	183.9307	=C-H stretching vibration of alkene
75	1698.78	1632.19	227.6343	=C-H stretching vibration of alkene
76	3169.14	3044.91	21.6467	
77	3170.17	3045.90	7.5132	
78	3177.81	3053.24	9.1562	
79	3183.31	3058.52	2.6031	
80	3185.09	3060.23	5.2050	
81	3189.66	3064.62	510.6961	Aromatic C-H bending vibration
82	3205.37	3079.72	9.3979	
83	3217.71	3091.58	6.2682	
84	3226.33	3099.86	3.8038	
85	3232.45	3105.74	2.2145	
86	3818.94	3669.23	88.6034	O-H stretching vibration of non-bonded O-H group
87	3819.20	3669.49	61.1431	O-H stretching vibration of non-bonded O-H group

benzene ring and a double bond and thus there is delocalisation of Π electrons reduces double bond character of C=O bond, causing absorption at a lower wave number or longer wavelength. Conjugation with an alkene or phenyl group causes absorption in the 1685-1666 cm^{-1} region. Additional conjugation may further cause slight reduction in frequency. Ketone show C-C (=0)-C stretching and bending vibration in the region 1300-1100 cm^{-1}.

3.6 Aliphatic double bond

Alkenes show C=C stretching, C-H stretching vibrations and in-plane &out-of-plane bending of C-H bond. Disubstituted trans alkenes, tri and tetra substituted alkenes absorb at or near 1670 cm^{-1}. Conjugation of an alkene double bond with aromatic ring produces enhanced alkene absorption near 1925 cm^{-1}. The most characteristic vibrational modes of alkenes are the out of plane C-H bending vibrations between 1000-650 cm^{-1}.

3.7 Thermochemical properties

The statistical thermo chemical analysis of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one is carried out considering the molecule to be at room temperature of 300 K and one atmospheric pressure. The standard thermodynamic functions: heat capacity (CV), entropy (S), and enthalpy (E) have been obtained at B3LYP/6-31G(d,p) level and are listed in Table 3.Thermodynamic properties helps to understand energetic, structural and reactivity of a molecule . The frequency calculations compute the zero point energies, thermal correction to internal energy and entropy as well as the heat capacity for a

Table 3 – Thermochemical properties of (2*E*)-1-
(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	159.659	63.190	130.034
Electronic	0.000	0.000	0.000
Translational	0.889	2.981	42.521
Rotational	0.889	2.981	34.284
Vibrational	157.882	57.228	53.229
Vibration 1	0.593	1.984	5.860
Vibration 2	0.594	1.982	5.387
Vibration 3	0.594	1.981	5.308
Vibration 4	0.602	1.955	3.608
Vibration 5	0.606	1.944	3.322
Vibration 6	0.612	1.922	2.924
Vibration 7	0.624	1.885	2.489
Vibration 8	0.642	1.827	2.053
Vibration 9	0.651	1.798	1.893
Vibration 10	0.653	1.792	1.861
Vibration 11	0.686	1.692	1.472
Vibration 12	0.716	1.605	1.235
Vibration 13	0.741	1.538	1.088
Vibration 14	0.744	1.530	1.072
Vibration 15	0.748	1.519	1.050
Vibration 16	0.754	1.501	1.017
Vibration 17	0.757	1.493	1.002
Vibration 18	0.783	1.426	0.890
Vibration 19	0.794	1.399	0.849
Vibration 20	0.824	1.323	0.746
Vibration 21	0.832	1.304	0.722
Vibration 22	0.872	1.213	0.618
Vibration 23	0.883	1.187	0.590
Vibration 24	0.914	1.122	0.527
Vibration 25	0.944	1.059	0.472

molecular system. These functions describe the thermodynamic stability of the system at the given conditions of pressure and temperature.

Zero-point correction	0.238407 (Hartree/Particle)
Thermal correction to Energy	0.254433
Thermal correction to Enthalpy	0.255378
Thermal correction to Gibbs Free Energy	0.193594
Sum of electronic and zero-point Energies	-879.493024
Sum of electronic and thermal Energies	-879.476998
Sum of electronic and thermal Enthalpies	-879.476053
Sum of electronic and thermal Free Energies	-879.537837

3.8 Nonlinear properties

Quantum chemical calculations have been very useful for predicting the molecular NLO properties of active compounds[15,16]. Hyperpolarizability is useful in understanding the relationship between the molecular structure and nonlinear optical properties. DFT has been used to calculate the total dipole moment (μ), the mean linear polarizability (α), the anisotropic polarizability ($\Delta\alpha$), the first-order hyperpolarizability (β) and the second-order hyperpolarizability (γ) in terms of x,y,z components by Gaussian 09 package for (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-oneThe mentioned NLO properties have

been calculated by using the following equations[17,18] and are summarized in Table 4.

$$\mu = (\mu^2_x + \mu^2_y + \mu^2_z)^{\frac{1}{2}} \qquad \cdots (1)$$

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad \cdots (2)$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha^2_{xy} + \alpha^2_{yz} + \alpha^2_{zx})]^{1/2} \qquad \cdots (3)$$

$$\beta = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \qquad \cdots (4)$$

$$\gamma = \frac{1}{5}[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})] \qquad \cdots (5)$$

The conversion factor of α, β and γ in atomic unit are 1 atomic unit (a.u.) = 0.1482×10^{-24} electrostatic unit (esu) for α, 1 a.u. = 8.6393×10^{-33} esu for β and 1 a.u. = 5.0367×10^{-40} esu for γ.

The above functions of the molecular system is calculated using B3LY/6-31G (d, p) method, based on (field-independent basis). Urea is one of the prototype molecules used in the study of the NLO properties of molecular systems and used as a threshold value for comparative purposes. The computed hyper-polarizability β is 1.568×10^{-30} esu and is about five times greater than urea β of urea is 0.3728×10^{-30} esu). Thus this molecule must acts as a prospective building block for nonlinear optical materials.

3.9 Mulliken atomic charges

We know that the atomic charges are very much dependent on how the atoms are defined. It also plays

Table 4 – Dipole moment (μ) in Debye, Mean Linear Polarizability (α) in a.u First order Hyperpolarizability (β) ina.u Second order Hyperpolarizability(γ) in a.u as calculated by DFT

Dipole moment μ in Debye		Mean Linear Polarizability α in a.u		First order Hyperpolarizability β in a.u		Second order Hyperpolarizability γ in a.u	
μ_X	-4.5146	α_{XX}	-100.4200	β_{XXX}	-182.6647	γ_{XXXX}	-7866.6750
μ_Y	-3.3629	α_{YY}	-104.2569	β_{YYY}	-59.1274	γ_{YYYY}	-1240.9333
μ_Z	-1.8986	α_{ZZ}	-108.6218	β_{ZZZ}	3.1636	γ_{ZZZZ}	-264.3958
Total μ	5.9410	α_{XY}	-19.4116	β_{XYY}	20.0019	γ_{XXXY}	-460.3914
		α_{XZ}	2.4498	β_{XXY}	20.1786	γ_{XXXZ}	279.2629
		α_{YZ}	-1.7101	β_{XXZ}	-60.0321	γ_{YYYX}	-191.5205
		Total α	-104.4329a.u.	β_{XZZ}	-1.0749	γ_{YYYZ}	24.9504
		$\Delta\alpha$	34.7630	β_{YZZ}	-0.1793	γ_{ZZZX}	11.3278
		α	1.54770×10^{-23}esu	β_{YYZ}	-10.8316	γ_{ZZZY}	2.0676
				β_{XYZ}	21.2935	γ_{XXXY}	-1570.5838
				Total β	181.4507a.u.	γ_{XXZZ}	-1481.6867
				β	1.568×10^{-30}esu	γ_{YYZZ}	-254.4656
						γ_{XXYZ}	-9.7624
						γ_{YYXZ}	-53.9418
						γ_{ZZXY}	-1.2037
						Total γ	-3197.0953a.u.
						γ	-1.6103×10^{-36}esu

an important role in the application of quantum chemical calculations to molecular systems. B3LYP level with 6-31G (d, p) basis set was used to calculate the Mulliken atomic charges. Calculated values of Natural, Mulliken and APT charges are given in Table 5 and plotted in Fig. 5. As seen in Table 5 and

Table 5 – Natural, Mulliken, APT Charges of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one. as calculated by B3LYP level with 6-31G (d, p) basis set

| S.No.	Atom No.	Natural Charge	Mulliken Charge	APT Charge
1	C 1	0.52119	0.379534	1.462552
2	C 2	-0.29247	-0.136402	-0.524199
3	H 3	0.24400	0.105561	0.024594
4	C 4	-0.17776	-0.102215	0.424328
5	H 5	0.23917	0.102098	0.025660
6	C 6	-0.11267	0.122337	-0.288879
7	C 7	-0.18859	-0.136411	0.139217
8	C 8	-0.18323	-0.117269	0.114542
9	C 9	-0.28769	-0.101949	-0.204519
10	H 10	0.24165	0.093256	0.033014
11	C 11	-0.31308	-0.134510	-0.221048
12	H 12	0.24247	0.096700	0.044403
13	C 13	0.34198	0.334154	0.756300
14	H 14	0.25510	0.103752	0.041197
15	H 15	0.23727	0.084054	0.006047
16	C 16	-0.24881	0.005854	-0.664788
17	C 17	0.40712	0.310506	0.757185
18	C 18	-0.17761	-0.136819	0.223677
19	C 19	-0.35300	-0.130890	-0.319763
20	C 20	-0.35470	-0.151660	-0.420360
21	H 21	0.24909	0.102374	0.048678
22	C 22	0.36644	0.339453	0.896714
23	H 23	0.26430	0.108906	0.061665
24	H 24	0.23493	0.075600	0.012140
25	O 25	-0.61416	-0.554797	-1.001345
26	O 26	-0.68227	-0.549447	-0.900671
27	O 27	-0.68992	-0.565960	-0.791034
28	O 28	-0.67838	-0.547858	-0.835573
29	H 29	0.52051	0.359051	0.481984
30	H 30	0.49410	0.321112	0.306119
31	H 31	0.49502	0.321886	0.312163
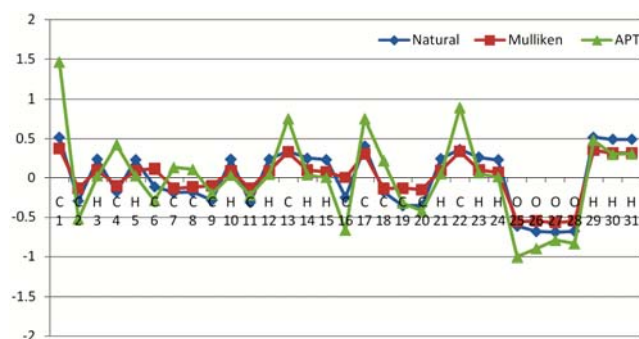
Fig. 5 – Natural, Mulliken, APT charges of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one.

Fig. 5 because of phenolic group on both the benzene rings α, β-unsaturated carbonyl group in aliphatic carbon chain the atomic charge distribution is different. All the four oxygen atoms are negatively charged but oxygen atom present at ortho position in phenyl ring A has maximum negative charge. This can be attributed to electron delocalisation due to carbonyl group. All the hydrogen atoms have positive charge. Of all the carbon atoms carbon atom number 1 has maximum positive charge indicating that at this carbon atom nucleophiles can easily attack.

3.10 UV-VISIBLE Spectral Studies and Electronic Properties

TD-DFT calculations facilitates quantum chemists a better understanding of observed electronic absorption spectrum in terms of Excitation energies (E), absorption wavelength (λ), oscillator strengths (f), molecular orbitals undergoing transitions, electronic transitions etc. Molecular orbitals undergoing excitation transition, transition energy and assignments of electronic transitions have been calculated and gathered in Table 6 and the UV –Visible spectra of title compound as obtained from TD-DFT calculations is shown in Fig. 6(a).

The maximum absorption wavelength corresponds to the electronic transition from the HOMO→LUMO contribution, which implies an electron density transfer as n-π* transition. This electronic absorption corresponds to the transition from ground to the first excited state and is mainly described by electron excitation from HOMO→LUMO. The λ_max is a function of substitution; the stronger is the donor character of the substitution, the more electrons are pushed into the molecule, and the larger is λ. The π-π* transitions are expected to occur relatively at lower wavelength, due to the consequence of the extended aromaticity of the benzene ring.

3.11 ECD spectroscopy

An optically active compound rotates the plane of linearly polarized light at a wavelength in which the chromophore of a molecule absorbs. Linearly polarized light may be decomposed to left and right circularly polarized waves and an optically active compound absorbs these lights differentially. The transmitted light is elliptically polarized and the difference in the absorption coefficient of the circular polarized waves is called circular dichroism (CD)[23,24]. The electronic circular dichroism (ECD) measurement of an optically active compound yields a value and a sign as a function of wavelength characterizing the optical transition, and contains information about the

Table 6 – Theoretical absorption spectrum of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-oneExcitationenergies (E), Absorption wavelength(λ) and   Oscillator strengths (f)

ExcitedState	Excitation energies (E)	Absorptionwavelength (λ)	oscillator strengths (f)	Excitation Transition(MO)	Transition energy (MO) Singlet A	assignments of electronic transitions
1	3.3460 ev	370.54 nm	0.0008	63->68	0.11349	n- Π*
				66->68	0.28894	
				67->68	0.60761	
				67->69	0.14418	
2	3.4831 ev	355.95 nm	0.0001	62 -> 68	0.17215	
				63 -> 68	0.21702	
				65 -> 68	0.13096	
				66 -> 68	0.53231	
				67 -> 68	-0.31658	
3	3.7114 ev	334.07 nm	0.0226	65 -> 68	-0.20187	
				65 -> 69	0.40572	
				66 -> 69	0.22752	
				67 -> 69	0.45212	

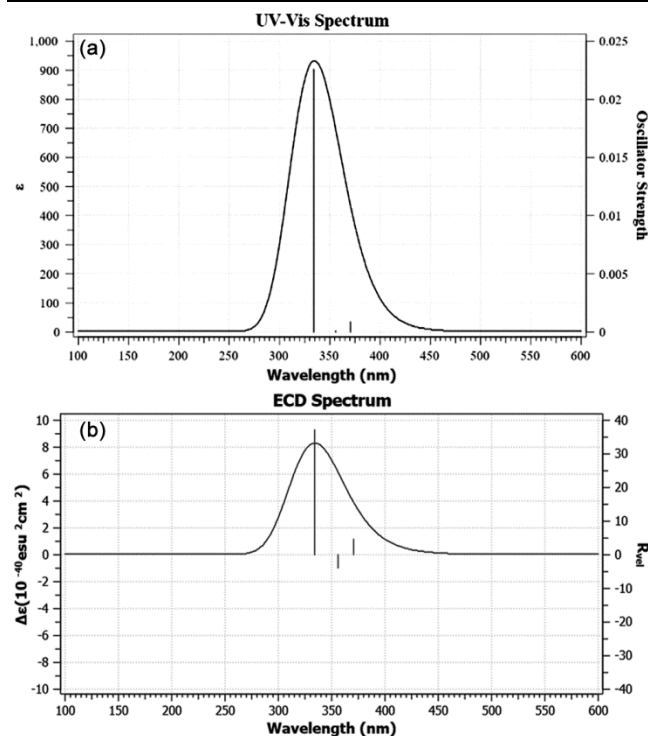Total Energy, E(TD-HF/TD-KS) = -879.314866842 Hartree

Fig. 6 – (a) UV-Visible spectra of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one and (b) ECD spectra of (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one.

absolute configuration or conformation of the compound[25]. Common chromophores in chalcones are two aromatic rings and a carbonyl group. The absorption bands of aromatic π–π* transitions lie in the UV range of 200−290 nm and the n–π* transitions of some carbonyl groups between 280 and 340 nm

and the absorption range will further extend due to conjugation. Aryl and carbonyl groups are achiral chromophores. For (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one a positive CE at 334 nm corresponds to R configuration. The ECD spectra for (2*E*)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one as obtained from DFT calculations have been shown in Fig. 6(b).

3.12 Frontier molecular orbital (FMO) analysis

HOMO and LUMO collectively form frontier molecular orbitals (FMOs).The highest occupied molecular orbital (HOMO) have higher energy and are rich in electrons, therefore have a good electron donating ability. On the contrary, lowest unoccupied molecular orbital (LUMO) indicates the electron accepting capability due to lower energy and deficiency of electrons. FMOs play a crucial role during molecular interactions. Furthermore, FMOs provide important information about the optical properties, electronic properties and reactivity of the molecule under investigation[15,16]. In this context, FMO analyses were carried out to predict the electronic properties of (2*E*)-1-(2,4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one at B3LYP level and 6-31G(d,p) basis set at DFT and has been shown in Fig. 7. Results of FMOs analysis consists of four important molecular orbital pairs, their gap energies (ΔE) and are presented in Table 7.

In terms of chemical hardness, if a molecule has a large HOMO–LUMO gap, it is hard. Conversely, if
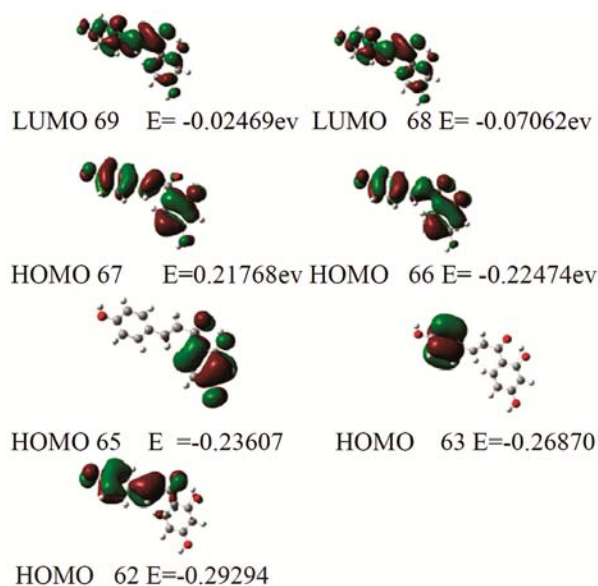
LUMO 69   E= -0.02469ev   LUMO 68 E= -0.07062ev

HOMO 67   E=0.21768ev   HOMO 66 E= -0.22474ev

HOMO 65   E =-0.23607   HOMO 63 E=-0.26870
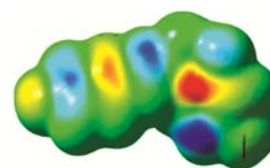
HOMO 62 E=-0.29294

Fig. 7

Fig. 8 – P(0, 0, 1, 0) Electron Density from Total SCF density (Isovalue=0.020000, Density=0.000400).
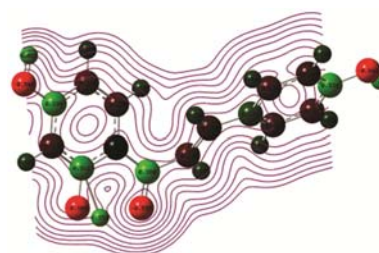

Fig. 9 – P(0, 0, 1, 0) Charge Density from Total SCF density (Isovalue=0.020000, Density=0.000400) ; Red negative and green positive charge.

Table 7 – Energy gap (ΔE) of Major Transitions

LUMO Energy (E_{LUMO})	HOMO Energy (E_{HOMO})	Energy gap (ΔE) ($E_{LUMO}-E_{HOMO}$)
68 (-0.07785ev)	63 (-0.26870 ev)	0.19085 ev
68 (-0.07785ev)	66 (-0.22474ev)	0.14689 ev
68 (-0.07785ev)	67 (-0.23189 ev)	0.15404 ev
69(-0.02469ev)	67 (-0.23189 ev)	0.20720 ev
68 (-0.07785ev)	62 (-0.29294 ev)	0.21509 ev
68 (-0.07785ev)	65 (-0.23607 ev)	0.15822 ev
69(-0.02469ev)	65 (-0.23607 ev)	0.21138 ev
69(-0.02469ev)	66(-0.22474ev)	0.20005 ev

Table 8 – Calculated values of reactive descriptors

Parameter	Relation	Calculated value
Ionization Energy(I)	$-E_{HOMO}$	0.23189
Electron Affinity(A)	$-E_{LUMO}$	0.07785
Chemical Potential(ϕ)	$-(I + A)/2$	-0.15487
Absolute hardness(η)	$(I - A)/2$	0.07702
Softness(S)	$\dfrac{1}{\eta}$	12.98364
Electronegativity(χ)	$(I + A)/2$	0.15487
Electrophilicity index (ω)	$\phi 2/2\eta$	0.15570
Electron donating capability(ω^-)	$\dfrac{(3 I + A)2}{16(I - A)}$	0.24276697
Electron accepting capability (ω^+)	$\dfrac{(I + 3A)2}{16(I - A)}$	0.087896975

the HOMO–LUMO gap is small, it is soft. One can also relate molecular stability to hardness, which means that the molecule with smaller HOMO–LUMO gap is more reactive.

Energies of HOMO, LUMO and their energy gaps are further used to describe the stability and reactivity by forecasting global reactivity descriptors[19-22].The calculated values of reactive descriptors are gathered in Table 8.

3.13 Electrostatic potential and electron density surfaces

The electrostatic potential and electron density surfaces for(2E)-1-(2,4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one was computed using with B3LYP level and 6-31G(d,p) basis set at DFT and are shown in fig. 8 & 9.The distribution of electrostatic potential and electron density surfaces depends on the type of substitution atoms and also depend on negative & positive charges. From this figure, the density distribution on the molecule varies from

negative charge on oxygen atoms to positive charge on hydrogen atoms.

4 Conclusions

To understand the structure and reactivityof(2E)-1-(2,4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-onewe have carried out an extensive study of the geometry, dipole moment, electrostatic potential (ESP), atomic charge distribution, polarizability, hyperpolarizability, chemical potential, electrophilicity, chemical hardness and chemical softnesses for (2E)-1-(2,4-dihydroxyphenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one using the B3LYP/6-31G(d) level of theory. The differences between the observed and scaled frequencies of the most of the fundamentals are

very small. Electrostatic potential (ESP), Mulliken population Analysis (MPA) and Natural population Analysis (NPA) reveal that the most possible sites for nucleophilic attack are C_2 C_{13} C_{17} and C_{22} and for electrophilic attack are O_{25}, O_{26} O_{27} and O_{28} among the atoms of (2E)-1-(2, 4-dihydroxyphenyl)-3-(4-hydroxyphenyl)prop-2-en-1-one. The magnitude of the molecular hyperpolarizability (β) shows that the Chalcone studied has much greater than that of the urea hence this molecule has better NLO activity.

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