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Scaled Quantum mechanical studies of the molecular structure and vibrational spectra of (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl) prop-2-en-1-one

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Abstract: The FT-IR and FT-Raman spectra of (2E)-3-(4-bromophenyl)-1-(2-methoxy phenyl) prop-2-en-1-onein the solid phase were recorded. The fundamental vibrational wavenumbers, intensities of vibrational bands and the optimized geometrical parameters of the compound were evaluated using DFT (B3LYP) method with 6-311++G(d,p) basis set. The stable geometry of the compound was determined from the potential energy surface scana. Complete vibrational assignments and Natural Bond Orbital (NBO) analysis for the title compound were carried out. The dipole moment (μ), polarizability (α) and hyperpolarizability (β) of the investigated molecule is calculated by using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods on the finite field approach. Besides, Molecular Electrostatic Potential (MEP) and thermodynamical properties are described from the computational process. The electron density-based local reactivity descriptor such as Fukui functions are calculated to explain the chemical selectivity or reactivity site in(2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one. Finally, the calculations are applied to simulated FT-IR and FT-Raman spectra of the title compound which show good agreement with observed spectra.

Key words : FT-IR, FT-Raman, NBO, NLO, DFT.

Introduction

Chalcones belong to flavonoid family. Chemical name is (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl) prop-2-en-1-one, they consist of open-chain flavonoids in which the two aromatic rings are joined by a threecarbon, α -unsaturated carbonyl system. A vast number of naturally occurring chalcones are polyhydroxylated in the aryl rings. The radical quenching properties of the phenolic groups present in many chalcones have raised interest in using the compounds or chalcone rich plant extracts as drugs or food preservatives. Chalcones have been reported to possess many useful properties, including anti-inflammatory, antimicrobial, antifungal, antioxidant, cytotoxic, anticancer activities. Many chalcones have been described for their high antimalarial activity. Chalconeis a derivative with 4-bromophenyl and 2-methoxy rings bonded at the opposite ends of a propenone group, the biologically active region [1-5].

A through literature analysis made over a decade reveal the need for analyzing the title compound theoretically to support experimental observations. Hence an attempt has been made in present work to analyze

this title compound theoretically and support these results experimentally. To our knowledge and literature survey reveals that, there are no theoretical calculations or detailed vibrational analysis have been performed on 2(E) molecule so far. Asystematic study on the molecule structure and vibrational spectra help in understanding the property of title molecule in depth insight. Vibrational spectra of the tilte compound have been analyzed on the basis of potential energy distribution (PED). The change in electron density(ED) in the σ^* and π^* antibonding orbitals and stabilization energies E(2) have been calculated by natural bond orbital (NBO)analysis to give clear evidence of stabilization originating in the hyperconjugation of hydrogen-bonded interaction. By analyzing the total (TDOS) and $\alpha\beta$ DOS density of states, the molecular orbital composition and their contributions to the chemical bonding were studied.

Experimental details

The compound 2(E) -3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-onewas prepared by following the procedure reported by Sreevidya *et al.*[6] for the preparation of chalcones. The chalcone formed was purified by recrystallization from absolute alcohol(M.P.453-455K). The FT-IR spectrum of the sample was recorded in the region 4000-400 cm⁻¹ in evacuation mode using KBr pellet technique with 1.0 cm resolution on a PERKINELMER FT-IR spectrophotometer. The FT-Raman spectrum of the sample was recorded in the region 4000-100 cm⁻¹ in pure mode using Nd; YAG laser of 100 Mw with 2 cm resolution on BRUKER RFS 27 at SAIF, IIT, Chennai, India.

Computational details

The optimized structure of the title compound, corresponding energy and vibrational harmonic frequencies were calculated by using DFT (B3LYP) / 6-311++G(d,P) basis set using GAUSSIAN 03W program package [7]. Without any constraint on the geometry the energy of the title molecule was minimized, whole intramolecular forces were brought to be zero. The geometry was optimized at B3LYP level by using 6-311++G(d,p) basis set. The frequency calculation delivered the fundamental vibrational frequencies, optimized geometrical parameters, energy, thermodynamical data such as entropy, enthalpy and heat capacity. Also IR and Raman spectra were stimulated. Mulliken population analysis determined the distribution of electrons into the molecular orbitals. The symmetries of the vibrational modes were determined by using the standard procedure [8] of decomposing the traces of the symmetry operation into the irreducible representations. By combining the result of the Gauss view program [9] with symmetry considerations, vibrational frequency assignments were performed. Calculation of potential energy distribution (PED) and the prediction of IR and Raman intensities were done with VEDA 4 program [10]. The NBO analysis and MEP calculations were performed on the title molecule. NBO give clear evidence stabilization originating from hyperconjugation of various intramolecular interactions [11-13]. The Mulliken populations were reported. The molecular orbital compositions and their contributions to the chemical bonding are studied by Total density states (TDOS) and sum of α and β electron density of states (αβTDOS). Furthermore, various non-linear optical properties of 2(E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-onesuch as dipole moment, anisotropy of polarizability and first order hyper polarizability were also computed on theoretical computations.

Prediction of Raman intensities

The Raman activities (S_i) calculated by Gaussian 03 program have been suitably adjusted by the scaling procedure with MOLVIB and subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [14].

$$I = f(v_o - v_i)^4 S_i$$

$$v_i[1-exp(hcv/K_bT]]$$

Where v_o is the exciting frequency (in cm), v_i is the vibrational wave number of the *ith* normal mode, h,c and k are universal constants, and the f is the suitably chosen common scaling factor for all the peak intensities. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes are used with full width at half maximum of 10 cm⁻¹ [15].

Results and Discussion

Geometrical structure

The optimized structure parameters of (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one was calculated at B3LYP levels with the 6-311++G(d,p) basis set and are listed in Table 1. in accordance with the atom numbering scheme as obtained from CHEMCRAFT software Fig 1. The table 1 of comparison for the experimental XRD data available from the literature [16] and the calculated bond angle and bond length for (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one is given in Table1. While comparing these values we can see that both are nearly the same, in case of any slight deviation is due to the fact that the theoretical calculations belong to the molecule in gaseous phase and the experimental results belong to the solid phase [17,18]. In spite of the slight difference in the calculated geometrical parameters, they represent a good approximation and they form the base for calculating other parameters such as vibrational frequencies and thermodynamic properties[19-21].



Fig 1. Optimized structure of (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one

Table 1. Optimized geometrical parameters	bond length and b	bond angles of title mo	ecule by B3LYP/6-
311++G(d,p) in comparison with experiment	tal values		

		B3LYP/6-	Parameter		B3LYP/6-
Parameter table	Experimental	311++G(d,p)	table	Experimental	311++G(d,p)
Bond length					
C ₁ - C ₂	1.517	1.505	C ₂ - C ₃ - H ₂₁	120	121
C ₁ - O ₄	1.208	1.224	C ₁₃ - C ₃ - H ₂₁	120	119
C ₁ - C ₅	1.517	1.503	C ₃ - C ₁₃ - C ₁₄	120	119
C ₂ - C ₃	1.337	1.345	C ₃ - C ₁₃ - C ₁₈	120	120
C ₂ - H ₂₀	1.1	1.086	$C_6 - C_5 - C_{10}$	120	120
C ₃ - C ₁₃	1.503	1.47	$C_5 - C_6 - C_7$	120	120
C ₃ - H ₂₁	1.1	1.081	$C_5 - C_6 - O_{11}$	120	120
C ₅ - C ₆	1.42	1.43	$C_5 - C_{10} - C_9$	120	120
C ₅ - C ₁₀	1.42	1.402	C ₅ - C ₁₀ - H ₂₅	120	120
C ₆ - C ₇	1.42	1.403	C ₇ - C ₆ - O ₁₁	120	121
C ₆ - O ₁₁	1.355	1.347	C ₆ - C ₇ - C ₈	120	121
C ₇ - C ₈	1.42	1.389	C ₆ - C ₇ - H ₂₂	120	120
C ₇ - H ₂₂	1.1	1.08	C ₆ - O ₁₁ - C ₁₂	120	120
C ₈ - C ₉	1.42	1.39	C ₈ - C ₇ - H ₂₂	120	119
C ₈ - H ₂₃	1.1	1.084	C ₇ - C ₈ - C ₉	120	120
C ₉ - C ₁₀	1.42	1.389	C ₇ - C ₈ - H ₂₃	120	119
C ₉ - H ₂₄	1.1	1.083	C ₉ - C ₈ - H ₂₃	120	120
C ₁₀ - H ₂₅	1.1	1.075	$C_8 - C_9 - C_{10}$	120	119
O ₁₁ - C ₁₂	1.4	1.422	C ₈ - C ₉ - H ₂₄	120	120

C ₁₂ - H ₂₆	1.11	1.088	C ₁₀ - C ₉ - H ₂₄	120	120
C ₁₂ - H ₂₇	1.11	1.095	C ₉ - C ₁₀ - H ₂₅	120	120
C ₁₂ - H ₂₈	1.11	1.095	O ₁₁ - C ₁₂ - H ₂₆	109	109
C ₁₃ - C ₁₄	1.42	1.404	O ₁₁ - C ₁₂ - H ₂₇	109	110
C ₁₃ - C ₁₈	1.42	1.406	O ₁₁ - C ₁₂ - H ₂₈	109	110
C ₁₄ - C ₁₅	1.42	1.392	H ₂₆ - C ₁₂ - H ₂₇	109	109
C ₁₄ - H ₂₉	1.1	1.085	H ₂₆ - C ₁₂ - H ₂₈	109	109
C ₁₅ - C ₁₆	1.42	1.39	H ₂₇ - C ₁₂ - H ₂₈	109	109
C ₁₅ - H ₃₀	1.1	1.082	C ₁₄ - C ₁₃ - C ₁₈	120	119
C ₁₆ - C ₁₇	1.42	1.394	C ₁₃ - C ₁₄ - C ₁₅	120	120
C ₁₆ - Br ₁₉	1.88	1.915	C ₁₃ - C ₁₄ - H ₂₉	120	120
C ₁₇ - C ₁₈	1.42	1.388	C ₁₃ - C ₁₈ - C ₁₇	120	120
C ₁₇ - H ₃₁	1.1	1.082	C ₁₃ - C ₁₈ -H ₃₂	120	120
C ₁₈ - H ₃₂	1.1	1.083	C 15- C14 -H29	120	120
Bond angles			C ₁₄ - C ₁₅ - C ₁₆	120	120
C ₂ - C ₁ - O ₄	120	119	C ₁₄ - C ₁₅ - H ₃₀	120	120
$C_2 - C_1 - C_5$	120	119	C ₁₆ - C ₁₅ - H ₃₀	120	120
$C_1 - C_2 - C_3$	120	120	C ₁₅ - C ₁₆ - C ₁₇	120	120
C ₁ - C ₂ - C ₂₀	120	120	$C_{15} - C_{16} - Br_{19}$	120	120
O ₄ - C ₁ - C ₅	120	120	C ₁₇ - C ₁₆ - Br ₁₉	120	120
$C_1 - C_5 - C_6$	120	120	C ₁₆ - C ₁₇ - C ₁₈	120	120
$\overline{C_1 - C_5 - C_{10}}$	120	121	$C_{16} - C_{17} - H_{31}$	120	120
C ₃ - C ₂ - H ₂₀	120	118	C ₁₈ - C ₁₇ - H ₃₁	120	120
$\overline{C_2 - C_3 - C_{13}}$	120	120	$C_{17} - C_{18} - H_{32}$	120	120

This molecule has sixteen C - C bond lengths, three C - O bond length, thirteen C - H bond lengths and one C - Br bond length. It is observed that the calculated C - C bond distances are higher than the C - N bond lengths, they are found to beslight difference at all levels of calculations. From theoretical values, we found most of the optimized bond lengths are ingood agreement with experimental bonds lengths, but bond angles are slightly longer and shorter than that of experimental values.

Vibrational Assignments

The experimental FT-IR and FT-Raman spectra for (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one are shown in Fig 2 and Fig 3. The vibrational frequencies calculated at B3LYP/6-311++G(d,p) levels were scaled to a factor 0.9641. The vibrational frequencies along with the approximate description about each normal mode of vibration obtained using the basis set B3LYP/6-311++G(d,p) are given in Table 2. The relative intensities were obtained by dividing the computed value by the intensity of the strongest line. Computed intensities and the observed values show intermediate deviation since the computed wave numbers corresponds to the isolated molecular state whereas the observed wave numbers correspond to the solid state spectra. ChemCraft, which is a graphical interface, was used to assign the calculated harmonic wave numbers usingdisplacement vectors to identify the motion of modes.The predicted vibrational wave numbers and the experimental data are well in agreement with each other.

	Obse	erved	Calculated frequencies(cm-1)		(cm-1)	Vibrational modes	
S.No	frequenc	ies(cm-1)	DFT/6-3	311++G(a	l,p)		(>10% PED)
	FT-IR	FT- Raman	unscaled	scaled ^a	IR ^b	Raman ^c	
90	3305(w)	3300(w)	3292	3174	4	111	v CH (94)
89	3234(w)	-	3217	3101	8	154	v CH (95)
88	-	3210(w)	3205	3090	15	30	v CH(90)
87	-	3204(w)	3204	3089	2	140	v CH (93)
86	3201(w)	3200(w)	3201	3086	3	81	v CH (89)
85	-	-	3189	3075	18	176	v CH (96)
84	3198(vw)	3190(w)	3188	3073	1	20	v CH(97)
83	-	3176(w)	3170	3057	3	85	v CH (97)
82	3100(vw)	3160(w)	3164	3050	6	48	v CH (95)
81	-	-	3156	3042	8	46	v CH (96)
80	-	3018(w)	3139	3026	16	110	v CH (92)
79	3060(w)	3062(m)	3069	2959	34	86	v CH (100)
78	3005(w)	3018(w)	3007	2899	75	224	v CH (92)
77	-	-	1678	1618	304	866	v OC (79)
76	-	-	1675	1615	59	1783	v CC(57) +β HCCC(14)
75	-	1639(s)	1639	1580	45	89	v CC(66)
74	1633(ms)	1620(vs)	1623	1565	63	2352	v CC(31)
73	1572(ms)	1589(s)	1604	1547	55	305	v CC(37)
72	1566(s)	1563(ms)	1597	1539	12	97	$v CC(45) + \beta CCC(10)$
71	-	-	1519	1464	42	22	β HCC(94)
70	-	-	1514	1459	78	65	β HCH (67)
69	-	-	1498	1444	120	22	β HCC(25) + β HCH(29)
68	-	-	1497	1443	9	15	β HCH (67)+tHCOC(17)
67	1484(s)	-	1489	1435	1	35	v CC (10)+ β HCC(29) + β HCH (21)
66	-	1404(vw)	1463	1410	50	18	β HCC(42) + β HCH (45)
65	1418(s)	-	1433	1381	22	77	$v CC (32) + \beta HCC(22)$
64	-	-	1371	1322	17	159	$v CC(12) + \beta HCC(43)$
63	1351(s)	-	1358	1309	29	385	β HCC(64)
62	-	-	1332	1285	3	7	v CC(66)
61	-	-	1327	1279	8	26	β HCC(76)
60	-	1306(w)	1313	1266	48	96	$v CC(23) + v OC(13) + \beta HCC(10)$
59	-	1286(w)	1298	1251	205	74	v OC(23)
58	1268(s)	1272(w)	1283	1237	20	37	v CC(12)
57	-	1253(ms)	1251	1206	150	473	v CC(43)
56	-	-	1228	1184	311	137	$v CC(18) + \beta HCC(10)$
55	-	1206(w)	1209	1165	13	347	β HCC(72)
54	-	-	1202	1159	24	14	β HCC(13) + t HCOC(56)
53	-	1176(ms)	1189	1146	84	3	β HCC (72)
52	1168(ms)	-	1164	1122	1	2	β HCC(28) + t HCOC(72)
51	-	-	1162	1120	24	31	$v CC(30) + \beta HCC(18)$
50	1134(ms)	1123(w)	1135	1094	12	2	$v CC(27) + \beta HCC(55)$
49	1068(ms)	1087(ms)	1086	1047	28	108	v CC(27) + v BrC(10)
48	-	-	1085	1046	47	17	v CC (29)

Table 2.Vibrational wave numbers obtained for at DFT/6-311++G(d,p) [(harmonic frequency cm⁻¹, IR intensities (K mmol⁻¹, Raman intensities (units)].

47	-	-	1049	1011	47	4	$v OC(65) + \beta CCC(13)$
46	-	1032(w)	1042	1004	136	339	$v CC(18) + \beta CCC(28)$
45	-	-	1022	985	66	60	β CCC(85)
44	1001(ms)	-	1007	971	34	0	t HCCC(87)
43	983(ms)	-	980	945	1	0	t HCCC(72) + t CCCC(12)
42	-	964	978	943	1	0	t HCCC(73) + t CCCC(11)
41	-	-	959	924	1	2	t HCCC(68) + t CCCC(10)
40	945(w)	-	930	896	0	1	t HCCC(74)
39	-	-	893	861	1	10	t $CCCC(29)$ + out of tor $OCCC(14)$
38	-	-	861	830	3	10	$\gamma CC(12) + \beta CCC(39)$
37	851(w)	848(vw)	852	821	30	1	t HCCC (35)+out of CCCC(11)
36	-	-	830	800	3	0	t HCCC(77)
35	-	-	825	796	7	0	t HCCC(62)
34	782(ms)	-	819	789	10	62	$\gamma \text{ OC}(18) + \beta \text{ CCC}(24)$
33	-	769(vw)					$t \operatorname{HCCC}(18) + t \operatorname{CCCC}(10) + \text{out of}$
			771	743	14	4	torsion OCCC(17)
32	717(s)	722()	751	724	57	0	t HCCC(69) + out of torsion
31	_	723(W)	724	724	3/ 17	1	$\frac{OCCC(17)}{VCC(10) + 0.000CC(18)}$
30	_	_	734	/08	1/	1	$\frac{1}{\sqrt{CC(10) + \beta CCC(18)}}$
20	-	-	/21	695	2	25	r = PrC(11) + 0.0000(12)
29	669(W)	687(W)	680	656	28	35	$v BrC(11) + \beta CCC(13)$ t CCCC (23) + out of torsion
20	-	-	671	647	2	0	CCCC(25)
27	647(w)	658(w)	650	627	15	5	$\beta \text{ OCC}(18) + \beta \text{ CCC}(25)$
26	-	633(w)	638	615	19	5	β CCC(37) + β OCC(15)
							$\frac{\beta \text{ OCC}(34) + \beta \text{ CCC}(11) + \beta}{\beta \text{ OCC}(34) + \beta \text{ CCC}(11) + \beta}$
25	-	573(w)	578	557	3	27	COC(17)
24	550(ms)	-	565	545	3	13	β CCC(40)
22	542())		521	510	2	0	t HCCC(29) + t CCCC(13) + out of $CCCC(24)$
23	543(ms)	-	531	512	2	0	$\frac{00000(34)}{1000000000000000000000000000000000000$
22	_	_	497	479	23	0	BrCCC(15) + out CCCC(22)
21	438(w)	_	444	428	1	3	$\beta CCC(17) + \beta COC(17)$
20	-	_	431	415	0	0	t CCCC(55)
19	404(w)	-	413	398	0	0	$t \operatorname{HCCC}(12) + t \operatorname{CCCC}(64)$
18	-	385(vw)	387	373	7	1	$v CC(10) + \beta CCC(33)$
17	-	-	381	367	5	3	$v CC (22) + \beta OCC(23)$
16	-	-	319	308	2	1	$v Br C(29) + \beta COC (15)$
							out of torsion BrCCC(36) + out
15	-	310(vw)	313	302	0	1	CCCC(4) + t CCCC(12)
14	-	-	282	272	0	1	$t \operatorname{HOCC}(25) + t \operatorname{HCOC}(20)$
13	-	-	275	265	5	1	$\beta \text{ OCC}(29) + \beta \text{ COC}(30)$
10			222	224	0	1	t CCCC(40) + t COCC(10) + t
12	-	211()	233	224	1	1	$\frac{0}{0} \frac{0}{10} \frac{1}{10} + 0 \frac{1}{10} \frac{1}{10$
10	-	211(W)	150	154	1	1	$\beta CCC(11) + \beta BrCC(49)$
10	-	155(W)	139	154	2	0	
9	-	138(W)	138	133	1	2	t CCC(56) + out of tor BrCCC(22)
8	-	119(VW)	101	12/		1	v CC(10) + p CCC(24)
/	-	105(W)	101	98	0	5	t UUU(45) + t HOUU(12) t HCOC(10)+ t CCCC(10)+ t
6	-	88(w)	97	94	3	1	COCC(60)
5	-	65(w)	51	49	1	1	$\beta \operatorname{CCC}(52) + \operatorname{v} \operatorname{CC}(29)$
L		('')			-	-	· · · · · · · · · · · · · · · · · · ·

4	-	-	36	35	0	0	t $CCCC(55)$ + out of tor $CCCC(19)$
3	-	-	22	22	0	1	t CCCC(89)
2	-	-	16	16	3	1	t CCCC(79)
1	-	_	10	10	0	1	$t \operatorname{HCCC}(10) + t \operatorname{CCCC}(47)$

Note : s: strong, vs: very strong, m: medium, ms: medium strong, w: weak, v:stretching, β : in plane bending, γ : out of plane bending, t: torsion, sym: symmetric stretching,asym: asymmetric stretching,

a Scaling factor: 0.961 for DFT(B3LYP)/6-311++G(d,p).

b Relative absorption intensities normalized with highest peak absorption equal to 100.

c Relative Raman intensities normalized to 100.



Wavenumber cm⁻¹

Fig.2. (a) Experimental (b) theoretical FT-IR spectra of (2*E*)-3-(4-bromophenyl)-1-(2-methoxyphenyl) prop-2-en-1-one



Wavenumber cm⁻¹

Fig.3. (a) Experimental (b) theoretical FT-Raman spectra of (2*E*)-3-(4-bromophenyl)-1-(2-methoxyphenyl) prop-2-en-1-one

C-H Vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000 cm⁻¹[22] which is the characteristic region for the ready identification of C-H vibration. In these compounds C-

H vibration absorption bands are usually weak; in many cases it is too weak for detection. Scaled vibrations assigned to the aromatic C H stretching computed in the range 3174, 3101, 3090, 3089, 3086, 3075, 3073, 3057, 3050, 3042, 3026, 2959, 2899 cm⁻¹ by B3LYP/6-311++G(d,p) method shows good agreement to the experimental FT-IR at 3060, 2983 cm⁻¹ and FT-Raman at 3062 and 3018 cm⁻¹

C-C Vibrations

The C-C aromatic stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra covering the spectral range from 1500 – 1650cm⁻¹[23,24]. In general, the bands are of variable intensity and according to Varsanyi, the five bands in this region are observed at 1489,1433, 1371,1332,1283,1228,1162. Neville and Shrvell have identified the IR bands at 1470, 1484, 1561, 1575, 1590cm⁻¹ in diazepam and closely related compounds of benzodiazepines due to aromatic CC stretching vibrations. Based on these factors, in the present study the stronger C-C vibrations occurs at 1590, 1600cm⁻¹ in the FT-IR spectrum and 1577, 1596cm⁻¹ in the FT-Raman spectrum.

C = O Vibrations

The carbonyl stretching frequency has been most extensively studied by infrared spectroscopy [25]. This multiple bonded group is high polar and therefore give rise to an intense infrared absorption band. In the present study the carbonyl stretching vibrations are found in the region of 1780 - 1700 cm [26]. Inour present study, the strong band at 1775 cm⁻¹ in FT-IR and 1737 cm⁻¹ as a weak band in FT-Raman spectrum are assigned to C – Ostretching vibration shows small deviation calculated by B3LYP/6-311++G(d,p) method at 1678 cm⁻¹ with PED contribution of 90%, the shift of the C – Ostretching frequency to the low frequency side indicate the presence of a strong intermolecularhydrogen bonding, as discussed above in this manuscript. The C – Oout of plane bending are observed as intense bands in the IR spectrum in the expected regions [27] at 782 cm⁻¹ in FT-IR spectrum.

C – Br Vibrations

The vibrations belonging to the bond between the ring and thehalogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of the molecular symmetry andthe presence of heavy atoms on the periphery of molecule. Generally,the C – Br absorption is obtained in the region between850 and 550 cm⁻¹[28]. Therefore, the strong band found at669 cm⁻¹ in the FT-IR spectrum has been designated to C – Br stretching mode of vibration and at 687 cm⁻¹ in the FT-Raman spectrum with 70% PED contribution. The band identified at 310 cm⁻¹ in Raman is assigned to the C – Br out of torsion-plane mode.

NLO properties

Non-linear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. NLO is at the forefront of current research because of its importance in providing 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 [29-31]. Organic molecules that exhibit extended p conjugation, in particular, show enhanced second order NLO properties. [32,33].

The first hyperpolarizability(β) of this novel molecular system and the related properties (μ,α,β_0) of LAO are calculated using the B3LYP/6-311++G(d,p) basis set, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpoarizability is a third-rank tensor that can be described by a 3 x 3 x 3 matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Klein man symmetry [34]. It can be given in the lower tetrahedral. The components are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogenous, this expansion becomes:

$$\begin{split} &E=E^{O}-\mu\alpha F\alpha-1/2\alpha\alpha\beta F\alpha F\beta-1/6\beta\alpha\beta\gamma F\alpha F\beta F\gamma+.... \\ &The total static dipole moment is \\ &\mu=(\mu_{x}^{2}+\mu_{y}^{2}+\mu_{z}^{2})^{1/2} \\ &The isotropic polarizability is \end{split}$$

 $\begin{aligned} \alpha_0 &= \alpha_{xx} + \alpha_{yy} + \alpha_{zz}/3 \\ \text{The polarizability anisotropy invariant is} \\ \alpha &= 2^{1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6 \alpha^2_{xx}]^{1/2} \\ \text{and the average hyperpolarizability is} \\ \beta &= (\beta^2_x + \beta^2_y + \beta^2_z)^{1/2} \\ \beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_y &= \beta_{yyy} + \beta_{xxy} + \beta_{yyz} \\ \beta_z &= \beta_{zzz} + \beta_{xxy} + \beta_{yyz} \end{aligned}$

Where E° is the energy of the unperturbed molecules, F is the field at the origin and are the components of dipole moment, polarizability and first order hyperpolarizabilities, respectively. The total static dipole moment (μ), polarizability (α) and the first order hyperpolarizability (β), using the x,y,z components are defined as follows. The calculated hyperpolarizability values of (2*E*)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one are listed in Table 3. According to the present calculation values of dipole moment and first order hyperpolarizability of (2*E*)-3-(4-bromophenyl)prop-2-en-1-one from B3LYP/6-311++G (d,p) basis set are 1.4348 Debye and 1.5741 esu as shown in Table 3. Total dipole moment of the title molecule is approximately only one time greater than those of the urea (1.3732 D) and first hyperpolarizability of the molecule is approximately four times greater than those of urea (0.372 esu).Based on these facts, it could be concluded that the present materialhas a reasonably good propensity for nonlinear optical activity.

Table 3. The electric dipole moments (Debye), polarizability (in esu), β components and β tot (10⁻³⁰esu) value of title compound calculated by B3LYP/ 6-311++G(d,p) method.

Parameter	B3LYP/6- 311++G(d,p)	Parameter	B3LYP/6- 311++G(d,p)
μ _x	1.092362	βxxx	1101.8834
μ_{y}	-0.930407	βxxy	1174.2724
μ _z	-0.0000397	βxyy	767.9546
μ(D)	1.4348	βууу	211.45786
$\alpha_{\rm xx}$	340.4961	βzxx	-0.22492
α_{xy}	80.909	βxyz	0.05998
α_{yy}	263.5495	βzyy	0.2361
α_{xz}	0.00022	βxzz	40.9022
$\alpha_{\rm yz}$	-0.00057	βyzz	-74.8852
α_{zz}	108.7203	βzzz	-0.1822
a (e.s.u)	1.611x 10 ⁻²³	βtot (e.s.u)	1.574×10^{-23}
Δa (e.s.u)	2.3879x10 ⁻⁴⁸		

NBO analysis

NBO analysis transforms molecular orbital wave functions into one-center (lone pair) and two-center (bond) representations [35]. The advantage of NBO analysis is that they provide insight into the interactions between various parts of the molecule [36]. The bond-antibond and lone-pair-antibond interactions can be calculated by two difference procedures following the NBO method [37]. The first one is an indirect procedure as suggested by Weinhold, which involves comparison of barrier energies calculated with and without the Fock matrix element (F_{ij}) [38]. The second procedure involves the estimations of all possible interactions between "filled" (donor) Lewis type NBO s and "empty" (acceptor) non-Lewis NBOs, by considering their energetic importance using second order perturbation theory. Since these interactions lead to the donation of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals, they are referred to as "delocalization" corrections to the zeroth-order natural Lewis structure. For each donor NBO (i) and acceptor (j), the stabilization energy E(2) associated with delocalization i -> j is represented as:

$$E(2) = \Delta E_{ij} = q_i (F_{ij})^2 / (\varepsilon_j - \varepsilon_i)$$

Where q_i is the donor orbital occupancy, F_{ij} is the off-diagonal and ε_j , ε_i are diagonal elements specifying the respective orbital energies of the NBO Fock matrix.

NBO analysis has been performed on the molecule the B3LYP/6-311+ at +G(d,p) level in order to elucidate the intra – molecular, rehybridisation and de-localization of electron density within the molecule. The strong intramolecular hyper conjugative interaction of the σ and π electrons of C – C to the antibond C - C bond in the ring leads to stabilization of some part of the ring as evident from Table 4. The intramolecularhyperconjugative interactions of the σ and π electrons of C – H to the antibond C – H bond in the ring leads to stabilization of some part of ring as evident from the Table 4. The intramolecular hyperconjugative interactions of σ (C₁₀ - H₂₅) orbital to σ^* (C₃ - H₂₁) and σ (C₃ - H₂₁) orbital to σ^* (C₁₀- H₂₅) leads to strongest stabilization energy of 206 k J/mol and 200 k J/mol. For $\pi(C_2 - C_3)$ orbital to $\pi^*(C_1 - O_4)$ shows the stabilization energy of 29.35 k J/mol. Similarly $\pi(C_5 - C_6)$ bonding orbital to antibonding orbital π^* (C₁ - O₄) and (C₉ - C₁₀) shows the highest energy of 27.78 k J/mol and 24.37 k J/mol. Therefore, the maximum energy delocalization takes place in the π to π^* transition. The E(2) values and types of the transition are shown in Table 4.

							E(j) -	
Donor	Туре	ED/e	Acceptor	Туре	ED/e	E(2)	E(i)	F(i,j)
C ₁ - C ₂	σ	1.97431	C ₁ - O ₄	σ*	1.98743	3.77	1.38	0.064
			C ₂ - C ₃	σ*	1.9734	3.61	1.38	0.063
			C ₃ - C ₁₃	σ*	1.95997	2.96	1.37	0.057
C ₁ - O ₄	σ	1.98743	C ₁ - C ₂	σ*	1.97431	3.72	1.67	0.071
			C ₂ - C ₃	σ*	1.9734	1.1	1.7	0.039
			C ₅ - C ₁₀	σ*	1.95942	1.66	1.7	0.048
	π	1.92106	C ₂ - C ₃	π*	1.80093	10.36	0.39	0.058
			C ₅ - C ₆	π*	1.59105	7.12	0.4	0.053
C ₁ - C ₅	σ	1.95997	C ₁ - C ₂	σ*	1.97431	5.49	1.34	0.077
			C ₁ - O ₄	σ*	1.98743	3.76	1.37	0.064
			C ₂ - H ₂₀	σ*	1.96957	2.67	1.13	0.049
C ₂ - C ₃	σ	1.9734	C ₁ - C ₂	σ*	1.97431	3.07	1.36	0.058
			C ₁ - O ₄	σ*	1.98743	3.91	1.39	0.066
			C ₂ - H ₂₀	σ*	1.96957	1.13	1.15	0.032
	π	1.80093	C ₁ - O ₄	π*	1.92106	29.35	0.32	0.088
			C ₉ - C ₁₀	π*	1.97004	1.37	0.32	0.019
			C ₁₃ - C ₁₄	π*	1.60785	19.73	0.32	0.075
C ₂ - H ₂₀	σ	1.96957	C ₁ - C ₂	σ*	1.97431	1.17	1.15	0.033
			C ₁ - O ₄	σ*	1.98743	0.98	1.17	0.03
C ₃ - H ₂₁	σ	1.7786	C ₁ - C ₂	σ*	1.97431	0.56	1.05	0.023
			C ₂ - H ₂₀	σ*	1.96957	4.37	0.85	0.057
			C ₃ - H ₂₁	σ*	1.7786	22.95	1.31	0.155
			C ₉ - C ₁₀	σ*	1.97004	3.8	1.08	0.06
			C ₁₀ - H ₂₅	σ*	1.77473	200.28	1.31	0.461
C ₅ - C ₆	σ	1.95613	C ₁ - C ₂	σ*	1.97431	2.44	1.36	0.051
			C ₁ - C ₅	σ*	1.95997	7.15	1.35	0.088
			C ₅ - C ₁₀	σ*	1.95942	7.74	1.39	0.093
			C ₆ - C ₇	σ*	1.9704	6.97	1.38	0.088
	π	1.59105	C ₁ - O ₄	π*	1.92106	27.78	0.31	0.087
			C ₅ - C ₆	π*	1.59105	1.7	0.32	0.021
			C ₇ - C ₈	π*	1.68114	18.45	0.31	0.069
			C ₉ - C ₁₀	π*	1.97004	24.37	0.31	0.079
C ₇ - C ₈	σ	1.97033	C ₆ - C ₇	σ*	1.9704	4.9	1.38	0.073
			C ₆ - O ₁₁	σ*	1.98823	4.41	1.12	0.063
			C ₇ - H ₂₂	σ*	1.97071	1.94	1.14	0.042
			C ₈ - C ₉	σ*	1.97111	4.45	1.38	0.07
			C ₈ - H ₂₃	σ*	1.97882	1.3	1.15	0.035
			C ₉ - H ₂₄	σ*	1.97648	3.3	1.15	0.055

Table 4.Second order perturbation theory analysis of Fock matrix in NBO basis.

	π	1.68114	C ₅ - C ₆	π*	1.59105	25.36	0.32	0.082
			$C_9 - C_{10}$	π^*	1.68065	19.38	0.31	0.07
C ₇ - H ₂₂	σ	1.97071	C ₅ - C ₆	σ*	1.95613	3.94	1.15	0.06
			C ₆ - C ₇	σ*	1.9704	1.52	1.16	0.038
C ₉ - C ₁₀	σ	1.97004	C ₉ - H ₂₄	σ*	1.97648	1.43	1.14	0.053
			C ₁₀ - H ₂₅	σ*	1.77473	1.61	1.61	0.047
			C ₅ - C ₆	π*	1.59105	19.63	0.31	0.072
			C ₇ - C ₈	π*	1.97033	24.4	0.31	0.078
			$C_5 - C_{10}$	σ^*	1.95942	4.15	1.16	0.062
	π	1.68065	C ₈ - H ₂₃	σ*	1.97882	0.69	0.92	0.023
			$C_9 - C_{10}$	σ*	1.97004	1.4	1.16	0.036
C ₉ - H ₂₄	σ	1.97648	C ₁₀ - H ₂₅	σ*	1.77473	1.17	1.39	0.038
			C ₁ - C ₅	σ*	1.95997	0.53	1.04	0.022
			C ₃ - C ₁₃	σ*	1.95997	3.99	1.06	0.061
			C ₃ - H ₂₁	σ*	1.7786	206.57	1.3	0.465
C ₁₃ - C ₁₄	σ	1.95716	C ₁₅ - H ₃₀	σ*	1.97405	2.89	1.12	0.051
			C ₁₈ - H ₃₂	σ*	1.97094	2.83	1.14	0.051
			C ₂ - C ₃	π*	1.80093	21.93	0.31	0.079
			C ₁₅ - C ₁₆	π*	1.67329	24.95	0.29	0.077
			C ₁₇ - C ₁₈	π*	1.96266	20.46	0.31	0.073
C ₁₅ - C ₁₆	σ	1.97374	C ₁₃ - C ₁₄	π*	1.60785	18.62	0.33	0.071
			C ₁₃ - C ₁₈	π^*	1.95302	20.8	0.33	0.075
			C ₁₃ - C ₁₄	σ*	1.95716	3.43	1.13	0.056
C ₁₇ - C ₁₈	σ	1.96266	C ₁₈ - H ₃₂	σ*	1.97094	1.52	1.15	0.038
			C ₁₃ - C ₁₄	π*	1.60785	22.47	0.32	0.077
			C ₁₅ - C ₁₆	π*	1.67329	22.21	0.3	0.073
			C ₁₃ - C ₁₈	σ*	1.95302	3.52	1.13	0.057
C ₁₈ - H ₃₂	σ	1.97094	C ₁₇ - H ₃₁	σ*	1.9747	0.71	0.92	0.023
			C ₁ - C ₂	σ*	1.97431	1.58	1.29	0.041
			C ₁ - C ₅	σ*	1.95997	1.15	1.28	0.035
			C ₅ - C ₆	σ*	1.95613	1.02	1.15	0.031
$LP(1)O_4$	σ	1.98125	C ₁₂ - H ₂₇	σ*	1.993	0.85	0.87	0.024
			C ₁₂ - H ₂₈	σ^*	1.993	0.86	0.87	0.025
$LP(1)O_{11}$	σ	1.9607	$C_5 - C_6$	π*	1.59105	30.74	0.35	0.099
			$C_{15} - C_{16}$	σ*	1.97374	1.73	1.63	0.048

Chemical reactivity

Global and local reactivity descriptors

The energy gap between HOMO and LUMO is a critical parameter to determine molecular electrical transport properties. By using HOMO and LUMO energy values for a molecule, the global reactivity descriptors of molecule such as hardness, chemical potential, softnesss, electronegativity and electrophilicity index as well as local reactivity have been defined [39-43]. Pauling introduced the concept of electronegativity as the power of an atom in a molecule to attract electrons to it. Hardness (η), chemical potential (μ) and electronegativity (χ) and softness are defined as follows.

$$\begin{split} \chi &= -\frac{1}{2} \left(E_{LUMO} + E_{HOMO} \right) \\ \mu &= -\chi = \frac{1}{2} \left(E_{LUMO} + E_{HOMO} \right) \\ \eta &= \frac{1}{2} \left(E_{LUMO} + E_{HOMO} \right) \end{split}$$

Softness is a property of molecule that measures the extent of chemical reactivity. It is the reciprocal of hardness.

 $S = 1/2\eta$

Considering the chemical hardness, large HOMO-LUMO gap means a hard molecule and small HOMO – LUMO gap means a soft molecule. One can also relate the stability of the molecule to hardness, which measures that the molecule with least HOMO – LUMO gap means it is more reactive. Recently Parr et al. have defined a new descriptor to qualify the global electrophilic power of a molecule as electrophilicity index (ω), which defines a quantitative classification of a global electrophilic nature of a molecule Parr et al. have proposed electrophilicity index (ω) as a measure of energy lowering due to the maximum electron flow between donor and acceptor. They defined electrophilicityindex(ω) as follows

 $\omega = \mu^2/2\eta$

Using the above equations, the chemical potential, hardness and electrophilicity index have been calculated for (2E)-3-(4-bromophenyl)-1-(2- methoxyphenyl)prop-2-en-1-one and their values are shown in Table 5. The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [44-46]. The calculated value of electrophilicity index describes the biological activity of (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one .

Table 5. Condensed Fukui table f_k and descriptors $(sf)_k$ for 2(E)-3-(4-bromophenyl)-1-(2-methoxyphenyl) prop-2-en-1-one

Atoms	$\mathbf{f_k}^+$	$\mathbf{f}_{\mathbf{k}}$	$\mathbf{s}_{\mathbf{k}}^{\dagger}\mathbf{f}_{\mathbf{k}}^{\dagger}$	s kf k	
C ₁	-0.0183	0.0353	-0.0052	0.01	
C ₂	-0.1725	-0.0465	-0.0492	-0.0132	
C3	0.0927	0.0923	0.0264	0.0263	
O4	0.286	0.1278	0.0815	0.0364	
C5	-0.0071	-0.0185	-0.002	-0.0052	
C6	0.0179	-0.0233	0.0051	-0.0066	
C7	0.0746	0.0451	0.0212	0.0128	
C8	0.055	0.0358	0.0156	0.0102	
C9	0.0677	0.0401	0.0193	0.01144	
C10	-0.0093	0.0423	-0.0026	0.012	
011	-0.0413	-0.0177	-0.0117	-0.005	
C12	-0.0095	-0.0027	-0.0027	-0.0007	
C13	0.058	0.0057	0.0165	0.0016	
C14	0.0455	0.0229	0.0129	0.0065	
C15	-0.0236	-0.0053	-0.0067	-0.0015	
C16	0.0496	0.0486	0.0141	0.0138	
C17	-0.0065	0.0124	-0.0018	0.0035	
C18	0.0366	0.0527	0.0104	0.014	
Br19	0.1036	0.1236	0.0295	0.0352	
H20	0.0338	0.0586	0.0096	0.0167	
H21	0.0256	0.026	0.0073	0.0074	
H22	0.0368	0.0395	0.0104	0.0112	
H23	0.055	0.0535	0.0156	0.0152	
H24	0.0511	0.0431	0.0145	0.0122	
H25	-0.0115	-0.0159	-0.0032	-0.0045	
H26	0.0336	0.0264	0.0095	0.00753	
H27	0.0371	0.0242	0.0105	0.0069	
H28	0.0371	0.0243	0.0105	0.0069	
H29	0.021	0.0396	0.0059	0.0113	
H30	0.031	0.0342	0.0088	0.0097	
H31	0.0299	0.0421	0.0085	0.012	
H32	0.0201	0.0204	0.0057	0.0058	

Local reactivity descriptors

Fukui functions $(f_k^*; f_k^*; f_k^o)$, local softness $(s_k^*; s_k^*; s_k^o)$ and localelectrophilicity indices $(\omega_k^*; \omega_k^o; \omega_k^o)$ [47,48] for selected atomicsites in have been listed in Table 5. Using Hirshfeld atomic charges of neutral, cation and anionstates of the compound, the fukui functions are calculated using the following equations:

 $f_k^+ = [q(N+1)-q(N)]$ for nucleophilic attack $f_k = [q(N)-q(N-1)]$ for electrophilic attack $f_k^\circ = 1/2 [q(N+1)-q(N-1)]$ for radical attack Local softness and electrophilicity indices are calculated usingthe following equations $s_k^+ = Sf_k^+, s_k^- = Sf_k, s_k^\circ = Sf_k^\circ$ $\omega_k^+ = \omega f_k^+, \omega_k^- = \omega f_k, \omega_k^\circ = \omega f_k^\circ$ where +,-,o signs show nucleophilic, electrophilic and radical attack respectively.

The maximum values of all three local electrophilic reactivity descriptors $(f_k^+; s_k^+; \omega_k^+)$ at atom O4>Br19>C3>C7 indicate that this site is prone to nucleophilic attack. In the same way, the maximum values of the nucleophilic reactivity descriptors $(f_k^-; s_k^-; \omega_k^-)$ at O4>Br19>C3>H20 indicate that this site is more prone to electrophilic attack.

Molecular electrostatic potential

Electrostatic potential maps, also known as electrostatic potential energy maps, or molecular electrical potential surfaces, illustrate the charge distributions of molecules three dimensionally. The purpose of finding the electrostatic potential is to find the reactive site of the molecule. These maps allow us to visualize variably charged regions of a molecule. Knowledge of the charge distributions can be used to determine how molecules interact with one another. Molecular electrostatic potential (MESP) mapping is very useful in the investigation of the molecular structure with its physiochemical property relationships [49-52]. Total SCF electron density surface mapped with molecular electrostatic potential of is shown in Fig 4. The molecular electrostatic potential surface which is a 3D plot of electrostatic potential mapped onto the iso-electron density surface is red electron rich or partially negative charge; blue-electron deficient or partially positive charge; light blue-slightly electron deficient; yellow electrons. Nitrogen has a higher electronegativity value would consequently have a higher electron density around them. Thus the spherical region corresponds to nitrogen atom would have a red portion on it. The MESP of (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one clearly indicates the electron rich centres of nitrogen, oxygen and Cl atoms.



Fig 4. Molecular electrostatic potential of (2*E*)-3-(4-bromophenyl)-1-(2- methoxyphenyl)prop-2-en- 1-one Thermodynamic properties

The total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies, i.e., E = Et + Er + Ev + Ee. The statistical thermo chemical analysis of 2 2E)-3-(4-bromophenyl)-1-(2-

methoxyphenyl)prop-2-en-1-oneis carried out considering the molecule to be at room temperature of 298.15 K and one atmospheric pressure. On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions: heat capacity ($C_{p,m}^{\circ}$), entropy (S_{m}°) and enthalpy (H_{m}°) were obtained and listed in Table 6. As it is evident from Table 6, all the values of $C_{p,m}^{\circ}$, S_{m}° , H_{m}° increases with the increase of temperature from 100K to 1000K, which is attributed to the enhancement of the molecular vibration while the temperature increases because at a constant pressure (db = 1atm) values of $C_{p,m}^{\circ}$, S_{m}° , H_{m}° are equal to the quantity of temperature [53]. The correlations between these thermodynamic properties and temperatures are fitted by quadratic formulas as follows and corresponding fitting factors (\mathbb{R}^{2}) for these thermodynamic properties are found to be 0.999, 0.999 and 0.999 for heat capacity, entropy and enthalpy, respectively. The temperature dependence correlation graphs are shown in Fig 5. Scale factors have been recommended [54] for an accurate prediction in determining the zero-point vibration energies, heat capacities, entropies and enthalpies.

Table6. Thermodynamic properties at different temperatures at B3LYP/6-311++G(d,p) level

	S	Ср	ΔH
I (K)	(J/mol.K)	(J/mol.K)	(kJ/mol)
100	365.28	110.5	7.25
200	464.43	184.92	21.98
298	552.76	263.14	43.95
300	554.39	264.62	44.43
400	641.16	340.78	74.78
500	724.4	405.6	112.2
600	803.17	458.18	155.49
700	877.11	500.62	203.5
800	946.29	535.28	255.35
900	1011.05	563.99	310.36
1000	1071.75	588.05	368





Fig 5. Correlation graphs of thermodynamic properties at different temperature of the (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one

 $C_{p,m}^{o} = 9.03811 + 0.98938T - 4.11358x10^{-4} T^{2} (R^{2} = 0.999)$ $S_{m}^{o} = 265.485 + 1.0306 T - 2.24464 x 10^{-4} T^{2} (R^{2} = 0.999)$ $H_{m}^{o} = -10.9284 + 0.11264T + 2.70227 x 10^{-4} T^{2} (R^{2} = 0.999)$

All these thermodynamic data provides helpful information forfurther study on 2(E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-onemolecule. They can be used to compute the other thermodynamicparameters according to relationships of thermodynamicfunctions and determine the directions of chemical reactionsaccording to the second law of thermodynamics. Dipole momentreflects the molecular charge distribution and is given as a vectorin three dimensions. Therefore, it can be used an illustrator to depict charge movement across the molecule. Direction of the dipolemoment vector in a molecule depends on the centers of negative and positive charges. Dipole moments are strictly identified for neutral molecules. For charged systems, its value dependson the choice of origin and molecular orientation. As a result the dipole moment of 2(E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one molecule was observed theoretically 1.4348D by B3LYP/6-31++G(d,p) method.

Total sum of alpha and beta electronsDOS



Fig 6. The calculated TDOS diagram of (2E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-one



Fig 7. The calculated αβDOS diagram of (2E)-3-(4-bromophenyl)-1-(2- methoxyphenyl)prop-2-en-1- one

In the boundary region, neighboring orbitals may show quasi degenerate energy levels. In such consideration of only the HOMO and LUMO may not yield a realistic description of frontier orbitals. For this reason, the total DOS (TDOS) and sum of α and β electron density of states [55-57], in terms of Mullikenpopulation analysis were calculated and created by convoluting the molecular orbital information with Gaussian curves of unit height and full width at half maximum (FWHM) of 0.3 e V by using Gausssum 2.2 program [58]. The TDOS and $\alpha\beta$ DOS of 2(E)-3-(4-bromophenyl)-1-(2-methoxyphenyl)prop-2-en-1-oneare plotted in Fig 6 and Fig 7. They provide a pictorial representation of MO (molecule orbital) compositions and their contributions to the chemical bonding. The most application of the DOS plots is to demonstrate MO compositions and their contribution to the chemical bonding through the positive and negative charges provide TDOS and $\alpha\beta$ DOS diagrams. The $\alpha\beta$ DOS shows the bonding, sum of positive and negative electron with nature of the interaction of two orbitals, atoms or groups. In this case, the title molecule consists of 80α electrons and 80 β -electrons, totally 160 electrons are occupied in density of states. The way designate a pictorial representation for cations and anions is essentially similar to that of neutral atoms in their ground state. Because of the short range of absorption, alphas are not, in general, dangerous to life unless the source is ingested or inhaled, in which case they become extremely dangerous. A positive value of the $\alpha\beta$ DOS indicates a bonding interaction, negative value means that there is an anti-bonding interaction and zero value indicates nonbonding interaction [59].HOMO orbitals are localized on the ring and their contributions are about 78%. The LUMO orbitalsare localized on the ring and their contributions are 89% of the compound.

Conclusion

The spectral studies such as FT-IR and FT-Raman for 2(E)-3-(4-bromophenyl)-1-(2-methoxyphenyl) prop-2-en-1-onewas carried out with quantum chemical computations. A complete vibrational and molecular structure analysis has been performed based on the quantum mechanical approach by B3LYP calculations with 6-311++G(d,p) basis set. The vibrational assignment with PED was calculated. The predicted NLO properties of title compound are much greater than those of urea. NBO analysis was made and it was indicated the intra molecular charge transfer between the bonding and anti-bonding orbitals. Furthermore, the thermodynamicparameters and properties of the compound have been calculated. The correlations between the statistical thermodynamics andtemperature are also obtained. It was seen that the heat capacities, entropies and enthalpies increase with the increasing temperatureowing to the intensities of the molecular vibrations increase withincreasing temperature. And also Fukui functions; localsoftness and electrophilicity indices for the selected atomic sites in the molecule have been calculated. Therefore, we hope the results of this present study will help researchers to analyze and synthesizenew materials.

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