Spectrochimica Acta Part A 75 (2010) 32–36

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

Spectroscopic studies of inclusion complex of β-cyclodextrin and benzidine diammonium dipicrate

H. Hamdi, R. Abderrahim*, F. Meganem

Laboratory of Organic Synthesis, Department of Chemistry, Faculty of Science of Bizerte, 7021 Jarzouna, Bizerte, Tunisie

ARTICLE INFO

Article history:
Received 11 March 2009
Received in revised form 13 August 2009
Accepted 12 September 2009

Keywords:
β-Cyclodextrin
Benzidine diammonium
Dipicrate
Inclusion complex

ABSTRACT

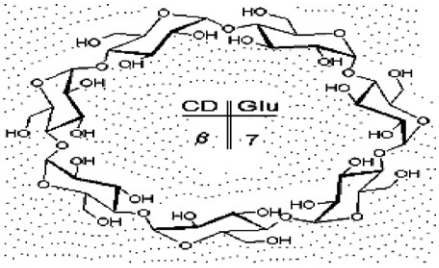
Formation of inclusion complex between benzidine diammonium dipicrate and β-cyclodextrin with stoichiometry 1:2 (guest–host) has been established by UV, ^{1}H NMR, ^{13}C NMR, IR spectra and powder X-ray diffractometry. ^{1}H NMR studies are used to confirm the inclusion and to provide information on the geometry of dipicrate inside the cavity of β-cyclodextrin.

1. Introduction

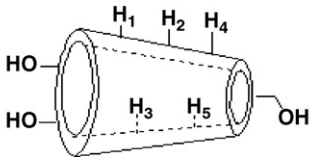
The supramolecular chemistry is that discipline of chemistry which involves all intermolecular interactions where covalent bonds are not established between the interacting species. The majority of these interactions are of the host–guest type. Among the majority of host, the cyclodextrin seemS to be the most important host to form inclusion complexes especially with wide variety of guest molecules with suitable polarity and dimension [1,2].

The cyclodextrins are cyclic oligosaccharides (A) obtained from simple enzymatic degradation. The most important structural feature of these compounds is the hydrophobic internal cavity and hydrophilic external surfaces (B) [3]. The inclusion complex between the cyclodextrin host and the guest is determined by several weak forces, including Van der Waals, hydrophobic dipole–dipole and hydrogen bonding interactions [4].

Cyclodextrins are widely used in pharmaceutical industry [5] with the aim of enhancing drug solubility in aqueous solutions, reducing toxicity and to control the rate of release.



(A)



(B)

Benzidine is often used to produce dyes. The major class of dyes are derived from benzidine and are used primarily to colour textiles, leather, and paper. However it is also one of the serious organic contaminations and it is usually difficult to treat industrial waste and living sewage. To solve the problem environmental cyclodextrin [6] can increase solubility of some contaminations, reduce their toxicity and catalyze their decomposition. On account of all the previous reasons, we report here the synthesis of benzidine diammonium dipicrate and the synthesis and spectroscopic studies of the new inclusion complex formed from dipicrate and β-cyclodextrin which makes the solubility of benzidine in water increase.

* Corresponding author. Tel.: +216 98948066.
E-mail address: Abderrahim_raoudha@yahoo.fr (R. Abderrahim).

1386-1425/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.saa.2009.09.018

2. Experimental

2.1. Apparatus

IR spectra were recorded on Perkin Elmer Paragon 1000 PC spectrometer using a sample dispersed in spectroscopically pure potassium bromide pellets. Spectra resolution was 4 cm^{-1}.

^1H NMR and ^{13}C NMR spectra were recorded with DMSO-d_6 solvent containing TMS (tetramethylsilane) on a Bruker 300 spectrometer (^1H: 300 MHz, ^{13}C: 75.47 MHz). The chemical shifts (δ) are reported in ppm relative to TMS (internal reference). For the ^1H NMR, the multiplicities of signals are indicated by the following abbreviations: s: singlet, d: doublet, t: triplet, q: quartet, m: multiple.

The powder X-ray diffraction patterns were obtained by PHILIPS PW 1729 diffractometer. The UV–visible spectrum was recorded in the range 200–400 nm with an UV JENWAY 6405 spectra photometer equipped with a stoppered quartz cell with 1.0 cm optical path length.

DSC–TGA analysis was performed using TA DSC-TGA SDT-2960 instrument in flowing N_2 with an average heating rate of 5 °C/min between room temperature and 450 °C.

2.2. Reagents

β-Cyclodextrin, picric acid, benzidine-3,3′-diamine were obtained from Aldrich Chemical Co. Other chemical reagents of analytical reagent grade were used as commercial.

2.3. Synthesis of benzidine diammonium dipicrate

10^{-4} mol (0.0229 g) of picric acid was dissolved in diethyl ether and 5×10^{-5} mol (0.0092 g) of benzidine-diamine dissolved in diethyl ether was slowly dropped into β-CD–diethyl ether solution with sufficient stirring. The stirring operation was kept for at least 24 h at room temperature. At the end of the reaction, a great deal of yellow crystal precipitate, the dipicrate was obtained by filtration. The product was washed with dichloro methane for three times. The product obtained was confirmed by powder X-ray diffractometry, ^1H NMR, ^{13}C NMR, IR and UV spectra.

2.4. Synthesis of inclusion complex

0.5×10^{-3} mol (0.5675 g) of β-cyclodextrin and 0.25×10^{-3} mol (0.16 g) of benzidine diammonium dipicrate were dissolved by 30 mL distilled water and 20 mL EtOH respectively. Then benzidine diammonium dipicrate–EtOH solution was dropped into β-cyclodextrin aqueous solution with continuous stirring. The stirring operation was left for 72 h at room temperature after which it gave birth to a yellow solid product, inclusion complex of benzidine diammonium dipicrate and β-cyclodextrin (β-CD) that was obtained by filtration. The yellow precipitate was washed with ether for three times in turn, respectively to clean the residual guest and host monomers. Then it was dried in vacuum oven at 40 °C for 48 h (yield = 80%). Elemental analysis: % C: 42.43; % H: 5.23; % N: 3.67.

The structure of inclusion complex was confirmed by powder X-ray diffractometry UV absorption, IR, ^1H NMR, ^{13}C NMR spectra.

3. Results and discussion

3.1. X-ray powder diffraction

The formation of the inclusion complex was confirmed by X-ray diffractometry [7]. Fig. 1 refers to the powder X-ray pattern of dipicrate, β-cyclodextrin monomer, inclusion compound and physical mixture in molar ratio 1:2 (guest:host). The powder X-ray pattern of the inclusion compound shown in Fig. 1 was different from that of dipicrate and β-cyclodextrin monomer. The difference between the spectra of dipicrate, the β-cyclodextrin and the spectra of inclusion compound is due to the interactions of β-cyclodextrin with dipicrate and produces a new structure.

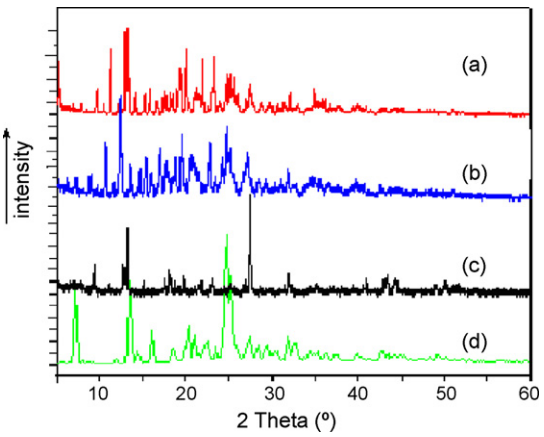


Fig. 1. Powder X-ray diffractometry of (a) physical mixture in molar ratio 1:2 (guest:host), (b) inclusion compound, (c) β-cyclodextrin and (d) dipicrate.

3.2. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

The thermogravimetric analysis and differential scanning calorimetry of β-cyclodextrin, physical mixture in molar ratio 1:2 (guest:host) and inclusion compound are shown in Fig. 2.

Thermogravimetric analysis has mainly been applied to demonstrate the different behaviour of an inclusion compound relative to its physical mixture of component compound [8].

Thermogravimetric analysis of inclusion compound shows a weight loss at 250 °C. The weight loss should correspond to the beginning of the degradation of the complex.

DSC analysis further supports the formation of a dipicrate: β-CD inclusion compound. A comparison of the TGA and DSC (Fig. 2) traces of the complex, the physical mixture and β-CD showed significant differences. The difference between them confirms the formation of the complex. The melting point was determined by TGA trace and are listed in Table 1.

Table 1
Melting point of dipicrate, β-cyclodextrin and inclusion compound.

	Peak	Melting point (°C)
Benzidine diammonium dipicrate	Exothermic	253.6
β-Cyclodextrin	Endothermic	300
Inclusion complex (β-cyclodextrin/dipicrate)	Endothermic	239

Table 2
Absorption spectral data of dipicrate and inclusion complex.

	λ_{max} (nm)	A	ε (L mol cm^{-1})
Benzidine	280	0.812	27,066
Diammonium dipicrate	355	0.978	32,600
Complex	288	0.377	12,566
(β-Cyclodextrin/dipicrate)	363	0.433	14,433

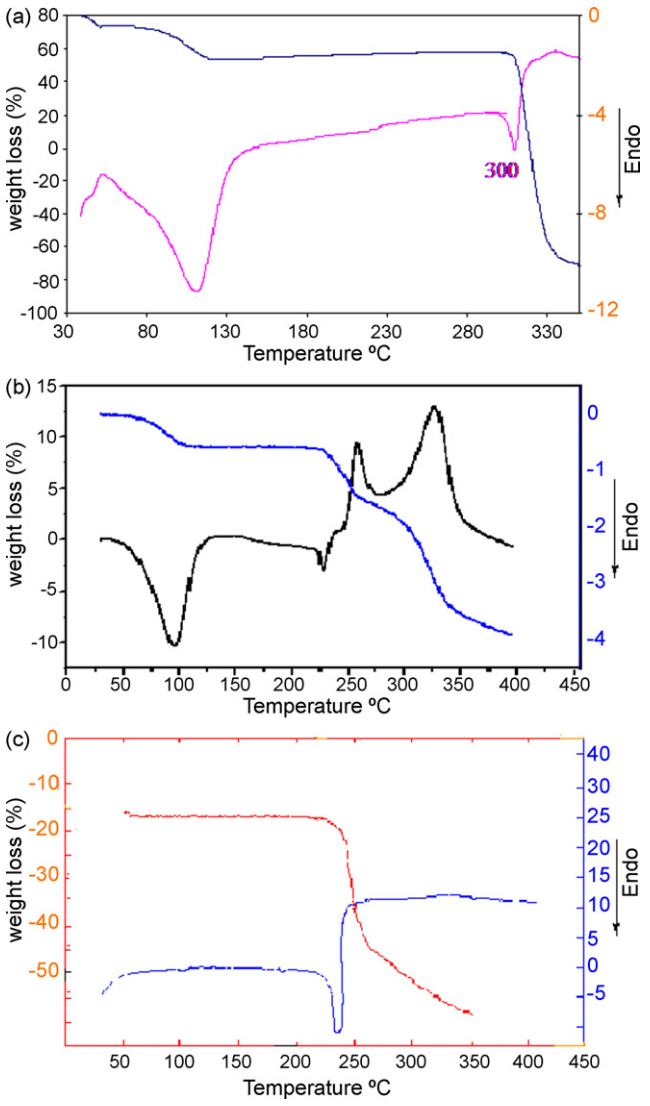


Fig. 2. Thermogravimetric analysis and differential scanning calorimetry thermograms of (a) β-cyclodextrin, (b) physical mixture in molar ratio 1:2 and (c) inclusion compound.

3.3. Absorption spectra

Absorption spectral data of dipicrate and inclusion complex in the mixture of water and ethanol (60/40, v/v) ($C = 3 \times 10^{-5}$ M) are listed in Table 2.

Fig. 3 shows the absorption spectra of dipicrate and inclusion complex. We establish that the absorption peaks of dipicrate at 280 and 355 nm were slightly shifted to longer wavelengths. This finding indicates the formation of dipicrate–β-CD inclusion complex.

The concentration of dipicrate and β-CD in the filtrate was determined by UV spectroscopy. The UV spectrum of the filtrate in the mixture of water/ethanol (60/40, v/v) and in the $C = 3 \times 10^{-5}$ M was shown to be nearly identical with the UV spectrum of the inclusion complex, then we can suggest that the solution still contains dipicrate and β-CD with 1:2 molar ratio (guest:host).

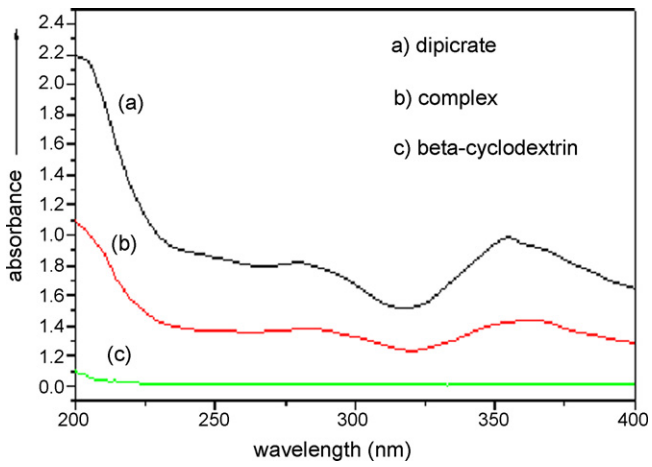


Fig. 3. Absorption spectra of (a) dipicrate, (b) inclusion complex and (c) β-CD.

3.4. Infrared spectral studies

In comparison with dipcrate, the $^{+}NH_3$ stretching vibrations were in the region (3040, 3240 and 3400 cm^{-1}) and symmetrical/asymmetrical $^{+}NH_3$ vibrations (2450, 2600 cm^{-1}) are largely affected in the inclusion compound 3318 and 2922 cm^{-1}, respectively. The symmetrical/asymmetrical NO_2 (1300, 1500 cm^{-1}) are also affected by the complexation (1330, 1490 cm^{-1}).

The C=C bending vibration of aromatic (1450, 1500, and 1600 cm^{-1}) is also blue shifted to 1433, 1490, 1555 cm^{-1}, respectively.

In comparison with β-CD, the C–O vibration of primary and secondary alcohol were in the region (1100, 1050 cm^{-1}) respectively these are largely affected in the complex (1080, 1029 cm^{-1}).

The intensity diminishing in the inclusion compound FTIR spectrum can prove the inclusion because the inclusion complex between the cyclodextrin host and the guest causes the change of the microenvironment of the guest, host and the formation of hydrogen bonding between the heteroatom of the guest and the primary hydroxyl group at the edge of the β-CD cavity. These reasons induce a decrease of the value of the absorption of stretching and bending vibration modes of different groups such as C–O (alcohol), $^{+}NH_3$, C=C, NO_2 group.

All the frequencies of different group were affected by the complexation. This finding indicates that dipicrate is included in the β-CD cavity.

3.5. ^{1}H NMR spectrum

The ^{1}H NMR has proved to be a useful tool in the study of cyclodextrin inclusion complex [9–11]. Direct evidence for the formation of dipicrate and the inclusion complex can be obtained by ^{1}H NMR and ^{13}C NMR spectra. The information gained from NMR spectroscopy relies on the observation of selective line broadening and/or chemical shift of displacement of ^{1}H NMR spectral signals

Table 3
Chemical shifts δ and $\Delta\delta$ of protons of β-cyclodextrin in free host, dipicrate in free guest and inclusion complex.

	H_2	H_4	H_3	H_5 and H_{6ab}	H_1	H_i	H_e	H_p
δ (β-Cyclodextrin)	3.299	3.281	3.608	3.420	4.811			
Dipicrate						7.380	7.740	8.610
δ(Dipicrate–β-cyclodextrin)	3.291	3.279	3.543	3.340	4.803	7.240	7.670	8.572
$\Delta\delta$	−0.008	−0.003	−0.065	−0.080	−0.008	−0.140	−0.070	−0.038

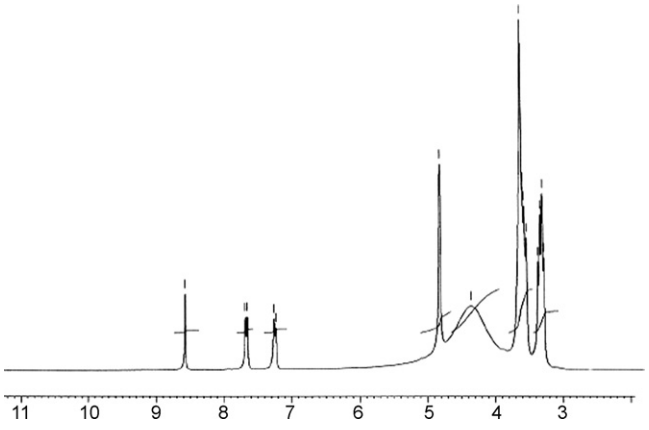


Fig. 4. ^{1}H NMR spectra in DMSO-d_6 of the inclusion complex (dipicrate–β-CD).

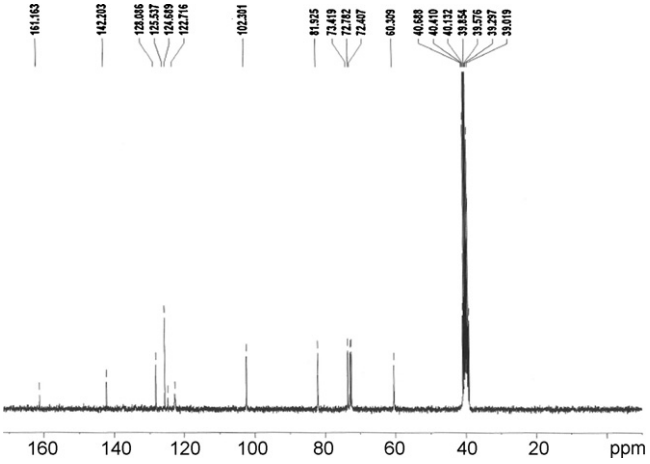


Fig. 5. ^{13}C NMR spectra in DMSO-d_6 of the inclusion complex.

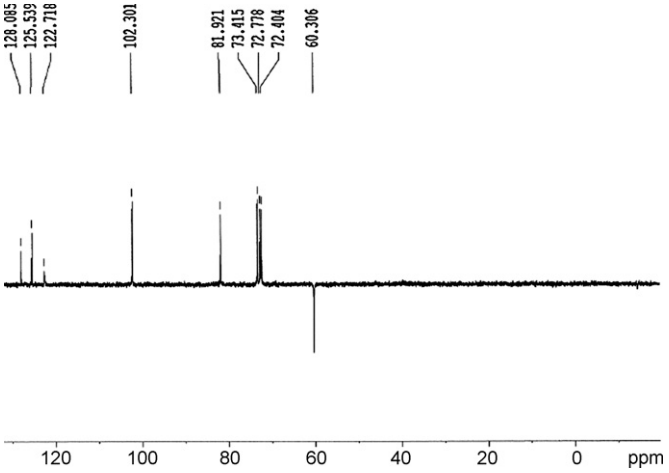


Fig. 6. ^{13}C NMR spectra in DMSO-d_6 of the inclusion complex (Dept 135).

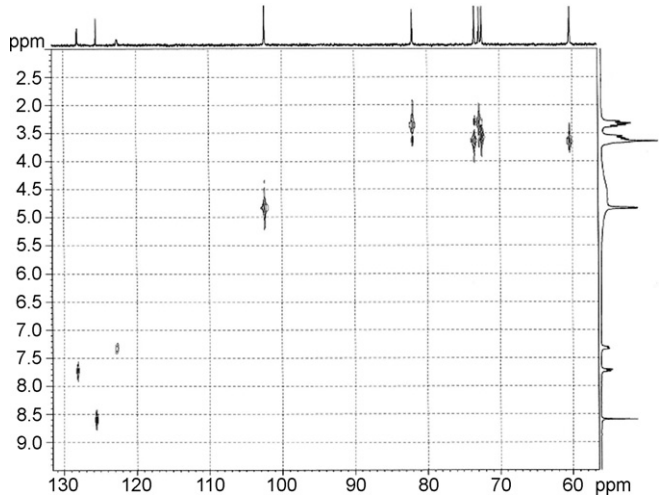


Fig. 7. ^{13}C NMR spectra of correlation ^{1}H–^{13}C.

of the guest and host protons [9–11]. It is well known that H_5 and H_3 protons are located in the interior of the β-cyclodextrin's cavity, and it is, therefore, likely that the inclusion of dipicrate with β-CD will affect the chemical shifts of theses two protons [12,13].

The significant distinction between the ^{1}H NMR spectra of dipicrate, β-CD and the inclusion complex of dipicrate with β-CD in DMSO-d_6 (Fig. 4) confirm that the inclusion complex was formed. The value of chemical shifts for different protons in β-CD, dipicrate and dipicrate–β-CD inclusion complex was listed in Table 3.

The complexation causes an upfield shift of β-CD protons; a great upfield was recorded for H_5 and H_3. (Table 4) However, the variation of the shift is not the same for all protons. H_3 signal shows an upfield shift of about 0.065 ppm. Since H_3 is located in the interior of the cavity, we suggest that H_5 signal shows approximately similar amount of upfield shift because both are located inside the cavity and will suffer similar amount of shielding. The upfield shift observed for H_5 and H_3 confirms the inclusion inside the cavity. However, an exact value of the shift was hard to be determined due to the complication in the spectrum upfield on inclusion. Further confirmation was obtained by observing the changes in the chemical shifts of dipicrate.

The ^{1}H NMR spectrum of dipicrate in DMSO-d_6 has revealed that dipicrate has four types of protons: the H_i doublet at δ 7.38, the H_e appears as a doublet at δ 7.74; the H_p signal appears as singlet at δ 8.61 and the H_a ($^{+}NH_3$) at 3.5.

The phenyl ring of dipicrate made the signals of protons (H_3 and H_5) upfield shift. Whereas the chemical shifts of H_1, H_2, H_4 and H_{6ab}, which are on the outer surface of β-CD, were only slightly affected by the guest molecule, the chemical shifts of H_i, H_e, H_p of dipicrate was affected by the complexation.

The ^{1}H NMR spectrum of an inclusion complex between dipicrate and β-CD has revealed a broad signal attributed to the protons of OH of the water molecules within the β-CD cavity

Table 4
Chemical shifts δ of carbons in β-CD in free host, dipicrate in free host and inclusion complex.

	C_1	C_2	C_3	C_4	C_5	C_6
δ (β-CD) in free host	101.91	71.93	72.34	81.52	72.94	59.87
δ (β-CD) in the complex	102,30	72.78	72.40	81,92	73.42	60
	$C(H_i)$	$C(H_p)$	$C(H_e)$	$C(NO_2)$	$C(H_{ii})$	$C(^{+}NH_3)$
δ (Dipicrate) in free guest	122.50	125.43	127.90	160.88	124.33	141.90
δ (Dipicrate) in the complex	122.70	125.50	128.00	161.10	124.60	142,20

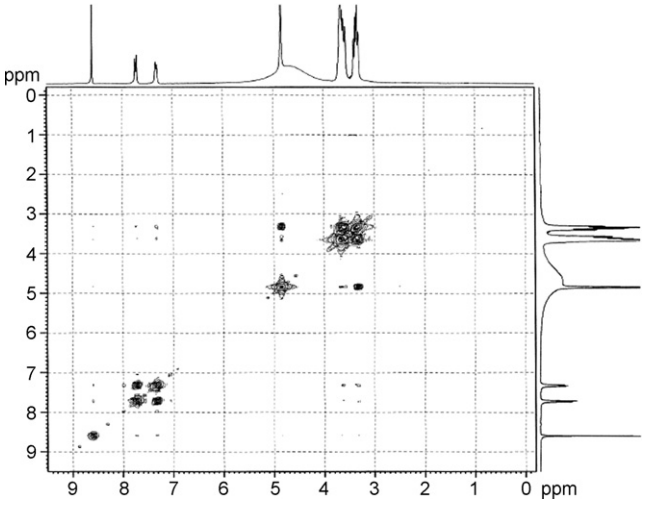


Fig. 8. ^{1}H–^{1}H NOE spectra of the inclusion complex dipicrate–β-CD.

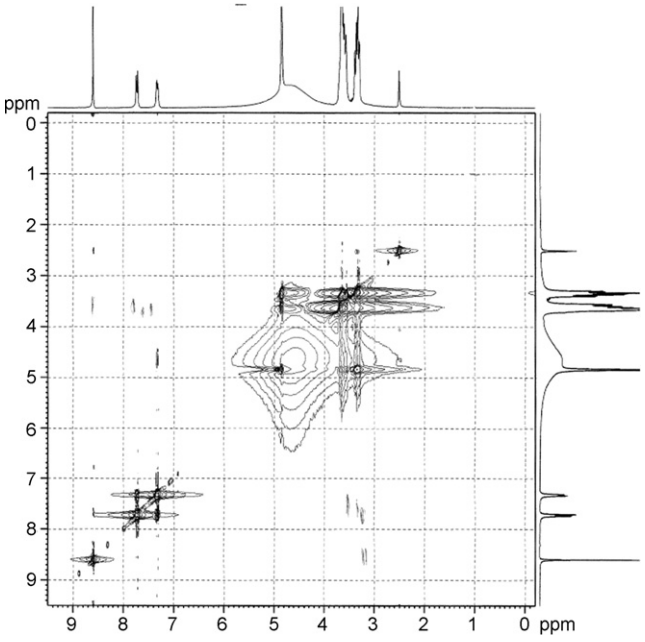


Fig. 9. ^{1}H–^{1}H COSY spectra of the inclusion complex dipicrate–β-CD.

3.6. ^{13}C NMR spectrum

The ^{13}C NMR spectra with proton decoupling, the spectra of dept 135 and the spectrum of correlation ^{1}H–^{13}C (Fig. 7) were used for attributing the different types of carbons. The ^{13}C NMR spectrum of inclusion complex in DMSO-d_6 consists of 12 types of carbons, six types of β-CD: C_1–C_6 and six types of dipicrate ($C(H_i)$, $C(H_p)$, $C(H_e)$, $C(NO_2)$, $C(H_{ii})$, $C(^{+}NH_3)$) (Fig. 5).

The chemical shift of the carbon (C6 methylene) was obtained by the ^{13}C spectra dept 135 (Fig. 6) and the chemical shift for different types of carbons in dipicrate were obtained by the ^{13}C spectrum (Fig. 5) and these assignments were confirmed by the spectra of correlation ^{1}H–^{13}C (Fig. 7, NMR 2D).

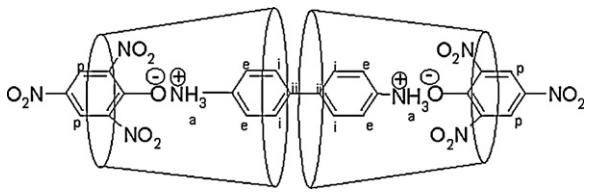


Fig. 10. Approach of an incoming cyclodextrin molecules to benzidine diammonium dipicrate molecule.

4. Stoichiometry of the inclusion complex

The stoichiometry of the complex of dipicrate with β-CD at 25 °C was determined by ^{1}H NMR, ^{1}H–^{1}H NMR NOE (Figs. 8 and 9) or by using UV–vis spectroscopy.

The ratio of dipicrate to β-CD in inclusion complex can be determined by the peak area of proton of dipicrate and β-CD in inclusion complex respectively. The integrated intensities of H_4 in β-CD resonance and the dipicrate H_i resonance are approximately 14 and 4 respectively. These values confirm that the ratio of dipicrate to β-CD in inclusion complex is 1:2.

The NOE experiments were particularly useful for the determination of structural arrangements of molecular complexes.

Figs. 8 and 9 showed ^{1}H–^{1}H NMR NOE (NOESY) and ^{1}H–^{1}H NMR COSY spectra in DMSO-d_6. It can be seen from these spectrums, that the presence of the correlation between the H_i of dipicrate with the H_3 and H_5 of β-CD, with strong intensity suggested that the dipicrate completely entered into two hydrophobic cavities of two β-CDs (Fig. 10).

The chemical shifts of H_i, H_p, H_e located in the hydrophobic cavity of β-CD were also significantly affected by the protons H_3 and H_5 of the host molecule because of the intermolecular interaction (formation of hydrogen bonding) between dipicrate and β-CD. From these results, we can suggest that the ratio of dipicrate ion to β-CD in inclusion complex is 1:2 (guest:host).

Acknowledgement

Authors thank the Secretary of State for Scientific Research and Technology (UR-05/12) for the financial support of this work, code.

References

[1] K.A. Connors, Chem. Rev. 97 (1997) 1335–1357.
[2] J. Szejtli, Chem. Rev. 98 (1998) 1743–1753.
[3] J. Szejtli, Akademiai Kiado: Budapest, 1982.
[4] Y. Inoue, T. Hakushi, Y. Liu, L.H. Tong, B. Shen, D.S. Jin, J. Am. Chem. Soc. 115 (1993) 475–481.
[5] D. Duchene, D. Wouessidjewe, Drug Dev. Ind. Pharm. 16 (1990) 175–182.
[6] T.B. Boving, M.L. Brusseau, J. Contam. Hydrol. 42 (2000) 5167.
[7] T. Pralhad, K. Rajendrakumar, J. Pharm. Biomed. Anal. 34 (2004) 333–339.
[8] C. Von Plessing Rossel, J.S. Carreno, M. Rodriguez-Baeza, J.B. Alderete, Quim Nova. 23 (2000) 749–752.
[9] A.A. Abdel-shafi, Spectrochim, Acta Part A 57 (2001) 1819.
[10] H. Scheneider, J. Hacket, F.V. Rudiger, Chem. Rev. 98 (1998) 1755.
[11] A. Mucci, L.M.A. Vadelli, F. Forni, P. Ventura, G. Salvioli, J. Chem. Soc., Perkin Trans. 2 (1996) 2347.
[12] H. Gunther, La spectroscopie de RAM, Masson, Paris, 1993.
[13] D. Duchene, C. Vaution, F. Glomot, STR Pharma. 1 (4) (1985) 323–332.