Journal of Molecular Liquids 216 (2016) 716–723

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Review

A combined DFT and experimental study of proline/β-cyclodextrin inclusion complex

Amal Zaboub [a], Fatiha Madi [b,*], Rachid Merdes [a], Messaouda Mohamedi [a], Leila Nouar [b]

[a] Laboratory of Applied Chemistry, Department of Material Sciences, Faculty of Mathematical, Informatics and Material Sciences, University of 08 Mai 1945, BP 401, Guelma, Algeria
[b] Laboratory of Computational Chemistry and Nanostructures, Department of Material Sciences, Faculty of Mathematical, Informatics and Material Sciences, University of 08 Mai 1945, BP 401, Guelma, Algeria

ARTICLE INFO

Article history:
Received 28 August 2015
Received in revised form 24 January 2016
Accepted 25 January 2016
Available online xxxx

Keywords:
B3LYP/3-21G$^+$
Pro
β-CD
Absorption spectra
FTIR spectroscopy

ABSTRACT

The binding of the L-proline (Pro) amino acid with β-cyclodextrin (β-CD) was investigated theoretically by B3LYP/3-21G$^+$ method and experimentally by UV–visible and FTIR techniques. Two modes of complexation were considered for studying such complex; in A complex the pyrrolidine ring of the guest was directed toward secondary hydroxyls of β-CD, while in B complex the pyrrolidine was directed toward primary one. Energetic analysis indicates that the formed complexes are stable and both host and guest were deformed after complexation. Electronic properties given by TD-DFT calculation and NBO analysis clearly demonstrate that a charge transfer was occurring between Pro and β-CD molecules.

Contents

1. Introduction

Cyclodextrins (CDs) are cyclic oligosaccharides with central hydrophobic cavities and hydrophilic exterior edges. Cyclodextrins are composed of 5–12 α-(1–4)-linked D(+) glucopyranose units linked in macrocyclic ring. The most widely used (CDs) are α, β, and δ (CDs). The ability of β-CD to form inclusion complexes with different products is well known. In particular, β-CD has an internal cavity shaped like a truncated cone of about 8 Å deep and 6.0–6.4 Å in diameter. This cavity possesses a relatively low polarity that can accommodate guest organic molecules inside. The formation of inclusion complexes of organic

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* Corresponding author.
E-mail address: fatiha_madi@yahoo.fr (F. Madi).

http://dx.doi.org/10.1016/j.molliq.2016.01.082
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molecules with cyclodextrins is important for their pharmaceutical and technological applications [1–3].

The study of inclusion complexes of organic molecules with cyclodextrins (CDs) has attracted the interest of many experimental [4–6] and theoretical chemists during the past decades. Computational methods in combination with experimental techniques have been mainly focused on the conformational study of inclusion complex of natural CDs or their derivatives. At present, there are a great number of theoretical methods used in molecular modeling for supermolecular systems such as the complexes of CDs or their derivatives with guest molecules [7–9].

L-Proline (Pro), as an amino acid, contains an amino group and a carboxylic acid. Pro is the only naturally occurring amino acid with a secondary α-amino group, which explains its more basic character with respect to many other α-amino acids. Pro and its derivative are often used as asymmetric catalysts in organic reaction. Pro is an osmoprotectant and therefore is used in many pharmaceutical, biotechnological applications. In brewing, proteins rich in Pro combine with polyphenols to produce haze (turbidity) [10–11].

The proline can catalyze the reaction of aldol with various arom by formation of inclusion complex with β-cyclodextrin. Moreover, the formation of proline/cyclodextrin inclusion complex was studied experimentally but until now no theoretical of such complex was done to propose a model for the inclusion complex [12–13].

In this paper, we have investigated the inclusion processes of Pro into β-CD cavity experimentally and using a B3LYP/3-21G$^+$ level of theory with the aim to give some insights about the geometry, electronic properties and the driving forces governing the formation of the inclusion complex.

2. Material and molecular modeling

2.1. Preparation of the inclusion complex

L-Proline (Pro) and β-cyclodextrin (β-CD) were purchased from Sigma and Aldrich chemical company and used as such. Solid L-Pro/β-CD inclusion complex was prepared using co-precipitation method [14]. Briefly, β-CD (10^{-4} M) was dissolved in 50 ml of a mixture of ethanol and distilled water (10:90, *v*/v) at 55 °C on a hot plate. After cooling the solution to 35 °C, L-Pro (10^{-4}) was added to produce L-Pro/β-CD complex (1:1). After that, the mixtures were stirred for 4 h at 35 °C and later maintained overnight at 4 °C. The cold precipitated L-Pro/β-CD inclusion complexes were recovered by vacuum-filtration and then dried in a convection oven at 50 °C for 24 h. Finally, the inclusion complex was further analyzed using FT-IR, UV visible.

Absorption spectral measurements were carried out with Perkin Elmer instrument Lambda 25 UV–visible spectrometer in the range 190 nm–800 nm. The Fourier Transform infrared spectra were recorded for powdered samples of Pro, β-CD and Pro/β-CD crystals using JASCO FT-IR Model 410 spectrophotometer by KBr pellet technique in the range of 400–4000 cm^{-1}. Band positions are reported in reciprocal centimeters (cm^{-1}).

2.2. Computational procedure

The initial structure of zwitterionic form of Pro was constructed using Hyperchem program [15]. The starting geometry of β-CD was taken from Chem-Office 3D ultra (version 10, Cambridge software). Then the two structures Pro and β-CD were optimized by B3LYP/3-21G$^+$ level of theory [16].

The complex is formed by introducing the Pro in β-CD cavity according to two models illustrated in Scheme 1.

In all optimizations of the host, guest and inclusion complexes, the B3LYP/3.21G$^+$ level of theory was used. The calculations and the analysis of results were done by Gaussview and Gaussian09 programs respectively [17]. The calculations of maximum visible absorption of the studied complexes were performed by the TD-DFT method the solvent effects on the conformational equilibrium have been investigated using the PCM model for water ($\varepsilon = 78.39$) as a solvent with B3LYP/3.21G$^+$ method. Finally the natural bond orbital analyses (NBO) were applied as a powerful approach for the evaluation of the intermolecular interactions between β-CD and Pro molecules.

3. Results and discussion

3.1. Absorption spectral studies

UV–Vis technique has been widely applied to study inclusion complexes of cyclodextrins for the determination of constant stability [18, 19]. In our study we are limited on studying the electronic absorption of Pro, β-CD and Pro/β-CD inclusion complex for comparison with theoretical TD-DFT calculation.

The electronic absorption spectra of Pro, β-CD and Pro/β-CD inclusion complex, recorded in water in the range 190 nm to 800 nm are presented in Fig. 1. From the spectra, it is observed that the pure Pro, β-CD and Pro/β-CD inclusion complex show good absorption in the UV regions. The absorption spectrum of Pro shows a λ_{max} at 202 nm assigned to n–π* transition, while that of β-CD shows absorption band at 204 nm (σ–σ* transition). When Pro and β-CD are mixed together; it is observed that new absorption peak (198 nm) appears in the visible region where neither donor nor acceptor has any absorption. This wavelength band is broad and has an increased intensity which is indicative of formation of the inclusion complex.

3.2. FTIR spectroscopy

FTIR is a useful technique for confirming the formation of the inclusion complex. The FTIR spectra of Pro (a), β-CD (b) and Pro/β-CD(c) inclusion are shown in Fig. 2.

The formation of the inclusion complex is further confirmed when the characteristic bands C=O and $^+NH_2$ of Pro are shifted upon inclusion into β-CD cavity. These bands in free Pro are observed at 1626 and 2988 cm^{-1} for C=O and asymmetrical vibration of $^+NH_2$ respectively. While, in the inclusion complex, C=O and $^+NH_2$ are observed at 1649 and 2921 cm^{-1}.

The broader O–H stretching band of the inclusion complex in the range of 3000–3500 cm^{-1} corresponds to the multiple O–H functional groups of β-CD molecule.

Since the amount of guest molecules included in the inclusion complex does not exceed 10%, the FT-IR spectrum of the guest molecules is usually obscured by cyclodextrin. Fig. 2 shows that the FT-IR spectrum of Pro is almost obscured by the very intense and broad β-CD bands in the physical mixture.

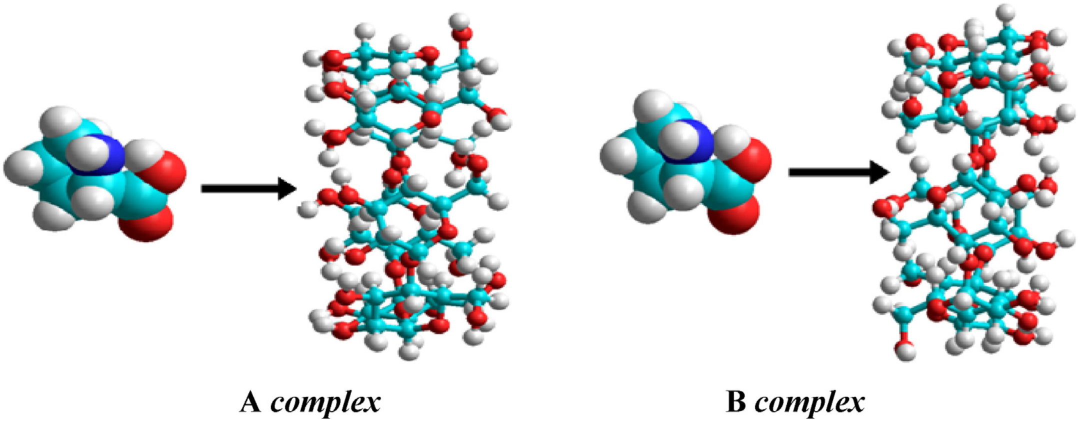
Additionally to experimental IR spectrum, the calculated one is obtained by B3LYP/3-21G$^+$ for A complex the favored model. The theoretical spectrum present the absorption bands of CO and NH_2^+ at 1651 and 2946 cm^{-1} respectively. A small difference between experimental and calculated vibration modes is observed. This discrepancy can come from the formation of intermolecular hydrogen bonding. Also, we note that the experimental results belong to solid phase and theoretical calculations belong to gaseous phase.

3.3. Molecular modeling

3.3.1. Energy

The complexation energy (ΔE) upon complexation between Pro and β-CD is defined in Eq. (1):

$$\Delta E = E_{complex} - (E_{\mathrm{Pro}} + E_{\beta-\mathrm{CD}}) \quad (1)$$



Scheme 1. The proposed structure of Pro/β-CD complex for A and B complexes.

where E_{complex}, E_{Pro} and $E_{\beta\text{-CD}}$ represent the relatives energies of complex, free Pro and free β-CD respectively.

The deformation energy of the guest or the host molecule can be obtained by Eqs. (2) and (3):

$$E_{deformation}(Guest) = E[G]_{sp}^{opt} - E[G]_{opt} \tag{2}$$

$$E_{deformation}(Host) = E[H]_{sp}^{opt} - E[H]_{opt} \tag{3}$$

where $E_{deformation}$ (guest) stands for the deformation energy of the Pro guest, $E[G]_{sp}^{opt}$ is the single point energy of the Pro using its geometry in the optimized complex, and $E[G]_{opt}$ is the energy of the optimized geometry of the guest.

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. The frontier orbital gap helps to characterize the chemical reactivity and kinetic stability of the molecule. 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 eigenvalues of HOMO and LUMO and their energy gap reflect the chemical activity of the molecule. A greater HOMO–LUMO energy gap has been taken as an indication of a high stability of the title molecule [20].

The highest occupied molecular orbital (HOMO) of Pro/β-CD complex and the lowest unoccupied molecular orbital (LUMO) are shown in Fig. 3. The HOMO and LUMO orbitals are localized on both host and guest molecules signifying that mutual interactions are established between Pro and β-CD. (See Fig. 4.)

The HOMO–LUMO energy gap $\Delta(HOMO\text{–}LUMO)$ of the A complex is predicted to be −7.03 eV which is greater than the B complex by 1.52 eV in water (0.32 eV in vacuum) for the B3LYP/3-21G^{+}).calculation.

The calculated complexation energy for Pro/β-CD for A and B complexes with and without solvent are mentioned in Table 1. The complexation energies in vacuum were found equal to −24.03 kcal/mol for A model and to −23.80 kcal/mol for B model; corresponding to a difference between the two models equal to 0.23 kcal/mol. Generally, the complex with more negative complexation energy is considered the most favored one (A complex).

It is well known that generally the formation of the inclusion complexes involving β-CD takes place in aqueous solution; so, the binding behavior of β-CD and Pro in solution seems to be more important than their in vacuum. For this, we undertook B3LYP/3-21G^{+} calculations in solutions in order to examine the influence of the salvation effect on the complexation energy, deformation energy and dipole moments of the inclusion complexes. The results of calculations listed in Table 1 confirm those obtained in vacuum and the energy difference in H_2O between the two models is 3.07 kcal/mol in favor of A complex. The computed deformation energies given in Table 1 indicate that β-CD is more deformed (>19 kcal/mol) in the two models during the inclusion process allowing the guest molecule to accommodate easily. Thus, the guest molecule needs only about 3 kcal/mol to adopt inside the β-CD cavity for A and B complexes. These results are confirmed with calculation carried out in vacuum.

Compared the dipole moment of the two complexes in vacuum, we can obtain that the dipole moment of B complex is 8 Debye smaller than

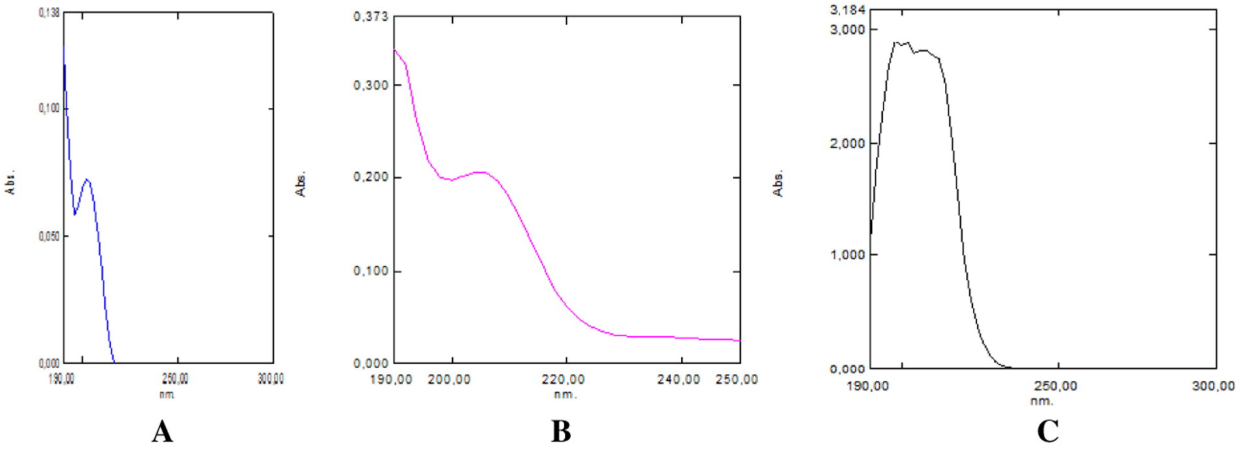
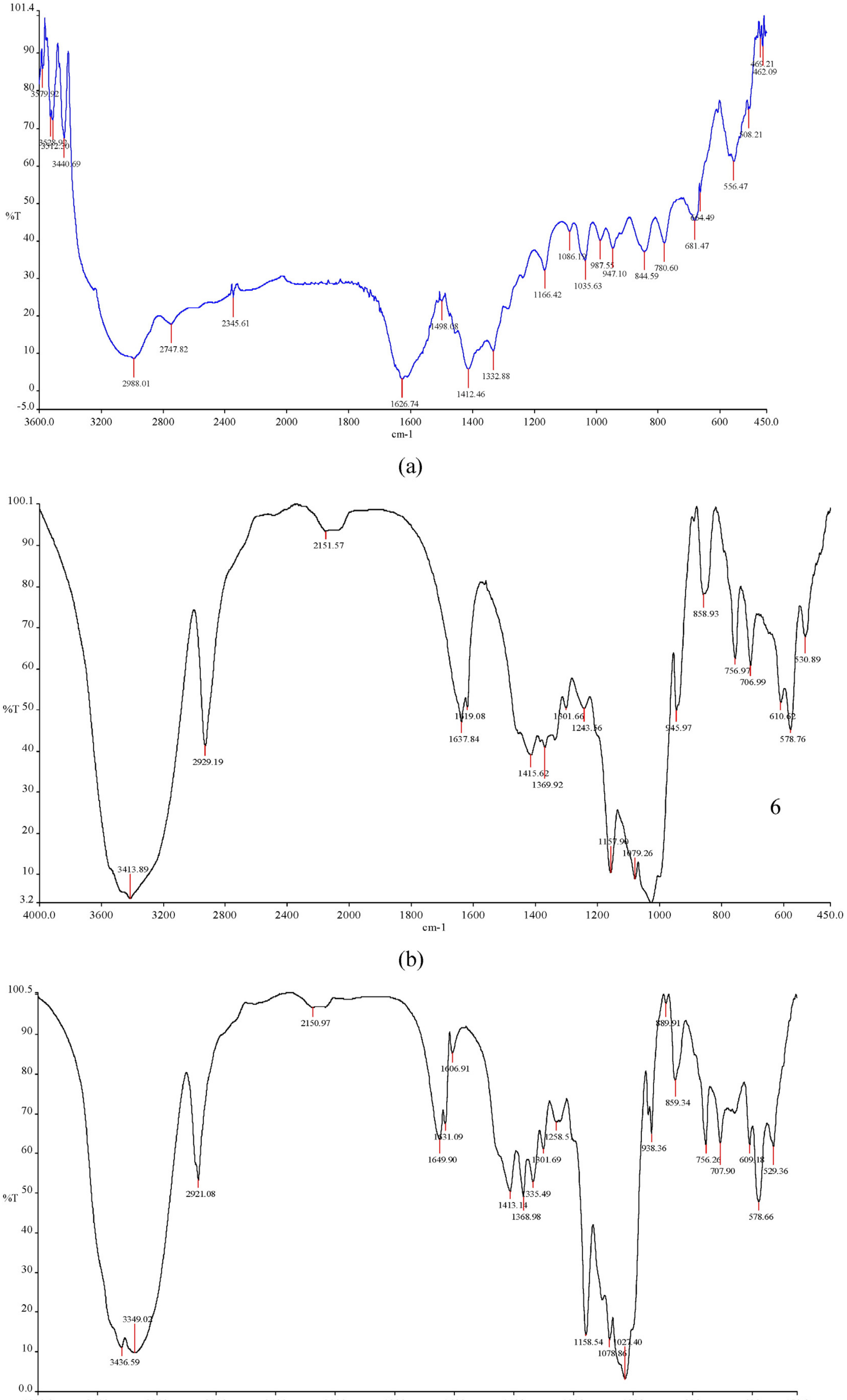


Fig. 1. Absorption spectra of (a) Pro, (b) β-CD and (c)Pro/β-CD.


101.4
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80
70
60
50
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30
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10
0
-5.0
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3579.92
3528.92
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2988.01
2747.82
2345.61
1626.74
1498.08
1412.46
1332.88
1166.42
1086.19
1035.63
987.55
947.10
844.59
780.60
681.47
664.49
556.47
508.21
469.21
462.09
3600.0
3200
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2400
2000
1800
1600
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1200
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3413.89
2929.19
2151.57
1637.84
1619.08
1415.62
1369.92
1301.66
1243.56
1157.90
1079.26
945.97
858.93
756.97
706.99
610.62
578.76
530.89
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3436.59
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1649.90
1631.09
1606.91
1413.14
1368.98
1335.49
1301.69
1258.5
1158.54
1078.86
1027.40
938.36
889.91
859.34
756.26
707.90
609.18
578.66
529.36
4000.0
3600
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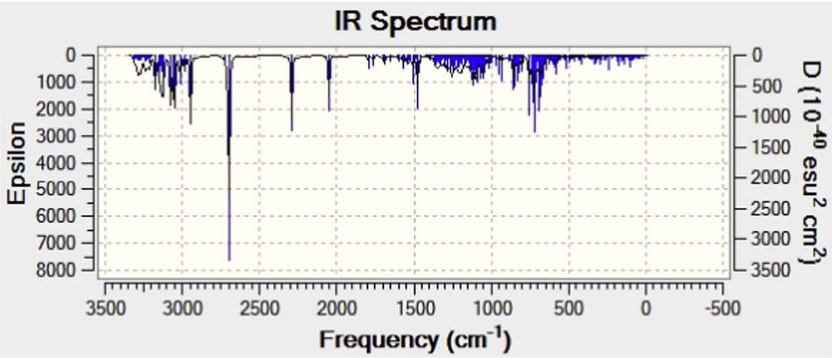
cm-1

(a)

(b)

(c)



(d)

Fig. 2. FT-IR spectra of (a) Pro (b) β-CD, (c) the inclusion complex of Pro/β-CD and (d) the calculated Pro/β-CD inclusion complex.

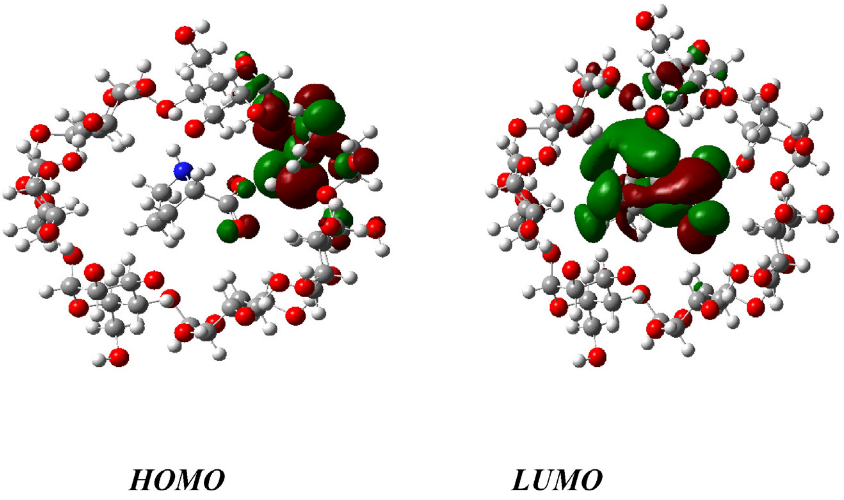


Fig. 3. Plots of molecular orbitals.

that of A complex, which means that the dipole moment of the complex have a closed relation with the polarity of the guest molecule.

3.3.2. Geometrical parameters

The optimized structural parameters (bond lengths) of the Pro molecule in a free and complexed form (Table 2) have been obtained by using the B3LYP/3-21G$^+$).level of theory.

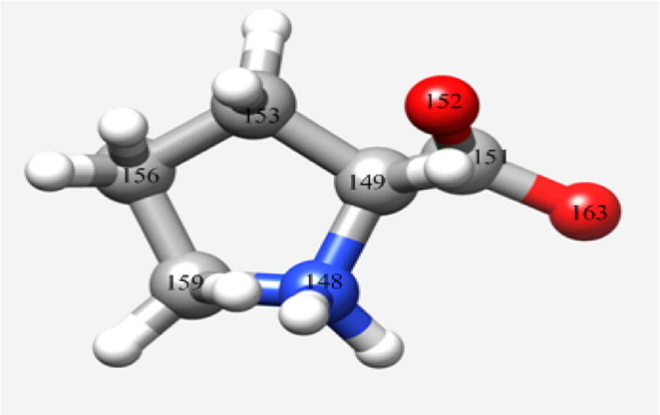


Fig. 4. Molecular structure and atomic numbering of Pro.

As shown in Table 2, the calculated bond distances of Pro guest are little changed upon complexation into β-CD cavity. The important modification has occurred in the COO$^-$ group of Pro. Thus is explained by the formation of intermolecular H-bond between the two oxygen's of COO$^-$ and the hydrogen's of hydroxyl groups of β-CD (See NBO section).

Comparing the calculated bond distances of free Pro with the experimental results we can found that the deviation is comprised between 0.004 and 0.118 Å. This divergence may be due to the fact that the calculations are performed for the isolated molecules (vacuum) while the experimental parameters are recorded in solid phase.

Table 1
Energies of the studied complexes (B3LYP/3-21G$^+$).

	In vacuum		In water	
	A complex	B complex	A complex	B complex
ΔE (kcal/mol)	−24.03	−23.80	−14.87	−11.80
HOMO (eV)	−6.84	−6.49	−6.39	−5.73
LUMO (eV)	−0.36	−0.33	0.64	−0.22
Δ(HOMO–LUMO) (eV)	−6.48	−6.16	−7.03	−5.51
DEF (Pro) (kcal/mol)	1.77	3.68	3.08	3.82
DEF (β-CD) (kcal/mol)	29.33	19.25	32.06	−22.85
μ (Debye)	12.20	4.16	14.65	6.71

Table 2
Bond distances (Å) of Pro before and after inclusion in β-CD, (B3LYP/3-21G$^+$ calculation).

	Free Pro	Pro in A complex	Pro in B complex	Experimental [7]
N_{148}–C_{149}	1.469	1.537	1.474	1.490
N_{148}–C_{159}	1.506	1.538	1.514	1.510
C_{149}–C_{151}	1.523	1.581	1.525	1.536
C_{149}–C_{153}	1.556	1.521	1.555	–
C_{156}–C_{159}	1.553	1.557	1.568	–
C_{156}–C_{153}	1.549	1.554	1.550	–
C_{151}–O_{152}	1.228	1.246	1.259	1.238
C_{151}–O_{163}	1.391	1.315	1.344	1.273

Table 3
Main calculated transitions for Pro/β-CD inclusion complex (B3LYP/3-21G$^+$).

		E (eV)	*f*	Configuration	Main attribution
Complex 1	Band 1	5.466	0.0005	H → L (13.02%)	Pro/β-CD
				H → L+4 (32.18%)	Pro/β-CD
	Band 2	6.197	0.0018	H-5 → L(7.52%)	Pro/β-CD
				H-5 → L+4 (15.68%)	Pro/β-CD
	Band 3	6.298	0.0038	H → L (66.60%)	Pro/β-CD
				H → L+2 (8.11%)	Pro/β-CD
Complex 2	Band 1	4.1806	0.0032	H → L (98.91%)	Pro/β-CD
	Band 2	5.3236	0.0017	H → L+1 (74.26%)	Pro/β-CD
	Band 3	5.4408	0.0019	H → L+1 (9.57%)	Pro/β-CD
				H → L+5 (43.16%)	Pro/β-CD
				H → L+8 (10.07%)	Pro/β-CD

3.3.3. Electronic properties

The TD-DFT method is able to detect accurate absorption wavelengths at a relatively small computing time which correspond to vertical electronic transitions computed on the ground state geometry, especially in the study of solvent effect for vertical excitation energy of electronic spectra [21,22]. To investigate the nature of electronic transitions, the electronic spectra of the studied complexes were calculated using the time-dependent density functional theory.TD-DFT approach at the B3LYP/3-21G$^+$ level on the basis of fully optimized ground-state structure. Calculations are performed in water at PCM model.

The calculated energies of excited states with oscillator strength are collected in Table 3.

From Table 3, the TD-DFT absorption spectrum (Fig. 5) of A complex shows three bands at 226.82, 200.06 and 196.84 nm assigned to H → L+4, H-5 → L+4 and H → L transitions respectively. The transition H → L is comparable to experimental results (198 nm).

The calculated UV–Vis spectrum of B complex (Fig. 6) reveals also three absorption bands at 296.57, 232.90 and 227.88 nm with transitions assignment to H → L, H → L+1 and H → L+5. The compositions of the occupied and virtual MOs are very useful to assign the character of each electronic transition. It can be seen from (Fig. 3) that H and L orbitals are localized on β-CD guest and Pro respectively. The contribution of frontier molecular orbitals indicates clearly that a charge transfer has occurred between host and guest compounds in the studied complex.

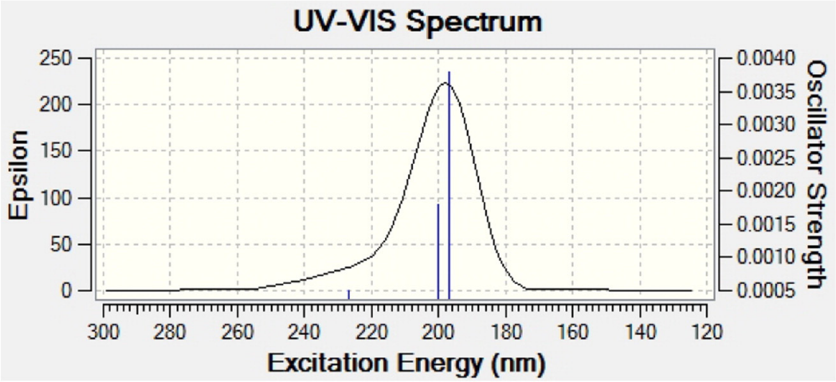


Fig. 5. TD-DFT calculated absorption spectra of Pro/β-CD A complex.

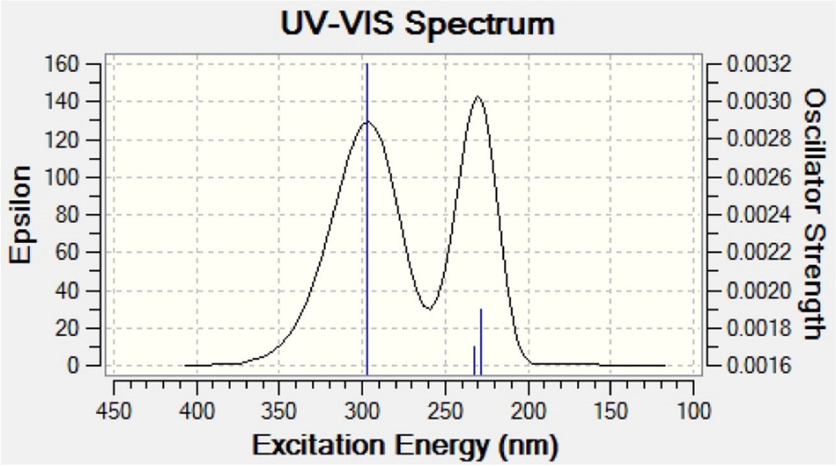


Fig. 6. TD-DFT calculated absorption spectra of Pro/β-CD B complex.

Table 4
Donor–acceptor interactions and stabilization energies $E^{(2)}$ (kcal/mol) in vacuum.

Donor	Acceptor	$E^{(2)}$ (kcal/mol) B3LYP/3-21G^{+}
Pro/β-CD (A complex)		
β-CD proton donor and Pro proton acceptor		
LP (1) O55	σ* C149–H150	2.58
LP (1) O6	σ* N148–H162	5.89
LP (2) O56	σ* N148–H162	13.17
Pro proton donor and β-CD proton acceptor		
LP (2) O152	σ* C29–H109	1.15
LP (1) O164	σ* O63–H137	17.78
LP (2) O164	σ* O63–H137	1.37
LP (2) O164	σ* C23–H102	1.17
Pro/β-CD (B complex)		
β-CD proton donor and Pro proton acceptor		
σ O63–H135	σ* O163–H164	4.80
LP (1) O63	σ* O163–H164	2.45
LP (2) O63	σ* O163–H164	51.54
LP (1) O75	σ* C159–H161	1.78
LP (1) O76	σ* N148–H162	5.01
Pro proton donor and β-CD proton acceptor		
LP (1) N148	C35–H116	4.95
LP (1) O152	σ* C17–H95	2.05
LP (1) O152	σ* O63–H135	6.60
LP (2) O152	σ* O63–H135	23.31
LP (1) O163	σ* C29–H109	1.29
LP (2) O163	σ* C23–H102	1.36
σ O163–H164	σ* O63–H135	1.07

3.3.4. NBO analysis

The NBO analysis was performed by B3LYP/3-21G^{+} level of theory in vacuum at the optimized geometries. The Table 4 illustrate only the interactions with stabilization $E^{(2)} \geq 1$ kcal/mol.

As can be seen from Table 4 for A complex, the following occupied orbitals of β-CD: LP (1) O55 and LP (1) O56 plays an important role to donate proton to vacant orbitals σ* C149–H150, σ* N148–H162 respectively of Pro molecule.

When Pro acts as proton donation the following orbitals: LP (2) O152 and LP (1) O163 participate to proton donation to: σ* C29–H109, σ* O63–H137 and σ* C23–H102.

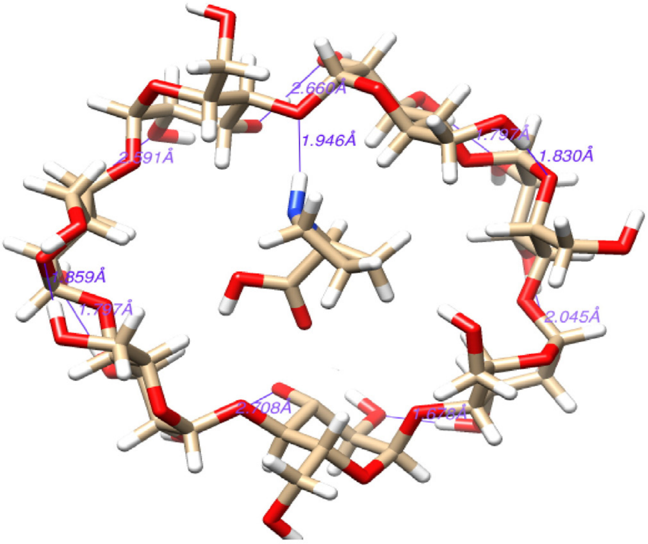
In the case of B complex, the occupied orbitals of β-CD donate proton to unoccupied orbital of Pro with stabilization energies comprised between 1.78 and 51.54 kcal/mol. In the other hand, the unoccupied orbitals of β-CD accept proton from Pro with stabilization energies ranges of 1.07 and 23.31 kcal/mol. Additionally, the formation of intramolecular H-bond was observed between O152 of Pro and H135 with stabilization energy equal to 23.31 kcal/mol.

3.3.5. Structure

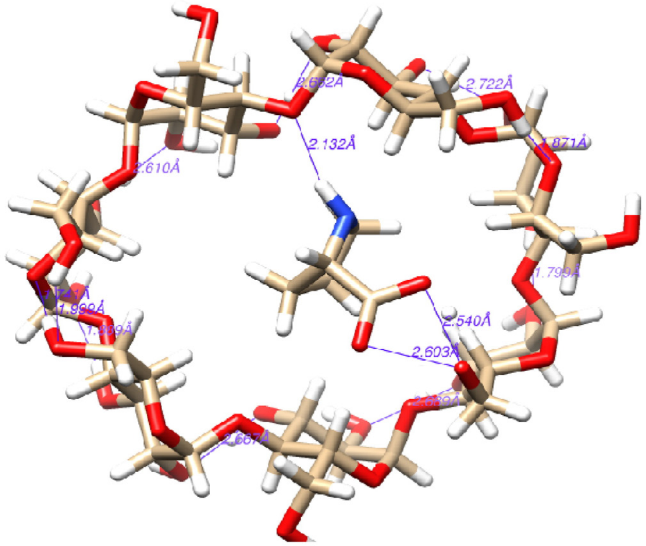
The structures of A and B complexes obtained with B3LYP/3-21G^{+} optimization are shown in Fig. 7. For both complex, the Pro is totally encapsulated in β-CD cavity; in A complex, Pro guest is included in β-CD cavity and COO^{-} group is pointed to the external portal (primary hydroxyl). While in B complex the COO^{-} group is oriented to secondary hydroxyl.

The structural analysis of the studied complexes shows the presence of stronger inter conventional H-bond formed between Pro and β-CD host molecule. For inter H-bond in A complex, this is formed between H162 (NH) and O56(interglucosidic oxygen of β-CD) at 1.946 Å.

In the case of B complex, three H-bonds were established: the first H-bond with a length of 2.132 Å was formed between H162 (NH) and O76 of β-CD. The second was formed between O152 (COOH) and H135 of primary OH of β-CD positioned at 2.540 Å and the third H-bond with a length of 2.603 Å was formed between O163 (COO^{-}) and H135 of β-CD.



A complex



B complex

Fig. 7. Geometric structures of Pro/β-CD complexes optimized by B3LYP/3-21G^{+}.

4. Conclusion

In this paper we report theoretical results of B3LYP/3-21G^{+} calculation and experimental FTIR and UV–visible spectra of the inclusion complexes formed between Pro and β-CD. The results showed that the studied complex is stables and Pro guest is totally included into β-CD cavity. Electronic excitation given by TD-DFT and NBO calculation clearly demonstrates that a charge transfer has occurred between Pro and β-CD molecules.

Acknowledgments

This study was supported by the Algerian Ministry of Higher Education and Scientific Research and General Direction of Scientific Research as a part of projects CNEPRU.

References

[1] K.A. Cannors, The stability of cyclodextrin complexes in aqueous solutions, Chem. Rev. 97 (1997) 1326–1357.

[2] J. Szejtli, Chem. Rev. 98 (1998) 1743, http://dx.doi.org/10.1021/cr970022c.

[3] H. Dodziuk, Cyclodextrins and their Complexes: Chemistry, Analytical Methods, Applications, Wiley, Weinheim, 2006.

[4] K.J. Siebert, The effect of beer pH on colloidal stability and stabilization — a review and recent findings, Tech. Q. Master Brew. Assoc. Am. 47 (2010) 1–5.

[5] K.P. Sharad, Advances in the chemistry of proline and its derivatives: an excellent amino acid with versatile applications in asymmetric synthesis, Tetrahedron Asymmetry 22 (2011) 1817–1847.

[6] A. Antony M P, G.S. Suresh K, F. Madi, S. Sorimuthu, M. Sundar R, Encapsulation of phenylalanine and 3,4 dihydroxyphenylalanine into β-cyclodextrin: spectral and molecular modeling studies, J. Mol. Struct. 1079 (2015) 370–382.

[7] F. Madi, D.E. Khatmi, N. Dhaoui, A. Bouzitouna, M. Abdaoui, A. Boucekkine, Molecular model of CENS piperidine β-CD inclusion complex: DFT study, C. R. Chim. 12 (2009) 1305–1312.

[8] F. Madi, L. Largate, L. Nouar, D. Khatmi, Theoretical study of the inclusion processes of ethyl p-hydroxybenzoate with β-cyclodextrin: PM3MM and ONIOM2 calculations, J. Taiwan Inst. Chem. Eng. 43 (2012) 868–872.

[9] A. Farcas, A. Fifere, I. Stoica, F. Farcas, A. Resmerita, Thermal analysis and theoretical study of α-cyclodextrin azomethine [2]-rotaxane formation by semi-empirical method PM3, Chem. Phys. Lett. 514 (2011) 74–78.

[10] M. Sunnie, P. Maren, B. Mu-Hyun, D. Clemmer, DL-Proline, Acta Crystallogr. C, ISSN 0108-2701.

[11] Y. Sheena Mary, L. Ushakumarib, B. Harikumarc, H. Tresa Varghesed, C. Yohannan Panicker, FT-IR, FT-Raman and SERS spectra of L-proline, J. Iran. Chem. Soc. 6 (2009) 138–144.

[12] L. Kegang, H. Daniel, W. Wolf-D, Aldol reactions in water using a β-cyclodextrin-binding proline derivative, Synlett 14 (2007) 2298–2300.

[13] L. Yu, H. Bao-Hang, L. Bin, Z. Yi-Min, Z. Peng, C. Yun-Ti, W. Takehiko, I. Yoshihisa, Molecular recognition study on supramolecular system. Synthesis of modified cyclodextrins and their inclusion complexation thermodynamics with L-tryptophan and some naphthalene derivatives, J. Org. Chem. 63 (1998) 1444–1454.

[14] R. Periasamy, S. Kothainayaki, R. Rajamohan, K. Sivakumar, Carbohydr. Polym. 114 (2014) 558e566.

[15] Hypercube, Inc., USA, Hyperchem, Release 7.51 for windows 2002, Hypercube, Inc., 2002

[16] B. Ferenc, H. Antonio, M. Hans, B. Ioan, Structure and vibrational spectroscopy of the fenbufen-β-cyclodextrin inclusion complex, Vib. Spectrosc. 69 (2013) 30–39.

[17] Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009 (GaussView v 5.0.9 Visualizer and Builder).

[18] K. Srinivasan, T. Stalin, Studies on inclusion complexes of 2,4-dinitrophenol, 2,4-dinitroaniline, 2,6-dinitroaniline and 2,4-dinitrobenzoic acid incorporated with β-cyclodextrin used for a novel UV absorber for ballpoint pen ink, J. Incl. Phenom. Macrocycl. Chem. 78 (2014) 337–350.

[19] S.J. Khouri, I.A. Abdel-Rahim, E.M. Shamaileh, A thermodynamic study ofα-, β-, and δ-cyclodextrin-complexed m-methyl red in alkaline solutions, J. Incl. Phenom. Macrocycl. Chem. 77 (2013) 105–112.

[20] G. Mariappan, N. Sundaraganesan, Spectral and structural studies of the anti-cancer drug flutamide by density functional theoretical method, Spectrochim. Acta A 117 (2014) 604–613.

[21] M. Shukla, N. Srivastava, S. Saha, Investigation of ground state charge transfer complex between paracetamol and p-chloranil through DFT and UV–visible studies, J. Mol. Struct. 1021 (2012) 153–157.

[22] O.R. Shehab, A.M. Mansour, Charge transfer complexes of arylaminomethyl-1H-benzimidazole with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone: experimental and DFT studies, J. Mol. Struct. 1047 (2013) 121–135.