Stereoselectivity and Regioselectivity of the Cycloaddition Dimerization of allyl 3-(2-pyridyl) acrylate and allyl 3-(2-pyrrol) acrylate: DFT Calculations

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Abstract. A theoretical study of the photochemical dimerization of allyl 3-(2-pyridyl) acrylate and allyl 3-(2-pyrrol) acrylate is reported. The reactions gave dimers with high regioselectivity and stereoselectivity through [2+2] cycloaddition mechanism. All calculations were computed by density functional theory method, B3LYP, in conjunction with the 6-31G(d) basis set. Conformation analysis, geometric parameters and IR spectrum for the target dimers were also studied. Conformation 2 of allyl 3-(2-pyridyl) acrylate and conformation 9 for allyl 3-(2-pyrrol) acrylate were found to be the most stable structures among the different conformations. Vibration frequencies and IR absorption intensities were calculated for the conformers 2 and 9 using the same computational method. In addition, thermodynamic parameters for the reactions of most stable conformations were analysed. The HOMO and LUMO molecular orbitals and the energy gap between them were estimated for the stable conformations.

1. Introduction
In dimerization of organic compounds, cycloaddition reaction of alkenes to form cyclobutane dimers is one of the most studied reaction [1]. Recently, it was found that in the presence of benzophenone, the irradiation of methyl 3-(2-furyl)acrylate gave a mixture of two isomeric dimers [2]. It is also reported that this reaction results in the triplet state of the molecule [3]. In 1992, D’Auria and co-workers found that this triplet state is achieved via energy transfer from benzophenone. Recently, different approaches were used to study photochemical dimerization. For instance, the photodimerisation of cytosine, using CASSCF/CASPT2 study, shows that the most probable reaction occurs along the potential energy hyper surface [4-6]. In the investigations of diradical species, density functional theory (DFT) was largely used [7-9]. It was found that calculations with DFT method give rise to better interaction energies for corannulene dimers than other methods [10]. The dimers of five diazanaphthalenes (DAPs)n were investigated by means of several methods to elucidate their dimer’s preferred relative energies, geometries and nature of the interactions between monomer units [11]. The results indicate that DFT method provides binding energies that are closer to the estimated values. The [2+2] cycloaddition reaction, in particular, represents a significant strategy with high atom economy for the preparation of cyclobutane derivatives. The importance of the cyclobutane containing compounds has been widely demonstrated as target molecules as well as useful building blocks for the construction of complex structures [12]. In particular, cyclobutanes can undergo fragmentation and ring-expansion reactions, due to the inherent ring strain, for the synthesis of both acyclic and cyclic systems [13]. There are different strategies that have been published to show the reactivity of these substrates [14].

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This study reports a DFT calculation on two photochemical cycloaddition dimerization reactions, namely, allyl 3-(2-pyridyl) acrylate and allyl 3-(2-pyrrol) acrylate, in order to show the effect of nitrogen heterocyclic ring (pyridine and pyrrole) on the dimerization pathways. This paper also reports the regio- and stereoselective behaviour of the dimerization reactions.

2. Computational Details

Gaussian09 package was used and all the computations were based on DFT method using the B3LYP functional [15, 16] and the 6-31G(d) basis set. Frequency calculations were performed to ensure that a transition state has only one imaginary frequency and a local minimum has no imaginary frequencies. All energies and thermodynamic parameters reported in this paper were obtained from the frequency calculations at the same level of theory.

3. Results and Discussion

3.1. Allyl 3-(2-pyridyl) acrylate

Stereo- and regioselectivity for allyl 3-(2-pyridyl) acrylate 1 was explained using DFT calculation at B3LYP/6-31G(d) level of theory. In order to investigate the most stable conformation, six different stereo and regioselectivity conformers were built and optimized. It was found that allyl 3-(2-pyridyl) acrylate 1 gave the corresponding dimer 2, (see Scheme 1) with high stereo- and regioselectivity.

The suggested stereo and regioselective cyclobutane derivatives that can be obtained in the dimerization are shown in Figure 1, and their energies are listed in Table 1. It can be noted that different structures with different diastereomers give different energies. The most stable structure was found to be 2 among all due to its lowest electronic energy and the lowest value of dipole moment.

Table 1. Electronic energies of the diastereomers of dimerization of allyl 3-(2-pyridyl) acrylate 1.

| Conf. | electronic energy (kcal/mol) | Relative energy (kcal/mol) | DM (Debye) | E_{LUMO}-E_{HOMO} (kcal/mol) |
|-------|-------------------------------|----------------------------|------------|-----------------------------|
| 2     | -791879.3                     | 0                          | 0.972      | -138.17                     |
| 3     | -791865.4                     | 13.94                      | 3.381      | -133.48                     |
| 4     | -791875.9                     | 3.35                       | 3.840      | -136.88                     |
| 5     | -791874.7                     | 4.65                       | 1.291      | -133.27                     |
| 6     | -791874.5                     | 4.80                       | 3.997      | -131.83                     |
| 7     | -791874.6                     | 6.68                       | 4.132      | -133.34                     |
The evaluation of the global reactions in terms of the thermodynamic parameters allows us to determine the stability of the proposed products and therefore, the feasibility of the reactions. Thermodynamic parameters were computed for all optimized structures. The results obtained during dimerization of 1 are collected in Table 2. All conformation reactions are entropically disfavoured and endothermic. The values of Gibbs free energy in all cases were found to be greater than zero, which refer non-spontaneous reactions. The heat of formation for conformation 2 was found to be the lowest.
and this indicates the highest stability of conformation 2. The lowest value of free energy, \( \Delta G \), is (186.33 kcal/mol), and lowest value of entropy, \( \Delta S \), is (-45.26 kcal/mol), for conformation 2 also indicate the stability of this conformation.

### Table 2. Thermodynamic parameters for dimerisation of 1 for all conformations.

| Conformation | \( \Delta H \) (kcal/mol) | \( \Delta G \) (kcal/mol) | \( \Delta S \) (cal/mol.K) |
|--------------|--------------------------|--------------------------|--------------------------|
| 2            | 186.37                   | 199.87                   | -45.26                   |
| 3            | 200.04                   | 216.37                   | -54.77                   |
| 4            | 189.51                   | 203.70                   | -47.60                   |
| 5            | 191.06                   | 206.11                   | -50.47                   |
| 6            | 191.05                   | 205.64                   | -48.94                   |
| 7            | 190.82                   | 204.70                   | -46.53                   |

The vibrational frequencies were calculated to determine the characteristic functional groups of the conformation 2 as the final product of dimerization of compound 1. The FT-IR spectrum was plotted between the percent transmittance against wavenumber and is shown in Figure 3. Table 1 lists the observed IR frequencies and empirical band assignments of the most stable dimer 2. The ring C-C, bonds stretching vibration occur in the regions 1050-1110 cm\(^{-1}\). The ring C-H stretching vibrations are observed at 3100-3150 cm\(^{-1}\). However, the ring C-H bending vibrations occur in the region 500-1500 cm\(^{-1}\). The C3-pyridyl and C4-pyridyl stretching vibrations are observed in 3217.5 cm\(^{-1}\) and 3279.3 cm\(^{-1}\), respectively. The C-C ring deformation occurs around 876 cm\(^{-1}\).

![Figure 3: IR spectrum for structure 2.](image)
Table 3. Some vibrational frequencies and IR absorption intensities of structure 2

| Frequency (cm⁻¹) | Intensity (km/mol) | Assignment          |
|-----------------|--------------------|---------------------|
| 3217.5          | 13.3024            | C₁-Pyridine stretching |
| 3279.3          | 14.4904            | C₃-Pyridine stretching |
| 3146.7          | 1.3481             | C₁-H₆ stretching     |
| 3122.1          | 1.7109             | C₃-H₃ stretching     |
| 1488.3          | 18.6629            | C₃-H₅ bending        |
| 1110.4          | 25.4008            | C₁-C₂ stretching     |
| 1057.5          | 8.8362             | C₃-C₄ stretching     |
| 876.7           | 1.8909             | C₁-C₂-C₃-C₄ ring deformation |
| 700.6           | 3.2017             | C₂-H₇ bending        |
| 507.9           | 5.7490             | C₁-H₆ bending        |

Table 4 lists the optimized geometrical parameters (bond angle and length) of structure 2. The ring C-C bond length are observed in the range of (1.550 - 1.555 Å). The ring C-H bond lengths are found in the range of (1.090 - 1.100 Å). The C₃-Pyridyl and C₄-Pyridyl lengths are found to be 1.510 Å and 1.505 Å respectively. The H₅-C₃-Pyridyl and H₈-C₄-Pyridyl bond angles were calculated at 41.32 and 40.87 degree, respectively.

Table 4. Some geometry parameters of structure 2

| Bond       | distance (Å) | Bonds       | Angle (°) |
|------------|--------------|-------------|-----------|
| C₁-C₂      | 1.552        | H₆-C₁-R₉   | 41.9      |
| C₁-C₃      | 1.553        | H₅-C₃-Pyd  | 41.3      |
| C₁-H₆      | 1.097        | H₇-C₂-R₁₀  | 40.5      |
| C₁-R₉      | 1.508        | H₆-C₁-Pyd  | 40.9      |
| C₃-H₅      | 1.096        | C₁-C₂-C₃-C₄| 18.6      |
| C₃-Pyd     | 1.510        | H₈-C₁-C₃-H₈| 155.2     |
| C₂-H₇      | 1.091        | H₇-C₂-C₄-H₆| 158.4     |
| C₂-R₁₀     | 1.507        |             |           |
| C₄-H₈      | 1.092        |             |           |
| C₄-Pyd     | 1.505        |             |           |

It is known that the occupation and the energies of the molecular orbitals (MO) give better insight on the excitation, reactivity and hence the stability of the studied molecular structure. Among the MOs, the highest occupies molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) are the most important as the energy difference between these orbitals quantifies the excitation energy of the compound. The energies of the HOMO and LUMO for the reactant and the suggested conformations are shown in Figure 4. As shown in figure, the energy band gap (E_{LUMO} - E_{HOMO}) for conformation 2 is the highest, -138.2 kcal/mol.
3.2. Allyl 3-(2-pyrryl) acrylate

The cycloaddition, regioselective and stereoselective reaction of allyl 3-(2-pyrryl) acrylate, 8 was explained using DFT calculations. It is reported that allyl 3-(2-pyrryl) acrylate 8, gave the corresponding dimer 9, (see Scheme 2) with high stereo- and regioselectivity. Six different stereo conformers of the product were built and optimized and listed in Figure 5. The calculated energies of the proposed six conformers are listed in Table 5. The most stable structure was found to be 9 among all as it has the lowest electronic energy as shown in Table 5.

![Scheme 2. Dimerization of allyl 3-(2-pyrryl) acrylate 8.](image-url)
Figure 5. The optimized structures dimerization of allyl 3-(2-pyrryl) acrylate

Table 5. Energies for diastereomers of dimerization of allyl 3-(2-pyrryl) acrylate 8.

| Conformation | electronic energy (kcal/mol) | Relative energy (kcal/mol) | DM (Debye) | E_{LUMO} - E_{HOMO} (kcal/mol) |
|--------------|------------------------------|---------------------------|------------|--------------------------------|
| 9            | -744038.4                    | 0                         | 2.02       | -124.35                        |
| 10           | -744031.5                    | 6.87                      | 1.38       | -113.86                        |
| 11           | -744034.2                    | 4.23                      | 3.37       | -120.40                        |
| 12           | -744034.6                    | 3.79                      | 2.65       | -115.52                        |
| 13           | -744034.5                    | 3.94                      | 3.70       | -123.39                        |
| 14           | -744036.5                    | 1.84                      | 3.82       | -110.65                        |
Thermodynamic parameters were computed for all optimized structures. The results obtained for the dimerization of \( \text{8} \) were collected in Table 6. It is clear from table that all reactions are entropically disfavored and endothermic. Gibbs free energy for all reactions has positive value and this indicates the nonspontaneous characteristics of these reactions. The heat of formation for conformation \( \text{9} \) was found to be the lowest which indicates the highest stability. The lowest values of \( \Delta G \) and \( \Delta S \) of the conformation \( \text{9} \) also indicate the stability of this conformation.

![Figure 6. Diastereomers energies for dimerization of allyl 3-(2-pyrryl) acrylate \( \text{8} \).](image)

Table 6. Thermodynamic parameters for all conformations.

| Conformations | \( \Delta H \) (kcal/mol) | \( \Delta G \) (kcal/mol) | \( \Delta S \) (cal/mol.K) |
|---------------|--------------------------|--------------------------|--------------------------|
| \( \text{9} \) | 215.63                   | 227.22                   | -38.87                   |
| \( \text{10} \) | 222.60                   | 237.75                   | -50.83                   |
| \( \text{11} \) | 219.67                   | 232.68                   | -43.65                   |
| \( \text{12} \) | 219.40                   | 231.88                   | -41.88                   |
| \( \text{13} \) | 219.68                   | 231.63                   | -40.06                   |
| \( \text{14} \) | 217.57                   | 230.62                   | -43.77                   |

The vibrational frequencies were calculated to determine the characteristic functional groups of conformer \( \text{9} \) of the dimerization reaction. The FT-IR spectrum was plotted between the percent transmittance against wavenumber and is shown in Figure 7. Table 7 lists some of the calculated IR frequencies, their intensities and the empirical band assignments of the dimer \( \text{9} \). The C-C, bonds that participate in the ring formation, stretching vibration occur in the regions (1100 - 950 cm\(^{-1}\)). The ring C-H stretching vibrations are observed at (3000 - 3150 cm\(^{-1}\)). However, the ring C-H bending vibrations occur in the region (500 - 1500 cm\(^{-1}\)). The \( \text{C}_3\)-pyrryl and \( \text{C}_4\)-pyrryl stretching vibrations are observed in 1625 cm\(^{-1}\) and 1631 cm\(^{-1}\), respectively. The C-C ring deformation occurs around 1050 cm\(^{-1}\).
Figure 7. IR spectrum for structure 9.

Table 7. Some vibrational frequencies and IR absorption intensities of structure 9

| Frequency (cm$^{-1}$) | Intensity (km/mol) | Assignment               |
|-----------------------|--------------------|--------------------------|
| 1631.6                | 10.0911            | $C_4$-(Pyrryl) stretching|
| 1625.6                | 1.2279             | $C_3$-Pyrryl Stretching  |
| 3126.1                | 4.4206             | $C_1$-$H_6$ stretching   |
| 3099.3                | 4.0553             | $C_3$-$H_5$ stretching   |
| 1107.9                | 6.0247             | $C_1$-$C_2$ stretching   |
| 956.4                 | 2.2985             | $C_3$-$C_4$ stretching   |
| 1048.5                | 12.2903            | $C_1$-$C_2$-$C_4$-$C_3$ ring deformation |
| 3143.1                | 3.6074             | $C_2$-$H_7$ bending      |
| 515.9                 | 8.7401             | $C_1$-$H_6$ bending      |
| 1516.6                | 7.5077             | $C_3$-$H_5$ bending      |
| 966.9                 | 27.8104            | $C_1$-$C_3$ stretching   |
| 3019.9                | 22.1954            | $C_4$-$H_8$ stretching   |
| 1280.7                | 27.3840            | $C_4$-$H_8$ bending      |
The optimized geometrical parameters (bond angle and length) of structure 9 are listed in Table 8. The ring C-C bond lengths are observed in the range of 1.551 to 1.572 Å. The ring C-H bond lengths are found in the range of 1.091 to 1.100 Å. The C3-Pyrryl and C4-pyrryl lengths are found to be 1.485 Å and 1.489 Å, respectively. The H5-C3-Pyrryl and H8-C4-pyrryl bond angles were calculated at 109.15 Å and 111.44 Å, respectively.

Table 8. Some geometry parameters of structure 9

| Bond         | distance (Å) | Bonds                | Angle (°) |
|--------------|--------------|----------------------|-----------|
| C1-C2        | 1.551        | H6-C1-R9             | 110.8     |
| C1-C3        | 1.572        | H5-C3-Pyrryl         | 109.2     |
| C1-H6        | 1.092        | H7-C2-R10            | 111.9     |
| C1-R9        | 1.509        | H6-C4-Pyrryl         | 111.4     |
| C3-H4        | 1.094        | C1-C2-C3-C4          | 19.8      |
| C3-Pyrryl    | 1.485        | H6-C1-C3-H5          | 158.6     |
| C2-H7        | 1.091        | H7-C2-C2-C2-H8       | 159.1     |
| C2-R10       | 1.507        |                      |           |
| C4-H8        | 1.100        |                      |           |
| C4-Pyrryl    | 1.489        |                      |           |

Figure 8. HOMO and LUMO energy for reactant and conformers.

The HOMO and LUMO energies for the reactant and conformers are shown in Figure 8. As shown in figure, the HOMO-LUMO gap for conformer 9 is largest, -124.35 kcal/mol, and this makes the conformation 9 the most stable among other conformations.

On comparing the two reactions studied and the results indicate that the dimerization of allyl 3-(2-pyridyl) acrylate is found to be more preferred than the dimerization of allyl 3-(2-pyrryl) acrylate. This is due to the larger energy gap of dimerization of allyl 3-(2-pyridyl) acrylate. Pyridine, a six member heterocyclic ring, makes the dimerization reaction more feasible than pyrrole, a five member heterocyclic ring.

4. Conclusions

The dimerization of allyl 3-(2-pyridyl) acrylate and allyl 3-(2-pyrryl) acrylate were studied using the B3LYP functional in conjunction with the 6-31G(d) basis set. Geometric parameters and IR spectrum of conformers 2 and 9 were studied and were found to be the most stable structures. Thermodynamic parameters for the most stable conformers were studied. The lowest values of heat of formation, Gibbs
free energy, and entropy indicate the stability of conformations 2 and 9. The HOMO-LUMO energy gaps for the stable conformations were found to be larger than the others, and this also confirm the stability of structures 2 and 9.

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