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Spectroscopic Characterization of (E)-1,4-Bis(3,4-dimethoxyphenyl) but-1-ene Ligand: IR and NMR Analysis Using DFT Methods

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Abstract:

In this study, the molecular structure of (E)-1,4-bis (3,4-dimethoxyphenyl) but-1-ene ($C_{20}H_{24}O_4$) ligand was thoroughly investigated using Density Functional Theory (DFT/B3LYP). Computational calculations employing the 6-311++G(d,p) basis set and the PM6 semi-empirical model yielded optimized geometries that closely matched experimental X-ray data. Vibrational frequencies computed via DFT/B3LYP provided precise spectral information, facilitating accurate vibrational assignments. The comparison of optimized geometric parameters and 1H and 13C NMR chemical shifts with experimental data demonstrated excellent agreement, validating the computational approach. Furthermore, electronic properties such as frontier molecular orbitals (HOMO-LUMO) and molecular electrostatic potential (MEP) distributions were analyzed based on theoretical calculations. These insights into electronic structure and MEP offer valuable understanding of the ligand's reactivity and interaction potentials in various chemical environments.

Keywords: IR; NMR; DFT; MEPs

1.Introduction

(E)-1,4-Bis (3,4-dimethoxyphenyl) but-1-ene, abbreviated as DMBDB, is a significant ligand in organometallic chemistry. Organometallic chemistry explores the interactions of organic molecules with metal atoms and their catalytic effects on transformations. DMBDB finds extensive use in metal-catalyzed organic syntheses [1-2]. Particularly, it plays a crucial role in reactions such as ring-opening metathesis polymerization (ROMP), which converts terminal alkenes into polymer chains [3].

In ROMP reactions, DMBDB coordinates with metallocene-type metal catalysts to control the growth of polymer chains. It is also utilized in other organic syntheses, including cross-coupling reactions, where a metal catalyst facilitates the formation of bonds between two different organic molecules [4].

Metal-catalyzed reactions play a vital role in organic chemistry by simplifying the synthesis of complex molecules, often required in industries such as pharmaceuticals, where synthesis pathways are typically multi-step processes. Metal catalysts enhance efficiency and streamline organic syntheses [5].

(E)-1,4-Bis (3,4-dimethoxyphenyl) but-1-ene is an alkene derivative characterized by a four-carbon butene chain with two phenyl groups and dimethoxy (CH_3OCH_3) groups attached to these phenyl groups [6]. The alkene group denotes the presence of a double bond, defining the molecule's stereochemical structure. The prefix "(E)" indicates that the double bond is in a trans configuration, situated between the two phenyl groups [7].

2. Computer Details

2.1. DFT Calculations

The ground-state molecular simulation of the molecule was performed using the Gaussian 09W program package [10], applying density functional theory (DFT) methods, and the output files were visualized using Gaussian View 5 software [11]. Calculations were carried out using the B3LYP hybrid functional with the LYP correlation functional, employing the 6-311++G(d,p) basis set [12-13].

3. Results And Discussion

3.1. Analysis of Molecular Geometry Structure

(E)-1,4-Bis (3,4-dimethoxyphenyl) but-1-ene, known as DMBDB, was synthesized by Felmer Latayada and colleagues [14]. The crystal structure of this synthesized molecule has been documented in the Cambridge Structural Database (CSD) under the code CCDC 1537460. The experimental structure and atomic numbers of DMBDB are depicted in Figure 1.

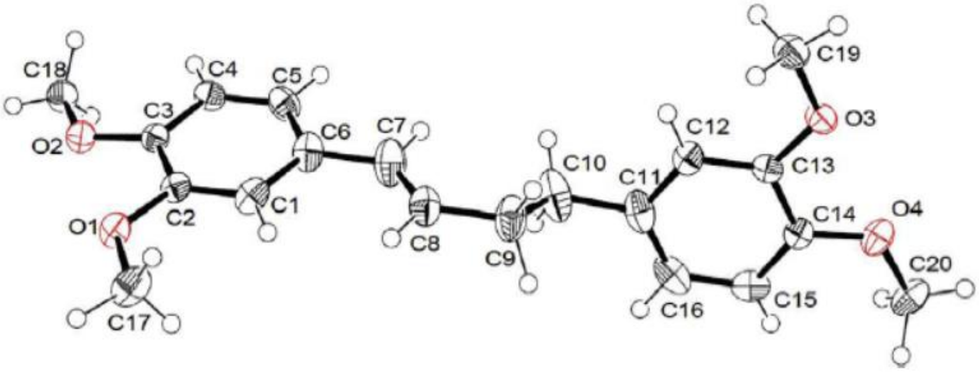

Figure 1. Experimental structure of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene ligand [14]

To investigate the theoretical geometric structure of the DMBDB molecule and compare it with experimental data obtained from the Cambridge Structural Database (CSD), Density Functional Theory (DFT) calculations were performed using the Gaussian 09 [10] program. The calculations employed the B3LYP functional with the 6-311++G(d,p) basis set [11].

The DFT/B3LYP/6-311++G(d,p) method was employed to optimize the stable structure of DMBDB, integrating the crystal structure data retrieved from CSD. The optimized molecular structure is depicted in Figure 2.

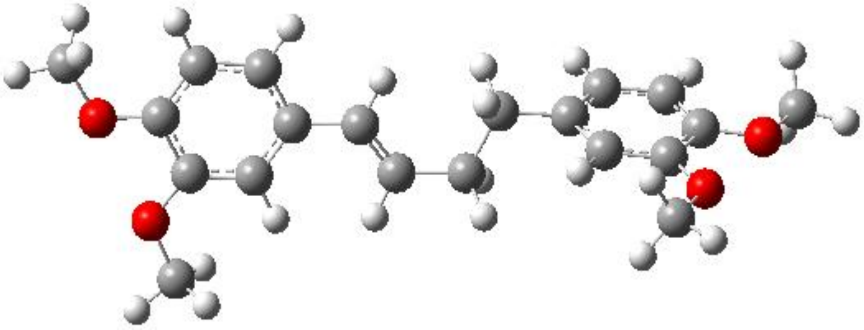

Figure 2. Optimized geometry of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene ligand calculated using the B3LYP/6-311++G(d,p) method

This methodological approach ensures that the theoretical model aligns closely with experimental findings, facilitating a comprehensive analysis of the molecular geometry. The use of DFT/B3LYP methodology with the specified basis set allows for accurate prediction and optimization of molecular structures, vital for understanding the chemical and physical properties of complex organic molecules like DMBDB. This integrated computational and experimental approach enhances our understanding of molecular structures and their dynamic behaviors in various chemical environments.

By validating theoretical predictions against experimental data, this study provides a robust foundation for further exploring the functional characteristics and potential applications of DMBDB in diverse fields of organic chemistry.

The bond lengths (Å) and bond angles (º) of (E)-1,4-Bis(3,4-dimethoxyphenyl) but-1-ene (DMBDB) molecule were theoretically computed and compared with experimental values as listed in Table 1.

Density Functional Theory (DFT) calculations using the Gaussian 09 [10] program with the B3LYP functional and 6-311++G(d,p) basis set [11] were employed to determine these parameters. The optimized molecular structure was obtained using the DFT/B3LYP/6-311++G(d,p) method, ensuring accurate prediction of bond lengths and angles. Figure 2 illustrates the optimized geometric structure of DMBDB.

Table 1 presents the calculated bond lengths and bond angles alongside experimental values retrieved from the literature or databases such as the Cambridge Structural Database (CSD). This comparative analysis between theoretical predictions and experimental data provides insights into the structural characteristics and molecular dynamics of DMBDB. The theoretical calculation of these parameters is crucial for understanding the molecular geometry and its impact on the chemical properties and reactivity of DMBDB in various applications, including catalysis and organic synthesis.

Bond Lengths			**Bond Angles**		
	X-ray [14]	**B3LYP**		**X-ray [14]**	**B3LYP**
C20-O4	1.42540	1.41876	C20-O4-C14	117.34257	118.16043
O4-C14	1.36907	1.36279	O4-C14-C13	115.10199	115.89288
C14-C15	1.37784	1.38944	O4-C14-C15	125.53976	125.12869
C15-C16	1.39819	1.40067	C14-C13-O3	115.24233	115.67339

C16-C11	1.38209	1.38850	C14-C13-C12	119.84160	119.51596
C11-C10	1.51508	1.51312	C13-O3-C19	117.06922	118.40474
C11-C12	1.38976	1.40573	C13-C12-C11	121.56461	121.58339
C12-C13	1.38165	1.39047	C12-C11-C10	118.85915	120.24586
C13-O3	1.36173	1.36200	C11-C10-C9	115.37617	112.73673
O3-C19	1.43787	1.41903	C10-C11-C16	123.39775	121.49311
C10-C9	1.46482	1.53838	C15-C16-C11	121.92357	120.95645
C9-C8	1.50126	1.50509	C10-C9-C8	116.10698	116.47808
C8-C7	1.31269	1.33943	C9-C8-C7	127.15780	126.75901
C7-C6	1.47772	1.47031	C8-C7-C6	129.00047	127.66643
C1-C6	1.40213	1.41109	C7-C6-C1	121.20639	123.07075
C5-C6	1.38253	1.39383	C7-C6-C5	121.21717	119.16321
C5-C4	1.39223	1.39853	C6-C5-C4	122.94505	121.35715
C1-C2	1.37878	1.38621	C5-C4-C3	118.84012	120.61074
C3-C2	1.39511	1.41946	C4-C3-O2	124.72256	125.22438
C3-C4	1.38638	1.38892	C3-O2-C18	117.18541	118.20928
C3-O2	1.36941	1.36020	C17-O1-C2	118.08366	118.42623
C18-O2	1.43057	1.41958	O1-C2-C1	123.96801	124.77867
C17-O1	1.43386	1.41914	O1-C2-C3	114.48862	115.39952
O1-C2	1.37408	1.36161	C1-C2-O1	123.96801	124.77867

Table 1. Geometric parameters bond lengths (Å) and bond angles (o) of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene ligand.

3.2. Electronic Properties

The highest occupied molecular orbital (HOMO) [15] and the lowest unoccupied molecular orbital (LUMO) are fundamental orbitals involved in chemical reactions [16]. The HOMO energy represents the molecule's ability to donate electrons (π-donor), while the LUMO energy describes its ability to accept electrons (π-acceptor). These electronic characteristics are pivotal in understanding the reactivity and behavior of molecules.

The electronic properties of the DMBDB molecule were theoretically calculated using the B3LYP method with the 6-311++G(d,p) basis set [11]. The HOMO and LUMO energies were computed to analyze the electronic structure parameters. Table 2 compares these theoretical calculations with experimental data.

Determining the HOMO and LUMO energies provides insights into the electronic structure of DMBDB, which are crucial for understanding its role in various chemical processes, including catalysis and molecular recognition. These calculations serve as a foundation for predicting and interpreting the molecule's reactivity and interaction capabilities in different applications.

.	
Parameters	**B3LYP /6-311++G(d,p)**
EHOMO (eV)	-5.45239
ELUMO (eV)	-0.83186
ΔE = ELUMO-EHOMO (eV)	4.62053
I (eV)	5.45239
A (eV)	0.83186
χ (eV)	3.142125
η (eV)	2.310265
S (eV^{-1})	0.091703
ETOTAL (a.u)	-1077.7035

Table 2. Molecular orbital energy calculations of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene ligand

LUMO and HOMO are critical concepts in determining the electronic structure of a molecule [17]. These terms denote the energies of the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) within the molecule. ELUMO and EHOMO refer specifically to the energy levels of these orbitals. In-depth analysis of the electronic structural properties of the DMBDB molecule involves visualizing the LUMO and HOMO orbitals, detailed in Figure 3. These analyses provide significant insights into the nature of molecular interactions, while determining the ELUMO and EHOMO values serves as a fundamental source of information for understanding the molecule's physical and chemical properties.

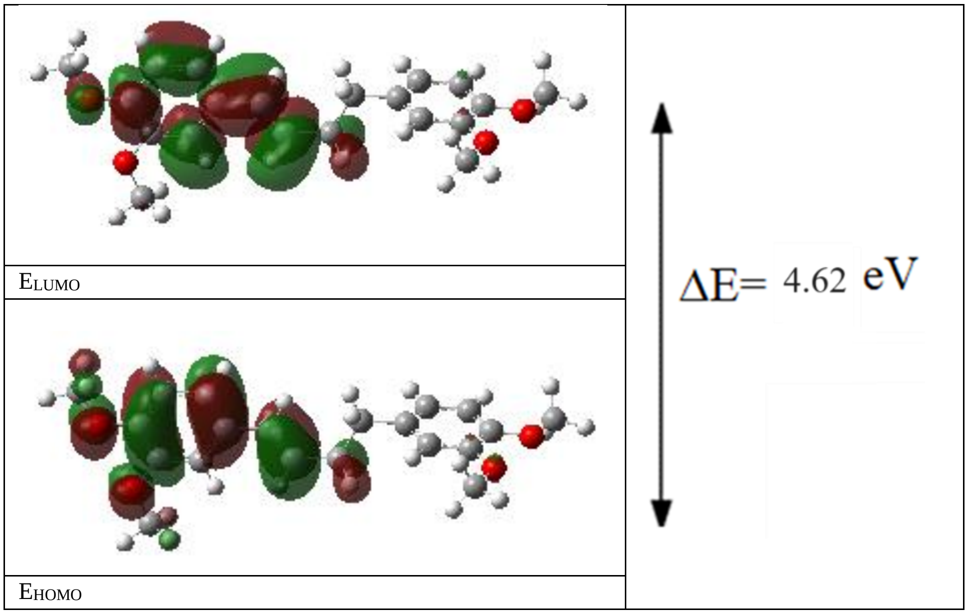

Figure 3. 3D orbital energies of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene ligand.

Upon examining the drawings of the HOMO and LUMO orbitals, a conclusion emerges that corroborates both this study and previous experimental research. According to the electrostatic potential mapping, electron density increases along the green-red direction. In other words, points indicated in red in the drawings are electron-rich. Furthermore, the positioning of the HOMO orbitals serves as an indicator of activity. Since reactions occur through interactions involving the HOMO and LUMO orbitals, atoms where these orbitals are located exhibit a propensity for reaction.

Understanding the distribution and energy levels of HOMO and LUMO orbitals is crucial for predicting and interpreting the chemical reactivity of molecules like DMBDB. This analysis not only validates theoretical predictions with experimental findings but also provides insights into the electronic properties governing molecular interactions and reactivity pathways. By visualizing the spatial arrangement and energy characteristics of these orbitals, researchers gain deeper insights into how DMBDB interacts in various chemical environments, thereby informing the design of new molecules and materials with tailored electronic properties.

3.3. Molecular Electrostatic Potential Surfaces (MEPS)

The optimized structures of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene (DMBDB) molecule were computed using the B3LYP/6-311++G(d,p) method, and the three-dimensional Molecular Electrostatic Potential (MEP) maps of these structures are depicted in Figure 4. MEP mapping [18] visualizes the electron density and potential reactive regions of the molecule using a color scale, providing crucial insights into molecular reactivity and structural activity.

Negative MEP values (red/orange colors) indicate electron-rich regions, whereas positive MEP values (blue colors) represent electron-deficient regions. This analysis serves as a valuable tool for understanding the chemical reactivity, structural features, and hydrogen bonding capabilities of the DMBDB molecule.

By visualizing the distribution of electrostatic potential on the molecular surface, researchers can gain significant understanding of how DMBDB interacts chemically and structurally in various contexts. This information is essential for designing molecules with specific electronic properties and predicting their behavior in complex chemical environments.

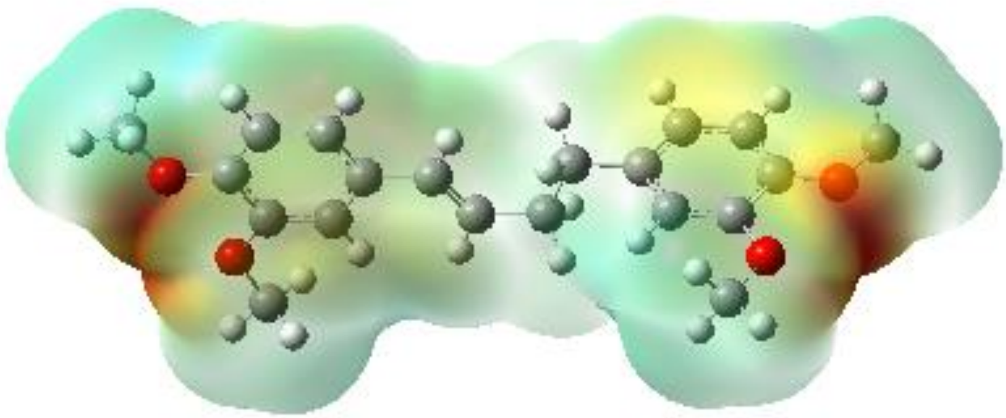

Figure 4. Molecular electrostatic surface map of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene ligand.

The electron density shows a uniform distribution throughout the molecule. The surface revealed in the MEP map also indicates molecular size, shape, and electrostatic potential values. In the MEP map of the neutral molecule, electron-rich regions are depicted in red, while electron-deficient regions appear in blue. Upon closer examination of the figure, it was found that in the neutral form, the regions with the highest electron density are around the oxygen atoms, and the regions with the lowest electron density are in the N-H region.

3.4. Infrared Spectrum

The vibration spectrum of the DMBDB molecule has been thoroughly investigated in the mid-infrared region (4000-400 cm⁻¹). In this study, the vibrational frequencies of the molecule were theoretically calculated and compared with experimentally obtained spectra. Table 3 illustrates the theoretical and experimental assignments of vibration spectra.

Theoretical calculations were conducted using Density Functional Theory (DFT) and supported by the 6-311++G(d,p) basis set. The experimental vibration spectrum delineates specific vibrational modes of the molecule and their wavenumbers (cm⁻¹). These analyses provide a valuable tool for understanding the nature of chemical bonds, molecular structures, and thermodynamic properties of DMBDB.

Assigments	Exp.	B3LYP/6-311++G(d,p)
ʋ(C=C)	1601	1642.42
ʋ(C=C)	1582	1613.43
ʋ(C=C))	1512	1545.64

Table 2. Experimental and theoretical wavenumber and labeling of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene ligand.

The C=C stretching vibration band of the DMBDB molecule appeared at 1601 cm⁻¹. These vibrational bands were theoretically calculated at 1642.42 cm⁻¹ using the B3LYP/6-311++G(d,p) level of theory. The obtained results demonstrate that the theoretical calculations are in good agreement with experimental data. This concordance indicates accurate characterization of the molecule's structural features and vibrational modes, contributing to understanding the spectral properties of the molecule.

In conclusion, this study on the vibration spectrum of the DMBDB molecule establishes an important foundation for analyzing and designing molecular structures in the fields of organic chemistry and materials science.

3.5 NMR Spectrum

The combined use of NMR and computational simulation methods is essential for predicting and interpreting the structure of large biomolecules. In this study, 13C and 1H NMR chemical shift calculations were performed using the B3LYP method with the 6-311++G(d,p) basis set for the optimized geometry. Table 3 presents the experimental and theoretical 1H and 13C isotropic chemical shifts of the DMBDB molecule (all values referenced to TMS in ppm).

	Deneysel	**Teorik**		
^{1}H		**GIAO**	**CSGT**	**IGAIM**
H_{-C20}	6.90	7.0341	7.3065	7.3074
H_{-C19}	6.86	6.7828	7.0024	6.9995
H_{-C18}	6.81	6.7050	6.9861	6.9873
H_{-C17}	6.80	6.5929	6.9695	6.9680
H_{-C10}	6.77	6.5420	6.9154	6.9114
H_{-C9}	6.75	6.5291	6.8919	6.8900
H_{-C8}	6.36	6.4997	6.8409	6.8367
H_{-C7}	6.13	6.3744	6.5996	6.5987
H_{-C16}	3.90	4.0737	4.5862	4.5833
H_{-C15}	3.90	4.0527	4.5610	4.5581
H_{-C14}	3.90	4.0310	4.5526	4.5496
H_{-C13}	3.89	4.0082	4.5520	4.5489
H_{-C12}	3.87	3.5759	4.2215	4.2191
H_{-C11}	3.87	3.5666	4.2207	4.2183
H_{-C6}	3.87	3.5662	4.1888	4.1864
H_{-C5}	2.74	3.5650	4.1877	4.1859
H_{-C4}	2.74	3.5365	3.3048	3.3051
H_{-C3}	2.51	3.5265	3.1742	3.1743
H_{-C1}	2.51	3.5184	3.0556	3.0551
^{13}C				
C_{20}	149.1	156.1888	154.6453	154.6381
C_{19}	149.0	155.9046	154.5592	154.5520
C_{18}	148.7	155.5257	154.4226	154.4147

C_{17}	148.3	154.1067	153.0303	153.0221
C_{10}	134.5	140.7770	140.1170	140.1089
C_9	130.9	135.2365	134.4395	134.4283
C_8	130.0	132.6802	132.6099	132.5908
C_7	128.1	131.2638	131.7270	131.7088
C_6	120.2	125.4482	124.4220	124.4003
C_5	118.8	123.9117	122.5102	122.4898
C_4	111.8	112.7579	111.4595	111.4435
C_3	111.2	111.6542	110.7060	110.6863
C_2	111.1	111.1878	110.3614	110.3416
C_1	108.5	106.0232	104.1420	104.1250
C_{16}	55.9	54.3039	54.5796	54.5559
C_{15}	55.9	54.2801	54.4745	54.4506
C_{14}	55.8	54.2275	54.4134	54.3895
C_{13}	55.8	54.2270	54.3687	54.3451
C_{12}	35.6	40.6373	41.8562	41.8370
C_{11}	35.1	26.1814	36.8802	36.8670

Table 3. Experimental and theoretically calculated 13C and 1H isotropic NMR chemical shifts of (E)-1,4-bis(3,4-dimethoxyphenyl)but-1-ene ligand (all values in ppm).

4. Results

In this study, the molecular structure of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene (C20H24O4) has been extensively investigated using Density Functional Theory (DFT/B3LYP). Calculations were performed employing the 6-311++G(d,p) basis set and the PM6 semi-empirical model. The optimized geometry of the molecule was found to be consistent with X-ray data, and the vibration frequencies calculated using the DFT/B3LYP method were accurately reproduced to facilitate reliable vibrational assignments. Additionally, optimized geometric parameters and 1H and 13C NMR chemical shifts were compared with experimental data, showing excellent agreement between calculated and experimental results.

Furthermore, molecular electrostatic potential (MEP) analysis was conducted to determine the distribution of electron densities in various regions of the molecule. These analyses provided important insights into the chemical properties and reactivity of (E)-1,4-bis(3,4-dimethoxyphenyl) but-1-ene.

This study demonstrates that the DFT/B3LYP method and PM6 model are effective approaches for accurately predicting the structure and properties of complex organic molecules. The findings offer a valuable foundation for molecular design and advanced pharmaceutical research.

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