



Spectroscopic and computational investigation of a novel charge transfer complex via hydrogen bonding between β -cyclodextrin with DDQ and TCNE: NBO, AIM, NLO and DFT analysis



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Abstract

Charge transfer complex study remains of paramount importance in material science research. A novel charge transfer complex CTC including hydrogen bonding between the donor β -cyclodextrin with the π -acceptors tetracyanoethylene (TCNE) and dichlorodicyanobenzoquinone (DDQ) have been synthesized and characterized experimentally and theoretically. The solid complex was prepared and characterized by ¹H NMR and FT-IR spectroscopies, the complex was formed in 1:1 ratio, with good evidences for existing both charge transfer and hydrogen bonding in its molecular structure. Density functional theory B3LYP/DFT at the basis set 6-31G (d,p) has been running out in gas phase to support the experimental results. The optimization energy, complexation energy, geometrical parameters, Mullikan atomic charges, LUMO and HOMO energies as well as non-linear optical (NLO) were calculated and interpreted; they strongly referred the high stability of the complex to the existence of charge transfer beside hydrogen bonding in the formed. In addition, Bader's atoms-in-molecule (AIM) and natural bonding orbital (NBO) calculations were analysed and discussed; they clearly demonstrate that a charge transfer was occurring between DDQ, TCNE and β -CD molecules. Theoretical studies propose that hydrophobic interaction and hydrogen bonding play significant role in determining the stability of the complexes. Keywords: β -Cyclodextrin, charge transfer complex, DDQ, TCNE, natural bonding orbital, B3LYP/DFT, nonlinear optical

1. Introduction

The study of the charge-transfer (CT) interaction of donor (β -CD) and π -acceptors (DDQ and TCNE) has been a great deal of interest. The charge transfer complexes originated from interaction between donor and acceptor molecules [1-3]. The CT complexes are of great significance in material science in recent years, and have found applications in solar cells [4], organic semiconductors [5,6], superconductors, photo catalysts [7] and biological systems, due to their electrical conductivity and optical properties [8]. These complexes can also be used as drug receptor binding mechanisms [9], corrosion inhibitors and micro emulsion agents. CT complexes have attracted further attention in the field of DNA binding [10–12], antibacterial, antimicrobial studies and quantitative estimation of drugs [13,14].

The Hydrogen bonding which exists between the electron donor and the electron acceptor plays a pivotal role for the formation of such type of CT

complexes and to ascertain their stability [15,16]. Such CT complexes are characterized by spectroscopic studies wherein a new absorption band is perceived in the absorption spectrum of the complex that does not

appear in the spectrum of discrete donor or acceptor [17–19]. This new absorption band is observed due to transfer of charge from ground state HOMO of the donor to the excited state LUMO of the acceptor [20].

β -cyclodextrin (β -CD) is a cyclic oligosaccharide derived by enzymatic hydrolysis of common starch. Due to its peculiar chemical structure, constituted of an external hydrophilic surface and a hydrophobic cavity, β -CD can form inclusion complexes with a variety of organic molecules, thereby improving some of their properties, such as solubility, stability and bio-availability [21–23]. Moreover, the presence of oxygen atoms can also give it the ability to form charge transfer complexes. The main forces involved in the complexation process are electrostatics, van der

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Receive Date: 26 November 2021, Revise Date: 21 December 2021, Accept Date: 31 December 2021

DOI: [10.21608/ejchem.2021.108057.4943](https://doi.org/10.21608/ejchem.2021.108057.4943)

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waals, hydrophobic interactions, hydrogen bonding and charge transfer interactions [24–26].

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) is commonly known as electron acceptor used in chemical synthesis. It is involved in processes of energy storage and utilization and therefore plays a vital role in biological reactions [27]. Some of these reactions are considered as simple models for biochemical processes [28]. Due to the importance of

DDQ as a famous and readily available π -acceptor, its charge transfer complexes have been the subject of extensive studies with different donors [29–30].

Likewise, it is known that the Tetracyanoethylene (TCNE) is one of the most versatile organic compounds as it is used in many different reactions, having a strong coupling of the intra and intermolecular vibrations [31].

The π -electron acceptors 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetracyanoethylene (TCNE) are known to form stable colored charge transfer complexes (CTC) with many donors' bases [32]. β -cyclodextrin is used as a donor because their hydroxyl groups can provide additional hydrogen bonds with guests (acceptors) [33]. Owing to their particular structures, they have the ability to form host-guest complexes with a wide range of guests [34]. The subject wants to make a study of charge transfer complexes using β -CD not only that it contains donor atoms, but that it can also stabilize the complexes. We want to see to what extent the inclusion phenomenon stabilizes the charge transfer complex.

So, the object of these studies is to prepare the new charge-transfer complexes between β -CD as a donor and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) or Tetracyanoethylene (TCNE) as π -acceptors. The obtained charge transfer complexes were structurally characterized using infrared fourier transform-infrared spectroscopy (FT-IR) and the nuclear magnetic resonance (^1H NMR) spectroscopy.

In order to support the measured work, density functional theory (DFT) has been applied using the hybrid B3LYP method at the basis set 6-31 G (d,p). The computations will include the optimization energy, complexation energy, geometrical parameters and reactivity parameters. Moreover, the natural bond orbital analysis (NBO) and Bader's atoms in molecule (AIM) analysis were applied as a powerful approach for the evaluation of the intermolecular interactions between β -cyclodextrin and acceptors (DDQ and TCNE). The nonlinear optical (NLO) properties magnitude of molecules is dependent on the first order hyperpolarizability. The NLO property of molecules and their hyperpolarizabilities have become an important field of extensive research [35–39]. A very important aim of this work is to match the experimental work with the calculated one. The

molecular structures of the donor and acceptors are shown in figure 1.

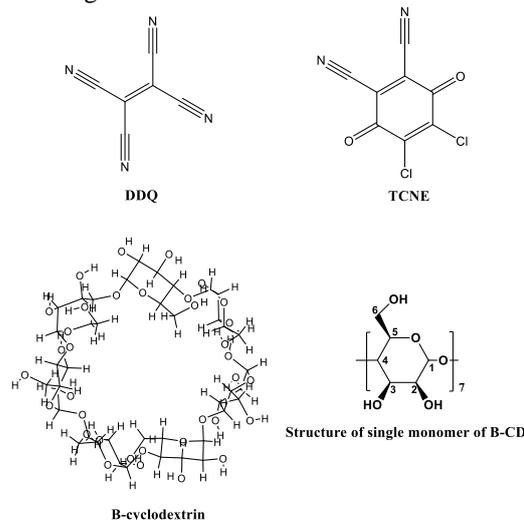


Fig.1. Structures of the β -cyclodextrin donor and the π -acceptors.

2. Experimental

2.1. Reagents

β -cyclodextrin (β -CD; $\text{C}_{42}\text{H}_{70}\text{O}_{35}$; 1135), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; $\text{C}_8\text{Cl}_2\text{N}_2\text{O}_2$; 227) and tetracyanoethylene (TCNE; C_6N_4 ; 128.09) π -acceptors (figure 1) were obtained from Sigma-Aldrich Chemical Company, USA and were used without further purification. Commercially available spectroscopic grade solvent was purchased from Merck Chemical Company and was also used as received.

2.2. Preparation of (β -CD/DDQ) and (β -CD/TCNE) charge transfer complexes

Tetracyanoethylene (TCNE), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and β -cyclodextrin (β -CD) were purchased from Sigma and Aldrich chemical company and used as such. The two solid CTC(β -CD/DDQ) and (β -CD/TCNE) have been prepared in 1:1 ratio of DDQ, TCNE and β -CD. For each complex, 1.0 mmol β -CD in water (10 ml) was added drop wise to 1 mmol of each acceptor in methanol (10 ml). The mixtures were stirred for about overnight and allowed to evaporate slowly at room temperature. Change in colors was observed upon mixing solution of the β -CD with any of the acceptors. These observed new colors are dark red-brick for (β -CD/DDQ); pale yellow for (β -CD/TCNE). These changes in colors represent strong evidence of the supramolecular interaction between the donor (β -CD) and each of the π -acceptors (DDQ, TCNE). These complexes were characterized using spectroscopic techniques (FT-IR; ^1H NMR).

2.3. Instrumental analyses

2.3.1. Infrared spectra

The infrared spectra within the range of 4000-400 cm^{-1} for the solid CT complexes were recorded on a spectrum one perkin Elmer FT-IR spectrophotometer.

2.3.2. ^1H NMR spectra

Proton nuclear magnetic resonance spectroscopy (^1H NMR) was collected by the Scientific and Technical research center in physico-chemical analysis (CRAPC), Algeria, on a Bruker spectrometer operating at 400.13 MHz. The measurements were performed at ambient temperature using D_2O (Deuterium oxide) as a solvent and TMS (tetramethylsilane) as an internal reference. The chemical shifts δ are expressed in parts per million (ppm).

3. Computational details

The initial structure of free molecules and their complexes was constructed using Hyperchem 7.5 molecular modeling package [40]. We started with the optimization of the substrates: β -CD, DDQ and TCNE by DFT methods using the B3LYP/6-31G (d,p) basis set functional. The most stable geometries of two complexes β -CD/DDQ and β -CD/TCNE were found by semi-empirical PM6 method. As an output to the semi-empirical, we make use of density functional calculations. All the computations were performed using Gaussian 09W [41] program and Gauss-View [42] 5.0 molecular visualization program package on the personal computer. To investigate the thermodynamic parameters of the binding process, the statistical thermodynamic calculation was carried in vacuum by (DFT/ B3LYP 6-31G (d,p)) method. Natural bond orbital (NBO) and Bader's atoms-in-molecule (AIM) were performed to explore the nature and strength of intermolecular interactions between β -CD and π -electron acceptors (DDQ and TCNE) in the complexes [43,44]. The HOMO-LUMO gap was also approximated using the HOMO to LUMO excitation energy obtained by DFT-B3LYP/6-31G (d,p) calculation. Moreover, various other molecular parameters like dipole moment, polarizability and first order hyperpolarizability have been also presented for the present complex.

4. Results and discussion

4.1. Vibrational frequencies

FT-IR spectra are important technique to prove the formation of charge transfer (CT) complexes as a result of the change in frequency of functional groups of DDQ and TCNE than that of pure β -cyclodextrin after formation of CT complexes (β -CD/DDQ) and (β -CD/TCNE). The FT-IR spectra bands of free donor β -cyclodextrin, free acceptors (DDQ, TCNE), and of their corresponding CT complexes are shown in figure2 and figure3, while the assignments of their characteristic FT-IR spectral bands are reported in Table 1. The formation of CT complexes during the reaction of β -cyclodextrin with TCNE and DDQ is strongly supported by observing of main infrared bands of the donor and acceptors in the product spectra. The FT-IR spectrum of the distinguished bands in the free donor (β -CD) shows the following vibration: A wide band correspond to the stretching vibrational ν (O-H) observed at 3283.58 cm^{-1} , and ν (C-H) vibration at 2925.37 cm^{-1} . The IR spectrum of β -cyclodextrin is characterized by other stretching modes at 1026.86 cm^{-1} , assigned in ν (C-O).

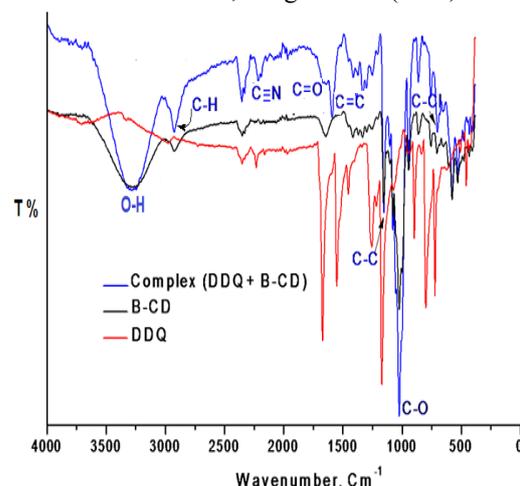


Fig. 2. Infrared spectra of β -CD; DDQ and its corresponding CT complexes

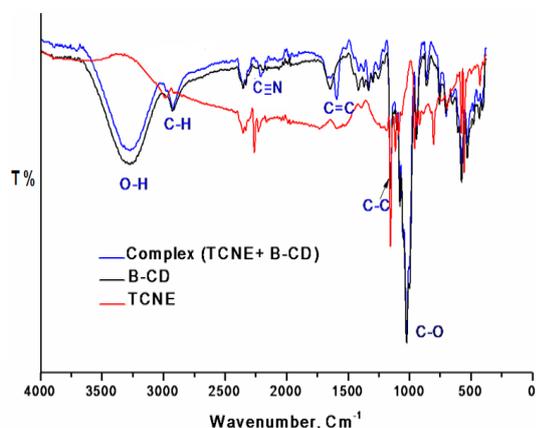
However, the bands of the donor and acceptors in the complexes spectra reveal shifts in the frequencies and difference in intensities compared with those of the free donor and acceptors.

The formation of CT complexes during the reaction of donor with TCNE and DDQ is strongly supported by observing of main infrared bands of the donor and acceptors in the product spectra.

Table 1: Infrared frequencies (cm^{-1}) and tentative assignments for β -cyclodextrin, DDQ, TCNE and the charge transfer complexes.

β -CD	DDQ	TCNE	CTC		Assignments
			β -CD/DDQ	β -CD/TCNE	
3283.58s			3273.34s	3268.23s	ν (O–H)
2925.37m			2921.96m	2920.25m	ν (C–H)
1415.77m			1410.66m	1414.07m	ν (C–H) of CH_2
1026.86m			1023.45m	1021.74m	ν (C–O)
	2229.42w		2217.48w		ν (C \equiv N)
	1639.23s		1644.34br		ν (C=O)
	1552.12m		1582.94m		ν (C=C)
	1168.44s		1151.38m		ν (C–C)
	701.06s		697.65m		ν (C–Cl)
		2255.01w		2224.30w	ν (C \equiv N)
		1577.82m		1589.76m	ν (C=C)
		1154.79m		1163.32m	ν (C–C)

Note: s: strong, w: weak, m: medium, br : broad

**Fig. 3.** Infrared spectra of β -CD; TCNE and its corresponding CT complexes.

The FT-IR spectrum of the $[(\beta\text{-CD}) (\text{DDQ})]$ complex indicated that the band resulting in ν (C \equiv N) vibration of the free acceptor DDQ changed in frequency and decreased in intensity in the complexes upon CT complexation. As a representative example, the ν (C \equiv N) vibration of free DDQ is observed at 2229.42 cm^{-1} , while in its complex, ν (C \equiv N) appears at the lower wavenumber value (2217.48 cm^{-1}). It is clear that ν (C \equiv N) of DDQ is decreasing during complexation. The characteristic band of the ν (O–H) group observed at 3283.58 cm^{-1} in the free donor β -CD is shifted to 3273.34 cm^{-1} in the complex, and its intensity as decreased. These observations clearly confirm that the OH group in the β -CD donor and the C \equiv N group in the DDQ acceptor participated in the complexation process. The groups of bands assigned to the vibrations ν (C=O) and ν (C=C) appear at 1639.23 cm^{-1} and 1552.12 cm^{-1} , respectively, in the free DDQ, with a shift towards

the higher wavenumbers at 1644.34 cm^{-1} and 1582.94 cm^{-1} , respectively.

The FT-IR spectrum of the $[(\beta\text{-CD}) (\text{TCNE})]$ complex, shows that the vibration ν (C \equiv N) is observed at 2259.71 cm^{-1} in the free TCNE is shifted to 2220.35 cm^{-1} in the complex, and its intensity as decreased. The characteristic band of the ν (O–H) group observed at 3283.58 cm^{-1} in the free donor β -CD is shifted to 3268.23 cm^{-1} in the complex, and its intensity as decreased. The characteristic bands of C–C and C=C observed at 1153.24 cm^{-1} and 1535.63 cm^{-1} of free TCNE, respectively, are shifted to 1162.40 cm^{-1} and 1589.49 cm^{-1} .

Generally, there are small changes in wavenumber values and intensities of the free reactants (β -CD, TCNQ and DDQ) upon complexation. These changes and shifts in positions of some of the peaks could be understood on the basis of the expected symmetry and electronic structure modifications in both donor and acceptor units in the formed complex compared to the free molecules. The presence of various hydrogen bond donor groups of the β -cyclodextrin, like alcohol (–OH) and (–CH) facilitate the hydrogen bonding and charge transfer interactions with acceptor molecules (TCNE and DDQ).

4.2. ^1H NMR spectra

^1H NMR spectra of complexes present the persuasive confirmation of the complexation pathway by observing most of signals of the free reactants with some expected shift due to the changes in electronic density upon complexation. Chemical shifts and the changes of the chemical shifts of protons in $[(\beta\text{-CD}) (\text{TCNE})]$ and $[(\beta\text{-CD}) (\text{DDQ})]$ complexes compared with the pure compound of β -CD (Figure. 4 and Figure. 5).

Table 2: ¹H-NMR Chemical shifts (δ, ppm) for CH protons of β-Cyclodextrin before and after complexation with DDQ and TCNE in D₂O solution.

Compound	H-1	H-2	H-3	H-4	H-5	H-6
β-CD	5.047	3.606	3.801	3.459	3.781	3.624
β-CD /DDQ	5.042	3.556	3.932	3.325	3.817	3.839
Δδ	-0.005	-0.050	+0.131	-0.134	+0.036	+0.215
β-CD /TCNE	5.043	3.591	3.944	3.327	3.823	3.851
Δδ	-0.004	-0.015	+0.143	-0.132	+0.042	+0.227

Δδ(complexed-free)

In the structure of CD, it is known that the H-3 and H-5 hydrogens are located inside the conical cavity, particularly, the H-3 protons are placed near the wider rim while H-5 protons are placed near the narrower rim and the other H-1, H-2 and H-4 protons are located at the exterior of cyclodextrins [45]. If a guest molecule is incorporated into the β-CD cavity (H-3 and H-5), the screening constants of the β-CD protons inside the cavity should be sensitive to the change environment, but that of the outside protons (H-1, H-2, H-4 and H-6) should not. This should result in chemical shift changes of the inside protons.

Table 2 shows the chemical shifts observed for H-1, H-2, H-3, H-4, H-5 and H-6 for pure β-Cyclodextrin [46] and its charge transfer DDQ and TCNE complexes. The largest chemical shift changes were observed for H-3 (0.131 ppm) followed by H-5 (0.036 ppm) in DDQ and for H-3 (0.143 ppm) followed by H-5 (0.042 ppm) in TCNE. It is observed that the values of chemical shift for protons of β-Cyclodextrin (H-3 and H-5) after formation of CT increased, this phenomena prove that formation of inclusion and charge transfer complex.

5. Theoretical results:

5.1. Geometry optimization:

5.1.1. Binding energy, structural geometry and Mulliken atomic charges

Full geometry optimizations of free molecules, CTC1: [(β-CD) (DDQ)] and CTC2: [(β-CD) (TCNE)] were performed without any constrain in the gaseous state at the same level of theory (B3LYP/6-31G (d,p)). The optimized structures were checked as minima on the potential energy surfaces by frequency calculations. A view of the optimized structures and its atoms numbering is shown in Figure 6; based on these structures the bond lengths, bond angles and Dihedral angle of β-CD, DDQ, TCNE, CTC1 and CTC2 were calculated and these values are listed in Tables 4 and 5.

The stabilization energy (ΔE_{stb}) and interaction energy (ΔE_{int}) upon complexation between β-CD and π-electron acceptors (DDQ and TCNE) can be calculated for the minimum energy structures

according to the following equations:

$$\Delta E_{\text{stb}} = E_{\text{complex}} - (E_{\text{guest_opt}} + E_{\text{host_opt}}) \quad (1)$$

$$\Delta E_{\text{int}} = E_{\text{complex}} - (E_{\text{guest_sp}} + E_{\text{host_sp}}) \quad (2)$$

Where E_{complex} , $E_{\text{host_opt}}$ and $E_{\text{guest_opt}}$ are the energies from full-geometry optimization of complex, host β-CD and guest (DDQ or TCNE) respectively; $E_{\text{guest_sp}}$ and $E_{\text{host_sp}}$ are the corresponding single-point energies in the complexed states. The calculated complexation energy for [(β-CD) (TCNE)] and [(β-CD) (DDQ)] complexes are mentioned in Table 3. The complexation energies were found equal to -2963,679.10³ Kcal/mol for [(β-CD) (TCNE)] complex and to -3614,768.10³ Kcal/mol for [(β-CD) (DDQ)].

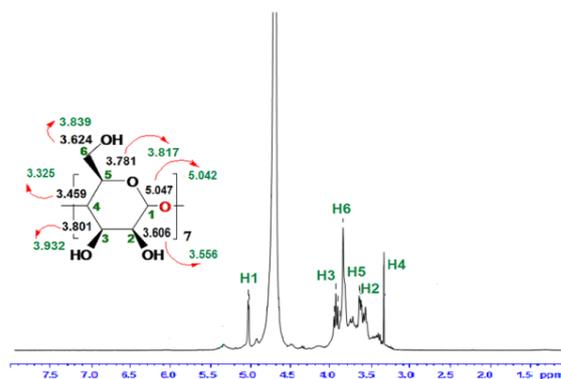


Fig. 4. ¹H-NMR spectra of the complex [(β-CD) (DDQ)].

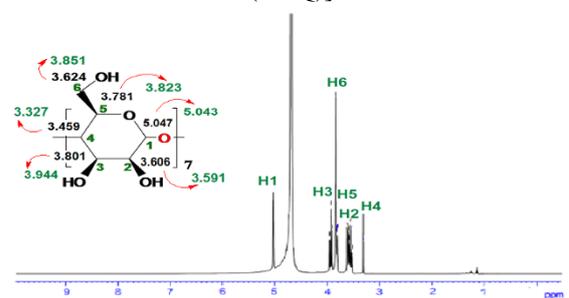


Fig. 5. ¹H-NMR spectra of the complex [(β-CD) (TCNE)].

Table 3: binding energy (ΔE) values of $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes calculated by B3LYP/6-31G (d,p) method.

Energies (kcal/mol)	$[(\beta\text{-CD})$ (DDQ)]	$[(\beta\text{-CD})$ (TCNE)]
ΔE_{stb} (kcal/mol)	3.800	4.000
ΔE_{int} (kcal/mol)	3.600	3.800

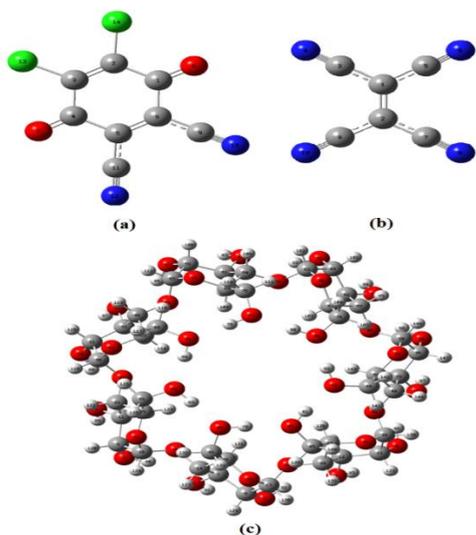


Fig. 6. Molecular structure of: (a) DDQ, (b) TCNE and (c) $\beta\text{-CD}$, optimized by B3LYP/6-31G (d,p) with numbering of the atoms used in the present work in vacuum.

From Figure 6, the interaction between the two reagents (donor and acceptor) was manifested by several variations in bond lengths, bond angles and dihedral angles in both molecules. In face-to-face configuration, it was obvious that the structural modifications were distributed over a large number of bonds in both molecules.

In the DDQ molecule, the lengths of the relatively sensitive bonds C148=O155, C149–C1161, C151=O154 and C150–C1160 were deviated from -0.0004 to -0.0054 Å. For C153–C156, C148–C149, C150–C151, C148–C153 and C151–C152 the changes located in the range 0.0014 to 0.0063 were also noticed.

In the TCNE molecule, the lengths bonds C152 \equiv N153, C148–C150 C154 \equiv N155, C149–C156, C156 \equiv N157, C149–C154, C148–C152 and C148=C149 were deviated from 0.0011 to 0.0041 Å.

In the opposite plane, several modifications in almost all constituent bonds were undergone in the $\beta\text{-CD}$ molecule. In $[(\beta\text{-CD}) (\text{DDQ})]$, the main bond lengths deviations were observed in O57–H79 and O71–H84 with deviations of 0.0144 and 0.0156 Å, respectively. The deviations of adjacent bonds O73–

H82, O57–H79 and O76–H80 were 0.0146 Å, 0.0149 Å and 0.0154 Å, in $[(\beta\text{-CD}) (\text{TCNE})]$.

For the angles and in CTC1, the most significant deviations of 3.5256 Å° and -93.475 Å° were noticed respectively for C153–C156 \equiv N157 and C148–C153=C152. Likewise, in CTC2 the deviations of bond angles C149–C156 \equiv N157, C156–C149=C148 and C148–C150 \equiv N151 were 1.0864 , 1.3461 and 3.5506 Å°, respectively. It was also noted that the dihedral angles underwent large changes. For instance, in CTC1 the deviations for C148–C153–C156 \equiv N157 and C148–C153=C152–C158 were very remarkable and equal 128.877 and 354.886 Å°. For the CTC2, the dihedral angles of C149=C148–C152 \equiv N153, C149=C148–C150 \equiv N151 and C154–C149=C148–C150 are -15.756 , 324.377 and 357.359 Å° respectively.

To complement this structural prediction, the Mulliken population analysis was exploited to compute atomic charge in order to know which atoms in the reagents were affected upon the formation complex and in which direction the charge transfer process will occurred. In CT complexes phenomena, estimation of Mulliken atomic charges plays a very imperative part in the application of quantum mechanical calculations to the molecular systems [47, 48]. These determined Mulliken atomic charges are shown in Tables 6. As shown in Figure 6, the C1 and C2 (labeled respectively C148 and C149 atoms in CT complexes) in the free TCNE have both a positive values with 6-31G (d,p) basis set. The corresponding value is $+0.19728$ e.

As we can see in Fig. 7, two hydrogen bonds are observed in optimized structure of $[(\beta\text{-CD}) (\text{TCNE})]$ complex. The first H-bond comes through the interaction of N155 in TCNE with H79 at 1.96 Å°. The second H-bond is located with N157 (C \equiv N) and H80 of $\beta\text{-CD}$ with distance of 2.06 Å°.

It was found that the negative charges upon N155 and N157 atoms in acceptor (TCNE) decreases

significantly upon complexation with donor molecule. This is associated with a decrease in the positive charge of H79 from $+0.35841$ e to $+0.35030$ e for 6-31G (d,p) basis and a decrease in the positive charge of H80 from $+0.35827$ e to $+0.33387$ e for 6-31G (d,p) basis set. Another hand, the C148...C149 bond distance of TCNE was decreased from 1.3723 Å° to 1.3682 Å° value at 6-31G (d,p) basis set in free and in complexed state (Table 4).

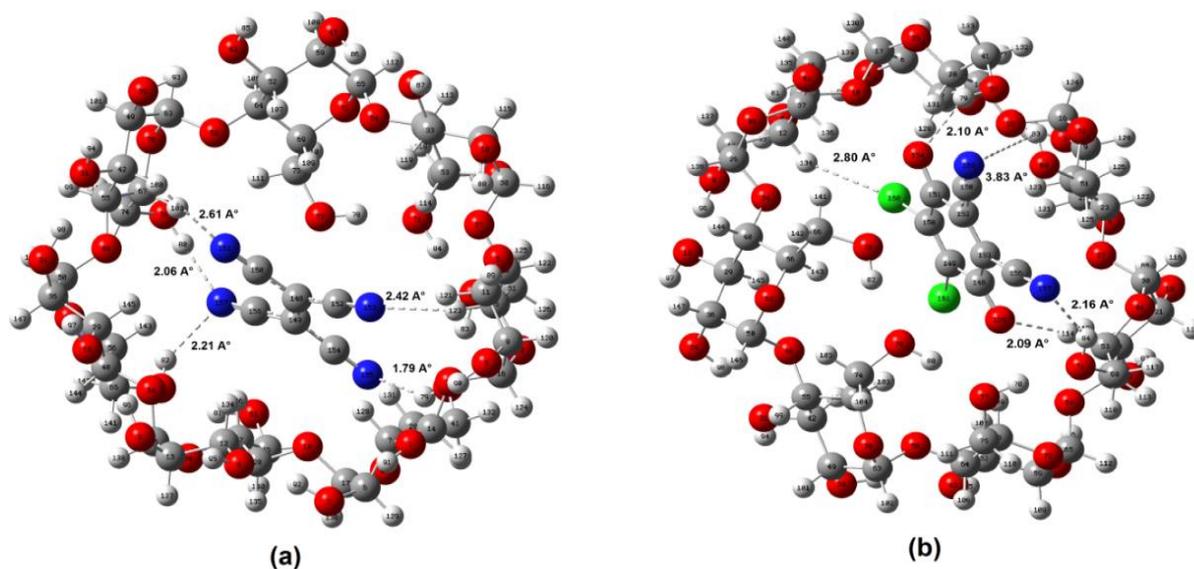


Fig. 7. The intermolecular hydrogen bond between b-CD and derivatives; (a) H-bond in [(β -CD) (TCNE)]; (b) H-bond in [(β -CD) (DDQ)]

Table 4: Bond lengths selected (\AA) of optimized free and complexed ligand with DDQ acceptor calculated by B3LYP/6-31G (d,p) method.

β -CD	DDQ	CTC1	$\Delta\delta$
O71-H84 (0.9831)		0.9675	0.0156
O60-H83 (0.9833)		0.9766	0.0067
O61-H81 (0.9829)		0.9676	0.0153
O57-H79 (0.9832)		0.9688	0.0144
O73-H82 (0.9830)		0.9674	0.0156
O76-H80 (0.9831)		0.9838	-0.0007
O77-H78 (0.9831)		0.9814	0.0017
C35-H123 (1.0956)		1.0971	-0.0015
C42-H100 (1.1007)		1.1004	0.0003
C53-H114 (1.0956)		1.0952	0.0004
C12-H134 (1.1006)		1.0988	0.0018
	C148-C149 (1.4956)	1.4939	0.0017
	C148-C153 (1.5034)	1.4981	0.0053
	C153-C156 (1.4268)	1.4254	0.0014
	C148=O155 (1.2136)	1.2140	-0.0004
	C156=N157 (1.1625)	1.1624	0.0001
	C149-Cl161 (1.7184)	1.7197	-0.0013
	C150-C151 (1.4956)	1.4913	0.0043
	C151-C152 (1.5034)	1.4971	0.0063
	C152-C158 (1.4268)	1.4267	0.0001
	C158=N159 (1.1625)	1.1622	0.0003
	C150-Cl160 (1.7184)	1.7250	-0.0066
	C151=O154 (1.2136)	1.2190	-0.0054
	Bond angles ($^\circ$)		
	C153-C156=N157 (178.7427)	175.2171	3.5256
	O155=C148-C153 (120.2425)	120.7284	-0.4859
	Cl161-C149=C150 (123.0121)	122.9483	0.0638
	C148-C153=C152 (27.7541)	121.2300	-93.475
	Dihedral angle ($^\circ$)		
	C148-C153-C156=N157 (177.9728)	49.0958	128.877
	O155=C148-C153=C152 (178.7619)	178.9474	-0.1855
	Cl161-C149-C148-C153 (-178.8004)	-179.4562	0.6558
	C148-C153=C152-C158 (180.0000)	-174.8860	354.886

Table 5: Bond lengths selected (Å) of optimized free and complexed ligand with TCNE acceptor calculated by B3LYP/6-31G (d,p) method.

β -CD	TCNE	CTC2	$\Delta\delta$
O71–H84 (0.9831)		0.9822	0.0011
O60–H83 (0.9833)		0.9798	0.0035
O61–H81 (0.9829)		0.9797	0.0032
O57–H79 (0.9832)		0.9683	0.0149
O73–H82 (0.9830)		0.9684	0.0146
O76–H80 (0.9831)		0.9677	0.0154
O77–H78 (0.9831)		0.9792	0.0039
C35–H123 (1.0956)		1.0929	0.0027
C42–H100 (1.1007)		1.0968	0.0039
C28–H131 (1.0956)		1.0948	0.0008
	C150 \equiv N151 (1.1627)	1.1624	0.0003
	C148=C149 (1.3723)	1.3682	0.0041
	C152 \equiv N153 (1.1627)	1.1616	0.0011
	C148–C150 (1.4296)	1.4282	0.0014
	C154 \equiv N155 (1.1627)	1.1609	0.0018
	C148–C152 (1.4296)	1.4265	0.0031
	C156 \equiv N157 (1.1627)	1.1607	0.0020
	C149–C154 (1.4296)	1.4270	0.0026
	C149–C156 (1.4296)	1.4277	0.0019
	Bond angles ($^\circ$)		
	C149–C156 \equiv N157 (178.9316)	177.8452	1.0864
	C156–C149–C154 (116.9834)	118.5475	-1.5641
	C156–C149=C148 (121.5198)	120.1737	1.3461
	C148–C150 \equiv N151 (178.9172)	178.9172	3.5506
	Dihedral angle ($^\circ$)		
	C149=C148–C152 \equiv N153 (-179.8478)	-164.0913	-15.756
	C149=C148–C150 \equiv N151 (-179.8211)	144.5562	324.377
	C154–C149=C148–C150 (179.9921)	-177.3670	357.359

Likewise, the positive charges of C148 and C149 of TCNE in [(β -CD) (TCNE)] complex are changing from 0.19728 e to 0.24401 e and 0.25476 e, suggesting that an appreciable amount of electronic charge has been transferred from ligand to TCNE acceptor.

The length of intramolecular bonds C154...N155 and C156...N157 is also decreased from 1.1627 Å (In the free TCNE) to 1.1609 Å and 1.1607 Å, respectively for 6-31G (d,p) basis set, this is due to the effect of the hydrogen bond. Other interactions have been established between N151...H100, N153...H123 and N157...H82 with inter-atomic distances: 2.61 Å, 2.42 Å and 2.21 Å, respectively.

In the case of [(β -CD) (DDQ)] complex, three H-bonds were established: the first H-bond with a length of 2.16 Å was formed between N157 (C \equiv N) and H84 of β -CD. The second was formed between O154 (C=O) and H79 of β -CD positioned at 2.10 Å and the third H-bond with length of 2.09 Å was formed between O155 (C=O) and H114 of β -CD. Other interactions are also found between C1160...H134 and N159...H83 where the bond distances are respectively 2.80 Å and 3.83 Å. It was found that the negative charges upon O154 and

O155 atoms in acceptor (DDQ) decreases significantly upon complexation with donor molecule. This is associated with a decrease in the positive charge of H79 from +0.35841 e to +0.34348 e for 6-31G (d,p) basis and an increase in the positive charge of H131 from +0.12429 e to +0.14735 e for 6-31G (d,p) basis set.

It should also be noted that the bond lengths of O57...H79, O73...H82 and O76...H80 are significantly modified after complexation (Tables 4 and 5) where the bond distances are changed from 0.9832 Å, 0.9830 Å and 0.9831 Å to 0.9683 Å, 0.9684 Å and 0.9677 Å in [(β -CD) (TCNE)] and to 0.9688 Å, 0.9674 Å and 0.9838 Å in [(β -CD) (DDQ)], respectively.

Another important point is that the Mulliken charges corresponding to the two chlorine atoms in DDQ molecule acceptor are entirely modified, to spend from an identical value of 0.11920 e and 0.11918 e to 0.09431 e and 0.081476 e, respectively for C1160 and C1161.

Similar results were found in the analysis of bonds lengths before and after complexation of TCNE and DDQ with biological molecule β -CD (see Tables 4 and 5). An decreased in O57...H79 bond length by 0.9683 Å and 0.9688 Å, respectively in [(β -CD) (TCNE)] and [(β -CD)

(DDQ)] complexes, and the atomic charges of these atoms (O57 and H79) were observed to be decreased upon complexation. This can be noted that there exists a strong hydrogen bonding interaction between N155...H79 and O154...H79.

In $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes, the two nitrogens (N157 of DDQ and N157 of TCNE) showed an increased Mulliken

atomic charges (-0.50695 e and -0.55140 e). On the other hand, the charges of H80 and H84 atoms of $\beta\text{-CD}$ were observed to be 0.36385 e and 0.33660 e in CTC1, but in CTC2 were found to be 0.33387 e and 0.37087 e, respectively. These findings clearly confirm the CT between both acceptor-donor molecules.

Table 6: Mulliken atomic charge distribution of some centers in $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes; CTC1 and CTC2, in gas phase.

Atom	In CTC1	In CTC2	Atom	In CTC1	In CTC2
$\beta\text{-CD}$					
O1: -0.57002	-0.58838	-0.58276	C53: 0.14756	0.15264	0.14700
O2: -0.58355	-0.60864	-0.61586	O57: -0.59970	-0.57474	-0.59545
O3: -0.58328	-0.61274	-0.59593	O60: -0.59985	-0.60693	0.62577
O4: -0.56997	-0.59049	-0.59464	O61: -0.59925	-0.55547	0.61009
O5: -0.56982	-0.59949	-0.57994	O71: -0.59958	-0.57765	-0.62370
C6: 0.15590	0.16762	0.16178	O76: -0.59950	-0.62135	-0.57499
C7: 0.15566	0.16080	0.15438	O77: -0.59979	-0.61086	-0.62550
O8: -0.58320	-0.62704	-0.60628	H79: 0.35807	0.34348	0.35030
C9: 0.15594	0.15859	0.16130	H80: 0.35795	0.36385	0.33387
O10: 0.58320	-0.61864	-0.59439	H81: 0.35737	0.31589	0.36118
C11: 0.15523	0.17049	0.15769	H82: 0.35772	0.34862	0.33696
C12: 0.15519	0.16197	0.17148	H83: 0.35809	0.36235	0.36999
O18: -0.52484	-0.53521	-0.54180	H84: 0.35773	0.33660	0.37087
O19: -0.56996	-0.59817	-0.58914	H100: 0.10004	0.11410	0.14451
C20: 0.15330	0.15148	0.15624	H114: 0.12458	0.15728	0.13612
C28: 0.14764	0.15003	0.15999	H120: 0.10807	0.11225	0.11092
C29: 0.15532	0.16076	0.15535	H121: 0.09995	0.11189	0.11604
C30: 0.36030	0.37344	0.36083	H122: 0.10027	0.10668	0.10221
C35: 0.14717	0.12530	0.12481	H123: 0.12433	0.10666	0.16831
C40: 0.15294	0.16101	0.13489	H130: 0.10695	0.11199	0.10763
C41: 0.02404	0.03147	0.01987	H131: 0.12420	0.14735	0.13715
C42: 0.15495	0.16298	0.15327	H132: 0.12791	0.12241	0.14286
C50: 0.36019	0.36759	0.35333	H133: 0.11266	0.13150	0.12333
C51: 0.02404	0.05274	0.01920	H134: 0.10010	0.11749	0.11061
DDQ					
C148: 0.46637	0.47337		O155: -0.38247	-0.44853	
C149: -0.15244	-0.12062		C156: 0.29467	0.32784	
C150: -0.15237	0.12507		N157: -0.42986	-0.50695	
C151: 0.46629	0.51369		C158: 0.29466	0.29997	
C152: 0.08457	0.20164		N159: -0.42990	-0.45136	
C153: 0.08450	0.11236		Cl160: 0.11920	0.09431	
O154: -0.38243	-0.48374		Cl161: 0.11918	0.08147	
TCNE					
C148: 0.19728		0.24401	N153: -0.41851		-0.47098
C149: 0.19728		0.25476	C154: 0.31987		0.39097
C150: 0.31987		0.36363	N155: -0.41851		-0.51204
N151: -0.41851		-0.47808	C156: 0.31987		0.41144
C152: 0.31987		0.35004	N157: -0.41851		-0.55140

1.2. HOMO-LUMO and reactivity parameters

Molecular orbitals and their properties such as energy are very useful for scientists and are very important parameters for quantum chemistry. The most important orbitals in a molecule which determine how the molecule interacts with other species are the frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule [49]. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule. The chemical reactivity and site selectivity of the molecular systems have been determined by the B3LYP/6-31G (d,p) method. Global reactivity descriptors: chemical potential (μ), global hardness (η), chemical softness (S) and electrophilicity index (ω) were calculated using the energies of frontier molecular orbital E_{HOMO} and E_{LUMO} and given by Eqs (3)-(6).

$$\mu = (E_{\text{HOMO}} + E_{\text{LUMO}}) / 2 \quad (3)$$

$$\eta = (E_{\text{LUMO}} - E_{\text{HOMO}}) / 2 \quad (4)$$

$$S = 1/\eta \quad (5)$$

$$\omega = \mu^2 / 2\eta \quad (6)$$

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies of $[(\beta\text{-CD}) (\text{TCNE})]$ and $[(\beta\text{-CD}) (\text{DDQ})]$ complexes and the structural parameters μ , η , S and ω are shown in Table 7.

The energy gap reflected the chemical activity of the molecules. The LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents the ability to donate electron. Moreover, a lower HOMO-LUMO energy gap explained the eventual stability of the complex.

We examine the four important molecular orbitals (MOs): the second highest and highest

occupied MOs and the lowest and the second lowest unoccupied MOs which we denote HOMO-1, HOMO, LUMO and LUMO+1, respectively. These MOs for gas phase are represented in Figure 8 and Figure 9. The HOMO-LUMO energy gap of both $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes are respectively -2.694 eV and -2.294 eV. We can conclude, from the reported results in Table 7 that $[(\beta\text{-CD}) (\text{DDQ})]$ complex had the lowest HOMO-LUMO energy gap this indicates that the complex $[(\beta\text{-CD}) (\text{DDQ})]$ is the most stable and his electron density changed more easily than $[(\beta\text{-CD}) (\text{TCNE})]$ complex.

1.1. Natural bond order (NBO) analysis

To better understand the intermolecular interaction of the $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes, natural bond orbital analysis [50] has been carried out with DFT/6-31G (d,p) method, which provides much information about the nature and strength of intermolecular interactions from the viewpoint of local orbital interactions and their second order perturbation energy ($E^{(2)}$). Table 8 lists the $E^{(2)}$ values of selected interactions between the local orbitals where BD, LP, BD* denote the occupied bonding orbitals, the lone pairs and the empty antibonding orbitals, respectively.

It can be seen from these results that a great number of nonbonding-antibonding and bonding-antibonding interactions occur between the host molecule ($\beta\text{-CD}$) and guests (DDQ and TCNE) (Fig. 7).

The interactions energies of these contacts are in the range of 0.07 kcal/mol–3.17 kcal/mol for $[(\beta\text{-CD}) (\text{DDQ})]$ and 0.08 kcal/mol–9.44 kcal/mol for $[(\beta\text{-CD}) (\text{TCNE})]$. The interactions are explained in detail as follows.

Table 7: (LUMO+1, LUMO, HOMO, HOMO-1) energies, chemical potential (μ) (eV), hardness (η) (eV), chemical softness (S) (eV) and electrophilicity (ω) (eV) of the charge transfer complexes calculated by B3LYP/6-31G (d,p) method.

Parameters	$[(\beta\text{-CD}) (\text{DDQ})]$	$[(\beta\text{-CD}) (\text{TCNE})]$
$E_{\text{LUMO}+1}$ (eV)	-2.367	-1.717
E_{LUMO} (eV)	-4.357	-4.628
E_{HOMO} (eV)	-7.051	-6.922
$E_{\text{HOMO}-1}$ (eV)	-7.140	-6.998
$E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)	-2.694	-2.294
μ (eV)	-5.704	-5.775
η (eV)	1.347	1.147
S (eV)	0.742	0.871
ω (eV)	12.077	14.538

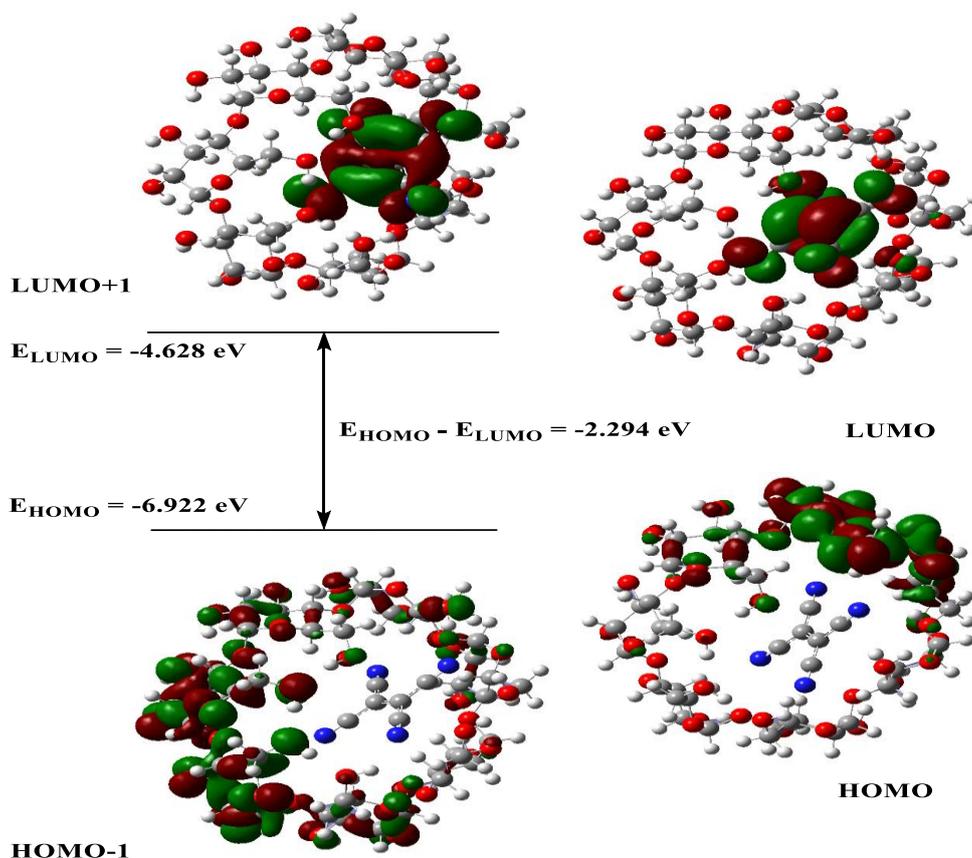


Fig. 8. Spatial plot of frontier molecular orbitals for $[(\beta\text{-CD}) (\text{TCNE})]$ complex.

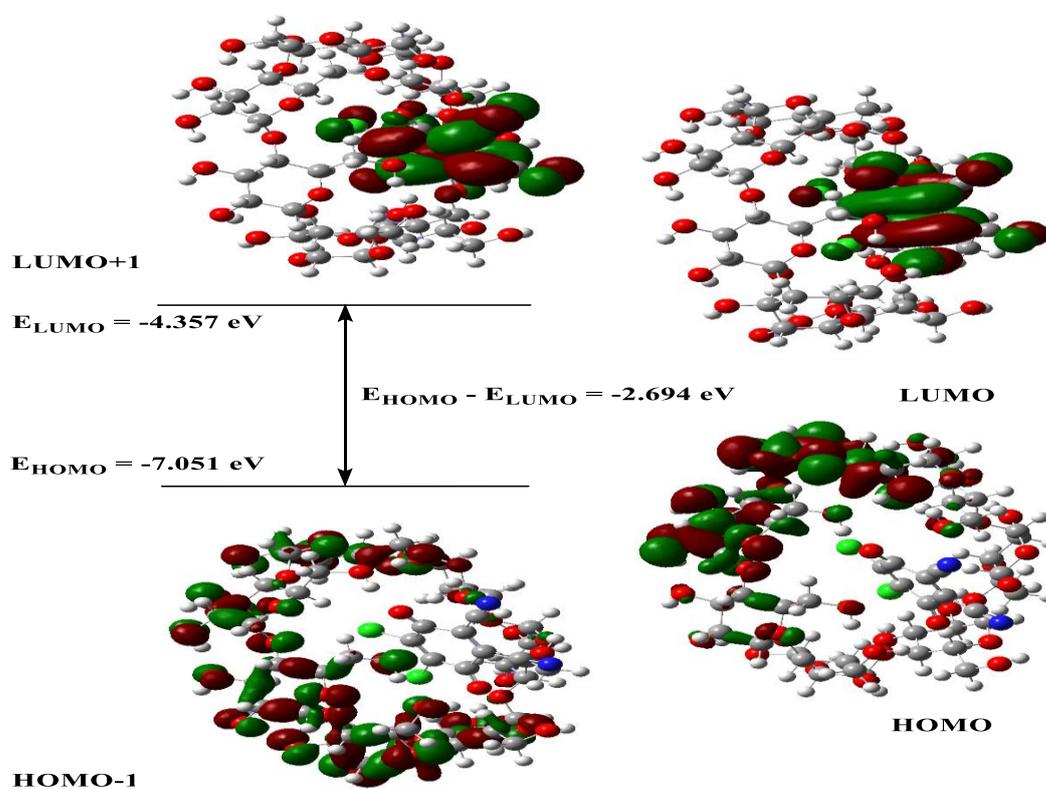


Fig. 9. Spatial plot of frontier molecular orbitals for $[(\beta\text{-CD}) (\text{DDQ})]$ complex.

Table 8: The partial electron donor orbitals, electron acceptor orbitals and the corresponding energies $E^{(2)}$ (kcal/mol) for $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes by DFT/6-31G (d,p).

Complex	Donor NBO(i)	Acceptor NBO(j)	$E^{(2)}$ (kcal/mol)
DDQ/ β -CD	β -CD donor and DDQ acceptor		
	LP (1) O 60	BD*(1) C 158-N 159	0.46
	BD (1) C 12-H 134	BD*(1) C 150-Cl 160	0.19
	BD (1) O 71-H 84	BD*(2) C 156-N 157	0.29
	LP (1) O 18	BD*(1) C 150-Cl 160	0.10
	DDQ donor and β -CD acceptor		
	LP (1) N 157	BD*(1) O 71-H 84	2.70
	BD (1) C 156-N 157	BD*(1) O 71-H 84	0.07
	BD (2) C 156-N 157	BD*(1) O 71-H 84	1.63
	LP (1) O 155	BD*(1) C 53-H 114	3.17
	BD (2) C 148-O 155	BD*(1) C 53-H 114	1.71
	LP (1) Cl 160	BD*(1) C 12-H 134	0.62
	LP (1) O 154	BD*(1) O 57-H 79	2.57
	BD (2) C151-O 154	BD*(1) O 57-H 79	1.00
	BD (1) C 150-Cl 160	BD*(1) C 12-H 134	0.09
	LP (1) Cl 160	BD*(1) C 7-H 128	0.27
	TCNE/ β -CD	β -CD donor and TCNE acceptor	
LP (1) O 61		BD*(2) C 156-N 157	0.12
LP (2) O 61		BD*(3) C 156-N 157	0.58
BD (1) O 61-H 81		BD*(2) C 156-N 157	0.10
LP (1) O 57		BD*(2) C 154-N 155	0.13
BD (1) O 57-H 79		BD*(2) C 154-N 155	0.77
LP (1) O 76		BD*(1) C 156-N 157	0.11
BD (1) O 76-H 80		BD*(1) C 156-N 157	0.21
BD (1) C 28-H 131		BD*(3) C 152-N 153	0.08
TCNE donor and β -CD acceptor			
LP (1) N 153		BD*(1) C 35-H 123	2.93
BD (2) C 152-N 153		BD*(1) C 35-H 123	0.08
LP (1) N 155		BD*(1) O 57-H 79	9.44
BD (1) C 154-N 155		BD*(1) O 57-H 79	0.24
BD (2) C 154-N 155		BD*(1) O 57-H 79	1.40
LP (1) N 157		BD*(1) O 73-H 82	2.53
BD (3) C 156-N 157		BD*(1) O 73-H 82	1.20
LP (1) N 157		BD*(1) O 76-H 80	7.29
BD (3) C 156-N 157		BD*(1) O 76-H 80	0.59
LP (1) N 151		BD*(1) C 42-H 100	1.42

In $[(\beta\text{-CD}) (\text{DDQ})]$ complex, an important interaction is observed between LP (1) O155 of DDQ and BD*(1) C53-H114 of β -CD and corresponds to 3.17 kcal/mol. Another important interaction is observed between LP (1) N157 and BD*(1) O71-H84 corresponds to 2.70 kcal/mol. Moreover, we also distinguish a nonbonding–antibonding interaction between both partners, this interaction is established between BD (2) C156-N157 and vacant antibond BD*(1) O71-H84 with value of stabilization energy (1.63 kcal/mol). All the interactions described are typical of Vander Waals forces. By against, when DDQ acts as a donor, the presence of intermolecular H-bond corresponding to both electron donor–acceptor orbitals: BD (2) C151-O154 toward BD*(1) O57-H79, LP (1) Cl160

toward BD*(1) C12-H134, BD (2) C148-O155 toward BD*(1) C53-H114 and LP (1) O154 toward BD*(1) O57-H79 results in stabilization of 1.00, 0.62, 1.71 and 2.57 kcal/mol, respectively.

In the case of $[(\beta\text{-CD}) (\text{TCNE})]$ complex, it is also noted that there exists a strong hydrogen bonding interaction between N155 and H79 which can be characterized by the orbital interaction LP (1) N155 toward BD*(1) O57-H79 and the corresponding energy value of this interaction is 9.44 kcal/mol. Another important interaction is observed between LP (1) N157 and BD*(1) O76-H80 corresponds to 7.29 Kcal/mol. Two other interactions are observed: the first between LP (1) N151 and BD*(1) C42-H100 and the second between LP (1) N153 and BD*(1) C35-H123 with a

stabilization energy of 1.42 and 2.93 Kcal/mol, respectively.

According to the results obtained from NBO calculations, we can conclude that the charge transfer between occupied and unoccupied orbitals of host-guest and the intermolecular hydrogen interactions are the major contributions of the stabilization of the complex.

1.1. Nonlinear optical properties (NLO)

Theoretical investigations have been done in order to understand the microscopic origin of nonlinear behavior of the studied molecule. The study involves

the calculation of dipole moment (μ), polarizability (α) and first hyperpolarizability (β) tensors for the title molecule. The Gaussian 09 output provides six polarisable components and each represents α_{xx} , α_{xy} , α_{yy} , α_{xz} , α_{yz} , α_{zz} respectively. For hyperpolarisability in the output we will get ten Hyper polar components and each represents β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{xzz} , β_{yzz} , β_{zzz} respectively.

Using the x, y and z components, the magnitude of the total static dipole moment, isotropic polarizability and first order hyperpolarizability can be calculated by the following equations [51]:

$$\mu_{\text{tot}} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \quad (7)$$

$$\alpha = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \quad (8)$$

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (9)$$

$$\beta_{\text{tot}} = [(\beta_{xxx} + \beta_{xxy} + \beta_{xxz})^2 + (\beta_{yyy} + \beta_{xyy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2} \quad (10)$$

All NLO identifiers obtained from the equations above have been computed at DFT/6-31G (d,p) levels of theory to provide its nonlinear properties and are listed in Table 9. The highest dipole moment has been determined as 5.1089 D for [(β -CD) (DDQ)] while the lowest one has been predicted as 2.1245 D for [(β -CD) (TCNE)].

Polarizability of [(β -CD) (DDQ)] and [(β -CD) (TCNE)] are calculated to be $(-80.8959 \times 10^{-24})$ and $(-75.6231 \times 10^{-24})$ esu, respectively.

The magnitude of the molecular hyperpolarizability β , is one of key factors in NLO system. The calculated first static hyperpolarizability β value is equal to 2.8178×10^{-30} esu and 0.9266×10^{-30} esu for [(β -CD) (DDQ)] and [(β -CD) (TCNE)], respectively and which is about 7 and 2 times greater than those of urea (for urea β is 0.3728×10^{-30} esu) [52]. Thus, the high value of dipole moment and first order hyperpolarizability are representing the NLO potential of the present complex.

1.1. Bader's atoms in molecules (AIM) analysis

It is known that Bader's topological analysis of electron density $\rho(r)$ could be widely employed to study the intermolecular interactions [53–57]. In this approach, the location of bond critical point (BCP), the value of electron density $\rho(r)$ and its Laplacian charge density $\nabla^2\rho(r)$ at the BCP provide vital information of the nature and strength of the interactions in the formation of complexes. According to the criteria, the electron density $\rho(r)$ values at the BCPs range from 0.002–0.040 a.u. [58]. Similarly, the $\nabla^2\rho(r)$ values at the BCPs vary from 0.024–0.139 a.u. [58]. The intermolecular interactions between the host molecule (β -CD) and guests (DDQ and TCNE) identified via an AIM analysis [59] are shown in Figs. 11 and 12. The values of electron densities, and its laplacian, potential energy density, kinetic energy density and total energy at the BCPs are tabulated in Table 10.

As shown in Table 10 and Figure 10, there exist three different hydrogen bonding interaction in [(β -CD) (DDQ)] complex: O...H, Cl...H and N...H. At the important BCP between O155 and H114, the charge density $\rho(r)$ and its laplacian $\nabla^2\rho(r)$ are 0.0164 a.u. and 0.0666 a.u., respectively. This BCP also has the highest value of the total energy $H(r)=0.0482$ a.u. Two other BCPS are observed: Cl160...H128 and O154...H79 with a charge density $\rho(r)$ of 0.0047 a.u. and 0.0142 a.u., respectively. The presence of five BCPS in [(β -CD) (DDQ)] reveal that there exist intermolecular interactions between DDQ and β -CD.

In the [(β -CD) (TCNE)] complex, five (N...H) bond critical points (BCPs) of intermolecular hydrogen bonds have been observed. The maximum amount of electron density (0.0193 a.u.) attributed to the interaction (N155...H79) is related to the laplacian ($\nabla^2\rho(r)=0.0978$ a.u.) and ($H(r)=0.0010$ a.u.).

Likewise, the BCP linked to the interaction between H100 and N151 also has a lower charge density (0.0070 a.u.) and a laplacian equal to 0.0256 a.u. with $H(r)=0.0014$ a.u.

As shown in Table 10, all the charge densities at the BCPs are relatively small, and their laplacian are positive; it indicates that the intermolecular interactions are typical close-shell interaction

The respective NBO and AIM results seem to be concordant with respect to the nature of the main reactive sites and their interaction energies, although the theoretical bases of two theoretical approaches were different. Figs. 10 and 11 illustrated a graphical correlation between the perturbation energy values of the interactions between the two orbitals located on both ends of the bond paths, and the electronic densities of the corresponding critical

points. The greater was the perturbation energy, the greater was the electronic density. Consequently, the AIM results gained were in agreement with those of NBO analysis.

6. Conclusion

Two new intermolecular charge transfer complexes are formed when β -CD electron donor and both TCNE and DDQ π -electron acceptors interact.

The formation of CT complexes was analyzed using spectroscopic techniques (^1H NMR and FTIR) and studied by computational molecular modeling using the hybrid B3LYP method at the basis set 6-31 G (d,p). It was established that the 1:1 $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes were formed. Characterization of the solid-state complexes by FT-IR and ^1H NMR confirms the existence of interaction CT between β -CD and acceptors (DDQ and TCNE).

Table 9: Calculated dipole moment (μ), mean polarizability (α : 1a.u = 0.1482×10^{-24} esu) and the mean first hyperpolarizability (β : 1a.u = 8.6393×10^{-33} esu) of $[(\beta\text{-CD}) (\text{DDQ})]$ and $[(\beta\text{-CD}) (\text{TCNE})]$ complexes by DFT/6-31G (d,p) method.

Parameters	$[(\beta\text{-CD}) (\text{DDQ})]$	$[(\beta\text{-CD}) (\text{TCNE})]$
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μ, D		
μ_x	1.1151	-0.9884
μ_y	2.4721	-1.8645
μ_z	-4.3297	-0.2459
μ	5.1089	2.1245
Polarizability		
α_{xx}	-532.7838	-508.5661
α_{xy}	1.3120	-13.1103
α_{yy}	-517.5080	-495.4679
α_{xz}	-10.4001	-9.6392
α_{yz}	6.0024	-7.5920
α_{zz}	-587.2783	-526.7995
α (a.u)	-545.8567	-510.2778
α [10^{-24} esu]	-80.8959	-75.6231
First		
Hypolarizability		
β_{xxx}	27.6487	-29.6212
β_{yyy}	22.9674	-71.9374
β_{zzz}	71.7486	3.0716
β_{xyx}	73.4107	30.8195
β_{xyy}	25.3357	74.1887
β_{xzz}	29.1582	-27.5290
β_{xyx}	81.4490	60.5808
β_{yyz}	-41.4961	-57.7181
β_{xzz}	78.8013	1.0967
β_{yyz}	-375.7601	-187.7123
β_{zzz}	326.1719	107.2645
β (a.u)	2.8178	0.9266
β [10^{-30} esu]		

Table 10: Topological parameters calculated by atoms in molecules (AIM).

Complex	BCPs	$\rho(r)$	$\nabla^2\rho(r)$	$V(r)$	$G(r)$	$H(r)$	$-G/V$
DDQ/β-CD	O155....H114	0.0164	0.0666	-0.0162	0.0644	0.0482	3.9753
	C1160....H128	0.0047	0.0178	-0.0024	0.0034	0.0010	1.4166
	C1160....H134	0.0061	0.0253	-0.0036	0.0050	0.0014	1.3888
	O154....H79	0.0142	0.0647	-0.0153	0.0157	0.0004	1.0261
TCNE/β-CD	N157....H84	0.0131	0.0592	-0.0129	0.0138	0.0009	1.0697
	N151....H100	0.0070	0.0256	-0.0040	0.0054	0.0014	1.3500
	N153....H123	0.0099	0.0352	-0.0073	0.0080	0.0007	1.0958
	N157....H82	0.0124	0.0549	-0.0119	0.0128	0.0009	1.0756
	N157....H80	0.0158	0.0755	-0.0170	0.0179	0.0009	1.0529
	N155....H79	0.0193	0.0978	-0.0223	0.0233	0.0010	1.0448

$\rho(r)$: critical point electron density, $\nabla^2\rho(r)$: critical point laplacian, $V(r)$: critical point potential energy density, $G(r)$: lagrangian form of kinetic energy density, $H(r)$: critical point total energy (all units are expressed in a.u.)

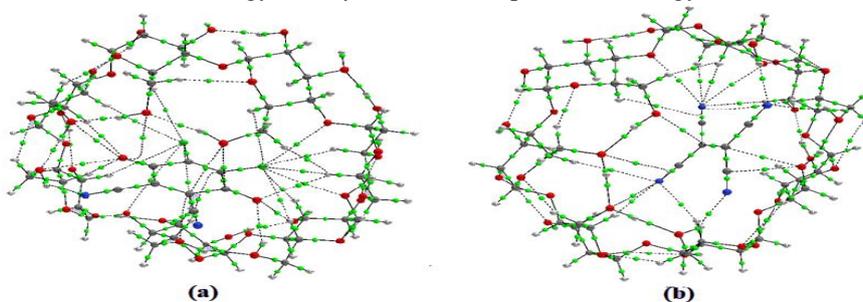


Fig. 10. AIM molecular graphs of (a): $[(\beta\text{-CD}) (\text{DDQ})]$ and (b): $[(\beta\text{-CD}) (\text{TCNE})]$ complexes showing different types of interactions.

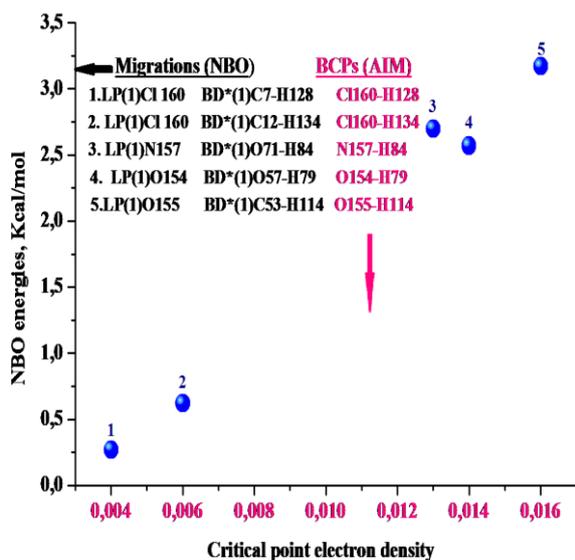


Fig. 11. Graphical correlation of [(β -CD) (DDQ)] between the perturbation energies ($E^{(2)}$ in kcal/mol) and the electronic densities ρ (BCP) of the corresponding critical points.

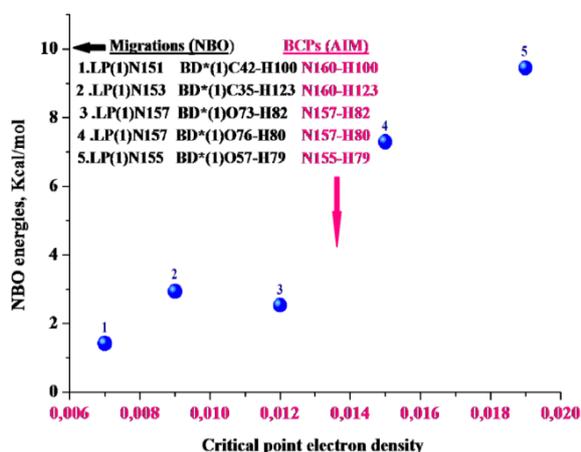


Fig.12. Graphical correlation of [(β -CD) (TCNE)] between the perturbation energies ($E^{(2)}$ in kcal/mol) and the electronic densities ρ (BCP) of the corresponding critical points.

Natural bond order analysis and frontiers of molecular HOMO and LUMO orbitals calculations indicate the presence of interaction charge transfer and clearly justify the complexes formation.

The static first and second order hyperpolarizability values are found be many folds higher than urea molecule and [(β -CD) (DDQ)] complex is highly NLO active than [(β -CD) (TCNE)] complex. Global chemical reactivity descriptors were calculated and explained about the chemical stability of the studied molecules.

Finally, the NBO and AIM analyses were performed to confirm the existence of

intermolecular hydrogen bonds for the complexes [(β -CD) (DDQ)] and [(β -CD) (TCNE)].

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