

STRUCTURE AND ELECTRONIC PROPERTIES OF 4HP2M3B BY DFT METHOD

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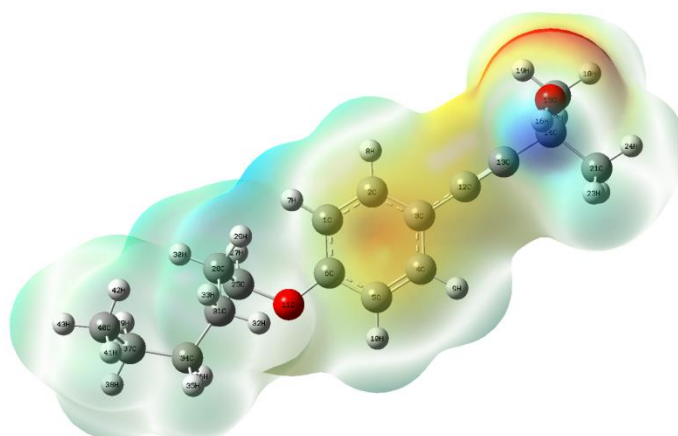
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ABSTRACT

4-(4-n-hexyloxyphenyl)-2-methyl-3-butyn-2-ol compound synthesized by O-Alkylation of 4-iodophenol with 1-bromohexane under basic condition provide the ether followed by coupling with 2-methyl-3-butyn-2-ol under Sonogashira reaction conditions to give the protected phenylacetylene. Single point energy was calculated for optimized the compound which helps the accurate path for the further computational studies. Molecular Electrostatic Potential map drawn using Gauss View output software and illustrates the charges among the atoms. This transitional compound used as the involving agent for laboratory component.

Keywords: 4-(4-N-Hexyloxyphenyl)-2-Methyl-3-Butyn-2-Ol, Total Energy Distribution, Molecular Electrostatic Potential.

GRAPHICAL ABSTRACT



I. INTRODUCTION

In recent decades, there has been increasing interest and research activity on the electrical and vibrational properties of organic systems [1]. A. R. Reddy et al analyzed the behavior of electrons which are easily affected by an external optical field because they are relatively weakly bound to the nucleus [2]. A. Rudge et al have shown that the orbital orbits relocated can be extended over the entire molecule which provides a tremendous and fast polarization [3]. It can be used to significantly reduce the transmittance of a device exposed to high technology entries it is the base [4, 5]. The high optical non-linearity makes it a promising material for optoelectronic and non-linear optical applications [6].

2methyl3butin2ol and its derivatives are known for their importance in biology and materials science. The interesting properties of 2methyl3butin2ol (2M3BY) fascinate agrochemical manufacturers and specialized chemists. Monoamine oxidase for the Mannich reaction [7]. It has been reported that 2methyl3buten2ol is efficiently substituted by MBY in baits to trap IPS typographus and also [8]. Samar Al Jitan et al have correlated the strength of basic catalyst sites and their activity [9]. Their properties are determined by triple bonding and are implicated in semi hydrogenation of nanoparticles [10-12].

The target compound was synthesized by reacting 4iodophenol with 1bromohexane in the presence of anhy K_2CO_3 undergoes O-alkylation to give the ether, which was then coupled with 2methyl3butin2ol under Sonogashira reaction conditions to provide the protected phenylacetylene [13].

This letter 4HP2M3B has been examined with both the observed methods and the calculation methods. The literature review concluded that there are no publications of the title compound 4HP2M3B using theoretical methods. From the equilibrium molecular structure, vibrational parameters and assignments help determine

the results of the internal properties of molecules. Electronic transitions, molecular orbital space, visual representation of charges, intra-charge interactions are predicted using DFT methods using the hybrid base set.

SYNTHESIS AND CHARACTERIZATION

PREPARATION OF 4-N-HEXYLOXYDOBENZENE

The 100 ml flask was equipped with a magnetic stirrer, a water condenser, and an argon inlet filled with acetone (40 ml), 4iodophenol (1 g, 4.54 mmol, 1 equiv), anhydrous K₂CO₃ (3.13 g, 22, 7 mmol, 5 equivalents), and hexyl bromide (1.5 g, 9.08 mmol, 2 equivalents) were then coated with argon for a certain time. After septum closure, the reaction mixture was refluxed for 12 h with vigorous stirring and filtered while hot through the celite layer. The crude mass obtained by evaporating the solvent from the filtrate was extracted to CH₂Cl₂ and the organic layer was washed with brine and dried on Na₂SO₄. Evaporation of the solvent yields crude oil, which is purified by column chromatography using silica gel (100200 mesh). Eluted with hexane followed by a 10% mixture of EtO Hexane yielded a colorless oil product. R_f = 0.6 in 10% EtOAhexan; a pale yellow liquid; yield: 1.0 g (83.8%); IR (KBr tablets): maximum in cm⁻¹ 2923, 2857, 1615 and 1582; ¹H NMR (200MHz, CDCl₃): 7.52 (d, J = 9.0Hz, 2H, Ar), 6.5 (d, J = 9.0, 2H, Ar), 3.8 (t, J = 6.6, 2H, 1 × OCH₂), 1,751.2 (m, 8H₄ × CH₂), 0.88 (t, J = 6.8, 3H, 1 × CH₃); FAB mass: 289.2

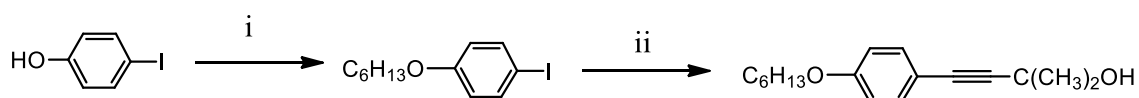
PREPARATION OF 4-(4-N-HEXYLOXYPHENYL)-2-METHYL-3-BUTYN-2-OL (4HP2M3B)

Mixture of 2methyl3butyn2ol (1.1 ml, 11.45 mmol, 1.1 equiv.), 4nhexyloxyiodobenzene (3 g, 10.41 mmol, 1 equiv), Triphenylphosphine (109.5 mg, 0.41 mmol, 0.04 equiv.), Bis (triphenylphosphine palladium (II) chloride (43.8) mg, 0.01 mmol, 0.006 equiv), copper (I) iodide (79.5 mg, 0.41 mmol, 0.04 equiv) equivalent), THF (10 ml) and triethylamine (10 ml) were heated under reflux for 12 h under inert atmosphere.

The reaction mixture was filtered and evaporated under vacuum. The obtained pale yellow solid was dissolved in CH₂Cl₂ (20ml) and the resulting solution was washed with 0.2M HCl (aq), 5% NaOH (aq), water and saline, and then dried on anhydrous Na₂SO₄. The solid was thus purified by column chromatography using (neutral) alumina

Elution with a 10% mixture of EtOAhexane yielded a pure product. R_f = 0.3 in 10% EtOAhexane; a viscous yellow liquid; yield: 2.39 g (92.6.0%); IR (KBr pellets): up to cm⁻¹ 3363, 2929, 2864, 2230 and 1601; ¹H NMR (400MHz, CDCl₃): 7.35 (d, J = 8.8Hz, 2H, Ar), 6.83 (d, J = 8.8, 2H, Ar), 4.01 (t, J = 6.6, 2H, 1 × OCH₂), 2.06 (s, 1H, 1 × OH), 2.3 0.98 (m, 39H, 1 × CH₃ 15 × CH₂, 6 × CH), 1.01 (s, 3H, 1 × CH₃), 0.91 (d, J = 5.44, 3H, 1 × CH₃), 1,761.3 (m, 8H. 4 × CH₂), 1.65 (s, 6H, 2 × CH₃) and 0.92 (t, J = 7.1, 3H, 1 × CH₃); FAB Mass: 260.5 [M]⁺ Calculated for C₁₇H₂₄O₂.

SCHEME FOR THE PREPARATION OF 4-(4-N-HEXYLOXYPHENYL)-2-METHYL-3-BUTYN-2-OL (4HP2M3B)



i) 1-Bromohexane, anhy. K₂CO₃, acetone, reflux, 12 hrs

ii) 2-Methyl-3-butyn-2-ol, CuI, Ph₃P, (Ph₃P)₂PdCl₂, THF, Et₃N, reflux, 12 hrs

COMPUTATIONAL DETAILS

The program GAUSSIAN 09W is used to predict the quantum calculations of 4HP2M3B with the original version as well as the three functional parameters by applying the method of combining BeckeLeeYangParr level with different basis sets on a personal computer core with 1.9 GHz Intel Core i3 processor to obtain the fully optimized geometry [14]. Gaussian software is a hyperlocalization tool for developing areas of computational physics such as structural analysis, reaction mechanisms, potential energy values, and charge distribution and excitation energies of compounds [15]. Single point energy calculation calculates the energy of specific molecular structures and the properties of the molecule that were initially predicted. Geometric optimization calculates the equilibrium structure of the molecule, optimizes the transition structure, and minimizes the energy in dynamic basis sets [16]. The scale coefficients are started by optimizing the least squares of the calculated data with the experimental data to fit both experimental and theoretical results. Oscillation

assignments with total energy distribution (TED) were calculated and interpreted using a proportional quantum mechanical program using VEDA 4.0 software to analyze the vibrational energy distribution [17-19]. A high level of accuracy as is normally considered as well as achievable related by the GAUSSVIEW program is achieved by assigning the vibrational frequencies of the molecules.

Electron vibration frequency and electronic properties such as HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) orbital energy distributions, atomic charge distribution Mulliken particle and thermodynamic parameters are resolved by time-dependent DFT (TDDFT) [20]. Energy absorption spectrum and energy difference plot taken from Gauss View 5.0 program [21]. Electrostatic potential map element (MEP) has been plotted. Finally, studies are performed to find the state densities of different atoms, the total state densities and band gap studies are found using theoretical demo.

STRUCTURAL PARAMETERS

The structure of the synthesized compound was drawn with Gauss View 09W input program. The design has been optimized with some of the Gaussian 09W hybrid base kits. The global minimization energy is 812,687 AU derived from the base set B3LYP / 631 (d, p), which is a good result compared to the other base sets. The optimized structure of 4HP2M3B is shown in Fig. 1. The optimized parameters are shown in Table 1. The symmetry of the C1 point group corresponds to the compound 4HP2M3B. Some differences in carbon and carbon bond lengths have been published. A higher value was found for the bond length CC, which combines with oxygen. The other bonded bonds are not greater than the oxygen combination for the CC bond. Oxygen carbon is the lowest of all bond lengths. The hexyloxy group has been attached to the para position of the benzene ring which can exist in various conformations. The interaction of the 2-methyl-3-bitin-2-ol alkyne group with the ring substituent is of great importance for determining its structural and vibrational properties. Changes in the charge distribution on the carbon atom can change the frequency or length of the CH bond with the benzene ring [22-23].

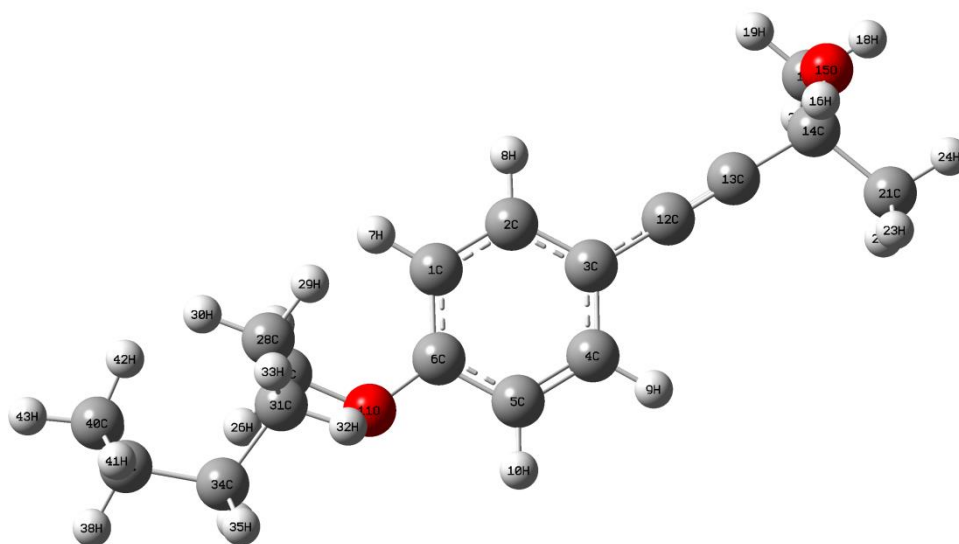


Fig 1. Optimized structure of 4HP2M3B

TOPOLOGICAL ATOMIC CHARGE DISTRIBUTION

Mulliken population and Natural Population Analysis (NPA) are the best analytical methods to find the topical atomic charges. The recent study predicted the atomic charges using the highest basis set in B3LYP for Mulliken method. The atomic charges of 4HP2M3B is tabulated the comparative results in Table 2 and shown the charge distribution in Fig. 2 by the above mentioned method.

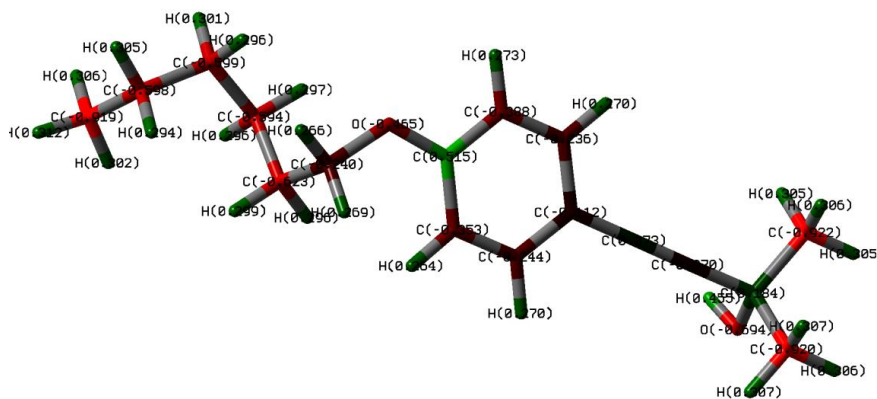


Fig 2. Topological atoms charge analyses of 4HP2M3B

From the results, concluded the C3, C6, C13 and C14 are electro positivity charge in the table because of that carbons are bonding with the oxygen and triplet charge. Other carbon showed the electro negativity through the Mulliken charge analysis. This is due to the attachment of the new substituent molecules. For that reason, the new substituent molecules like O11 and O15 show the required electro negativity. The hydrogen atoms have electro positivity because of this; they are joined together with the electro negative atoms of oxygen and carbon. In the carbons, C6 is able to network by the negatively signed part of the receptor easily because of it is the most positively charged part. In the contrast, C21 is able to interact with the donor atom because of its most negatively charged part. Oxygen can form a bond with a proton and other electrophilic atoms while sharing its free electron pair. Oxygen is able to share its free electron pair to form a bond with a proton and other electrophilic atoms.

MOLECULAR ELECTROSTATIC POTENTIAL

The visual representations are mostly welcomed one, while compared with other studies. Molecular electrostatic potential (MEP) is the versatile used visual illustration to find out the reactivity of the molecule which explains through its colors [24], hydrogen bonding interactions and biological detection methods [25]. The electrophilic and nucleophilic attacks are demonstrated by two different colors. The MEP's of 4HP2M3B is calculated and drawn by the computational method in Fig. 3. The colors are increased in the order of red, yellow, green, blue shades. The red color starts from negative region for electrophilic reactivity and blue ends with positive region for nucleophilic reactivity regions. The values of the regions are increased from red to blue (-7.528 to 7.528) for the title molecule. The Carbon and Oxygen groups are almost negative electrostatic potential for electrophilic attack. The hydrogen atoms are the positive one for nucleophilic attack. The Mulliken population and NPA analysis are showing the electronic charges distribution of the molecules, which are identified with the support of MEP maps.

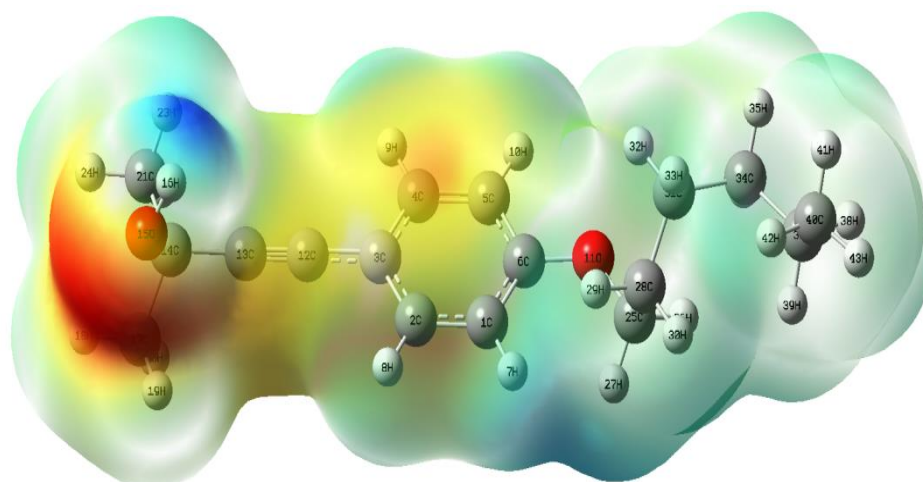


Fig 3. MEP map for 4HP2M3B

II. CONCLUSION

The research the experimental FT-IR, FTR spectroscopic studies are investigated for the first time. The theoretical spectra are predicted using computational methods and well agreed with experimental results. The molecular structure was characterized by ¹H Nuclear Magnetic Resonance Spectroscopy, Infrared Spectroscopy, Mass Spectroscopy and Elemental Analysis. Structure of the compound is confirmed using the computational spectral studies and geometrical parameters. 2M3B has been an acetylene precursor on the synthesis of suicide in activators for monoamine oxidase. The moiety 2M3B is bonded with 4-(4-n-hexyloxyphenyl) it enhances the hyperpolarizability. This study is helpful for further studies like MEP, Topological atomic charge distribution and thermo dynamical studies. The vibrational assignments of the 4HP2M3B are assigned with TED value. Thermodynamic parameters also tabulated.

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Table 1. Selected Optimized Geometrical Parameters Of 4hp2m3b

Bond Length		Bond Angle		Dihedral Angel	
C1-C2	1.401	C2-C1-C6	119.95	C6-C1-C2-C3	-2.32
C1-C6	1.400	C2-C1-H7	120.08	C6-C1-C2-H8	177.82
C1-H7	1.070	C6-C1-H7	119.97	H7-C1-C2-C3	178.21
C2-C3	1.402	C1-C2-C3	119.96	H7-C1-C2-H8	-1.65
C2-H8	1.070	C1-C2-H8	119.98	C2-C1-C6-C5	3.88
C3-C4	1.402	C3-C2-H8	120.05	C2-C1-C6-O11	-175.41
C3-C12	1.543	C2-C3-C4	120.00	H7-C1-C6-C5	-176.65
C4-C5	1.403	C2-C3-C12	119.88	H7-C1-C6-O11	4.06
C4-H9	1.070	C4-C3-C12	120.12	C1-C2-C3-C4	-0.70
C5-C6	1.402	C3-C4-C5	119.98	C1-C2-C3-C12	179.27
C5-H10	1.071	C3-C4-H9	119.99	H8-C2-C3-C4	179.16
C6-O11	1.423	C5-C4-H9	120.03	H8-C2-C3-C12	-0.87
O11-C25	1.423	C4-C5-C6	119.85	C2-C3-C4-C5	2.16
C12-C13	1.213	C4-C5-H10	120.13	C2-C3-C4-H9	-178.19
C13-C14	1.533	C6-C5-H10	120.02	C12-C3-C4-C5	-177.81
C14-O15	1.433	C1-C6-C5	120.14	C12-C3-C4-H9	1.84
C14-C17	1.544	C1-C6-O11	119.65	C2-C3-C14-O15	12.81
C14-C21	1.544	C5-C6-O11	120.20	C2-C3-C14-C17	-104.92
O15-H16	0.958	C6-O11C25	113.00	C2-C3-C14-H21	133.02
C17-H18	1.062	C13-C14-O15	109.43	C4-C3-C14-O15	-169.42
C17-H19	1.061	C13-C14-C17	109.51	C4-C3-C14-C17	72.85
C17-H20	1.064	C13-C14-C21	109.34	C4-C3-C14-H21	-49.21
C21-H22	1.070	O15-C14-C17	109.45	C3-C4-C5-C6	-0.60
C21-H23	1.071	O15-C14-C21	109.42	C3-C4-C5-H10	179.43
C21-H24	1.072	C17-C14-C21	109.67	H9-C4-C5-C6	179.75
C25-H26	1.063	C14-C15-H16	109.79	H9-C4-C5-H10	-0.21
C25-H27	1.062	C14-C17-H18	109.81	C4-C5-C6-C1	-2.42
C25-C28	1.532	C14-C17-H19	109.41	C4-C5-C6-O11	176.87
C25-C37	1.670	C14-C17-H20	109.84	H10-C5-C6-C1	177.54
C25-H39	1.146	H18-C17-H19	109.26	H10-C5-C6-O11	-3.17
H26-C34	0.891	H18-C17-H20	109.19	C1-C6-O11-C25	-106.81
H26-C37	1.059	H19-C17-H20	109.32	C5-C6-O11-C25	73.90
C28-H9	1.063	C14-C21-H22	85.21	C6-O11-C25-H26	177.52

C28-H30	1.072	C14-C21-H23	81.49	C6-O11-C25-H27	56.95
C28-C31	1.532	C14-C21-H24	140.55	C6-O11-C25-C28	-63.55
C31-H32	1.063	H22-C21-H23	138.38	C6-O11-C25-C37	137.43
C31-H33	1.065	H22-C21-H24	86.38	C6-O11-C25-H39	106.03
C31-C34	1.531	H23-C21-H24	79.63	C13-C14-O15-H16	60.33
C34-H35	1.074	O11-C25-H26	109.07	C17-C14-O15-H16	-179.66
C34-H36	1.062	O11-C25-H27	110.27	C21-C14-O15-H16	-59.46
C34-C37	1.538	O11-C25-C28	109.20	C13-C14-C17-H18	177.02
C37-H38	1.077	O11-C25-C37	107.49	C13-C14-C17-H19	57.12
C37-H39	1.077	O11-C25-H39	82.57	C13-C14-C17-H20	-62.89
C37-C40	1.544	H26-C25-H27	109.74	O15-C14-C17-H18	57.06
C40-H41	1.037	H26-C25-C28	108.93	O15-C14-C17-H19	-62.85
C40-H42	1.099	H27-C25-H39	75.21	O15-C14-C17-H20	177.15
C40-H43	1.055	H27-C25-C28	109.61	C21-C14-C17-H18	-62.99

Table 2. Mullikan Atomic Charges (A.U.) For 4hp2m3b.

S.No.	Mulliken Charge	B3LYP/6-31g(d,p)	S.No.	Mulliken Charge	B3LYP/6-31g(d,p)
1	C1	-0.112	23	H23	0.239
2	C2	-0.086	24	H24	0.206
3	C3	0.033	25	C25	-0.056
4	C4	-0.103	26	H26	0.179
5	C5	-0.106	27	H27	0.090
6	C6	0.290	28	C28	-0.328
7	H7	0.088	29	H29	0.069
8	H8	0.101	30	H30	0.172
9	H9	0.102	31	C31	-0.217
10	H10	0.148	32	H32	0.107
11	O11	-0.554	33	H33	0.088
12	C12	-0.046	34	C34	-0.137
13	C13	0.020	35	H35	0.027
14	C14	0.095	36	H36	0.174
15	O15	-0.543	37	C37	-0.196
16	H16	0.316	38	H38	0.093
17	C17	-0.283	39	H39	0.143
18	H18	0.111	40	C40	-0.328
19	H19	0.122	41	H41	0.149
20	H20	0.111	42	H42	0.123
21	C21	-0.626	43	H43	0.128
22	H22	0.197			