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Graphical Abstract





Synthesis, Spectral Analysis and Quantum Chemical Studies on Molecular Geometry of (2E,6E)-2,6-bis(2-chlorobenzylidene)cyclohexanone: Experimental and Theoretical Approaches.

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Abstract

(2E,6E)-2,6-bis(2-chlorobenzylidene) cyclohexanone was synthesized and characterized by proton and carbon nuclear magnetic resonance, infrared, ultraviolet-visible, mass spectral analysis and X-ray crystallography techniques. Quantum Chemical calculations were done using Becke3-Lee-Yang-Parr with 6-31, 6-311, 6-311+ and 6-311++G (d, p) as basis sets and CAM-B3LYP with 6-31G(d,p) as the basis set. A good correlation between calculated and experimental spectroscopic data has been accomplished. Ultraviolet-Visible spectrum of the molecule was recorded in the region 200-500 nm and the electronic properties and composition were obtained using Time Dependent Density Functional Theory method. X-ray parameters (bonds, bond angles and torsion angles), Electric dipole moment, Mulliken atomic charges, polarizability and first static hyperpolarizability values have been calculated. Hyperconjugative interactions were studied with the help of natural bond orbital analysis. The thermodynamic properties of the compound were calculated at different temperatures.

Keywords: Cyclohexanone, Density functional theory, Hyperpolarizability, Natural Bond Orbital, Non linear optical, Molecular Electrostatic Potential.

1. Introduction

The Claisen-Schmidt reaction (cross-aldol reaction) is a condensation reaction of aldehydes and carbonyl compounds leading to β -hydroxycarbonyl compounds and has been playing important role in synthetic organic chemistry. Subsequent dehydration of β -hydroxycarbonyl compounds afford α -alkylidene or α -arylidene compounds. Such an introduction of alkylidene or arylidene moieties at the α -position of carbonyl compounds has also been a quite useful synthetic tool in the natural product chemistry [1-6]. Although studies on the Claisen-Schmidt reaction have been focused on α -alkylidene and α -arylidene-carbonyl compounds, interest in α, α' -bisalkylidene and α, α' -bisarylidene-carbonyl compounds is still increasing. Particularly, α, α' -bis(substituted benzylidene)cycloalkanones have been attracting much attention due to not only their intriguing biological activities such as antiangiogenic, [7-8] quinine reductase inducer [9], cytotoxic [10,11] and cholesterol-lowering activity [12], but also because of their large second-harmonic generation coefficient that is good enough for nonlinear optical materials [13]. These derivatives are also the important precursors for the synthesis of pyrimidine derivatives [14], 2,7-disubstituted tropones [15] and synthetic intermediates to functionalize α , β -position during the total synthesis of natural products such as cystodytins [16].

To the best of our knowledge, neither quantum chemical calculations, nor the vibrational analysis study of (2E,6E)-2,6-bis(2-chlorobenzylidene)cyclohexanone has been reported yet. The present paper deals with the synthesis and characterization of titled compound with the aim to provide a complete description on the X-ray crystallography, molecular geometry, molecular vibration, electronic features and Ultraviolet (UV)

spectroscopic investigation employing the Becke3-Lee-Yang-Parr (B3LYP) and Coulomb Attenuating Method (CAM-B3LYP) as different basis sets. Vibrational spectral analysis has been carried out the basis of calculated potential energy distribution (PED). A comprehensive investigation of geometrical and electronic structure in the ground state and first excited state, dipole moment, polarizability, first static hyperpolarizability along with Molecular electrostatic potential (MESP) surface and contour map may lead to better understanding of structural and spectral characteristic of the title compound under investigation. Electronic absorption spectra, Mulliken atomic charges, Global reactivity descriptors and thermodynamic properties at different temperatures were also investigated using Density functional theory (DFT). Nonlinear optical (NLO) study divulges the nonlinear properties of the molecule. Stability of the title molecule arising from hyper-conjugative interactions and charge delocalization has been investigated using natural bond orbital (NBO) analysis. The theoretical results were found to be in coherence with the measured experimental data.

2. Materials and Method

All chemicals were purchased from Sigma-Aldrich and reagents were used without further purification, unless otherwise specified. Infrared (IR) spectrum was recorded on Perkin-Elmer Fourier transform infra-red spectrophotometer. Proton and Carbon Nuclear Magnetic Resonance (¹H and ¹³C-NMR) spectra were recorded on Bruker 300 MHz instrument using Chloroform (CDCl₃) as a solvent. All Chemical shifts are reported in parts per million (p.p.m.) using Tetramethylsilane (TMS) as internal standard. The Positive Electron Spray Ionization (ESI) high resolution mass spectrometry (MS) of compound was recorded on Agilent 6520(Q-TOF) mass spectrophotometer (systronic-2203) instrument using chloroform as a solvent. Melting point (m.p.) was determined in a melting point apparatus and is uncorrected.

2.1 Procedure for the Synthesis of (2E,6E)-2,6-bis(2-chlorobenzylidene)cyclohexanone (C) and spectral recording

The synthetic route [17] for the proposed compound is illustrated in **Scheme 1**. A mixture of Cyclohexanone (**A**) (1 mmol), 2-Chloro benzaldehyde (**B**) (2 mmol) and 20 mol% of NaOH in alcohol (25 ml) was stirred for 15 min. The resulting mixture was washed with water for several times and recrystalized from ethanol. The title compound was obtained as yellow crystalline solid. Yield: 93.9%; m.p.:124°C; Retention Factor (R_f) value: 0.338 using Hexane: Ethyl acetate (8.0:2.0 v/v) as mobile phase; IR (KBr) vmax: 3021 (=CH stretching); 2950 (Aromatic stretching of C-H); 1615 (C=O stretching); 1480 (Aromatic C=C stretching); 1258 (C-O stretching vibration); 748 (C-Cl stretching); ¹H NMR (CDCl₃) : δ = 1.87 (s, 2H), 2.45-2.49 (s, 4H), 7.33 (s, 2H), 7.50-7.61 (m, 6H), 7.74 (s, 2H); ¹³C NMR (CDCl₃) : δ = 22.9, 28.3, 127.1, 129.5, 129.9, 130.1, 130.6, 134.9, 135.9, 140.2, 189.9; MS, *m/z*: M⁺ 343; Anal. Calcd for C₂₀H₁₆Cl₂O: C, 69.98; H, 4.70; Found: C, 67.77; H, 5.16.

<Scheme 1>

3. Computational methods

All the calculations of synthesized compound were carried out with help of Gaussian 09 program package [18] using hybrid functional B3LYP [19] and CAM-B3LYP [20] and 6-31, 6-311, 6-311+ and 6-311++ G(d, p) as basis sets. The ¹H and ¹³C-NMR chemical shifts were calculated. B3LYP invokes Becke's three parameter (local, non local, Hartree-Fock) hybrid exchange functional (B3), with Lee-Yang-Parr correlation functional (LYP) [21]. UV-Vis spectra, electronic transitions and electronic properties such as highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) were computed with the help of time-dependant DFT (TD-DFT) method with similar hybrid functional and basis set. The molecular structures were visualized with the help of Gauss View [22]. Potential energy

distribution (PED) along with internal coordinates was calculated by Gar2ped software [23]. The second-order Fock matrix was used to evaluate the donor-acceptor interactions in the Natural Bond Order (NBO) basis [24].

4. Result and discussion

4.1 Molecular geometry

The most relevant structural parameters (bond lengths, bond angles and dihedral angles) of title compound were determined by DFT calculations using B3LYP/CAM-B3LYP functional 6-31G(d, p) as basis sets which are given in **Table S1**. Geometry optimization was carried out without any symmetry constraints. The atoms numbering of molecule used in this paper is reported in **Fig. 1**. The optimized structure of title compound was compared with the experimental structure [25]. The agreement between the optimized and experimental crystal structure is quite good showing that the geometry optimization almost exactly reproduces the experimental conformation. The molecular structure of title compound belongs to C1 point group symmetry. So it can be used to calculate various molecular and spectroscopic parameters, such as electronic properties, electric moments and vibrational wave numbers.

<Fig. 1>

4.2 ¹H and ¹³C NMR spectroscopy

¹H and ¹³CNMR chemical shifts were calculated with Gauge Independent Atomic Orbital (GIAO) approach using DFT with B3LYP and CAM-B3LYP functional and 6-31, 6-311, 6-311+ and 6-311++ G(d, p) as basis sets [26]. The experimental and calculated values of ¹H and ¹³C NMR chemical shifts of the title compound are given in **Table 1** and **Table 2** respectively. The experimental ¹H and ¹³C NMR spectra of the title compound are given in supplementary **Fig. S1** (Supporting information) and **Fig. S2** respectively. The correlation

graph between the experimental and calculated chemical shifts for ¹H and ¹³C NMR are shown in **Fig. 2** and **Fig. 3** respectively.

<Table 1>

<Table 2>

<Fig. 2 and Fig. 3>

4.3 UV-Visible absorption spectroscopy

The UV-Visible spectrum of compound C (Fig. 4) has been studied by TD-DFT method using B3LYP 6-31, 6-311, 6-311+ and 6-311++ G/(d, p) and CAM-B3LYP functional as 6-31 G/(d, p) basis sets and solvent effect has been taken into consideration by implementing Integral Equation Formalism Polarisable Continuum Model (IEFPCM). The simulated UV data and related properties such as the vertical excitation energies, oscillator strength (f), percentage contribution of probable transition and corresponding absorption wavelength have been tabulated in **Table 3** and compared with experimental UV data. When experimental results compared with the quantum chemical calculations, the CAM-B3LYP method gives better agreement. Calculations by B3LYP functional predict one intense electronic transition at 396.54 nm with an oscillator strength f = 0.0775 in chloroform which is in good agreement with the measured experimental data ($\lambda_{exp.} = 364$ nm in chloroform) as shown in Fig. 4. This electronic absorption corresponds to the transition from the molecular orbital HOMO (89) to the LUMO (90) with 13.9% contribution, HOMO-2 (87) to LUMO with 33.143% contribution and from HOMO-3 (86) to LUMO with 13.9% contribution. In the title compound these transitions appears to be due to $\pi \to \pi^*$ transition. Molecular orbitals of the compound and their electronic transitions are shown in **Fig. 5** which shows the distributions and energy levels of the HOMO -3, HOMO -2, HOMO and LUMO orbitals at the B3LYP/ 6-31G (d, p) level for the title compound. HOMO is mainly localized on the phenyl ring

containing chloro group, slightly delocalized on carbon atoms of cyclohexane ring and on oxygen atom of carbonyl group. HOMO-2 is delocalized over the cyclohexanone ring, carbonyl group which is attached to the cyclohexane ring. HOMO-3 is localized on phenyl ring containing chloro group. LUMO is localized on cyclohexane ring with slight delocalization over phenyl ring, carbonyl groups attached to cyclohexane ring. The value of the energy gap between HOMO and LUMO is 4.02 eV. The lowering of the HOMO-LUMO band gap is essentially a consequence of the large stabilization of the LUMO due to the strong electron-acceptor ability of the electron-acceptor group. Higher the energy of HOMO, the easier it is for HOMO to donate electrons where as it is easier for LUMO to accept electrons when the energy of LUMO is low. This shows the chemical reactivity of the title compound and proves the occurrence of eventual charge transfer within the molecule. Experimental UV-Visible spectrum of title compound is given in Supplementary **Fig. S3**.

<Table 3>

<Fig. 4>

<Fig. 5>

4.4 Molecular electrostatic potential analysis

The MESP is a map of electrostatic potential over constant electron density of molecules. The importance of MESP lies in the fact that it simultaneously displays the molecular size and shape as well as positive, negative and neutral electrostatic potential regions in terms of the color grading scheme which is very useful in the investigation of the most probable binding receptor site along with the size and shape of the molecules [27,28]. To predict the reactive sites of electrophilic and nucleophilic attack for the investigated molecules of MESP at the B3LYP/6-31 G optimized geometry were calculated in **Fig. 6**. The negative (red) regions of the MESP are relative to the electrophilic reactivity, and the positive (blue and yellow) regions are related to nucleophilic reactivity. As seen from Figure there is one possible site on

the title compounds for electrophilic attack. The negative regions are mainly localized on the oxygen atom (Red region) of C=O group O36 is the most negative regions so, carbonyl group is the binding site for electrophilic attack. The maximum positive regions are localized on H23, H26, H29, H31, H32 and H33 atoms of the benzene ring, which can be considered as possible sites for nucleophilic attack.

<Fig. 6>

4.5 Natural bond orbital analysis

NBO analysis has an appealing aspect of highlighting the individual bonds and lone-pair energy that play a vital role in the chemical processes [29,30]. It is an important tool for studying hybridization, co-valence, hydrogen-bonding and Van der Waals interactions. The result of interaction is a loss of occupancy from the concentration of electron NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j) the stabilization energy E(2) associated with the delocalization $i \rightarrow j$ is as follows:

$$\mathbf{E}(\mathbf{2}) = \Delta \mathbf{E}\mathbf{i}\mathbf{j} = \mathbf{q}\mathbf{i}\frac{(\mathbf{F}\mathbf{i}\mathbf{j})\mathbf{2}}{(\mathbf{E}\mathbf{j} - \mathbf{E}\mathbf{i})} \qquad (1)$$

In other words, NBO provides supplementary structural information. Second-order perturbation theory analysis of the Fock matrix in NBO basis for (2E,6E)-2,6-bis(2-chlorobenzylidene)cyclohexanone presented in supplementary **Table S2.** The higher E(2) value (stabilization energy or energy of hyperconjugative interaction) points towards the greater interaction between electron donors and electron acceptors (i.e. the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation in the system). Delocalization of electron density between occupied Lewis-type (bonding or lone pair) NBO's and unoccupied (antibonding or Rydberg) non-Lewis NBO's correspond to a stabilizing donor–acceptor interaction. In compound **C** some of the important $\pi \rightarrow \pi^*$ interactions *viz* π (C8-C9) $\rightarrow \pi^*$ (C5-C7)/ π^* (C10-C13)/ π^* (C11-C12); π (C15-C16) $\rightarrow \pi^*$ (C2–

C14)/ $\pi^*(C17-C20)/\pi^*(C18-C19)$ are responsible for the delocalization of respective π electrons of phenyl ring, the molecule being stabilized by energy in the region of 25.29~226.15 kJ/mol. Other interactions involving the lone pair of electrons with the antibonding π electrons corresponds to $n_3(C137) \rightarrow \pi^*(C8-C9)$, $n_3(C138) \rightarrow \pi^*(C15-C16)$ and $n_2(O31) \rightarrow \pi^*(C29-C30)$ stabilizing the molecule with 12.08 kJ/mol energy.

4.6 Non linear optical analysis

NLO effect is the forefront of current research because of its importance in providing the key functions of frequency shifting, optical modulation, optical switching, optical logic and optic memory for the emerging technologies in areas such as telecommunications, signal processing and optical interconnections [31-33]. Nonlinear optics deals with the interaction of applied electromagnetic fields in various materials to generate new electromagnetic fields, altered in wavenumber, phase or other physical properties. Organic molecules able to manipulate photonic signals efficiently are of importance in technologies such as optical communication, optical computing, and dynamic image processing [34,35]. The first hyperpolarizability of the title compound was calculated using B3LYP/ 6-31, 6-311, 6-311+, 6-311++G and CAM-B3LYP functional with 631-G/(d,p) basis set based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of electric field. The first hyperpolarizability is a third rank tensor that can be described by a 3 x 3 x 3 matrix. The 27 components of the matrix can be reduced to 10 components due to Kleinman symmetry [36]. The complete equations for calculating the magnitude of total dipole moment μ , the average polarizability α_{tot} and the first hyperpolarizability β_{tot} using the x,y,z components is as follows:

$$\mu_{tot} = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$
(2)
$$\alpha_{tot} = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$
(3)

1 /

$$\left\langle \boldsymbol{\beta} \right\rangle = \left[\left(\boldsymbol{\beta}_{xxx} + \boldsymbol{\beta}_{xyy} + \boldsymbol{\beta}_{xzz} \right)^2 + \left(\boldsymbol{\beta}_{yyy} + \boldsymbol{\beta}_{yzz} + \boldsymbol{\beta}_{yxx} \right)^2 + \left(\boldsymbol{\beta}_{zzz} + \boldsymbol{\beta}_{zxx} + \boldsymbol{\beta}_{zyy} \right)^2 \right]^{\frac{1}{2}}$$
(4)

Since the value of the polarizabilities α and the hyperpolarizability of Gaussian output are reported in a atomic mass units (a.u.), the calculated values have been converted into electrostatic units (esu) (α : 1 a.u = 0.1482×10⁻²⁴ esu; β : 1 a.u. = 0.0086393×10⁻³⁰ esu). The results of electronic dipole moment μ i, polarizability α ij and first order hyperpolarizability Bijk are listed in supplementary **Table S3**. The calculated dipole moment as 6-31, 6-311, 6-11+, 6-311++/G (d,p) basis set is equal to 5.5329 D, 5.1022 D, 4.8088 D and 4.8071 D respectively for B3LYP level and 5.019 D for CAM-B3LYP level. The calculated polarizability α_{tot} , as 6-31, 6-311, 6-311+, 6-311++/G (d,p) basis set is equal to 38.65822 $\times 10^{-24}$ esu, 40.27641×10^{-24} esu, 43.28655×10^{-24} esu and 43.35537×10^{-24} esu respectively for B3LYP and 36.09673 $\times 10^{-24}$ esu for CAM-B3LYP level. The calculated first hyper polarizability of the title compound as 6-31, 6-311, 6-311+, 6-311++/G (d,p) basis set is 3.697×10^{-30} esu, 3.575×10^{-30} esu, 4.956×10^{-30} esu and 4.93×10^{-30} esu respectively for B3LYP level and 2.432×10^{-30} esu for CAM-B3LYP level and these values are greater (28.43, 27.5, 38.12 and 37.92 times for B3LYP level and 18.70 times for CAM-B3LYP level) than that of the standard NLO material urea $(0.13 \times 10^{-30} \text{esu})$ [37]. We conclude that the title compound is an attractive object for future studies of nonlinear optical properties.

4.7 Thermodynamic Properties

The values of some thermodynamic parameter of title compound, including zero-point vibrational energy, rotational temperatures, rotational constants, energies at standard temperature 298.15 K were obtained at the using B3LYP 6-31, 6-311, 6-311+, 6-311++G and CAM-B3LYP functional with 631-G/(d,p) basis set (supplementary **Table S4**). The standard statistical thermodynamic functions, heat capacity (CV) and entropy (S) were obtained at various temperatures (100-500 K) for the title compound on the basis of vibrational analysis using B3LYP and CAM-B3LYP functional with different basis sets and are listed in

supplementary **Table S5**. The total energy and vibrational values are somewhat higher when calculated in CAM-B3LYP than B3LYP. The rotational constants and rotational temperature values are similar in all the cases. It is observed that standard statistical thermodynamic functions increase with temperature ranging from 100 to 500 K, due to the fact that the molecular vibrational intensities increase with temperature [38, 39]. The correlation equations among heat capacities, entropies and temperatures were fitted by quadratic formulas and the corresponding fitting factors (R^2) for these thermodynamic properties are given in equation (5-14). The corresponding fitting equations are as follows and the correlation graphics are <Fig. 7 > shown in **Fig. 7**.

$$CV = 4.99 + 0.253T - 5.10^{-5}T^{2} (R^{2} = 0.9996) \text{ using B3LYP 6-31G(d,p)} (5)$$

$$S = 67.725 + 0.3048T - 6.10^{-5}T^{2} (R^{2} = 1) \text{ using B3LYP6-31G(d,p)} (6)$$

$$CV = 7.6073 + 0.2253T - 2.10^{-5}T^{2} (R^{2} = 0.9998) \text{ using B3LYP 6-311G(d,p)} (7)$$

$$S = 66.705 + 0.305T - 6.10^{-5}T^{2} (R^{2} = 1) \text{ using B3LYP 6-311G(d,p)} (8)$$

$$CV = 5.1715 + 0.2536T - 5.10^{-5}T^{2} (R^{2} = 0.9994) \text{ using B3LYP 6-311+G(d,p)} (9)$$

$$S = 67.594 + 0.3061T - 7.10^{-5}T^{2} (R^{2} = 1) \text{ using B3LYP 6-311+G(d,p)} (10)$$

$$CV = 5.1538 + 0.2537T - 5.10^{-5}T^{2} (R^{2} = 0.9994) \text{ using B3LYP 6-311+G(d,p)} (11)$$

$$S = 67.486 + 0.3058T - 6.10^{-5}T^{2} (R^{2} = 1) \text{ using B3LYP 6-311+HG(d,p)} (12)$$

$$CV = 5.487 + 0.2454T - 4.10^{-5}T^{2} (R^{2} = 0.9994) \text{ using CAM-B3LYP} (13)$$

$$S = 68.176 + 0.3011T - 6.10^{-5}T^{2} (R^{2} = 1) \text{ using CAM-B3LYP} (14)$$

These thermodynamic data may provide helpful information for the further study of title compound. They can be used to compute the other thermodynamic energies according to the relationships of thermodynamic functions and estimate directions of chemical reactions

according to the second law of thermodynamics in thermo chemical field [40]. All thermodynamic calculations were done in gas phase and they could not be used in solution.

4.8 Vibrational spectral analysis

Experimental FT-IR spectra of synthesized compound C has been recorded in the range of 4000-450 cm⁻¹ where as theoretical vibrational analysis of the compound were performed by DFT using B3LYP and CAM-B3LYP level with 6-31G (d,p) basis set. The theoretical IR spectrum is shown in Supplementary **Fig. S4.** The observed infrared and calculated wave numbers are scaled down by a single scaling factor 0.9679 [41] by DFT using B3LYP level with 6-31G (d,p) basis set and the assigned wavenumbers of calculated vibrational modes by B3LYP along with their PED are given in **Table 4.** Experimental IR spectrum of title compound is given in **Fig. S5.**

<Table 4>

4.8.1 C=O and C-O vibrations

The appearance of strong bands in the FT-IR between 1690-1800 cm⁻¹ [42] in aromatic compounds shows the presence of carbonyl group and is due to the C=O stretching motion. The wavenumber due to C=O stretch mainly depends on the bond strength which in turn depends upon inductive, conjugative, field and steric effects. In the present study, the strong band at 1615 cm⁻¹ in FT-IR spectrum is assigned to C=O stretching mode. The calculated C=O stretching mode at 1606.86 cm⁻¹, whereas the band at 1251.41 cm⁻¹ is assigned to stretching vibration of C-O which shows the good agreement with the experimental value at 1258 cm⁻¹.

4.8.2 =**C**–**H** vibrations

The aromatic C–H stretching vibrations are normally found between 3100 and 3000 cm⁻¹ due to aromatic C–H stretching vibrations [43]. The wavenumbers calculated at 3086.48 cm⁻¹ is assigned to =C–H stretching vibrations. A strong band appeared at 3021 cm⁻¹ in FTIR spectrum is assigned to =C–H ring stretching vibrations.

4.8.3 C=C vibration

In aromatic hydrocarbon, skeletal vibrations involving carbon-carbon stretching within ring are absorbed in the region between 1600 and 1585 cm⁻¹ [44]. The benzene ring possesses six ring stretching modes, of which the four with the highest wavenumbers (occurring near 1600, 1580, 1490 and 1440 cm⁻¹) are good group vibrations. The wavenumber calculated at 1458.05 cm⁻¹ assigned to the C=C stretching vibration in the benzene ring which show good agreement with experimental value at 1480 cm⁻¹.

4.8.4 C-Cl vibration

The vibrations belonging to the bond between the ring and chlorine atoms are worth to discuss here since mixing of vibrations is possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule [45, 46]. Mooney [47, 48] assigned vibrations of C-Cl, Br, and I in the wavenumber range of 1129-480 cm⁻¹. The C-Cl stretching vibrations give generally strong bands in the region 710-505 cm⁻¹. For simple organic chlorine compounds, C-Cl absorptions are in the region 750-700 cm⁻¹. For the title compound C, the band observed at 748 cm⁻¹ in the IR spectrum and 734.51 cm⁻¹ (DFT) is assigned as the C-Cl stretching mode.

4.9 Chemical reactivity

4.9.1 Global reactivity descriptors

Global reactivity descriptors are highly successful in predicting global reactivity trends. The energies of frontier molecular orbital (ε_{LUMO} , ε_{HOMO}), band gap ($\varepsilon_{LUMO} - \varepsilon_{HOMO}$), ionization

potential (IP), electron affinity (EA), electronegativity (χ), global hardness (η), chemical potential (μ), global electrophilicity index (ω), global softness (S) [49-53] and additional electronic charge (ΔN_{max}) of reactant A, B and product C have been calculated using following equations. [(15)-(22)] and listed in **Table 5**.

<Table 5>

$$IP = -\varepsilon_{HOMO}$$
(15)

$$EA = -\varepsilon_{LUMO}$$
(16)

$$\chi = -\frac{1}{2} (\varepsilon_{LUMO} + \varepsilon_{HOMO})$$
(17)

$$\eta = \frac{1}{2} (\varepsilon_{LUMO} - \varepsilon_{HOMO})$$
(18)

$$\mu = -\chi = \frac{1}{2} (\varepsilon_{LUMO} + \varepsilon_{HOMO})$$
(19)

$$\omega = \frac{\mu^2}{2\eta}$$
(20)

$$S = \frac{1}{2\eta}$$
(21)

$$\Delta N_{max} = -\frac{\mu}{\eta}$$
(22)

According to Parr et al., electrophilicity index (ω) is a global reactivity index similar to the chemical hardness and chemical potential. This is positive and definite quantity. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge (ΔN) from the environment. The direction of the charge transfer is completely determined by the electronic chemical potential of the molecule because an electrophile is a chemical species capable of accepting electrons from the environments. Therefore its energy must decrease upon accepting electronic charge and its electronic chemical potential must be negative.

Electrophilic charge transfer (ECT) [54] is defined as the difference between the ΔN_{max} values of interacting molecules. If we consider two molecules A and B approach to each other (i) if ECT > 0, charge flow from B to A (ii) if ECT < 0, charge flow from A to B. ECT is calculated using equation given below:

$$ECT = \left(\Delta N_{\max}\right)_{A} - \left(\Delta N_{\max}\right)_{B} \quad (23)$$

where
$$(\Delta N_{\text{max}})_A = -\frac{\mu_A}{\eta_A}$$
 and $(\Delta N_{\text{max}})_B = -\frac{\mu_B}{\eta_B}$ (24)

For the sake of simplicity, reactants cyclohexanone and 2-chlorobenzaldehyde and product benzylidine cyclohexanone are abbreviated as A, B & C respectively.

Ionization potential (IP), electron affinity (EA), electronegativity (χ), global hardness (η), chemical potential (μ), global electrophilicity index (ω), global softness (S) and additional electronic charge (ΔN_{max}) were calculated for reactants A and B as well as for the product C, using the energies of frontier molecular orbitals $\varepsilon_{\text{LUMO}}$, $\varepsilon_{\text{HOMO}}$ which are tabulated in **Table 5**. ECT was calculated from the values of additional electron charge (ΔN_{max}) of reactant A and B using the equation (23).

The calculated value of ECT > 0 (ECT = 0.690), for reactant molecules cyclohexanone (A) (1 mmol), 2-chlorobenzaldehyde (B) indicates charge flow from B to A. Therefore, the reactant molecules B act as global nucleophile (electron donor) and A as global electrophile (electron acceptor). The high value of electrophilicity index (ω) = 4.456 eV for product C than from reactant (B) shows that it is strong electrophile than reactant (B).

4.9.2 Local reactivity descriptors

Fukui function (FF) is one of the widely used local density functional descriptors to model chemical reactivity and site selectivity. Using Hirshfeld population analysis of neutral, cation and anion state of molecule, Fukui Functions are calculated using following equations:

$$f_{K}^{+} = \left[q\left(N+1\right) - q\left(N\right)\right] \text{for nucleophilic attack}$$
(25)

$$f_{K}^{-} = \left[q(N) - q(N-1)\right]$$
 for electrophilic attack (26)

$$f_{K}^{0} = \frac{1}{2} \Big[q \big(N+1 \big) - q \big(N-1 \big) \Big] \text{ for radical attack} \quad (27)$$

Where, N, N-1, N+1 are total electrons present in neutral, anion and cation state of molecule respectively.

In addition local softnesses s_k^+ , s_k^- , s_k^0 and electrophilicity indices (ω_k^+ , ω_k^- , ω_k^0) are also used to describe the reactivity of atoms in a molecule. These local reactivity descriptors associated with a site k in a molecule are defined with the help of the corresponding condensed to atom variants of Fukui function, using the following equations-

$$s_{K}^{+} = Sf_{K}^{+}, \ s_{k}^{-} = Sf_{K}^{-}, \ s_{K}^{0} = Sf_{K}^{0}$$
(28)
$$\omega_{K}^{+} = \omega f_{K}^{+}, \ \omega_{K}^{-} = \omega f_{K}^{-}, \ \omega_{K}^{0} = \omega f_{K}^{0}$$
(29)

Where +, -, 0 signs show nucleophilic, electrophilic and radical attack respectively. The maximum values of all the three local reactivity descriptors $(f_k^{\pm}, s_k^{\pm}, \omega_k^{\pm})$ indicate that it site is more prone site for nucleophilic or electrophilic attack than all other atomic sites in reactants.

Fukui functions (f_k^+, f_k^-) , local softnesses (s_k^+, s_k^-) and local electrophilicity indices (ω_k^+, ω_k^-) [52, 53] for selected atomic sites of molecule have been listed in supplementary **Table S6**.

In product, the relative high value of local reactivity descriptors $(f_k^+, s_k^+, \omega_k^+)$ in **Table S6** at C2, C9, C16 and O36 indicate that these sites are prone to nucleophilic whereas the relative high value of local reactivity descriptors $(f_k^-, s_k^-, \omega_k^-)$ at C1, C8 and C15 indicate that this site is more prone to electrophilic attack. Thus synthesized molecule may be used as intermediate for the synthesis of further new heterocyclic compounds.

5. Conclusion

In the present study, we have carried out the combined experimental and theoretical spectroscopic analysis of (2E,6E)-2,6-bis(2-chlorobenzylidene)cyclohexanone for the first time, using FT-IR, ¹H, ¹³C NMR, UV-Vis techniques and DFT. In general, a good correspondence between experimental and calculated normal modes of vibrations has been observed. X-ray studies helped in establishing the structure with optimized geometric parameters (bond lengths, bond angles and dihedral angles) are determined by DFT theory and compared with the experimental data. NLO behavior of the title molecule has been investigated by dipole moment, polarizability and first hyperpolarizability. It is concluded that the lowest singlet excited state of the molecule is mainly derived from the HOMO \rightarrow LUMO ($\pi \rightarrow \pi^*$) electron transition. NBO results reflected the charge transfer within the molecule. The calculated first hyper polarizability of the title compound as 6-31, 6-311, 6-311+, 6-311++/G (d,p) basis set is 3.697×10^{-30} esu, 3.575×10^{-30} esu, 4.956×10^{-30} esu and 4.93×10^{-30} esu respectively for B3LYP level and 2.432×10^{-30} esu for CAM-B3LYP level and these values are greater (28.43, 27.5, 38.12 and 37.92 times for B3LYP level and 18.70 times for CAM-B3LYP level) than that of the standard NLO material urea (0.13 $\times 10^{-30}$ esu), implies that the title molecule may be useful as a nonlinear optical material. The electronic properties are also calculated and compared with the experimental UV-Vis spectrum. NBO analysis reveals that the some important intramolecular charge transfer can induce large nonlinearity to the title molecule and the high intramolecular hyper-conjugative interaction around the ring can induce the large bioactivity in the compound.

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Legends of figure / table / scheme-

Fig. 1. Optimized geometry of the title compound using B3LYP/6-31G(d,p) level of theory.
Fig 2. Correlation graph between experimental and calculated ¹H NMR chemical shift using B3LYP (a) 6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++ /G(d, p) and CAM-B3LYP (e) 6-31G (d, p).

Fig 3. Correlation graph between experimental and calculated ¹³C NMR chemical shift using B3LYP (a) 6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++ /G(d, p) and CAM-B3LYP (e) 6-31G (d, p).

Fig 4. Calculated UV-visible spectrum of compound C.

Fig. 5. Molecular orbitals (HOMO →LUMO, HOMO-2 →LUMO and HOMO-3→LUMO) of the compound at the B3LYP/6-31G(d,p) basis set.

Fig. 6. 3 D plots of the molecular electrostatic potential of title compound.

Fig 7. Correlation graphs of heat capacity calculated at various temperatures using B3LYP/6-31G(d,p) (a), B3LYP/6-311G(d,p) (b), B3LYP/6-311+G(d,p) (c), B3LYP/6-311++G(d,p) (d) and CAM-B3LYP /6-31G (d, p) (e).

Table 1. Experimental and Calculated ¹H chemical shifts of title compound using B3LYP (a)6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++/G(d, p) and CAM-B3LYP (e) 6-31G (d, p).

Table 2. Experimental and Calculated ¹³C chemical shifts of title compound using B3LYP (a) 6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++ /G(d, p) and CAM-B3LYP (e) 6-31G (d, p).

Table 3. Experimental and theoretical absorption wavelength λ (nm), excitation energies E (eV) of title compound using B3LYP (a) 6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++ /G(d, p) and CAM-B3LYP (e) 6-31G (d, p).

Table 4. The recorded (FT-IR) and computed vibrational wavenumbers by B3LYP/6-31G(d,p), IR activities along with the assignments of vibrational modes of compound based on PED results.

Table 5. Calculated ε_{LUMO} , ε_{HOMO} , energy band gap $\varepsilon_{LUMO} - \varepsilon_{HOMO}$, ionization potential (IP), electron affinity (EA), electronegativity (χ), global hardness (η), chemical potential (μ), global electrophilicity index (ω), global softness (S) and additional electronic charge (ΔN_{max}) in eV for reactant A, B and product C using B3LYP/6-31G(d,p).

Scheme 1. Synthesis of (2E,6E)-2,6-bis(2-chlorobenzylidene)cyclohexanone.



Fig. 1. Optimized geometry of the title compound using B3LYP/6-31G(d,p) level of theory.



Fig 2. Correlation graph between experimental and calculated ¹H NMR chemical shift using B3LYP (a) 6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++ /G(d, p) and CAM-B3LYP (e) 6-31G (d, p).



Fig 3. Correlation graph between experimental and calculated ¹³C NMR chemical shift using B3LYP (a) 6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++ /G(d, p) and CAM-B3LYP (e) 6-31G (d, p).



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Fig. 6. 3D plots of the molecular electrostatic potential of title compound.





Fig 7. Correlation graphs of heat capacity calculated at various temperatures using B3LYP/6-31G(d,p) (a), B3LYP/6-311G(d,p) (b), B3LYP/6-311+G(d,p) (c), B3LYP/6-311++G(d,p) (d) and CAM-B3LYP /6-31G (d, p) (e).

Table 1. Experimental and Calculated ¹ H chemical shifts of title compound using B3LY
with 6-31, 6-311, 6-311+, 6-311++ and CAM-B3LYP with 6-31G/(d, p)basis set

Atom	¹ H NMR Calculated							
110.		I	B3LYP		CAM-B3LY	YP		
	6-31G	<mark>6-311G</mark>	<mark>6-311+G</mark>	<mark>6-311++G</mark>	6-31G	Exp		
21	8.23	<mark>7.54</mark>	<mark>7.53</mark>	<mark>8.20</mark>	8.33	7.59		
22	7.47	<mark>6.61</mark>	<mark>6.78</mark>	<mark>7.39</mark>	7.48			
23	7.46	<mark>6.71</mark>	<mark>6.45</mark>	<mark>7.23</mark>	7.48	7.31		
24	7.41	<mark>6.67</mark>	<mark>7.18</mark>	<mark>6.39</mark>	7.43	}		
25	7.42	<mark>6.70</mark>	<mark>6.49</mark>	<mark>7.26</mark>	7.40			
26	2.87	<mark>1.98</mark>	<mark>1.73</mark>	<mark>2.75</mark>	1.88	2.50		
27	2.73	1.78	<mark>1.45</mark>	<mark>2.53</mark>	1.70	2.48		
28	1.53	<mark>0.44</mark>	<mark>0.26</mark>	<mark>1.44</mark>	0.33	ן 1.87-		
29	1.74	<mark>0.87</mark>	<mark>0.55</mark>	<mark>1.70</mark>	0.60	£ 1.93		
30	2.73	<mark>1.78</mark>	<mark>2.53</mark>	<mark>1.45</mark>	1.70	2.47		
31	2.87	<mark>1.98</mark>	<mark>1.73</mark>	<mark>2.75</mark>	1.87	2.49		
32	7.47	<mark>6.78</mark>	<mark>7.39</mark>	<mark>6.61</mark>	7.48)		
33	7.46	<mark>6.71</mark>	<mark>6.45</mark>	<mark>7.23</mark>	7.48			
34	7.41	<mark>6.67</mark>	<mark>7.18</mark>	<mark>6.39</mark>	7.43	7.61		
35	7.42	<mark>6.70</mark>	<mark>7.26</mark>	<mark>6.49</mark>	7.40	J		
39	8.23	7.54	<mark>7.53</mark>	<mark>8.20</mark>	8.33	7.34		
	C							

Atom	¹³ C NMR Calculated								
110.		В	CAM-B3LYP						
	6-31G	6-311G	6-311+G	6-311++G	6-31G	Exp			
1	184.28	<mark>186.13</mark>	<mark>190.02</mark>	<mark>189.96</mark>	189.11	189.98			
2	137.79	<mark>139.37</mark>	<mark>140.79</mark>	<mark>140.70</mark>	137.51	135.86			
3	34.06	<mark>25.841</mark>	<mark>24.62</mark>	<mark>24.71</mark>	32.10	28.34			
4	29.15	<mark>20.70</mark>	<mark>19.90</mark>	<mark>20.07</mark>	22.71	22.91			
5	137.79	<mark>139.37</mark>	<mark>140.79</mark>	<mark>140.70</mark>	137.51	135.86			
6	34.06	<mark>25.84</mark>	<mark>24.62</mark>	<mark>24.71</mark>	28.16	28.34			
7	136.63	<mark>136.95</mark>	<mark>138.56</mark>	<mark>138.79</mark>	138.36	130.56			
8	134.21	<mark>135.80</mark>	<mark>136.24</mark>	<mark>135.87</mark>	135.09	134.86			
9	143.28	<mark>144.05</mark>	<mark>145.66</mark>	<mark>145.29</mark>	141.48	140.24			
10	128.30	<mark>129.91</mark>	<mark>130.29</mark>	<mark>130.37</mark>	128.17	129.49			
11	135.14	<mark>131.41</mark>	<mark>132.12</mark>	<mark>132.07</mark>	131.18	129.96			
12	124.25	<mark>125.64</mark>	<mark>125.97</mark>	<mark>125.97</mark>	125.99	130.10			
13	127.87	<mark>129.73</mark>	130.25	<mark>130.24</mark>	142.37	127.14			
14	136.63	<mark>136.95</mark>	<mark>138.56</mark>	<mark>138.79</mark>	146.67	130.56			
15	134.21	<mark>135.80</mark>	<mark>136.24</mark>	<mark>135.87</mark>	135.09	134.86			
16	143.28	<mark>144.05</mark>	<mark>145.66</mark>	<mark>145.29</mark>	141.48	140.24			
17	128.30	<mark>129.91</mark>	<mark>130.29</mark>	<mark>130.37</mark>	129.75	129.49			
18	129.70	<mark>131.41</mark>	<mark>132.12</mark>	<mark>132.07</mark>	131.18	129.96			
19	124.25	<mark>125.64</mark>	<mark>125.97</mark>	<mark>125.97</mark>	125.99	130.10			
20	127.87	<mark>129.73</mark>	<mark>130.25</mark>	<mark>130.24</mark>	129.26	127.14			

Table 2. Experimental and Calculated ¹³C chemical shifts of title compound using B3LYP with 6-31, 6-311, 6-311+, 6-311++ and CAM-B3LYP with 6-31G/(d, p)basis set

Table 3. Experimental and theoretical absorption wavelength λ (nm), excitation energies E (eV) of title compound using B3LYP (a) 6-31G, (b) 6-311, (c) 6-311+ (d) 6-311++ /G(d, p) and CAM-B3LYP (e) 6-31G (d, p).

Model	Electronic transitions (molecula r orbitals	Energy (in eV)	Calculated λ_{max} (in nm)	Oscillatory Strength (f)	Percent contributio n of probable	Observe d λ _{max} (in nm)
	involved)				transition	
B3LYP				(
6-31G (d,p)	86-90	3.1267	396.54	0.0775	1.69	364
	87-90				33.14	
	89-90				13.90	
<mark>6-311G (d,p)</mark>	<mark>86-90</mark>	<mark>4.6307</mark>	<mark>347.1</mark>	<mark>0.8036</mark>	<mark>1.72</mark>	<mark>364</mark>
	<mark>87-90</mark>				<mark>14.40</mark>	
	<mark>89-90</mark>				<mark>33.44</mark>	
<mark>6-311G+ (d,p)</mark>	<mark>85-90</mark>	<mark>4.5801</mark>	<mark>351.22</mark>	<mark>0.7563</mark>	<mark>8.93</mark>	<mark>364</mark>
	<mark>87-90</mark>				<u>10.42</u>	
	<mark>89-90</mark>				<mark>30.14</mark>	
<mark>6-311G++(d,p)</mark>	<mark>85-90</mark>	<mark>4.5788</mark>	<mark>351.36</mark>	<mark>0.7571</mark>	<mark>8.75</mark>	<mark>364</mark>
	<mark>87-90</mark>	Y			<mark>10.50</mark>	
	<mark>89-90</mark>				<mark>30.25</mark>	
Ċ						
CAM- B3LYP	85-90	3.4835	355.92	0.0372	37.77	364
6-31G (d,p)	85-94				2.872	
	87-90				1.026	
	89-90				6.15	

Table 4. The recorded (FT-IR) and computed vibrational wavenumbers by B3LYP/6-31G (d,p), IR activities along with the assignments of vibrational modes of compound based on PED results.

				Theoretical
				wavenumber
<mark>Mode</mark>	<mark>Unscale</mark>	Scaled	I_{IR}	Vibrational Assignment (PED in %)
	<mark>d</mark>		(km/	
			mol)	
1	<mark>17.28</mark>	<mark>16.72</mark>	<mark>1.03</mark>	τ (C1-C2) (39) τ _{asy} (C1-C2) (16) δ _{asy} (O36-C5-C1-C6) (16)
4	52.20	50 60	0.62	B(C15, C15, C16) (14) $B(C15, H25, C18)$ (4) $B(C15, C26, C16)$ (30) π (C26, C15, C17, C16) (36) $S(C26)$
4	<u>32.20</u>	<mark>30.00</mark>	0.05	$p(C13-C30-C10)(39) m_{asy}(C30-C13-C17-C10)(30) b(C30-C5-C1-C6)(8) b(C36-C2-C1-C3)(7) b(C14-C3-C2-C4)(3)$
5	70.85	<u>68 57</u>	0.05	$\beta(C15-C16)(3)\delta(C50-C2-C1-C5)(7)\delta(C14-C5-C2-C4)(3)$ $\beta(C15-C16)(31)\pi_{ext}(C36-C15-C17-C16)(31)\delta(C36-C16)(31)$
~	10100		0.00	C2-C1-C3) (13) δ_{asy} (O36-C5-C1-C6) (13) β (C15-H25-
				C18) (5) π (H25-C15-H29-C18) (3)
<mark>6</mark>	<mark>84.41</mark>	<mark>81.70</mark>	<mark>0.03</mark>	δ(O36-C2-C1-C3) (43) δ _{asy} (O36-C5-C1-C6) (43) β(C15-
				<mark>O36-C16) (5) π(O36-C15-C17-C16) (4)</mark>
<mark>8</mark>	<mark>117.22</mark>	<mark>113.45</mark>	<mark>0.02</mark>	τ(C1-C2) (48) $τ$ (C1-C2) (36) $δ$ (O36-C2-C1-C3) (4)
0	150.07	145.05	0.15	$\delta(036-C5-C1-C6)$ (4) $\delta(C14-C3-C2-C4)$ (4)
9	<mark>150.07</mark>	145.25	0.15	$\beta(C_{20}-C_{16}-C_{15})$ (43) $\beta(C_{15}-C_{17}-C_{16})$ (32) $\beta(C_{13}-C_{9}-C_{8})$
11	177 36	171.66	0.46	$(0) \ m(030-C13-C17-C10) \ (3) \ p_{asy}(C6-C10-C9) \ (3)$ $\delta(O36, C2, C1, C3) \ (49) \ \delta(O36, C5, C1, C6) \ (49)$
1 <u>1</u> 15	275 53	266 68	<u>0.40</u> <u>4 2</u>	$\delta(036-C2-C1-C3)(34) \delta_{-}(036-C5-C1-C6)(34) \beta(C20-C2-C1-C3)(34) \delta_{-}(036-C5-C1-C6)(34) \beta(C20-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C2-C2-C1-C6)(34) \beta(C20-C2-C2-C2-C2-C2-C2-C2-C2-C2-C2-C2-C2-C2-$
10	<u>213.33</u>	200.00		$C_{16}C_{15}C_{1$
<mark>17</mark>	<mark>308.35</mark>	<mark>298.45</mark>	<mark>1.6</mark>	τ (C1-C2) (36) τ_{asy} (C1-C2) (24) δ_{asy} (C6-C2-C1) (15)
				$\delta_{asy}(C15-C17-C16)$ (9) $\delta_{asy}(C1-C3-C2)$ (4)
<mark>18</mark>	<mark>373.24</mark>	<mark>361.25</mark>	<mark>0.42</mark>	δ(C20-C16-C15) (28) δ(C6-C2-C1) (22) τ(C1-C2) (12)
				$\delta_{asy}(O36-C2-C1-C3)$ (8) $\delta_{asy}(O36-C5-C1-C6)$ (8) $\tau_{asy}(C1-C1)$
20	410.07	007 60	114	C2) (5) δ_{asy} (C15-C17-C16) (5) δ (C13-C9-C8) (4)
<mark>20</mark>	<mark>410.87</mark>	<u>397.68</u>	<mark>11.4</mark>	$\delta(C15-C17-C16)$ (48) $\delta_{asy}(C20-C16-C15)$ (37) $\delta_{asy}(C13-C0, C2)$ (5) $\delta(C2, C10, C2)$ (5)
21	<u>/31 56</u>	417 70	10.02	8(C15, C17, C16)(46) = (C20, C16, C15)(31) = (C8)
<mark>21</mark>	431.30	41/./0	10.92	$C_{10}-C_{9}$ (5) $\delta(C_{13}-C_{9}-C_{8})$ (4) $\beta_{asy}(C_{5}-C_{36}-C_{16})$ (3)
<mark>24</mark>	<mark>464.89</mark>	<mark>449.96</mark>	1.03	$\delta(C6-C2-C1)$ (40) $\delta_{asv}(C15-C17-C16)$ (27) $\delta(C20-C16-C16)$
				C15) (7) δ (C1-C3-C2) (6) τ (C1-C2) (5)
<mark>25</mark>	<mark>471.73</mark>	<mark>456.58</mark>	<mark>6.86</mark>	<mark>β(C5-O36-C16) (36) π_{asy}(O36-C15-C17-C16) (34) δ(C6-</mark>
				C2-C1) (4) δ_{asy} (C15-H25-C18) (4) δ_{asy} (C1-C3-C2) (3)
<mark>26</mark>	<mark>478.78</mark>	<mark>463.41</mark>	<mark>13.93</mark>	δ (C6-C2-C1) (36) π _{asy} (O36-C15-C17-C16) (19) β(C5-O36-
20	540.27	5 21 C 2	<u> </u>	C16) (18) $\delta_{asy}(036-C2-C1-C3)$ (8) $\delta_{asy}(036-C5-C1-C6)$ (8)
<mark>28</mark>	<mark>549.27</mark>	<mark>531.05</mark>	<mark>0.03</mark>	$O(C0-C2-C1)$ (42) $O_{asy}(O30-C2-C1-C3)$ (13) $O_{asy}(O30-C3-C1-C3)$ (13) $O_{asy}(O30-C3-C3)$ (13) $O_{asy}(O30-C3-C1-C3)$ (13) $O_{asy}(O30-C3-C1-C3-C1-C3)$ (13) $O_{asy}(O30-C3-C1-C3-C1-C3)$ (13) $O_{asy}(O30-C3-C1-C3-C1-C3)$ (13) $O_{asy}(O30-C3-C1-C3-C1-C3-C1-C3)$ (13) $O_{asy}(O30-C3-C1-C3-C1-C3-C1-C3)$ (13) $O_{asy}(O30-C3-C1$
				$C_{16}(C_{15}) = C_{16}(C_{15}) = C_{1$
<mark>31</mark>	<mark>606.35</mark>	<mark>586.88</mark>	<mark>5.15</mark>	$v(C1-C2) (17) \delta_{asv}(C1-C3-C2) (15) v_{asv}(C15-C18) (11)$
-				$v_{asy}(C16-C17)$ (8) $v_{asy}(C18-C19)$ (8) $v(C1-C5)$ (8) $v(C15-C19)$
				C16) (6) δ_{asy} (C15-C17-C16) (5) v_{asy} (C17-C20) (3)
<mark>32</mark>	<mark>635.75</mark>	<mark>615.34</mark>	<mark>2.07</mark>	δ(C1-C3-C2) (45) δ(O36-C2-C1-C3) (20) δ(O36-C5-C1-
				C6) v(C9-C10) δ_{asv} (C6-C2-C1) (4)

<mark>33</mark>	<mark>667.47</mark>	<mark>646.04</mark>	<mark>0.16</mark>	δ(C15-C17-C16) (46) δ _{asy} (C20-C16-C15) (37) δ(C13-C9-
<mark>34</mark>	<mark>695 39</mark>	<mark>673 06</mark>	<mark>50 49</mark>	C8) (5) $\delta_{asy}(C8-C10-C9)$ (5) $\delta(C15-C17-C16)$ (49) $\delta_{aut}(C20-C16-C15)$ (40) $\delta_{aut}(C13-C16)$
<mark></mark>	070.07	075.00	50.15	C9-C8) (6) δ(C8-C10-C9) (5)
<mark>35</mark>	<mark>705.02</mark>	<mark>682.38</mark>	<mark>0.29</mark>	δ(C15-C17-C16) (47) δ _{asy} (C20-C16-C15)(41) δ(C13-C9-
26	710.20	<u>690 51</u>	2 10	$\frac{(28)}{(6)} (6) \delta_{asy}(C8-C10-C9) (5)$
<mark>30</mark>	/12.38	<mark>689.51</mark>	<mark>2.19</mark>	$0(C15-C17-C16)(45) 0_{asy}(C20-C16-C15)(13) \beta_{asy}(C5-C16-C16)(7) \delta(C8-C10-C9)(5) \pi(C36-C15-C17-C16)(5)$
				$v_{asv}(C15-C18)$ (4) $v_{asv}(C4-C6)$ (3) $v_{asv}(C5-C6)$ (3)
<mark>38</mark>	<mark>748.9</mark>	<mark>724.86</mark>	<mark>42.4</mark>	δ (C20-C16-C15) (36) δ _{asy} (C15-C17-C16) (33) τ(C1-C2)
				(7) δ (C13-C9-C8) (5) τ_{asy} (C1-C2) (4) δ asy(C8-C10-C9) (3)
<mark>41</mark>	<mark>784.41</mark>	<mark>759.23</mark>	<mark>79.98</mark>	$\delta(C15-C17-C16)$ (41) $\delta_{asy}(C20-C16-C15)$ (26) $\tau(C1-C2)$
<mark>42</mark>	825 71	799 20	<mark>16 78</mark>	$\delta(C15-C17-C16)$ (59) $v_{asy}(C15-C18)$ (12) $\delta_{asy}(C20-C16-C8)$ (4)
·	023.11	177.20	10.70	C(2) = C(2) +
<mark>43</mark>	<mark>838.75</mark>	<mark>811.82</mark>	<mark>5.53</mark>	δ(C15-C17-C16) (62) $ν$ _{asy} (C15-C18) (11) $δ$ _{asy} (C20-C16-
4 7	002 50	055 01		C15) (11) δ (C8-C10-C9) (7)
<mark>45</mark>	<mark>883.58</mark>	<mark>855.21</mark>	<mark>8./6</mark>	π (H25-C15-H29-C18) (38) δ (C15-H25-C18) (31) β_{asy} (C5- O36 C16) (9) π (O36 C15 C17 C16) (6) δ_{asy} (C15 C17
				$C_{16}(4) v(C_{15}-C_{18}) (4)$
<mark>47</mark>	<mark>923.87</mark>	<mark>894.21</mark>	<mark>10.16</mark>	ν(C15-C18) (17) δ(C6-C2-C1) (15) δ(C1-C3-C2) (11)
				$δ_{asy}$ (C15-C17-C16) (8) $ν_{asy}$ (C4-C6) (7) δ(O36-C2-C1-C3)
				(7) $\delta(\text{O36-C5-C1-C6})$ (7) $\tau(\text{C1-C2})$ (6) $\delta_{\text{asy}}(\text{C6-C2-C1})$ (5)
<mark>/8</mark>	940 21	910.02	0.32	v(C1-C2)(3) $\delta(C20-C16-C15)(21)v = (C15-C18)(20)\delta(C6-C2-C1)$
-0	740.21	<mark>910.02</mark>	0.52	(11) π (H21-C2-C15-C14) (9) δ (O36-C2-C1-C3) (7)
				δasy(O36-C5-C1-C6) (7) $τasy(C14-C15)$ (3)
<mark>52</mark>	<mark>971.07</mark>	<mark>939.89</mark>	<mark>20.88</mark>	τ(C1-C2) (19) π_{asy} (H25-C15-H29-C18) (16) δ_{asy} (C15-H25-
				C18) (12) δ_{asy} (C1-C3-C2) (10) τ_{asy} (C1-C2) (10)
				$O_{asy}(C20-C10-C15)(0) \pi_{asy}(H21-C2-C15-C14)(0) O_{asy}(C6-C2-C1)(5)$
<mark>53</mark>	<mark>986.86</mark>	<mark>955.18</mark>	<mark>67.99</mark>	$\delta(C6-C2-C1)$ (21) $v_{asv}(C15-C18)$ (17) $\delta(O36-C2-C1-C3)$
				(12) δ _{asy} (O36-C5-C1-C6) (12) β(C5-O36-C16) (5)
<u> </u>	000.2	0000	0.72	$\beta(C20-C16-C15)$ (4) $v_{asy}(C5-C6)$ (4)
<mark>54</mark> 57	998.3 1040-37	900.25 1015.68	$\frac{0.73}{140.3}$	$\pi(H_{23}-C_{13}-H_{23}-C_{18})$ (45) $\theta(C_{13}-H_{23}-C_{18})$ (40) $\theta(C_{15}-C_{17}-C_{16})$ (23) η (C15 C18) (23) θ (C5 O36)
<u></u>	1047.37	1013.00	9 9	$C_{16}(14) \beta_{acv}(C_{20}-C_{16}-C_{15}) (10) \nu_{acv}(C_{17}-C_{20}) (6)$
			-	$v_{asy}(C19-C20)$ (5) $v_{asy}(C18-C19)$ (5)
<mark>61</mark>	1081.27	<mark>1046.56</mark>	<mark>3.64</mark>	τ(C1-C2) (28) δ_{asy} (C20-C16-C15) (15) τ_{asy} (C1-C2) (14)
				$\delta_{asy}(C1-C3-C2)$ (12) $v_{asy}(C17-C20)$ (7) $\delta_{asy}(C15-C17-C16)$
<mark>63</mark>	1147 55	1110 71	85 23	$(5) v_{asy}(C19-C20) (3) v(C15-C18) (3) \delta(C20-C16-C15) (49) v(C17-C20) (24) \delta (C13-C9-C8)$
	11 -11.55	1110./1	05.25	(7) v(C16-C17) (4) $v_{asv}(C10-C13)$ (3) $v_{asv}(C18-C19)$ (3)
<mark>64</mark>	<mark>1165.68</mark>	<mark>1128.26</mark>	<mark>295.8</mark>	ν(C1-C2) (16) δ(C20-C16-C15) (15) δ(O36-C2-C1-C3)
			<mark>9</mark>	(13) $\delta_{asy}(O36-C5-C1-C6)$ (13) v(C17-C20) (8) v _{asy} (C1-C5)
70	1220.05	1100.27	1 70	(8) $\tau_{asy}(C1-C2)$ (5) $\tau(C1-C2)$ (5) $\nu(C16, C17)$ (20) $\nu(C18, C10)$ (21) $\nu(C15, C16)$ (15)
<mark>70</mark>	1239.03	1199.27	<mark>4.72</mark>	$\delta_{auv}(C1-C3-C2)$ (8) $v_{auv}(C15-C18)$ (4) $v(C9-C10)$ (15)
				v(C11-H35) (3)
<mark>71</mark>	<mark>1292.92</mark>	<mark>1251.41</mark>	<mark>319.0</mark>	v(C1-C2) (18) v(C16-C17) (18) δ(C6-C2-C1) (9) v _{asy} (C1-

			<mark>2</mark>	C5) (9) δ(O36-C2-C1-C3) (7) δ _{asy} (O36-C5-C1-C6) (7)
				$\delta(C15-C17-C16)$ (7) v(C15-C18)(6) v(C4-C6) (3)
<mark>75</mark>	<mark>1328.38</mark>	<mark>1285.73</mark>	<mark>53.01</mark>	$v(C15-C18)$ (33) $v_{asy}(C17-C20)$ (21) $v_{asy}(C15-C16)$ (10)
				$v(C16-C17)$ (8) $v(C19-C20)$ (6) $v_{asy}(C18-C19)$ (6) $v_{asy}(C8-C19)$
				C11) (4)
<mark>77</mark>	<mark>1349.1</mark>	<mark>1305.79</mark>	<mark>13.16</mark>	$v(C15-C18)$ (32) $v_{asy}(C17-C20)$ (17) $v_{asy}(C15-C16)$ (8)
				v(C16-C17) (7) v(C19-C20) (6) δ(O36-C2-C1-C3) (5)
				$\delta_{asy}(O36-C5-C1-C6)$ (5) $v_{asy}(C18-C19)$ (4) $v_{asy}(C8-C11)$ (4)
<mark>78</mark>	<mark>1364.04</mark>	<u>1320.25</u>	<mark>2.1</mark>	$v(C15-C18)$ (16) $v_{asy}(C4-C6)$ (16) $v_{asy}(C17-C20)$ (12)
				$\delta(036-C2-C1-C3)$ (7) $\delta(036-C5-C1-C6)$ (7) $v_{asy}(C15-C16)$
				$(7) v(C19-C20) (5) v(C16-C17) (5) v_{asy}(C18-C19) (4)$
7 0	107615	1001 07	0.00	$\delta_{asy}(C6-C2-C1)$ (3)
<mark>/9</mark>	<u>13/6.15</u>	<mark>1331.97</mark>	<mark>0.09</mark>	$v(C4-C6)$ (44) $v_{asy}(C15-C18)$ (11) $v(C17-C20)$ (9) $v_{asy}(C3-C4)$ (6) $S(C4-C6)$ (11) (5) $v_{asy}(C3-C4)$ (11) (11) (11) (11) (11) (11) (11) (1
0.4	1404 20	1426 67	17 50	(4) (6) $\delta(C6-C2-C1)$ (5) $V_{asy}(C5-C6)$ (4)
<mark>84</mark>	<mark>1484.32</mark>	1436.67	<mark>17.39</mark>	0(C6-C2-C1)(23)V(C17-C20)(19)0(C15-C17-C16)(9)
				$O_{asy}(CO-C2-C1)(9) O(C20-C10-C15)(0) O(C1-C5-C2)(5)$
<mark>07</mark>	1506 11	1458 05	72 22	$V_{asy}(C15-C16)$ (4) $V_{asy}(C5-C0)$ (4) $V_{asy}(C4-C0)$ (4) S(C20 C16 C15) (20) y(C17 C20) (18) y(C0 C10) (4)
<mark>07</mark>	1300.41	<mark>1436.05</mark>	12.23	8(C15 C17 C16)(13) + (C15 C18)(10) + (C13 C0)
				$C(C13-C17-C10)(13) V_{asy}(C13-C18)(10) V_{asy}(C13-C9-C8)(10) V_{asy}(C13-C9-C8)(10) V_{asy}(C13-C9-C9-C8)(10) V_{asy}(C13-C9-C9-C9-C8)(10) V_{asy}(C13-C9-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9-C9-C9)(10) V_{asy}(C13-C9-C9)(10) V_{asy}(C13-C9)(10) V_{asy}(C13-C9)(10) V_{asy}(C13-C9)(10) V_{asy}(C13-C9)(10) V_{asy}(C13-C9)(10) V_{asy}(C13-C9)(10) V_{asy}(C13-C9)$
92	1642 41	1589 68	<mark>9 54</mark>	$\delta(C15-C17-C16)$ (23) $\nu(C15-C18)$ (15) $\nu(C17-C20)$ (13)
)	1072.71	1507.00	<mark>).JT</mark>	$\delta = (C20 - C16 - C15) (13) \chi = (C18 - C19) (11) \chi = (C16 - C17)$
				(9)
<mark>94</mark>	1660.16	1606.86	<mark>416.4</mark>	$\delta(C6-C2-C1)$ (19) $\delta_{ee}(O36-C2-C1-C3)$ (12) $\delta(O36-C5-C1-C3)$
-			4	C6) (12) δ (C6-C2-C1) (11) v(C17-C20) (9) δ (C15-C17-
				C16) (6) v_{asv} (C15-C16) (5) δ_{asv} (C1-C3-C2) (4) v(C1-C2)
				(4) $v(C15-C18)$ (3) $v_{asv}(C5-C6)$ (3)
<mark>95</mark>	<mark>1736.99</mark>	<mark>1681.23</mark>	<mark>72.7</mark>	δ(O36-C2-C1-C3) (24) δ(O36-C5-C1-C6) (24) β _{asy} (C6-C2-
				C1) (24) δ(C1-C3-C2) (21)
<mark>97</mark>	<mark>3006.66</mark>	<mark>2910.14</mark>	<mark>46.41</mark>	δ (C1-C3-C2) (35) τ _{asy} (C1-C2) (17) ν _{asy} (C3-H27) (12)
				v_{asy} (C6-H30) (12) τ (C1-C2) (11) ν (C4-C6) (5) δ (C6-C2-
_				C1) (3)
<mark>98</mark>	<mark>3045.8</mark>	<mark>2948.03</mark>	<mark>35.5</mark>	δ (C6-C2-C1) (34) ν(C4-H28) (19) τ(C1-C2) (13) ν(C4-
				H29) (11) v_{asy} (C4-C6) (10) δ (C1-C3-C2) (4) τ_{asy} (C1-C2)
100	2001.00		20.10	(4)
<mark>100</mark>	<u>3091.88</u>	<mark>2992.63</mark>	<mark>39.12</mark>	$\tau(C1-C2)$ (25) $\tau_{asy}(C1-C2)$ (15) $v_{asy}(C4-H29)$ (14) $v_{asy}(C6-H21)$ (12) v_{as
				$(12) V_{asy}(C3-H20) (12) o(C1-C3-C2) (9) V(C4-C0)$
102	2188 20	2085.04	2.05	(7) y(C8 H30) (45) y (C14 H21) (45)
102 106	3100.29 3200.0	3106.96	2.05 21.09	$v(CO^{-115}) (45) v_{asy}(C14^{-1121}) (45)$ $\delta(C20, C16, C15) (52) \delta_{-1} (C15, C17, C16) (24) \delta_{-1} (C12)$
100	<mark>3209.9</mark>	5100.80	<mark>21.98</mark>	$0(C20-C10-C13)(33) 0_{asy}(C13-C17-C10)(24) 0_{asy}(C13-C20-C20)(6)$
<mark>111</mark>	<u>3777 75</u>	3124 13	16 46	$\delta(C^{2}0, C^{1}6, C^{1}5) = (26) \psi_{-}(C^{1}5, C^{1}8) = (20) - \delta_{-}(C^{1}5, C^{1}7)$
111	<u>5221.15</u>	5124.15	10.40	$C_{16}(11) v_{asy}(C_{13}-C_{13}) (20) v_{asy}(C_{13}-C_$
				$(11)^{v_{asy}(-10-C1)}(11)^{v_{asy}(-1)-C20}(0)^{-0}(0)^{-0}(-1)$

Proposed assignment and potential energy distribution (PED) for vibrational modes: types of vibrations: v- symmetric stretching; v_{asy} - asymmetric stretching; β - in-plane bending; β_{asy} - asymmetric in-plane bending; π -out-of-plane bending; δ - linear bend; τ - torsion ; τ_{asy} - asymmetric torsion.

Table 5. Calculated ε_{LUMO} , ε_{HOMO} , energy band gap $\varepsilon_{LUMO} - \varepsilon_{HOMO}$, ionization potential (IP), electron affinity (EA), electronegativity (χ), global hardness (η), chemical potential (μ), global electrophilicity index (ω), global softness (S) and additional electronic charge (ΔN_{max}) in eV for reactant A, B and product C using B3LYP/6-31G(d,p).

437
ΔN_{max}
1.797
1.107
2.093



Scheme 1: Synthesis of (2E,6E)-2,6-bis(2-chlorobenzylidene)cyclohexanone

Highlights

- Chemical structures were characterized using spectroscopic techniques.
- A good agreement between the calculated and experimental wavenumbers shows precise assignment of normal mode vibrations in the entire spectral region.
- The HOMO, LUMO and MESP surfaces are analyzed to discuss the chemical reactivity in the molecules.
- A number of reactivity parameters has been calculated to further explain their chemical reactivity

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