Functionalized Nano Graphene Platelets as Green Catalyst to Synthesize New and Known Benzoyl-1,4-diazanaphthalene and Study of Their Local Aromaticity

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\textbf{ABSTRACT}

Functionalized graphene has been prepared and employed for the solvent-free synthesis of some novel and known benzoyl-1,4-diazanaphthalene from the condensation of various arylglyoxals with 4-benzoyl-1,2-phenylenediamine. Catalyst loads as low as 0.003 g could be used leading to high yields of pure products. Magnetic, geometry, and electronically based indices have been also employed to investigate the correlation between aromaticity variation in new formed ring (ring A) and yield of reaction.

\textbf{Introduction}

Synthesis of aromatic diazanaphthalenes such as quinoxalines, quinazolines, and quinolines has remained the goal of many research groups over the years because of their wide range of applications (1–3). The general method for the synthesis of quinoxalines is the condensation of 1,2-aryldiamines with 1,2-dicarbonyl compounds under reflux in ethanol as solvent and in using acetic acid (4) as catalyst. However, several methods have been recently developed for the synthesis of this class of 1,4-diazanaphthalenes (quinoxalines) based on the condensation of aryl diamines with 1,2-dicarbonyl/\(\alpha\)-bromoketone/\(\alpha\)-hydroxyketone compounds using various reagents (5–10).

Nanocatalysts emerged as a sustainable alternative to the conventional catalysts (11). Although various catalysts have been used in chemical reactions, the metal-free catalysts like graphene oxide (GO) is emerging as a new class of carbocatalysts due to its special features including stability, safety, insolubility in common solvents, and recyclability (12–14). Herein, a new and simple route to benzoylquinazolines using GO catalyst is described.

From another point of view, the relation between yield of reaction and aromaticity degree of the new ring formed during cyclization has been also investigated. Aromaticity is considered as one of the most important concepts (15–8) to predict behavior that in turn helps to design useful materials which have not been prepared previously (19). Turning to heterocyclic compounds, the importance of the concept of aromaticity is even greater (20, 21) In our research, we have concentrated on results obtained by means of accepted definitions of
aromaticity refer to magnetic, geometry, and electronically based indices presented in most aromatic species, which are briefly introduced later. Our aim is to study the relation between yield of reaction and degree of aromaticity of new ring formed during cyclization in synthesize of some derivatives of benzoyl quinoxaline.

**Results and discussion**

According to Scheme 1, the modified Hummers method was employed for the preparation of graphene oxide (GO). The acidic and oxidative nature of the oxygen functionalities allows it to act as a solid acid or green oxidant.

As can be seen in Figure 1A, the scanning electron microscopy (SEM) shows the morphology of the GO nanoplatelets. Crumpled thin layers with wrinkles and folds on the surface of GO is well observed. Figure 1B shows the XRD pattern of the GO in its dry state. In the XRD pattern, the clear diffraction bands are centered at $2\theta \sim 101$ corresponding to the (002) plane of the GO.

In continuation of our study on developing green methodologies (22–24), we have now found that the GO can be used as an efficient catalyst for the condensation of 4-benzoyl-1,2-phenylenediamine (1) with aryl glyoxales 2 at room temperature to afford benzoylquinoxalines 3 (Scheme 2).

**Scheme 1.** Synthesis of geraphene oxide.

**Scheme 2.** Synthesis of benzoylquinoxalines using GO.
For establishing the simple and suitable conditions to prepare corresponding quinoxaline derivatives using GO, the treatment of 1 with phenyl glyoxal (2a) was chosen as a model. During the optimization experiments including several catalyst amounts and solvents, it was observed that the condensation reaction can be efficiently carried out under solvent-free conditions by adding 0.003 g of GO as catalyst in a short time span of 14 min. The use of excess amounts of the catalyst does not show marked influence on the product yield.

In order to prove the general applicability of this method, after optimizing the reaction conditions, we have treated 1 with aryl glyoxals 2. The results are summarized in Table 1.

Although the generally mechanistic details of this reaction have not been fully proved, a feasible pathway, as indicated in Scheme 3, might involve the activation of the carbon joined to hydroxyl groups by acidic protons of GO followed by catalyzed N-C coupling. The irreversibility of the reaction implies that reaction product is thermodynamically stable. However, the driving force for all of these reactions is cycloaromatization.

Since GO is insoluble in water, they can be recovered through filtration after the catalytic reaction and is also reusable. Hence, this catalyst is expected to contribute to green and sustainable innovation. To investigate the recyclability of GO in the model reaction, the catalyst was reused for five cycles without significant loss in activity (Figure 2).

Quantitative study on local aromaticity has been performed on new aromatic ring formed during cyclization in benzoylquinoxaline derivatives (labeled as ringA in Figure 3.) For this purpose it is used some quantitative descriptors including magnetic index (NICS), geometry-based index (HOMA) and electronically indices (PDI and FLU) to study the correlation between the local aromaticity in this ring and yield of reaction. The analyses were carried out by comparing the aromaticity of ring(A) obtained from different derivatives of aryl glyoxal containing typical substituents with different behavior in inductive (F) and resonance (R) effect (such as NO$_2$, Cl, F, and OCH$_3$).

Table 2 lists data for quantitative measures of aromaticity of ring(A). It would be mentioned that using different derivatives of aryl glyoxal may have influence on $\pi$-electron delocalization in ring(A) as well as violation of symmetry of $\pi$-electron density distribution in this ring which may be caused by substitution of the carbon atom by a nitrogen atom.

All used indices indicate a good correlation between variation of aromaticity of ring(A) and yield of reaction by the use of aryl glyoxal bearing different substituents (Table 3). It means that increase in the yield of reaction due to use of aryl glyoxal containing withdrawing substituent can be accompanied with more aromatic character in ring(A). Contrary electron-donating substituent with strong resonance power leads to decrease in the yield of reaction which can be along with reduction in aromaticity of ring(A). Moreover, Table 3 presents correlations between data from different indices (such as HOMA, PDI, FLU, and NICS) used for study of the local aromaticity of ring(A). A good correlation coefficients (R) can be observed between two electronically-based index (R = 0.94) as well as good correlation between HOMA and PDI values (R = 0.95). Also, both data from geometry and electronically based indices correlate better with NICS values than with NICS(1). It should be noted that a high correlation may be related to HOMA vs. NICS values in this system (R = 0.98).

**Experimental**

**Materials and instruments**

Chemicals were purchased from Aldrich. Aryl glyoxals have been synthesized according to previous report (25). GO was prepared using modified Hummers method from flake graphite.
Table 1. Synthesis of benzoyl-1,4-diazanaphthalene using GO.

| Entry | Product | Time (min) | Yield\(^a\)(%) |
|-------|---------|------------|----------------|
| 3a    | ![Product](image1) | 14 | 89 |
| 3b    | ![Product](image2) | 7 | 98 |
| 3c    | ![Product](image3) | 12 | 94 |
| 3d    | ![Product](image4) | 10 | 85 |
| 3e    | ![Product](image5) | 12 | 87 |
| 3f    | ![Product](image6) | 15 | 90 |
| 3g    | ![Product](image7) | 12 | 90 |
| 3h    | ![Product](image8) | 9 | 95 |
| 3i    | ![Product](image9) | 12 | 93 |
| 3j    | ![Product](image10) | 10 | 96 |

\(^a\) Isolated yields.
Scheme 3. Suggested mechanism for the synthesis of benzoyl-1,4-diazanaphthalene 3 using GO catalyst.

(Merck Company). The reactions were monitored by thin layer chromatography (TLC; silica-gel 60 F$_{254}$, n-hexane: ethyl acetate). IR spectra were recorded on a FT-IR JASCO-680 and the $^1$H NMR spectra were obtained on a Bruker-Instrument DPX-400 MHz Avance 2 model. SEM studies of the nanostructures were carried out with a JEOL JEM 3010 instrument operating at an accelerating voltage of 300 kV. X-Ray diffraction (XRD, D8, Advance, Bruker, AXS) patterns were obtained for characterization of the heterogeneous catalyst. Melting points were measured on an electrothermal KSB1N apparatus.

**Computational details**

The calculations carried out in these researches have been done with GAUSSIAN03 program (26). The molecular geometries of all diamine rings have been fully optimized at B3LYP level of theory and 6–311+G** basis set. Each stationary point was then characterized at the same level of theory by computing the vibrational frequencies within the harmonic approximation to make sure that the resulting structures were the minima. Moreover, their wave functions at the same level of theory have been used to characterize topological properties of the electronic charge density. The AIM2000 package (27) was employed for computing the atomic overlap
matrices (AOM) and delocalization indices. The values of \( \delta_{\text{ref}} \) (C-C) in benzene and \( \delta_{\text{ref}} \) (C-N) in pyridine were calculated at the B3LYP/6–311++G** level of theory to be 1.395e 1.310e, respectively.

**Harmonic oscillator model of aromaticity (HOMA)**

The geometry-based index for calculation of aromaticity which is known as (HOMA) defined by as follows (28–30):

\[
\text{HOMA} = 1 - \frac{\alpha}{n} \sum \left( R_{\text{opt}} - R_i \right)^2
\]

where \( n \) is the number of bonds taken into account; \( \alpha \) is a normalization factor equal to 257.7 or 93.52 for CC or CN bond respectively (it is fixed to give HOMA = 0 for a model non-aromatic system and 1 for the system with all bonds equal to the optimal value) \( R_{\text{opt}} \) - which is assumed to be realized when full delocalization of \( \pi \)-electrons occurs (\( R_{\text{opt}} = 1.388 \) or \( R_{\text{opt}} = 1.334 \) for CC or CN bonds, respectively) and \( R_i \) stands for a running bond length.

**Table 2.** HOMA, PDI, FLU, NICS, NICS(1), and NICS(1)\(_{\text{zz}} \) values for ring(A) and yield of reaction in some derivatives of benzoyl quinoxaline.

| X      | Ring | HOMA | PDI  | FLU  | NICS | NICS(1) | NICS(1)\(_{\text{zz}} \) | Yield |
|--------|------|------|------|------|------|---------|-----------------|------|
| 4NO\(_2\) | (A)  | 0.810 | 0.0720 | 0.0200 | -4.8 | -10.2 | -24.8 | 98   |
| 3NO\(_2\) | (A)  | 0.808 | 0.0710 | 0.0204 | -4.8 | -10.2 | -24.2 | 94   |
| 4Cl    | (A)  | 0.801 | 0.0708 | 0.0207 | -4.5 | -10.1 | -24.4 | 90   |
| 4F     | (A)  | 0.800 | 0.0707 | 0.0208 | -4.5 | -10.1 | -24.2 | 90   |
| 3OCH\(_3\) | (A) | 0.795 | 0.0700 | 0.0211 | -4.4 | -9.6 | -23.6 | 87   |
| 4OCH\(_3\) | (A) | 0.790 | 0.0690 | 0.0231 | -4.1 | -9.7 | -23.4 | 85   |
Table 3. Correlation coefficients and regressions between HOMA, PDI, FLU, NICS, NICS(1), NICS(1)_{ZZ} values for ring(A) and yield of reaction and correlation coefficients between data from different aromaticity indices in some derivatives of benzoyl quinoxaline.

| HOMA vs. Yield | PDI vs. Yield | FLU vs. Yield | NICS vs. Yield | NICS(1) vs. Yield | NICS(1)_{ZZ} vs. Yield |
|----------------|--------------|---------------|----------------|-------------------|------------------------|
| \( y = 606.73 \) | \( y = 4454.6 \) | \( y = -3599.4 \) | \( y = -16.75 \) | \( y = -13.87 \) | \( y = -8.21 \) |
| \( x = -395.12 \) | \( x = -223.76 \) | \( x = 166.31 \) | \( x = 15.029 \) | \( x = -47.581 \) | \( x = -107.17 \) |
| \( R = 0.97 \) | \( R = 0.95 \) | \( R = 0.83 \) | \( R = 0.94 \) | \( R = 0.84 \) | \( R = 0.90 \) |

| PDI vs. FLU | PDI vs. NICS | PDI vs. NICS(1) | PDI vs. NICS(1)_{ZZ} |
|--------------|--------------|----------------|----------------------|
| \( y = 0.1269 \) | \( y = -0.1276 \) | \( y = -34.223 \) | \( y = -30.51 \) |
| \( x = 0.031 \) | \( x = 0.123 \) | \( x = 22.884 \) | \( x = 14.445 \) |
| \( R = 0.95 \) | \( R = 0.89 \) | \( R = 0.98 \) | \( R = 0.88 \) |

| FLU vs. NICS | FLU vs. NICS(1) | FLU vs. NICS(1)_{ZZ} |
|--------------|----------------|----------------------|
| \( y = 225.39 \) | \( y = 175.74 \) | \( y = 404.51 \) |
| \( x = -9.254 \) | \( x = -13.677 \) | \( x = -32.602 \) |
| \( R = 0.93 \) | \( R = 0.72 \) | \( R = 0.85 \) |

**Quantitative descriptors of \( \pi \)-electron delocalization**

Two-center delocalization index \( \delta (A, B) \) is defined from the double integration of the exchange-correlation density over the atomic basins (31, 32). The term \( \delta (A, B) \) is a quantitative measure of the number of electrons delocalized or shared between atomic basins \( A \) and \( B \). For a closed shell system the delocalization index can be expressed as

\[
\delta(A, B) = \sum_{i,j} 4 S_{ij}^A S_{ji}^B
\]

where \( S_{ij}^A \) is the overlap between doubly occupied orbitals \( i \) and \( j \) over the basin of atom \( A \).

Para delocalization index (PDI) is proposed as the average of delocalization indices of para related atoms in a given six-membered ring (33),

\[
PDI = \frac{\delta (1, 4) + \delta (2, 5) + \delta (3, 6)}{3}
\]

The aromatic fluctuation index (FLU) is based on the fact that aromaticity is related to the cyclic delocalized circulation of \( \pi \)-electrons and it is constructed not only by considering the amount of electron sharing between contiguous atoms, which should be substantial in aromatic molecules, but also taking into account the similarity of electron sharing between adjacent atoms (34, 35). FLU is defined as

\[
FLU = \frac{1}{n} \sum_{A-B} \left( \frac{V(B)}{V(A)} \right)^\alpha \left( \frac{\delta(A, B) - \delta_{ref}(A, B)}{\delta_{ref}(A, B)} \right)^2
\]

where the summation runs over all adjacent pairs of atoms around ring, \( n \) equals the number of atoms of the ring, and \( V(A) \) is the global delocalization of atom \( A \):

\[
V(A) = \sum_{B \neq A} \delta(A, B)
\]
\( \delta(A, B) \) and \( \delta_{\text{ref}}(A, B) \) are the delocalization indices for the atomic pairs of \( A \) and \( B \) and its reference value, respectively, and \( \alpha \) is a simple function to ensure the first term in is always greater or equal to 1,

\[
\alpha = \begin{cases} 
1, & V(B) > V(A) \\ 
-1, & V(B) \leq V(A) 
\end{cases}
\]

**Nucleus independent chemical shift (NICS)**

The magnetic index (36) have been used as successful index in describing the aromatic character of heterocyclic system (37–39) for calculation of aromaticity in ring(A). NICS has been defined as the negative value of the absolute shielding computed at the geometric center of a ring system. Rings with negative NICS values qualify as aromatic, and the more negative the NICS value, the more aromatic are the rings. The values calculated at 1 Å are denoted as NICS (1), whereas the component of NICS (1) corresponding to the principal axis perpendicular to the ring plane is denoted as NICS (1)zz (40).

**Preparation of GO catalyst**

A flask containing graphite (1 g) and NaNO\(_3\) (0.75 g) was placed in an ice-water bath. H\(_2\)SO\(_4\) (75 mL) was added with stirring and then KMnO\(_4\) (4.5 g) was slowly added over about 1 h. After vigorously stirring for 5 days at room temperature, 5% H\(_2\)SO\(_4\) (140 mL) aqueous solution was added over about 1 h with stirring, and the temperature was kept at 98°C. The temperature was reduced to 60°C, 3mL of H\(_2\)O\(_2\) (30 wt% aqueous solution) was added, and the mixture was stirred for 2 h at room temperature. As prepared, GO was suspended in ultrapure water to give a brown dispersion, which was subjected to dialysis to completely remove residual salts and acids. The resulting purified GO powders were collected by centrifugation and air-dried. GO powders were dispersed in water to create a 0.05 wt% dispersion. The dispersion was then exfoliated through ultrasonication for 1 h, which the bulk GO powders were transformed into GO nanoplatelets.

**General procedure for the synthesis of 3 using GO**

A mixture of aryl glyoxal (1 mmol), 4-benzoyl-1,2-phenylenediamine (1.1 mmol), and GO (0.003 g) was grounded at room temperature. The progress of the reaction was monitored by TLC (hexane/EtOAc, 7:3). After the completion of the reaction, the solid was dissolved in hot EtOH and filtered to separate the catalyst. Pure product 3 was obtained by recrystallization from EtOH.

**Spectral data for novel compounds**

2-(4-Nitrophenyl)-6-benzoylquinoxaline (3b)

IR (KBr) cm\(^{-1}\): 3070, 1651, 1534, 1600, 1349, 1298; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta = 9.40 \) (s, 1H), 8.45–8.38 (m, 5H), 8.23 (s, 2H), 7.83 (s, 2H), 7.59 (s, 1H), 7.48 (s, 2H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): \( \delta = 195.4, 150.7, 149.1, 143.8, 142.0, 141.2, 138.9, 136.9, 133.1, 132.2, 130.8, 130.3, 130.1, 130.0, 128.6, 124.4; \) Anal. Calcd for C\(_{21}\)H\(_{13}\)N\(_3\)O\(_3\): C, 70.98; H, 3.69; N, 11.83; O, 13.51. Found: C, 71.15; H, 3.61; N, 11.98.
2-(4-Methoxyphenyl)-6-benzoylquinoxaline (3d)
IR (KBr) cm⁻¹: 3050, 2970, 1650, 1598, 1297; ¹H NMR (400 MHz, CDCl₃): δ = 9.30 (s, 1H), 8.39 (s, 1H), 8.16 (s, 4H), 7.82 (d, 2H, J = 7.2 Hz), 7.57 (t, 1H, J = 7.6 Hz), 7.46 (t, 2H, J = 7.6 Hz), 7.02 (d, 2H, J = 8.4 Hz); ¹³C NMR (100 MHz, CDCl₃): δ = 195.6, 162.1, 152.8, 144.2, 144.1, 140.1, 137.4, 137.2, 132.8, 132.3, 130.2, 130.1, 129.8, 129.4, 128.6, 128.5, 114.8, 55.5; Anal. Calcd for C₂₂H₁₆N₂O₂: C, 77.63; H, 4.74; N, 8.23. Found: C, 77.80; H, 4.88; N, 8.37.

2-(4-Chlorophenyl)-6-benzoylquinoxaline (3g)
IR (KBr) cm⁻¹: 3100, 1649, 1597, 1300; ¹H NMR (400 MHz, CDCl₃): δ = 9.32 (s, 1H), 8.42 (s, 1H), 8.16 (d, 4H, J = 7.6 Hz), 7.82 (s, 2H), 7.57–7.40 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ = 195.5, 152.1, 150.2, 144.1, 144.07, 144.04, 143.1, 137.3, 132.9, 132.3, 130.4, 130.2, 130.1, 129.6, 129.0, 128.6; Anal. Calcd for C₂₁H₁₃ClN₂O: C, 73.15; H, 3.80; N, 8.12. Found: C, 73.25; H, 3.71; N, 8.17.

2-(4-Fluorophenyl)-6-benzoylquinoxaline (3f)
IR (KBr) cm⁻¹: 3092, 1651, 1598, 1298; ¹H NMR (400 MHz, CDCl₃): δ = 9.30 (s, 1H), 8.42 (s, 1H), 8.18 (s, 4H), 7.82 (d, 2H, J = 8.8 Hz), 7.56 (d, 1H, J = 8.6 Hz), 7.47 (d, 2H, J = 8.4 Hz), 7.20 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): 195.6, 166.3, 152.2, 144.1, 140.5, 138.0, 137.1, 132.9, 132.3, 130.4, 130.2, 130.0, 129.9, 129.8, 128.5, 116.6, 116.3; Anal. Calcd for C₂₁H₁₃FN₂O: C, 76.82; H, 3.99; N, 8.53. Found: C, 76.90; H, 3.81; N, 8.57.

Conclusion
In conclusion, we have devised efficient synthetic approaches for the synthesis of some benzoyl-1,4-diazanaphthalene. The condensation has been proficiently performed under solvent-free conditions using graphene oxide nanoplatelate. Mild reaction conditions, operational simplicity, catalyst recyclability, avoidance of solvent, and high isolated yields of pure products offer suitable prospects for the industrial applicability of the present protocol. In addition, magnetic, geometry, and electronically based indices have been employed to investigate the correlation between aromaticity variation in new formed ring (A) and yield of reaction. It has been shown that all used indices can reasonably describe that maximum aromaticity is characterized when aryl glyoxal with electron accepting substituents is used as percursor in synthesise of benzoylquinoxalines. It can be concluded that change in yield of reaction, which are affected by the consequences of substituent effect in aryl glyoxal, may be as a result of perturbation in π-electron delocalization and shift in degree of aromaticity of ring A in these reactions. Generally, good correlations are also exist between data resulted from different aromaticity indices.

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