Density Functional Study on the Adsorption of 5-Membered N-Heterocycles on B/N/BN-Doped Graphene: Coronene as a Model System

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Supporting Information

ABSTRACT: Adsorption of seven 5-membered N-heterocycles on B/N/BN-doped graphene (with coronene as a model system) has been studied using density functional theory (DFT). The geometry of the complexes validated the involvement of both π···π stacking and N–H···π interaction in the adsorption process. The stability of the complexes is measured in terms of stabilization energy, and the results suggested that the complexes are stable enough (stabilization energies are in the range of 7.61–14.77 kcal mol⁻¹). Studies confirmed the stability of complexes in the solvent phase too irrespective of the dielectric of the solvent. Dispersive force is the major mode of interaction in stabilizing the complexes. Natural bond orbital analysis indicated a small contribution from electrostatic and covalent interactions. Thermochemical analysis revealed that the complexation is exothermic in nature and favorable at a lower temperature. Adsorption of N-heterocycles exerts a nominal impact on the electronic properties of the undoped/doped graphene. The study presents a simple approach to introduce an arbitrary functionality to undoped/doped graphene by preserving its electronic properties.

1. INTRODUCTION

Graphene is a tri-coordinated two-dimensional (2D) material, which possesses extraordinary thermal, mechanical, electrical, and optical properties.† These properties have triggered tremendous interest in scientific communities toward its application in the field of nanophotonics, nanoelectronics, nanocomposites, biosensors, drug delivery, and many more.‡–§ Apart from these, different groups are also associated with its application in environment pollution remediation, which is one of the most pressing and current issues.‖ To have full potential of the aforesaid applications, adequate procedures and approaches are desired for exploring graphene in nanotechnology and material sciences.¶

Functionnalization of graphene is one of the most commonly used approaches that led to modification of the nanomaterial for its application in multiple areas.⁵,⁶ Although functionalization is executed by both covalent and noncovalent modes of interaction, the latter is preferred because it does not affect the extended π-conjugation of the graphene sheet to a significant extent (useful properties remain intact).⁹,¹⁰ In addition to this, noncovalent interaction is impermanent and a comparatively simple adsorption/desorption process introduces flexibility in treating the adsorbent.⁹

Recent years have witnessed a number of studies on the adsorption of aromatic molecules on the surface of graphene sheets.⁹–¹² Such interaction is also considered to be a suitable model for interaction between two graphene surfaces.¹³ Apart from this, interaction with aromatic moieties has also been explored in tailoring the electronic structure of graphene sheets.¹⁴ A number of theoretical efforts have been focused on the interaction of aromatic hydrocarbons (linear and fused) with graphene sheets.¹⁵–¹⁶ The presence of heteroatoms or substituents on the aromatic moieties is reported to have some impact on the adsorption energies.¹⁷,¹⁸ For example, interaction between hexafluorobenzene and graphene is significantly stronger than that between benzene and graphene.¹² Similarly, compared with benzene, pyridine and pyridazine are adsorbed preferably on graphene surface.⁹ Moreover, substituents present on aromatic moieties also enhance the interaction with graphene.¹⁷,¹⁸

N-Heterocycles are central to the chemical reactions that occur in all organisms and are the key constituents of both RNA and DNA.¹⁹ In addition to these, N-heterocycles are also present in coenzymes that mediate metabolic transformations.¹⁹ Adsorption of the N-heterocycles is of notable interest because N-heterocycles like pyridine are quite useful from drug

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delivery and diagnostic points of view. 20 5-Membered N-heterocycles are also useful in different areas. A pyrrole ring is important from the viewpoint of porphyrin and corrin macrocycles. Similarly, aromatic compounds bearing imidazole and triazole moieties are important from the perspective of fluorescence and DNA studies. Apart from this, imidazole and triazole compounds are important from both agrochemical and pharmaceutical viewpoints. Tetrazole is acidic in nature and has been used in drugs as a replacement of -COOH groups with no loss of activity. However, compounds with four or more N atoms are explosive in nature. For example, pentazole is highly explosive. Apart from their usefulness, some of these heterocyclic compounds and their derivatives are also toxic in nature.

Even though adsorption of aromatic moieties on graphene is extensively studied, reports on adsorption of N-heterocycles on B/N/BN-doped graphene are relatively scarce. To the best of our knowledge, only Petrushenko et al. have reported the adsorption of pyridine, pyrimidine, pyrazine, pyridazine, and 1,3,5 triazine on a graphenelike boron nitride–carbon heterostructure (GBNCH). This stimulated the interest of studying the adsorption of 5-membered N-heterocycles on B/N/BN-doped graphene systems. In addition, doping disturbs the π-electron delocalization and introduces polarity in the molecule and, therefore, might improve its adsorptive capacity for various molecules at interfacial regions. Therefore, it becomes imperative to have some understanding on the interactions between B/N/BN-doped graphene and N-heterocycles.

Here, physical adsorption of a series of isoelectronic 5-membered N-heterocycles on B/N/BN-doped graphene is studied in the light of density functional theory (DFT). The following N-heterocycles are considered for the study: pyrrole, imidazole, pyrazole, 1,2,3-triazole, 1,2,4-triazole, tetrazole, and pentazole. However, the choice of a suitable model graphene system is crucial. It should be so chosen that it is practicable from the viewpoint of computational demand and provides results that are consistent with the experimental observations. Considering these and in line with the literature, coronene is employed as a model graphene system. To scrutinize the effect of the size of the considered graphene model system on the adsorption of heterocycles, four larger graphene model systems, viz., C42H16, C48H18, C54H18, and C66H20 are also considered and their interactions with pyrrole and imidazole are studied as representative cases. Substitutional doping of the B/N/BN unit on the ring at the center of coronene is taken into consideration. Furthermore, the effects of complexation on HOMO energy (energy of the highest occupied molecular orbital, $E_{\text{HOMO}}$), HOMO–LUMO gap (energy of the lowest unoccupied molecular orbital, $E_{\text{LUMO}}$), and UV–visible absorption spectra are studied. Apart from these, the number of dopants is increased from one to three and its effect on the aforesaid properties is also studied. Furthermore, effects of solvent dielectric on the stability of the complexes are also scrutinized. Our study is expected to reveal the role of dopant along with the role of N atom present on adsorbent in the adsorption process.

2. RESULTS AND DISCUSSION

For the study, substitutional doping is considered in coronene with B (electron-deficient), N (electron-rich), and BN (isoelectronic with CC) units bearing no charges. In this article, undoped/doped coronene is symbolized as Cor with dopants indicated within the parenthesis. For example, B-
Doped coronene is represented as Cor(B) and its complexes with considered N-heterocyclic compounds such as pyrrole (Pyr), imidazole (Im), pyrazole (Pz), 1,2,3-triazole (123-tria), 1,2,4-triazole (124-tria), tetrazole (Tetra), and pentazole (Penta) are represented as Cor(B)-Pyr, Cor(B)-Im, Cor(B)-Pz, Cor(B)-123-tria, Cor(B)-124-tria, Cor(B)-Tetra, and Cor(B)-Penta.

Electrostatic potential of a system is a physical property, and it reveals the resultant spatial effect of nuclei and electrons and thereby provides useful information in predicting the possibility of interactions between two moieties. Hence, molecular electrostatic potential (ESP) surfaces of undoped/doped Cor and the considered N-heterocyclic systems are obtained and are depicted in Figure 1. Referring to Figure 1, the charge distribution over the surface of the considered N-heterocycles varies depending upon the position and number of N atoms present in the heterocycles. The red area in the ESP surfaces stands for the electron-rich (negatively charged) region, whereas the blue area represents a relatively electron-deficient (positively charged) region. In the case of N-heterocycles, the region around the H atom attached to the N atom is relatively electron-deficient, whereas the region around the N atom with a lone pair is electron-rich, Figure 1a–g. Similarly, there exists a negatively charged region over the surface of Cor (Figure 1h); however, upon doping, irrespective of its nature, the charge distribution over the surface of Cor is perturbed, Figure 1i–n. Variation in the charged region over the surface of N-heterocyclic systems and the undoped/doped Cor surface suggests the possibility of multiple modes of interactions between the considered moieties and thereby would influence the adsorption process.

Again, doping influences the delocalized π-electrons (aromaticity) and therefore is expected to influence the possible π-interactions (π⋯π, N–H⋯π, C–H⋯π, lone pair⋯π interactions) to a certain extent. Hence, aromaticity at the site of complexation is estimated using the HOMA index. According to the literature, a system with HOMA > 0.5 is aromatic, HOMA < 0 is antiaromatic, and for the range 0 < HOMA < 0.5, the system is non-aromatic. Among the considered systems, Cor is the most aromatic with HOMA = 0.87. Upon doping, variation in HOMA values is observed depending on the nature and number of dopants. Except Cor(3B), all of the doped Cor are aromatic in nature, and the calculated HOMA values for Cor(B), Cor(3B), Cor(N), Cor(3N), Cor(BN), and Cor(3BN) are 0.69, 0.08, 0.80, 0.69, 0.65, and 0.85, respectively. Suitability of the HOMA index is validated by estimating the HOMA values for C6H6 (0.99) and B3N3H6 (0.94) as reference and comparing the results with the reported values. The observed variation in aromaticity

Figure 2. Optimized geometries of (a) Cor-Pyr, (b) Cor-Im, (c) Cor-Pz, (d) Cor-123-tria, (e) Cor-124-tria, (f) Cor-Tetra, (g) Cor-Penta (h) Cor(B)-Pyr, (i) Cor(B)-Im, (j) Cor(B)-Pz, (k) Cor(B)-123-tria, (l) Cor(B)-124-tria, (m) Cor(B)-Tetra, and (n) Cor(B)-Penta obtained at the ωB97-XD/6-311++G(d,p) level of theory.
predicts the key role of the dopant in adsorption of the N-heterocyclic system on the undoped/doped Cor surface. The ESP surface and aromaticity predict the viability of adsorption of N-heterocycles on undoped/doped Cor where doping is anticipated to have a significant role in the stability of the complex. Recent studies also confirmed suitability of the ESP surface in predicting the likelihood of interaction between two moieties involving similar type of interactions.

2.1. Geometry of the Complexes. The presence of substituent plays a key role in controlling the geometry and properties of the complexes involving π···π stacking. From chemical intuition, the presence of heteroatom in a π-conjugated system would also influence the geometry of the studied complexes, measured in terms interlayer separation ($d_{\pi-\pi}$, distance between the Bq atoms placed at the ring center at the site of complexation). Apart from this, interlayer separation and degree of π-orbital interaction are also crucial from the viewpoint of an organic semiconductor. Although the considered heterocycles possibly would interact via C−H···N, N−H···π, and lone pair−π interactions, due to favorable and maximum π-orbital overlap, π−π stacking, i.e., face-to-face orientation between the systems, is taken into consideration. The optimized geometries of the complexes formed by Cor and Cor(3B) with the considered N-heterocycles are shown in Figure 2 as representative cases, and the interlayer separation involving N-heterocycles are not exactly over the center of the ring, i.e., the N-heterocyclic compound is displaced to a certain extent with the interlayer separation of 3.37−3.52 Å. Displacement of the N-heterocyclic compound is also observed for the complexes with doped Cor irrespective of the nature of dopants, possessing variable interlayer separation (3.21−3.94 Å), Table 1. Similar displacement of the monomers is also reported on benzene dimers formed via π···π stacking. The observed interlayer separation is in good agreement with the reported values for adsorption of aromatic molecules on graphene via π···π stacking interaction. Petrushenko et al. have reported the interlayer separation within the range of 3.17−3.34 Å for similar type of complexes involving GBNCH. A distance of ~3.40 Å is also reported for adsorption of substituted pyridine on graphene surface. On increasing the number of dopants from 1 to 3, the interlayer separation decreases. For example, for the complexes involving Cor(3B), Cor(N)-123-tria, and Cor(3B)Pyr, the interlayer separation is less (3.21−3.39 Å) than that for the complexes with Cor, Cor(B), Cor(N), and Cor(BN) (3.35−3.62 Å), Table 1. Therefore, a stronger interaction is anticipated between the N-heterocycle and Cor(3B), Cor(N), and Cor(BN). Unlike the benzene dimer (parallel displaced), considered N-heterocycles are not exactly parallel to the molecular plane of undoped/doped Cor. In addition to this, the considered N-heterocycles possess lone pair electrons on the N atom (except in Pyr) that do not contribute to the delocalized π-electrons and experience additional interaction with undoped/doped Cor. As the number of lone pairs increased, such interactions between the systems are expected to be stronger and may result in more slanting. For example, higher slanting is observed in the case of complexes involving tetrazole and pentazole irrespective of the nature and number of dopants, Figure 2. The literature also confirmed the slanting of N-heterocycles on interaction with an aromatic moiety. Petrushenko et al. have attributed this slanting to the dipole moment ($\mu$) of the heterocycles. It is seen that the dipole moment of Pyr ($\mu = 1.95$ D) is the lowest among the chosen set of N-heterocycles, which exhibits minimum slanting in the complexes, whereas for Tetra ($\mu = 5.66$ D) and Penta ($\mu = 4.15$ D), the slanting is maximum, Figure 2. Again, the dipole moments of Im, Pz, 123-tria, and 124-tria are 3.95, 2.44, 4.71, and 5.99 D, respectively. Although 124-tria possesses the maximum $\mu$ value, the slanting is comparatively less than that in Tetra and Penta, Figure 2. This indicates that the dipole moment is not the only criterion that controls the slanting in geometries of the considered systems.

Apart from interlayer separation, N−H···π distances in the complexes are also measured ($d_{N−H···π}$ distance between the H atom and Bq atom placed at the center of the arene ring closest to it) and are shown in Table 1. The $d_{N−H···π}$ varies (2.44−3.33 Å) depending upon the nature of the N-heterocycles. The observed results are in line with the reported values for the N−H···π interaction. However, the earlier literature on adsorption of N-heterocycles did not report anything about the involvement of N−H···π interactions. In the case of complexes with doped Cor, $d_{N−H···π}$ decreases with an increase in the number of N in the heterocyclic ring (especially for Tetra and Penta), suggesting the key role of N−H···π interaction in stabilizing their complexes, Table 1. For example, in the case of complexes involving Cor(N), $d_{N−H···π}$ decreases in the following order: Cor(N)-Im (2.90) > Cor(N)-Pz (2.78) > Cor(N)-Pyr (2.77) > Cor(N)-123-tria (2.75) > Cor(N)-124-tria (2.73) > Cor(N)-Tetra (2.65) > Cor(N)-Penta (2.44); values are in angstrom.

### Table 1. $d_{\pi-\pi}$ and $d_{N−H···π}$ Distances (in Å) for the Complexes Obtained at the $ω$B97XD/6-311++G(d,p)

| Complex   | $d_{\pi-\pi}$ | $d_{N−H···π}$ | Complex   | $d_{\pi-\pi}$ | $d_{N−H···π}$ |
|-----------|---------------|---------------|-----------|---------------|---------------|
| Cor-Pyr   | 3.37          | 2.93          | Cor(N)-124-tria | 3.36          | 2.78          |
| Cor-Im    | 3.35          | 3.33          | Cor(N)-Tetra  | 3.45          | 2.64          |
| Cor-Pz    | 3.43          | 3.05          | Cor(N)-Penta  | 3.54          | 2.44          |
| Cor-123-tria | 3.46         | 2.84          | Cor(N)-Pyr    | 3.24          | 2.77          |
| Cor-124-tria | 3.42         | 2.64          | Cor(N)-Im     | 3.23          | 2.90          |
| Cor-Tetra | 3.49          | 2.65          | Cor(N)-Pz     | 3.21          | 2.78          |
| Cor-Penta | 3.52          | 2.61          | Cor(N)-123-tria | 3.21         | 2.75          |
| Cor(B)-Pyr | 3.44         | 2.99          | Cor(N)-124-tria | 3.21         | 2.73          |
| Cor(B)-Im | 3.50          | 2.95          | Cor(N)-Tetra  | 3.27          | 2.65          |
| Cor(B)-Pz | 3.46          | 3.03          | Cor(N)-Penta  | 3.94          | 2.44          |
| Cor(B)-123-tria | 3.56      | 2.97          | Cor(N)-Pyr    | 3.35          | 2.93          |
| Cor(B)-124-tria | 3.51     | 2.86          | Cor(N)-Im     | 3.51          | 2.91          |
| Cor(B)-Tetra | 3.49         | 2.80          | Cor(N)-Pz     | 3.38          | 3.35          |
| Cor(B)-Penta | 3.49        | 2.66          | Cor(N)-123-tria | 3.41         | 3.15          |
| Cor(3B)-Pyr | 3.24        | 2.67          | Cor(N)-124-tria | 3.37         | 2.86          |
| Cor(3B)-Tetra | 3.35        | 2.83          | Cor(N)-Tetra  | 3.62          | 2.55          |
| Cor(3B)-Pz | 3.29          | 2.64          | Cor(N)-Penta  | 3.50          | 2.49          |
| Cor(3B)-123-tria | 3.40       | 2.92          | Cor(N)-Pyr    | 3.27          | 2.79          |
| Cor(3B)-124-tria | 3.37      | 2.91          | Cor(N)-Im     | 3.29          | 2.92          |
| Cor(3B)-Tetra | 3.41        | 2.66          | Cor(N)-Pz     | 3.28          | 2.93          |
| Cor(3B)-Penta | 3.37        | 2.52          | Cor(N)-123-tria | 3.36         | 2.85          |
| Cor(N)-Pyr | 3.42          | 3.20          | Cor(N)-124-tria | 3.30         | 2.83          |
| Cor(N)-Im | 3.40          | 2.76          | Cor(N)-Tetra  | 3.35          | 2.78          |
| Cor(N)-Pz | 3.37          | 3.07          | Cor(N)-Penta  | 3.39          | 2.65          |
| Cor(N)-123-tria | 3.43        | 3.03          |               |               |               |
the complexes can be attributed to the simultaneous involvement of π···π, N−H···π, and lone pair···π interactions. Voloshina et al. have also attributed the slating of pyridine on graphene surface to the simultaneous involvement of π···π and lone pair···π interactions between the two.12

It is to be mentioned that adsorption of the N-heterocycles does not lead to notable changes on the geometries of the undoped/doped Cor except for Cor(3B). In the complexes with Cor(3B), significant distortion in the molecular plane (buckling) of Cor(3B) is observed (Figures 2h–n) upon complexation. This is probably due to the presence of larger B atoms (three longer B–C bond) in the ring of the Cor(3B) system. Also, the process of complexation does not bring about any significant (<0.005 Å) changes in the individual bond length in the ring at the site of complexation, indicative of π-interaction. However, complex formation with Cor(3B) brought about comparatively larger changes in B-C bond distances (up to 0.01 Å) along with its molecular plane. Studies on geometries of the complexes thus suggest the simultaneous involvement of π···π stacking and N−H···π interaction in the adsorption process.

2.2. Stabilization Energies of the Complexes. Aromatic stacking or π···π stacking is intuitively repulsive, and such interaction is stabilized by key contributions from dispersive, electrostatic, and solvophobic interactions.37 Although the geometry of the complexes indicated the presence of N−H···π interaction along with π···π stacking, accurate estimation of these interactions is challenging. The coupled cluster approach with perturbative triples on extrapolation to the complete basis set limit (CCSD(T)-CBS) is reported to produce results consistent with experimental observation.38 Nevertheless, its computational demand has limited the use of the CCSD(T)-CBS method to smaller systems only. Moreover, the second-order Möller–Plesset (MP2) perturbation theory is computationally less expensive (compared with CCSD(T)), but its accuracy is reported to be dependent on the type of basis set used.39 Hobza et al. suggested the use of the MP2/cc-pVTZ level of theory for this purpose, which would also be prohibitively expensive for the considered systems.40 DFT methods are computationally more convenient than CCSD(T) and MP2 calculations and hence, in this study, DFT functionals are used. However, proper selection of the functional (dispersion-corrected) and basis set is important for accurate estimation of π···π stacking.49 For this purpose, MP2/cc-pVTZ calculations are performed on the complexes formed by undoped/B/N/BN-doped Cor with Pyr (as the representative case) and the results are compared with those obtained from various DFT functionals and basis sets, as shown in Table 2. It is seen that compared to the results obtained with the MP2/cc-pVTZ calculation (shown within parentheses in the second column of Table 2), the results produced by the ωB97-XD functional are closer than those obtained from the M06-2X level calculation. This validates the suitability of the ωB97-XD functional over the M06-2X functional for studying the complexes. Recently, ωB97-XD functional is also used for studying the adsorption of aromatic molecules on graphene.51,52 To find out the appropriate basis set, stabilization energies of the complexes are obtained at the ωB97-XD/6-311++G(d,p), ωB97- XD/6-311+G(d,p), ωB97- XD/cc-pVTZ, and ωB97- XD/def2TZVP levels of theories, given in Table 2. Considering the result obtained from the MP2/cc-pVTZ calculation as the standard, for the complex of undoped Cor, the ωB97- XD/6-311++G(d,p) level of theory produces more comparable result (differs by 0.91 kcal mol⁻¹).

Similarly, for the complexes with B-doped, N-doped, and BN-doped pyrene, ωB97- XD/cc-pVTZ (varies by 0.07 kcal mol⁻¹), ωB97-XD/def2TZVPP (varies by 0.01 kcal mol⁻¹), and ωB97- XD/6-311+G(d,p) (varies by 0.88 kcal mol⁻¹) levels of theories, respectively, produce results that are in close agreement with the MP2/cc-pVTZ calculation. Therefore, with a bit of compromise to the accuracy and considering the computational cost, use of the ωB97- XD/6-311++G(d,p) level of theory for geometry optimization is not at all a bad choice (varies by <0.92 kcal mol⁻¹ from that obtained with MP2 calculation).

The SE values calculated at the ωB97- XD/6-311++G(d,p) level of theory (in gas phase) are provided in Table 2. Depending on the nature of heterocycles involved in complexation, the SE value varies in the range of 7.61–14.77 kcal mol⁻¹, and complexes are expected to be moderately stable. For example, in the case of undoped Cor, the SE values decrease in the order Cor-124-tria (9.67) > Cor-Tetra (9.41) > Cor-123-tria (9.24) > Cor-Pyr (9.07) > Cor-Pz (8.98) > Cor-Im (8.59) > Cor-Penta (8.35); values are in kcal mol⁻¹. The observed SE values are in good agreement with the reported values.9,10,12 Zarudnev et al. have reported the SE value of 7.90 kcal mol⁻¹ for adsorption of Im on graphene (obtained at the M05-2X/6-31++G(d,p) level of theory) surface.10 Although Im and Pz are isomeric/isoelectronic, SE values are relatively higher for Cor-Pz complexes (which may be attributed to the higher contribution from the N−H···π interaction, as evident from the N−H···π distance). This validates the importance of the position of N in the heterocycles in stabilizing the complexes. Similar results are also observed for complexes with 123-tria and 124-tria. This also suggests lower stability of the complexes formed by the N-heterocyclic compound where N is present adjacent to each other. Again, the Cor-Penta complex possesses lowest SE values, which may be attributed to the smaller π···π contribution (maximum slanting) in stabilizing the complexes. Upon doping, the SE values, i.e., the stability of the complexes, increase irrespective of the nature of dopants for most of the cases, Table 2. For example, the SE values for the complexes involving Pyr follow the following order: Cor(3B)-Pyr (14.68) > Cor(NB)-Pyr (12.60) > Cor(NBN)-Pyr (11.45) > Cor(N)-Pyr (9.94) > Cor(B)-Pyr (9.62) ≈ Cor(NBN)-Pyr (9.61) > Cor-Pyr (9.07); values are in kcal mol⁻¹. Apart from this, with an increase in the number of dopants, the SE values are further increased, Table 2. Even though the above order is not true for all of the heterocycles, the SE is always higher when the number of dopants is increased from 1 to 3. Like undoped Cor, the complexes formed by doped Cor with Penta possess the lowest SE values except in the case of the Cor(NBN)-Penta complex, which possesses the SE of 10.63 kcal mol⁻¹. Thus, doping facilitates the adsorption process and thereby enhances the stability of the complexes. Even though the literature suggested the relationship between the SE values and dipole moment of the N-heterocycles, the obtained results do not establish such relationship between the two parameters (neither with the dipole moment of undoped/doped Cor nor with that of N-heterocycles).9

To scrutinize the effect of functionals and basis sets on the stability of the complexes, SEs are calculated at different levels of theories, and the results are shown in Table 2. The estimated SE values differ by some extent depending upon the functional employed for the study. For instance, use of the ωB97- XD functional estimates higher SEs (by 1.00–3.00 kcal mol⁻¹) of the complexes compared to those from the M06-2X
| complexes      | oB97-XD/6311++ G(dp) | M06-2X/6−311++ G(dp) | oB97-XD/6−311++ G(dp) | oB97-XD/cc-pVTZ   | oB97-XD/def2 tzvpp | oB97-XD/cc-pVTZ   |
|----------------|---------------------|---------------------|---------------------|------------------|-------------------|------------------|
| Cor-Pyr        | 9.07 (9.98°)        | 7.16                | 8.87                | 8.50             | 8.46              | 8.61             |
| Cor-Im         | 8.59                | 6.60                | 8.44                | 8.10             | 8.09              | 8.28             |
| Cor-Pz         | 8.98                | 7.49                | 8.79                | 8.46             | 8.42              | 8.50             |
| Cor-123-tria   | 9.24                | 7.84                | 9.05                | 8.69             | 8.67              | 8.79             |
| Cor-124-tria   | 9.67                | 7.92                | 9.47                | 9.10             | 9.11              | 9.20             |
| Cor-Tetra      | 9.41                | 8.10                | 9.19                | 8.78             | 8.76              | 8.89             |
| Cor-Penta      | 8.35                | 7.52                | 8.18                | 7.81             | 7.78              | 7.86             |
| Cor(B)-Pyr     | 9.62 (9.19°)        | 8.27                | 9.45                | 9.12             | 9.07              |                  |
| Cor(B)-Im      | 10.61               | 9.20                | 10.43               | 10.03            | 9.98              |                  |
| Cor(B)-Pz      | 9.19                | 7.84                | 9.03                | 8.74             | 8.69              |                  |
| Cor(B)-123-tria| 9.31                | 7.90                | 9.14                | 8.82             | 8.77              |                  |
| Cor(B)-124-tria| 11.19               | 9.96                | 11.00               | 10.59            | 10.55             |                  |
| Cor(B)-Tetra   | 10.11               | 8.93                | 9.90                | 9.50             | 9.47              |                  |
| Cor(B)-Penta   | 8.11                | 7.32                | 7.99                | 7.76             | 7.68              |                  |
| Cor(N)-Pyr     | 14.68               | 16.61               | 14.53               | 14.04            | 13.98             |                  |
| Cor(N)-Im      | 13.73               | 8.30                | 13.59               | 13.16            | 13.12             |                  |
| Cor(N)-Pz      | 12.46               | 11.22               | 12.34               | 11.98            | 11.92             |                  |
| Cor(N)-123-tria| 12.99               | 11.74               | 12.88               | 12.47            | 12.40             |                  |
| Cor(N)-124-tria| 14.77               | 13.53               | 14.57               | 14.16            | 14.12             |                  |
| Cor(N)-Tetra   | 12.72               | 11.61               | 12.53               | 12.25            | 12.16             |                  |
| Cor(N)-Penta   | 10.78               | 10.19               | 10.66               | 10.46            | 10.32             |                  |
| Cor(N)-Pyr     | 9.94 (9.31°)        | 8.43                | 9.80                | 9.38             | 9.32              |                  |
| Cor(N)-Im      | 10.04               | 8.68                | 9.87                | 9.48             | 9.45              |                  |
| Cor(N)-Pz      | 9.34                | 8.00                | 9.18                | 8.84             | 8.78              |                  |
| Cor(N)-123-tria| 9.31                | 7.95                | 9.14                | 8.76             | 8.70              |                  |
| Cor(N)-124-tria| 10.23               | 8.84                | 10.06               | 9.71             | 9.70              |                  |
| Cor(N)-Tetra   | 9.54                | 8.62                | 9.44                | 9.01             | 8.97              |                  |
| Cor(N)-Penta   | 8.53                | 7.84                | 8.48                | 8.18             | 8.08              |                  |
| Cor(3N)-Pyr    | 12.60               | 11.59               | 12.46               | 12.03            | 11.94             |                  |
| Cor(3N)-Im     | 12.07               | 8.81                | 11.93               | 11.49            | 11.49             |                  |
| Cor(3N)-Pz     | 11.53               | 10.67               | 11.43               | 11.05            | 10.97             |                  |
| Cor(3N)-123-tria| 11.51               | 10.31               | 11.43               | 11.02            | 10.95             |                  |
| Cor(3N)-124-tria| 12.75               | 10.82               | 12.65               | 12.21            | 12.16             |                  |
| Cor(3N)-Tetra  | 11.69               | 11.12               | 11.60               | 11.17            | 11.11             |                  |
| Cor(3N)-Penta  | 10.37               | 9.83                | 10.31               | 10.00            | 9.91              |                  |
| Cor(3BN)-Pyr   | 9.61 (10.49°)       | 7.65                | 9.46                | 9.15             | 9.12              |                  |
| Cor(3BN)-Im    | 11.44               | 9.82                | 11.30               | 10.93            | 10.85             |                  |
| Cor(3BN)-Pz    | 7.92                | 6.02                | 7.81                | 7.58             | 7.54              |                  |
| Cor(3BN)-123-tria| 8.30                | 6.77                | 8.16                | 7.88             | 7.83              |                  |
| Cor(3BN)-124-tria| 11.46               | 9.60                | 11.32               | 10.93            | 10.88             |                  |
| Cor(3BN)-Tetra | 7.61                | 5.94                | 7.44                | 7.26             | 7.23              |                  |
| Cor(3BN)-Penta | 10.63               | 9.83                | 10.53               | 10.26            | 10.18             |                  |
| Cor(3BN)-Pyr   | 11.45               | 9.25                | 11.35               | 11.20            | 11.13             |                  |
Moreover, SEs estimated with the 6-31++G(d,p) basis set are marginally lower (<0.25 kcal mol\(^{-1}\)) than those obtained with the 6-311++G(d,p) basis set. Addition of extra diffuse function leads to a nominal impact on the SEs of the complexes, Table 2. For example, SE values for the Cor-Pyr complex are 9.07 and 8.87 kcal mol\(^{-1}\) obtained, respectively, at \(\omega\)B97-XD/6-311++G(d,p) and \(\omega\)B97-XD/6-31++G(d,p) levels of theory. On the other hand, the SE values calculated with cc-pVTZ and def2TZVPP basis sets in combination with the \(\omega\)B97-XD functional are lower (up to 0.66 kcal mol\(^{-1}\)) as compared to those with the \(\omega\)B97-XD/6-311++G(d,p) level of theory. For instance, the SE values for the Cor-Pyr complex are 9.07, 8.50, and 8.46 kcal mol\(^{-1}\) obtained with 6-311++G(d,p), cc-pVTZ, and def2TZVPP basis sets in association with the \(\omega\)B97-XD functional. Thus, apart from the functional, the choice of a suitable basis set is also crucial. Jacobs et al. have also suggested the importance of a suitable DFT functional and basis set for estimating the noncovalent interactions.39

To verify the accuracy of single-point calculations for estimating the SEs, the geometries of the complexes formed by undoped Cor (as the representative case) are re-optimized at the \(\omega\)B97-XD/cc-pVTZ level of theory, and the calculated SE values are shown in Table 2 (column 7). The SE values obtained from re-optimization and single-point calculations are very close, with SEs obtained from re-optimization being higher by <0.20 kcal mol\(^{-1}\) only. The results thus validate the suitability of the used protocol (computationally cheaper) for scrutinizing the effect of the functional and basis set on the SEs.

To examine the role of solvent phase in the stability of the complexes, solvent phase calculations are performed in cyclohexane (ch), ethanol (eth), DMSO and water (wat) as model solvents, represented in Table 3. It is seen that the presence of solvent phase exerts some impact on the stability of the complexes. Compared to those in the gas phase, in cyclohexane, SE values decreased by ~2.00 kcal mol\(^{-1}\) except in the case of complexes formed by Cor(3B) and Cor(3N) with Im, Pz, 123-tria, and 124-tria; SE values decreased up to 7.07 kcal mol\(^{-1}\) (Table 3). In solvents with a higher dielectric (ethanol), SE values further drop up to 2.58 kcal mol\(^{-1}\) (compared to those in cyclohexane). However, with a further increase in the dielectric of the solvent, i.e., in the case of DMSO and water, no prominent effect on the SEs is observed (<0.10 kcal mol\(^{-1}\), compared to that in ethanol), Table 3. Earlier studies have shown a notable impact of solvents on SEs of complexes formed through relatively stronger noncovalent interactions, such as hydrogen bonding and cation···π, whereas for weaker interactions, such as B···H···π, the effect of solvent is nominal.42,43 Although SE is decreased in the presence of a solvent phase, the complexes are stable enough in the solvent phase irrespective of their dielectrics.

To analyze the size effect, SE values are calculated (optimized) for the complexes involving Pyr and Im with four relatively larger graphene model systems with different sizes, viz., \(C_{42}H_{16}\), \(C_{48}H_{18}\), \(C_{54}H_{18}\), and \(C_{66}H_{20}\) (Supporting Information Figure S1). Compared to those of undoped Cor, the corresponding SE values for the complexes increase by 1.57−2.21 kcal mol\(^{-1}\) upon increasing the size of the considered graphene sheet. For example, Cor-Pyr possesses an SE value of 9.07 kcal mol\(^{-1}\) and in the case of \(C_{42}H_{16}\)-Pyr, \(C_{48}H_{18}\)-Pyr, \(C_{54}H_{18}\)-Pyr, and \(C_{66}H_{20}\)-Pyr complexes, the SE values are calculated to be 10.64, 10.94, 11.04, and 11.12 kcal mol\(^{-1}\), respectively. Similarly, the SE value for the Cor-Im

Table 2. continued

| complexes     | \(\omega\)B97-XD/6-31++G(d,p) | \(\omega\)B97-XD/6-311++G(d,p) | \(\omega\)B97-XD/cc-pVTZ | \(\omega\)B97-XD/def2TZVPP |
|---------------|-----------------------------|------------------------------|--------------------------|---------------------------|
| Cor(3BN)-Im   | 11.04                       | 10.83                        | 10.78                    | 10.74                     |
| Cor(3BN)-Pz   | 10.10                       | 9.98                         | 9.96                     | 9.94                      |
| Cor(3BN)-123-tria | 9.94               | 9.75                         | 9.76                     | 9.73                      |
| Cor(3BN)-124-tria | 9.87               | 9.68                         | 9.67                     | 9.65                      |
| Cor(3BN)-Tetra | 9.80                        | 9.68                         | 9.68                     | 9.67                      |
| Cor(3BN)-Penta | 9.74                        | 9.69                         | 9.69                     | 9.68                      |
| Cor(3BN)-Penta | 9.64                        | 9.59                         | 9.59                     | 9.58                      |
| Cor(3BN)-Tetra | 9.53                        | 9.49                         | 9.49                     | 9.48                      |
| Cor(3BN)-Penta | 9.43                        | 9.34                         | 9.34                     | 9.33                      |
| Cor(3BN)-Tetra | 9.34                        | 9.24                         | 9.24                     | 9.23                      |
| Cor(3BN)-Penta | 9.24                        | 9.14                         | 9.14                     | 9.13                      |
| Cor(3BN)-Tetra | 9.14                        | 9.04                         | 9.04                     | 9.03                      |
| Cor(3BN)-Penta | 9.04                        | 8.94                         | 8.94                     | 8.93                      |
| Cor(3BN)-Tetra | 8.94                        | 8.84                         | 8.84                     | 8.83                      |
| Cor(3BN)-Penta | 8.84                        | 8.74                         | 8.74                     | 8.73                      |
| Cor(3BN)-Tetra | 8.74                        | 8.64                         | 8.64                     | 8.63                      |
| Cor(3BN)-Penta | 8.64                        | 8.54                         | 8.54                     | 8.53                      |
| Cor(3BN)-Tetra | 8.54                        | 8.44                         | 8.44                     | 8.43                      |
| Cor(3BN)-Penta | 8.44                        | 8.34                         | 8.34                     | 8.33                      |
| Cor(3BN)-Tetra | 8.34                        | 8.24                         | 8.24                     | 8.23                      |
| Cor(3BN)-Penta | 8.24                        | 8.14                         | 8.14                     | 8.13                      |
| Cor(3BN)-Tetra | 8.14                        | 8.04                         | 8.04                     | 8.03                      |

\(a\) SE values obtained from optimization.
\(b\) SE values obtained from single-point calculation.
\(c\) SE values obtained from MP2/cc-pVTZ level of theory.
model has also been used in a number of occasions.\textsuperscript{25} Therefore, considering the computational demand and a bit of compromise to the accuracy, use of Cor as a graphene dopant is not at all a bad choice for such study. This model has also indicated the same for systems with SEs around this range.\textsuperscript{10,43}

In addition, this may also lead to effective removal of N-heterocycles, leading to environment treatments.

2.3. Nature of Interaction and Charge Transfer

Noncovalent interaction arises from the contribution from a number of interactions such as electrostatic, induction, exchange, and dispersion that act either parallelly or antiparallelly.\textsuperscript{44} Depending upon the studied systems (presence of substituent, dopants, etc.) and involved interaction (strong/weak), contributions from each of these interactions vary. Generally, the nature of $\pi\cdots\pi$ stacking is primarily dispersive along with some contribution from electrostatic interaction.\textsuperscript{9,45,46} Because the geometry of the complexes suggested the additional involvement of N–H···N interaction, it is imperative to realize the nature of interaction in stabilizing the complexes.

Although qualitative, the nature of involved interaction can be predicted using appropriate DFT functionals.\textsuperscript{43,47} As per the literature, this can be achieved by calculating the SEs of the complexes’ DFT functional that encounters dispersion interaction along with all other interactions and functionals that encompass other interactions except the dispersion interaction. A comparison between these two would qualitatively provide the role of dispersion interaction. The above protocol is adopted by Li et al. to have some idea about the magnitude of charge transfer ($\Delta q$) in the complexation process.\textsuperscript{47} As a result, natural bond orbital analysis is performed to calculate the charge at a particular site before the nature of interaction in stabilizing the complexes, which are in good agreement with the documented report for $\pi\cdots\pi$ stacking.\textsuperscript{9,45,46}

Moreover, qualitative interpretation about the role of electrostatic and covalent components can be predicted from the magnitude of charge transfer ($\Delta q$) in the complexation process.\textsuperscript{47}

For an effective carrier, a feebly weak or a significantly strong interaction is unfavorable. However, the SEs obtained for the complexes are $<$15.00 kcal mol$^{-1}$ and therefore it would be wise to anticipate that N-heterocycles might be effectively adsorbed and get released suitably from the surface of undoped/doped Cor, i.e., graphene. The literature has also indicated the same for systems with SEs around this range.\textsuperscript{10,43}

### Table 3. Stabilization Energies (in kcal mol$^{-1}$) of the Complexes in Solvent the Phase Calculated at the $\omega$B97-XD/6-311++G(d,p) Level of Theory

| complexes | SE$_{\text{hh}}$ | SE$_{\text{eth}}$ | SE$_{\text{DMSO}}$ | SE$_{\text{w}}$ |
|-----------|----------------|----------------|----------------|----------------|
| Cor-Pyr   | 7.86           | 6.71           | 6.66           | 6.63           |
| Cor-Im    | 7.19           | 6.34           | 6.25           | 6.23           |
| Cor-Pz    | 8.12           | 7.18           | 7.15           | 7.13           |
| Cor-123-tria | 7.87       | 6.83           | 6.81           | 6.78           |
| Cor-124-tria | 8.05       | 6.90           | 6.82           | 6.79           |
| Cor-Tetra | 7.89           | 6.34           | 6.29           | 6.28           |
| Cor-Penta | 6.88           | 5.64           | 5.62           | 5.61           |
| Cor$_{\text{3B}}$-Pyr | 8.71       | 7.61           | 7.56           | 7.54           |
| Cor$_{\text{3B}}$-Im | 9.41       | 7.82           | 7.75           | 7.71           |
| Cor$_{\text{3B}}$-Pz | 8.37       | 7.32           | 7.27           | 7.25           |
| Cor$_{\text{3B}}$-123-tria | 8.09     | 6.73           | 6.68           | 6.66           |
| Cor$_{\text{3B}}$-124-tria | 9.52     | 7.47           | 7.29           | 7.25           |
| Cor$_{\text{3B}}$-Tetra | 8.42       | 6.69           | 6.64           | 6.63           |
| Cor$_{\text{3B}}$-Penta | 6.74       | 5.69           | 5.63           | 5.59           |
| Cor$_{\text{3B}}$-Pyr | 12.60      | 10.98          | 10.86          | 10.82          |
| Cor$_{\text{3B}}$-Im | 6.66           | 4.95           | 4.88           | 4.85           |
| Cor$_{\text{3B}}$-Pz | 6.87           | 5.70           | 5.66           | 5.64           |
| Cor$_{\text{3BN}}$-123-tria | 6.90     | 5.09           | 5.02           | 4.98           |
| Cor$_{\text{3BN}}$-124-tria | 7.98     | 5.40           | 5.30           | 5.26           |
| Cor$_{\text{3BN}}$-Tetra | 10.91      | 8.56           | 8.46           | 8.42           |
| Cor$_{\text{3BN}}$-Penta | 9.51       | 7.80           | 7.73           | 7.70           |
| Cor$_{\text{3BN}}$-Pyr | 9.22       | 7.95           | 7.88           | 7.85           |
| Cor$_{\text{3BN}}$-Im | 8.94           | 7.97           | 7.91           | 7.86           |
| Cor$_{\text{3BN}}$-Pz | 8.58           | 7.70           | 7.67           | 7.66           |
| Cor$_{\text{3BN}}$-123-tria | 8.14     | 6.99           | 6.97           | 6.95           |
| Cor$_{\text{3BN}}$-124-tria | 8.55     | 7.35           | 7.27           | 7.24           |
| Cor$_{\text{3BN}}$-Tetra | 8.01       | 6.68           | 6.59           | 6.57           |
| Cor$_{\text{3BN}}$-Penta | 6.89       | 5.75           | 5.73           | 5.72           |
| Cor$_{\text{3BN}}$-Pyr | 11.27      | 9.69           | 9.60           | 9.56           |
| Cor$_{\text{3BN}}$-Im | 7.93           | 6.40           | 6.34           | 6.32           |
| Cor$_{\text{3BN}}$-Pz | 10.16       | 8.84           | 8.79           | 8.76           |
| Cor$_{\text{3BN}}$-123-tria | 5.77      | 4.59           | 4.14           | 4.14           |
| Cor$_{\text{3BN}}$-124-tria | 6.78       | 4.68           | 4.64           | 4.62           |
| Cor$_{\text{3BN}}$-Tetra | 10.77      | 8.99           | 8.91           | 8.86           |
| Cor$_{\text{3BN}}$-Penta | 8.46       | 6.21           | 6.13           | 6.11           |
| Cor$_{\text{3BN}}$-Pyr | 8.49       | 7.33           | 7.29           | 7.28           |
| Cor$_{\text{3BN}}$-Im | 10.13       | 8.26           | 8.16           | 8.12           |
| Cor$_{\text{3BN}}$-Pz | 7.29           | 6.92           | 6.85           | 6.83           |
| Cor$_{\text{3BN}}$-123-tria | 7.18     | 6.61           | 6.54           | 6.53           |
| Cor$_{\text{3BN}}$-124-tria | 9.49     | 7.28           | 7.21           | 7.18           |
| Cor$_{\text{3BN}}$-Tetra | 6.24       | 5.46           | 5.41           | 5.40           |
| Cor$_{\text{3BN}}$-Penta | 8.76       | 6.80           | 6.72           | 6.69           |
| Cor$_{\text{3BN}}$-Pyr | 9.43       | 8.13           | 8.07           | 8.04           |
| Cor$_{\text{3BN}}$-Im | 9.63       | 8.51           | 8.43           | 8.40           |
| Cor$_{\text{3BN}}$-Pz | 8.81       | 7.92           | 7.81           | 7.79           |
| Cor$_{\text{3BN}}$-123-tria | 8.75     | 7.66           | 7.59           | 7.55           |
| Cor$_{\text{3BN}}$-124-tria | 9.13     | 7.75           | 7.67           | 7.61           |
| Cor$_{\text{3BN}}$-Tetra | 8.21       | 6.87           | 6.77           | 6.77           |
| Cor$_{\text{3BN}}$-Penta | 6.75       | 5.52           | 5.41           | 5.40           |
and after complexation (charge transfer is defined as follows: $\Delta q = q_1 - q_2$ (charge at the pyrrolelike N atom before complexation) – $q$ (charge at the same site after complexation)), presented in Table 4. From $\Delta q$ values, it would be possible to predict whether an interaction is charge-controlled (electrostatic) or orbital-controlled (covalent). An interaction with a sufficiently small $\Delta q$ value is considered to be charge-controlled or electrostatic, whereas for orbital-controlled or covalent interaction, the $\Delta q$ value is larger. Table 4 shows variable charge transfer upon complexation depending upon the nature of both the monomers. For example, $\Delta q$ values for complexes formed by undoped Cor are significantly small (<0.003 e$^-$) except with Tetra and Penta for which relatively higher $\Delta q$ values (0.0079 and 0.0107 e$^-$) are observed, Table 4. Thus, for Cor-Tetra and Cor-Penta complexes, the contribution from the covalent component is relatively larger, whereas for the rest, the electrostatic contribution is comparatively larger. Similarly, for doped Cor, irrespective of

| complexes      | HF/6-311++G(d,p) | B3LYP/6-311++G(d,p) | $\Delta q$ |
|----------------|-----------------|-------------------|------------|
| Cor-Pyr        | −6.27           | −6.45             | 0.0010     |
| Cor-Im         | −5.34           | −3.90             | −0.0014    |
| Cor-Pz         | −5.55           | −4.09             | −0.0003    |
| Cor-123-tria   | −3.94           | −2.69             | −0.0028    |
| Cor-124-tria   | −3.33           | −2.15             | −0.0012    |
| Cor-Tetra      | −2.86           | −1.90             | −0.0079    |
| Cor-Penta      | −2.61           | −1.46             | −0.0107    |
| Cor(3B)-Pyr    | −7.64           | −4.51             | −0.0019    |
| Cor(3B)-Im     | −4.65           | −2.97             | −0.0046    |
| Cor(3B)-Pz     | −6.27           | −4.25             | −0.0065    |
| Cor(3B)-123-tria | −4.27  | −2.54             | −0.0065    |
| Cor(3B)-124-tria | −3.03  | −1.80             | −0.0070    |
| Cor(3B)-Penta  | −2.40           | −1.67             | −0.0119    |
| Cor(N)-Pyr     | 1.69            | −1.52             | −0.0073    |
| Cor(N)-Im      | −3.79           | −2.93             | −0.0118    |
| Cor(N)-Pz      | −7.51           | −3.71             | −0.0091    |
| Cor(N)-123-tria| −6.46           | −2.26             | −0.0107    |
| Cor(N)-124-tria| 1.81            | −1.23             | −0.0132    |
| Cor(N)-Penta   | −3.17           | −0.80             | −0.0137    |
| Cor(N)-Pyr     | −5.65           | −4.02             | 0.0028     |
| Cor(N)-Im      | −5.01           | −3.06             | 0.0009     |
| Cor(N)-Pz      | −5.60           | −3.91             | −0.0015    |
| Cor(N)-123-tria| −4.17           | −2.86             | −0.0039    |
| Cor(N)-124-tria| −3.49           | −2.03             | 0.0010     |
| Cor(N)-Tetra   | 2.89            | −1.57             | −0.0088    |
| Cor(N)-Penta   | −2.47           | −0.46             | −0.0070    |
| Cor(3N)-Pyr    | −2.75           | −2.55             | 0.0022     |
| Cor(3N)-Im     | −3.19           | −2.71             | −0.0016    |
| Cor(3N)-Pz     | −4.78           | −2.36             | 0.0013     |
| Cor(3N)-123-tria| −1.92       | −1.74             | −0.0018    |
| Cor(3N)-124-tria| 0.73            | −1.40             | −0.0017    |
| Cor(3N)-Tetra  | −2.18           | −4.90             | −0.0087    |
| Cor(3N)-Penta  | −0.17           | 2.69              | −0.0142    |
| Cor(3N)-Pyr    | −5.96           | −4.32             | 0.0007     |
| Cor(3N)-Im     | −2.99           | −1.99             | −0.0031    |
| Cor(3N)-Pz     | −6.20           | −4.70             | −0.0010    |
| Cor(3N)-123-tria| −5.33           | −3.90             | −0.0020    |
| Cor(3N)-124-tria| −1.89           | −1.10             | −0.0069    |
| Cor(3N)-Tetra  | −3.04           | −1.90             | −0.0080    |
| Cor(3N)-Penta  | −0.61           | 0.61              | −0.0152    |
| Cor(3N)-Pyr    | −5.14           | −3.78             | −0.0018    |
| Cor(3N)-Im     | −4.63           | −3.19             | −0.0070    |
| Cor(3N)-Pz     | −4.87           | −3.71             | −0.0056    |
| Cor(3N)-123-tria| −4.24           | −2.98             | −0.0076    |
| Cor(3N)-124-tria| −3.30           | −2.16             | −0.0087    |
| Cor(3N)-Tetra  | −3.18           | −1.97             | −0.0104    |
| Cor(3N)-Penta  | −3.21           | −2.16             | −0.0113    |
the nature of dopants, complexes with Tetra and Penta possess higher Δq values (0.0070–0.0170 e\(^{-}\)), indicating a higher covalent contribution, Table 4. Apart from this, most of the complexes formed by Cor(B), Cor(3B), and Cor(3BN) are associated with higher Δq values (0.0046–0.0170 e\(^{-}\)) irrespective of the considered N-heterocycle and thereby indicating a higher covalent contribution in their complexes, Table 4. On the other hand, for complexes formed by doped Cor(N), Cor(3N), and Cor(3BN) with Pyr, Im, Pz, 123-tria, and 124-tria, the electrostatic contribution is large with relatively lower Δq values, Table 4. The literature also suggested the secondary role of electrostatic interaction in stabilizing the B–H\(^{\cdots}\pi\) interaction with Δq values around 0.002 e\(^{-}\).\(^{43,47,48}\)

Therefore, it can be concluded that adsorption of the considered N-heterocycles is largely stabilized by dispersive interaction with secondary contribution from both electrostatic and covalent interactions depending on the natures of dopant and N-heterocycles.

2.4. Thermochemical Analysis. Enthalpy change upon complexation (ΔH) provides useful information about the stability of complexes.\(^{49}\) Apart from this, to predict the thermodynamic driving force, ΔH of complexation is estimated (at 298 K); its values are shown in Table 5. The estimated ΔH values are all negative (range from −4.80 to −12.88 kcal mol\(^{-1}\), Table 5), revealing the exothermic nature of complexation. Moreover, free energy change (ΔG) for the process of complexation is more reliable (comprises both enthalpy and entropy factors) and has been extensively used for examining the spontaneity of a process.\(^{53}\) Hence, ΔG values are also estimated (at 298 K) in the gas phase, and the values are provided in Table 5. The ΔG values are positive (0.12–4.49 kcal mol\(^{-1}\)) with a few exceptions for which negative ΔG (−0.04 to −2.45 kcal mol\(^{-1}\)) values are observed. Small positive ΔG values can be attributed to the entropy compensation resulting from complexation.\(^{49}\) Apart from this, higher stability of the corresponding complexes at a relatively low temperature is also revealed from the observed ΔG values. Generally, negative ΔG values are common in complexes with stronger interactions (cation···π, hydrogen bonding, etc.), whereas positive ΔG values are frequently observed in the case of complexes with weaker such as B–H\(^{\cdots}\pi\) interaction.\(^{42,43,49}\) The thermochemical study indicated that the adsorption of N-heterocycles is enthalpy-driven with the entropy factor restricting the spontaneity of the process.

Apart from gas phase, solvent phase ΔG values for the complexation are also calculated (at 298 K) by considering the complexes involving undoped Cor as the representative case. For this purpose, the geometry of the concerned complexes is re-optimized in solvent phases (cyclohexane, ethanol, and water), and the calculated ΔG values are presented in Table 6. Unlike those in the gas phase, the calculated ΔG values are all positive in solvent phases. However, it is observed that ΔG\(_{\text{solvent}} > ΔG_{\text{gas}}\). The difference between ΔG\(_{\text{solvent}}\) and ΔG\(_{\text{gas}}\) is significant.
is calculated to be in the range of 0.04–3.25 kcal mol\(^{-1}\). The results advocate that the complexation is not spontaneous in solvent phases, Table 6. With the increase in solvent dielectrics, \(\Delta G\) increases (becomes more positive, i.e., \(\Delta G_{\text{inh}} < \Delta G_{\text{sol}}\)). Although the \(\Delta G\) value becomes more positive with an increase in the solvent dielectric, values are not large enough (<5.0 kcal mol\(^{-1}\)) to prohibit the complexation, Table 6. The complexes are thus expected to be stable at lower temperatures.

### 2.5. HOMO—LUMO Perspective and UV—Visible Absorption Spectra

HOMO energy (\(E_{\text{HOMO}}\)) provides the electron-donating ability of a species, and in association with \(E_{\text{LUMO}}\) it measures the stability (HOMO—LUMO gap or \(E_{\text{LUMO}} - E_{\text{HOMO}}\)) and the control of the absorption spectra of the system under consideration.\(^{50}\) Hence, \(E_{\text{HOMO}}\) and the HOMO—LUMO gap are estimated using the TD-DFT calculation. For this purpose, the B3LYP hybrid functional is used in combination with the 6-31++G(d,p) basis set. Zhang et al. also have validated the use of hybrid functional in predicting the energies frontier molecular orbitals (FMOs).\(^{51}\) Apart from this, the ability of the B3LYP functional to produce results that are in close agreement with the experimental results has also fueled its use for TD-DFT calculations.\(^{63}\) To validate this fact, TD-DFT calculations are performed on undoped Cor (in THF as experimental result is available in THF) with B3LYP, CAM-B3LYP, \(\omega B97-XD\), and M06-2X functionals in association with the 6-31++G(d,p) basis set and a strong band for each at 306, 275, 271, and 276 nm, respectively. The experimental absorption spectrum in THF of Cor is reported to be 301 nm, suggesting the suitability of B3LYP functionals.\(^{52}\) In addition, the HOMO—LUMO gap of undoped Cor calculated from TD-DFT calculation is 4.06 eV, whereas the experimental result reported it to be 3.29 eV.\(^{53}\) Calculated gas phase \(E_{\text{HOMO}}\) and \(E_{\text{LUMO}} = E_{\text{HOMO}}\) of undoped/doped Cor along with its corresponding complexes obtained at the B3LYP/6-31++G(d,p) level of theory are shown in Table 7. As expected, \(E_{\text{HOMO}}\) of doped Cor varies (−3.36 to −5.66 eV) compared to that of undoped Cor (−5.74 eV) depending upon the nature of the dopants with significant effect on Cor(N) and Cor(BN), for which \(E_{\text{HOMO}}\) is increased by >2.00 eV, Table 7. Electron-rich N makes the Cor sheet electron-rich and thereby increases (less negative) the \(E_{\text{HOMO}}\) to a significant extent. Although relatively less, \(E_{\text{HOMO}}\) values for rest of the doped Cor also increase upon doping. A similar variation in \(E_{\text{LUMO}}\) values is also reported for B/N/BN-doped graphene.\(^{50}\) Compared with undoped Cor (4.06 eV), the HOMO—LUMO gap also varies (1.08–3.92 eV) on doping. Upon complexation, both drop and rise in \(E_{\text{HOMO}}\) values are observed. In some cases, the observed variation is insignificant, whereas in some others, it is relatively larger, Table 7. Compared to those of free Cor, \(E_{\text{HOMO}}\) values for the Cor-Pyr complex are increased by 0.20 eV, whereas for Cor-Im and Cor-Pz complexes, no variation in \(E_{\text{HOMO}}\) values is observed. On the other hand, for Cor-123-tria, Cor-124-tria, Cor-Tetra, and Cor-Penta complexes, \(E_{\text{HOMO}}\) values are increased up to 0.15 eV. Similar trends in \(E_{\text{HOMO}}\) values are also observed for most of the complexes involving doped Cor. However, except a few, in most of the complexes, the HOMO—LUMO gap remained similar (changed by <0.10 eV) upon complexation.

### Table 7. \(E_{\text{HOMO}}\) and HOMO—LUMO Gap (in eV) for Undoped/Doped Cor and Its Corresponding Complexes Obtained at the B3LYP/6-31++G(d,p) Level of Theory

| complex          | \(E_{\text{HOMO}}\) | HOMO—LUMO gap | complex          | \(E_{\text{HOMO}}\) | HOMO—LUMO gap |
|------------------|---------------------|----------------|------------------|---------------------|----------------|
| Cor              | −5.74               | 4.06           | Cor(N)–123-tria  | −3.42               | 1.66           |
| Cor-Pyr          | −5.54               | 3.84           | Cor(N)–124-tria  | −3.41               | 1.66           |
| Cor-Im           | −5.76               | 4.06           | Cor(N)–Tetra     | −3.63               | 1.77           |
| Cor-Pz           | −5.76               | 4.04           | Cor(N)–Penta     | −3.62               | 1.76           |
| Cor-123-tria     | −5.81               | 4.04           | Cor(BN)–123-tria | −3.39               | 1.72           |
| Cor-124-tria     | −5.87               | 4.04           | Cor(BN)–124-tria | −3.40               | 1.73           |
| Cor-Tetra        | −5.89               | 4.05           | Cor(BN)–Pyr      | −3.41               | 1.70           |
| Cor-Penta        | −5.88               | 4.04           | Cor(BN)–Pz       | −3.41               | 1.73           |
| Cor(3B)–Penta    | −5.66               | 3.92           | Cor(3B)–123-tria | −3.44               | 1.71           |
| Cor(3B)–Pyr      | −5.48               | 3.82           | Cor(3B)–124-tria | −3.46               | 1.69           |
| Cor(3B)–Im       | −5.62               | 3.79           | Cor(3B)–Pyr      | −3.69               | 1.77           |
| Cor(3B)–Pz       | −5.75               | 3.82           | Cor(3B)–Penta    | −3.69               | 1.77           |
| Cor(3B)–123-tria | −5.79               | 3.94           | Cor(BN)–123-tria | −5.42               | 3.47           |
| Cor(3B)–124-tria | −5.77               | 3.85           | Cor(BN)–124-tria | −5.60               | 3.49           |
| Cor(3B)–Tetra    | −5.68               | 3.94           | Cor(BN)–Tetra    | −5.61               | 3.44           |
| Cor(3B)–Penta    | −5.82               | 3.98           | Cor(BN)–Penta    | −5.62               | 3.47           |
| Cor(N)–Pyr       | −5.25               | 1.11           | Cor(BN)–Pyr      | −5.35               | 3.32           |
| Cor(N)–Im        | −5.38               | 1.11           | Cor(BN)–Im       | −5.29               | 3.24           |
| Cor(N)–Pz        | −5.34               | 1.11           | Cor(BN)–Pz       | −5.31               | 3.27           |
| Cor(N)–123-tria  | −5.37               | 1.08           | Cor(BN)–123-tria | −5.31               | 3.25           |
| Cor(N)–124-tria  | −5.47               | 1.13           | Cor(BN)–124-tria | −5.40               | 3.28           |
| Cor(N)–Tetra     | −5.49               | 1.12           | Cor(BN)–Tetra    | −5.37               | 3.28           |
| Cor(N)–Penta     | −5.55               | 1.19           | Cor(BN)–Penta    | −5.43               | 3.28           |
| Cor(3N)–Im       | −5.50               | 1.14           | Cor(3N)–Penta    | −5.44               | 3.28           |
| Cor(3N)–Pyr      | −3.36               | 1.69           | Cor(3N)–Pyr      | −3.36               | 1.69           |
| Cor(3N)–Pz       | −3.31               | 1.65           | Cor(3N)–Pz       | −3.31               | 1.65           |
| Cor(3N)–123-tria | −3.45               | 1.72           | Cor(3N)–124-tria | −3.45               | 1.72           |
| Cor(3N)–Tetra    | −3.34               | 1.66           | Cor(3N)–Tetra    | −3.44               | 1.66           |

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The recent literature also reported insignificant variation (in HOMO−LUMO gap) in the case of complexation between N-heterocycles and GBNCHs. Only in the case of Cor-Pyr, Cor(B)-Pyr, Cor(B)-Im, Cor(B)-Pz, and Cor(3N)-Tetra complexes, variations in the HOMO−LUMO gap are relatively larger (up to 0.22 eV). Insignificant changes in the HOMO−LUMO gap
suggest that adsorption of N-heterocycles does not perturb the electronic properties of the undoped/doped Cor systems to a significant extent. Petrushenko et al. also echoed a similar effect of complexation on the electronic properties of the GBNCH.

To further validate the effect of complexation on electronic properties, UV–visible absorption spectra of the monomers and their corresponding complexes are studied in THF, the result of which is shown in Figure 3a–h, and $\lambda_{\text{max}}$ values with corresponding excitation energies ($E$), oscillator strength ($f$), and the dominant transition are presented in the Supporting Information Table S1 (undoped/doped Cor) and Table S2 (complexes). As mentioned, undoped Cor possesses a strong absorption maximum at 306 nm corresponding to the HOMO → LUMO transition and can be attributed to HOMO − 1 → LUMO and HOMO → LUMO + 1 transitions. Upon doping, a significant red shift in the absorption maxima is observed. In the case of Cor(B) (two bands at 386 and 502 nm), Cor(3B) (one band at red shift in the absorption maxima is observed. In the case of Cor(BN) (one band) and Cor(3BN) (two bands except $\pi$–$\pi^*$ transitions. Upon doping, a significant red shift in the absorption maxima is observed. In the case of Cor(B) (two bands at 386 and 502 nm), Cor(3B) (one band at 1044 nm), and Cor(N) (two bands at 460 and 580 nm), red-shifted low-intensity absorption maxima are observed (Figure 3a and Supporting Information Table S1). On the other hand, for Cor(BN) (one band at 585 nm), Cor(B) (one band at 326 nm), and Cor(3BN) (two bands at 272 and 357 nm), high-intensity bands are observed, Supporting Information Table S1. As expected, upon complexation, no shift in the absorption spectra of Cor complexes is observed (lower intensity), Figure 3b. However, in the case of complexes with Cor(B) (visible region) and Cor(3B) (beyond the visible region > 1000 nm), red-shifted (up to 250 nm) absorption maxima are observed (Figure 3c,d and Supporting Information Table S2). In addition, in the case of Cor(B), for complexes formed with Pz, 123-tria, 124-tria, Tetra, and Penta, the N–H stretching frequencies are obtained and the observed results are shown in Table 8. In free N-heterocycles, i.e., in Pyr, Im, Pz, 123-tria, 124-tria, Tetra, and Penta, the N–H stretching frequencies are observed at 3735, 3727, 3730, 3715, 3723, 3720, and 3704 cm$^{-1}$, respectively. Upon complexation, a red shift (lower wave number) in the corresponding stretching frequencies is observed, Table 8. In some cases, the observed shift is nominal (<20 cm$^{-1}$), whereas in some cases, the shift is quite pronounced (up to 120 cm$^{-1}$). For example, in the case of complexation involving Pyr, a nominal red shift is observed except in Cor(3B)-Pyr and Cor(3N)-Pyr complexes for which a shift of >30 cm$^{-1}$ is observed, Table 8. Like Pyr, similar red shifts are also observed for other N-heterocycles also. The N–H stretching depends not only on the nature of dopant but also on the nature of N-heterocycles involved in complexation. For instance, the observed shift is found to be relatively higher in the case of Cor(3B) and Cor(3N) complexes. Apart from this, as compared to the rest, the maximum red shift (up to 120 cm$^{-1}$) is observed in the case of complexes with Penta, Table 8. The result thus confirms the involvement of N–H–$\pi$ interaction in the adsorption process with a larger contribution in the case of Cor(3B), Cor(3N), and Penta complexes.

### 3. CONCLUDING REMARKS

In this study, DFT calculations are performed to study the physisorption of seven 5-membered N-heterocycles on B/N-BN-doped coronene. The study confirmed that complexes are moderately strong and stable in both gas and solvent phases. With an increase in the number of dopants, the stability of the complexes increases. In the adsorption process, $\pi$–$\pi^*$ stacking and N–H–$\pi$ interactions operate simultaneously. Dispersion interaction is the primary mode of interaction along with some contribution from both electrostatic and covalent modes of interaction in stabilizing the complexes. The process of complexation is exothermic in nature and enthalpy-driven. For most of the cases, physisorption of N-heterocycles exhibit little impact on the electronic properties of the considered undoped/doped Cor. The results thus could be an impetus for environmental remediation from toxic N-heterocyclic compounds. Apart from this, obtained SE values can also be exploited for the drug delivery purpose.

### 4. THEORETICAL AND COMPUTATIONAL DETAILS

DFT is one of the most widely used approaches for calculating the electronic structure of a system. It produces results with a

| systems   | Pyr | Imd | Pyra | 123-tria | 124-tria | Tetra | Penta |
|-----------|-----|-----|------|----------|----------|-------|-------|
| Free      | 3735| 3727| 3730 | 3715     | 3723     | 3720  | 3704  |
| Cor       | 3722| 3739| 3722 | 3690     | 3693     | 3694  | 3640  |
| Cor(B)    | 3727| 3706| 3720 | 3697     | 3705     | 3702  | 3646  |
| Cor(3B)   | 3704| 3700| 3702 | 3655     | 3686     | 3676  | 3646  |
| Cor(N)    | 3724| 3696| 3719 | 3699     | 3689     | 3667  | 3584  |
| Cor(3N)   | 3702| 3708| 3695 | 3674     | 3685     | 3674  | 3453  |
| Cor(BN)   | 3721| 3698| 3723 | 3707     | 3694     | 3667  | 3601  |
| Cor(3BN)  | 3710| 3711| 3710 | 3696     | 3692     | 3684  | 3646  |

| Table 8. N–H Stretching Frequencies (in cm$^{-1}$) Obtained at the ωB97-XD/6-311++G(d,p) Level of Theory |
sensible trade-off between computational efficiency and accuracy. Because in π·π stacking long-range dispersion interaction plays a key role, the DFT functional with dispersion interaction in combination with a sufficiently large basis set is preferred for estimating such interaction. From this viewpoint, two of the most popular DFT functionals, viz., ωB97-XD and M06-2X, are used for the study. The literature also suggested the suitability of these functionals in estimating the dispersion-dominating interactions. Therefore, the geometries are optimized with the ωB97-XD functional in association with the 6-311++G(d,p) basis set. The ωB97-XD functional is reported to be efficient for calculating the thermochemical parameters and estimating the strength of noncovalent interaction. Hessians calculations are performed to ensure the real minima, and absence of imaginary frequency confirmed the minima of the concerned geometries. To test the consistency of the ωB97-XD functional, the single-point calculation is also performed on the gas-phase-optimized geometries at the M06-2X level of theory. Truhlar et al. expressed the suitability of the M06-2X functional for studying the thermochemistry, kinetics, and noncovalent interactions. A similar protocol, i.e., single-point calculation, is also carried out at ωB97-XD/6-31+G(d,p), ωB97-XD/cc-pVTZ, and ωB97-XD/def2TZVP levels of theory to assess the role of the basis set. To validate the suitability of the single-point calculation, the complexes formed by undoped coronene are re-optimized with the ωB97-XD/cc-pVTZ level of theory (as a representative case).

Aromaticity at the site of complexation is estimated using the harmonic oscillator model of aromaticity (HOMA) and is defined as:

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

where \( n \) is the number of bonds in the considered ring; \( \alpha \) is the empirical constant, fixed for a particular bond type; \( R_{\text{opt}} \) is the optimal bond length; \( R_i \) is the individual bond length between the adjacent atoms; and \( j \) corresponds to the bond type. HOMA values are calculated using the following proposed values of \( \alpha/R_{\text{opt}} \) (Å): 78.6/1.387 (for C–C bond), 87.4/1.339 (for C–N bond), 118.009/1.4378 (for B–C bond), and 72.03/1.402 (for B–N bond) [31,32,60].

Stabilization energies (SEs) of the complexes are measured using the supermolecular model, according to which SE is the difference of the total ground-state energies of the monomers and the ground-state energy of the complex [for the complexation process, \( \text{Cor} + \text{N-heterocycle} \rightarrow \text{Cor}\cdots\text{N-heterocycle} \), where \( E \) is the total electronic energy of the respective systems]. It is well mentioned that estimation of SE by this model produces basis set superposition error (BSSE) and therefore to mitigate the issue the counterpoise (CP) correction method (N route) is used. The supermolecular model is also used for calculating the enthalpy change (\( \Delta H \)) and free energy change (\( \Delta G \)) during complexation, i.e., \( \Delta H = H_{\text{Cor}\cdots\text{N-heterocycle}} - (H_{\text{Cor}} + H_{\text{N-heterocycle}}) \) and \( \Delta G = G_{\text{Cor}\cdots\text{N-heterocycle}} - (G_{\text{Cor}} + G_{\text{N-heterocycle}}) \), where \( H \) and \( G \) are the enthalpies and free energies of the corresponding monomers and complexes.

To interpret the UV–visible absorption spectra of monomers and complexes, time-dependent density functional theory (TD-DFT) calculations are performed at the B3LYP/6-31++G(d,p) level of theory considering vertical excitations from the ground state to \( N = 10 \) states.

The polarizable continuum model (PCM, solvent is considered as continuous dielectric medium) is used for solvent phase calculations. The PCM model implements the self-consistent reaction field (SCRF) approach and defines solvent polarization in terms of electrostatic potential. To assess the role of solvent dielectric, single-point calculations are performed on the optimized geometries at the same level of theory. For this purpose, cyclohexane (\( \epsilon = 2.02 \)), ethanol (\( \epsilon = 24.85 \)), DMSO (\( \epsilon = 46.82 \)), and water (\( \epsilon = 78.35 \)) are considered as the model solvent systems.

All calculations are performed with the Gaussian 09 programme package, and Gauss View S.1 is used for viewing the systems.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02340.

**Optimized geometries of**

- **(a) C_{42}H_{16}**
- **(b) C_{48}H_{18}**
- **(c) C_{48}H_{15}**
- **(d) C_{64}H_{20}** (Figure S1); \( \Delta_{\text{max}} \) values and their corresponding oscillator strength (\( f \)), excitation energy (\( E \)) with dominant transition for each undoped/doped Cor (Table S1) and its complexes (Table S2) in THF obtained at the B3LYP/6-31+G(d,p) level of theory (PDF)

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#### Notes

The authors declare no competing financial interest.

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