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EXPERIMENTAL AND THEORETICAL STUDIES OF 6, 8-DICHLORO-2-(4-METHOXYPHENYL)-4*H*-CHROMEN-4-ONE

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ABSTRACT

6,8-dichloro-2-(4-methoxyphenyl)-4H-chromen-4-one was synthesized from chalcone and characterized by IR, NMR, and UV-VIS spectrophotometer. The optimized molecular geometry, bond lengths, bond angles, atomic charges, harmonic vibrational wave numbers and intensities of vibrational bonds of the titled compound has been investigated by Density Functional Theory (DFT) using standard B3LYP method with 6-311++G(d,p)basis set using Gaussian 03W package. The difference between the observed and scaled frequencies was small. The HOMO to LUMO transition implies an electron density transfer.

Keywords : chalcone, flavone, DFT calculation, FTIR, HOMO- LUMO.

INTRODUCTION

The flavones are naturally occurring heterocyclic compounds belonging to the flavonoid group. These are accumulating in almost any part of plant, from the roots to the flower petal, and used as dyes for wool [1]. Flavonoids have gained recent interest because of their broad biological and pharmaceutical activities [2-11]. The synthesized compound exhibited antibacterial and antifungal activity. The study of flavonoids is therefore of great practical and theoretical importance. A density functional theory and structure-activity relationship of different flavone compounds with anti-HIV-1 intgrase activity were reported by Lameira *et al.*[12]. Santiago Aparicio studied the flavones derivatives at B3LYP/6-311++G(d,P) theoretical level [13]. Lau *et al*. reported the ab initio and DFT conformational analysis of 5,7-dihydroxyflavone and 7,8-dihydroxyflavone[14]. The relative gas-phase acidities were determined for different flavonoids by Hugo *et al.* [15]. Raman and surface-enhanced Raman spectra of flavones and several hydroxy derivatives were studied by Teslova *et al.*[16]. The main objective of this paper is to present, more accurate vibrational assignments, bond lengths, bond angels, atomic charges and HOMO-LUMO of 6,8-dichloro-2-(4-methoxyphenyl)-4*H*-chromen-4-one (DMC) using DFT/B3LYP method. Literature survey reveals that to the best of our knowledge no DFT study of this molecule has been reported so far. Hence, a systematic study on vibrational spectra and structure of this compound has been carried out.

EXPERIMENTAL

Melting points was uncorrected. IR spectrum was recorded on a Perkin Elmer Model- spectrometer on KBr pellets. UV was recorded on Labindia/UV 3000^+ UV/ Vis Spectrophotometer. ^{1}H NMR spectrum was recorded on Nuclear Magnetic Resonance Spectrometer (300 MHz)Varian Mercury 300 using $CDCl_3$ as a solvent and TMS as internal standard. All chemicals needed for the synthesis were obtained from commercial source and used without further purification.

Synthesis of DMC

Aqueous KOH (1.12g, 0.02 mol) was added to the suspension of 3, 5-dichloro 2-hydroxyacetophenone (2.0504g, 0.01 mol) and p-methoxybenzaldehyde (1.3614g, 0.01 mol) in ethanol. The reaction mixture was stirred at room temperature for overnight. The reaction mixture was poured into ice cold water and acidified with HCl (1M). The solid obtained was filtered (chalcone) and crystallized from ethanol. Chalcone (0.65g, 0.002 mol) was dissolved in DMSO (20 ml), and a crystal of iodine was added to it. The mixture was refluxed 30-45 minutes. The solid obtained after dilution with excess of water was filtered, washed with aqueous 20% sodium thiosulphate till the product become colorless. The product was further purified by column chromatography using hexane: ethyl acetate (80:20 v/v) as an eluent. Fig. 1 shows experimental IR spectrum of DMC.

Yield 78%. m. p., 177-179^{0}C. ^{1}H NMR: δ 8.09 (d, 1H, H10), 7.72 (d, 1H, H11), 7.93 (d, 2H, H18 & H16), 7.04 (d, 2H, H20 & H21), 6.77 (s, 1H, H7), 3.90 (s, 3H, OCH3).

Computational details

The DFT calculations were performed on an Intel (R) Pentium (R) Dual Core personal computer using the Gaussian-03W program package[17] without any constraint on the geometry. Geometry of the titled compounds was first optimized at 6-311++G(d,p) basis set. Optimized structural parameters were used in the vibrational frequency calculations at DFT level to confirm the structure as minima. Using Gauss View 4.1.2 molecular visualization program, the vibrational frequency assignments and other parameters were made. All the calculations were done for the optimized structure in gas phase.

RESULTS AND DISCUSSION

Molecular geometry

DMC was subjected to geometry optimization in the ground state. The optimized structural parameters of DMC was calculated by DFT/B3LYP 6-311++G(d, p) basis set are listed in Table 1 in accordance with the atom numbering scheme given in Fig. 2. The self consistent field (SCF) energy of DMC at B3LYP level with the basis set 6-311++G(d,p) is found to be -1762.055 a.u. with Dipole Moment 5.7616 Debye. The bond lengths of C2-C3, C2-C5, C5-C9, C6-C8 and C8-C9 show double bond character (aromatic bond). Bond length of C3-C23 possesses single bond character. Bond length of C3-C23 is more than C4-C23 is due to A ring in the DMC. Similarly, the bond lengths of C12-C13, C12-C14, C13-C15, C15-C19, C14-C17 and C19-C17 show double bond character.

Mullikan atomic charges

We know that the atomic charges are very much dependent on how the atoms are defined. It also plays an important role in the application of quantum chemical calculations to molecular systems. The Mullikan atomic charges calculated at B3LYP level with 6-311++G(d,p) basis set are given in Table 2. As seen in Table 2, because of methoxy group in ring B and chlorine atom in A ring, the atomic charge distribution is different. The C23 has more negative charge (-0.9397e) and C1 has more positive charge. All hydrogen carry positive charge.

Electronic Spectra and HOMO-LUMO

The electronic absorption spectra of DMC was recorded in methanol. The experimental maximum wavelengths were 327 and 288 nm, respectively. Theoretical values of absorption spectra of the optimized structure were 346 and 312 nm, respectively. These were determined by using DFT/TD-SCF method at B3LYP/6-311++G(d,p) level. Theoretical values have a red shifts compared with experimental. Optimized geometry of DMC at DFT/ B3LYP/6-311++G(d,p) level is shown in Fig. 3. It shows that the frontier molecular orbital is mainly composed of p atomic orbital, so electronic transitions correspond to above electronic spectrum are assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. Fig. 4 shows the HOMO-LUMO.

Analysis of wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state and is explained by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). LUMO as an electron acceptor represents the ability to obtain an electron, and HOMO represents the ability to donate an electron. The LUMO, i.e., of π nature of A, B and C ring of titled compound is delocalized over the entire C – C and C- O bond, in contrast, the HOMO is located over A and B ring and chlorine atoms of ring A. The HOMO–LUMO transition implies an electron density transfer from A, C ring to B ring. The HOMO-LUMO energy is calculated at B3LYP/6-311++G(d,p) level. Energies of HOMO and LUMO are -0.32331, -0.22900 au., respectively and energy gap (ΔE) is -0.09431 au. ΔE reveals the chemical activity of the molecule.

Vibrational assignments

The spectral assignments of the titled compound have been made on the recorded FT-IR (solid phase) and theoretically predicted wave numbers by density functional B3LYP/6-311++G(d,p) method. None of the predicted vibrational frequencies have any imaginary frequency, implying that the optimized geometry is located at the local minimum point on the potential energy surface. There are 33 atoms having 87 fundamental modes of vibrations. This molecule possesses C1 symmetry. The scaling factor of 0.96 is used for DFT method. After scaling, the deviation from the experimental value is less. Comparison of the frequencies calculated at DFT method using 6-311++G(d,p) basis set with experimental values reveal that the B3LYP method shows very good agreement with experimental observation.

The selected calculated vibrational frequencies are numbered from largest to smallest fundamental wave number. The calculated and experimental wave numbers and intensities of the normal mode of vibrations and corresponding vibrational assignments for selected fundamental modes of vibrations of the DMC are given in Table 3. The band at 3077 cm^{-1} in FTIR spectrum of the DMC corresponds to symmetric C-H stretching of ring A, theoretically it is assigned at 3082 cm^{-1}. The bands in the range 3097-2892 cm^{-1} are due to C-H stretching vibrations. Experimental bands at 1645 cm^{-1} is due to C=O stretching and theoretically assigned at 1636 cm^{-1}. The C=C stretching is observed around 1600 cm^{-1} which is in close agreement with the computed frequency at 1585, 1559, 1526 cm^{-1} . The computed bands in 1444-825 cm^{-1} are assigned for C-H out of plane bending of ring A, B and C which are close to experimental values as tabulated in Table 3.

The C-H in plane bending vibrations of ring A, B and C are assigned within 1414-1057 cm^{-1} and experimentally these are recorded in the range 1312 - 1082 cm^{-1} for DMC. The C5-Cl stretching vibration is assigned at 806 cm^{-1} and experimentally this is observed at 829 cm^{-1}. C8-Cl stretching vibration is assigned at 682 cm^{-1} and experimentally it is observed at 648 cm^{-1}. The calculated bands assigned for C=C, CC, C-Cl stretching mode are in good agreement with the literature values [18].

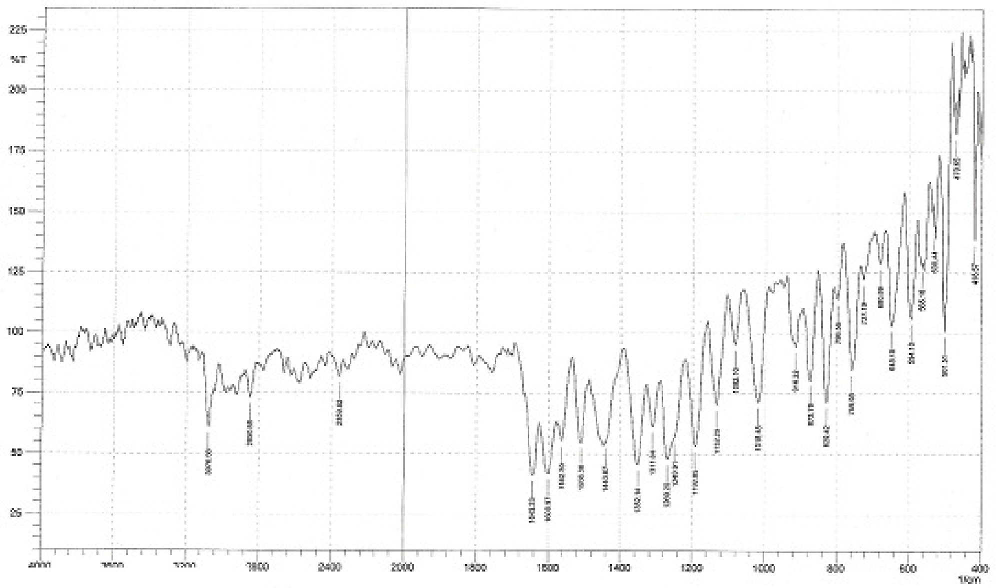

Fig.-1: Experimental IR spectrum of DMC.

Table-1: Selected geometrical parameters of DMC at B3LYP/6-311++G(d,p) level.

Geometrical parameters			
Bond	Bond length (Å)	Bond	Bond length (Å)
C1-C4	1.3583	C14-C17	1.3897
C2-C3	1.3973	C23-O24	1.2262
C2-C5	1.4030	C19-O25	1.3564
C5-C9	1.3846	C4-H7	1.0807
C6-C8	1.3813	C6-H10	1.0821
C8-C9	1.3991	C9-H11	1.0813
C6-C3	1.3995	C13-H16	1.0814
C3-C23	1.4869	C15-H20	1.0831
C4-C23	1.4497	C17-H21	1.0814
C1-C12	1.4685	C14-H18	1.0825
C2-O22	1.3597	C5-Cl31	1.7471
C1-O22	1.3660	C8-Cl30	1.7440
C12-C13	1.4083	C26-O25	1.4248
C12-C14	1.4009	C26-H27	1.0947
C13-C15	1.3828	C26-H28	1.0882
C15-C19	1.4011	C26-H29	1.0947
C19-C17	1.4002		
Bond angle $(^0)$			
C1-O22-C2	120.5	C5-C9-H11	120.0
C3-C23-C4	114.1	C1-C12-C13	120.7
C2-C5-C9	120.1	C1-C12-C14	121.4
C3-C6-C8	119.3	C12-C14-H18	120.4
C2-C5-Cl31	120.1	C12-C13-H16	119.6
C9-C8-Cl30	118.6	C12-C14-C17	121.5
C5-C2-O22	117.7	C13-C15-C19	120.4
C4-C23-O24	123.8	H27-H28-H29	60.30
C1-C4-H7	120.4	C19-O25-C26	118.9
C3-C6-C8	119.3	C15-C19-C17	119.4

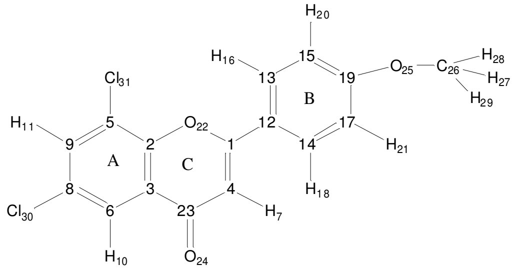

Fig.-2: Atom numbering scheme of DMC.

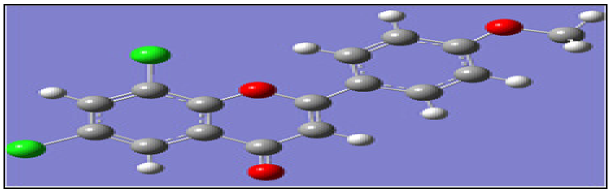

Fig.-3: Optimized structure of the studied molecule

Table-2 :Mullikan atomic charges for DMC at B3LYP/6-311++G(d,p) level.

S. No.	Atom	Charge	S. No.	Atom	Charge
1	C1	1.0528	17	C17	-0.2304
2	C2	-0.6859	18	H18	0.0809
3	C3	0.1373	19	C19	-0.6107
4	C4	-0.7720	20	H20	0.2053
5	C5	0.3123	21	H21	0.2176
6	C6	-0.6682	22	O22	0.0816
7	H7	0.2112	23	C23	-0.9397
8	C8	0.5941	24	O24	-0.2985
9	C9	-0.5230	25	O25	-0.1525
10	H10	0.2386	26	C26	-0.3128
11	H11	0.2231	27	H27	0.1824
12	C12	1.0487	28	H28	0.1824
13	C13	0.0778	29	H29	0.1553
14	C14	-0.5062	30	Cl30	0.5156
15	C15	-0.3645	31	Cl31	0.4154
16	H16	0.1595			

CONCLUSION

DMC has been synthesized and characterized by IR, UV-VIS and ^{1}H NMR spectroscopy. Vibrational assignments are also examined theoretically. The data obtained during the course of present investigation shows a better agreement between the experimental and computed data obtained by using the DFT method with 6-311++G(d,p) basis set. The LUMO-HOMO energy gap reveals the activity of DMC.

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Table-3: Selected experimental and theoretical vibrational assignments (cm^{-1}) of DMC at B3LYP/6-311++G(d,p) level.

Mode	Scaled	Intensity	Experimental	Assignment
87	3097	2		Ring C C4-H str, Ring B C14-H str (sym), Ring B C17-H str (sym)
86	3088	2		Ring A C9-H str, Ring B C13-H, C15-H str
85	3088	2		Ring A C9-H ,Ring B C13-H,C15-H str
84	3084	7		Ring A C6-H str
83	3082	6	3077	Ring A C4-H ,Ring B C14-H str (sym)

82	3065	1		Ring B CH_3 CH str (asym)
81	3062	6		Ring B CH str (asym)
80	3016	20		Ring B CH_3 CH str (asym)
79	2952	32		Ring B CH_3 CH str (asym)
78	2892	65		Ring B CH_3 CH str (sym)
77	1636	477	1645	C=O str
76	1585	91	1601	C1-C4 str, Ring B CC str
75	1572	386		Ring A,B,C,C=C str
74	1559	15	1562	Ring A quinoid str,C=C str
73	1599	15		Ring A,B,C,C=C str
72	1526	141	1508	Ring A,B,C,C=C str,CH ip bend
71	1481	208		Ring B quinoid str,CH ip bend
70	1444	63	1441	Ring B CH_3 CH oop bend
69	1435	10		Ring B CH_3 CH oop bend
68	1418	23		Ring B CH_3 CH oop bend
67	1414	261		Ring A CH ip bend
66	1396	13		Ring B CH ip bend
65	1375	31		Rng A CH ip bend
64	1315	441	1312	Ring A,B,C,CH ip bend
63	1289	11		Ring B CH ip bend
62	1287	3		Ring A CC str , CH ip bend
61	1277	62	1269	Ring A,B,C,C-C str, Ring A,B,C CH ip bend
60	1240	332	1250	Ring B C-OCH_3 str, Ring B CH ip bend
59	1230	43		Ring A,B,C,CH ip bend , Ring C CO str
58	1222	262		Ring C CH ip bend
57	1200	7	1192	ring C C19-O str
56	1169	33		Ring A CH ip bend
55	1156	71		Ring B CH ip bend
54	1154	141		Ring A,B,C,CH ip bend
53	1121	1		ring B CH (CH_3) oop bend
52	1103	23		Ring A,B,C,CH ip bend
51	1098	49	1082	Ring A,B,C,CH ip bend
50	1057	15		Ring A CH ip bend
49	1016	28	1018	C1 -O22 str, O25-C26(OCH_3) str
48	1003	86		C1 O22 str, O25-C26(OCH_3) str
47	981	5		Ring B quinoid str
46	949	0		Ring B CH oop bend

45	912	0	916	Ring B CH oop bend
44	894	26		Ring A,B,C CC def
43	891	5	874	Ring A CH oop bend
42	853	25		Ring A CC def
41	849	22		Ring A CH oop bend
40	825	0	829	Ring C CH oop bend , Rng B C13-H,C15-H oop bend
39	819	86		Ring B,C CH oop bend
38	806	7	829	C5-Cl str, Ring A C-C def
36	719	5	727	Ring A,B def
34	682	89	648	C8-Cl str, Ring A,B,C-C def

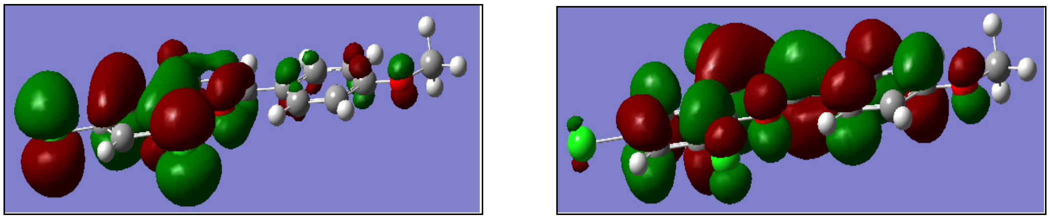
HOMO LUMO

Fig.-4: HOMO-LUMO of the studied molecule

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