

The electron density analysis of $\text{Cr}(\text{CO})_3\text{L}$ complexes (L=benzene and graphyne)

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ABSTRACT

In the present research, the electronic structure and bonding properties of the $\text{Cr}(\text{CO})_3\text{L}$ complexes (L= η^6 -benzene, η^6 -graphyne) was studied with MPW1PW91 quantum chemical computations. Quantum theory of atoms in molecules (QTAIM) was applied to elucidate these complexes Cr-CO bonds. The ellipticity (ε) and η values of the Cr-CO bonds were calculated. The amount of $\rho\pi$ - $d\pi$ back-donation of Cr-CO bonds were illustrated by calculation of the magnitude of the quadrupole polarization of carbon atoms. Delocalization index values of C-C bonds of the six-member rings was calculated. Percentage composition in terms of the specified groups of frontier orbitals was found in these complexes to the investigation of the feature in metal-ligand bonds. The nature of chemical bond between the π -ring and $\text{Cr}(\text{CO})_3$ fragments was demonstrated through energy decomposition analysis (EDA).

Keywords: Delocalization Index; Ellipticity; Graphyne Complex; Quantum Theory of Atoms In Molecules (QTAIM)

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INTRODUCTION

Graphyne (GY) is a novel type of non-natural carbon allotropes related to graphite/graphene (GR). The exclusive structures and fascinating electronic, optical and mechanical properties have been investigated. Graphyne was first described in 1987 [1], although in spite of many efforts graphyne has not yet prepared [2-6]. Attempts for synthesis of graphyne layers, crystals, and nanostructures occurred from theoretical researches. The graphyne compounds were prepared by the polymerization of molecules having carbon cage fragments [7-8]. Theoretical calculations of the structures of graphyne layer fragments and single graphyne layers and their properties were reported [9-17].

When the π -ligands are attached to metals, the ability of π ligands to undergo reactions is changed [18]. Therefore, the investigation of the structures of metal- π ligand complexes are useful

and interesting. For example, arene tricarbonyl chromium complexes are everywhere synthetic reagents that were interesting for chemists [19-26]. When a arene ligand is coordinated to a $\text{Cr}(\text{CO})_3$ metal fragment, the arene ring is activated to nucleophilic attack. Furthermore, it acts as a stereo directing group and provides a road for region, stereo and chemo appropriate preparations [27]. Several theoretical works dealt with studying the structures and properties of η^6 -arene chromium tricarbonyl complexes have been reported [28-30]. But, the interaction $\text{Cr}(\text{CO})_3$ metal fragment to graphyne has not reported. Then, we interested to the theoretical study of the structure and properties of $\text{Cr}(\text{CO})_3(\text{graphyne})$.

The major aim of the present investigation was to clarify the interaction of $\text{Cr}(\text{CO})_3$ with benzene and graphyne by the quantum mechanics method. The dipole moment, structural parameters, frontier orbital energies, electron density analysis and

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characterization of Cr-CO bond in these complexes was explored.

COMPUTATIONAL METHODS

All calculations were performed with the Gaussian 09 suite program [31]. The calculations of systems containing C, H, and O were described by the standard 6-311G(d,p) basis set [32-35]. The element standard Def2-TZVPPD basis set [36] was used for Cr element. Geometry optimization was performed through the application of Modified Perdew-Wang Exchange and Correlation (MPW1PW91) method [37]. Harmonic vibrational frequencies were calculated to verify that the optimization structures have no imaginary frequency.

The bonding interaction between the Cr(CO)₃ fragment and π -ring has been analyzed by means of the energy decomposition analysis implemented in Multiwfn3.3.9 package [38]. In this method, the instantaneous interaction energy (E_{int}) between the two fragments can be divided into three main components:

$$\Delta E_{\text{int}} = \Delta E_{\text{polar}} + \Delta E_{\text{els}} + \Delta E_{\text{Ex}}$$

E_{polar} is electron density polarization term (also called as induction term)

$$= E(\text{SCF last}) - E(\text{SCF 1st})$$

E_{els} is electrostatic interaction term, and E_{Ex} is an exchange repulsion term.

The GaussSum 3.0 software package was employed for evaluation of molecular orbital information by partial population density of states (PDOS) [39]. The full width at half maximum (FWHM) of 0.3 eV was considered. Moreover, GaussSum 3.0 software was used for the inclusive investigation of the atomic orbitals contributions to the molecular orbitals.

Quantum theory of atoms in molecules analysis (QTAIM) computations were performed with the AIMAll package [40]. QTAIM calculations were computed by using the basis sets for optimization

and MPW1PW91 method.

The degree of π -electron delocalization can be measured on the basis of Bader's "atoms in molecules" (AIM) theory by using the delocalization index (DI), $\delta(A,B)$, that is calculated by double integration of the exchange-correlation density over the basins of atoms A and B [41-42]:

$$\delta(A,B) = - \int_A \int_B \Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 -$$

$$\int_B \int_A \Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2 = -2 \int_A \int_B \Gamma_{\text{XC}}(\vec{r}_1, \vec{r}_2) d\vec{r}_1 d\vec{r}_2$$

The atom basin in the QTAIM theory is determined as the region in real space bound by Zero-flux gradient surfaces in the one electron density, $\rho(\mathbf{r})$, or by infinity. Quantitatively, δ gives an impression of the number of electrons delocalized (or shared) between A and B [42].

RESULTS AND DISCUSSION

Fig. 1 presents the structure of graphyne, (η^6 -benzene)Cr(CO)₃ and (η^6 -Graphyne)Cr(CO)₃ complexes. Dehydrobenzo[12]annulene (DBA) [43] can be regarded as the smallest unit of graphyne. Therefore, this molecule cluster (C₂₄H₁₂) was considered to be an appropriate model for theoretical study of graphyne [44]. The total electronic energy values of these molecules are gathered in Table 1. It has been proved that the electron density analysis base on quantum theory of atoms in molecules (QTAIM) can present important information about the large number of physical and chemical features of molecular systems [45-49].

Structural parameters

The computed Cr-CO bond distances of the (η^6 -benzene)Cr(CO)₃ and (η^6 -Graphyne)Cr(CO)₃ complexes are gathered Table 2. It can be found Cr-CO bonds in the (η^6 -Graphyne)Cr(CO)₃ complex are longer in compared to bonds of (η^6 -benzene)Cr(CO)₃ complex. The average values of OC-Cr-CO bond angles are (η^6 -benzene)Cr(CO)₃ and

Table 1. Absolute energy (E, a.u), dipole moment (μ , Debye), frontier orbital energies (E(HOMO) and E(LUMO), eV), HOMO-LUMO gap (eV) values of benzene, graphyne, (η^6 -benzene)Cr(CO)₃ and (η^6 -Graphyne)Cr(CO)₃ complexes (B=Benzene, G=Graphyne).

| Molecule | E | μ | E(HOMO) | E(LUMO) | Gap |
|-----------------------|------------|-------|---------|---------|------|
| Benzene | -232.2456 | 0.00 | -7.25 | -0.07 | 7.18 |
| Graphyne | -921.6071 | 0.00 | -5.84 | -2.20 | 3.64 |
| Cr(CO) ₃ B | -1616.8513 | 5.18 | -6.10 | -0.96 | 5.14 |
| Cr(CO) ₃ G | -2306.2063 | 4.82 | -5.89 | -2.47 | 3.42 |

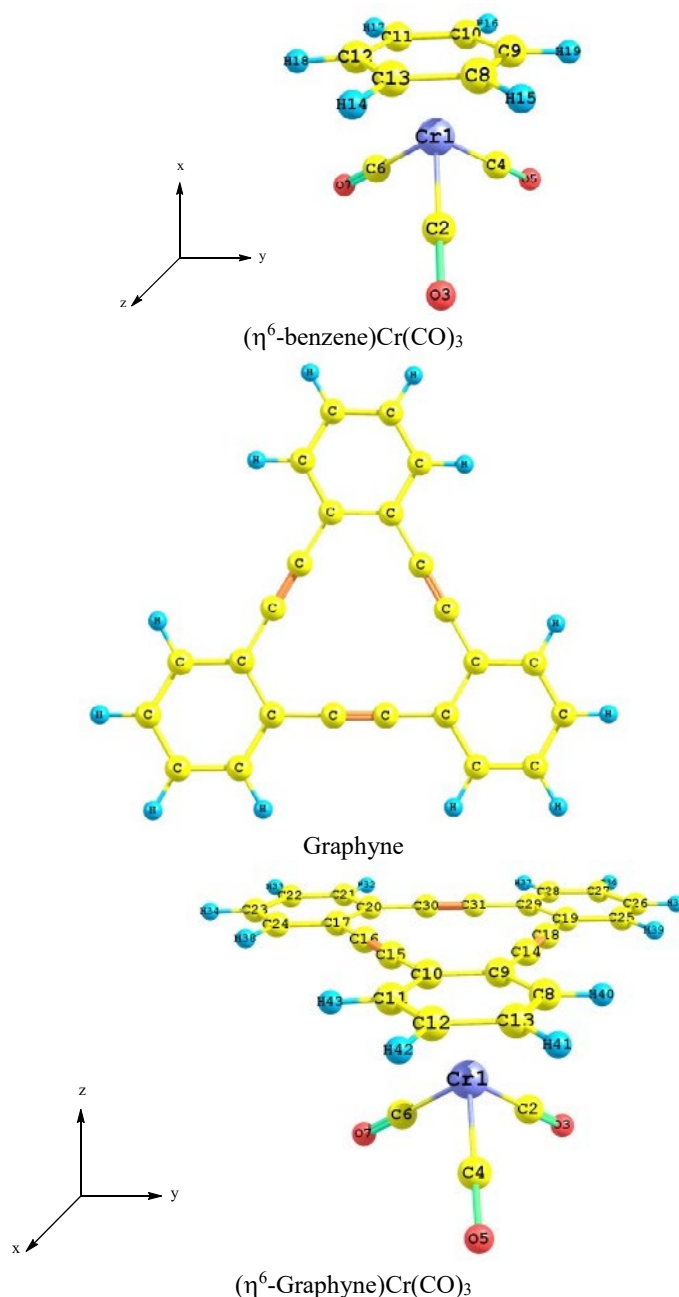


Fig. 1. The structures of graphyne, $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complexes.

$(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complexes are 88.72 and 88.48° , respectively. Also, the $\angle\text{Cr-C-O}$ bond angles values show the linear arrangement for these atoms in two studied complexes.

Electron density

The findings obtained from calculations of QTAIM may also describe this fact that the computed bond distances of Cr-CO in the $(\eta^6\text{-$

Graphyne) $\text{Cr}(\text{CO})_3$ complex is 0.006 \AA larger compared to the bonds of $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex (Table 2). The calculations of QTAIM indicate show that the density of electron on bond critical point (BCP) of Cr-C bonds of $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex is greater compared to Cr-C bonds of $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complex. On the other hand, computed bond of Cr-C4 of $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complex are 0.001 \AA shorter

Table 2. The bond distance (\AA) and QTAIM analysis results (a.u) of Cr-CO bond in $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complexes.

| Molecule | | r | ρ | H | G | K | V | L |
|----------------------------------|-------|-------|--------|---------|--------|--------|---------|--------|
| $\text{Cr}(\text{CO})_3\text{G}$ | Cr-C6 | 1.847 | 0.1305 | -0.0419 | 0.1752 | 0.0419 | -0.2171 | 0.5333 |
| | Cr-C4 | 1.840 | 0.1328 | -0.0436 | 0.1780 | 0.0436 | -0.2215 | 0.5376 |
| | Cr-C2 | 1.847 | 0.1306 | -0.0419 | 0.1753 | 0.0419 | -0.2172 | 0.5333 |
| $\text{Cr}(\text{CO})_3\text{B}$ | Cr-C4 | 1.841 | 0.1324 | -0.0432 | 0.1777 | 0.0432 | -0.2208 | 0.5379 |
| | Cr-C6 | 1.841 | 0.1324 | -0.0432 | 0.1778 | 0.0432 | -0.2210 | 0.5385 |
| | Cr-C2 | 1.841 | 0.1324 | -0.0432 | 0.1778 | 0.0432 | -0.2210 | 0.5381 |

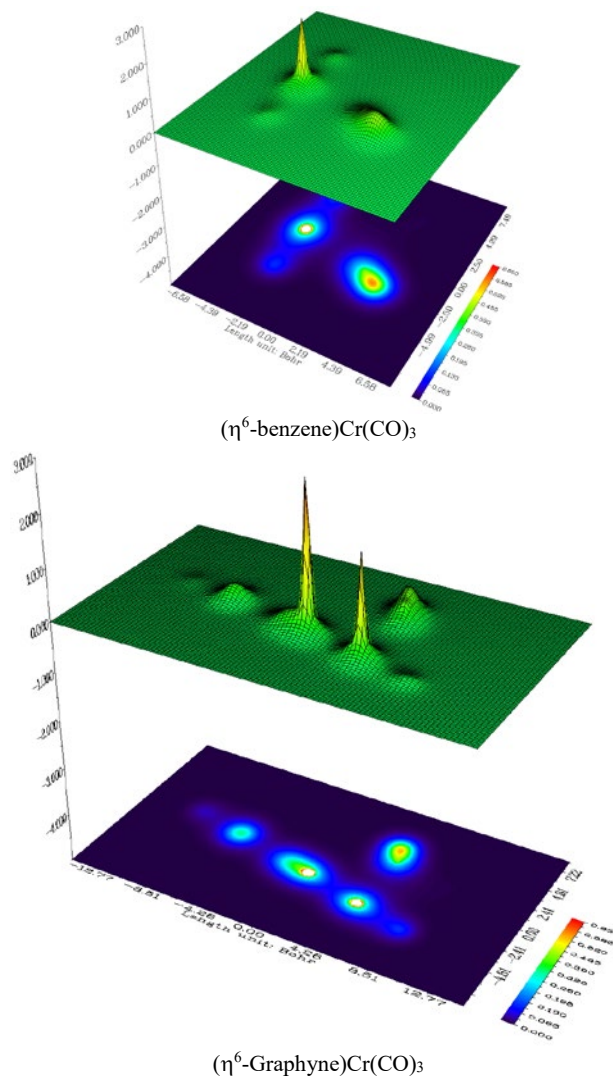


Fig. 2. Shaded surface maps with projection of electron density in the $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complexes in xz-plane.

compared to Cr-C2 bond of $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex (Table 2). The calculations of QTAIM indicate show that the density of electron on bond critical point (BCP) of Cr-C bond of $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex is less compared to Cr-C4 bond of $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complex. Fig. 2 presents shaded surface maps with a projection of electron

density of the $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complexes in xz-plane. It can be observed the most electron density on Cr atom in the studied complexes. On the other hand, electron density on Cr atom of $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ is lower than that of $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ in the electron density map and this might be because

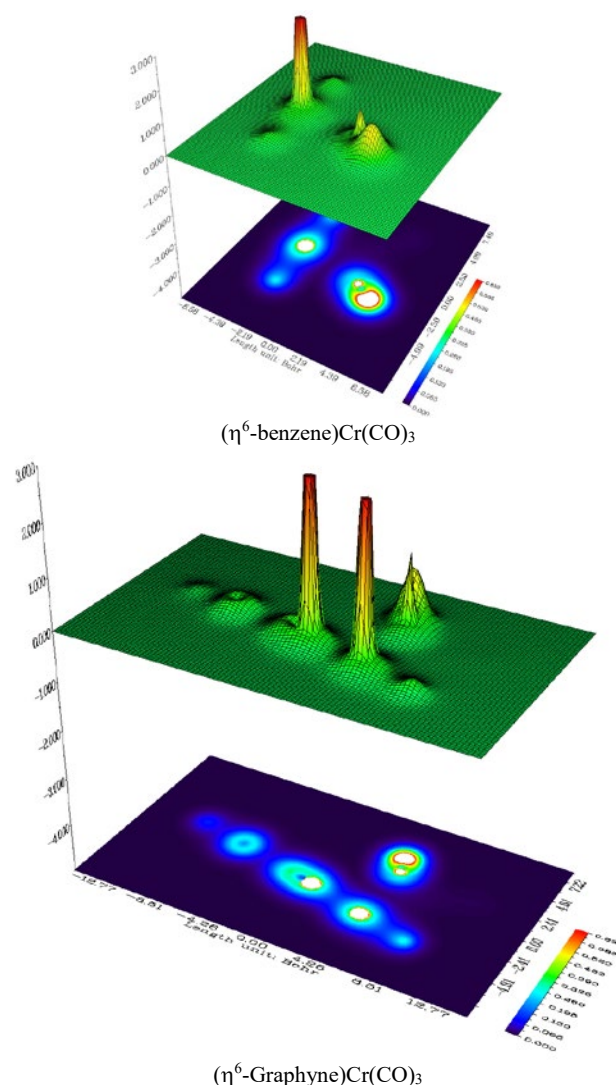


Fig. 3. Shaded surface maps with projection of Laplacian of electron density in the (η^6 -benzene) $\text{Cr}(\text{CO})_3$ complex (η^6 -Graphyne) $\text{Cr}(\text{CO})_3$ complexes in xz-plane.

of poor electron delocalization in (η^6 -benzene) $\text{Cr}(\text{CO})_3$ complex.

Laplacian of electron density

Table 2 indicates $\nabla^2\rho$ values of Cr-CO bonds are positive at related bond critical points (BCP), as it was observed in interactions of closed-shell. Fig. 3 reveals shaded surface maps with projection of Laplacian of electron density in the (η^6 -benzene) $\text{Cr}(\text{CO})_3$ complex (η^6 -Graphyne) $\text{Cr}(\text{CO})_3$ complexes in xz-plane.

Energy density

Table 2 indicates the energy density (H) has negative values are, as observed in interactions

of shared. This is in agreement with findings obtained for the M-C bonds in the complexes of organometallic [50] and transition metal carbonyl clusters [51], when a mixture of parameters of the closed-shell and shared are represented by the metal-ligand bonding.

Ellipticity

Ellipticity of electron density is defined as:

$$\varepsilon = \left[\frac{\lambda_1(r)}{\lambda_2(r)} \right] - 1$$

In this equation, λ_1 and λ_2 are the lowest and the second lowest eigenvalues of Hessian matrix of ρ ,

respectively. At bond critical point, λ_1 and λ_2 are both negative and exhibit the curvature of electron density perpendicular to the bond. The ellipticity values of the Cr-CO bond in the (η^6 -benzene)Cr(CO)₃ complex (η^6 -Graphyne)Cr(CO)₃ complexes are listed in Table 3. The Cr-CO bonds are almost linear, therefore their ellipticity values are very small. On the other hand, the ellipticity values of the Cr-CO bond in the (η^6 -benzene)Cr(CO)₃ complex are smaller than (η^6 -Graphyne)Cr(CO)₃ complexes.

η index

η index is defined as:

$$\eta = \frac{|\lambda_1(r)|}{\lambda_3(r)}$$

In this equation, λ_1 and λ_3 are the lowest and the highest eigenvalues of Hessian matrix of ρ , respectively. the $\eta < 1$ values of bond critical point are attributed to closed shell interactions and increases with increasing covalent character^{52, 53}. The η values of the Cr-CO bond in the (η^6 -benzene)Cr(CO)₃ complex (η^6 -Graphyne)Cr(CO)₃ complexes are listed in Table 3. It can be found, these values are less than unity. As a result, the interaction between Cr and carbonyl ligand is closed shell interaction type.

Atomic quadrupole moment as a measure of $d\pi$ - $p\pi^*$ back-bonding

The calculated dipole moments values of the studied complexes in vacuum phase and various solvents are listed Table 1. It can be seen, the less dipole moment values for (η^6 -Graphyne)Cr(CO)₃ complex in comparing to (η^6 -benzene)Cr(CO)₃

complex. On the other hand, the magnitude $|Q(A)|$ of the atomic quadrupole polarization is given in Table 3 for isolated and bound CO groups. The magnitude of the quadrupolar polarization moment is defined as [54]:

$$|Q(\Omega)| = \sqrt{\left(\frac{2}{3}\right)[Q_{xx}^2 + Q_{yy}^2 + Q_{zz}^2]}$$

The magnitude of the quadrupole polarization of carbon atom has been established as an evaluation of the amount of $p\pi$ - $d\pi$ back-donation within the QTAIM standard model [55-56]. When the CO molecule is coordinated, the increases in the magnitude of the quadrupole moment of a carbon are dramatic. As can be seen, $|Q(\Omega)|$ value increase in the complexes compared to free CO.

Delocalization index

QTAIM analysis gives a delocalization index for each bond between two neighboring atoms. The delocalization index is a degree of the number of electrons that are exchanged, shared or between two or basins or atoms. The Fermi hole density integration directs to and delocalization index (DI) and the localization index (LI). The delocalization Index as an electronic aromaticity criterion to several molecules has been used [57-58]. The CC delocalization indices of six-member ring of the studied complexes are collected in Table 4. The average of these values reveals minor changes of delocalization of the six-member ring in the studied complexes.

Molecular orbital analysis

The frontier orbital energy and HOMO-LUNO gap values of the (η^6 -benzene)Cr(CO)₃ and (η^6 -

Table 3. Ellipticity of electron density (ϵ), eta index (η) of Cr-CO bond, Atomic quadrupole moments of C in free CO, (η^6 -benzene)Cr(CO)₃ and (η^6 -Graphyne)Cr(CO)₃ complexes (atomic unit).

| | | Q_{xx} | Q_{yy} | Q_{zz} | $ Q(\Omega) $ | ϵ | η |
|-----------------------|-------|----------|----------|----------|---------------|------------|--------|
| CO | | -0.1120 | -0.1131 | 0.2251 | 0.2251 | - | - |
| Cr(CO) ₃ G | Cr-C6 | -0.9821 | 0.6148 | 0.3673 | 0.9924 | 0.1029 | 0.1755 |
| | Cr-C4 | 2.0605 | -1.4978 | -0.5627 | 2.1301 | 0.0954 | 0.1766 |
| | Cr-C2 | -1.0012 | 0.6370 | 0.3642 | 1.0135 | 0.1029 | 0.1755 |
| Cr(CO) ₃ B | Cr-C4 | 0.0799 | 0.6482 | -0.7281 | 0.7986 | 0.0848 | 0.1756 |
| | Cr-C6 | 0.0840 | -1.4935 | 1.4095 | 1.6781 | 0.0867 | 0.1755 |
| | Cr-C2 | 0.0791 | 0.7208 | -0.7999 | 0.8815 | 0.0845 | 0.1756 |

Table 4. Delocalization index (DI) of C-C bonds in the benzene, graphyne, (η^6 -benzene)Cr(CO)₃ and (η^6 -Graphyne)Cr(CO)₃ complexes (B=Benzene, G=Graphyne).

| Molecule | C8-C9 | C9-C10 | C10-C11 | C11-C12 | C12-C13 | C13-C8 |
|-----------------------|--------|--------|---------|---------|---------|--------|
| Cr(CO) ₃ B | 1.2043 | 1.1380 | 1.2041 | 1.1382 | 1.2040 | 1.1382 |
| Cr(CO) ₃ G | 1.1862 | 1.1966 | 1.1863 | 1.2055 | 1.1321 | 1.2055 |

Graphyne)Cr(CO)₃ complexes are gathered in Table 1. As seen, frontier orbitals are more stable in and (η⁶-Graphyne)Cr(CO)₃ complex compared to (η⁶-benzene)Cr(CO)₃.

The HOMO-LUMO gap is an appropriate factor for the electrical conductivity of a system. It is defined as the energy difference between the valence level (HOMO) and the conduction level (LUMO) in insulators and semiconductors and can be calculated using the following equation [59]:

$$\sigma \propto \exp\left(-\frac{E_g}{2k_b T}\right)$$

Where σ is electrical conductivity, k_b is Boltzmann's constant and T is the temperature.

One can see from Table 1, the HOMO-LUMO gaps of (η⁶-Graphyne)Cr(CO)₃ complex are smaller than (η⁶-benzene)Cr(CO)₃ complex. Therefore, when HOMO-LUMO gap values decrease, the electrical conductivity increases at a given temperature.

Total density of states (TDOS) and partial density of states (PDOS) investigations are useful for illustrations of the central features of bonding interactions of in the studied complexes (Fig. 4). The composition of the fragment orbitals contributing to the molecular orbitals is presented in the PDOS. It can be found, the frontier orbitals are fairly localized on graphyne ligand in (η⁶-Graphyne)Cr(CO)₃ complex. The most contributions in the HOMO and LUMO of the (η⁶-benzene)Cr(CO)₃ complex are attributed to Cr and carbonyl ligand.

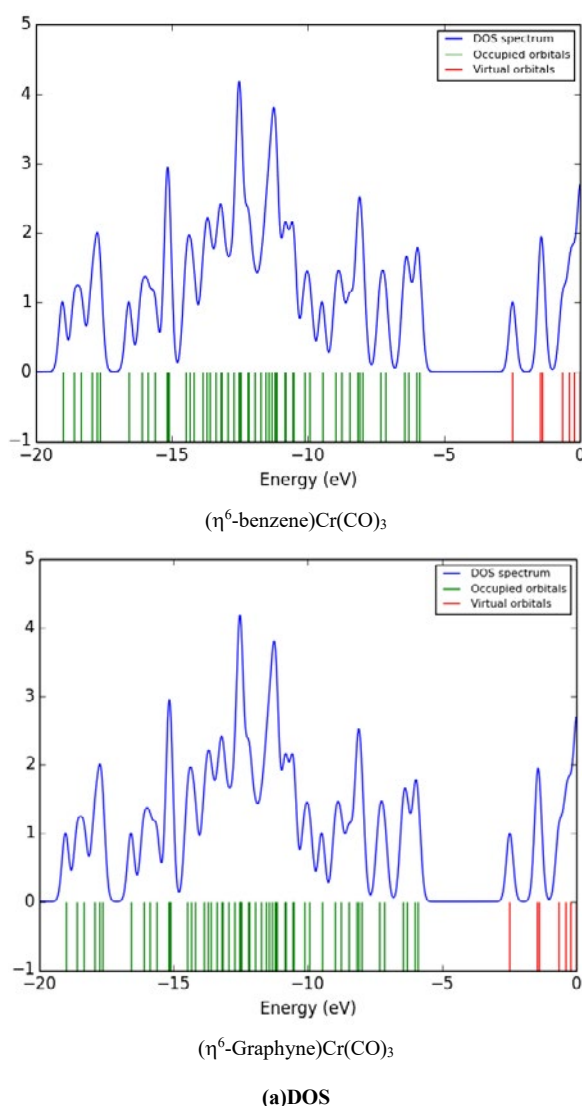
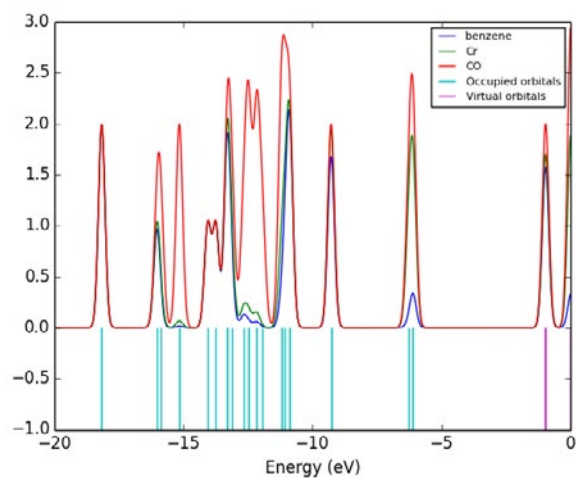
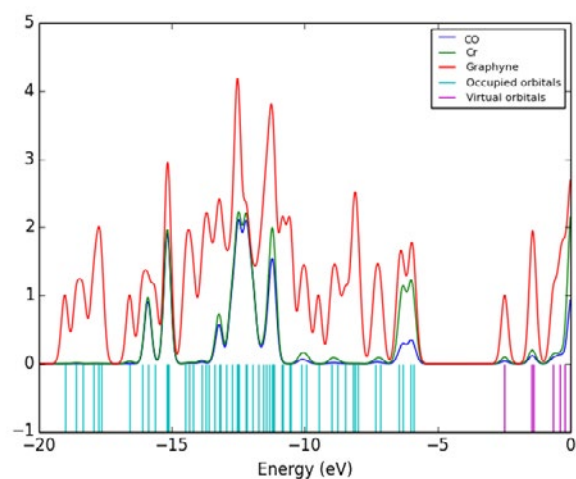


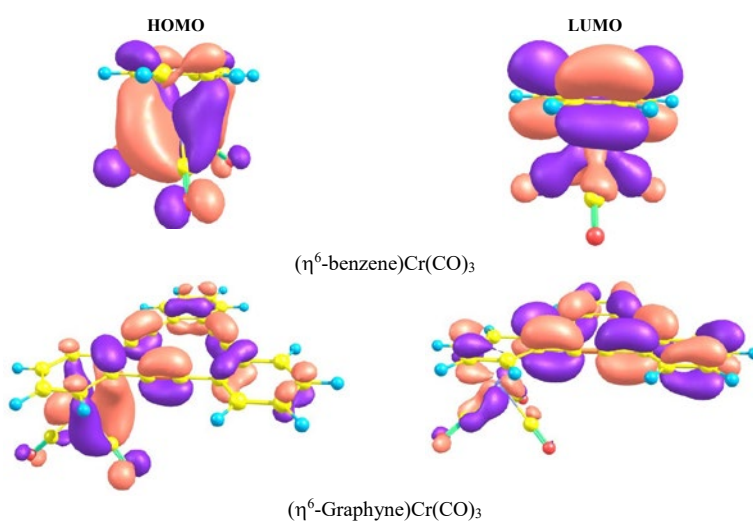
Fig. 4. (a)DOS, (b) PDOS and (c) the plots of frontier orbital in (η⁶-benzene)Cr(CO)₃ and (η⁶-Graphyne)Cr(CO)₃ complexes.



$(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$



$(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$
(b) PDOS



(c) Plots of frontier orbital

Continued Fig. 4. (a) DOS, (b) PDOS and (c) the plots of frontier orbital in $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complexes.

Fig. 4 reveals the plots of frontier orbital in $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ and $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complexes. These plots reveal orbital overlaps of metal and aromatic ring are more significant in $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex compared to $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complex. To get an insight into the influence of the optical and electronic properties, the distributions of the frontier orbitals for these molecules are investigated. percentage compositions in terms of the defined groups of frontier orbitals for $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex are Cr (60%), benzene(16%), CO(24%) in HOMO and Cr(6%), benzene(79%), CO(15%) in LUMO. The largest contribution of HOMO and LUMO arises from Cr and benzene ligand, respectively. For $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complex are Cr (39%), graphyne (45%), CO(16%) in HOMO and Cr(5%), graphyne (91%), CO(3%) in LUMO. Therefore, the largest contribution of HOMO and LUMO arises from graphyne ligand.

Energy decomposition analysis (EDA)

The nature of chemical bonds between the graphyne and benzene fragments with $\text{Cr}(\text{CO})_3$ has been investigated using an energy decomposition analysis (EDA). In $(\eta^6\text{-Graphyne})\text{Cr}(\text{CO})_3$ complex, the total interaction energy between graphyne and $\text{Cr}(\text{CO})_3$ is -63.52 kcal/mol, the polarization energy -59.76 kcal/mol stabilized the adduct, while the sum of electrostatic and exchanging energy stabilized the adduct by -3.74 kcal/mol.

In $(\eta^6\text{-benzene})\text{Cr}(\text{CO})_3$ complex, the total interaction energy between benzene and $\text{Cr}(\text{CO})_3$ is -67.40 kcal/mol, the polarization energy -74.75 kcal/mol stabilized the adduct, while the sum of electrostatic and exchanging energy destabilized the adduct by 7.35 kcal/mol.

The magnitude of the ΔE_{int} values shows that the interaction of benzene and $\text{Cr}(\text{CO})_3$ is stronger than graphyne with $\text{Cr}(\text{CO})_3$.

CONCLUSION

In the current research, MPW1PW91 method was used to demonstrate the structural, features and the nature of the Cr-CO bond in $\text{Cr}(\text{CO})_3\text{L}$ complexes (L= $\eta^6\text{-benzene}$, $\eta^6\text{-graphyne}$) complexes. These calculations indicate:

1. Frontier orbital analysis reveals that maximum contributions for HOMO and LUMO are the largest contribution of HOMO and LUMO arises from graphyne ligand in $\text{Cr}(\text{CO})_3(\eta^6\text{-graphyne})$ complex.

2. EDA analysis reveals that interaction of benzene and $\text{Cr}(\text{CO})_3$ is stronger than graphyne with $\text{Cr}(\text{CO})_3$.
3. Based on the results of the QTAIM analysis, there is a mixture of two parameters of the closed-shell and shared for Cr-CO bonds.
4. The increase in quadrupole polarization values in the complexes compared to free CO values show the $p\pi\text{-}d\pi$ back-donation in Cr-CO bonds.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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