Cyclohexanone-Based Chalcones as Alternatives for Fuel Additives

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ABSTRACT: The use of small molecules, such as chalcones and their derivatives, for more efficient fuels is in increasing demand due to environmental factors. Here, three crystal structures (BH I, II, and III) of cyclohexanone-based chalcones were synthesized and described by single-crystal X-ray diffraction and Hirshfeld surface analysis. The supramolecular modeling analysis on the hyperconjugative interaction energies and QTAIM analysis at the oB97XD/6-311+G(d,p) level of theory were carried out to analyze the intermolecular interactions in the solid-state. The structure−property relationship, frontier molecular orbital, molecular electrostatic potential, and the experimental calorific value analysis show that the three compounds are a good alternative to be used as an additive for some fuels. Our findings represent a further step forward in the development of cheaper and more efficient fuel additives and pose an opportunity for further investigation on similar analogues.

INTRODUCTION

The push from the exhaustion of fossil fuels and global warming problems has increased the demand for alternative bioenergy sources and improved the efficiency of current fuels.1 Regarding currently used biofuels, their energetic efficacy is affected by inherent stability, oxidation, and energy availability limitations.2 The use of small molecules for these purposes is an attractive alternative, once they usually are easily synthesized, cost-wise accessible, and serve for a myriad of different applications, including the modulation of protein−protein interactions, alteration of protein function, catalytic activity, and energy source for crucial chemical reactions.3 In fact, due to its physicochemical properties similar to cellulose, the small molecule α-cyclodextrin has been investigated as an accurate way to unveil the chemical mechanisms involved during high-temperature conversion to biofuel.

Chalcones and their analogues are either found in plants or obtained from specific synthetic pathways and have shown numerous applications as liquid crystal materials,4 pH sensors,5,6 nonlinear optical materials,7,8 as well as their remarkable biological properties: antitumor,9,10 anti-inflammatory,11 anti-fungal,12−14 antibacterial,12,15,16 and antioxidant.17−20 Some of these properties can be related to fuel applications, such as energy efficiency or additives,21−27 and often fuels such as ethanol and biofuels are prone to suffer from degradation and oxidation problems, mainly caused by micro-organisms28−34 or even the lower combustion capacity, therefore, a lower energy efficiency.35−39

Chalcone molecular structures have stimulated studies of their spatial conformation systems, such as π-electronic conjugations,40 cyclohexanone rings,41 electronic effects of substituents in the aromatic rings,42 interaction energies, and electronic properties obtained by density functional theory (DFT) calculations.43 Understanding these interactions has been applied to comprehend these physical chemistry systems and pharmaceutical and material properties. X-ray crystallography, Hirshfeld surface analysis, and theoretical studies are handy tools for this subject.

Based on these potentials as fuel additives previously described for chalcones, we hypothesized that cyclohexanone-based analogues would present the same physicochemical features needed to improve biofuel’s efficiency. Here we report the results of the (2E,6E)-2,6-bis(4-ethylbenzylidene)cyclohexanone (BH I), (2E,6E)-2,6-bis(2,4-dichlorobenzylidene)cyclohexanone (BH II), and (2E,6E)-2,6-bis(4-chlorobenzylidene)cyclohexanone (BH III) from single-crystal X-ray diffraction (XRD) and Hirshfeld surface (HS) analysis in order to describe its molecular and supramolecular architectures. In addition to molecular structure studies, theoretical calculations such as frontier molecular orbital (FMO), molecular electrostatic potential (MEP) map, hyperconjugative interaction energies, counterpoise procedure, quantum theory of atoms in molecules (QTAIM), and

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vibrational infrared (IR) spectra assignments were carried out at the ωB97XD/6-311+G(d,p) level of theory. Finally, we quantified their energetic potential using a calorimetric pump, which was then compared to ethanol, biodiesel, diesel, and butanol.

### EXPERIMENTAL AND COMPUTATIONAL PROCEDURES

**Synthesis and Crystallization.** The reaction was carried out at room temperature where BH I, II, and III were prepared by the reaction of cyclohexanone (3.00 mmol) and substituted benzaldehydes (2.00 mmol) in a minimum amount of absolute methanol (10 mL) as shown in Scheme 1. Then a 30% KOH solution was added and after a few minutes of continuous stirring, the reaction was completed, and the precipitate obtained was collected by filtration. Yellow product was obtained in 75% yield.

Crystals of BH I, II, and III were grown in dichloromethane inside a beaker with a known solvent volume. Then, the reaction mixture was kept at room temperature for slow evaporation for 96 h until the formation of crystals. All solvents and chemicals used in the synthesis were obtained from commercial sources and used without further purification. Thin-layer chromatography (TLC) was carried out using Silica gel 60 UV254 plates, and the solvent system was ethyl acetate–methanol (10 mL) as shown in Scheme 1. Then a 30% KOH solution was added and after a few minutes of continuous stirring, the reaction was completed, and the precipitate obtained was collected by filtration. Yellow product was obtained in 75% yield.

**Crystallographic Characterization.** Single-crystal XRD intensity data collection was performed on a Bruker APEX II CCD diffractometer fitted with MoKα radiation (0.71073 Å) at 120 K. The structures, using the ShelX refinement package, were solved by direct methods and refined by least-squares minimization using the ShelXL refinement package. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed geometrically and refined using a riding model with their Uiso set to 1.2 Ueq of the bonded carbon. The crystallographic information file (CIF) was prepared using Olex2. Also, the artwork representations for publication were prepared using the programs Ortep and Mercury (version 3.0). Intermolecular interactions were checked by the Platon software. The BH I, II, and III structures were deposited in the Cambridge Structural Database under codes 2120122, 2120123, and 2120124. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

**Hirshfeld Surface.** The HS consists of a spatial map to visualize the surface of the molecules. It is a useful tool that compares the electron density of a molecule to the entire crystal and measures the distribution of close contact interactions. A weight function \( w_s(r) \) for a molecule in a crystal was defined by eq 1,

\[
w_s(r) = \sum_{\text{a molecule}} \rho_a(r)/\sum_{\text{a crystal}} \rho_a(r)
\]

where \( \rho_a(r) \) is the electron density function of the atom, centered on the nucleus \( a \), defined by eq 2,

\[
\rho_a(r) = w_s(r) \rho_{\text{mol}}(r)
\]

\( \rho_{\text{mol}}(r) \) defines the molecular electron density. In an HS, \( d_s \), is the distance from the nearest nucleus to a molecule outside the surface, which provides the close intermolecular contacts, while \( d_v \) is the distance from inside to the surface, which provides studies of the molecule itself. The normalized contact distance \( d_{\text{norm}} \), which combines the normalized \( d_s \) and \( d_v \) with the van der Waals radius for each atom involved in this close contact to the surface, is given by eq 3 and was used to analyze intermolecular interactions.

\[
d_{\text{norm}} = (d_s - r_{vdw})/r_{vdw} + (d_v - r_{vdw})/r_{vdw}
\]
Table 1. Vibrational Assignments of the Theoretical and Experimental FT-IR for BH I, II, and III

| Vibrational modes | BH I | BH II | BH III |
|-------------------|------|-------|--------|
| $\nu$ (C\(_\text{sp}^3\)-H) \(^*=\) | 3084-3001 | 3095-3030 | 3088-3030 |
| $\nu$ (C\(_\text{sp}^2\)-H) \(^*=\) | 2965-2853 | 2972-2845 | 2929-2835 |
| $\nu$ (C=C) \(^*=\) | 1606, 1580, 1508, 1457 | 1600, 1580, 1468 | 1606, 1577, 1486 |
| $\nu$ (C=O) and $\nu$ (C\(_\text{sp}^2\)=C) \(^*=\) | 1663 | 1660 | 1667 |
| $\delta_\text{H}_\text{Ak}$ out of plane | 828 | 825 | 836 |
| $\nu$ (C-Cl) | 3001 | 3030 | 3030 |

These results were obtained at the $\omega$B97XD/6-311++G(d,p) level of theory in the gas phase. $\nu$ = stretching; $\delta$ = bending. \(^*=\)Scale factor 0.9461. \(^*=\)Ar = aromatic ring. \(^*=\)Alk = alkene.

In eq 3, the $r_{vdw}$ and $r_{vdw}$ represent the van der Waals radii. The shape index is a function of a surface that allows one to identify complementarity between molecules in the crystal packing structure and that can identify hydrophobic intermolecular interactions.\(^{51}\) Fingerprint plots provide a quantitative value for the types of intermolecular contacts, also known as frequency occurrences. The software Crystal Explorer 21.52 was used to generate HS intermolecular interactions and calculated 2D fingerprint plots.

\section*{CALORIFIC POWER}

The calorific value of fuel indicates energy released by combustion per unit mass. The test to determine the calorific value was carried out in a calorimetric pump with a combustor surround by water. This analysis followed the ASTM D4809 standard methodology using an IKA C200 equipment. The combustor is pressurized (30 bar), and the sample is heated by an electric current that promotes burning. Burning releases energy into the environment and exchanges heat with water, generating a change in its temperature. A high precision resistive sensor measures the change in temperature as a function of time and, after correlation with the sample mass obtained prior to burning, the result of the calorific value of the sample is reported.\(^{24,54}\)

\textbf{Theoretical Calculation.} The electronic structure calculations were carried out with the Gaussian 16\(^{55}\) program package for BH I, II, and III. Full geometry optimization was carried out using DFT, with exchange-correlation functional $\omega$B97XD\(^{56}\) and basis set 6-311++G(d,p). This functional includes empirical dispersion with long-range corrections, making it suitable for noncovalent interactions. The wave function for the natural bond orbital (NBO) analysis was carried out at the same level of theory, and the basis set superposition errors (BSSE) were corrected using the counterpoise procedure as implemented in the g04b program.\(^{57}\) Also, the studied electronic properties: the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and MEP were calculated. The QTAIM analysis, using the Multwfn program (version 3.7),\(^{58}\) was performed using the non-hydrogen atoms taken from the crystallographic data, while the hydrogen atoms were optimized using the same level of theory and were also calculated assignments of infrared vibrational frequencies.

\section*{RESULTS AND DISCUSSION}

\textbf{Solid-State Description.} Table 1 lists the main IR absorption bands and also Figure 1 shows the overlapping of the theoretical and experimental FT-IR spectra for BH I, II, and III. The values of DFT in vibrational frequencies for the results obtained at the $\omega$B97XD/6-311++G(d,p) level of theory were scaled by Wang et al. as 0.9461.\(^{59}\) The experimental measurements of $\nu$ (C=O) for BH I, II, and III occur at 1663, 1660, and 1667 cm\(^{-1}\), respectively, while the theoretical measurements absorb at 1683, 1688, and 1682 cm\(^{-1}\), respectively, considering the molecule was in the gas phase.

![Figure 1. Overlapping of the theoretical (red) and experimental (black) FT-IR spectra of (a) BH I, (b) BH II, and (c) BH III.](https://doi.org/10.1021/acsomega.1c07333)
Absorption peaks appear in the experimental $\nu(C\equiv C\cdots H)$ aromatic ring for BH I at 1606 cm$^{-1}$, 1580, 1508, and 1457 cm$^{-1}$; and for BH II these peaks appear at 1600, 1580, and 1468 cm$^{-1}$; and for BH III they appear at 1606, 1577, and 1486 cm$^{-1}$, while theoretically, these values appear for BH I at 1607 and 1482 cm$^{-1}$; for BH II at 1620, 1575, and 1440 cm$^{-1}$; and for BH III at 1617, 1591, and 1457 cm$^{-1}$. It is observed that the $\nu(C\equiv C\cdots H)$ for BH I, II, and III are in the range of 2965–2853 cm$^{-1}$, 2975–2845 cm$^{-1}$, and 2929–2835 cm$^{-1}$, respectively, while the DFT calculations assigned to the regions of 2957–2876 cm$^{-1}$, 2935–2859 cm$^{-1}$, and 2932–2849 cm$^{-1}$, respectively. Additionally, for BH the ring-puckering parameters appear in the cyclohexanone as a half boat conformation, which is described by Cremer and Pople.60 Additionally, for BH the ring-puckering parameters are 742 and 799 cm$^{-1}$, while the theoretical band appears in 746 and 785 cm$^{-1}$.

Figure 2 shows the BH I, II, and III asymmetric units as an Ortep diagram. With respect to BH I, the stereochemistry of the aromatic ring for BH I is crystallized in the orthorhombic system with $Z = 8$). The crystal packing of BH is formed by dihydrogen-bifurcated interaction along the $Z$ axis, which can be described as $C\equiv C\cdots H$ (Figure 3a).

C5=C2 is on an (E)-configuration. This molecule appears in the cyclohexanone as an envelope conformation confirmed by the ring-puckering parameters $Q = 0.5034 \text{ Å}$ and $\phi = 360^\circ$, as described by Cremer and Pople.60 Additionally, for BH I, the dihedral angle C2−C5−C6−C7 has $147.3^\circ$, as shown in Table 2. Also, for BH II and III, the stereochemistry of the C7=C8 and C12=C13 is on an (E)-configuration. These molecules appear in the cyclohexanone as a half boat conformation, which is confirmed by the ring-puckering parameters $Q = 0.5291 \text{ Å}$ and $\phi = 136.2^\circ$, as well as $Q = 0.5343 \text{ Å}$ and $\phi = 282.06^\circ$ for BH II and III, respectively. Furthermore, for BH II with dichloro-substituted, the dihedral angle C3−C4−C7−C8 and C12−

![Ortep diagram of ellipsoids at 50% probability level with the atomic numbering scheme for (a) BH, (b) BH II, and (c) BH III. Hydrogen atoms are in arbitrary radii.](image)

The BH I is crystallized in the orthorhombic system with noncentrosymmetric space group Cmc2$_1$. In this case, being a centrosymmetric molecule and lying on a crystallographic mirror plane, its asymmetric unit comprises only one-half-molecule ($Z = 0.5$) of the compound. The crystal packing of BH I appears in an infinite chain formed by C1−H$_{3b}$···O1 interaction along the $c$ axis, which can be described as $C1(5)$ (Figure 3a). Further, C$_{13}$−H$_{3b}$···H$_{13b}$−C$_{13}$ dihydrogen contact is possible to observe along the $a$-axis, also generating an infinite chain (Figure 3b). Figure 3c shows the packing of BH I, formed by dihydrogen contact at the center of the unit cell and the C$_{13}$−H$_{3b}$···O$_1$ interaction lying on a crystallographic mirror plane.

The BH II is crystallized in the orthorhombic system with centrosymmetric space group Pbcn, with one molecule in the asymmetric unit ($Z = 8$). The crystal packing of BH II is formed by C16−H$_{10a}$···O$_1$ and C$_{2b}$−H$_{2o}$···O$_1$ interactions, appearing as bifurcated interaction along the $b$ axis, which can be described as

| BH       | experimental | theoretical |
|----------|--------------|-------------|
| O1−C1−C2−C3 | -171.9 (2) | -179.0 |
| C1−C2−C3−C4 | -33.4 (2)  | -29.8  |
| C1−C2−C5−C6 | -176.2 (2) | -179.7 |
| C2−C3−C4−C5 | 59.9 (3)   | 59.0   |
| C2−C5−C6−C7 | -147.3 (2) | -145.9 |
| C5−C2−C3−C4 | 144.94 (18)| 147.3  |
| C8−C9−C10−C13 | -165.1 (3) | -178.1 |

**Table 2. Relevant Experimental and Theoretical Dihedral Angles (deg) for BH I, II, and III**

Relevant experimental and theoretical dihedral angles are given in Table 2. The important crystallographic parameters of BH I, II, and III are shown in Table 3. Detailed intermolecular interactions observed in all crystal structures are given in Table 4.
Table 3. Important Crystallographic Parameters of BH I, II, and III

| crystal data          | BH I         | BH II        | BH III       |
|-----------------------|--------------|--------------|--------------|
| empirical formula     | C_{24}H_{26}O | C_{24}H_{34}OCl | C_{24}H_{18}OCl |
| formula weight/g mol^{-1} | 330.45       | 412.11       | 343.23       |
| temperature/K         | 120(2)       | 120(2)       | 120(2)       |
| radiation type        | MoKα         | MoKα         | MoKα         |
| crystal system        | orthorhombic  | orthorhombic  | monoclinic   |
| space group           | Cmc2_1       | Pbcn         | P2_1/n       |
| unit cell dimensions  | a = 20.72(4)Å  | a = 14.26(2)Å | a = 9.82(9)Å |
|                       | b = 14.80(4)Å | b = 7.78(13)Å| b = 16.48(15)Å |
|                       | c = 6.03(12)Å | c = 31.37(5)Å| c = 10.46(10)Å |
| volume/Å³              | 1852.2(7)    | 3484.7(10)   | 1630.6(3)    |
| Z                     | 4            | 8            | 4            |
| density (calculated)/g cm^{-3} | 1.185       | 1.571        | 1.398        |
| F(000)                | 712          | 1680         | 712          |
| reflections collected  | 14571        | 61722        | 30834        |
| independent reflections | 2375 [R(int) = 0.0356] | 4366 [R(int) = 0.0856] | 4036 [R(int) = 0.0223] |
| data/restraints/parameters | 2375/1155 | 4366/0/238   | 4036/0/229   |
| goodness-of-fit on F^2 | 1.047        | 1.262        | 1.077        |
| final R indices [I > 2σ(I)] | R_1 = 0.0629, wR_2 = 0.0868 | R_1 = 0.0793, wR_2 = 0.0816 | R_1 = 0.0379, wR_2 = 0.0816 |
| final R indices [all data] | R_1 = 0.0448, wR_2 = 0.0917 | R_1 = 0.0676, wR_2 = 0.0785 | R_1 = 0.0325, wR_2 = 0.0785 |
| extinction coefficient | n/a          | n/a          | n/a          |
| largest diff. peak and hole/e Å^{-3} | 0.18−0.19 | 0.53 and −0.41 | 0.36 and −0.26 |

Table 4. Hydrogen-Bond Geometry (Å, deg) in the Crystal Structure of BH I, II, and III

| BH       | D–H–A      | D–H      | D–A      | H–A      | D–H–A     | symmetry code |
|----------|------------|----------|----------|----------|-----------|---------------|
| I        | C_{17}H_{20}O–O_1 | 0.98    | 3.277    | 2.55     | 130.08    | x, y, −1 + z  |
|          | C_{17}H_{18}O–O_{10}–C_{17} | 1.05    | 2.650    | 1.65     | 154.83    | −1 + x, y, z |
| II       | C_{10}H_{18}O–O_{10} | 0.96    | 3.506    | 2.54     | 177.00    | 1/2 − x, 1/2 + y, z |
|          | C_{10}H_{16}O–O_1   | 0.95    | 3.225    | 2.33     | 157.00    | 1/2 − x, −1/2 + y, z |
|          | C_{17}H_{14}O–Cl_1 | 0.97    | 3.587    | 2.74     | 146.00    | 1 − x, −y, 1 − z |
| III      | C_{10}H_{18}O–π    | 0.94    | 3.623    | 2.71     | 159.63    | −1/2 + x, 1.5 − y, −1/2 + z |
|          | C_{10}H_{10}O–Cl_1 | 0.97    | 3.799    | 2.89     | 154.87    | −1 + x, y, z |
|          | C_{14}H_{12}O–Cl_1 | 1.74    | 5.023    | 3.30     | 169.18    | −2 + x, y, −1 + z |

C_{17}^-(9), as shown in Figure 4a. Further, C_{17}−H_{18}⋯Cl_4 appears as a dimer around the inversion center along the c axis, which can be described as R_2^1(8) (Figure 4b). Figure 4c shows the packing of BH II, formed by C_{17}−H_{17}⋯Cl_3 lying at the center of the unit cell and around the inversion centers.

The BH III crystallized in the monoclinic system with centrosymmetric space group P2_1/n, with one molecule in the asymmetric unit (Z = 4). The crystal packing of BH III, differently from the other BHs, is formed by C_{6}−H_{6}⋯π interaction appearing in a zigzag chain along the a axis (Figure 5a). Further, bifurcated contacts through C_{10}H_{18}⋯Cl_1 and C_{1}−Cl⋯C_{1} in Figure 5b. Figure 5c shows the packing of BH III, formed by a zigzag chain lying on a crystallographic glide plane. On the other hand, at the center of the unit cell and around the inversion center, no interaction is observed.

In order to interpret the intermolecular interactions, we employed HS d_{norm} analysis. These interactions are verified in d_e and d_d indicating the distance within the molecule between the external and internal nucleus of the HS, respectively. Additionally, d_e and d_d correspond to acceptor and donor regions, respectively. The HS mapped over d_{norm} (range of −0.511 to 1.470 Å) is shown in Figure 6.

For BH I, the red spots correspond to a stronger C_{6}−H_{18}⋯O_1 contact (Figure 6a), which is also related to the shorter H⋯H contact (Figure 6b). In the same way, for BH II, the red spots correspond to C_{10}−H_{18}⋯O_2 and C_{9}−H_{20}⋯O_1 interactions, as shown in Figure 6c. Also, Figure 6d is related to a dimer C_{17}−H_{17}⋯Cl_3 interaction. The shape index HS also is a tool for the identification of hydrophobic interactions like π⋯π. The π⋯π stacking in the BH II is identified by the red and blue triangle in the shape index surface, as shown in Figure 6e. The distance between centroids, formed between the center of aromatic rings C_1−C_6 (Cg1) and C_15−C_20 (Cg3), is 3.88 Å providing additional stability for the structure. For BH III, the red spots correspond to C_{6}−H_{6}⋯π and C_{10}−H_{10}⋯Cl_1 interactions, as shown in Figure 6f, respectively. Also, Figure 6h is related to a halogen Cl⋯Cl contact.

The 2D fingerprint plot of BH I, II, and III is shown in Figure 7. From the 2D fingerprint plot, most contact is due to H⋯H interaction, which makes up 68.1% of the HS of BH I and is characterized by the thin spike of the fingerprint 2D plot. The contribution of O⋯H⋯O interactions of BH I represents 5.6% of the HS (Figure 7a). For BH II, the contribution of H⋯H and C⋯H⋯C interactions represents 23.5% and 15.3% of the HS, respectively. The polar dimer interactions Cl⋯H⋯Cl represents 32.7%. Another feature is the existence of C⋯C interaction, which is responsible for 5.1% of HS. The interaction O⋯H⋯O is characterized by the small spikes in the bottom of the fingerprint plot, representing 6.0% of the HS, as shown in Figure 7b. For BH III, most contact is due to H⋯H interaction which makes up 33.5% of the HS. The contribution of C⋯H/
H···C interactions of BH III represents 27.4% of the HS. The polar interaction Cl···H/H···Cl represents 22.5%. The contribution of Cl···Cl contacts are characterized by the thin spike at the center of the 2D fingerprint plot (Figure 7c).

The root mean squared (RMS) values predicted by the Mercury program package, 48 comparing calculated and experimental geometries, were 0.0047, 0.0131, and 0.0061 for BH I, II, and III, respectively. The overlay depicts a good correlation between the geometric parameters for all the structures. The difference for BH I (Figure 8a), representing about 7.29%, is around C8−C9−C12−C13 with experimental (−165.1°) and theoretical (−178.1°) dihedral angles, as shown in Table 2. The difference for BH II (Figure 8b), representing about 7.90%, is around C3−C4−C7−C8 with experimental (145.6°) and theoretical (−134.0°) dihedral angles. Additionally, another difference for BH II, representing about 12.5%, is around C7−C8−C9−C10 with experimental (−161.2°) and theoretical (−141.0°) dihedral angles, as shown in Table 2. The difference for BH III (Figure 8c), representing about 16.40%, is

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Intermolecular interactions depicting (a) C3−H3B···O1, (b) C13−H13B···H13B−C13 dihydrogen contact, and (c) the crystalline packing of BH I.

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Intermolecular interactions depicting (a) C10−H10A···O1 and C20−H20···O1, (b) C17−H17···Cl3, and (c) the crystalline packing of BH II.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** Intermolecular interactions depicting (a) C6−H6···π, (b) C10−H10A···O1 and C18−Cl2···Cl1, and (c) the crystalline packing of BH III.
around C12−C14−C15−C16 with experimental (−173.1°) and theoretical (−144.7°) dihedral angles, as shown in Table 2.

Supramolecular Modeling Analysis and Energy. The investigation into the chalcones’ chemical structure and its properties helps us to understand the activity of these molecules as a possible application in fuels. Actually, the world energy matrix has some fuels with advantages over fossil fuels. However, these fuels have stability, oxidation, and energy availability problems, as with ethanol and biodiesel.

The calorific value test for BH I, II, and III shows values of 7284.0 kcal/kg, 6430.2 kcal/kg, and 7298.7 kcal/kg, respectively (Table 5). In addition, we performed calorific value tests for gasoline (common type C), hydrated ethanol, and n-butanol for comparative parameters. Table 5 also presents different calorific values for various types of biodiesel.

The calorific value results reveal that BH I, II, and III have good energy availability, even a little lower than biodiesel (Figure 9). However, BH I and III (7284.0 and 7298.7 kcal/kg) have a higher calorific value than ethanol (6906.0 kcal/kg), while BH II presents a small difference compared to ethanol. Due to the susceptibility and good energy availability of chalcones, they...
The HOMO located mainly on the aromatic rings. It is a π-bonding orbital and is associated with fuels, since the high calorific value in fuels is associated with better performance.

The FMO obtained from Kohn–Sham analysis for BH I, II, and III was carried out at ωB97XD/6-311+G(d,p) level of theory, and they are shown in Figure 10. The FMO analysis of bond-antibonding interactions is a good approximation for ionization (Lewis base) and electron affinity (Lewis acid) energies. The HOMO, the electron donor for BH I, II, and III, is located mainly on the aromatic rings. It is a π-bonding orbital, which is characteristic of the electrophilic region. The HOMO energy for BH I, II, and III is negative (−185.79, −200.34, and −194.86 kcal/mol, respectively). The LUMO for BH I, II, and III is an π-antibonding orbital, and it is spread out through the molecular rings and the carbonyl group. The LUMO energy for BH I, II, and III is −10.69, −20.34, and −185.79 kcal/mol, respectively. These results show that the BH I, II, and III compounds are electrophilic species.

NBO analysis helps us better understand the nature of intermolecular interactions in the solid state. For the reason that one of the aims of this work is to explain the supramolecular arrangement of the BH I, II, and III compounds, the atomic coordinates of non-hydrogen atoms were taken directly from the crystallographic data. However, as the coordinates of the hydrogen atoms were not experimentally determined, it was necessary to optimize them using the wB97XD/6-311++G(d,p) level of theory. The same level of theory was used to obtain the necessary to optimize them using the wB97XD/6-311++G(d,p) level of theory. The same level of theory was used to obtain the

\[
E(2) = -\frac{\langle \sigma | F \sigma | \rangle^2}{\varepsilon_\sigma - \varepsilon_\tau} = -n_\sigma \frac{F_{ij}^2}{\Delta E}
\]

where \( \langle \sigma | F \sigma | \rangle^2 \) is the Fock matrix element between the \( i \) and \( j \) NBO orbitals. \( \varepsilon_\sigma \) and \( \varepsilon_\tau \) are the energies of \( \sigma \) and \( \tau \) NBO orbitals, respectively, and \( n_\sigma \) stands for the \( \sigma \) donor orbital population. NBO analysis provides a method for studying hyperconjugative interaction in a molecular system.91,92 The higher the \( E(2) \) value, the more intensive the interaction between electron donor and acceptor, respectively. Figure 11 shows the calculated NBO orbitals.

For BH I, Figure 11a shows the orbital interaction between the lone pair orbital of the O1 atom and the \( \sigma^* \) antibonding orbitals in BD-B100 (methyl palm)80 and BD-B100 (methyl palm)80. BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsky)94 9319.3 BD-B100 (sosnowsk
orbital of the Cl$_1$ atom and the $\sigma^*$ antibonding orbital of the C$_{10}$–H$_{10A}$ is shown in Figure 11g with a stabilization energy of 0.65 kcal mol$^{-1}$. Along with the halogen contact (Figure 11h) between the lone pair orbital of the Cl$_1$ atom and the $\sigma$ antibonding orbital of the Cl$_2$, a stabilization energy of 0.63 kcal mol$^{-1}$ is observed.

The MEP is a physicochemical tool that gives information about molecular interactions and helps predict the reactive sites to be targeted in a chemical reaction. The electrostatic potential at a given point $\rho(r)$ in the vicinity of a molecule can be calculated by eq 5:

$$V(r) = \sum \frac{Z_\alpha}{|r - R_\alpha|} - \int \frac{\rho(r')}{|r - r'|} \, dr'$$

where $V(r)$ is the potential energy by a positive unit charge at point $r$, $Z_\alpha$ is the nuclear charge of the atom $\alpha$ located at position $R_\alpha$, and $\rho(r')$ is the electron density.

The tridimensional MEP representation (Figure 12) for BH I, II, and III shows that the most negative region (red) is located on the oxygen atom of the carbonyl group, with a value of $-35.76$, $-30.93$, and $-30.12$ kcal/mol, respectively. On the other hand, the positive region (blue) is around the cyclohexanone hydrogen atoms, with a value of 12.29, 22.02, and 19.39 kcal/mol, respectively. In conclusion, due to C–H···O interactions in the crystal structures, we can assume an electrostatic attack on this carbonyl group’s region.

Also, the supramolecular modeling analysis on the hyper-conjugative interaction energies and QTAIM analysis, using theoretical calculations at the ωB97X-D/6-311++G(d,p) level of theory, were calculated to prove the existence of intermolecular interactions and to classify their nature. Figure 13 shows that, in quantum mechanic calculations, there are two types of interaction for BH I, II, and III in the solid-state, which we call here as side-to-side and head-to-head dimers. The basis set superposition errors (BSSE) were corrected using the counterpoise procedure as implemented in the g16 program. For BH I, Figure 13a shows that the side-to-side dimer interaction energy is $-10.60$ kcal/mol, showing powerful and attractive energy for dimers. The head-to-head interaction energy (Figure 13b) for BH I dimer is 1.19 kcal/mol. This interaction energy is negligible and repulsive for the dimers. Consequently, we can assume that the side-to-side interaction energies are the driving forces for the BH I molecular arrangement in the solid-state.

For BH II, Figure 13c shows that the side-to-side dimer interaction energy is $-19.59$ kcal/mol, showing powerful and attractive energy for dimers. The head-to-head interaction energy (Figure 13d) for the BH II dimer is $-0.53$ kcal/mol. Consequently, we can assume that both the side-to-side and head-to-head interaction energies are the driving forces for the BH II molecular arrangement in the solid-state.

For BH III, Figure 13e shows that the side-to-side dimer C$_6$–H$_{10A}$···π interaction energy is $-10.73$ kcal/mol. Further, another side-to-side dimer (i.e., C$_{10}$–H$_{10A}$···Cl$_2$) interaction energy is $-5.48$ kcal/mol, showing powerful and attractive energy for the molecule. As well as BH I, the head-to-head C$_{10}$–H$_{10A}$···Cl$_2$ dimer interaction energy (Figure 13f) for BH III is 0.31 kcal/mol. This interaction energy is also negligible and repulsive for the dimers. Consequently, we can assume that the side-to-side interaction energies are the driving forces for the BH III molecular arrangement in the solid state.

The QTAIM analysis was carried out to understand the chemical nature of dimers’ interactions. The interactions

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**Figure 9.** Calorific value for BH I, II, III, and fuels: biodiesel, diesel, hydrated ethanol, and s-butanol. The calorific value of biodiesel varies with its composition; therefore, we have a comparative parameter. We performed an average of the values described in Table S. Average of the values described in Table S.

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**Figure 10.** Frontier molecular orbitals derived from Kohn–Sham analysis at ωB97X-D/6-311++G(d,p) level of theory with the isovalue of 0.02 atomic units: the HOMO $\pi$-bonding orbital and the LUMO $\pi$-antibonding orbital for (a) BH I, (b) BH II, and (c) BH III.

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TABLE S

|          | BH I   | BH II  | Ethanol | Biodiesel | Diesel | Butanol |
|----------|--------|--------|---------|-----------|--------|---------|
| Calorific power (MJ kg$^{-1}$) | 7284   | 6430   | 7298    | 6906      | 9196   | 10235   | 8509   |

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**Figure 11c** shows the orbital interaction between the lone pair orbital of the O1 atom and the $\sigma^*$ antibonding orbital of the C$_{10}$–H$_{10A}$.
that occur in BH I are of type C₃⁻H₃B···O₁ short contact and C₁₃⁻H₁₃B···H₁₃B=C₁₃ dihydrogen contact, as shown by bond critical point (BCP) analysis (Figure 14). The BCP describes the stationary point between donor and acceptor atoms, confirming

Figure 11. Intermolecular donor–acceptor natural bond interactions in (a and b) C₃⁻H₃B···O₁ and C₁₃⁻H₁₃B···H₁₃B=C₁₃ for BH I; (c–e) C₁₀⁻H₁₀A···O₁, C₂₀⁻H₂₀B····O₁, and C₁₇⁻H₁₇···C₁₃ for BH II; and (f–h) C₆⁻H₆···π, C₁₀⁻H₁₀B···Cl₁, and C₁₈⁻Cl₂···Cl₁ for BH III.
the existence of hydrogen bonding interaction. The QTAIM’s electron density $\rho(r)$ at the BCP of proton-acceptor is 0.032 and 0.050 au for $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$ and $C_{13}^{} - H_{13B}^{} \cdots H_{13B}^{} - C_{13}^{}$, respectively. The positive Laplacians, 0.040 and 0.28 au for $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$ and $C_{13}^{} - H_{13B}^{} \cdots H_{13B}^{} - C_{13}^{}$, respectively, are observed for noncovalent hydrogen bonds interactions. The total energy density value $E(r)$ is small and negative for $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$ and $C_{13}^{} - H_{13B}^{} \cdots H_{13B}^{} - C_{13}^{}$ as shown in Table 6.

The interactions that occur in BH II are of type $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$ and $C_{20}^{} - H_{20}^{} \cdots O_1^{}$ short contact and $C_{17}^{} - H_{17}^{} \cdots C_{13}^{}$ dimer interaction, as shown by BCP analysis (Figure 15). The QTAIM’s electron density $\rho(r)$ at the BCP of proton-acceptor is 0.058, 0.087, and 0.019 au for $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$, $C_{20}^{} - H_{20}^{} \cdots O_1^{}$, and $C_{17}^{} - H_{17}^{} \cdots C_{13}^{}$, respectively. The positive Laplacians, 0.074, 0.30, and 0.093 au for $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$, $C_{20}^{} - H_{20}^{} \cdots O_1^{}$, and $C_{17}^{} - H_{17}^{} \cdots C_{13}^{}$, respectively, are observed for noncovalent hydrogen bonds interactions. The total energy density value $E(r)$ is small and negative for $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$ and $C_{20}^{} - H_{20}^{} \cdots O_1^{}$, as shown in Table 6. On the other hand, for $C_{13}^{} - H_{13B}^{} \cdots C_{13}^{}$, the total energy density value $E(r)$ is small and positive.

The interactions in BH III are of type $C_{6}^{} - H_{6}^{} \cdots \pi$, $C_{10}^{} - H_{10B}^{} \cdots C_{18}^{}$ short contact and halogen contact $C_{18}^{} - C_{13}^{} \cdots C_{13}^{}$, as shown by BCP analysis (Figure 16). The QTAIM’s electron density $\rho(r)$ at the BCP of proton-acceptor is 0.063, 0.053, and 0.025 au for $C_{6}^{} - H_{6}^{} \cdots \pi$, $C_{10}^{} - H_{10B}^{} \cdots C_{18}^{}$, and $C_{18}^{} - C_{13}^{} \cdots C_{13}^{}$, respectively. The positive Laplacians, 0.12, 0.19, and 0.014 au for $C_{6}^{} - H_{6}^{} \cdots \pi$, $C_{10}^{} - H_{10B}^{} \cdots C_{18}^{}$, and $C_{18}^{} - C_{13}^{} \cdots C_{13}^{}$, respectively, are observed for noncovalent hydrogen bonds interactions. The total energy density value $E(r)$ is small and negative for $C_{6}^{} - H_{6}^{} \cdots \pi$ and $C_{18}^{} - C_{13}^{} \cdots C_{13}^{}$, as shown in Table 6. On the other hand, for $C_{18}^{} - H_{18B}^{} \cdots C_{18}^{}$, the total energy density value $E(r)$ is small and positive. We can conclude from the QTAIM analysis that these interactions for all BH I, II, and III dimers can be classified as van der Waals or closed-shell interactions.

Energy availability is directly dependent upon the molecular structure, such as the number of carbons, chemical energy bond interactions, chemical stability, and molecular sites susceptible to the occurrence of reactions. Thus, its thermodynamic properties influence fuel energy efficiency. The difference in the calorific values between BH I, II, and III is related to their supramolecular arrangement formed by chemical energy interactions presented in these compounds. MEP calculation indicates the carbonyl group’s region where the burning reactions can occur, which can be involved with higher energy values. Additionally, the HOMO and LUMO are related to excitation energies and GAP energy ($E_{\text{GAP}} = E_{\text{LUMO}} - E_{\text{HOMO}}$) in

Figure 12. Molecular electrostatic potential surface mapped for (a) BH I, (b) BH II and (c) BH III showing the red-colored region rich in electrons and the blue-colored region, which is electron depleted. The density isovalue of $4.0 \times 10^{-4}$ electrons/bohr$^3$ was used to generate the molecular electrostatic potential surfaces.

Figure 13. Complexation energies obtained at the ωB97X-D/6-311+G(d,p) level of theory: side-to-side and head-to-head dimers, respectively, (a and b) $C_{1}^{} - H_{1B}^{} \cdots O_1^{}$ and $C_{13}^{} - H_{13B}^{} \cdots H_{13B}^{} - C_{13}^{}$ for BH I; (c and d) $C_{10}^{} - H_{10A}^{} \cdots O_1^{}$, $C_{20}^{} - H_{20}^{} \cdots O_1^{}$, and $C_{17}^{} - H_{17}^{} \cdots C_{13}^{}$ for BH II; and (e and f) $C_{6}^{} - H_{6}^{} \cdots \pi$, $C_{10}^{} - H_{10B}^{} \cdots C_{18}^{}$, and $C_{18}^{} - C_{13}^{} \cdots C_{13}^{}$ for BH III.
some situations can be an indicator of kinetic stability (large GAP values are associated with kinetic stability). For some compounds used to preserve fuels properties, this parameter is described in the literature (toluene derivative compounds used to preserve fuels properties, this parameter is information can support application studies or more specific the structure and its relationship with some properties. This analysis of the calori kinetic energy density to understand the BCP interaction and (b) head-to-head \( C_{17} \cdots H_{17} \cdots Cl_{3} \) interaction, showing the BCP in yellow.

CONCLUSIONS

In this work, three crystal structures of chalcone based on cyclohexanone core have been extensively characterized. All these molecules appear as the dienones in the (E,E)-configuration. For BH I, the cyclohexanone appears as an envelope conformation, and for BH II and III, it appears as a half-boat conformation. The crystal packing for BH I was investigated by C–H···C hydrogen bonding C–H···C dihydrogen contact and nonclassical hydrogen bonding C–H···O, which were observed on HS topological analysis (68.1% of H···H interaction and 5.6% of O···H interaction). The crystal packing for BH II was investigated by nonclassical hydrogen bonding C–H···O, C–H···Cl, and \( \pi \cdots \pi \) stacking, which were observed on HS topological analysis (6.0% of O···H interaction, 32.7% of Cl···H interaction, and 5.1% \( \pi \cdots \pi \) stacking). The crystal packing for BH III was investigated by C–H···\( \pi \) interaction, nonclassical hydrogen bonding C–H···Cl, and halogen Cl···Cl contacts, which were observed on HS topological analysis (27.4% of C···H interaction, 22.5% of Cl···H interaction, and 2.9% Cl···Cl contacts). The calculated and experimental geometries parameters depict a good correlation for all the structures.

The calorific value indicated good energy availability for these compounds, thus being able to support other studies of this application. Theoretical calculations using the counterpoise procedure conclude that the side-to-side interaction energies are the driving forces for the BH I, II, and III molecular arrangements in the solid state. We can conclude from the QTAIM analysis that these interactions for all BH I, II, and III dimers can be classified as van der Waals or closed-shell interactions. Additionally, FMO calculation indicates that the BH I, II, and III compounds are electrophilic species. Also, MEP

Table 6. QTAIM Parameters Describing Contacts and Intermolecular Interactions for BH I, II, and III [Electron Density at BCP \( \rho (r) \), Laplacian \( \nabla^{2} \rho (r) \), The Potential Electron Energy Density \( V(r) \), The Kinetic Electron Energy Density \( G(r) \), and The Total Electron Energy Density \( E(r) \).

| BCP interaction | \( \rho (r) \) | \( \nabla^{2} \rho (r) \) | \( V(r) \) | \( G(r) \) | \( E(r) \) | kind of interaction |
|-----------------|-------------|----------------|----------|-----------|--------|-----------------|
| BH I            |             |                 |          |           |        |                 |
| 1 \( C_{13} \cdots H_{13b} \cdots O_{1} \) | 0.03258 | 0.04070 | −0.01958 | 0.01488 | −0.00470 | weak |
| 2 \( C_{13} \cdots H_{13b} \cdots C_{13} \) | 0.05043 | 0.28115 | −0.10856 | 0.08942 | −0.01913 | weak |
| BH II           |             |                 |          |           |        |                 |
| 3 \( C_{10} \cdots H_{10a} \cdots O_{1} \) | 0.05882 | 0.07459 | −0.03009 | 0.02437 | −0.00572 | weak |
| 4 \( C_{9} \cdots H_{9b} \cdots O_{1} \) | 0.08763 | 0.30248 | −0.08025 | 0.07793 | −0.00231 | weak |
| 5 \( C_{17} \cdots H_{17} \cdots Cl_{3} \) | 0.01996 | 0.09355 | −0.02006 | 0.02172 | 0.00166 | weak |
| BH III          |             |                 |          |           |        |                 |
| 6 \( C_{12} \cdots H_{12} \cdots \pi \) | 0.06580 | 0.12316 | −0.03976 | 0.03527 | −0.0044 | weak |
| 7 \( C_{10} \cdots H_{10a} \cdots Cl_{3} \) | 0.05321 | 0.19465 | 0.01753 | 0.01556 | 0.03309 | weak |
| 8 \( C_{15} \cdots Cl_{2} \cdots Cl_{1} \) | 0.02586 | 0.01479 | −0.00782 | 0.00576 | −0.00206 | weak |
calculation indicates the susceptible electrophilic attack on this carbonyl group’s region.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07333.

1H NMR spectra and 13C NMR spectra of compounds BH I, II, and III (PDF)

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**Notes**
The authors declare no competing financial interest.

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