

A DFT study on the functionalization of C₂₀ Fullerene via its 1,3-dipolar cycloaddition with 4-pyridine nitrile oxide

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Abstract: Surface modification and functionalization of nano-materials is very useful so that it could extend their applications in many fields, especially metal ion adsorption, and catalytic process. As a result, in this project, we tried to investigate the addition of functional groups onto C₂₀ fullerene via its 1,3-dipolar cycloaddition reaction with 4-pyridine nitrile oxide. The obtained calculations proved that the 1,3-dipolar cycloaddition reaction between 4-pyridine nitrile oxide and C₂₀ fullerene could occur much faster than this reaction by ordinary organic species. In this study, all calculations were performed at B3LYP/6-31+G(d,p) level of the theory.

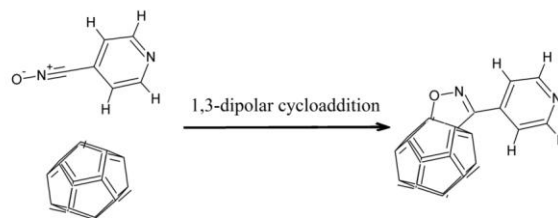
Keywords: Catalyst free reaction, C₂₀ Fullerene, DFT, 1,3-Dipolar cycloaddition, Functionalization of C₂₀.

Introduction

Having huge surface area-to-volume ratio [1], nano-particles have many applications in a variety of chemical processes, especially in metal ion adsorption [2], pollutants removal [3], and catalytic reactions [4]. Having low costs, and easy preparation, it makes carbon nano-tubes (CNTs), as one of the most suitable nano-material, to be served as a base for the synthesis of functionalized catalysts and sorbents [5]. Taking a look at the previously reported research in this field, it is clear that CNT- based catalysts, as nano sized compounds, are more efficient than their polymer based rivals [5-9]. So, such reports could encourage researchers to use these nano-size compounds.

Nano-fullerene small radius has been an important factor that is served as an impetus to encourage researchers to use them as suitable base for the catalytic complexes. To enable it to be used in biochemical [10], and chemical fields [11], fullerene C₆₀ is one of Nano Buckminster fullerenes which has already been successfully functionalized through exercising of several methods. Achievement which

have been made by the scientists in the functionalization of the C₆₀ fullerenes via 1,3-dipolar reaction [12,13] with 4-pyridine nitrile oxide [14] helped us to plan a scheme that consisted of 1,3-dipolar cycloaddition reaction between C₂₀ fullerene [15-17] and 4-pyridine nitrile oxide (Scheme 1). The Density Functional Theory that could estimate the exact $\Delta G^{0,\#}$ of several 1,3-dipolar reactions [18,19] was used to study some of the thermodynamic, and kinetic parameters of this reaction. In this work, we have used the DFT method at a trustable basis set to study the cycloaddition reaction of 4-pyridine nitrile oxide and C₂₀ fullerene which is illustrated in Scheme 1.



Scheme 1: 1,3-Dipolar cycloaddition reaction of C₂₀ fullerene with 4-pyridine nitrile oxide.

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Results and discussion

At first stage, a number of structures were considered for all species as input files. Then, these structures optimized to achieve more stable geometry. The entire calculations were carried out by Gaussian 03 chemical quantum package [20]. Using DFT method at the B3LYP/6-31+G(d,p) level of the theory, each structure was optimized [21-23]. The synchronous transit guided quasi-Newton (STQN) method [24, 25] was employed to find the transition state structures (TSs). Frequencies of all structures were taken to obtain the thermodynamic energies of each state. Using the intrinsic reaction coordinate (IRC) method, the accuracy of all TSs were then checked and confirmed [26, 27]. Also, the natural bond orbital (NBO) calculation [28, 29] was carried out to determine the electrical charge of each atom, both in the reactants and in the TSs. To calculate the electrophilicity constants of all the species, which showed in the table 1, Parr electrophilic relation was applied [30].

$$\omega = \mu^2 / 2\eta \quad (1)$$

Where, ω is electrophilicity, μ is the chemical potential, and η is the hardness of a species.

In this study, all calculations were performed at B3LYP/6-31+G(d,p) level of the theory, and, for each species, several geometries were proposed as input files. Then, they have been optimized at the fore-mentioned theoretical level. Finally, the more stable geometry for each species was selected as the best geometry for further calculations. Figure 1 shows the optimized structures of the reactants, products, and TSs.

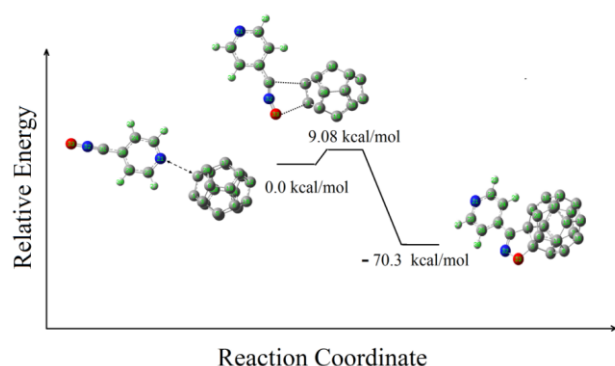


Figure 1: the relative Gibbs Energy surface during the reaction coordinate.

According to the table 1, the concerted mechanism of this reaction initiated with the formation of the C31-C1 and O33-C3 bonds, and the cleavage of C1-C3 and C31-N32 π bonds. In the TSs, the bond length of the C31-C1 and O33-C3 bonds are 2.63 and 2.47

angstrom, respectively. Using Pauling relation [31] to determining the related partial bond orders, the values of 0.024, 0.030, 0.967, and 0.935 were achieved for the C31-C1, O33-C3, C1-C3, and C31-N32 bonds, respectively. The calculated partial bond orders indicated that the C31-C1 and O33-C3 are only 2.4% and 3.0% formed, respectively. While, the π bonds in the C1-C3, and C31-N32 are 3.3% and 6.5% broken, respectively. The extent of broken and formed bonds in the TSs shows that a synchronous concerted mechanism occurs for the 1,3-dipolar cycloaddition reaction of C₂₀ fullerene with 4-pyridine nitrile oxide.

Table 1: Geometrical parameters of reactants, transition state and product at B3LYP/6-31+G(d,p) level.

	C(1)- C(3)	C(1)- C(31)	C(3)- O(33)	C(31)- N(32)	N(32)- O(33)
Reactants	1.41	–	–	1.17	1.22
TS	1.42	2.63	2.47	1.19	1.22
Product	1.58	1.51	1.42	1.29	1.41

Obtained results showed in table 2 indicate the charge distribution in the reactants, TSs, and the charge difference between TSs and reactant (Δ charge), employing Natural Bond Order calculations. These results show that a small negative charge increased on C1, and N32 atoms at the TSs. Also, the charge difference between the reactants, and TSs proves that electron donor groups (EDG), at C1 atom, accelerates the reaction, whereas at C3 position leads to opposite results.

Table 2: Distributed NBO charges on the reactant and TS at the B3LYP/6-31+G(d,p) level of theory.

	C (1)	C (3)	O (33)	N (32)	C (31)
Reactants	-0.092	-0.029	-0.385	0.190	0.224
TS	-0.164	0.024	-0.337	0.161	0.259
Δ (Charge)	0.072	-0.053	-0.048	0.029	-0.035

The imaginary frequency for the TSs was calculated to confirm the TS B3LYP/6-31+G(d,p). Activation energy (E_a), ΔG^\ddagger , ΔH^\ddagger , ΔS^\ddagger , and the reaction rate constant were shown in the table 3. Moreover, the Gibbs free energy barrier for the TS formation in gas phase is 9.09 kcal. mol⁻¹, and the calculated value of rate constant is 1.3×10^6 s⁻¹.mol⁻¹. The calculated rate constant for this reaction proves that the reaction is significantly faster compared to 1,3-dipolar cycloaddition reactions between usual organic

compounds such as norbornadiene [18], and dimethyl-acetylene-dicarboxylate [19].

Table 3: Theoretical kinetic and activation parameters for the cycloaddition reaction in gas phase and different solvents at 298.15K. ΔG^\ddagger , ΔH^\ddagger , and E_a are in $Kcalmol^{-1}$ and ΔS^\ddagger is in $cal\ mol^{-1}K^{-1}$.

	$\Delta G^{0,\ddagger}$	K(mol.s ⁻¹)	$\Delta H^{0,\ddagger}$	$\Delta S^{0,\ddagger}$	Ea
Gas phase	9.09	1.3(10 ⁺⁶)	2.63	-21.6(10 ⁻³)	3.22

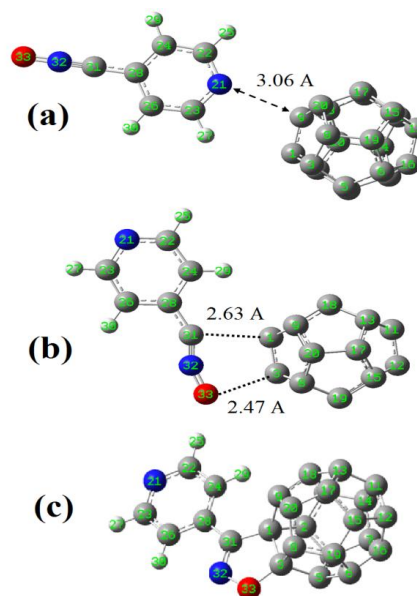
Furthermore, the achieved results indicate that the E_a of the process is about 3.22 $kcal.mol^{-1}$, that is significantly lower than E_a of ordinary 1,3 dipolar cycloadditions reactions. So, it could be concluded that the higher electrophilicity in the C₂₀ fullerene, compared to ordinary olefins, could be the root cause of this observation.

Table 4 shows that the electrophilicity of C₂₀ fullerene ($\omega = 0.403$) is significantly higher than those of normal dipolarophiles including 2, 3-dihydrofurane ($\omega=4.68 (10^{-2})$), maleic acid ($\omega=1.71 (10^{-1})$), and ethene ($\omega=7.67 (10^{-2})$). Even the strong electron-withdrawing groups such as Flour, Nitrile, Amide, and Nitro could not make the normal C=C bond to be better electrophile compared to C=C bond of C₂₀ fullerene. So, the high electrophilicity of C₂₀, may be the root cause of the high value of the rate constant for 1,3-dipolar cycloaddition reaction of C₂₀ fullerene with 4-pyridine nitrile oxide.

Table 4: The electrophilicity ω , of urea, and some of the C=C Bond derivatives calculated at B3LYP/6-31+G(d,p) level of theory.

Species	HOMO	LUMO	η	μ	ω
C(20) fullerene	-0.2024	-0.1327	0.03485	-0.1676	0.403
Trans-1,2-dinitro ethene	-0.3410	-0.1704	0.0852	-0.2557	0.384
Cis-1,2-ethene diamide	-0.2739	-0.0926	0.0906	0.1832	0.185
Cis-1,2-cyanoethene	-0.3003	-0.0729	0.1137	-0.1866	0.153
Cis-1,2-difluoro ethene	-0.2759	-0.0047	0.0135	-0.1403	7.29 (10 ⁻¹)
maleic acid	-0.2945	-0.0842	0.1051	-0.0189	1.71 (10 ⁻¹)
2,3-dihydrofurane	-0.2158	0.0101	0.1129	-0.1028	4.68 (10 ⁻²)
ethene	-0.2783	-0.0095	0.1349	-0.1439	7.67 (10 ⁻²)

Based on what was stated in the Scheme 2, the amount of Gibbs free energy surface of reactants, TSs, and product shows that the reaction is kinetically and thermodynamically favorable.



Scheme 2: The optimized structure of reactants, TS, and Product at B3LYP/6-31+G(d,p) level.

Conclusion

As previous reports have proved, the highly suitable agreement between theoretical and experimental $\Delta G^{0,\ddagger}$ of 1,3-dipolar cycloadditions could improve the perspective that the DFT method is able to calculate the $\Delta G^{0,\ddagger}$, and activation energy of 1,3-dipolar cycloaddition reactions between nitrile oxides and olefins.

Based on the obtained result, the activation energy of the process is about 3.22 $kcal.mol^{-1}$, which is significantly lower than the E_a of normal 1, 3-dipolar cycloadditions reaction of ordinary organic compounds. Also, the rate constant of the reaction is $1.3 \times 10^6\ mol^{-1}.s^{-1}$. That is, this reaction on C₂₀ fullerene is kinetically suitable and could occurs much faster compared to 1,3-dipolar reactions between 1,3-dipoles and the ordinary olefins. Moreover, the Gibbs energy surface shows that this reaction process is thermodynamically very favorable. So, it seems that 1,3-dipolar reaction could become a suitable procedure to functionalize C₂₀ fullerene.

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