Substituent effects and Mechanism Studies in CO2 Transformation to Benzoxazinone Derivatives as Worthwhile N-containing Heterocycles: insight from DFT simulation

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Substituent effects and Mechanism Studies in CO$_2$ Transformation to Benzoxazinone Derivatives as Worthwhile N-containing Heterocycles: insight from DFT simulation

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Abstract

Investigation of CO$_2$ transformation into value-added organic molecules is an interesting purpose in scientific communities. Here, the substitute effect exploration in CO$_2$ incorporation reaction toward benzoxazinones formation, as a bioactive heterocyclic compound, is the main studied issue. A profound understanding of the substituent effect is helpful toward the investigation of the kinetic and thermodynamic aspects of the reaction. The substituted aryynes, an imine compound, and atmospheric CO$_2$ have been reported as the starting reactants. The substituted functional groups show substantial consequences on the studied mechanisms. The obtained results show that mechanism A, in which the imine compound is added as a nucleophile to aryynes, is the most probable mechanism. The Energetic Span Model (ESM) was used in the kinetic studies, which indicates the turnover-frequency determining intermediate (TDI) and turnover-frequency determining transition state (TDTS) in the reaction progress. Also, Electron localization function (ELF) analyses reveal that the electron density of a developing monosynaptic basin on the carbon atom (V(C)) at the transition state shows a good linear correlation with the calculated energy values of TDTS. Electron-withdrawing and electron-releasing characters of the substituents have the main effects on the electron density of the developing basin at the transition states which change the TDTS energies.

Keywords: Carbon dioxide; Benzoxazinones; Energetic span model; Electron localization function.

Introduction

Human activities such, as burning fossil fuels for power production, manufacturing, and transportation are the origin of greenhouse gases emission. Regarding the reports, the CO$_2$ amount grows up from 280 ppm (parts per million) in the mid-1800s to 397 ppm in 2014, which shows an average growth of 2 ppm/year in the last 10 years [1]. Global warming, ocean acidification, and CO$_2$ fertilization are harmful consequences of unusual CO$_2$ emissions. To attain sustainable development, an effective understanding of increasing environmental problems and global climate-changing is necessary. Thus, practical approach innovations, such as climate change inhabitation, environment conservation and fossil fuel replacement by green energies, must be considered by
scientific communities. However, in addition to reducing fossil fuel usage and change in the energy resource, CO₂ capture and utilization as a feedstock to produce value-added compounds are other developing solutions among scientists [2,3]. CO₂ utilization, as a C1 source, has great direct or indirect potential uses. The direct use of CO₂ includes CO₂-enhanced oil recovery, beverage carbonation, food processing, the cleaning agent in the textile, etc., which have been applied for several decades [4]. However, the extent of these usages is small.

CO₂ can be transformed into various value-added chemicals such as formic acid [5], carboxylated structures [6,7], inorganic carbonates, ethylene/propylene carbonates, polycarbonates [8-11], biodegradable polymers [12-14], and various heterocycles [15-19]. A range of technologies based on CO₂ conversion for various product manufacturing was proposed [20]. CO₂, as an alternative to phosgene or carbon monoxide, is applied in the synthesis of heterocycles, which are the building block of the N-containing heterocyclic compound synthesis, such as oxazolidinones [21], imidazolidinones [22], quinazolines [23-25], etc.

N-containing heterocycles, as the biocompatible compounds, are used as pharmaceutical and agrochemical agents [26-28]. The derivatives such as benzothiazoles, benzimidazoles, and benzoazinone, are typical N-containing heterocycles that are extensively used as an antiviral, antibacterial, anticancer, antifungal, antibacterial agent, antihypertensive, and anti-inflammatory [29-32]. CO₂ incorporation by nucleophiles, as an efficient and green approach in heterocycle synthesis, has been investigated in recent years, frequently [33]. Based on the reports, CO₂ incorporation can be progressed through three routes including (1) nucleophilic addition to CO₂ followed by intramolecular cyclization to carboxylated cycle production; (2) concerted two-nucleophilic site attacks on CO₂ affording cyclic carbonyl compound; (3) cyclization due to nucleophilic attack on the reduced CO₂ [33].

Yoshida and coworker reported a CO₂ incorporation reaction in the six-membered heterocycle formation by using arynes and imines, which produces benzoazinone compounds [34]. Arynes possess different electron-releasing and electron-withdrawing substituents, which afford distinct effects on the thermodynamic and kinetic behaviors of the benzoazinone formation. The substituents have different effects on the hydrogen-less carbon atom of arynes as meta and para positions. Based on the Yoshida report, a zwitterion is obtained from the nucleophilic addition of imines to arynes, which is an excellent molecular scaffold for CO₂ capture. The aryne functional groups have undeniable effects on the CO₂ incorporation. Here, based on the previous experiences [35-40], a comprehensive mechanism study was performed on the benzoazinone formation, consists of two separate routes for the reaction progress. According to the obtained theoretical results at two computational levels, meta and para positions on the arynes have different behaviors against CO₂ or imines. The Energetic Span
Model (ESM), as a kinetic-quantum chemical model, was used to investigate the kinetic aspects of the reaction. Also, powerful quantum chemistry descriptors, such as Electron Localization Function (ELF) and Fukui Functions are applied to describe the observed substituent behavior in the reaction. Fig. 1 shows the overall reaction and the studied substituted arynes in the reaction.

Fig. 1 The overall reaction, and the substituted arynes, within atom numbering for the involved atoms in the reaction

Computational details

Geometry optimization and vibrational frequency calculations were carried out using M06-2X functional [41] by the Gaussian 09 software [42]. The calculations were performed by two different basis sets of 6-31+G(d,p) and 6-311++G(2d,p) [43,44]. According to Schlegel’s synchronous transit-guided quasi-Newton method (STQN), the structures of the transition states (TSs) were located and their accuracies were checked via the intrinsic reaction coordinate (IRC) calculations to specify the connection of the TS structure to the corresponding products and reactants [45]. The stationary points were determined by vibrational frequency calculations to check that the calculated reactants and products have positive vibrational frequencies and the TSs have only one imaginary frequency. The zero-point vibrational energy (ZPVE) correction was applied for the calculated thermodynamic and kinetic parameters based on the harmonic oscillator approximation and solvation corrections at 298.15 K and 1 atm. The solvent effects were evaluated in tetrahydrofuran (THF) as the solvent by conductor-like polarizable continuum model (CPCM) [46]. This method defines the cavity as a group of nuclear-centered spheres within a dielectric continuum. Topological analysis of the ELF was obtained by MultiWFN package [47].
Results and discussions

Two distinct mechanisms can be considered for the reaction, determined by A and B letters. Mechanism A is initiated by the nucleophilic addition of imine to meta/para position, while in mechanism B, it is assumed that the substituted arynes behave as the nucleophile species (Fig. 2). In1A and In2A, in which the electron density of the lone pair electrons are on the C3 and C4 atoms, are the outcomes of steps 1A and 1A', respectively. In steps 2A and 2A', CO2 molecule incorporates to C3 or C4 atoms, yielding In2 and In2', respectively, which are the common intermediates in both mechanisms. Steps 3 and 3', as the final steps of both mechanisms, are intramolecular nucleophilic additions, which proceed through different paths including si face and re face states. Indeed, according to Cahn-Ingold-Prelog sequence rules [48], linked carbon atoms to nitrogen (iminic carbon) of In2 and In2' are prochiral centers, in which nucleophilic species can be added to two different faces (Fig. 3). The outcomes of the re face approaching in both intermediates are two diastereomers with S configurations, and vice versa R configurations diastereomers for the si face approaching mode.
Fig. 2 Two possible mechanisms: mechanism A (blue lines) and mechanism B (red lines). Black lines illustrate the common steps of both mechanisms.

However, in mechanism B, arynes act as nucleophiles, in which the nucleophilic addition to the carbon atom of $\text{CO}_2$ leads to In1B and In2B formation. The bond formation between the electron-deficient carbon atoms of In1B and In2B and lone pair electrons of the iminic nitrogen atom in steps 2B and 2B' produces In2 and In2'. However, the obtained results in both calculated methods show that mechanism B is not a favorable mechanism for the reaction progress. Indeed, the optimized intermediates and transition states for some electron-withdrawing functional groups, such as CN, NO$_2$, Cl, and F are not achievable and all efforts to get their optimization structures were failed.
Mechanism B is only probable for limited functional groups, such as Et, Me, OMe and NMe$_2$. It can be concluded that the nucleophilic behavior of arynes against CO$_2$ molecule can be considered only for those having electron-releasing groups. Therefore, the local nucleophilicity of the involved arynes atoms in the reaction has a considerable difference.

Local nucleophilicity ($N_k$) (Eq(1)), at the atomic $k$ position, can be defined by the related condensed Fukui functions, $f_k^-$ (Eq(2)), in which $q_k(N)$ and $q_k(N-1)$ are natural atomic charges of the N and N-1 electronic states [49]. $N$, as the global nucleophilicity index, is calculated by Eq(3), in which $E_{\text{HOMO(Nu)}}$ and $E_{\text{HOMO(TCE)}}$ are the HOMO energies of the substituted arynes (nucleophilic species), and tetracyanoethylene (TCE), respectively. Global nucleophilicity is defined relative to TCE because it shows the lowest HOMO energy in the large series of molecules [49]. Table 1 represents the HOMO energies of the substituted arynes, natural atomic charges of N and N-1 electronic states for C3 and C4 atoms, calculated $f_k^-$, and $N$. Fig. 4 depicts the donor (nucleophilic) Fukui function isosurfaces and the obtained $N_k$ for C3 and C4 atoms.

$$N_k = N \cdot f_k^- \quad Eq(1)$$

$$f_k^- = q_k(N - 1) - q_k(N) \quad Eq(2)$$

$$N = E_{\text{HOMO(Nu)}}(eV) - E_{\text{HOMO(TCE)}}(eV) \quad Eq(3)$$
As shown in Fig. 4, \( N_k \) values for C3 and C4 atoms of arynes having electron-withdrawing substituents are substantially lower than the others. Therefore, the nucleophilicity character of these atoms in the substituted arynes by \( \text{NO}_2 \), CN, F, and Cl groups is lower than that of Et, Me, OMe, and NMe\(_2\). It is a logical reason for the justification of failed attempts to the optimization of intermediates and transition states in the substituted arynes owning electron-withdrawing groups.

**Table 1** HOMO energies (eV) of the substituted arynes, natural atomic charges of N and N-1 electronic states for C3 and C4 atoms, calculated \( f_k^- \), and \( N \) (eV)

|                | \( G \) | \( E_{\text{HOMO}} \) | \( q_N(C3) \) | \( q_N(C4) \) | \( q_{N-1}(C3) \) | \( q_{N-1}(C4) \) | \( N \) | \( f_k^-(C3) \) | \( f_k^-(C4) \) |
|----------------|--------|------------------------|---------------|---------------|-----------------|---------------|--------|----------------|----------------|
| **F**          | -0.3221| 0.0141                 | 0.0156        | 0.0559        | 0.0815          | 0.0629        | 0.0418 | 0.0659         |                 |
| **Cl**         | -0.3175| 0.0144                 | 0.0260        | 0.0551        | 0.0927          | 0.0675        | 0.0407 | 0.0667         |                 |
| **NO\(_2\)**   | -0.3473| 0.0139                 | 0.0663        | 0.0585        | 0.1161          | 0.0377        | 0.0447 | 0.0498         |                 |
| **CN**         | -0.3381| 0.0046                 | 0.0613        | 0.0538        | 0.1142          | 0.0469        | 0.0493 | 0.0529         |                 |
| **Et**         | -0.3109| 0.0163                 | -0.0132       | 0.0739        | 0.0525          | 0.0741        | 0.0576 | 0.0657         |                 |
| **Me**         | -0.3108| 0.0160                 | -0.0129       | 0.0717        | 0.0518          | 0.0742        | 0.0557 | 0.0646         |                 |
| **OMe**        | -0.2915| 0.0270                 | -0.0215       | 0.0720        | 0.0527          | 0.0935        | 0.0450 | 0.0742         |                 |
| **NMe\(_2\)** | -0.2543| 0.0449                 | -0.0596       | 0.0952        | 0.0230          | 0.1307        | 0.0503 | 0.0825         |                 |
| **TCE**        |         |                        |               |               |                 |              |        |                 | -0.3850        |

|                | \( G \) | \( E_{\text{HOMO}} \) | \( q_N(C3) \) | \( q_N(C4) \) | \( q_{N-1}(C3) \) | \( q_{N-1}(C4) \) | \( N \) | \( f_k^-(C3) \) | \( f_k^-(C4) \) |
|----------------|--------|------------------------|---------------|---------------|-----------------|---------------|--------|----------------|----------------|
| **F**          | -0.3231| 0.0128                 | 0.0177        | 0.0520        | 0.0817          | 0.0655        | 0.0418 | 0.0659         |                 |
| **Cl**         | -0.3181| 0.0139                 | 0.0273        | 0.0477        | 0.0971          | 0.0705        | 0.0407 | 0.0667         |                 |
| **NO\(_2\)**   | -0.3495| 0.0113                 | 0.0694        | 0.0591        | 0.1173          | 0.0392        | 0.0447 | 0.0498         |                 |
| **CN**         | -0.3401| 0.0033                 | 0.0650        | 0.0541        | 0.1144          | 0.0485        | 0.0493 | 0.0529         |                 |
| **Et**         | -0.3121| 0.0170                 | -0.0138       | 0.0719        | 0.0485          | 0.0765        | 0.0576 | 0.0657         |                 |
| **Me**         | -0.3122| 0.0170                 | -0.0137       | 0.0714        | 0.0483          | 0.0764        | 0.0557 | 0.0646         |                 |
| **OMe**        | -0.2929| 0.0289                 | -0.0219       | 0.0714        | 0.0481          | 0.0957        | 0.0450 | 0.0742         |                 |
| **NMe\(_2\)** | -0.2566| 0.0474                 | -0.0601       | 0.0943        | 0.0197          | 0.1320        | 0.0503 | 0.0825         |                 |
| **TCE**        |         |                        |               |               |                 |              |        |                 | -0.3886        |

Tables 2 and 1(S) represent the calculated thermodynamic and kinetic parameters for different steps of mechanisms A and B, respectively. The calculated activation Gibbs energy (\( \Delta G^* \)) for step 1 of both mechanisms shows that mechanism B is not a favorable mechanism. Indeed, the nucleophilic character of the substituted arynes versus CO\(_2\) is substantially lower than that of imines. Therefore, the reaction progress through the nucleophilic addition of imines is the most probable mechanism.
Fig. 4 Donor (nucleophilic) Fukui functions isosurfaces and nucleophilicity indexes ($N_{i}$) (e) for C4 and C5 atoms at M06-2X/6-31+G(d,p) (Blue color) and M06-2X/6-311++G(2d,p) (Red color) levels.
| Steps | $\Delta G^1$ | $\Delta H^1$ | $\Delta S^1$ | $\Delta G^{21}$ | $\Delta G^1$ | $\Delta H^1$ | $\Delta S^1$ | $\Delta G^{21}$ | $\Delta G^1$ | $\Delta H^1$ | $\Delta S^1$ | $\Delta G^{21}$ |
|-------|-------------|-------------|-------------|----------------|-------------|-------------|-------------|----------------|-------------|-------------|-------------|----------------|
| 6-31+G(d,p) | -22.19 | -26.18 | -13.39 | 3.26 | -18.79 | -24.82 | -20.22 | 4.65 | -19.16 | -25.21 | -20.29 | 5.08 |
| 1A | -24.69 | -28.53 | -12.87 | 3.26 | -35.20 | -47.41 | -40.97 | - | -35.58 | -46.38 | -36.22 | -|
| 2A | -33.93 | -44.50 | -35.46 | - | -34.67 | -46.97 | -42.31 | - | -18.57 | -20.19 | -5.45 | 2.10 |
| 2A' | -31.94 | -42.91 | -36.79 | - | -19.21 | -19.84 | -2.11 | 1.77 | -19.21 | -20.31 | -3.69 | 1.97 |
| 3 re | -19.46 | -21.38 | -6.44 | 1.99 | -20.40 | -19.49 | 1.84 | 1.64 | -17.45 | -19.67 | -7.42 | 2.42 |
| si | -19.47 | -21.38 | -6.42 | 1.99 | -19.52 | -19.16 | 1.23 | 1.61 | -17.84 | -20.16 | -7.78 | 1.94 |
| 6-31++G(2d,p) | -20.11 | -25.64 | -18.55 | 4.15 | -17.12 | -19.90 | -9.34 | 4.28 | -19.02 | -21.88 | -9.60 | 3.81 |
| 1A | -22.36 | -27.94 | -18.69 | 3.38 | -17.82 | -20.28 | -8.27 | 5.37 | -19.09 | -21.90 | -9.44 | 3.75 |
| 2A | -31.09 | -41.55 | -35.09 | - | -33.08 | -43.73 | -35.72 | - | -34.57 | -43.72 | -30.70 | -|
| 2A' | -29.24 | -40.04 | -36.25 | - | -32.66 | -43.37 | -35.94 | - | -32.79 | -43.61 | -36.28 | -|
| 3 re | -18.03 | -20.38 | -7.88 | 2.40 | -17.82 | -19.71 | -6.31 | 2.76 | -15.71 | -19.34 | -12.17 | 4.58 |
| si | -18.03 | -20.38 | -7.88 | 2.40 | -17.82 | -19.70 | -6.32 | 2.46 | -16.12 | -19.31 | -10.70 | 4.50 |
| 3' re | -16.14 | -18.17 | -6.82 | 2.39 | -17.56 | -19.37 | -6.05 | 2.55 | -16.88 | -18.71 | -6.12 | 2.90 |
| si | -16.14 | -18.17 | -6.82 | 2.39 | -16.37 | -18.84 | -8.27 | 2.40 | -17.52 | -19.06 | -5.14 | 2.66 |
| Mechanism A | | | | | | | | | | | | |
| Cl | -23.42 | -26.84 | -11.48 | 3.40 | -20.90 | -24.37 | -11.62 | 4.09 | -26.37 | -28.00 | -5.44 | 3.37 |
| 6-31+G(d,p) | -25.44 | -28.86 | -11.45 | 1.78 | -23.02 | -26.38 | -11.27 | 3.38 | -26.32 | -27.87 | -5.18 | 2.17 |
| 1A | -32.08 | -43.59 | -38.59 | - | -35.59 | -46.96 | -38.14 | - | -28.73 | -39.57 | -36.33 | -|
| 2A | -30.55 | -41.93 | -38.17 | - | -34.42 | -45.76 | -38.04 | - | -29.41 | -39.75 | -34.68 | -|
| 2A' | -19.21 | -20.58 | -4.61 | 1.03 | -19.93 | -21.53 | -5.37 | 1.42 | -17.41 | -19.73 | -7.78 | 2.12 |
| 3 re | -19.21 | -20.58 | -4.60 | 1.03 | -19.93 | -21.53 | -5.36 | 1.42 | -17.41 | -19.72 | -7.77 | 4.95 |
| si | -18.28 | -19.84 | -5.22 | 1.56 | -15.07 | -17.30 | -7.47 | 2.25 | -20.95 | -23.93 | -10.00 | 2.55 |
| 3' re | -18.28 | -19.84 | -5.22 | 1.56 | -16.86 | -18.69 | -6.16 | 2.25 | -20.95 | -23.93 | -10.01 | 2.55 |
| NO2 | | | | | | | | | | | | |
| 6-31++G(2d,p) | -19.86 | -24.72 | -16.30 | 5.44 | -18.81 | -22.42 | -12.12 | 4.71 | -24.74 | -26.25 | -5.09 | 2.90 |
| 1A | -21.81 | -26.71 | -16.45 | 3.45 | -20.86 | -24.38 | -11.81 | 3.62 | -24.88 | -26.23 | -4.51 | 1.88 |
| 2A | -29.14 | -40.55 | -38.26 | - | -33.21 | -43.89 | -35.82 | - | -25.40 | -36.65 | -37.73 | -|
| 2A' | -28.19 | -39.32 | -37.33 | - | -31.63 | -42.66 | -37.01 | - | -24.77 | -36.69 | -39.96 | -|
| 3 re | -18.32 | -19.82 | -5.01 | 1.59 | -18.66 | -20.82 | -7.24 | 2.21 | -17.16 | -19.01 | -6.17 | 1.87 |
| si | -18.32 | -19.81 | -5.01 | 1.61 | -18.66 | -20.82 | -7.24 | 2.20 | -17.17 | -19.00 | -6.17 | 1.86 |
| 3' re | -16.82 | -18.57 | -5.87 | 2.53 | -14.29 | -16.73 | -8.19 | 2.35 | -21.38 | -23.16 | -5.95 | 1.12 |
| si | -16.82 | -18.57 | -5.87 | 2.53 | -15.98 | -18.05 | -6.95 | 2.36 | -21.39 | -23.16 | -5.92 | 1.14 |

1 kcal mol$^{-1}$
2 kcal mol$^{-1}$K$^{-1}$
Mechanism A proceeds through two barrier energies for the nucleophilic addition (Fig. 5). The first transition state (TS) is an intermolecular TS, in which a C-N bond is formed, gradually. However, the second TS, as an intramolecular interaction, includes a C-O bond development. To have an insight into the most effective TS in reaction kinetics, the Energetic Span Model (ESM) was used [50-52].

**Fig. 5** C-N and C-O bond development during the reaction progress through TS1 and TS2 of mechanism A, respectively.

ESM is a powerful concept to describe the kinetic aspects of mechanism A. This model is applied to connect the energy profile acquired from the electronic-structure calculations to the turnover frequency (TOF) as an experimentally accessible quantity. TOF is described as the number of the productive cycles (N) per catalyst unit \([C_t]\) and time \((t)\) as illustrated in Eq (4) [53-56].

\[
TOF = \frac{1}{[C_t]} \frac{dN}{dt} \quad Eq(4)
\]

ESM significantly allows the estimation of TOF of each considered route within determining the most effective TS and intermediate on the kinetic aspects of the reaction in the studied mechanism. Based on the Kozuch and Shaik report [53], TOF is evaluated by Eq (5).
\[
\text{TOF} = \frac{k_B T}{h} \cdot \frac{e^{-\Delta G_r/RT} - 1}{\sum_{i,j} e^{(T_i-I_j-\delta G'_{i,j})/RT}} \quad \text{Eq}(5)
\]

Where, \(\Delta G_r\) is the overall reaction Gibbs energy, and \(T_i\) and \(I_j\) are the energies of the \(i\)th TS and the \(j\)th intermediate (In) in each step, respectively. \(k_B\) and \(h\) are the Boltzmann and Planck constants, respectively. \(R\) is the gas constant (1.98 cal mol\(^{-1}\)·K\(^{-1}\)), and \(T\) is the absolute temperature (298.15 K). According to Eq (6), \(\delta G'_{i,j}\) is equal to zero or \(\Delta G_r\).

\[
\delta G'_{i,j} = \begin{cases} 
\Delta G_r & \text{if } i \geq j \\
0 & \text{if } i < j
\end{cases} \quad \text{Eq}(6)
\]

All the TSs and intermediates of a given reaction have not the same effect on the TOF of the reaction. Degree of TOF control (\(X_{\text{TOF}}\)) is used to specify the effect of each In and TS on the TOF in ESM to evaluate the TOF determining intermediate (TDI) and the TOF determining transition state (TDTS). Campbell’s degree of rate control is a concept that develops the \(X_{\text{TOF}}\) [57,58], which measures the variation of TOF value by a small change in the TS or In energies. It can be calculated by Eq (7) [53].

\[
X_{\text{TOF},T_i} = \frac{\sum_{j} e^{(T_i-I_j-\delta G'_{i,j})/RT}}{\sum_{i,j} e^{(T_i-I_j-\delta G'_{i,j})/RT}}
\]

\[
X_{\text{TOF},I_j} = \frac{\sum_{i} e^{(T_i-I_j-\delta G'_{i,j})/RT}}{\sum_{i,j} e^{(T_i-I_j-\delta G'_{i,j})/RT}} \quad \text{Eq}(7)
\]

\[
\sum_i X_{\text{TOF},T_i} = 1 \quad \sum_j X_{\text{TOF},I_j} = 1
\]

After that TDI and TDTS are evaluated, TOF equation (Eq (5)) can be abbreviated as Eq (8) in which, \(\delta E\) is the energetic span of the route.

\[
\text{TOF} = \frac{k_B T}{h} \cdot e^{-\delta E/RT} \quad \text{Eq}(8)
\]

\[
\delta E = \begin{cases} 
T_{\text{TDTS}} - I_{\text{TDI}} & \text{if TDTS occurs after TDI} \\
T_{\text{TDTS}} - I_{\text{TDI}} + \Delta G_r & \text{if TDTS occurs before TDI}
\end{cases} \quad \text{Eq}(9)
\]
Table 3 represents the $X_{\text{TOF}}$ values for the involved TSs and intermediates for all steps of mechanism A and Fig. 6 depicts the Potential Energy Diagram (PED) for the reaction of Et-substituted aryne, as an example. Also, Fig. 7 depicts the involved species in the reaction. The obtained $X_{\text{TOF}}$ values for the TS and intermediate of step 1 are larger than others. Step 1 plays a key role in the TOF of the reaction, which means that In0 and TS1 of both routes are TDI and TDTS of the reaction for all studied groups, respectively. Since TDTS occurs after TDI, $\delta E$ is calculated by Eq (8-a). Table 4 shows the relative energy of the involved species, $\delta E$ (kcal.mol$^{-1}$) and TOF (s$^{-1}$) values in which the summation of the absolute energies of aryne, CO$_2$ and imine molecules was considered as the energy reference.

The comparison of the barrier energies related to the C-N and C-O bond developments through the ESM reveals the greater effect of the C-N bond formation in the reaction kinetics. Thus the effect of the functional groups on the barrier energy of step 1, as the TDTS of the reaction, is more considerable than step 2. Two distinguishable trends are observed in the TDTS energy values. Generally, TDTS energies for electron-releasing groups are larger than that of electron-withdrawing ones. ELF is a powerful concept for explaining the observed TDTS energy trend of the substituted groups.
| Table 3 Degree of TOF control ($X_{TOF}$) of the possible reaction routes for all functional groups in both calculated levels |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Et | Me | Cl | NMe₂ |
| **Steps** | **In** | **$X_{TOF,j}$** | **TS** | **$X_{TOF,ti}$** | **In** | **$X_{TOF,j}$** | **TS** | **$X_{TOF,ti}$** | **In** | **$X_{TOF,j}$** | **TS** | **$X_{TOF,ti}$** |
| **Route A 6-31+G(d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.99 | TS1 | 0.99 | In0 | 1.00 | TS1 | 1.00 | In0 | 0.98 | TS1 | 0.98 |
| 2A | In1A | 0.00 | TS2-re | 0.00 | In1A | 0.00 | TS2-re | 0.00 | In2 | 0.07 | TS2-re | 0.07 |
| 3 | In2 | 0.01 | TS2-re | 0.01 | In2 | 0.07 | TS2-re | 0.07 | In2 | 0.07 | TS2-re | 0.07 |
| **Route A' 6-311++G(2d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.99 | TS1' | 0.99 | In0 | 1.00 | TS1' | 1.00 | In0 | 0.58 | TS1' | 0.58 |
| 2A | In2A | 0.00 | TS2-re | 0.00 | In2A | 0.00 | TS2-re | 0.00 | In2 | 0.42 | TS2-re | 0.42 |
| 3 | In2' | 0.01 | TS2-re | 0.01 | In2' | 0.42 | TS2-re | 0.42 | In2' | 0.01 | TS2-re | 0.01 |
| **Route A 6-31+G(d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.76 | TS1 | 0.76 | In0 | 0.96 | TS1 | 0.96 | In0 | 0.99 | TS1 | 0.99 |
| 2A | In1A | 0.00 | TS2-re | 0.00 | In1A | 0.00 | TS2-re | 0.00 | In2 | 0.00 | TS2-re | 0.00 |
| 3 | In2 | 0.24 | TS2-re | 0.24 | In2 | 0.04 | TS2-re | 0.04 | In2 | 0.01 | TS2-re | 0.01 |
| **Route A' 6-311++G(2d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.81 | TS1' | 0.81 | In0 | 0.99 | TS1' | 0.99 | In0 | 0.82 | TS1' | 0.82 |
| 2A | In2A | 0.00 | TS2-re | 0.00 | In2A | 0.00 | TS2-re | 0.00 | In2 | 0.01 | TS2-re | 0.01 |
| 3 | In2' | 0.19 | TS2-re | 0.19 | In2' | 0.01 | TS2-re | 0.01 | In2' | 0.01 | TS2-re | 0.01 |
| **Route A 6-31+G(d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.78 | TS1 | 0.78 | In0 | 0.99 | TS1 | 0.99 | In0 | 0.94 | TS1 | 0.94 |
| 2A | In1A | 0.00 | TS2-re | 0.00 | In1A | 0.00 | TS2-re | 0.00 | In2 | 0.06 | TS2-re | 0.06 |
| 3 | In2 | 0.22 | TS2-re | 0.22 | In2 | 0.06 | TS2-re | 0.06 | In2 | 0.01 | TS2-re | 0.01 |
| **Route A' 6-311++G(2d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.90 | TS1' | 0.90 | In0 | 0.64 | TS1' | 0.64 | In0 | 0.66 | TS1' | 0.66 |
| 2A | In2A | 0.00 | TS2-re | 0.00 | In2A | 0.00 | TS2-re | 0.00 | In2 | 0.34 | TS2-re | 0.34 |
| 3 | In2' | 0.09 | TS2-re | 0.09 | In2' | 0.34 | TS2-re | 0.34 | In2' | 0.13 | TS2-re | 0.13 |
| **Route A 6-31+G(d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.90 | TS1 | 0.90 | In0 | 0.94 | TS1 | 0.94 | In0 | 0.85 | TS1 | 0.85 |
| 2A | In1A | 0.00 | TS2-re | 0.00 | In1A | 0.00 | TS2-re | 0.00 | In2 | 0.15 | TS2-re | 0.15 |
| 3 | In2 | 0.09 | TS2-re | 0.09 | In2 | 0.15 | TS2-re | 0.15 | In2 | 0.01 | TS2-re | 0.01 |
| **Route A' 6-311++G(2d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.84 | TS1' | 0.84 | In0 | 0.55 | TS1' | 0.55 | In0 | 0.76 | TS1' | 0.76 |
| 2A | In2A | 0.00 | TS2-re | 0.00 | In2A | 0.00 | TS2-re | 0.00 | In2 | 0.55 | TS2-re | 0.55 |
| 3 | In2' | 0.16 | TS2-re | 0.16 | In2' | 0.44 | TS2-re | 0.44 | In2' | 0.24 | TS2-re | 0.24 |
| **Route A' 6-31+G(d,p)** | | | | | | | | | | | | |
| 1A | In0 | 0.55 | TS1' | 0.55 | In0 | 0.76 | TS1' | 0.76 | In0 | 0.89 | TS1' | 0.89 |
| 2A | In2A | 0.00 | TS2-re | 0.00 | In2A | 0.00 | TS2-re | 0.00 | In2 | 0.55 | TS2-re | 0.55 |
| 3 | In2' | 0.11 | TS2-re | 0.11 | In2' | 0.44 | TS2-re | 0.44 | In2' | 0.24 | TS2-re | 0.24 |
### Table 4 TDI, TDTS, $\delta E$ (in kcal.mol$^{-1}$) and TOF (s$^{-1}$) values of the studied functional groups

| G   | Routes | M06-2X/6-31+G(d,p) |       |       |       | M06-2X/6-311++G(2d,p) |       |       |       |
|-----|--------|-------------------|-------|-------|-------|-----------------------|-------|-------|-------|
|     |        | TDI (kcal.mol$^{-1}$) | TDTS (kcal.mol$^{-1}$) | $\delta E$ (kcal.mol$^{-1}$) | TOF (s$^{-1}$) | TDI (kcal.mol$^{-1}$) | TDTS (kcal.mol$^{-1}$) | $\delta E$ (kcal.mol$^{-1}$) | TOF (s$^{-1}$) |
| Et  | A      | 5.77              | 11.19 | 5.43  | 6.5×10$^8$ | 7.61                  | 11.42 | 4.50  | 2.4×10$^8$ |
|     | A'     | 5.77              | 10.96 | 5.19  | 9.7×10$^8$ | 7.61                  | 11.36 | 3.75  | 8.9×10$^9$ |
| Cl  | A      | 6.76              | 10.16 | 3.40  | 2.0×10$^{10}$ | 5.01                 | 10.44 | 5.44  | 6.4×10$^8$ |
|     | A'     | 6.76              | 8.55  | 1.78  | 1.8×10$^{11}$ | 5.01                 | 8.46  | 3.45  | 1.5×10$^{10}$ |
| F   | A      | 6.47              | 9.73  | 3.26  | 2.0×10$^{10}$ | 6.01                 | 10.16 | 4.15  | 5.1×10$^9$ |
|     | A'     | 6.47              | 9.73  | 3.26  | 2.3×10$^{10}$ | 6.01                 | 9.39  | 3.38  | 1.7×10$^{10}$ |
| Me  | A      | 5.51              | 10.16 | 4.65  | 2.4×10$^9$ | 6.04                  | 10.32 | 4.28  | 4.3×10$^9$ |
|     | A'     | 5.51              | 10.59 | 5.08  | 1.2×10$^{10}$ | 6.04                 | 11.41 | 5.37  | 7.1×10$^8$ |
| NMe$_2$ | A     | 6.59              | 10.56 | 3.97  | 7.6×10$^9$ | 6.28                  | 10.73 | 4.46  | 3.3×10$^9$ |
|     | A'     | 6.59              | 11.46 | 4.88  | 1.6×10$^9$ | 6.28                 | 11.71 | 5.43  | 6.4×10$^8$ |
| CN  | A      | 6.46              | 10.04 | 3.58  | 1.4×10$^{10}$ | 6.00                 | 10.20 | 4.20  | 4.9×10$^9$ |
|     | A'     | 6.46              | 8.01  | 1.56  | 2.9×10$^{11}$ | 6.00                 | 8.22  | 2.21  | 8.2×10$^{10}$ |
| NO$_2$ | A     | 5.47              | 7.65  | 4.95  | 1.4×10$^9$ | 5.86                 | 8.76  | 2.90  | 3.9×10$^{10}$ |
|     | A'     | 5.47              | 8.84  | 2.55  | 5.4×10$^{10}$ | 5.86                 | 7.75  | 1.88  | 2.0×10$^{11}$ |
| OMe | A      | 6.69              | 10.78 | 4.09  | 6.2×10$^9$ | 6.48                 | 11.18 | 4.71  | 2.2×10$^9$ |
|     | A'     | 6.69              | 10.07 | 3.38  | 1.8×10$^{10}$ | 6.48                 | 10.09 | 3.62  | 1.2×10$^{10}$ |

Fig. 7 Involved species in the reaction of Et-substituted aryne, as an example
ELF analysis is another molecular descriptor, which can be applied for justification of the nucleophilic attack of the imine to the substituted arynes [59-61]. ELF analysis generates basin spaces, in which the probability of electron pair existence in these spaces is maximal. Generally, the basins are divided into core and valence kinds. The latter is specified by the synaptic order, i.e., the number of atomic valence shells that they participate [62]. Therefore, three main monosynaptic, disynaptic, and trisynaptic basins are distinguishable. A monosynaptic basin, V(A), related to a lone pair or non-bonding regions on atom A, V(A,B) as a disynaptic basin refers to the core of two nuclei of A and B, which describes a bonding region between A and B. A trisynaptic basin, V(A,B,C), corresponds to a three-center bond and so on. ELF concept is similar to the Lewis bonding model that provides a graphical representation of the molecular system. Based on this concept, two monosynaptic basins, V(C_x) and V(C_y) are merged into a new disynaptic basin V(C_x,C_y), corresponding to the formation of the new single C_x–C_y bond [63,64].

Based on the ELF terminology, involved basins in the reaction for the substituted arynes are disynaptic basins C2-C3 (V(C2,C3)), C3-C4 (V(C3,C4)) and C4-C5 (V(C4,C5) bonds. Also, the nitrogen atom of the imine compound has a monosynaptic basin, V(N). In TS1 and TS1’, the electron density of V(N) basin decreases and the disynaptic basin (V(C,N)) corresponding to the C-N bond is developed, gradually. Fig. 8 and Table 5 represent the involved basins in the reaction and their calculated electron density for steps 1A and 1A’, respectively.

Fig. 8 The position of the participating basins in the first steps of both routes in mechanism A
The reaction progress from the reactants to the TS1 and TS1' is followed by decreasing the electron density of V(C₄,C₅) and V(C₂,C₃) basins and increasing that for V(C₃,C₄) basin. Also, monosynaptic basins V(C₄) and V(C₃) corresponding to TS1 and TS1' are developed on the related carbon atoms, respectively. In the case of TS1', a good linear correlation can be seen between ΔG° values of TDSTs and the electron density of monosynaptic basin V(C₃). However, in TS1, the correlation for V(C₄) electron density values is not acceptable (Fig. 9). The difference between the electron densities of V(C₄,C₅) basins in arynes and TS1(ΔV(C₄,C₅)) is greater than that of V(C₂,C₃) basin in arynes and TS1' (ΔV(C₂,C₃)). As a result, in comparison to the nucleophilic addition of the imine...
to C4 in TS1', the addition to C3 atom in TS1 causes a larger decline in the electron densities of V(C4,C5) basins, making a significant electron density development for V(C4) basin. This addition to C4 atom results in a lower electron density growth for V(C3) basin.

**Fig. 9** Linear correlation between the electron density of V(C4) and V(C3) basins and $\Delta G^\neq$ of TDSTs

ELF analysis is followed by an evaluation of the electron density of the C1-G basin, in which G and C1 are the bonded atoms of the substituents to the aryne ring and carbon atom of the ring, respectively. Fig. 9 depicts the electron density contributions of the C1 and G atoms in the total electron density of C1-G basins (V(C1,G)) for both TS1 and TS1'. The obtained results show that in the nucleophilic addition to C3 atom (TS1), the contribution of C1 in electron density of V(C1,G) is greater than that of in the addition to C4 atom (TS1'). Also, the developed natural charge on the C4 atom in TS1 is more significant than the C3 natural charge in TS1'(Fig. 10). This can be related to the larger electron density of V(C4,C5) basins decreasing along the TS1 than that of V(C2,C3) basins in the TS1'. On the other hand, C4 and C3 atoms are in para and meta positions relative to substituted groups in TS1 and TS1', respectively. It seems that more effective interaction of developing electron density on C4 atom in para position with the substituted groups (G) causes further natural charge growth on this atom, indeed the substituted groups have more significant effects on the electron density of C4 atoms at TS1. These effects can be considered as a mixture of inductive and resonance effects. The poor linear correlation between $\Delta G^\neq$ values of the TDSTs and electron densities of V(C4) basin may be owning to these different effects.
of the substituents on the C4 position. Finally, in the case of In1A and In2A, the electron density of V(C₃,N) basins is somewhat greater than V(C₄,N).

Fig. 10 The electron density contributions (in a.u) of C1 (in green color) and G (in purple color) atoms in V(C₁,G) basins for both TS1 and TS1' and developed natural charges on C3 and C4 atoms at 6-31+G(d,p) (Blue color) and 6-311++G(2d,p) (Red color) levels (Hydrogen atoms have been omitted for more clarity)
Conclusion

Benzoxazinone formation by CO₂ incorporation can proceed through two mechanisms. In mechanism A, which is initiated by addition to the substituted arynes, the imine compound behaves as the nucleophile, while, in mechanism B the reaction is started by the nucleophilic addition of arynes to CO₂. The calculated results at M06-2X/6-31+G(d,p) and M06-2X/6-311++G(2d,p) levels showed that mechanism B proceeds within the large values of activation barrier energy in the first step. Generally, four stereoisomers can be considered for the final product. The results of X_TOF analyses in ESM reveal that TS1 and TS1' are TDTS of routes A and A', respectively. Also, In0 is considered as the TDI for both routes. ELF analysis was used to investigate the calculated TDTS energy trends. The reaction in step1 and 1' is followed by the electron densities of V(C₄) and V(C₃) basin development corresponding to the TS1 and TS1', respectively, which accomplishes by decreasing the electron density of V(C₄,C₅) and V(C₂,C₃) basins and increasing that for V(C₃,C₄) basin in TS1 and TS1', respectively. Therefore, the variation of V(C₄,C₅) and V(C₂,C₃) along with the reaction progress from the substituted arynes to the TSs has a remarkable effect on the electron densities of V(C₄) and V(C₃) basins. A good linear correlation can be seen between the TDTS energy values and V(C₃) electron densities. Nonetheless, this correlation was not considered for TS1. Furthermore, the greater contribution of C1 atom of arynes in the electron density of V(C₁,G) basin at TS1 than TS1' was another consequence of ELF analysis, which reveals that the interactions of the substituents groups and aryne ring in TS1 and TS1' are different, significantly.

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Availability of data and material The authors confirm that the data supporting the findings of this study are available within the supporting information as a separated word file includes Tables and Cartesian coordinates of the molecules.

Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.
**Ethical approval** This article does not contain any studies with human participants or animals performed by any of the authors.

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Figures

Figure 1

The overall reaction, and the substituted arynes, within atom numbering for the involved atoms in the reaction.
Two possible mechanisms: mechanism A (blue lines) and mechanism B (red lines). Black lines illustrate the common steps of both mechanisms.
Figure 3

Different nucleophile approaching modes in steps 3 and 3’
Figure 4

Donor (nucleophilic) Fukui functions isosurfaces and nucleophilicity indexes (Nk) (e) for C4 and C5 atoms at M06-2X/6-31+G(d,p) (Blue color) and M06-2X/6-311++G(2d,p) (Red color) levels.
Figure 5

C-N and C-O bond development during the reaction progress through TS1 and TS2 of mechanism A, respectively.
Figure 6

Potential Energy Diagram (PED) for the reaction of Et-substituted aryne
Figure 7
Involved species in the reaction of Et-substituted aryne, as an example

Figure 8
The position of the participating basins in the first steps of both routes in mechanism A
Figure 9

Linear correlation between the electron density of V(C4) and V(C3) basins and ΔG≠ of TDSTs
Figure 10

The electron density contributions (in a.u) of C1 (in green color) and G (in purple color) atoms in V(C1, G) basins for both TS1 and TS1' and developed natural charges on C3 and C4 atoms at 6-31+G(d,p) (Blue color) and 6-311++G(2d,p) (Red color) levels (Hydrogen atoms have been omitted for more clarity)

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