

Molecular Structure and Electronic Properties Of 2-Methyl-3-[(2-Methylphenyl) Carbamoyl] Phenyl Acetate by Using Density Functional Theory

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Abstract- The quantum chemical study of 2-methyl-3-[(2-methylphenyl) carbamoyl] phenyl acetate (2M3PA) have been studied in ground and first excited state using DFT method employing B3LYP/6-311++G(d,p) level of theory. Quantum chemical calculations of geometrical structure optimized parameter and molecular electrostatic potential surface (MESP) has been calculated by using DFT method. The highest occupied molecular orbital and lowest unoccupied molecular orbital has also been calculated by DFT method.

Indexed Terms- DFT, Optimize geometry, electronic property

I. INTRODUCTION

A recent supramolecular architecture study on 2-methyl-3-[(2-methylphenyl) carbamoyl] phenyl acetate (2M3PA) has been performed by *Prajina et al.* 2016[1]. In recent years, the physicochemical properties of active pharmaceutical ingredients have been improved widely with the use of co-crystals (Lemmerer & Bernstein, 2010). Supramolecular synthons- modular representation of primary recognition between functional groups are of great importance in providing an effective strategy for designing solids in crystal engineering.

The vibrational spectroscopic analysis is known to provide immensely invaluable molecular structure elucidation in synergy with quantum chemical calculations. In order to obtain a complete description of molecular dynamics, vibrational wavenumber calculations along with the normal mode analysis have been carried out at the DFT level employing the basis set 6-311++G(d,p). The optimized geometry of molecule under investigation and its molecular properties such as equilibrium energy, frontier orbital energy gap, molecular electrostatic potential energy

map has also been used to understand the properties and active sites of the molecule.

II. COMPUTATIONAL DETAILS

Quantum chemical study of the 2-methyl-3-[(2-methylphenyl) carbamoyl] phenyl acetate (2M3PA), has been performed within the framework of the density functional theory [2,3] with Becke's three-parameter hybrid exchange functional [4] with Lee–Yang–Parr correlation functionals (B3LYP) [5] and employing 6-311++ G(d,p) basis set using the Gaussian 09 program package [6].

III. RESULT AND DISCUSSION

3.1 Molecular Geometry Optimization and Energies: Geometry of the model 2M3PA was optimized for the calculation of its molecular properties using DFT at the B3LYP level, with the 6-311++G(d,p) basis set. The X-ray diffraction data of the 2M3PA was obtained from Cambridge Crystallographic Data Center. The optimized geometry of molecule (Fig. 1) under study is confirmed to be located at the local true minima on potential energy surface, as the calculated vibrational spectra contains no imaginary wavenumber. The optimized structural parameters (bond lengths, bond angles, dihedral angles) of 2M3PA have been calculated as shown in Table 1.

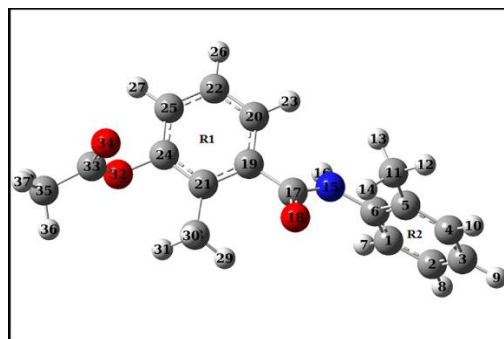


Fig. 1. The geometric structure of 2M3PA molecule.

For the title compound, all carbon-carbon bond lengths in six membered ring R1 and R2 lies in the range 1.98-1.41 Å and the endocyclic bond angle lie in the range 116.65 to 122.12 degree. In the ring all the endocyclic C-C-C angles are found to deviate from the usual value of 120.0. The bond angles C3-C4-C5 increases to 122.12 from 120 which is due to the presence of adjacent methyl group and the angles C19-C21-C24 decrease to 116.65 due to the presence of the adjacent acetate group. Based on the above comparison, it is clear that the calculated bond lengths and bond angles are very near to the standard values [7]. All the dihedral angle in rings is found to be very close to 0 or 180 degrees except the dihedral angles C6-N15-C17-C19(-177.34) and C16-N15-C17-O18 (164.17) which shows the rings in the title compound are almost planar except some non-planarity in between ring R1 and R2. Both the ring is tilted mutually as is evident from the torsion angles C6-N15-C17-C19(-177.34) and C16-N15-C17-O18 (164.17) (Table. 1) . This calculated bond length; bond angles are in full agreement with those standard bond lengths and bond angles.

Table 1: Optimize geometric parameter for 2M3PA

Parameter	Theoretical
C1-C2	1.39
C1-C6	1.39
C1-H7	1.08
C2-C3	1.39
C2-H8	1.08
C3-C4	1.39
C3-H9	1.08
C4-C5	1.40
C4-H10	1.08
C5-C6	1.40
C5-C11	1.50
C6-N15	1.42
C11-H12	1.09
C11-H13	1.09
C11-H14	1.09
N15-H16	1.00
N15-C17	1.38
C17-O18	1.21
C17-C19	1.50
C19-C20	1.40
C19-C21	1.41
C20-C22	1.39

C20-H23	1.08
C21-C24	1.39
C21-C28	1.50
C22-C25	1.38
C22-H26	1.08
C24-C25	1.38
C24-O32	1.40
C25-H27	1.08
C28-H29	1.08
C28-H30	1.09
C28-H31	1.09
O32-C33	1.37
C33-O34	1.19
C33-C35	1.50
C35-H36	1.09
C35-H37	1.08
C35-H38	1.09
C2-C1-C6	120.77
C2-C1-H7	120.14
C6-C1-H7	119.07
C1-C2-C3	119.36
C1-C2-H8	119.98
C3-C2-H8	120.64
C2-C3-C4	119.67
C2-C3-H9	120.33
C4-C3-H9	119.97
C3-C4-C5	122.12
C3-C4-H10	119.43
C5-C4-H10	118.43
C4-C5-C6	117.42
C4-C5-C11	120.19
C6-C5-C11	122.37
C1-C6-C5	120.61
C1-C6-N15	117.82
C5-C6-N15	121.50
C5-C11-H12	110.57
C5-C11-H13	111.25
C5-C11-H14	110.87
H12-C11-H13	108.21
H12-C11-H14	108.82
H13-C11-H14	106.98
C6-N15-C16	116.08
C6-N15-C17	125.05
C16-N15-C17	116.10
N15-C17-O18	122.95
N15-C17-C19	114.21
O18-C17-C19	122.81

C17-C19-C20	119.15
C17-C19-C21	120.21
C20-C19-C21	120.57
C19-C20-C22	120.92
C19-C20-H23	119.46
C22-C20-H23	119.58
C19-C21-C24	116.65
C19-C21-C28	123.48
C24-C21-C28	119.85
C20-C22-C25	119.40
C20-C22-H26	120.36
C25-C22-H26	120.22
C21-C24-C25	123.14
C21-C24-O32	118.74
C25-C24-O32	118.02
C22-C25-C24	119.29
C22-C25-H27	121.35
C24-C25-H27	119.34
C21-C28-H29	111.89
C21-C28-H30	110.37
C21-C28-H31	110.35
H29-C28-H30	106.63
H29-C28-H31	109.25
H30-C28-H31	108.20
C24-O32-C33	118.43
O32-C33-O34	123.49
O32-C33-C35	110.06
O34-C33-C35	126.44
C33-C35-H36	109.63
C33-C35-H37	109.41
C33-C35-H38	110.26
H36-C35-H37	109.74
H36-C35-H38	107.43
H37-C35-H38	110.32
C6-C1-C2-C3	0.71
C6-C1-C2-H8	179.93
H7-C1-C2-C3	-178.48
H7-C1-C2-H8	0.74
C2-C1-C6-C5	0.55
C2-C1-C6-N15	177.96
H7-C1-C6-C5	179.75
H7-C1-C6-N15	-2.83
C1-C2-C3-C4	-0.99
C1-C2-C3-H9	179.49
H8-C2-C3-C4	179.78
H8-C2-C3-H9	0.27
C2-C3-C4-C5	0.03

C2-C3-C4-H10	-178.93
H9-C3-C4-C5	179.53
H9-C3-C4-H10	0.56
C3-C4-C5-C6	1.19
C3-C4-C5-C11	-177.80
H10-C4-C5-C6	-179.82
H10-C4-C5-C11	1.17
C4-C5-C6-C1	-1.47
C4-C5-C6-N15	-178.79
C11-C5-C6-C1	-177.50
C11-C5-C6-N15	0.18
C4-C5-C11-H12	15.66
C4-C5-C11-H13	135.94
C4-C5-C11-H14	-105.13
C6-C5-C11-H12	-163.28
C6-C5-C11-H13	-43.00
C6-C5-C11-H14	75.92
C1-C6-N15-H16	-40.01
C1-C6-N15-C17	120.36
C5-C6-N15-C16	137.37
C5-C6-N15-C17	-62.24
C6-N15-C17-O18	3.80
C6-N15-C17-C19	-177.34
C16-N15-C17-O18	164.17
C16-N15-C17-C19	-16.97
N15-C17-C19-C20	-42.54
N15-C17-C19-C21	140.00
O18-C17-C19-C20	136.30
O18-C17-C19-C21	-41.14
C17-C19-C20-C22	-177.51
C17-C19-C20-H23	0.53
C21-C19-C20-C22	-0.08
C21-C19-C20-H23	177.97
C17-C19-C21-C24	177.86
C17-C19-C21-C28	-2.59
C20-C19-C21-C24	0.45
C20-C19-C21-C28	179.99
C19-C20-C22-C25	-0.45
C19-C20-C22-H26	179.05
H23-C20-C22-C25	-178.51
H23-C20-C22-H26	0.99
C19-C21-C24-C25	-0.31
C19-C21-C24-O32	176.22
C28-C21-C24-C25	-179.86
C28-C21-C24-O32	-3.32
C19-C21-C28-H29	-26.83
C19-C21-C28-H30	91.73

C19-C21-C28-H31	-148.71
C24-C21-C28-H29	152.68
C24-C21-C28-H30	-88.37
C24-C21-C28-H31	30.81
C20-C22-C25-C24	0.59
C20-C22-C25-H27	-179.76
H26-C22-C25-C24	-178.91
H26-C22-C25-H27	0.72
C21-C24-C25-C22	-0.21
C21-C24-C25-H27	-179.85
O32-C24-C25-C22	-176.77
O32-C24-C25-H27	3.57
C21-C24-O32-C33	97.67
C25-C24-O32-C33	-85.60
C24-O32-C33-O34	0.47
C24-O32-C33-C35	-179.30
O32-C33-C35-H36	63.95
O32-C33-C35-H37	-175.64
O32-C33-C35-H38	-54.13
O34-C33-C35-H36	-115.81
O34-C33-C35-H37	4.58
O34-C33-C35-H38	126.09

3.2 Electronic properties:

The highest occupied molecular orbital (HOMO) is the orbital that primarily acts as an electron donor and the lowest unoccupied molecular orbital (LUMO) is the orbital that largely acts as the electron acceptor. The frontier orbital energy gap helps characterize the chemical reactivity and kinetic stability of the molecule. The 3D plots of the frontier orbitals HOMO, LUMO and the Molecular electrostatic potential map (MESP) figures of molecules are shown in Fig 2 and Fig.3 respectively. It can be seen from the Fig. 2, that the HOMO is spread heavily over the phenyl ring region. The HOMO also shows appreciable π bonding character. In contrast the LUMO display Rydberg character at the alcoholic end and are located outside the molecule and oriented perpendicular to the molecular plane. Consequently, the HOMO to LUMO transition reflects the transfer of electron cloud mainly from phenyl ring to Rydberg type excited state. The electron thus transferred to the Rydberg state is very weakly bound to the rest of the molecule. This electron spends most of its time a long way from the molecule. The basis set 6-311++G (d,p) which includes asymptotically correct functions with slower radial decay to represent a more diffuse electron distribution

in addition to additional polarization functions, has been suitably chosen to describe the LUMO orbitals adequately. The value of the electrostatic potential (the energy of interaction of a positive test point charge with the nuclei and electrons of a molecule) mapped onto an electron iso-density surface may be employed to distinguish regions on the surface which are electron rich (subject to electrophilic attack) from those which are electron poor (subject to nucleophilic attack).

The 3D plots of Frontier molecular orbitals are shown in Fig. 2. The HOMO is delocalized over the benzene rings R2 and partly to the benzene ring R1 while LUMO is delocalized over the benzene rings only and shows antibonding character. This shows that a charge transfer takes place within the molecule. The frontier orbital energy gap is found to be 5.158 eV. Lower is the energy gap, more easily the electrons get excited from the ground to the excited state.

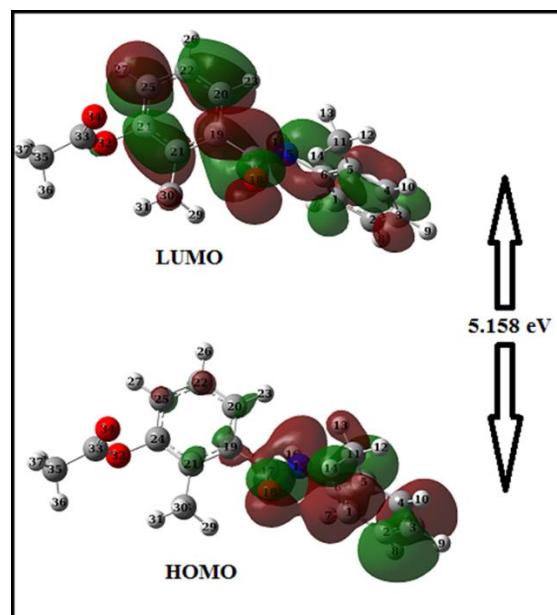


Fig. 2. HOMO, LUMO plots of 2M3PA molecule

The MESP for the title molecule is shown in Fig. 3. The MESP map in case of the 2M3PA clearly suggests that the potential swings wildly between alcoholic oxygen (dark red) and alcoholic hydrogen atoms which bear most the brunt of positive charge (blue).

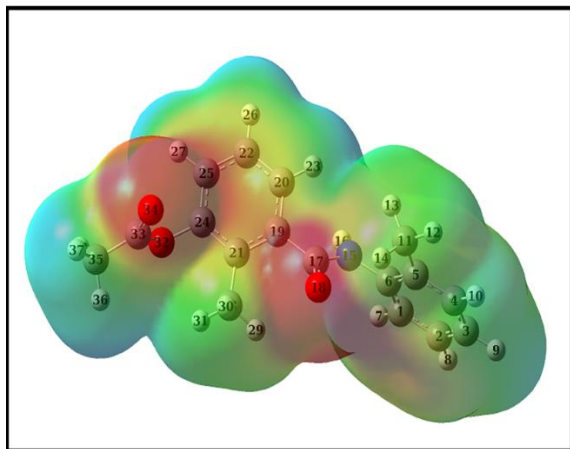


Fig. 3. MESP Surface for 2M3PA calculated at B3LYP/6-311**þ**G(d,p).

There is only one active electrophilic site [8]. The larger extent of spread of green colour which corresponds to a potential halfway between the two extremes red and blue colour suggests that most part of the molecule has almost the neutral potential. Such a representation provides more detailed information regarding electrostatic potential distribution, by showing the values in a manifold of spatial location around the molecule.

CONCLUSION

The optimized geometric parameters and vibrational harmonic wave numbers, of the compound have been calculated using DFT/B3LYP methods with 6e311**þ**G(d,p) basis set. In general, a good agreement between experimental and calculated normal modes has been observed. The calculated bond lengths and bond angle are in full agreement with those reported. The frontier orbital energy gap is found to be 5.158 eV. Lower is the energy gap, more easily the electrons get excited from the ground to the excited state. The molecular electrostatic potential map of the 2M3PA, has been used to understand the active sites of the molecule under study.

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