

## Synthesis, spectroscopic (NMR and FT-IR) and theoretical (HF and DFT) investigation of dimethyl (Z)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butendioate

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### Abstract

Dimethyl (z)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate has been synthesized using one-pot three component reaction between *N*-isocyaniminotriphenylphosphorane (Ph<sub>3</sub>PNNC), 3-methylcyclopentene-1,2-dione and dimethyl acetylenedicarboxylate. Also, optimized geometry and nuclear magnetic resonance (NMR) of the title compound are evaluated using HF and B3LYP methods and 6-311+G(d) basis set. Moreover, the <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values of the molecule are calculated and compared with experimental results. Frontier molecular orbitals (FMOs), total density of states (DOS), electronic properties, natural charges, NMR parameters and NBO analysis for product were calculated by theoretical calculations. Finally, molecular electrostatic potential (MEP) surface is obtained for understanding the active regions of molecule.

**Keywords:** *N*-Isocyaniminotriphenylphosphorane (Ph<sub>3</sub>PNNC); one-pot; DFT; NBO analysis; electronic properties.

### Introduction

Multicomponent processes are, at a premium, for the achievement of high level of diversity and brevity as they allow three or more simple and flexible building blocks to be combined in a practical, time-saving, and one-pot operation—giving rise to complex structures by simultaneous formation of two or more bonds [1]. During the past decade, the compounds with isocyanide moiety have usually been used as components in isocyanide-based

multicomponent reaction (IMCR) and as ligands in the synthesis of metal complexes [1,2]. The chemistry of the isocyanides began in 1859 when Lieke prepared allyl isocyanide as the first isocyanide [3]. In 1921, Passerini pioneered the use of isocyanides and successfully developed a three-component synthesis of  $\alpha$ -acyloxycarboxamide using the reaction of a carboxylic acid, an aldehyde, and an isocyanide [4]. Iminophosphoranes are important reagents in synthetic

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organic chemistry, especially in the synthesis of naturally occurring products and compounds with biological and pharmacological activity [5].

*N*-Isocyaniminotriphenylphosphorane ( $\text{Ph}_3\text{PNNC}$ ) is expected to have synthetic potential because it provides a reaction system in which the iminophosphorane group can react with a reagent having carbonyl functionality as well as the unique reactivity of an isocyanide moiety which acts as nucleophile and electrophile at the same time [6]. There are several reports for the use of *N*-isocyaniminotriphenylphosphorane ( $\text{Ph}_3\text{PNNC}$ ) in the synthesis of metal complexes [6] and heterocyclic compounds [7]. However, the ability of *N*-isocyaniminotriphenylphosphorane ( $\text{Ph}_3\text{PNNC}$ ) to act as metal-free catalyst remains almost unexplored [8]. In recent years, we have established a one-pot method for the synthesis of organophosphorus compounds [9-31].

In this work, a novel application in the field of isocyanide chemistry has been introduced. *N*-isocyaniminotriphenylphosphorane ( $\text{Ph}_3\text{PNNC}$ ) acts as a metal-free catalyst for the construction of heterocyclic building blocks dimethyl (*z*)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate *via* three components reaction (3-CR) using 3-methylcyclopentene-1,2-dione and dimethyl acetylenedicarboxylate. 1,2-diketones are dielectrophilic compounds whose reactivity at one carbonyl moiety is enhanced by the presence of the second carbonyl group. Thus, 1,2-diketones readily react with nucleophiles such as amines, alcohols, thiols and carbanions. 1,2-dicarbonyl compounds have a strong tendency to enolize. 3-Methyl-1,2-cyclopentanedione is present in coffee

and is capable of scavenging peroxyxynitrite [32]. It also has anti-inflammatory effects [33].

In recent years, computational chemistry has become an important tool for chemists and a well-accepted partner for experimental chemistry [34-36]. Also, in the present work, we investigate the energetic and structural properties of dimethyl (*z*)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate using the Density Functional Theory (DFT) and Hartree Fock (HF) methods with 6-311+G(d) basis set. The optimized geometry, FMO, MEP, electronic properties, chemical shift analysis, fundamental natural charge and NBO analysis of title compound were calculated.

## Experimental

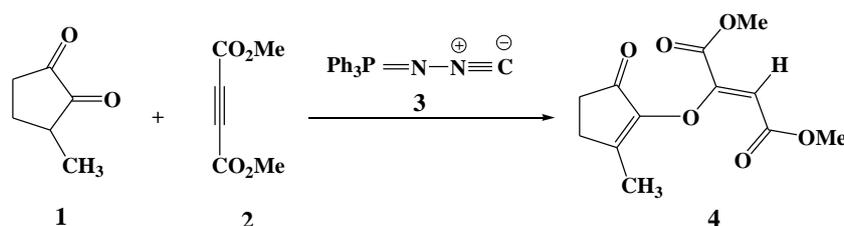
### General

The solvents and starting materials were obtained from Merck (Germany) and Fluka (Switzerland) and were used without further purification. The methods used to follow the reactions were TLC and NMR. TLC and NMR indicated that there is no side product. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. IR spectra were measured on a Shimadzu IR-460 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured ( $\text{CDCl}_3$  solution) with a BRUKER 250 spectrometer at 250 and 62.5 MHz, respectively. Flash chromatography columns were prepared from Merck silica gel powder.

### General procedure for the preparation of product

To a magnetically stirred solution of 3-methylcyclopentene-1,2-dione **1** (1 mmol) and *N*-isocyaniminotriphenylphosphorane **3** (1 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added dropwise a solution of dimethyl

acetylenedicarboxylate **2** (1 mol%) in  $\text{CH}_2\text{Cl}_2$  (5 mL) at  $-10^\circ\text{C}$  over 15 min (Scheme 1).



**Scheme 1.** Three-component synthesis of dimethyl (z)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate **4**

The mixture was stirred for 2 h at room temperature. The reaction mixture was stirred at the same conditions ( $-10^\circ\text{C}$ ) for 2 h, and then the mixture was allowed to warm up to room temperature and was stirred for 4 days. The solvent was removed under reduced pressure and the viscous residue was purified by flash column chromatography (silica gel powder; petroleum ether–ethyl acetate, 10:1). The solvent was removed under reduced pressure and the product **4** was obtained. The characterization data of the compound is given below:

**Dimethyl (z)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate**

Vicose Oil (Yield: 68%). IR (KBr):  $\nu = 2953.85; 1730.77; 1669.23; 1284.62, 1115.38$  and  $1030.77\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{H}}$ : 6.21 (s, 1H, vinylic); 3.75 and 3.66 (2s, 6H, 2 $\text{CH}_3$  of ester); 2.46–2.45 (m, 2H,  $\text{CH}_2$ ); 2.34–2.32 (m, 2H,  $\text{CH}_2$ ); 2.05 (s, 3H,  $\text{CH}_3$  of cyclopentenyl).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta_{\text{C}}$ : 199.91 (1C, C=O of ketone); 164.12 and 162.44 (2C, C=O of ester); 152 (1C, C of vinylic), 151.05 and 149.29 (2C, C of cyclopentenyl); 108.76 (1C, CH of vinylic), 52.90 and 51.60 (2C,  $\text{CH}_3$  of ester); 32.40 and 27.19 (2C,  $\text{CH}_2$ ); 14.79 (1C,  $\text{CH}_3$  of cyclopentenyl).

**Computational methods**

In this work, we have carried out quantum theoretical calculations and have optimized structure of title compound using HF and DFT (B3LYP) [37–39] methods with 6-311+G(d) basis set by the Gaussian 09W program package [40] and calculate its properties. The electronic properties such as dipole moment ( $\mu_D$ ), point group,  $E_{\text{HOMO}}$ ,  $E_{\text{LUMO}}$ , HOMO–LUMO energy gap ( $\Delta E$ ), natural charges, and electronic properties were detected [41]. The optimized molecular structure, HOMO and LUMO surfaces were visualized using GaussView 05 program [42]. Also we calculated NMR parameters using GIAO method such as  $^1\text{H}$  and  $^{13}\text{C}$  chemical shift [43] for the title structure by HF/6-311+G(d) and B3LYP/6-311+G(d) levels in the gas phase and the solvent phase. The electronic structure title compound were studied by using Natural Bond Orbital (NBO) analysis [44] using B3LYP/6-311+G(d) level in order to understand hyperconjugative interactions and charge delocalization.

**Results and discussion**

To the best of our knowledge, this is the first report for the use of *N*-isocyaniminotriphenylphosphorane ( $\text{Ph}_3\text{PNNC}$ ) **3** as metal-free catalyst in three component reaction between a

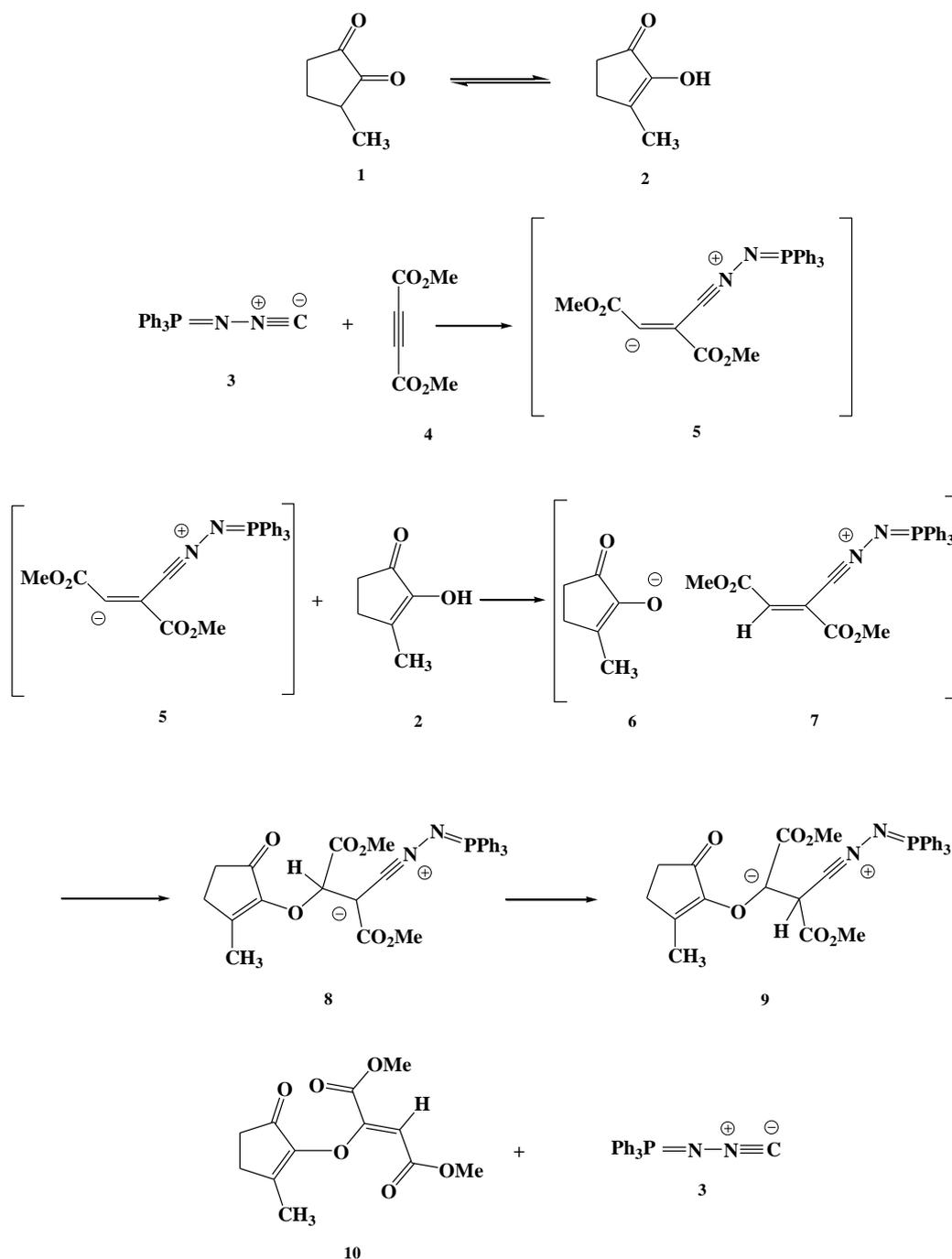
1,2-diketones compound and acetylenic ester.

Herein, we wish to report an approach for synthesis of dimethyl (z)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate *via* three-component reaction (3-CR) between 3-methylcyclopentene-1,2-dione **2** and dimethyl acetylenedicarboxylate **4** in the presence of *N*-isocyaniminotriphenylphosphorane (Ph<sub>3</sub>PNNC) **3** as a metal-free catalyst in high yields.

A mechanistic rationalization of this reaction is provided in Scheme 2. It is conceivable that the initial event is condensation of *N*-isocyaniminotriphenylphosphorane (Ph<sub>3</sub>PNNC) **3** and dimethyl acetylenedicarboxylate **4** entities to generate intermediate **5**. The addition of 3-methylcyclopentene-1,2-dione **2**

(enolic form) to intermediate **5** leads to conjugate base **6** and intermediate **7**. The next step may involve nucleophilic addition of conjugate base **6** to intermediate **7** which leads to intermediate **8**. The intermediate **8** then undergoes intramolecular hydrogen shift and is generated intermediate **9**. The final step may be the isolation of dimethyl (z)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate **10** by removing *N*-isocyaniminotriphenylphosphorane (Ph<sub>3</sub>PNNC) **3** from intermediate **9**.

The reaction which requires only 2 h, using *N*-isocyaniminotriphenylphosphorane (Ph<sub>3</sub>PNNC) as a metal-free catalyst, to be completed is more active than reported transition-metal-based catalysts procedures.

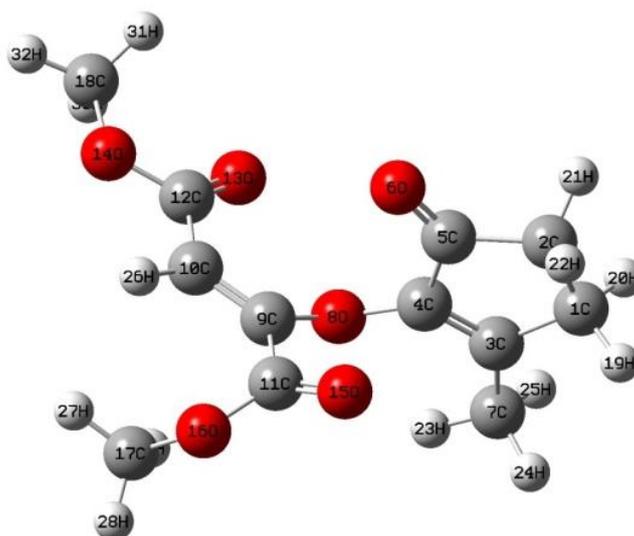


**Scheme 2.** A proposed reaction mechanism

### Optimized geometry

The optimized geometry of title compound is performed by HF and

B3LYP methods with 6-311+G(d) basis set (Figure 1).



**Figure 1.** The theoretical geometric structure of the title compound (optimized using the B3LYP/6-311+G(d) level)

The title compound has C1 point group symmetry. The total energy of the compound has been calculated by two methods HF/6-311+G(d) and

B3LYP/6-311+G(d) is -911.9489065 and -917.2542378 Hartree-Fock, respectively (Table 1).

**Table 1.** Energy (Hartree-Fock) and point group of the title compound calculated by HF and B3LYP methods with 6-311+G(d) basis set

|                       | HF/6-311+G(d) | B3LYP/6-311+G(d) |
|-----------------------|---------------|------------------|
| Energy (Hartree-Fock) | -911.9489065  | -917.2452378     |
| Point group           | C1            | C1               |

The optimized geometrical parameters of compound such as bond lengths (Å), bond angles (°) and torsion

angles (°) have been obtained by two methods are listed in Table 2.

**Table 2.** Optimized geometrical parameters of the title compound calculated by HF and B3LYP methods with 6-311+G(d) basis set

| Parameter       | HF    | B3LYP | Parameter       | HF      | B3LYP   |
|-----------------|-------|-------|-----------------|---------|---------|
| Bond lengths(Å) |       |       | Bond angles (°) |         |         |
| C1-C2           | 1.537 | 1.542 | C1-C2-C5        | 105.095 | 105.279 |
| C1-C3           | 1.512 | 1.511 | C1-C3-C4        | 110.846 | 110.514 |
| C2-C5           | 1.518 | 1.525 | C1-C3-C7        | 121.055 | 122.290 |
| C3-C4           | 1.323 | 1.342 | C2-C5-C4        | 106.294 | 106.157 |
| C3-C7           | 1.496 | 1.490 | C2-C5-O6        | 126.756 | 127.270 |
| C4-O8           | 1.363 | 1.375 | C3-C4-C5        | 112.316 | 112.481 |
| C5-O6           | 1.183 | 1.211 | C3-C4-O8        | 127.961 | 124.190 |
| O8-C9           | 1.339 | 1.361 | C4-C3-C7        | 128.100 | 127.196 |
| C9-C10          | 1.323 | 1.341 | C4-C5-O6        | 126.934 | 126.570 |

|         |       |       |                    |          |          |
|---------|-------|-------|--------------------|----------|----------|
| C9-C11  | 1.510 | 1.514 | C4-O8-C9           | 122.506  | 120.829  |
| C10-C12 | 1.488 | 1.477 | O8-C9-C10          | 121.802  | 121.925  |
| C10-H26 | 1.069 | 1.081 | O8-C9-C11          | 116.736  | 115.515  |
| C11-O15 | 1.180 | 1.202 | C9-C10-C12         | 124.406  | 125.539  |
| C11-O16 | 1.315 | 1.351 | C9-C11-O15         | 123.093  | 120.927  |
| C12-O13 | 1.183 | 1.206 | C11-O16-C17        | 117.168  | 124.040  |
| C12-O14 | 1.322 | 1.360 |                    |          |          |
| O14-C18 | 1.416 | 1.436 | Torsion angels (°) |          |          |
| O16-C17 | 1.419 | 1.438 | C3-C4-O8-C9        | -2.373   | 143.947  |
|         |       |       | C5-C4-O8-C9        | -116.940 | -44.230  |
|         |       |       | C7-C3-C4-O8        | 69.349   | -5.343   |
|         |       |       | C9-C10-C12-O13     | 32.487   | 7.144    |
|         |       |       | O13-C12-O14-C18    | -1.459   | -1.530   |
|         |       |       | O15-C11-O16-C17    | 1.589    | -155.086 |

According to the optimized structure, the cyclopentene ring is in planar. The C=O and C-O bond lengths is shorter than C-C bond lengths due to strong electron-withdrawing nature of oxygen atom. Also C=O bond lengths is shorter as compared to C-O bond lengths. In title compound, the C5-O6, C11-O15 and C12-O13 bond lengths vary from 1.183, 1.180, 1.183 Å by HF method to 1.211, 1.202, 1.206 Å by DFT method, whereas the C4-O8, O8-C9, C11-O16, C12-O14, O14-C18, O16-C17 bond lengths vary from 1.363, 1.339, 1.315, 1.322, 1.416, 1.419 Å by HF method to 1.375, 1.361, 1.351, 1.360, 1.436, 1.438 Å by DFT method. As seen from Table 1, the calculated bond angle C1-C3-C4 is 110.846 and 110.514° by HF and DFT methods respectively, which they are smaller than typical hexagonal angle of 120°

due to angle strain in cyclopentene ring. The calculated bond angle C1-C2-C5 is 105.095° and 105.279° by HF and DFT methods respectively. It is worth mentioning that they are smaller than typical angle of 108° for cyclopentene. The calculated bond angle C9-C10-C12 is 124.406 and 125.539° by HF and DFT methods respectively showing that they are greater than typical hexagonal angle of 120°.

#### NMR chemical shift analysis

In the present study, the theoretical <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values of title compound were calculated by HF and DFT/B3LYP methods with 6-311+G(d) basis set using GIAO method in the gas phase and the solvent CHCl<sub>3</sub>. Then calculated <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts were compared to the experimental values (Tables 3 and 4).

**Table 3.** Theoretical and experimental  $^1\text{H}$  and  $^{13}\text{C}$  isotropic chemical shifts for the title compound

| Atoms              | Experimental<br>( $\text{CDCl}_3$ ) | Theoretical   |                  | Assignment                            |
|--------------------|-------------------------------------|---------------|------------------|---------------------------------------|
|                    |                                     | HF/6-311+G(d) | B3LYP/6-311+G(d) |                                       |
| $^1\text{HNMR}$    |                                     |               |                  |                                       |
| H23                | 2.05                                | 2.82          | 2.22             | s, 3H, $\text{CH}_3$ of cyclopentenyl |
| H24                | 2.05                                | 1.26          | 1.35             |                                       |
| H25                | 2.05                                | 1.30          | 1.42             |                                       |
| H19                | 2.32                                | 1.95          | 2.06             | m, 2H, $\text{CH}_2$                  |
| H20                | 2.34                                | 1.97          | 2.06             |                                       |
| H21                | 2.45                                | 1.98          | 1.86             | m, 2H, $\text{CH}_2$                  |
| H22                | 2.46                                | 1.98          | 2.01             |                                       |
| H27                | 3.75                                | 3.27          | 3.43             | 2s, 6H, $2\text{CH}_3$ of ester       |
| H28                | 3.75                                | 3.40          | 3.48             |                                       |
| H29                | 3.75                                | 3.30          | 3.49             |                                       |
| H30                | 3.66                                | 3.44          | 3.32             |                                       |
| H31                | 3.66                                | 3.45          | 3.34             |                                       |
| H32                | 3.66                                | 3.28          | 3.08             |                                       |
| H26                | 6.21                                | 6.00          | 5.87             | s, 1H, vinylic                        |
| $^{13}\text{CNMR}$ |                                     |               |                  |                                       |
| C7                 | 14.79                               | 17.91         | 14.47            | 1C, $\text{CH}_3$ of cyclopentenyl    |
| C1                 | 27.19                               | 30.20         | 29.88            | 2C, $\text{CH}_2$                     |
| C2                 | 32.40                               | 33.23         | 34.17            |                                       |
| C18                | 51.60                               | 51.85         | 51.81            | 2C, $\text{CH}_3$ of ester            |
| C17                | 52.90                               | 52.49         | 57.75            |                                       |
| C10                | 108.76                              | 121.10        | 114.68           | 1C, CH of vinylic                     |
| C4                 | 149.29                              | 157.15        | 157.59           | 2C, C of cyclopentenyl                |
| C3                 | 151.05                              | 160.06        | 157.58           |                                       |
| C9                 | 152                                 | 159.95        | 156.54           | 1C, C of vinylic                      |
| C11                | 162.44                              | 167.33        | 168.16           | 2C, C=O of ester                      |
| C12                | 164.12                              | 171.05        | 168.34           |                                       |
| C5                 | 199.91                              | 202.55        | 203.60           | 1C, C=O of ketone                     |

**Table 4.** Theoretical and experimental  $^1\text{H}$  and  $^{13}\text{C}$  isotropic chemical shifts for the title compound. $\text{CHCl}_3$ 

| Atoms           | Experimental<br>( $\text{CDCl}_3$ ) | Theoretical   |                  | Assignment                            |
|-----------------|-------------------------------------|---------------|------------------|---------------------------------------|
|                 |                                     | HF/6-311+G(d) | B3LYP/6-311+G(d) |                                       |
| $^1\text{HNMR}$ |                                     |               |                  |                                       |
| H23             | 2.05                                | 2.34          | 2.40             | s, 3H, $\text{CH}_3$ of cyclopentenyl |
| H24             | 2.05                                | 1.45          | 1.66             |                                       |
| H25             | 2.05                                | 1.51          | 1.75             |                                       |
| H19             | 2.32                                | 2.08          | 2.34             | m, 2H, $\text{CH}_2$                  |
| H20             | 2.34                                | 2.13          | 2.30             |                                       |
| H21             | 2.45                                | 2.10          | 2.09             | m, 2H, $\text{CH}_2$                  |
| H22             | 2.46                                | 2.06          | 2.08             |                                       |
| H27             | 3.75                                | 3.47          | 3.52             | 2s, 6H, $2\text{CH}_3$ of ester       |
| H28             | 3.75                                | 3.48          | 3.40             |                                       |
| H29             | 3.75                                | 3.43          | 3.48             |                                       |
| H30             | 3.66                                | 3.53          | 3.40             |                                       |
| H31             | 3.66                                | 3.49          | 3.38             |                                       |

|                    |        |        |        |                          |
|--------------------|--------|--------|--------|--------------------------|
| H32                | 3.66   | 3.43   | 3.25   |                          |
| H26                | 6.21   | 6.05   | 5.51   | s, 1H, vinylic           |
| <sup>13</sup> CNMR |        |        |        |                          |
| C7                 | 14.79  | 18.31  | 15.0   | 1C, CH3 of cyclopentenyl |
| C1                 | 27.19  | 30.30  | 30.36  | 2C, CH2                  |
| C2                 | 32.40  | 33.89  | 35.17  |                          |
| C18                | 51.60  | 52.58  | 52.83  | 2C, CH3 of ester         |
| C17                | 52.90  | 53.59  | 57.54  |                          |
| C10                | 108.76 | 120.82 | 113.83 | 1C, CH of vinylic        |
| C4                 | 149.29 | 154.29 | 154.24 | 2C, C of cyclopentenyl   |
| C3                 | 151.05 | 167.53 | 168.72 |                          |
| C9                 | 152    | 161.78 | 162.87 | 1C, C of vinylic         |
| C11                | 162.44 | 169.03 | 171.32 | 2C, C=O of ester         |
| C12                | 164.12 | 172.43 | 171.01 |                          |
| C5                 | 199.91 | 209.63 | 205.63 | 1C, C=O of ketone        |

<sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported in ppm relative to TMS [35]. According to the results, there can be seen a good agreement between experimental and calculated values. The hydrogen atoms of CH<sub>3</sub> group appear at lower delta values rather than hydrogen atoms of CH<sub>2</sub> group due to shielding effect. The hydrogen atoms of CH<sub>2</sub> group appeared in recorded <sup>1</sup>H NMR at 2.32, 2.34, 2.45, 2.46 ppm while the theoretical values by HF and DFT/B3LYP methods appeared at 1.95, 1.97, 1.98, 1.98 ppm and 2.06, 2.06, 1.86, 2.06 ppm, respectively. The CH<sub>3</sub> protons of cyclopentenyl ring appeared at 2.05 ppm in experimental <sup>1</sup>H NMR spectrum while calculated chemical shift values for CH<sub>3</sub> protons appeared at 2.82, 1.26, 1.30 and 2.22, 1.35, 1.42 ppm by HF and DFT/B3LYP methods, respectively. According to experimental results, chemical shift value for CH<sub>3</sub> protons of ester groups (3.75 and 3.66 ppm) is greater than CH<sub>3</sub> protons of cyclopentenyl ring (2.05 ppm), due to the presence of electronegative oxygen atoms in ester groups. The calculated chemical shift values for CH<sub>3</sub> protons of ester groups appeared at 3.27, 3.40, 3.30, 3.44, 3.45, 3.28 and 3.43, 3.48,

3.49, 3.32, 3.34, 3.08 ppm by HF and DFT/B3LYP methods, respectively. From experimental <sup>13</sup>C NMR spectrum it is found that, C11, C12 and C5 atoms in carbonyl group have the highest chemical shift values (162.44, 164.12 and 199.91 ppm, respectively) compared to other carbon atoms of title compound in accordance to the presence of electronegative oxygen atoms and the anisotropic effect. Besides, the calculated chemical shifts for C11, C12 and C5 atoms are 167.33, 171.05, 202.55 and 168.16, 168.34, 203.60 ppm by HF and DFT/B3LYP methods, respectively. Also we investigated the relation between experimental and theoretical chemical shift values by comparing the experimental and calculated results and obtained linear function formula for Figures 2 and 3. According to the results, the experimental values are in good agreement with the theoretical values by B3LYP/6-311+G(d) level as compared to HF/6-311+G(d) level. Also, the results show the experimental values are close to the calculated values in the solvent phase rather than the gas phase.

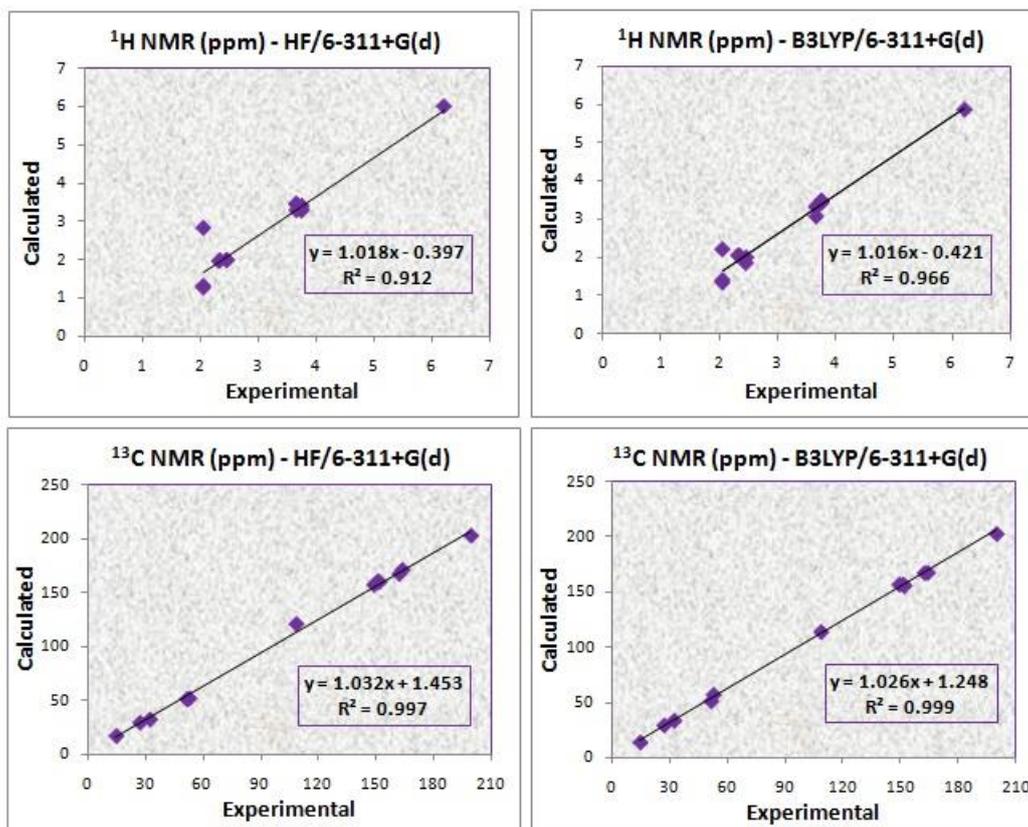


Figure 2. Correlation graphics of theoretical chemical shift values of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of the title compound

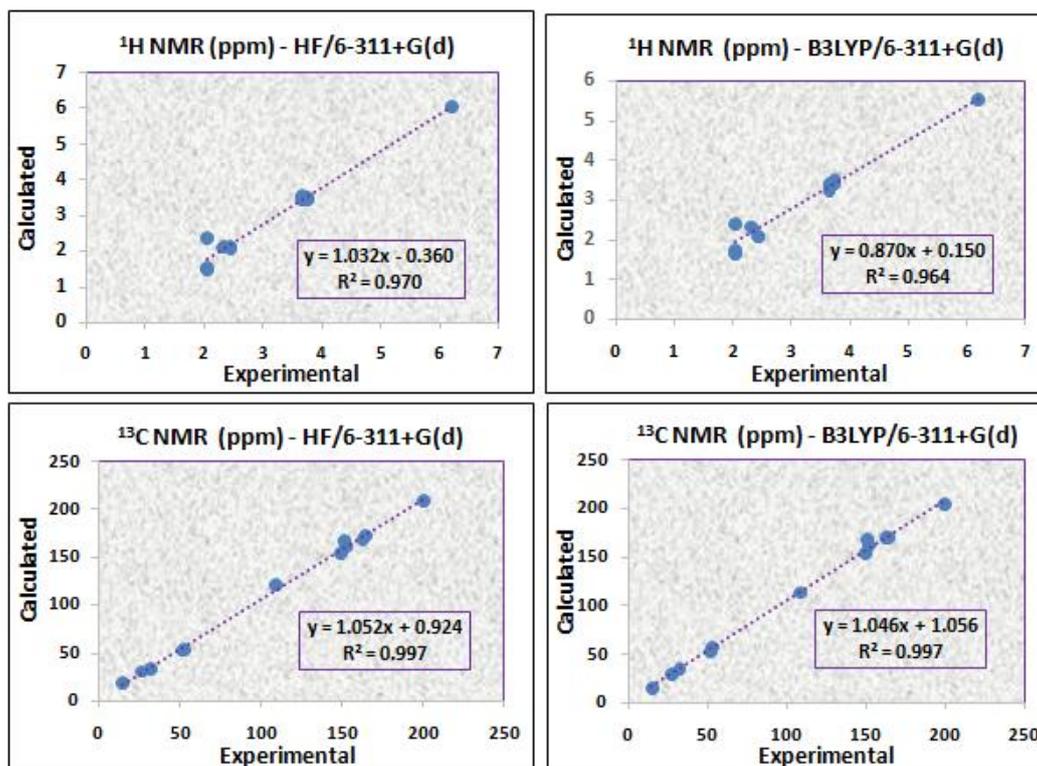


Figure 3. Correlation graphics of theoretical chemical shift values of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of the title compound in the solvent  $\text{CHCl}_3$

### Atomic charge

The atomic charges play an important role in molecular polarizability, dipole moment, electronic structure and lot of related properties of molecular systems. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transferring the molecule. We

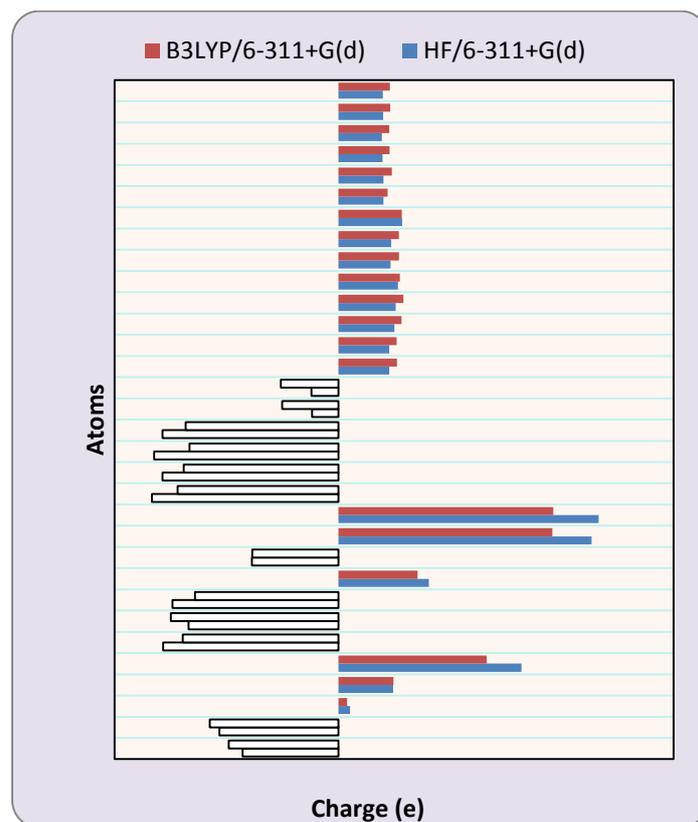
calculated the charge distributions for equilibrium geometry of molecule by NBO method (natural charge) using HF/6-311+G(d) and B3LYP/6-311+G(d) levels. The results of Natural Bond Orbital (NBO) [44,45] are listed in Table 5 (Atoms labeling is according to Figure 1).

**Table 5.** Natural Charge (NBO charges, e) of the title compound using the HF and B3LYP methods with 6-311+G(d) basis set

| HF/6-311+G(d)   |        |                 |        | B3LYP/6-311+G(d) |        |                 |        |
|-----------------|--------|-----------------|--------|------------------|--------|-----------------|--------|
| Atoms           | Charge | Atom            | Charge | Atoms            | Charge | Atom            | Charge |
| C <sub>1</sub>  | -0.343 | H <sub>19</sub> | 0.182  | C <sub>1</sub>   | -0.392 | H <sub>19</sub> | 0.210  |
| C <sub>2</sub>  | -0.425 | H <sub>20</sub> | 0.182  | C <sub>2</sub>   | -0.460 | H <sub>20</sub> | 0.209  |
| C <sub>3</sub>  | 0.042  | H <sub>21</sub> | 0.201  | C <sub>3</sub>   | 0.032  | H <sub>21</sub> | 0.226  |
| C <sub>4</sub>  | 0.196  | H <sub>22</sub> | 0.205  | C <sub>4</sub>   | 0.197  | H <sub>22</sub> | 0.233  |
| C <sub>5</sub>  | 0.655  | H <sub>23</sub> | 0.213  | C <sub>5</sub>   | 0.531  | H <sub>23</sub> | 0.220  |
| O <sub>6</sub>  | -0.627 | H <sub>24</sub> | 0.187  | O <sub>6</sub>   | -0.556 | H <sub>24</sub> | 0.217  |
| C <sub>7</sub>  | -0.536 | H <sub>25</sub> | 0.189  | C <sub>7</sub>   | -0.599 | H <sub>25</sub> | 0.217  |
| O <sub>8</sub>  | -0.593 | H <sub>26</sub> | 0.228  | O <sub>8</sub>   | -0.513 | H <sub>26</sub> | 0.227  |
| C <sub>9</sub>  | 0.324  | H <sub>27</sub> | 0.161  | C <sub>9</sub>   | 0.283  | H <sub>27</sub> | 0.177  |
| C <sub>10</sub> | -0.309 | H <sub>28</sub> | 0.162  | C <sub>10</sub>  | -0.308 | H <sub>28</sub> | 0.192  |
| C <sub>11</sub> | 0.906  | H <sub>29</sub> | 0.158  | C <sub>11</sub>  | 0.766  | H <sub>29</sub> | 0.183  |
| C <sub>12</sub> | 0.931  | H <sub>30</sub> | 0.156  | C <sub>12</sub>  | 0.769  | H <sub>30</sub> | 0.182  |
| O <sub>13</sub> | -0.667 | H <sub>31</sub> | 0.160  | O <sub>13</sub>  | -0.575 | H <sub>31</sub> | 0.186  |
| O <sub>14</sub> | -0.629 | H <sub>32</sub> | 0.159  | O <sub>14</sub>  | -0.553 | H <sub>32</sub> | 0.184  |
| O <sub>15</sub> | -0.659 |                 |        | O <sub>15</sub>  | -0.532 |                 |        |
| O <sub>16</sub> | -0.629 |                 |        | O <sub>16</sub>  | -0.546 |                 |        |
| C <sub>17</sub> | -0.094 |                 |        | C <sub>17</sub>  | -0.201 |                 |        |
| C <sub>18</sub> | -0.096 |                 |        | C <sub>18</sub>  | -0.206 |                 |        |

The total charge of the investigated molecules is equal to zero. Also, Figure 4 shows the results of natural charge in graphical form. The natural charge (NBO) analysis of the title compound shows that oxygen atoms (O<sub>6</sub>, O<sub>8</sub>, O<sub>13</sub>, O<sub>14</sub>, O<sub>15</sub> and O<sub>16</sub> atoms) have the highest values of negative charge. As seen in Table 5 and Figure 4, the values of natural charges of the carbons are both positive and negative. The carbon atoms of methyl groups (C<sub>7</sub>,

C<sub>17</sub> and C<sub>18</sub> atoms) bear negative charge, but C<sub>17</sub> and C<sub>18</sub> atoms have least negative charge as compared to C<sub>7</sub>, due to attachment of C<sub>17</sub> and C<sub>18</sub> to electron-withdrawing O atom. The highest positive charges is observed for C<sub>5</sub>, C<sub>11</sub> and C<sub>12</sub> atoms (carbon atoms of C=O group). According to results of natural charge analysis of title compound, all the hydrogen atoms have positive charge.



**Figure 4.** Natural charge distribution of the title compound

### Electronic properties

Quantum chemical methods are important for obtaining information about molecular structure and electrochemical behavior. A Frontier Molecular Orbitals (FMO) analysis [46]

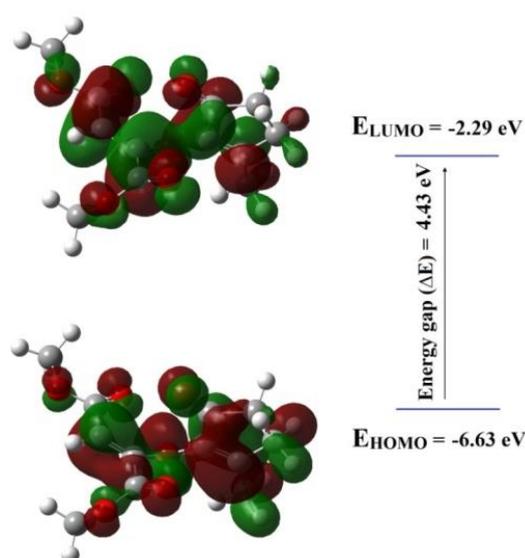
was done for the compound using B3LYP/6-311+G(d) level. FMO results such as  $E_{\text{HOMO}}$ ,  $E_{\text{HOMO}-1}$  and the HOMO-LUMO energy gap ( $\Delta E$ ) of title compound, are summarized in Table 6.

**Table 6.** Electronic properties of the title compound calculated by B3LYP method with 6-311+G(d) basis sets

| Property                                  | B3LYP/6-311+G(d) |
|---|------------------|
| $E_{\text{HOMO}}$ (eV)                    | -6.63            |
| $E_{\text{LUMO}}$ (eV)                    | -2.29            |
| Energy gap (eV)                           | 4.34             |
| Ionisation potential $I$ (eV)             | 6.63             |
| Electron affinity $A$ (eV)                | 2.29             |
| Electronegativity ( $\chi$ )              | 4.46             |
| Global hardness ( $\eta$ )                | 2.17             |
| Chemical potential ( $\mu$ )              | -4.46            |
| Global electrophilicity ( $\omega$ )      | 4.49             |
| Chemical softness $S$ (eV <sup>-1</sup> ) | 0.46             |
| Dipole moment (Debye)                     | 3.5527           |

The values of energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ) can act as an electron donor and the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ) can act as the electron acceptor [47]. The energy of HOMO (-6.63 eV) is directly related to the ionization potential, while the energy of LUMO (-2.29 eV) is related to the electron affinity. The HOMO and LUMO

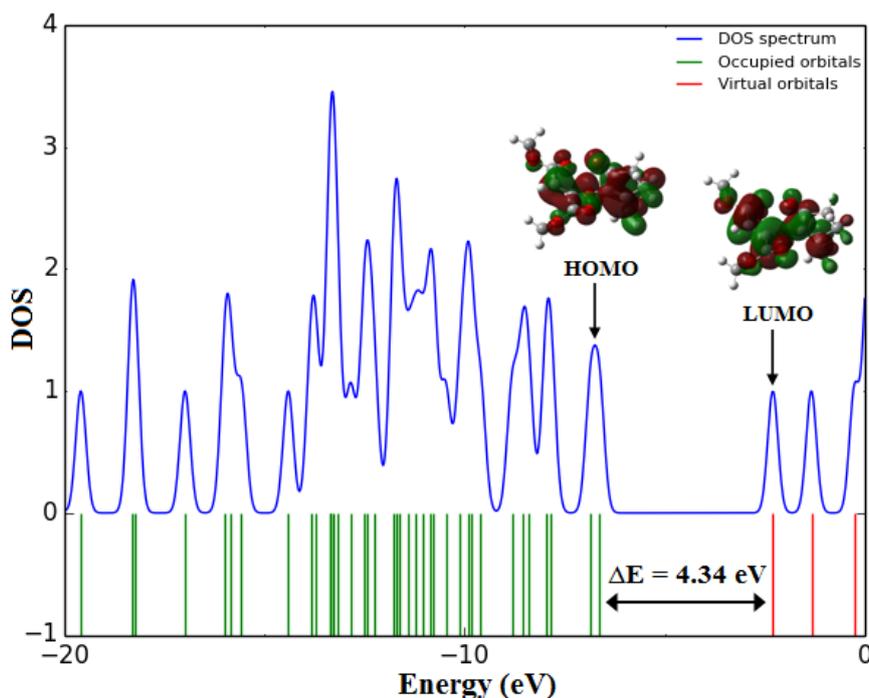
energy gap ( $\Delta E$ ) explains the eventual charge transfer interaction taking within the molecule. The title compound contains 67 occupied molecular orbital and 370 unoccupied virtual molecular orbital. The energies of two important molecular orbitals of compound in gas phase such as  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  were calculated as shown in the Table 6 and Figure 5.



**Figure 5.** Calculated Frontier molecular orbitals of the title compound (using the B3LYP/6-311+G(d))

As shown in Figure 5, the positive and negative phase is represented in green and red color respectively. According to Figure 5, charge transfer is taking place within molecule. The graphic pictures of orbitals show HOMO orbital of molecule is localized mainly on oxygen atoms and C=C bonds, whereas LUMO orbital of

molecule is localized mainly on oxygen atoms and C-C bonds. As seen in Table 6, the HOMO-LUMO energy gap ( $\Delta E$ ) of compound is 4.34 eV that reflect the chemical activity of the molecule. Also the calculated energy gap clearly is shown in DOS plot (Figure 6) [48,49].



**Figure 6.** Calculated DOS plots of the title compound (using the B3LYP/6-311+G(d))

A detail of quantum molecular descriptors of title compound such as ionization potential ( $I = -E_{HOMO}$ ), electron affinity ( $A = -E_{LUMO}$ ), global hardness ( $\eta = I - A/2$ ), electronegativity ( $\chi = (I + A)/2$ ), electronic chemical potential ( $\mu = -(I + A)/2$ ) and electrophilicity ( $\omega = \mu^2/2\eta$ ), chemical softness ( $S = 1/\eta$ ) [50] are calculated and are listed in Table 6. The global hardness ( $\eta$ ) corresponds to the HOMO-LUMO energy gap. A molecule with a small energy gap has high chemical reactivity, low kinetic stability and is a soft molecule, while a hard molecule has a large energy gap [51,52]. The ionization potential value (6.63 eV) obtained by DFT method also support the stability of the title molecule. Electronegativity ( $\chi$ ) is a measure of the power of an atom or a group of atoms to attract electrons [53] and the chemical softness ( $S$ ) describes the capacity of an atom or a group of atoms to receive electrons [54] Dipole moment ( $\mu_D$ ) is a good measure for the asymmetric nature of a structure [35].

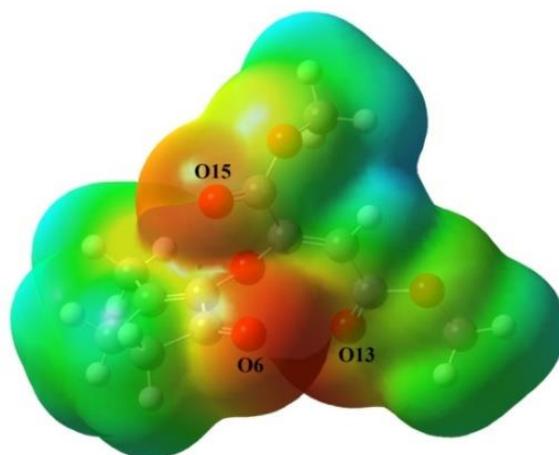
The size of the dipole moment depends on the composition and dimensionality of the 3D structures. The calculated dipole moment value shows that the molecule is highly polar in nature. As shown in Table 5, dipole moment and point group of title structure is 3.5527 Debye.

#### Molecular electrostatic potential (MEP)

The molecular electrostatic potential (MEP) was checked out by theoretical calculations using B3LYP/6-311+G(d) level. Molecular electrostatic potential shows the electronic density and is useful in recognition sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions. The different values of the electrostatic potential at the surface are represented by different colors. The negative areas (red, orange and yellow color) of MEP were related to electrophilic reactivity, the positive areas (blue color) ones to nucleophilic reactivity and green color is neutral

regions [55]. According to the MEP map in Figure 7, negative region of compound is mainly focused on O6, O13 and O15 atoms with more red color intensity which is caused by the

contribution of lone-pair electrons of oxygen atom. Therefore they are suitable sites for electrophilic attack. The positive potential sites (blue color) are around the hydrogen atoms.



**Figure 7.** Molecular electrostatic potential (MEP) map of the title compound calculated using the B3LYP/6-311+G(d) level

#### NBO analysis

Natural bond orbital (NBO) analysis is important method for studying intra- and inter-molecular bonding and interaction between bonds [56].

Electron donor orbital, acceptor orbital and the interacting stabilization energy resulting from the second-order micro disturbance theory are reported in Table 7.

**Table 7.** Significant donor–acceptor interactions and second order perturbation energies of the title compound calculated using the B3LYP/6-311+G(d) level

| Donor (i)        | Occupancy | Acceptor (j)         | Occupancy | E(2) <sup>a</sup><br>kcal/mol | E(j)-<br>E(i) <sup>b</sup><br>a.u. | F(i, j) <sup>c</sup><br>a.u. |
|------------------|-----------|----------------------|-----------|-------------------------------|------------------------------------|------------------------------|
| $\sigma$ (C1-C3) | 1.96824   | $\sigma^*$ (C3-C4)   | 0.02385   | 2.02                          | 1.27                               | 0.045                        |
|                  |           | $\sigma^*$ (C3-C7)   | 0.01853   | 0.81                          | 1.05                               | 0.026                        |
|                  |           | $\sigma^*$ (C4-O8)   | 0.03872   | 8.53                          | 0.96                               | 0.081                        |
| $\pi$ (C3-C4)    | 1.82552   | $\pi^*$ (C5-O6)      | 0.17431   | 23.22                         | 0.31                               | 0.076                        |
|                  |           | $\sigma^*$ (C7-H24)  | 0.00929   | 2.67                          | 0.66                               | 0.039                        |
|                  |           | $\sigma^*$ (O8-C9)   | 0.03698   | 1.15                          | 0.63                               | 0.025                        |
| $\pi$ (C9-C10)   | 1.86876   | $\pi^*$ (C11-O15)    | 0.20183   | 10.56                         | 0.34                               | 0.055                        |
|                  |           | $\sigma^*$ (C11-O16) | 0.10066   | 1.68                          | 0.65                               | 0.030                        |
|                  |           | $\pi^*$ (C12-O13)    | 0.25796   | 16.92                         | 0.32                               | 0.068                        |
| $\pi^*$ (C5-O6)  | 0.17431   | $\pi^*$ (C3-C4)      | 0.16302   | 60.61                         | 0.02                               | 0.068                        |
| $\pi^*$ (C9-C10) | 0.14857   | $\pi^*$ (C11-O15)    | 0.20183   | 56.32                         | 0.02                               | 0.063                        |
| n2(O6)           | 1.86506   | $\sigma^*$ (C2-C5)   | 0.06548   | 21.57                         | 0.64                               | 0.107                        |
|                  |           | $\sigma^*$ (C4-C5)   | 0.08073   | 20.52                         | 0.70                               | 0.109                        |
| n2(O8)           | 1.84423   | $\pi^*$ (C9-C10)     | 0.14857   | 0.53                          | 0.27                               | 0.011                        |
|                  |           | $\sigma^*$ (C9-C10)  | 0.01847   | 2.76                          | 0.97                               | 0.048                        |

|         |         |                     |         |       |      |       |
|---------|---------|---------------------|---------|-------|------|-------|
| n2(O13) | 1.83966 | $\pi^*(C9-C10)$     | 0.14857 | 17.12 | 0.36 | 0.071 |
|         |         | $\sigma^*(C10-C12)$ | 0.06022 | 18.58 | 0.68 | 0.103 |
|         |         | $\sigma^*(C12-O14)$ | 0.10639 | 33.63 | 0.61 | 0.130 |
|         |         | $\sigma^*(C18-H32)$ | 0.00907 | 0.79  | 0.65 | 0.021 |
| n2(O14) | 1.79390 | $\pi^*(C12-O13)$    | 0.25796 | 43.56 | 0.34 | 0.110 |
| n2(O15) | 1.82842 | $\pi^*(C3-C4)$      | 0.16302 | 1.34  | 0.32 | 0.019 |
|         |         | $\sigma^*(C9-C11)$  | 0.08816 | 18.79 | 0.64 | 0.100 |
| n2(O16) | 1.80424 | $\sigma^*(C11-O16)$ | 0.10066 | 30.76 | 0.62 | 0.126 |
|         |         | $\sigma^*(C11-O15)$ | 0.03156 | 3.46  | 0.93 | 0.053 |
|         |         | $\pi^*(C11-O15)$    | 0.20183 | 28.93 | 0.38 | 0.094 |
|         |         | $\sigma^*(C17-H28)$ | 0.01179 | 1.24  | 0.72 | 0.028 |
|         |         | $\sigma^*(C17-H29)$ | 0.01213 | 1.44  | 0.71 | 0.030 |

<sup>a</sup> E(2) means energy of hyperconjugative interactions.

<sup>b</sup> Energy difference between donor and acceptor i and j NBO orbitals.

<sup>c</sup> F(i, j) is the Fock matrix element between i and j NBO orbitals

The electron delocalization from filled NBOs (donors) to the empty NBOs (acceptors) describes a conjugative electron transfer process between them [49]. For each donor (*i*) and acceptor (*j*), the stabilization energy E(2) associated with the delocalization *i*→*j* is estimated [57]:

$$E^{(2)} = \Delta E_{ij} = q_i \frac{F(i,j)^2}{\epsilon_j - \epsilon_i}$$

where  $q_i$  is the donor orbital occupancy,  $\epsilon_j$  and  $\epsilon_i$  are diagonal elements and F(i,j) is the off diagonal NBO Fock matrix element. The resonance energy (E(2)) detected the quantity of participation of electrons in the resonance between atoms. The larger E(2) value, the more intensive is the interaction between electron donors and acceptor, i.e. the more donation tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system [56]. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non Lewis NBO orbitals correspond to a stabilization donor-acceptor interaction. NBO analysis has been performed for title compound at the B3LYP/6-311+G(d) level of energy

in order to elucidate the intramolecular, rehybridization and delocalization of electron density within the molecule. The strong, moderate and weak intramolecular hyperconjugative interactions of the title compound such as  $\pi \rightarrow \pi^*$ ,  $\pi^* \rightarrow \pi^*$ ,  $\sigma \rightarrow \sigma^*$ ,  $n \rightarrow \pi^*$  and  $n \rightarrow \sigma^*$  transitions are presented in Table 6. According to NBO analysis, the  $\sigma(C1-C3)$  orbital participates as donor and the anti-bonding  $\sigma^*(C3-C4)$ ,  $\sigma^*(C3-C7)$  and  $\sigma^*(C4-O8)$  orbitals act as acceptor with resonance energies (E(2)) of is 2.02 kcal/mol, 0.81 kcal/mol and 8.53 kcal/mol, respectively. These values indicate the most charge transfer from the  $\sigma(C1-C3)$  to  $\sigma^*(C4-O8)$  [ $\sigma(C1-C3) \rightarrow \sigma^*(C4-O8)$ ]. As can be seen in Table 7, the resonance energies of  $\pi \rightarrow \pi^*$  transitions are higher than  $\sigma \rightarrow \sigma^*$  transitions. The intramolecular hyperconjugative interactions of the  $\pi \rightarrow \pi^*$  transitions in double bonds that lead to a strong delocalization are such as  $C3-C4 \rightarrow C5-O6$ ,  $C9-C10 \rightarrow C11-O15$  and  $C9-C10 \rightarrow C12-O13$  with resonance energies (E(2)) 23.22 kcal/mol, 10.56 kcal/mol and 16.92 kcal/mol, respectively. The  $\pi^* \rightarrow \pi^*$  transitions have the highest resonance energies compared with other interactions of the title compound such as  $C5-O6 \rightarrow C3-C4$

and C9-C10→C11-O15 with resonance energies (E(2)) 60.61 kcal/mol 56.32 kcal/mol respectively, that lead to stability of the title compound. According to the n→σ\* interactions, the strongest interactions are due to n2(O13)→σ\*(C12-O14) and n2(O15)→σ\*(C11-O16) transitions with stabilization energies of 33.63 kcal/mol and 30.76 kcal/mol, respectively. Also according to the n→π\* interactions, the strongest interaction is due to n2(O14)→σ\*(C12-

O13) transition with stabilization energy of 43.56 kcal/mol.

The results of NBO analysis such as the occupation numbers with their energies for the interacting NBOs [interaction between natural bond orbital A and natural bond orbital B (A-B)] and the polarization coefficient amounts of atoms in title compound are presented using the B3LYP/6-311+G(d) \* level of energy is summarized in Table 8 (Atoms labeling is according to Figure 1).

**Table 8.** Calculated natural bond orbitals (NBO) and the polarization coefficient for each hybrid in selected bonds of the title compound using the B3LYP/6-311+G(d) level

| Occupancy (a.u.) | Bond (A-B) <sup>a</sup> | Energy (a.u.) | ED <sub>A</sub> (%) | ED <sub>B</sub> (%) | NBO   |
|------------------|-------------------------|---------------|---------------------|---------------------|---|
| 1.98044          | σ(C1-C2)                | -0.60517      | 50.32               | 49.68               | 0.7093 (sp <sup>2.68</sup> ) + 0.7049 (sp <sup>2.60</sup> )   |
| 1.96824          | σ(C1-C3)                | -0.62662      | 49.51               | 50.49               | 0.7036 (sp <sup>2.60</sup> ) + 0.7106 (sp <sup>2.32</sup> )   |
| 1.97788          | σ(C2-C5)                | -0.62197      | 51.34               | 48.66               | 0.7165 (sp <sup>2.86</sup> ) + 0.6975 (sp <sup>1.93</sup> )   |
| 1.97440          | σ(C3-C4)                | -0.75449      | 49.84               | 50.16               | 0.7060 (sp <sup>1.80</sup> ) + 0.7082 (sp <sup>1.41</sup> )   |
| 1.82552          | π (C3-C4)               | -0.28620      | 46.32               | 53.68               | 0.6806 (sp <sup>99.99</sup> ) + 0.7326 (sp <sup>99.99</sup> ) |
| 1.98444          | σ(C3-C7)                | -0.66140      | 51.16               | 48.84               | 0.7152 (sp <sup>1.94</sup> ) + 0.6989 (sp <sup>2.30</sup> )   |
| 1.97480          | σ(C4-C5)                | -0.66375      | 52.22               | 47.78               | 0.7226 (sp <sup>1.98</sup> ) + 0.6912 (sp <sup>1.99</sup> )   |
| 1.98368          | σ(C4-O8)                | -0.90873      | 31.53               | 68.47               | 0.5616 (sp <sup>3.02</sup> ) + 0.8274 (sp <sup>2.07</sup> )   |
| 1.99558          | σ(C5-O6)                | -1.08530      | 34.90               | 65.10               | 0.5908 (sp <sup>2.08</sup> ) + 0.8068 (sp <sup>1.34</sup> )   |
| 1.97782          | π (C5-O6)               | -0.37489      | 31.93               | 68.07               | 0.5650 (sp <sup>99.99</sup> ) + 0.8251 (sp <sup>99.99</sup> ) |
| 1.98642          | σ(O8-C9)                | -0.92574      | 67.86               | 32.14               | 0.8237 (sp <sup>2.11</sup> ) + 0.5670 (sp <sup>2.91</sup> )   |
| 1.97984          | σ(C9-C10)               | -0.78905      | 50.20               | 49.80               | 0.7085 (sp <sup>1.34</sup> ) + 0.7057 (sp <sup>1.59</sup> )   |
| 1.86876          | π (C9-C10)              | -0.31164      | 47.64               | 52.36               | 0.6902 (sp <sup>99.99</sup> ) + 0.7236 (sp <sup>99.99</sup> ) |
| 1.98006          | σ(C9-C11)               | -0.69381      | 51.31               | 48.69               | 0.61563 (sp <sup>2.17</sup> ) + 0.6977 (sp <sup>1.68</sup> )  |
| 1.97375          | σ(C10-C12)              | -0.68949      | 51.45               | 48.55               | 0.7173 (sp <sup>2.09</sup> ) + 0.6968 (sp <sup>1.61</sup> )   |
| 1.99310          | σ(C11-O15)              | -1.06925      | 34.96               | 65.04               | 0.5913 (sp <sup>2.11</sup> ) + 0.8065 (sp <sup>1.59</sup> )   |
| 1.97980          | π (C11-O15)             | -0.44279      | 31.95               | 68.05               | 0.5653 (sp <sup>49.31</sup> ) + 0.8249 (sp <sup>44.65</sup> ) |
| 1.99229          | σ(C11-O16)              | -0.93932      | 31.59               | 68.41               | 0.5620 (sp <sup>2.51</sup> ) + 0.8271 (sp <sup>2.03</sup> )   |
| 1.99575          | σ(C12-O13)              | -1.09488      | 35.36               | 64.64               | 0.5947 (sp <sup>1.88</sup> ) + 0.8040 (sp <sup>1.45</sup> )   |
| 1.98192          | π (C12-O13)             | -0.39095      | 30.62               | 69.38               | 0.5533 (sp <sup>1.00</sup> ) + 0.8330 (sp <sup>1.00</sup> )   |
| 1.99296          | σ(C12-O14)              | -0.91187      | 31.27               | 68.73               | 0.5592 (sp <sup>2.68</sup> ) + 0.8290 (sp <sup>2.14</sup> )   |
| 1.99187          | σ(O14-C18)              | -0.82823      | 69.12               | 30.88               | 0.8314 (sp <sup>2.51</sup> ) + 0.5557 (sp <sup>3.71</sup> )   |
| 1.98843          | σ(O16-C17)              | -0.84753      | 69.27               | 30.73               | 0.8323 (sp <sup>2.37</sup> ) + 0.5544 (sp <sup>3.69</sup> )   |
| 1.97154          | σ(C1-H19)               | -0.50853      | 60.57               | 39.43               | 0.7783 (sp <sup>3.42</sup> ) + 0.6279 (s)                     |
| 1.97055          | σ(C2-H21)               | -0.50857      | 61.12               | 38.88               | 0.7818 (sp <sup>3.26</sup> ) + 0.6236 (s)                     |
| 1.98715          | σ(C7-H23)               | -0.51409      | 60.99               | 39.01               | 0.7809 (sp <sup>3.14</sup> ) + 0.6246 (s)                     |
| 1.96775          | σ(C10-H26)              | -0.54552      | 61.09               | 38.91               | 0.7816 (sp <sup>2.45</sup> ) + 0.5913 (s)                     |
| 1.99415          | σ(C17-H27)              | -0.55473      | 59.23               | 40.77               | 0.7696 (sp <sup>2.77</sup> ) + 0.6385 (s)                     |
| 1.99411          | σ(C18-H30)              | -0.53570      | 59.48               | 40.52               | 0.7713 (sp <sup>2.76</sup> ) + 0.6365 (s)                     |

<sup>a</sup>A-B is the bond between atom A and atom B. (A: natural bond orbital and the polarization coefficient of atom; A-B: natural bond orbital and the polarization coefficient of atom B).

The size of polarization coefficients shows the importance of the two hybrids in the formation of the bond. The differences in electronegativity of the atoms involved in the bond formation are reflected in the larger differences in the polarization coefficients of the atoms (C-O and C-H bonds). The calculated bonding orbital for the  $\sigma(\text{C4-O8})$  bond is the  $\sigma=0.5616\text{sp}^{3.02} + 0.8274\text{sp}^{2.07}$  with high occupancy 1.98368a.u. and low energy -0.90873a.u.. The polarization coefficients of C4= 0.5616 and O8= 0.8274 shows importance of O8 in forming C4-O8 bond compared with C4 atom. Also the calculated bonding orbital for the  $\pi(\text{C12-O13})$  is  $\sigma=0.5533\text{sp}^{1.00} + 0.8330\text{sp}^{1.00}$  with high occupancy 1.98192a.u. and energy -0.39095a.u.. The polarization coefficients of C12= 0.5533 and O13= 0.8330 shows importance of O13 in forming C12-O13 bond compared with C12 atom. The difference in polarization coefficients is small when similar atoms are involved in bond formation (C-C bonds). As shown in Table 7, the calculated bonding orbital for the  $\sigma(\text{C1-C2})$  bond is  $\sigma=0.7093\text{sp}^{2.68} + 0.7049\text{sp}^{2.60}$  with energy -0.60517a.u. and high occupancy 1.98044a.u.. The polarization coefficients of C1= 0.7093 and C2= 0.7049 shows low difference in polarization coefficients C1 and C2 atoms in C1-C2 bond and importance of two atoms in forming bond.

### Conclusion

In conclusion, we are reporting a new MCR by a sequence of multicomponent reaction for the preparation of dimethyl (z)-2-[(2-methyl-5-oxo-1-cyclopentyl)oxy]-2-butenedioate. Due to the easy availability of the synthetic approach and use of *N*-isocyaniminotriphenylphosphorane

(Ph<sub>3</sub>PNNC) as a metal-free catalyst, this new synthetic approach has the shows a high potential in the synthesis of such compounds, which are considerable interest as potential potent biologically active compounds or pharmaceuticals. In the present study also, the electronic properties and geometric parameters of compound have been analyzed using the DFT/B3LYP and HF methods with 6-311+G(d) basis set. From the theoretical and experimental <sup>1</sup>H and <sup>13</sup>C NMR chemical shift values, it can be seen experimental values are in good agreement with the theoretical values by B3LYP/6-311+G(d) level compared with HF/6-311+G(d) level. The natural charge (NBO) analysis of the title compound shows that oxygen atoms (O6, O8, O13, O14, O15 and O16 atoms) have the highest values of negative charge. The FMO analysis suggests that charge transfer is taking place within the molecule. From the MEP map, it can be seen negative region of the title compound is mainly focused on O6, O13 and O15 atoms, therefore they are suitable site for electrophilic attack. According to the results of NBO analysis, the intramolecular hyperconjugative interactions of  $\pi^*(\text{C5-O6}) \rightarrow \pi^*(\text{C3-C4})$  and  $\pi^*(\text{C9-C10}) \rightarrow \pi^*(\text{C11-C15})$  have the highest energies compared with interactions that leads to strong stabilization energy of 60.61 kcal/mol and 56.32 kcal/mol, respectively.

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