Theoretical Investigation of Br2 and Cl2 Detection by the Pristine and Co-Doped Graphyne

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Research Article

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Theoretical investigation of Br_2 and Cl_2 detection by the pristine and Co-doped graphyne

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Abstract

The Br_2 and Cl_2 interaction with the intrinsic, and Co-doped graphyne nanosheets has been explored by density functional theory calculations. Two vertical and parallel configurations were identified for Br_2 and Cl_2 adsorption. Calculations showed that the adsorption of Br_2 was stronger than Cl_2 on the graphyne nanosheet. Neither Br_2 nor Cl_2 could make serious changes to the HOMO-LUMO gap (E_g) and electrical resistance pf pristine sheet. By manipulating the structure of pristine graphyne by Co atom, its reactivity and sensitivity dramatically improved toward Br_2 and Cl_2 gases. Compared to the Cl_2, the Br_2 much more decreases the electrical resistance and E_g of the Co-doped graphyne (~ -40.25%). Thus, the Co-doped graphyne may selectively recognize the Br_2 gas in the presence of Cl_2. The computed recovery time value for Br_2 from the surface of the Co-doped graphyne is 36.4 *s*, which shows that the graphyne, as a sensor, benefits from a short recovery time to detect Br_2.

Keywords: Density functional theory, Adsorption, Nanosheet, Graphyne, Sensor

1. Introduction

Releasing toxic gases into the environment is now a major problem, so many researchers are working to produce different sensors to detect these gases. Chlorine is a dense yellow and green gas with a suffocating odor and a boiling point of -34 °C. Chlorine is used as an oxidizing agent in alternative reactions. 85% of pharmacies use chlorine or its compounds in their production process [1]. Exposure to Cl_2 gas causes irritation, pain, and blisters on the skin, and excessive inhalation can cause blurred vision, nausea, and vomiting. Bromine is also a toxic substance that has a wide range of uses, such as chemical intermediates, pharmaceuticals, agricultural chemicals, insecticides, dyes, etc [2]. Bromine gas breathing causes problems such as headache, cough, dizziness, and respiratory problems and so on. Therefore, it seems that finding a cheap, reliable, and simple method for detecting Cl_2 and Br_2 is important in many cases. The adsorption of Cl_2 and Br_2 on various nanostructures has been investigated [3-5]. Nanosheets are two-dimensional structures which have aroused considerable interest in the sensor industry due to their great sensitivity, fast response time, and large surface to volume ratio [6-9]. Graphyne is one of the carbon allotropes which has been produced by Bughman et al. [10]. It contains carbon atoms with sp and sp^2 hybridizations. In six-membered rings of graphyne, carbon atoms hybridize to form sp^2. The hexagons are connected together by triple carbon-carbon linkages (–C≡C–). These triple bonds are the main factor that distinguish graphyne from graphene. This distinction is due to the different optical and electronic properties. For example, wider band gap is observed in graphyne due to different kinds of C-C bonds.

The interaction of different molecules with the surface of nanostructures is investigated because of potential applications such as storages, electronic devices[11], and chemical sensors

[12-15]. In the case of sensors, changes in the electrical conductivity are expected to be evident and the adsorption of gas molecules onto them should be stable, but in most cases, this does not happen and the gases are physically adsorbed [16, 17]. In physical adsorptions, there is not noticeable change in the electrical conductance of nanostructures. To improve the sensing performance of nanostructures, some atoms have been replaced by impurity atoms [18-20]. Recent theoretical studies on Co-doped graphyne nanosheet have shown that these structures are useful for hydrogen storage [21]. In the current study, the interaction between graphyne and chlorine, as well as the graphyne and bromine will be investigated using structure analysis, electronic properties, energy, and so on. The aim of this manuscript is to survey the effects of the Cl_2 and Br_2 on the electronic properties of graphyne in order to design sensor.

2. Computational methods

A graphyne nanosheet was selected as a model with 86 carbons and its ends include hydrogen (H) atoms. Calculations such as energy calculations, geometry optimization, and state density analysis on the pure and Co-doped graphyne were performed at B3LYP density functional improved with an experimental dispersion factor (B3LYP-D). The 6-31G (d) basis set was used and all calculations were done by using GAMESS software [21]. We used GaussSum [22] software to show the density of state (DOS) diagram. Previous researches have indicated that the B3LYP density functional is used for nanostructures and it has defensible performance in this field [23, 24]. After a Cl_2 adsorption and at another time adsorption of a Br_2 molecule onto the pristine and Co-doped graphyne, the adsorption energy (E_{ad}) is obtained as follows:

$$E_{ad} = E(X_2) + E(\text{graphyne}) - E(X_2/\text{graphyne}) - E_{BSSE} \quad (1)$$

Here E (X_2) is the X_2 molecule energy (X = Cl or Br), E (graphyne) is the pristine graphyne nanosheet energy, and E (X_2/graphyne) is the energy of the graphyne on which Cl_2 or Br_2 is adsorbed. The positive energy of the adsorption energy shows that this adsorption is exothermic. Basis set superposition error (BSSE) is corrected for the all interactions.

3. Results and discussion

3.1. Pure graphyne

Graphyne nanosheet is a type of carbon allotrope in which single, resonance bonds (in its hexagonal ring) and triple bonds in the –C≡C– linkage can be observed, as shown in Fig. 1. In the graphyne, there are two kinds of carbon atoms. One is sp-hybridized (tagged as C_a), which connects carbon hexagons, and the other is sp^2-hybridized hexagons (tagged as C_b). After the optimization, the bond length between the two C_b atoms becomes 1.42 Å, which indicates the presence of resonance in the hexagonal rings. The existence of a short bond length between the two C_a atoms (1.22 Å) suggests that a triple bond is formed between them. It has also been previously shown [25] that the bond length between two single carbons is 1.53 Å, while in this configuration, the bond length between C_a and C_b (1.41 Å) is much shorter than a π bond. Due to the presence of C_a atoms in graphyne, this configuration is somewhat less stable in terms of energy than graphene [26]. The calculated HOMO-LUMO gap (E_g) is about 2.57 eV, demonstrating a semiconducting character.

Different possible primary adsorption geometries were taken into account to achieve the most stable complex of a Cl_2 or Br_2 adsorbed on the sheet. For each molecule, we predicted two local minima (Figs. 2 and 3). In one configuration the X_2 (X = Cl or Br) interacts vertically with the C_a atom through, and in another configuration the X_2 interacts horizontally with the sheet. Configuration **A** indicates a weak physical interaction between the graphyne and Cl_2, the Cl_2

interacting in parallel with the graphyne surface (Fig. 2). The E_{ad} is 4.3 kcal/mol, which indicates the physical nature of this interaction. However, configuration **A** is somewhat more stable than the **B** configuration (E_{ad} = 3.2 kcal/mol). Similarly, for Br_2 adsorption, the configuration **C** (Fig. 3) is stronger than the configuration **D.** Configuration **C** has an E_{ad} of 8.98 kcal/mol, and the Br_2 molecule is located at a distance of 3.01 Å from the graphyne nanosheet. By X_2 adsorption, both of valence and conduction levels in the pristine graphyne change slightly. It is clear that after the adsorption process because of the weak adsorption of Cl_2 and Br_2, the E_g of graphyne cannot change dramatically. The E_g decreases from 2.57 eV in the pure graphyne to 2.50 and 2.44 eV in **A** and **C** complexes, respectively. Thus, the pristine graphyne is not a proper sensor for detection of X_2 gases.

3.2. Co-doped graphyne

Moreover, the impact of substituting one C_a or C_b atom by a Co atom was investigated on the graphyne construction and electronic and sensing properties (Fig. 4). The construction of the doped graphynes are significantly changed because the Co atom is bigger than the carbon atom. Here, we show the Co-doped graphynes (Co@graphyne) by symbols **Co.1** and **Co.2**, that Co atom replaces a C_a and C_b atom in the graphyne, respectively. The calculated bond length for Co-C_a (Co-C_b) bond in the Co-doped graphyne is 1.67 (1.87) Å, which is much longer than the corresponding C-C bond. The impurity Co creates new electronic states inside the E_g. As shown in Table. 2, the E_g of **Co.1** is 2.46 eV and that of **Co.2** is 2.41 eV.

Then, X_2 adsorption was investigated by placing X_2 around Co atom with different initial directions as shown in Figs. 5 and 6. For each Co@ graphyne sheet (**Co.1** and **Co.2**), one different adsorptive configuration of Cl_2 and Br_2 is found. To adsorb Cl_2 in Co@graphyne, configuration **L**

(Cl_2/Co.2) creates an E_{ad} of 13.6 kcal/mol, that is higher than that of **J** (Cl_2/Co.1, E_{ad} = 11.1 kcal/mol). In comparison, we find that the adsorption of Cl_2 on the Co@graphyne is more energy-efficient than that on the bare graphyne. In configurations **J** and **L**, the Cl atoms of Cl_2 were located above the Co atom with the bond lengths of 2.58 and 2.38 Å. To adsorb Br_2 on the Co@graphyne, configuration **M** (Br_2/Co.2) causes an E_{ad} of 24.1 kcal/mol, that is more stable than the configuration **K** (Br_2/Co.1) with the E_{ad} = 18.0 kcal/mol. In configurations **K** and **M**, the Br atoms of Br_2 were located above the Co atom with the bond lengths of 2.29 and 2.15Å. The results obtained from the E_{ad} and E_g of the Cl_2 and Br_2 adsorption on the Co@graphyne are summarized in Table 2. Doping Co can strengthen the interaction of these gases with the sheet, which is greater for the Br_2 molecule. It should be noted that the larger size of Br_2 compared to the Cl_2 produces an instantaneous dipole moment which strengthens its interaction with the Co as an electron-deficient site. Co has a partial positive charge of 0.65 |e| based on the natural bond orbital (NBO) analysis. As a result, the adsorption of Br_2 on the Co@graphyne is stronger than that of the Cl_2 gas.

3.3. Sensing and electronic properties

Partial DOS diagram of the Br_2 molecule and Co@graphyne indicates a shift in the HOMO and LUMO (Fig. 8). According to this diagram, it can be concluded that the electronic properties of the Co@graphyne have become more sensitive to the Br_2 in comparison to the pure graphyne. The value of E_g in the doped **K** and **M** sheets alters from 2.46 and 2.41 eV to 1.71 and 1.44 eV in the complexes, respectively (Table 2). Therefore, according to the information obtained, the E_g value of the **M** graphyne has decreased (by approximately 40.25%) in the complex form. It results in the electrical conductivity variation of the doped nanosheet based on the below formula:

$$\sigma \propto exp\ (\frac{-Eg}{2kT}) \quad (2)$$

In eq. 2, k is the Boltzmann constant and σ is the electric conductivity [27], and at a given temperature, the lower the value of E_g, the higher the electrical conductivity. Thus, a significant decrease is observed in E_g in the Co@graphyne when the adsorption procedure causes an increase in the electrical conductance of the complex.

To further scrutinize the sensitivity of extrinsic and intrinsic graphynes, the changes in the work function (Φ) of the sheets upon the charge transfer have been investigated. Φ is defined as the lowest amount of work or energy needed to relocate the electron from the level of Fermi to the vacuum. When gas adsorption, changes the Φ of an adsorbent, it can change the intensity of field emission [28]. In addition, the density of electron current can be obtained as follows:

$$j\ =\ AT^2\ exp\ (\frac{-\Phi}{kT}) \quad (3)$$

Where T is the temperature (K), A is called the Richardson constant (A/m^2). The Φ is computed as follows:

$$\Phi = E_{inf} - E_F \quad (4)$$

Where E_F designates the energy of the Fermi level and E_{inf} designates the electrostatic potential at infinity, which is presumed to be equal to 0. We subtracted Φ of the sheet from that of the complexes and obtained Φ changes (ΔΦ).

The Φ of the pure graphyne is approximately 3.90 eV (calculated in Table 1), which changes slightly after the adsorption of Cl_2 and it can be ignored. However, after the adsorption of Br_2 through the **M** graphyne (Fig. 6, Table 2), its Φ decreases significantly from 3.90 to 3.21 eV (by approximately 17.7%). As mentioned before, Eq. 2 shows that the electron current density is

related to the Φ exponentially. Consequently, after the adsorption of Br_2, the emitted electron current density from the Co@graphyne can be dramatically amplified. Therefore, we think that Co doping can be considered an effective method to increase the sensitivity of graphyne to Br_2, which could not be distinguished by the intrinsic graphyne.

3.4. Recovery time

We know that very strong interactions cannot be desirable in gas detection, because of having a strong interaction between the two involved. Strong interactions show that the molecule will be difficult to be desorbed from the surface and the device may suffer from a long recovery time. It seems that the adsorption of Br_2 on the surface of Co@graphyne may be reversible because of the moderate E_{ad} based on the following equation:

$$\tau = \nu_0^{-1} exp\left(\frac{E_{ad}}{kT}\right) \quad (5)$$

Where ν_0 is the attempt frequency, *T* the temperature; and k the Boltzmann's constant (~ 2×10^{-3} kcal/mol.K). At 298 K and the ultra-violet light ($\upsilon \sim 10^{16}\ s^{-1}$), τ computed for the desorption of Br_2 from the surface of the Co@graphyne nanosheet is 36.4 s, which shows that the Co@graphyne has a short τ as a sensor to detect Br_2. As a comparison, τ value for various chemical agents such as SO_2/Al-doped h-BN [29], adrucil/Si-doped phagraphene [30], metronidazole/B_{36} borophene [31], phosgene/BN nanocones-180 [42], and cathinone/$B_{12}N_{12}$ [43], is 27.6, 0.02, 1.53, 0.48 and 0.54 s, respectively.

4. Conclusion

The adsorption of Br_2 and Cl_2 gases on the surface of pristine graphyne, and Co@graphyne has been studied by DFT. The results showed that Cl_2 and Br_2 prefer to be absorbed in parallel with

the graphyne surface with E_{ad} of 4.3 and 9.0 kcal/mol. It was found that the Cl_2 and Br_2 molecules were weakly adsorbed onto the pristine BC_3 with low E_{ad} and much distance. Adsorption of Cl_2 and Br_2 On pristine graphyne and Co@graphyne is found to be exothermic in order of $Cl_2 < Br_2$. After the adsorption of the Cl_2 and Br_2, there was low change in the electronic properties of the pure graphyne. The Cl_2 and Br_2 prefer to be absorbed in parallel with the Co@graphyne surface with E_{ad} of 13.8 and 24.1 kcal/mol, respectively. After the adsorption of the Cl_2, there was low change in the electronic properties of the Co@graphyne. However, the Br_2 molecule had a strong interaction with the Co@graphyne. After the adsorption of Br_2, there is significant destabilization in the HOMO level of the Co@graphyne. Therefore, there was a considerable reduction in its E_g leading to an increase in the electrical conductance. The results suggest that Co doping may be a promising way to increase the sensitivity of graphyne toward Br_2 significantly. The computed τ value for Br_2 from the surface of the Co@graphyne is 36.4 *s*, which shows that the graphyne, as a sensor, benefits from a short τ to detect Br_2.

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Figure captions

Fig. 1. Optimized structure of graphyne and its density of states (DOS).

Fig. 2. Models for two stable adsorption states for a Cl_2 molecule on the pure graphyne, distances are in Å.

Fig. 3. Models for two stable adsorption states for a Br_2 molecule on the pure graphyne, distances are in Å.

Fig. 4. Optimized structures of different Co-doped graphyne.

Fig. 5. Models for two stable adsorption states for one of the Br_2 and one of the Cl_2 molecule on the Co-doped graphyne, distances are in Å.

Fig. 6. Models for two stable adsorption states for one of the Br_2 and one of the Cl_2 molecule on the Co-doped graphyne, distances are in Å.

Fig. 7. The HOMO/LUMO profile of Co-doped graphyne/Br_2 nanostructure complex.

Fig. 8. Partial DOS plot of Co-doped graphyne/Br_2 nanostructure complex.

Table 1. Calculated adsorption energy of Cl_2 and Br_2 (E_{ad}, kcal/mol), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level energies (E_F) and HOMO–LUMO energy gap (E_g) for pristine graphyne.

Structure	E_{ad}	E_{HOMO}	E_F	E_{LUMO}	E_g	$\Delta E_g(\%)$	Φ	$\%\Delta\Phi$
Graphyne	-	-5.18	-3.90	-2.61	2.57	-	3.90	-
A	4.3	-5.15	-3.90	-2.65	2.50	-2.72	3.90	0.00
B	3.2	-5.17	-3.93	-2.68	2.49	-3.11	3.93	0.64
C	9.0	-5.07	-3.85	-2.63	2.44	-5.06	3.85	-1.28
D	6.0	-5.13	-3.89	-2.65	2.48	-3.50	3.89	-0.26

Table 2. Calculated adsorption energy of Cl_2 and Br_2 (E_{ad}, kcal/mol), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), Fermi level energies (E_F) and HOMO–LUMO energy gap (E_g) for Co-doped graphyne.

Structure	E_{ad}	E_{HOMO}	E_F	E_{LUMO}	E_g	$\Delta E_g(\%)$	Φ	$\%\Delta\Phi$
Co.1	-	-5.11	-3.88	-2.65	2.46	-	3.88	-
J	11.1	-4.87	-3.75	-2.63	2.24	-8.9	3.75	-3.3
K	18.0	-4.25	-3.40	-2.54	1.71	-30.0	3.40	-12.3
Co.2	-	-5.10	-3.90	-2.69	2.41	-	3.90	-
L	13.6	-4.76	-3.70	-2.63	2.13	-11.6	3.70	-4.4
M	24.1	-3.93	-3.21	-2.49	1.44	-40.2	3.21	-17.7

Fig. 1.

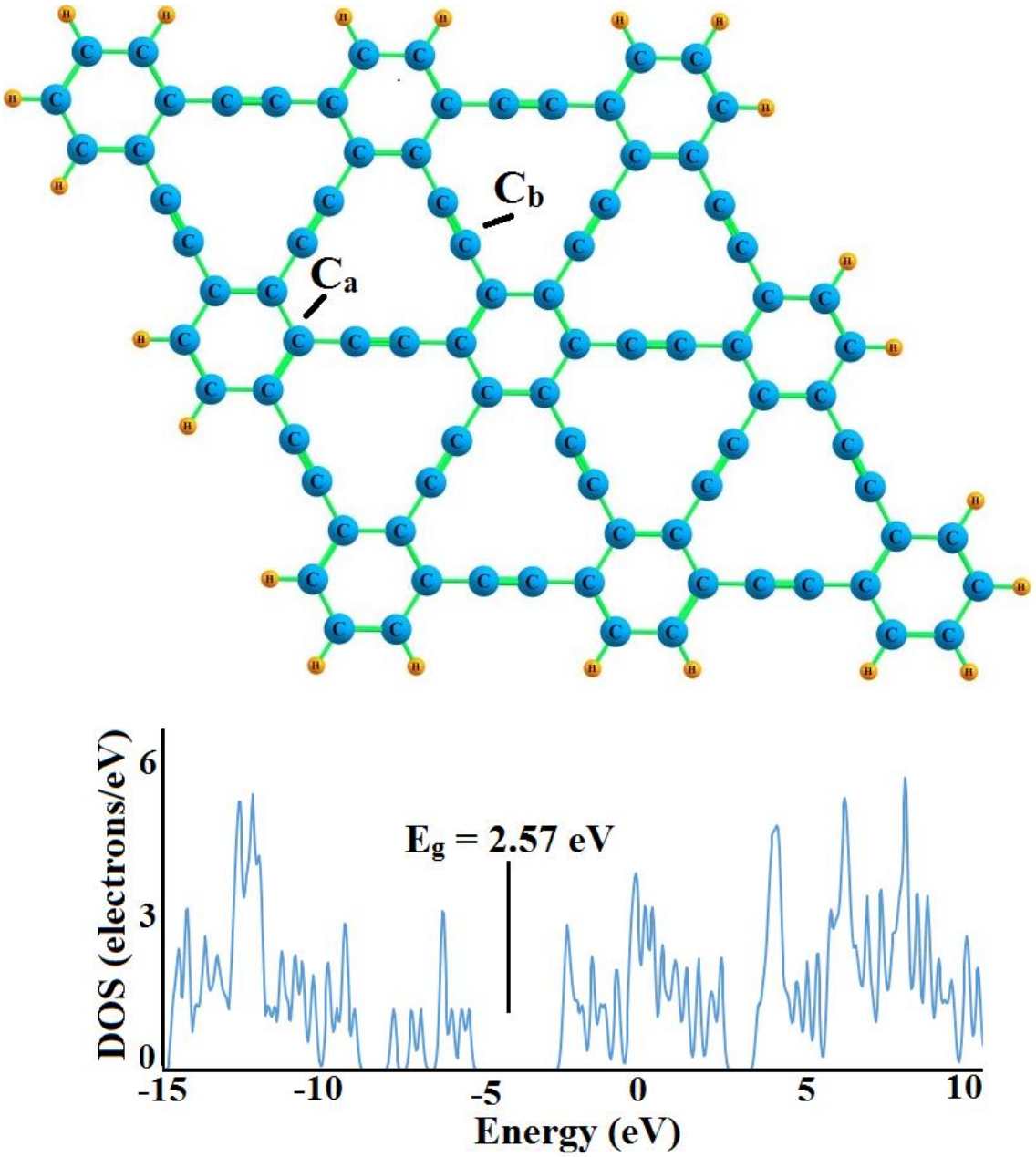


Fig. 2.

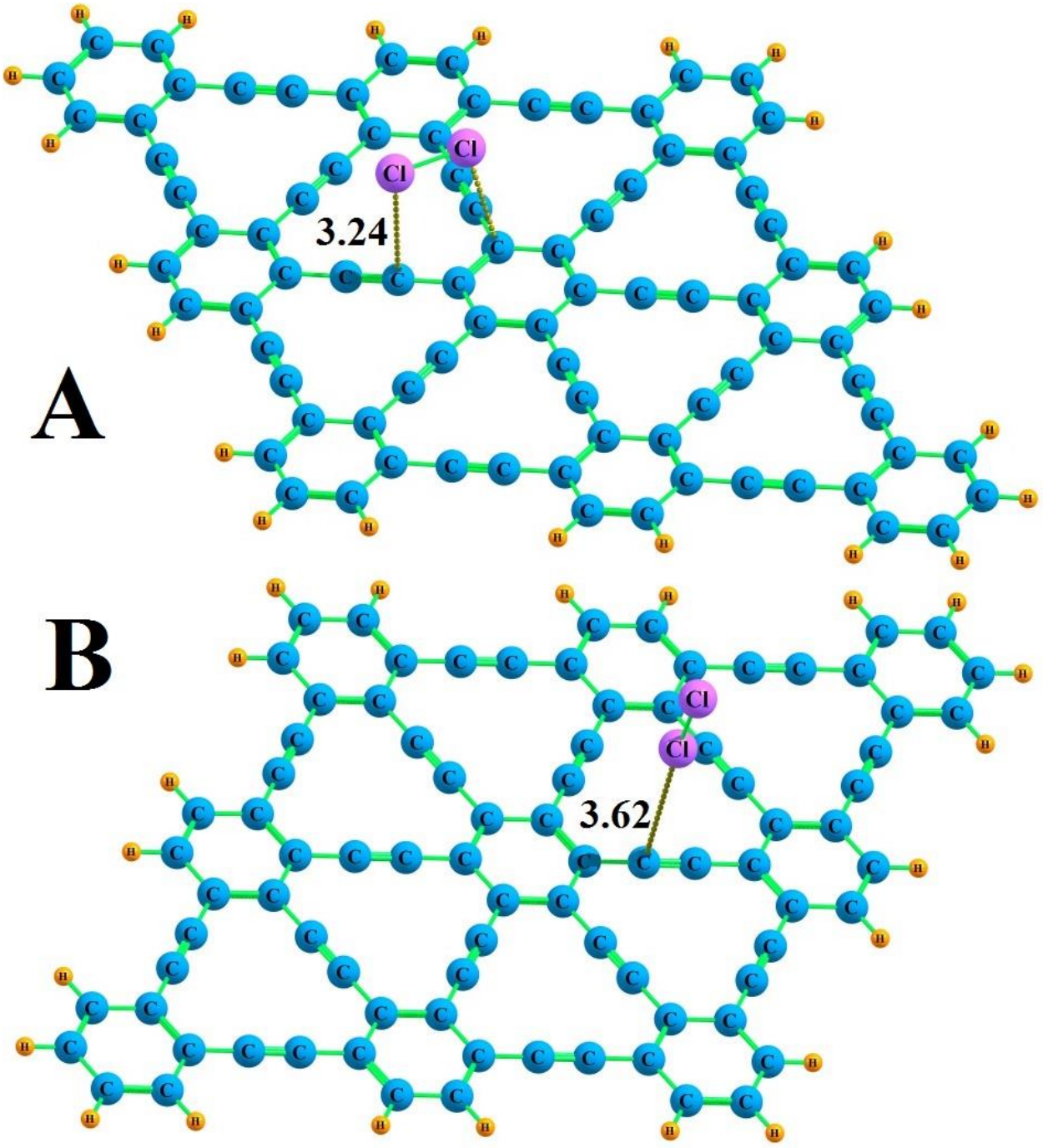
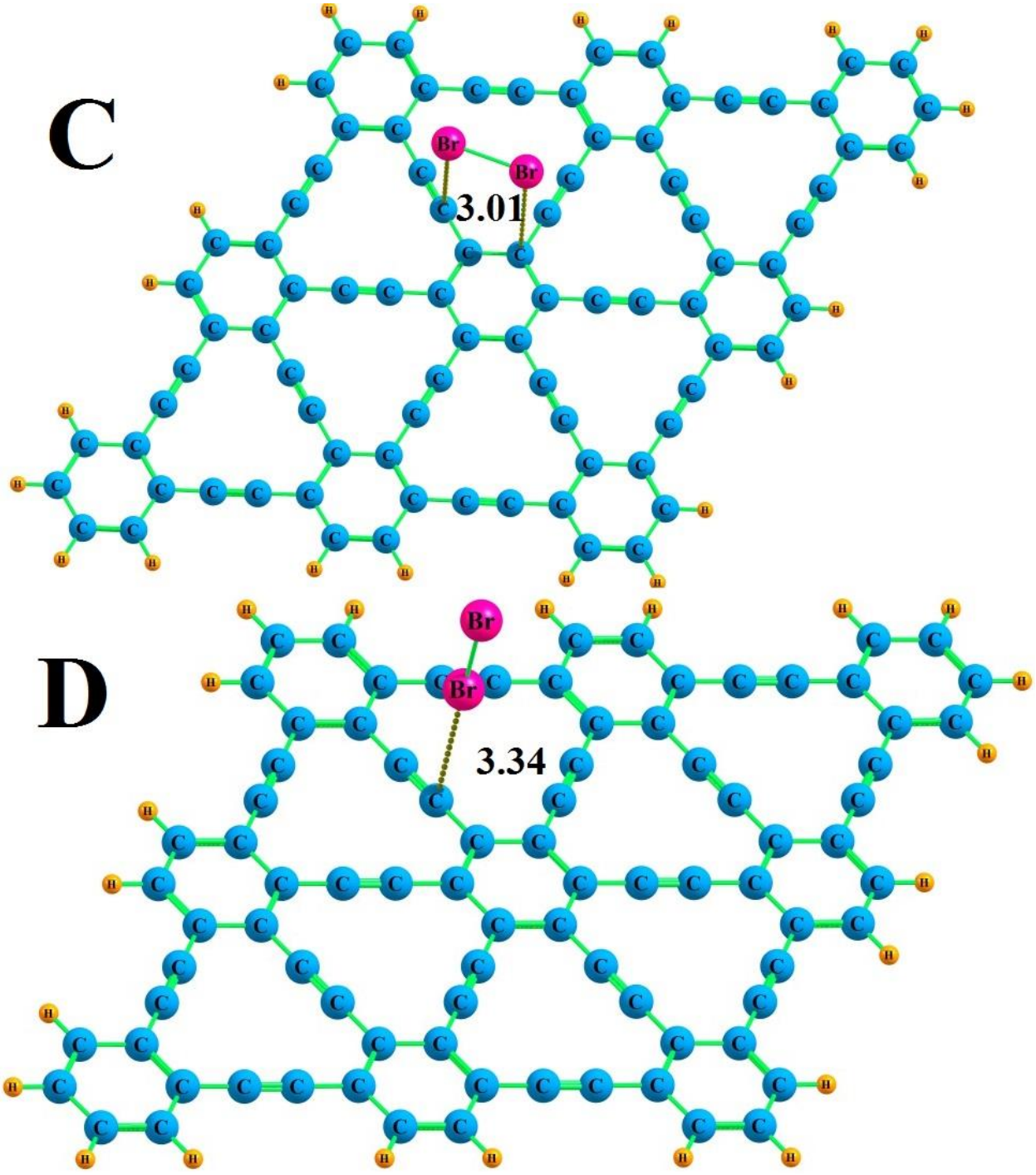


Fig. 3.



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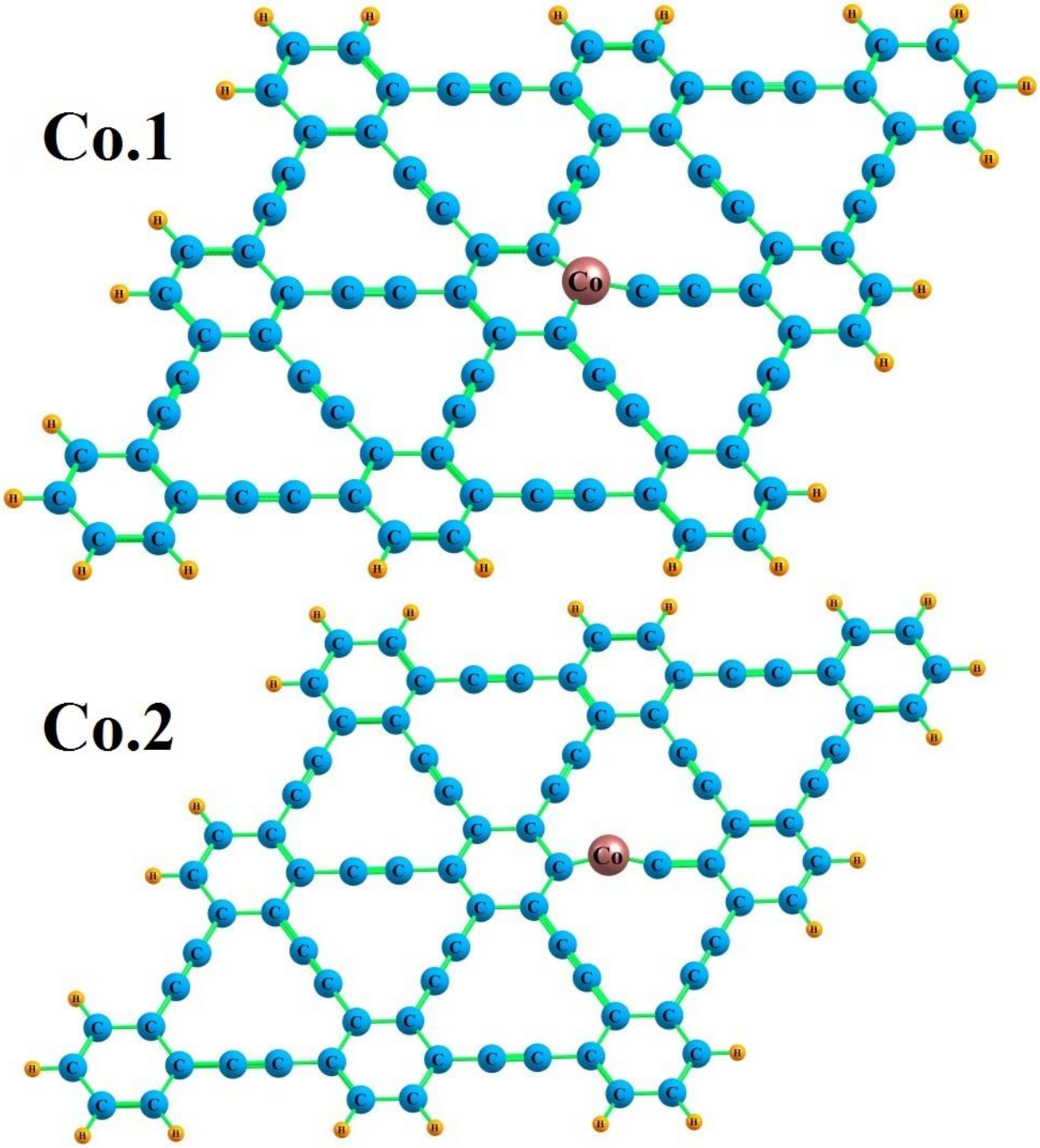


Fig. 5.

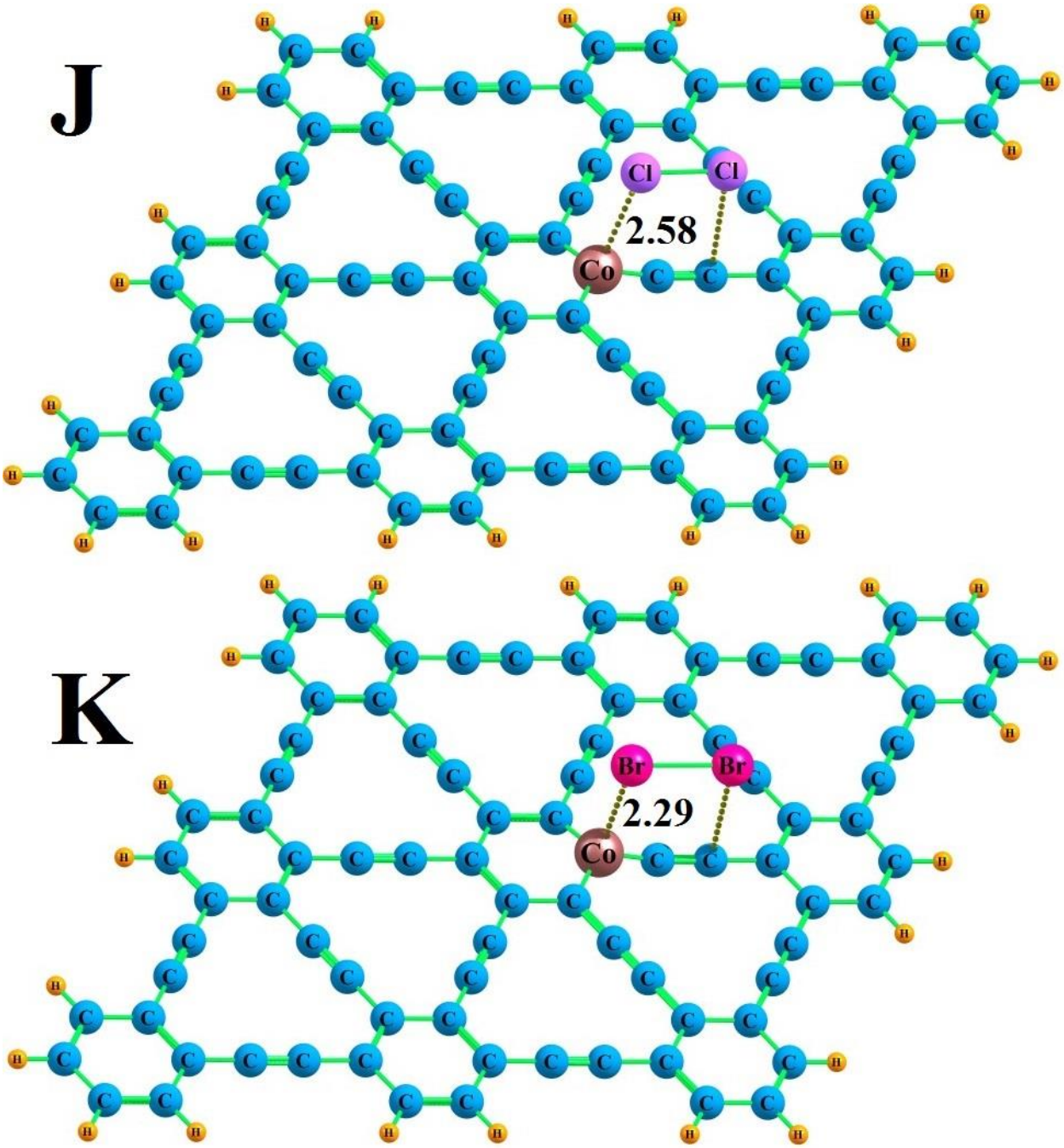


Fig. 6.

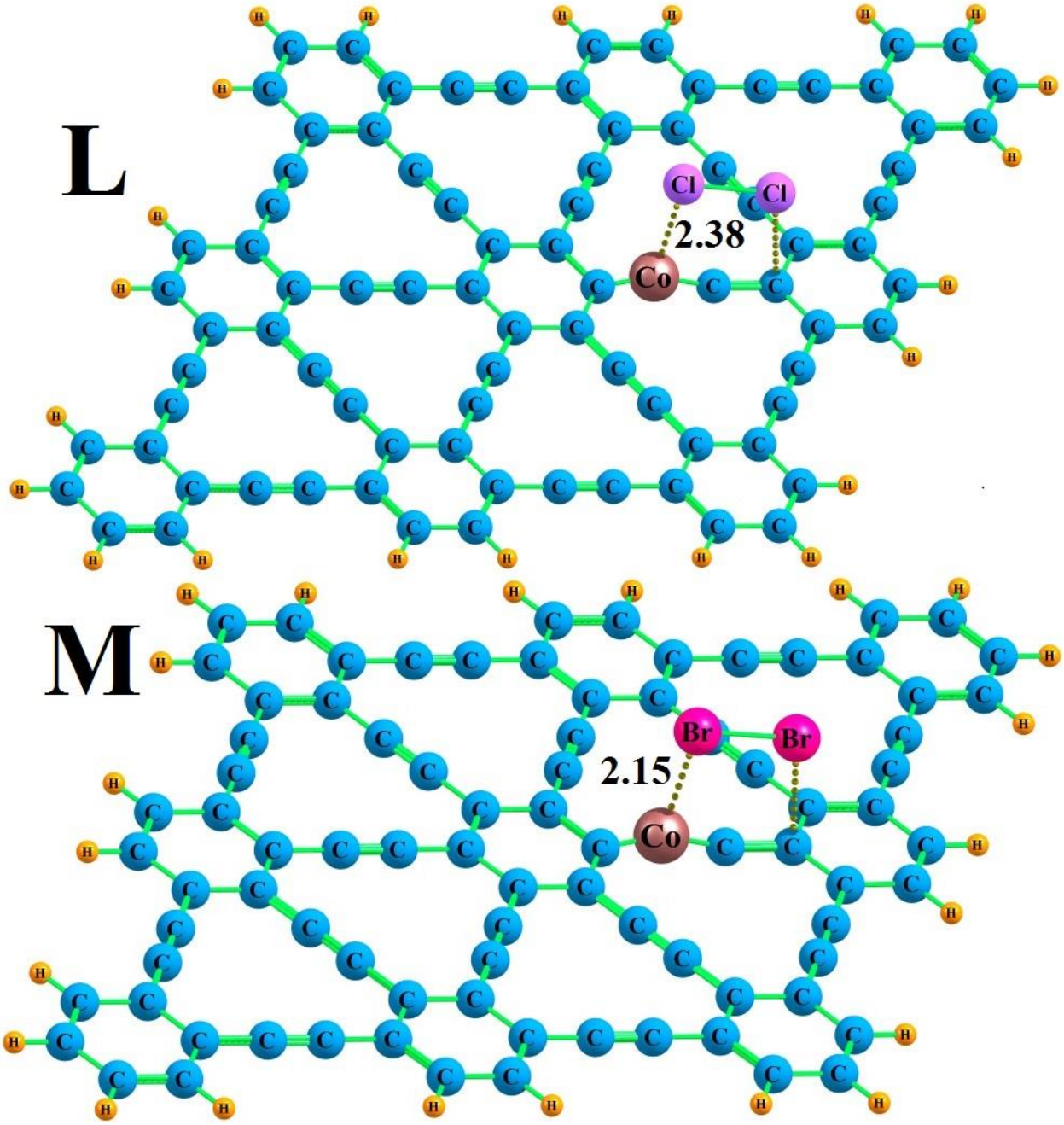


Fig. 7.

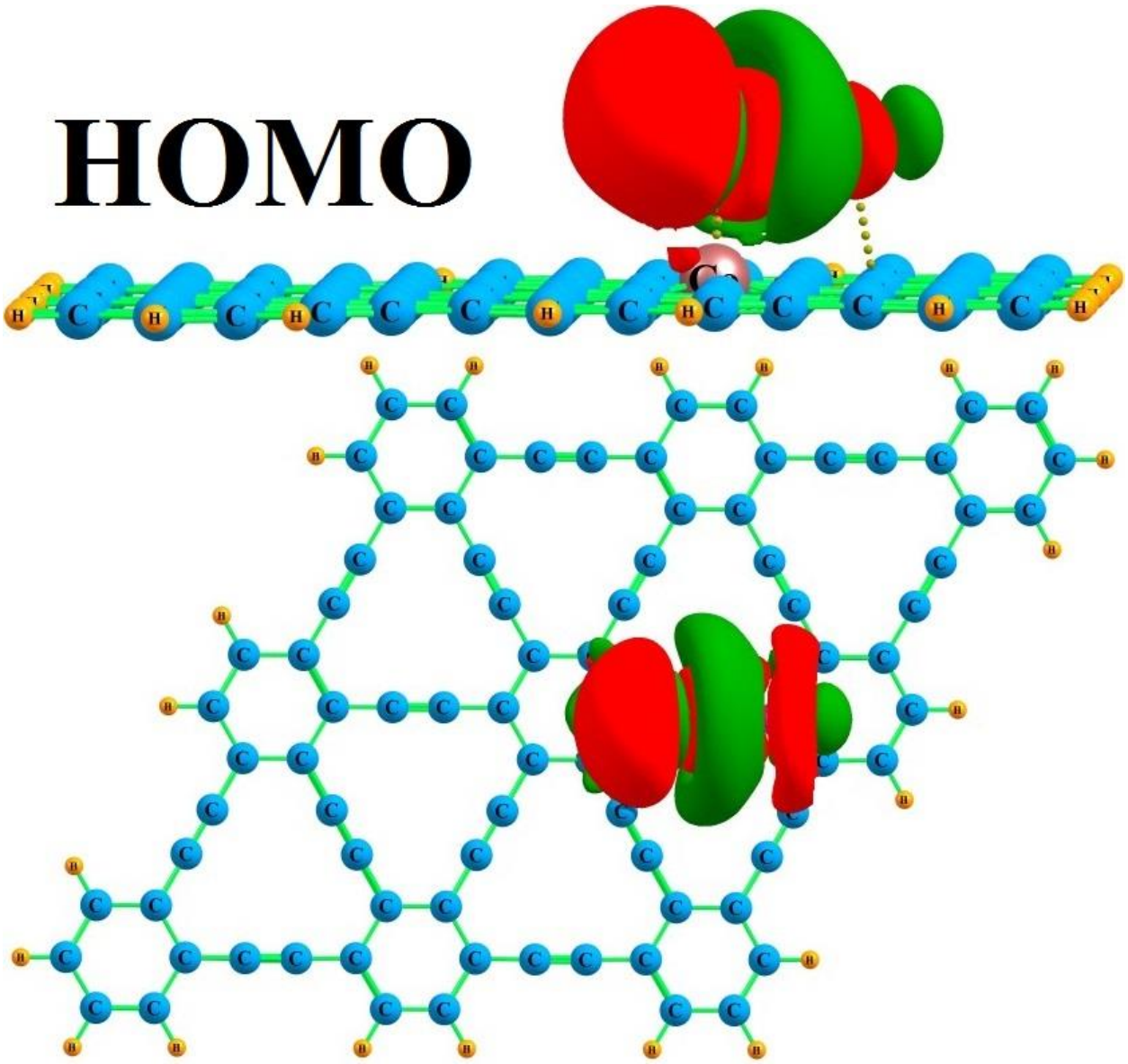
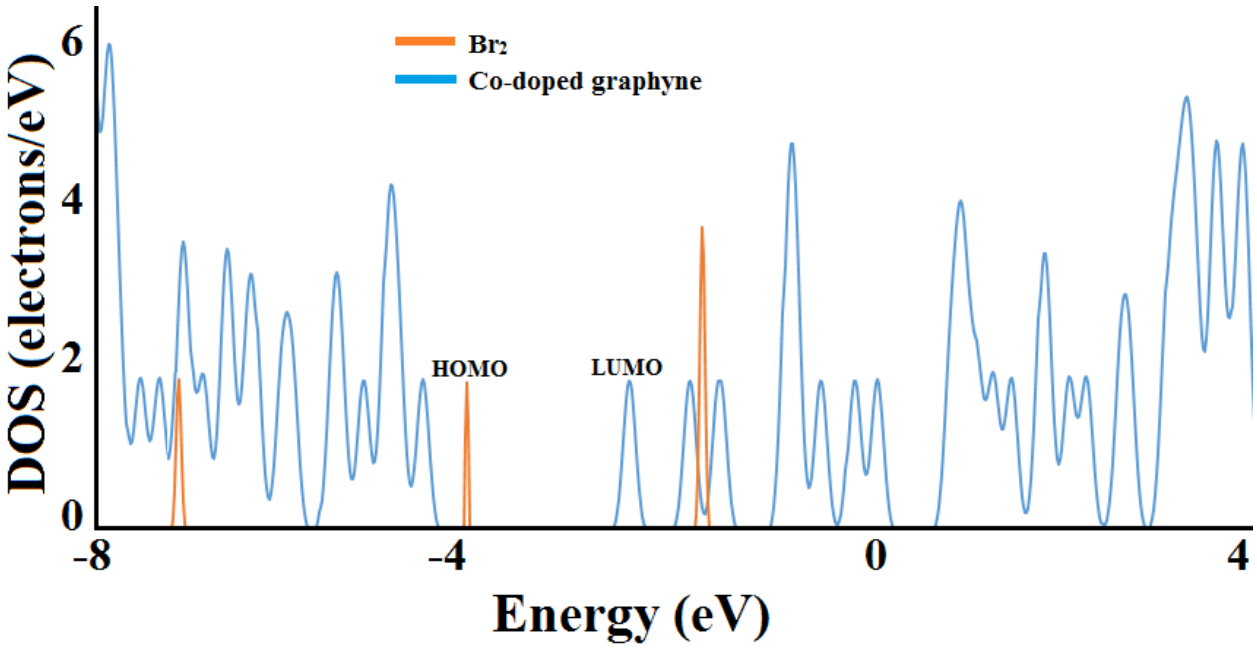


Fig. 8.


Br2
Co-doped graphyne
DOS (electrons/eV)
6
4
2
0
HOMO
LUMO
-8
-4
0
4
Energy (eV)

Declarations

Funding: Not applicable

Conflicts of interest/Competing interests: There is no conflict of interest

Availability of data and material: All data will be available if required.

Code availability: Not applicable

Authors' contributions: Not applicable

Ethics approval: We approved all Ethics

Consent to participate Not applicable

Consent for publication Not applicable

Availability of data and material Not applicable

Authors' contributions Not applicable

Figures

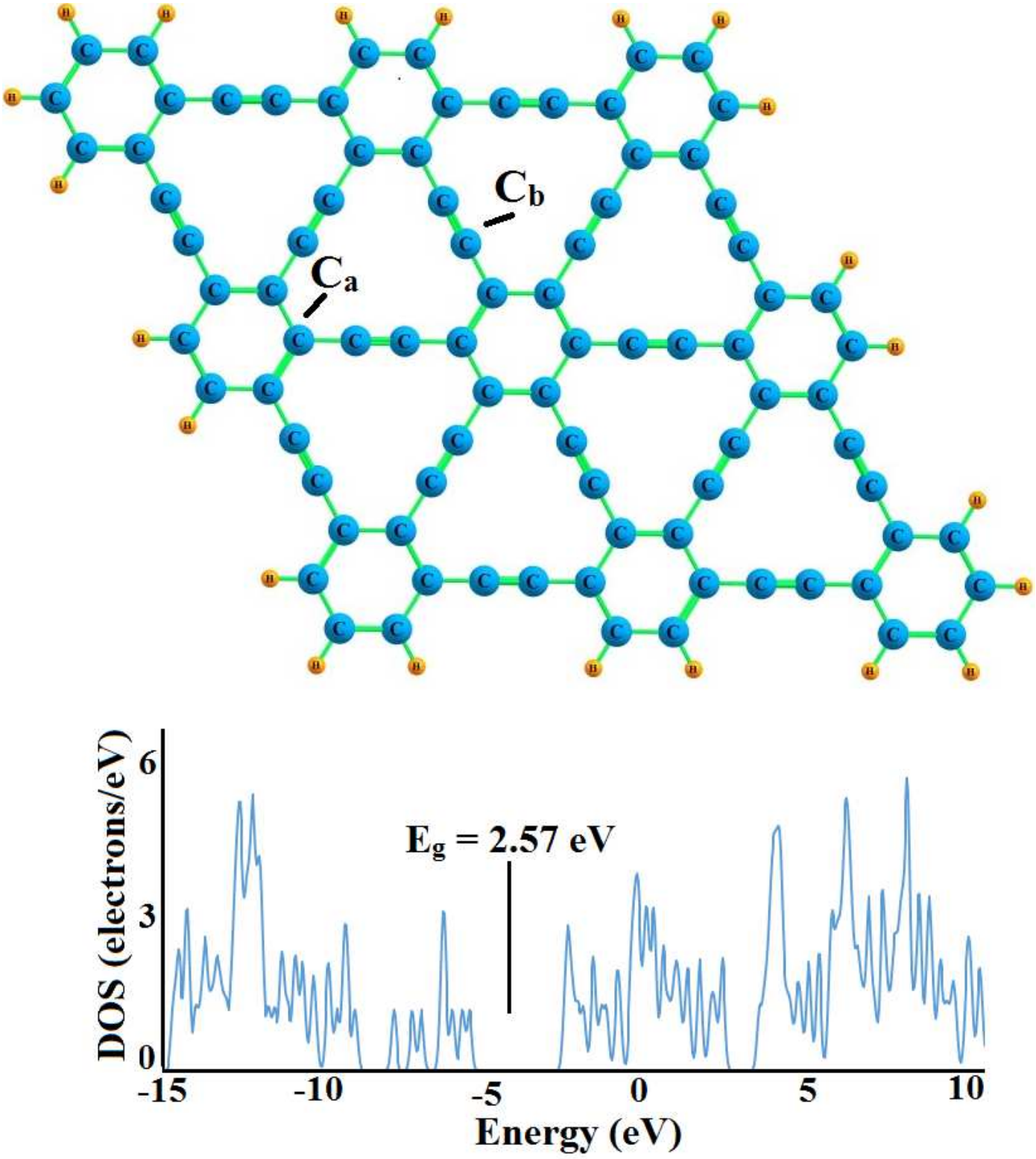


Figure 1

Optimized structure of graphyne and its density of states (DOS).

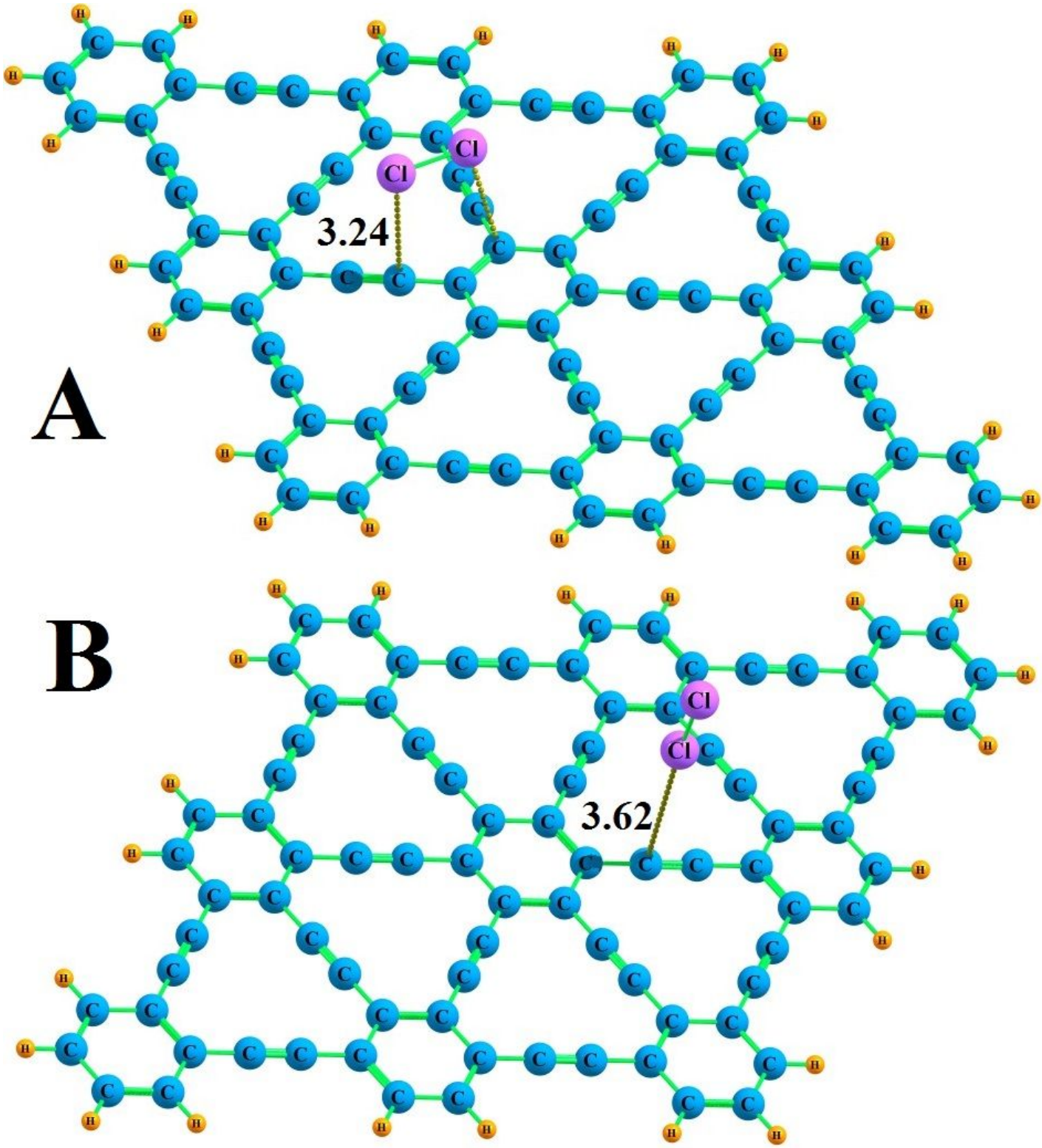


Figure 2

Models for two stable adsorption states for a Cl2 molecule on the pure graphyne, distances are in Å.

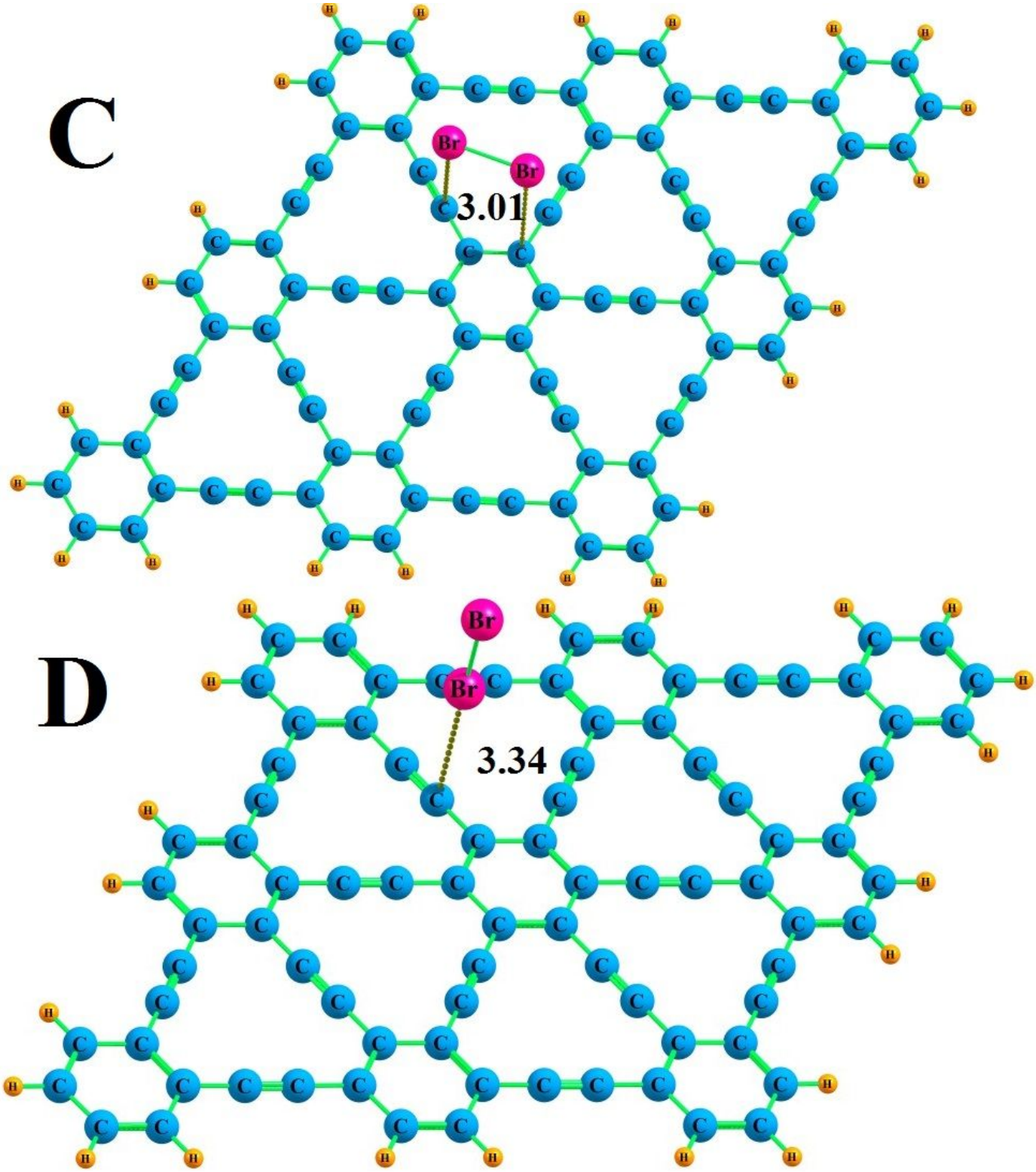


Figure 3

Models for two stable adsorption states for a Br2 molecule on the pure graphyne, distances are in Å.

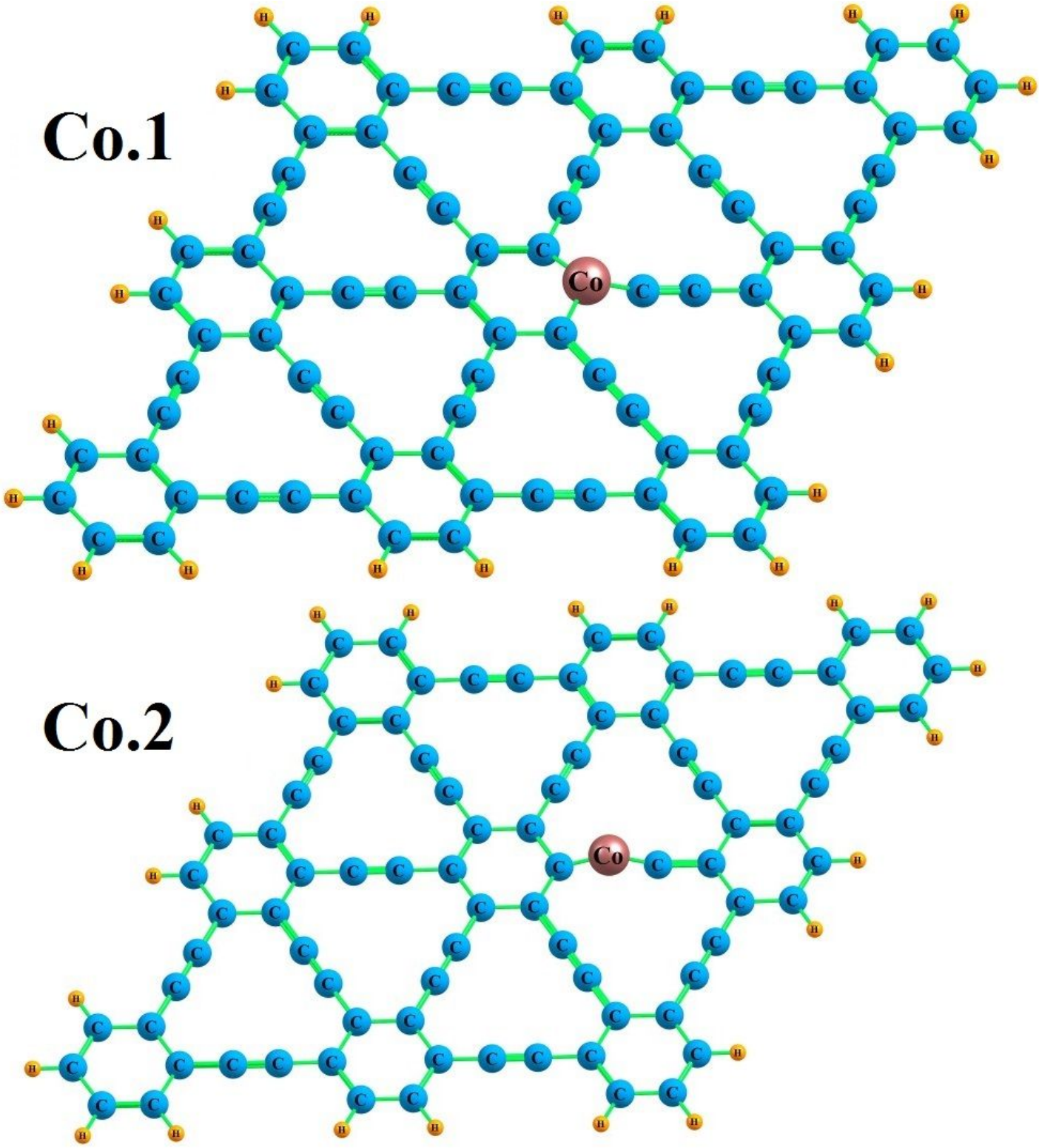


Figure 4

Optimized structures of different Co-doped graphyne.

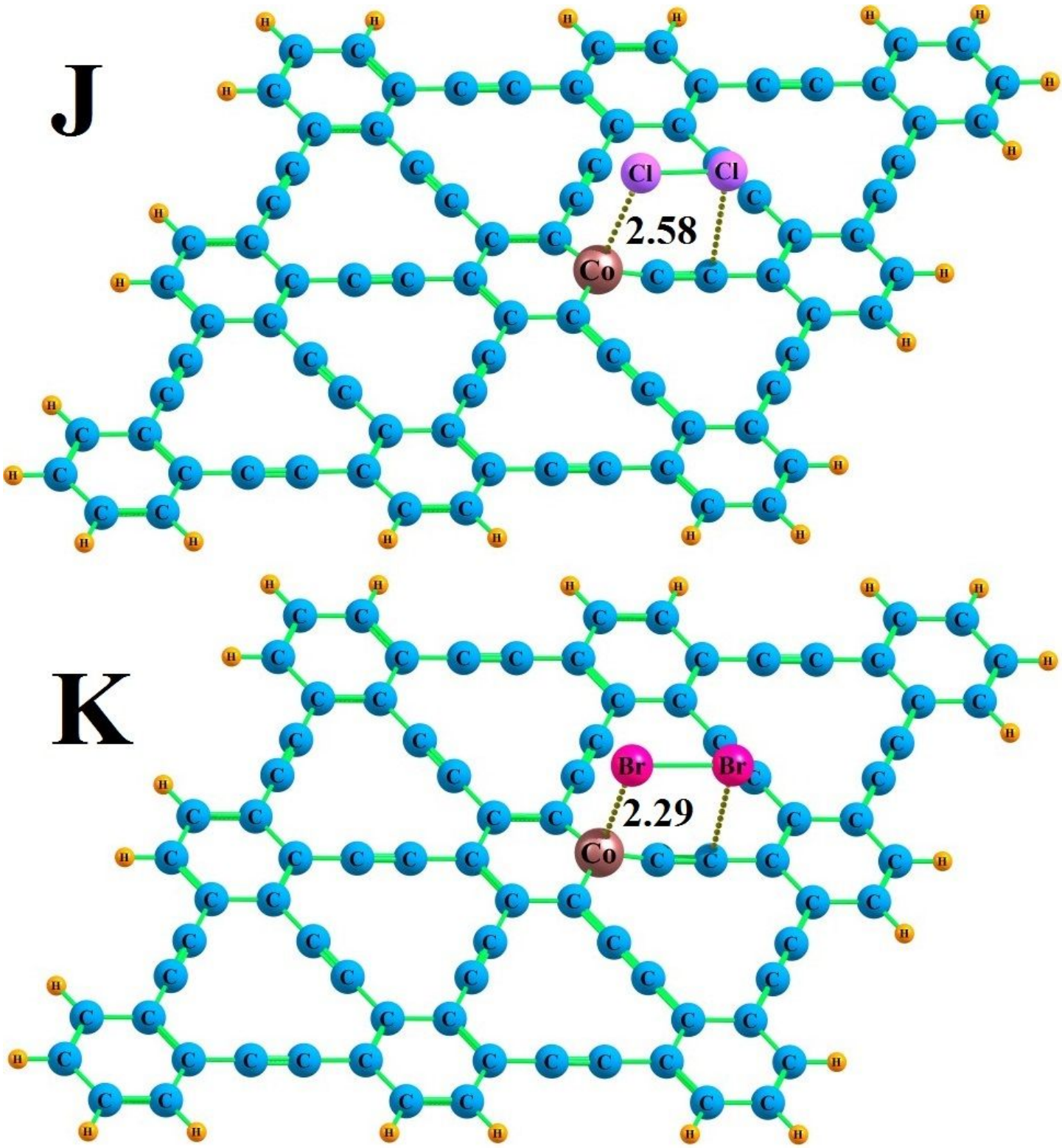


Figure 5

Models for two stable adsorption states for one of the Br2 and one of the Cl2 molecule on the Co-doped graphyne, distances are in Å.

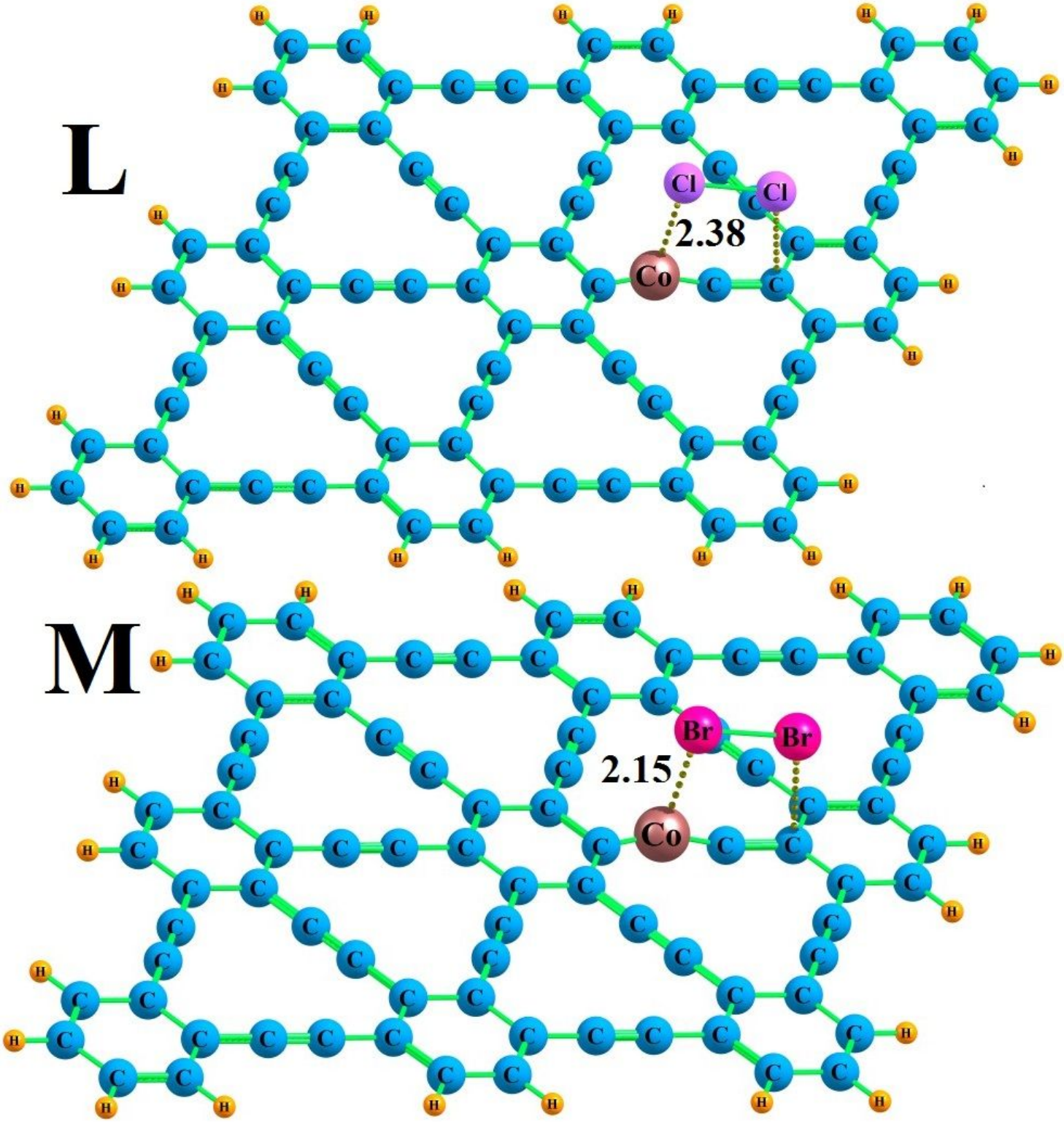


Figure 6

Models for two stable adsorption states for one of the Br2 and one of the Cl2 molecule on the Co-doped graphyne, distances are in Å.

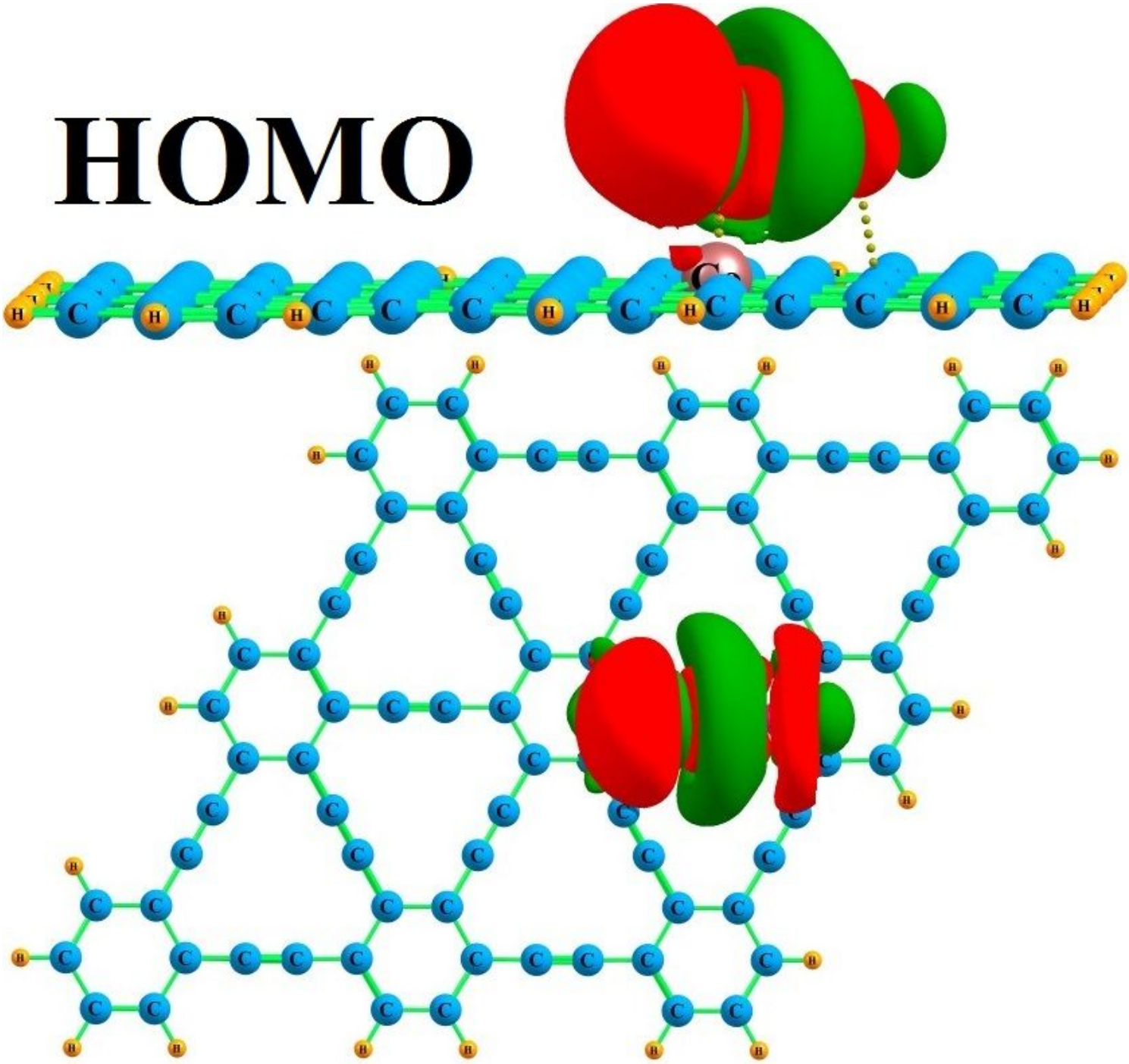


Figure 7

The HOMO/LUMO profile of Co-doped graphyne/Br2 nanostructure complex.

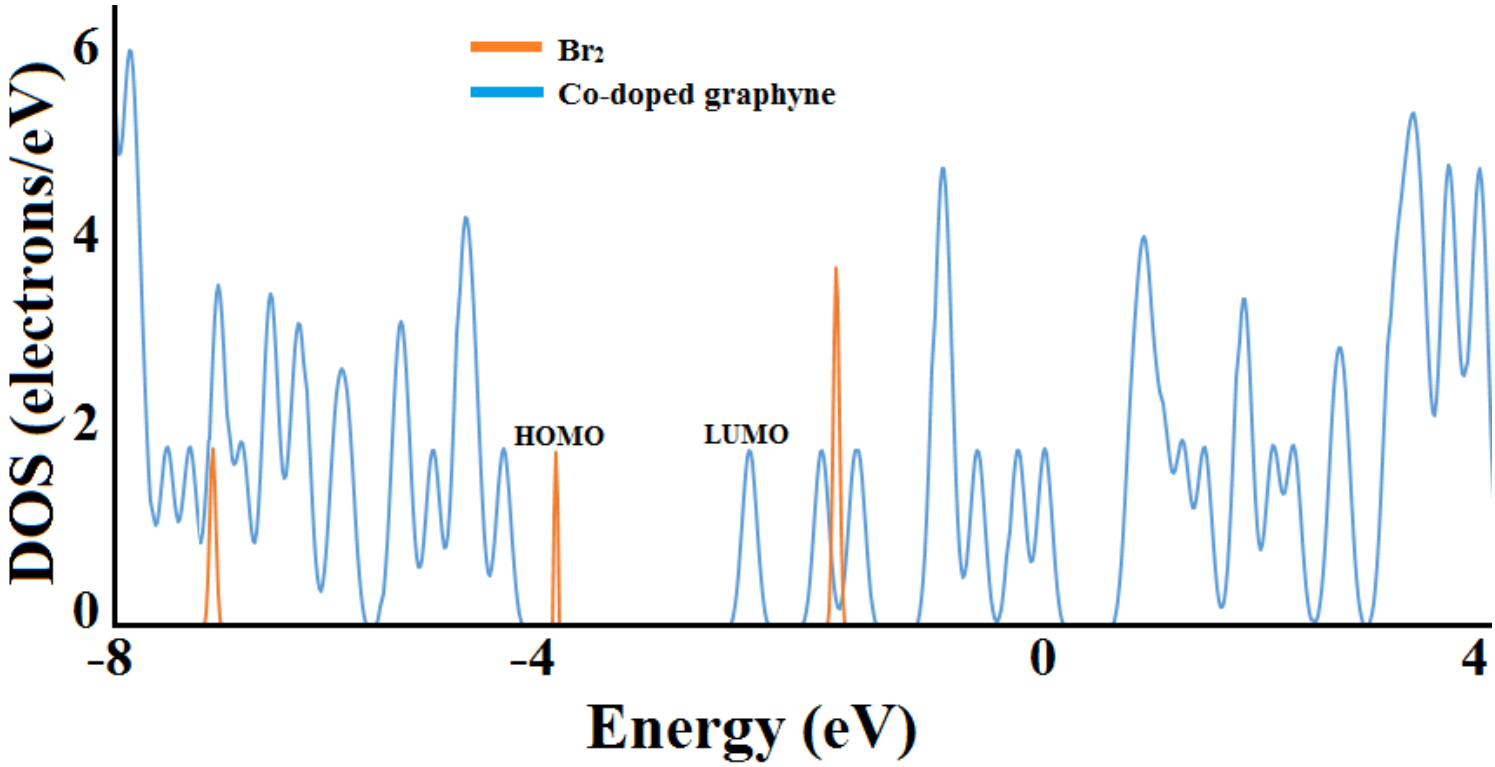


Figure 8

Partial DOS plot of Co-doped graphyne/Br2 nanostructure complex.