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Chapter

Possibility of Complexation of the Calix[4]Arene Molecule with the Polluting Gases: DFT and NCI-RDG Theory

Bouzid Gassoumi, Fatma Ezzahra Ben Mohamed, Houcine Ghalla and Rafik Ben Chaabane

Abstract

The calix[4]arenes (abbreviated as CX[4]) are characterized by a specific hydrophobic cavity formed by a four cyclically phenol groups to encapsulate a gas or small molecules. Recently, the CX[4] molecule is used in a specific media and in pharmaceutical drug delivery. The pollution problem will be a vital subject in the future because the increase of the explosions of the gaseous pollutants in the environment. In this report, we have encapsulated the polluting gases NO_3, NO_2, CO_2 and N_2 by the calix[4]arene molecule. In this work, The binding energies of the CX[4]-gas has been calculated including the BSSE (Basis Set Superposition Error) counterpoise (CP). The red-shift of the O-H bonding interactions obtained by adding the gas in the sensitive area of calix[4]arene is clearly explained by the infrared spectrum analysis. The Molecular electrostatic potential (MEP) of the stable CX[4]-gas complexes have been investigated in the endo-vs. exo-cavity regions. Finally, the non-covalent interactions analyses of the stable host-guests complexes have been estimated by using DFT calculations.

Keywords: complexation, specific gases, H-bonding, molecular electrostatic potential and binding energy

1. Introduction

The recognition of the electrostatic and magnetic properties in the selective guest in microscopic systems facilitates to know several anionic cationic or neutral guests' complexes [1–5]. In this work, the CX[4] molecule is specified by its own chemical composition and the hydrophobic cavity form [6]. This molecule is characterized by specific parameters such as the diameter and the height, which facilitates the encapsulation of the cationic, anionic, neutral guests or small molecules [7–9]. Also, the cavity of the CX[4] molecule have attracted the researchers to test a new guest materials to be functional in the medical [10–12] or micro-biological field [13, 14]. In literature, we have noted that there are some works which discuss the encapsulation of the CX[4] with gases molecules (CH_4, NH_3 and C_2H_2) [15–18]. In our work, we have studied the photo-physical properties of the CX[4]-gas complexes (CX[4]-NO_3, CX[4]-NO_2, CX[4]-CO_2 and CX[4]-N_2). We discuss the

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possibility of the encapsulation of these gases by the CX[4] molecule to show the sensibility of this molecule to the polluting gases outside or inside the cavity. We have chosen the NO_3, NO_2, CO_2 and N_2 gas as guest's because they can be formed a dipole-dipole interactions and a CH...π hydrogen-bonding with the CX[4] molecule. By using the density functional theory (DFT) calculations, we have described the dynamic stabilities of the endo-vs. exo-cavity of the CX[4]-gas complexes. The vibrational properties of the CX[4]-gas complexes have been studied. The Molecular electrostatic potential studies of these host-guests complexes have been performed. The Non-covalent interaction via RDG function are very important to know the nature of the interactions between the specific guests and the CX[4] molecule.

2. Computational method

The stable structures of the studied systems (CX[4] and CX[4]-gas) have been calculated with the DFT method by using the B3LYP [16, 19–21] coupled to the D3BJ (empirical Becke and Johnson damping dispersion corrections) in combination with the 6-31 + G(d) basis set, as implemented in GAUSSIAN 09 package [22] and the Gauss View [23] as a visual program. We have been calculated the binding energies of the CX[4]-gas take into account the Basis Set Superposition Error (BSSE) counterpoise (CP) correction energy of Boys and Bernardi [24].

The binding energies are given by the following formula:

$$\ddot{A}E_{CX[4]-gas} = E_{CX[4]-gas} - E_{CX[4]} - E_{gas} + BSSE \quad (1)$$

where $E_{CX[4]\text{-}gas}$, $E_{CX[4]}$ and E_{gas} are the total energies of host-guest and host or guest molecules. The electronic parameters of the studied complexes are very effective to show the sensibility of the specific gas inside or outside the cavity. We analyzed then the infrared spectrum of these complexes using the DFT/B3LYP-D3 method. The nature of the interaction between the CX[4] molecule and the pollutant gases is better explained using the Non covalent interaction via RDG analysis [25].

3. Results and discussions

3.1 Geometry optimizations

The CX[4]-gas complexes have been optimized at the DFT/B3LYP-D3 (**Figure 1**). In this study, we have placed the NO_3, NO_2, CO_2 and N_2 gas in the exo or endo-cavity positions. **Table 1** presents the Binding energy E_b (in (kcal/mol)) of CX[4]-gas complexes. The binding energy value of the CX[4]-CO_2 is equal to 21.33 kcal/mol (see **Figure 1**). We show that, the CX[4]-$CO_{2(endo)}$ complex is more stable than that of CX[4]-$CO_{2(exo)}$. In addition, from the CX[4]-NO_3 complex, the NO_3 gas has placed in the endo or the exo-cavity position. In this situation, we have obtained a divergence in the case of the interaction of CX[4] with NO_3 outside the cavity that is why, we have tested the case where the NO_3 gas perpendicular to the 4-fold axis of CX[4] and a parallel position of the NO_3 (NO_3 parallel to the 4-fold axis). We have been noted a very weak energy of the CX[4]-$NO_{3(perp.)}$ complex in comparison with the CX[4]-$NO_{3(paral.)}$ complex. Moreover, we have noted that the interaction between the CX[4] molecule and the $NO_{3(paral.)}$ is stabilized by a low dipole moment. We have calculated

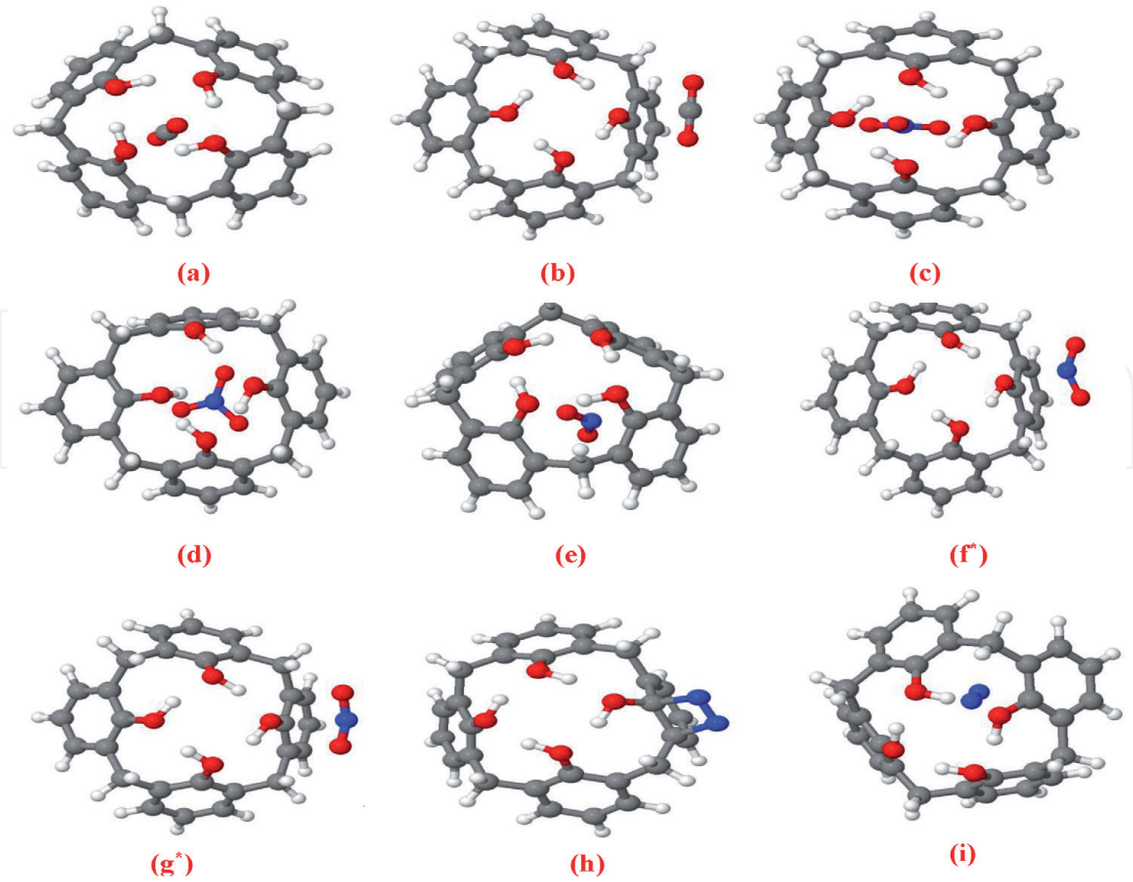


Figure 1.
Optimized geometries of the CX[4]-$CO_{2(endo)}$ (a), CX[4]-$CO_{2(exo)}$ (b), CX[4]-$NO_{3(paral.)}$ (c), CX[4]-$NO_{3(perp.)}$ (d), CX[4]-$NO_{2(endo)}$ (e), CX[4]-$NO_{2(exo)}$ (f), CX[4]-$NO_{2(exo)}$ (g*), CX[4]-$N_{2(endo)}$ (h) and CX[4]-$N_{2(exo)}$ (i) complexes using B3LYP-D3BJ/6-31 + G(d) method (top view).*

Complexes	E_b	BSSE	E_b (with BSSE)
CX[4]-$NO_{3\ (paral.)}$	24.62	6.17	
CX[4]-$NO_{3(perp.)}$	16.51	6.05	22.56
CX[4]-$N_{2(exo)}$	16.89	1.70	18.59
CX[4]-$N_{2(endo)}$	16.90	1.80	18.70
CX[4]-$NO_{2(exo)f^*}$	18.17	1.82	19.99
CX[4]-$NO_{2(exo)g^*}$	18.11	1.80	19.91
CX[4]-$NO_{2(endo)}$	17.83	2.71	20.54
CX[4]-$CO_{2(endo)}$	18.62	2.71	21.33
CX[4]-$CO_{2(exo)}$	18.10	2.71	20.81

Table 1.
Binding energy E_b (in (kcal/mol)) of CX[4]-gas complexes.

two positions for the guest N_2: the N_2 gas located on the outside of cavity and this gas located perpendicular to the 4-fold axis of CX[4] molecule. We have shown that the CX[4]-$N_{2(endo)}$ has a very strongest energy, which explain that this geometry is more stable than CX[4]-$N_{2(exo)}$ (see **Table 1**). The binding energy (E_b) of the stable complex is equal to 18.90 kcal/mol. Finally, from the CX[4]-$NO_{2(exo)}$ complex, we note that the NO_2 gas is located in the outside of the H-link network of the phenolic hydroxyl groups. The binding energy of the CX[4]-$NO_{2(endo)}$ complex is equal to 20.54 kcal/mol (see **Table 1**). As we see, The binding energy of the CX[4]-$NO_{2(endo)}$

complex is higher than that of CX[4]-$CO_{2(exo/endo)}$. Therefore, The CX[4]-$NO_{2(endo)}$ complex is more stable than others, which is explained by the lowest dipole moment.

3.2 Red-shifted of O-H bonds

The reorganization of the O...H stretching vibration has been calculated after the system perturbation with the pollutant gases. Moreover, The IR spectrum calculation of the four stable complexes is given in **Figure 2**. In literature, Furel et al. have been studied the experimental infrared spectrum of the CX[4] molecule. In this work, we have analyzed the stretching region of the IR spectrum between 2900 and 3500 cm^{-1}, respectively 3254 (OH), 3168(OH asymmetric), 3045($C_{ar.}H$), 2951 (asym. CH2), 2916 cm^{-1}(sym.CH2). The infrared spectrum of the CX[4]-gas have been compared to the IR spectra of the free CX[4] molecule (See **Figure 2**). In addition, to take into account the an-harmonic effect our calculated frequencies scaled by 0.956. However, we have noted that, the CX[4]-CO_2 is characterized by two peaks located in the vicinity of 3177 cm^{-1} and 3181 cm^{-1}respectively. The CX[4]-N_2 complex have the same results. These tow peaks are specified by the O-H asymmetric stretching vibration. We have shown that the frequency band located at 3160 cm^{-1} is corresponding to the O-H stretching vibration of the phenol O-H groups. Concerning the CX[4]-NO_2 complex, we have noted the appearance of the two peaks in the neighborhood of 3170 cm^{-1} and 3193 cm^{-1}. These peaks are corresponding to the vibrations of the O-H and O-H asymmetric bonds. Finally, we have shown a burst of the OH peak in the CX[4]-NO_3 gas what form four peaks located in the vicinity of 2928 cm^{-1} (asym.CH2), 3100 cm^{-1}(asym.OH), 3204 cm^{-1}(OH) and 3298 cm^{-1}(free OH) respectively. The noted values for the comparing of the red-shifted O-H vibration between the CX[4]-gas and the free CX[4]molecule are 44 cm^{-1}, 24 cm^{-1} and 9 cm^{-1} for CX[4]-NO_3, CX[4]-NO_2, CX[4]-CO_2 and CX[4]-N_2 successively.

3.3 Molecular electrostatic potential study

In **Figure 3(a–d)**, we have been created the MEP map of the stable host-guests. These graphs indicate the relation between the supra-molecular structure and the physic-cal-chemical properties of the CX[4]-gas complexes. In this work, we have explained the more nucleophile or electrophile sites in these stable host-guests. The color code of the maps varying from −0.005 to 0.005 (isoval = 0.001). From **Figure 3**, we show that the electrophilic sites surrounded by N atoms and the nucleophilic sites surrounded by O atoms. In addition, these host-guests complexes are characterized by the existence of the positive charges located at the level of the phenolic branch.

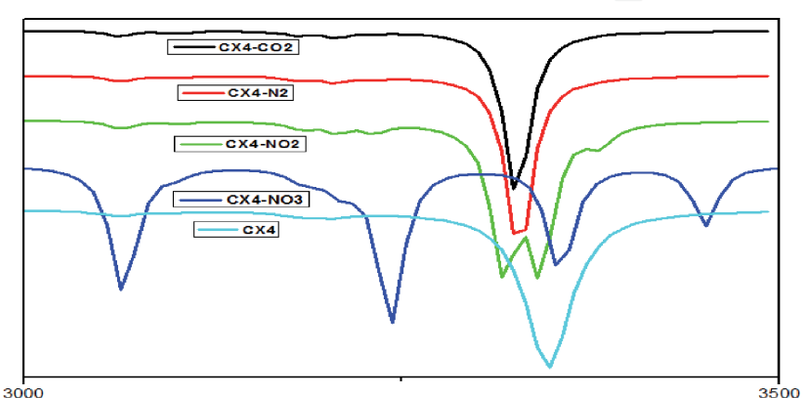


Figure 2.
Infrared spectrum of the stable host-guests complexations (H-bonding region (the unit is cm^{-1})).

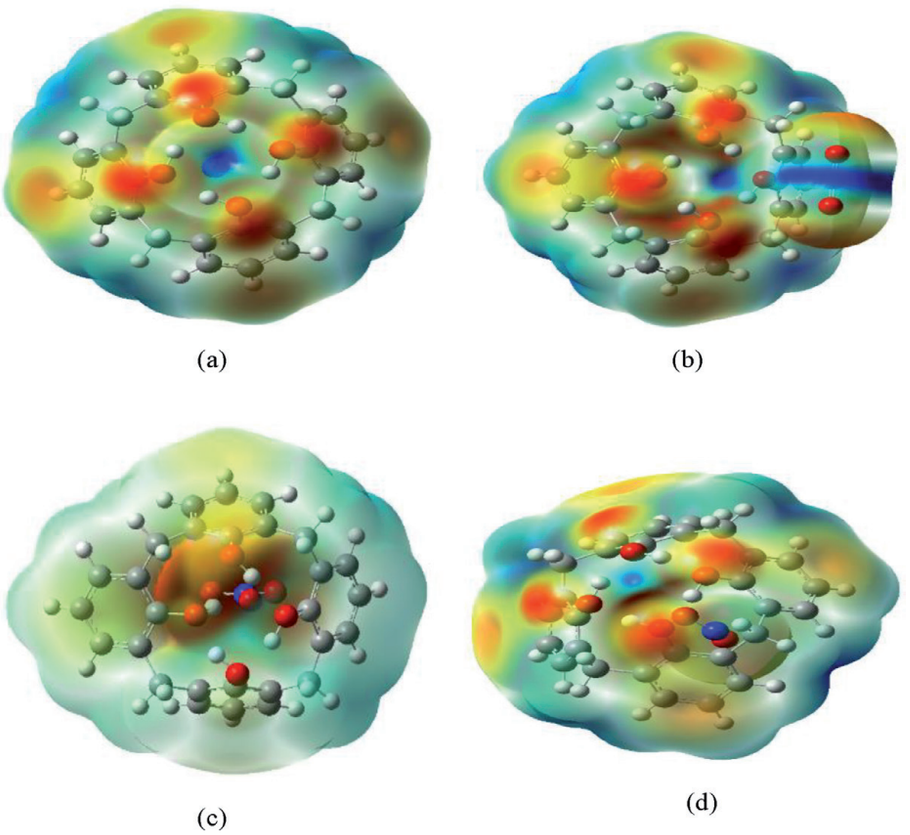


Figure 3.
Molecular electrostatic potential analysis of the CX[4]-CO_2 (a), CX[4]-N2 (b), CX[4]-NO_2 (c) and CX[4]-NO_3 (d) complexes calculated by B3LYP-D3/6–31 + G(d) level.

This part demonstrates how the MESP can explore the region of the unravel molecular interactions between the CX[4] molecule and these hosts.

3.4 Non covalent interactions analysis

Figure 4(a) shows the existence of a weak van der Waals (VdW) type interactions between CO_2 gas and CX[4]. Concerning the CX[4]-N_2 complex (**Figure 4(b)**), we show a green color between the guest and the host that indicates the existence of the weak Van der Waals interactions and the blue color at the lower edge level indicates the existence of the O-H-bonding type interactions. Also, we have shown clearly a red color located in the center of the phenol rings indicates a strong repulsion. The NCI-plots have been confirmed these results (see **Figure 4**). In addition, from CX[4]-NO_2 (**Figure 4(c)**) complex, we find the existence of a red color which explain the steric effect interactions, blue color (hydrogen bonds type interactions) and a green color (week van der Waals type interactions). The type of majority bonds of the links between the NO_3 gas and the CX[4] molecule is the weak VdW type interactions. The NCI-RDG analysis shows that the VdW type interactions and the hydrogen bonding interactions between the guest and the host are very necessary for the stability of the encapsulated complexes.

4. Conclusion

The CX[4] and the CX[4]-gas complexes have been optimized using the density functional theory (DFT). Our work has clearly explained the sensibility of the pollutant gas inside the cavity, which is very important in comparison with the gas

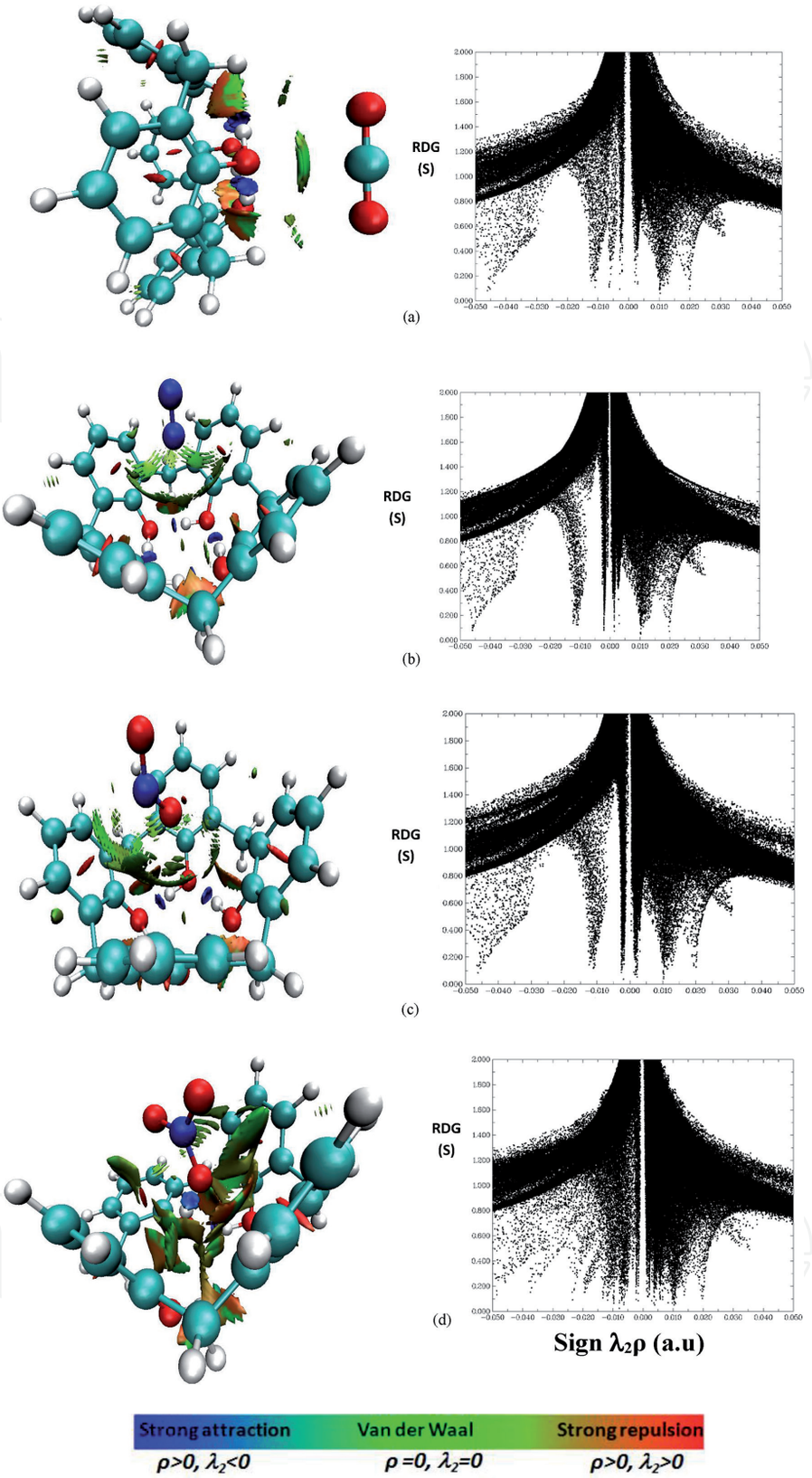


Figure 4.
NCI-RDG plots of the electron density and its reduced gradient of the inclusion complexes for CX[4]-gas (CX[4]-CO_2(a), CX[4]-N_2(b), CX[4]-NO_2(c) and CX[4]-NO_3(d)). The iso-surfaces were constructed with RGD = 0.5a.u and the colors scaling from −0.01 to −0.01 a.u.

located outside the cavity. The IR spectrum study has explained the role of the NO_3 gas in the red-shifted of the O-H bonds in comparison with the other gases. The MEP results is clearly explained the charge distribution reactivity. The NCI-RDG analysis clearly shows the strong interactions of the gas NO_3 and NO_2 with the endo-cavity

environments of the CX[4] molecule. Finally, the non-covalent interactions analyses show that the calix[4]arene maybe useful for encapsulated the pollutant gas in the future. The sensitivity of the calix[4]arene molecule for these polluting gases opens a way to test the interaction of CX[4] with other types of biological molecules (proteins).

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