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COMPUTATIONAL ANALYSIS OF 6,7-DIMETHOXY-2,2-DIMETHYL-4-CHROMANONE BY DENSITY FUNCTIONAL THEORY CALCULATIONS

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Abstract:

The present study aims at determining the optimized molecular geometry of 6,7-dimethoxy-2,2-dimethyl-4-chromanone (DDC), using DFT method and 6-311++G(d,p) basis set. The ^{1}H and ^{13}C NMR spectra of DDC have been recorded and compared with the theoretically calculated values using the gauge independent atomic orbital (GIAO) method. The electronic properties such as HOMO and LUMO energies are performed by time-dependent DFT (TD-DFT) approach. Natural bond (NBO) analysis gives clear evidence of stabilization originating in the hyper conjugation of hydrogen–bonded interactions. Information about the size, shape, charge density distribution and site of chemical reactivity of the molecules has been obtained by mapping electron density isosurface with electrostatic potential (ESP). The theoretical calculations are achieved with the help of Gaussian 09 software package, Gauss view 5.0.9 visualization program, NBO 3.1 program and Molvib program.

Key Words: DFT, Vibrational Analysis, NBO Analysis, HOMO- LUMO; MEP, NMR, 6,7-dimethoxy-2,2-dimethyl-4-chromanone.

Introduction:

Computational chemistry or molecular modelling is a set of techniques for investigating chemical problems on a computer. Theoretical or computational chemistry, with the aid of computer technology applies the knowledge of chemistry, physics and mathematics to probe the problems raised at the molecular level. Computational chemistry advances research activities in all areas of research. The questions that are investigated computationally are: molecular geometry, the energies of molecules and transition state, chemical reactivity, IR, UV, and NMR spectra and the physical properties of substances. Density functional theory (DFT) calculations are based on the Schrödinger equation. The premise behind DFT is that the energy of a molecule is determined from the electron density. The electron density is measurable and so is much easier to explain certain chemical properties. The DFT technique has become very popular in recent years as it is both accurate and economical [1-2]. Hence, the research paper emphasizes the spectroscopic and density functional theory (DFT) studies of 6,7-dimethoxy-2,2-dimethyl-4-chromanone (DDC), using computational methods.

Software and Computational Details:

All theoretical calculations were performed with the help of a personal computer using Gaussian 09 [3] software package. The B3LYP functional and standard 6-311++G* basis set were used to optimize the geometries of all the structures. In order to establish the agreement between the simulated and observed frequencies, scaling of the computed frequencies was indispensable.Normal coordinate analysis is nowadays commonly used as an aid in the interpretation of the vibrational spectra of large molecules. The normal coordinate analysis is achieved by utilizing the program Molvib [4]. It is developed using mass-weighted Cartesian coordinates, which eliminates the redundancy problems arising when internal valence coordinates are used. The minimal root mean square (RMS) deviation between the experimental and scaled frequencies confirms the reliability of the assignments of the fundamental modes. Gauss view 5.0.9 visualization program [5] has been utilized to construct the molecular electrostatic potential surface (MEP) and the shape of the frontier molecular orbitals, namely, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). NBO 3.1 [6] program implemented in Gaussian 09 package was used to perform the natural bond orbital (NBO) calculations.

Molecular Geometry:

To find the most stable conformer of DDC, its input geometry was optimized without imposing any external constraints on the geometrical parameters and the resultant optimized geometry has been used as input for vibrational frequency calculations. The labelled optimized structure of DDC is given in Figure 1. The global minimum energy obtained from the optimized structure is -806.123 Hartree.

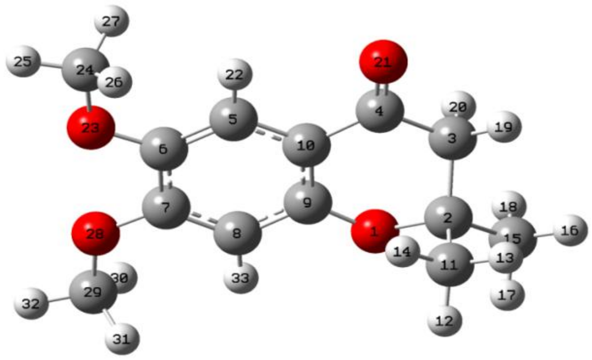


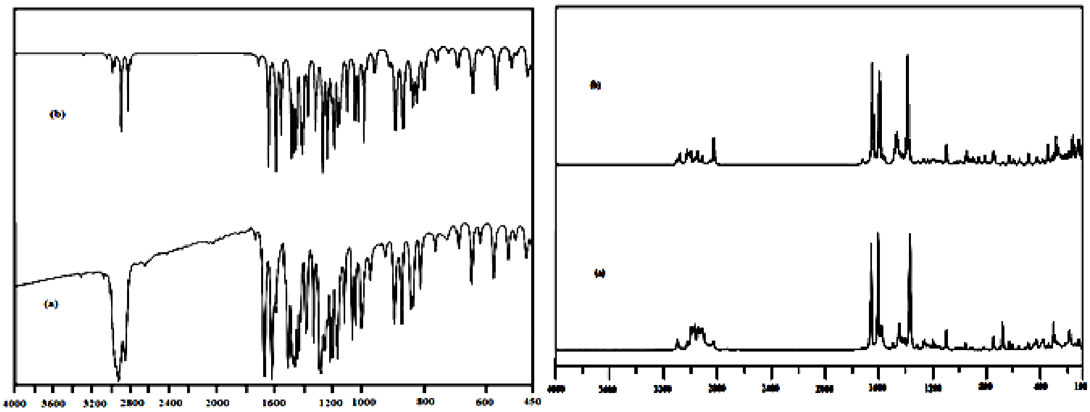
Figure 1

The dimethyl group substituted to the C2 atom tends to affect the hexagonal structure of the pyrone ring to a greater extent. At the point of substitution of the dimethyl group, O1–C2–C3 bond angle is 108.91º, which is very much less than the other bond angles of the ring. As C2 atom is pulled away from the ring due to steric repulsion caused by the methyl group carbons, C2–C3 and C2–O1 bond lengths are found to be greater than the other C–C and C–O bond lengths of the ring. The methoxy groups substituted to C6 and C7 atoms have no effect on the ring symmetry of the benzene ring, which is obvious from the dihedral angles of the benzene ring. But the planar geometry between the benzene and pyrone ring is affected by the dimethyl substitution. This is evident from the dihedral angle C8–C9–C10–C4, which has the value -177º.

Spectral Analysis:

In order to establish the vibrational assignments of DDC, a non-redundant set of 93 local symmetry coordinates were constructed by combining the standard internal coordinates.The 93 normal modes of DDC are distributed among the symmetry species as Γ_{3N-6}= 63 (in-plane) + 30 (out-of-plane). For visual comparison, the observed and simulated FT-IR and FT-Raman spectrum of DDC produced in common frequency scales, are portrayed in Figure 2. The scaling procedure has reduced the RMS error between unscaled and experimental frequencies to 2.7 cm^{-1}. The assignments of all the fundamental vibrational modes of DDC were made based on the results of PED output obtained from normal coordinate analysis. The important vibrational assignments are explained below:

The C–H stretching vibrations of heteroaromatic structure appear in the region 3100–3000 cm^{-1}. The two C–H stretching vibrations are simulated at 3181 and 3100 cm^{-1} and the experimental peak is identified in both IR and Raman at 3100 cm^{-1}. The in-plane bending vibrations are predicted at 1271 and 1257 cm^{-1} and the experimental counterparts of these vibrations falls at 1275 cm^{-1} (Raman) and 1260 cm^{-1} (IR). The out-of-plane bending vibrations are identified in IR at 806 and 760 cm^{-1}.For these vibrations the calculated values are at 809 and 761 cm^{-1}. In the case of CH_2group, the C–H stretching vibrations are simulated at 2970 and 2932 cm^{-1} and one of these vibrations is found in Raman spectrum at 2970 cm^{-1}. In the present study, the four CH_2 bending vibrations are assigned in the frequency range 1500–800 cm^{-1}. Two of these CH_2 bending vibrations are identified in IR at 1330 and 840 cm^{-1}, and one in Raman at 1440 cm^{-1}. These vibrations agree well with the calculated vibrational frequencies.



Figures 2: Comparison of observed and calculated FT-IR, FT-Raman spectra of DDC (a) observed and (b) calculated

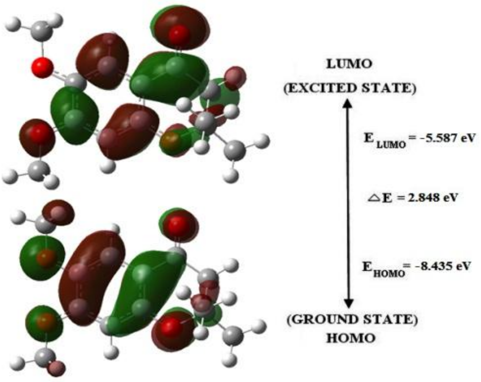
A methyl group is associated with nine fundamental vibrations. The presence of two methyl groups in DDC gives rise to eighteen fundamental vibrations. These vibrations are assigned as follows: The asymmetric vibrations are simulated at 3080, 3020, 3015 and 3000 cm^{-1} and symmetric vibrations are calculated at 2915 and 2860 cm^{-1}. Only three of the asymmetric vibrations are active in Raman at 3080, 3016 and 3000 $cm^{-1.}$ The symmetric stretching vibrations are found in Raman and IR spectrum at 2915 and 2860 cm^{-1}, respectively. The four antisymmetric bending vibrations are present at 1480 and 1455 cm^{-1} in IR and at 1505 and 1465 cm^{-1} in Raman. The two symmetric bending vibrations are simulated at 1416 and 1398 cm^{-1} and only one is found in both the spectra at 1415 cm^{-1}. The titled molecule has twoCH_3ipr and CH_3opr bands (i.e. in-plane and out-of-plane rocking modes). Both the CH_3ipr modes are identified experimentally in IR at 1165 and 1110 cm^{-1}, but only one CH_3opr mode is identified in IR and Raman spectrum at 1010 and 1008 cm^{-1}, respectively. The tCH_3 twisting mode vibrations are active in Raman at 212 and 190 cm^{-1}. The eighteen fundamental vibrations of the two methoxy groups substituted with C6 and C7 atoms are assigned as follows: The asymmetric stretching vibrations are found in IR at 3020 cm^{-1} (OCH_3 ops), 2930 cm^{-1} (OCH_3 ips) and in the Raman spectrum at 3030 cm^{-1} (OCH_3 ops), 2950 cm^{-1} (OCH_3 ips). The theoretical frequencies of these vibrations fall at 3030, 3021, 2950 and 2930 cm^{-1}. The symmetric stretching vibrations (OCH_3 ss) are calculated at 2899 and 2830 cm^{-1}. One of these vibrations is found at 2830 cm^{-1} in Raman spectrum. The bending vibrations are predicted at 1500, 1491 cm^{-1} (OCH_3 ipb), 1487, 1474 cm^{-1} (OCH_3 opb) and 1425, 1385 cm^{-1} (OCH_3 sb). Both the symmetric bending vibrations (OCH_3 sb) are found in IR at 1425 and 1385 cm^{-1}, but only one of the asymmetric bending vibrations is found in IR at 1500 cm^{-1}. One of the OCH_3 ipr vibrations shows peak in IR and Raman at 1210 cm^{-1}. The other vibration calculated at 1121 cm^{-1} is not found in the experimental spectra. The out-of-plane rocking vibrations of DDC (OCH_3 opr) are found in IR at 895 and 870 cm^{-1}. The twisting mode vibrations ($tOCH_3$) are calculated at 202 and 155 cm^{-1} and one $tOCH_3$ mode is found in Raman at 156 cm^{-1}.

NMR Analysis:

Theoretical calculations of chemical shift help us to assign the experimental chemical shifts of the titled molecule. The electronegative oxygen atom attached with C4 atom reduces the electron density around it, thereby influencing the chemical shift of C4 to fall in the downfield region at 190.94 ppm. Next to C4, C6 and C7 atoms have higher chemical shifts among the ring carbons, due to the methoxy group substitution in these atoms. The carbon atom C9 also produces chemical shift in downfield at 144.02 ppm, due to O1 atom in its neighbourhood. The methyl carbons C11 and C15 give peak at 26.57 ppm, whereas the methoxy carbons C24 and C29 give peak at 56.14 ppm. The atoms C2 and C3 give peak at 79.53 and 48.37 ppm, which agrees with the simulated chemical shift values. The protons directly attached to the ring, H22 and H33 give signal at 7.3 and 6.4 ppm, respectively. The protons H19 and H20, attached with C3, have their chemical shift at 2.67 ppm. The doublet present around 3.9 ppm is assigned to the methoxy protons and the sharp peak at 1.46 ppm is assigned to the methyl protons. The correlation coefficient between the experimental and theoretical chemical shifts is found to be 0.991 for ^{1}H NMR and 0.999 for ^{13}C NMR.

Frontier Molecular Orbitals:

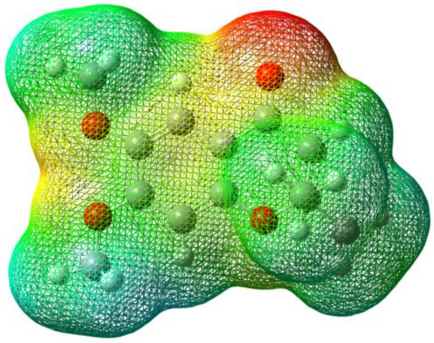
The visualized molecular orbitals are shown in Figure 3. At both HOMO and LUMO levels, the functional groups $-CH_3$ and $-OCH_3$ have minimum contribution. The calculated energy band gap of the molecule, obtained by determining the energy difference between the HOMO and LUMO level, is 2.848 eV. The high chemical reactivity of DDC is revealed from the low frontier orbital gap.



The small HOMO-LUMO energy gap results in small hardness value [7], which implies that the title molecule is a soft molecule with high reactivity.

Analysis of Molecular Electrostatic Potential (MEP):

The MEP map portrayed in Fig. 10.9 helps us to predict the molecular reactive sites of DDC. All the oxygen atoms of the molecule are suitable for the electrophilic attack and the fact is also confirmed by the NAO charges on the oxygen atoms of DDC. The methyl and methoxy group hydrogens are covered with blue region and this shows the positive electrostatic potential experienced by these atoms. So, hydrogen atoms act as electrophilic sites of the molecule. The chromanone ring is mapped with green colour, which suggests the zero potential in these regions.



Natural Bond Orbital Analysis:

The natural bonding orbital (NBO) analysis has been reported to determine the stabilization originating due to hyper conjugative interactions. The intensive interactions determined from NBO analysis are discussed here.The strong interactions that arises from the lone pair electrons of electron donating atoms to the anti-bonding orbitals are LP(2)O1 → π*(C5–C10), LP(2)O21 →σ*(C3–C4), σ*(C4–C5), LP(2)O23 → π*(C6–C7) and LP(2)O28 → π*(C8–C9), with stabilization energies 28.25, 20.48, 18.29, 29.23 and 33.44 kcalmol^{-1}, respectively. The other interactions that produce large stabilizing energies are π(C5–C10) → π*(C4–O21), π*(C6–C7) and π*(C8–C9); π(C6–C7) → π*(C5–C10) and π*(C8–C9); π(C8–C9) → π*(C5–C10) and π*(C6–C7). The E(2)value for these interactions are 23.86, 20.20, 14.34, 14.62, 19.25, 22.55 and 13.45 kcalmol^{-1}, respectively.

Conclusion:

This paper reveals the complete structural information and electronic properties of DDC. The FT-IR and FT-Raman studies show good correlation with theoretically simulated FT-IR and FT-Raman spectra. All the fundamental vibrational modes of the titled compounds were assigned, based on the PED output. The lower energy gap value of the molecule explains the charge transfer interactions within the molecule and its enhanced bioactivity. The absolute chemical shift values were determined from the theoretically predicted NMR spectra and the experimental ^{1}H and ^{13}C NMR chemical shift values agree well with the theoretical values.

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