

**A Continuous Spectroscopic Investigation of Polyaromatic Hydrocarbons
(Acenaphthylene and Acenaphthene) and a Biological π Acceptor (Folic acid)**

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Centre of Chemistry Research, Ministry of Science and Technology, Jadriyia, Baghdad, Iraq

Abstract

The complexation between folic acid and typical polyaromatic hydrocarbons (Acenaphthylene and Acenaphthene) was studied by using FTIR and UV spectra with pH changing. The experiments confirmed that combination was through π - π donor-acceptor interaction and inducing the protonation process in folic acid upon strengthening electron accepting ability of the acid so the changing of their charge distribution and the surroundings became necessarily. In another words, this inferred that not only biotransformation process of folic acid, but also the toxicity of polyaromatic hydrocarbons could be more understood.

Keywords: Folic acid, Acenaphthylene, Acenaphthene, Spectroscopic studies

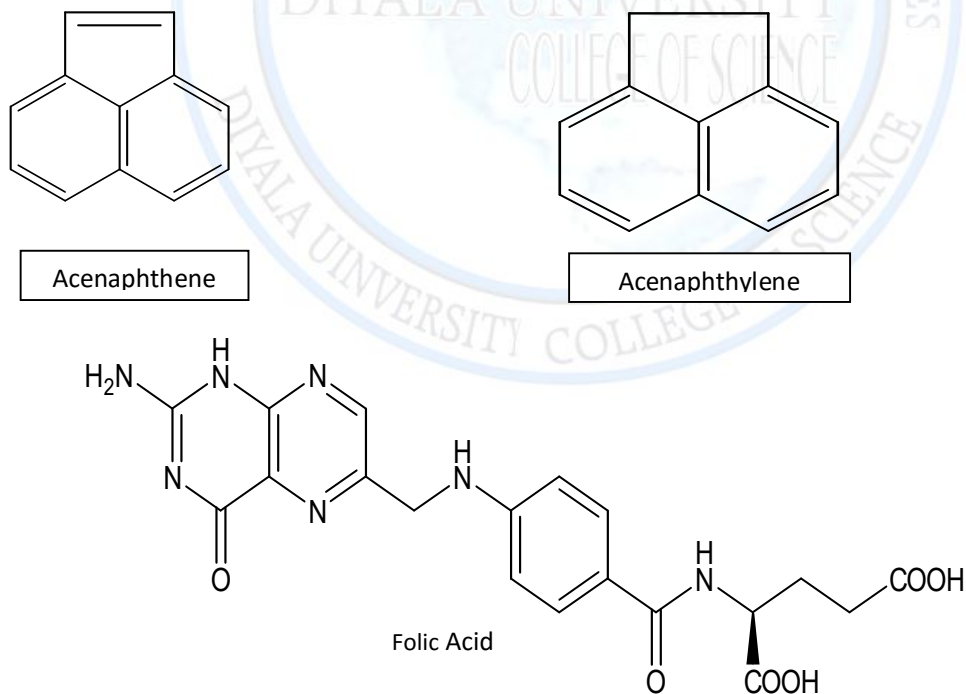
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Introduction

Folic acid (See scheme -1-), (N- [4-[[[2-Amino-1,4-dihydro-4-oxo-6-pteridiny] methyl] amino] benzoyl] -L-glutamic acid), hematopoietic vitamin presents, free or combined with one or more additional molecules of L(+) glutamic acid, in liver, kidney, mushrooms, spinach, green leaves, and grasses [1]. Folic acid (Scheme -1-), which plays as a key in one-carbon metabolism, is essential for biosynthesis of several compounds. The pterin ring changed by reductase enzyme to tetrahydrofolate which receives one carbon fragments from donors (monocarbonic units) such as serine, glycine, and histidine then transfers them to intermediates in the synthesis of amino acids, purines, thymine, and pyrimidine found in DNA [2,3].

Polyaromatic hydrocarbons are a group of organic compounds consisting of two or more fused benzene rings. They are priority pollutants in many industrial areas and occur in living organisms at significant concentrations near these sites [4].



Scheme -1-: Structures of Folic acid, Acenaphthene, and Acenaphthylene.

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The natural levels of ultraviolet radiation in sunlight enhance the toxicity of polyaromatic hydrocarbons in aquatic animals [5] and aquatic plants [6] which results from oxidation to more toxic form [7], photosensitization reaction [8], or combination of both of them [9]. Polyaromatic hydrocarbons toxicity and transformation have been demonstrated [10, 11]. For example, benzo[α]pyrene is converted in the liver to an epoxy diol that can induce mutation leading to the uncontrolled growth of certain cells [12,13,14].

As an experimental model phenanthrene (π donor) with o- phenanthroline or pyridine (humic π acceptor) that forms π - π complex give a primary explanation of the dependence of the environmental transformation of polyaromatic hydrocarbons on the surrounding [15]. Recently, Y. He et al reported that these process of polyaromatic hydrocarbons are strongly depended on the on the interaction between polyaromatic hydrocarbons and the coexisting compounds [16].

The aim of this paper is to study the complexation between folic acid and two typical polyaromatic hydrocarbons (Acenaphthylene and Acenaphthene) (Scheme -1-) by using FTIR and UV spectroscopies and compared the obtained results with recent studies.

Experimental section [16]

Materials: *(All materials were from BDH Chemicals Ltd Poole, England)*

0.01 g Acenaphthylene (or Acenaphthene) was dissolved in 100 mL methanol, and the supernatant liquid was taken out as Acenaphthylene (or Acenaphthene) saturated solution. 0.01g folic acid in 100 mL 1:1 methanol/water (v: v). Also HCl, NaOH were used for pH adjustment.

Experimental methods

FTIR spectroscopy:

Microscopic FTIR-spectra of the complex formed between folic acid and Acenaphthylene (or Acenaphthene) as well as the spectra of folic acid and Acenaphthylene (or Acenaphthene)

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were recorded at FTIR spectrophotometer (IR Prestige - 21, Shimadzu, Japan) after packed with potassium bromide at room temperature. Solid folic acid and Acenaphthylene (or Acenaphthene) were used directly to obtain microscopic FTIR spectra, while the samples of complex were prepared by mixing the appropriate quantity of folic acid with Acenaphthylene (or Acenaphthene).

UV absorption spectroscopy:

UV absorption spectra were recorded as follows: seven of 5.0×10^{-5} mol l⁻¹ folic acid working solutions in 1:1 methanol/water (v:v) were respectively adjusted to pH 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0 with HCl and NaOH, which were tagged as group I.

Then 50 μ l Acenaphthylene (or Acenaphthene) saturated solutions were respectively added into each 10ml of the solutions from group I, which was tagged as group II. Acenaphthylene (or Acenaphthene) solution of the same concentration without folic acid were used as spectra control. The UV absorption spectra of the test solutions were recorded using a UV-Vis spectrophotometer (UV-1650 PC, Shimadzu, Japan) against a solvent blank (for group I) or Acenaphthylene (or Acenaphthene) blank (for group II).

Results and Discussion

FTIR spectroscopy is an appropriate technique to understand the functionalization of organic compound reactions. The FTIR spectrum of pure folic acid is characterized by number of bands. According to J. Zhang et al [17], the bands between (3600-3000) are due to hydroxyl stretching and NH- stretching vibrations. The C=O bond stretching vibration of carboxyl group appears at 1967 cm⁻¹ and 1636 cm⁻¹ belongs to C=O bond stretching vibration of -CONH₂ group and the band at 1604 cm⁻¹ relates to the bending mode of NH- vibration and at 1419 cm⁻¹ corresponds to OH deformation band of phenyl skeleton.

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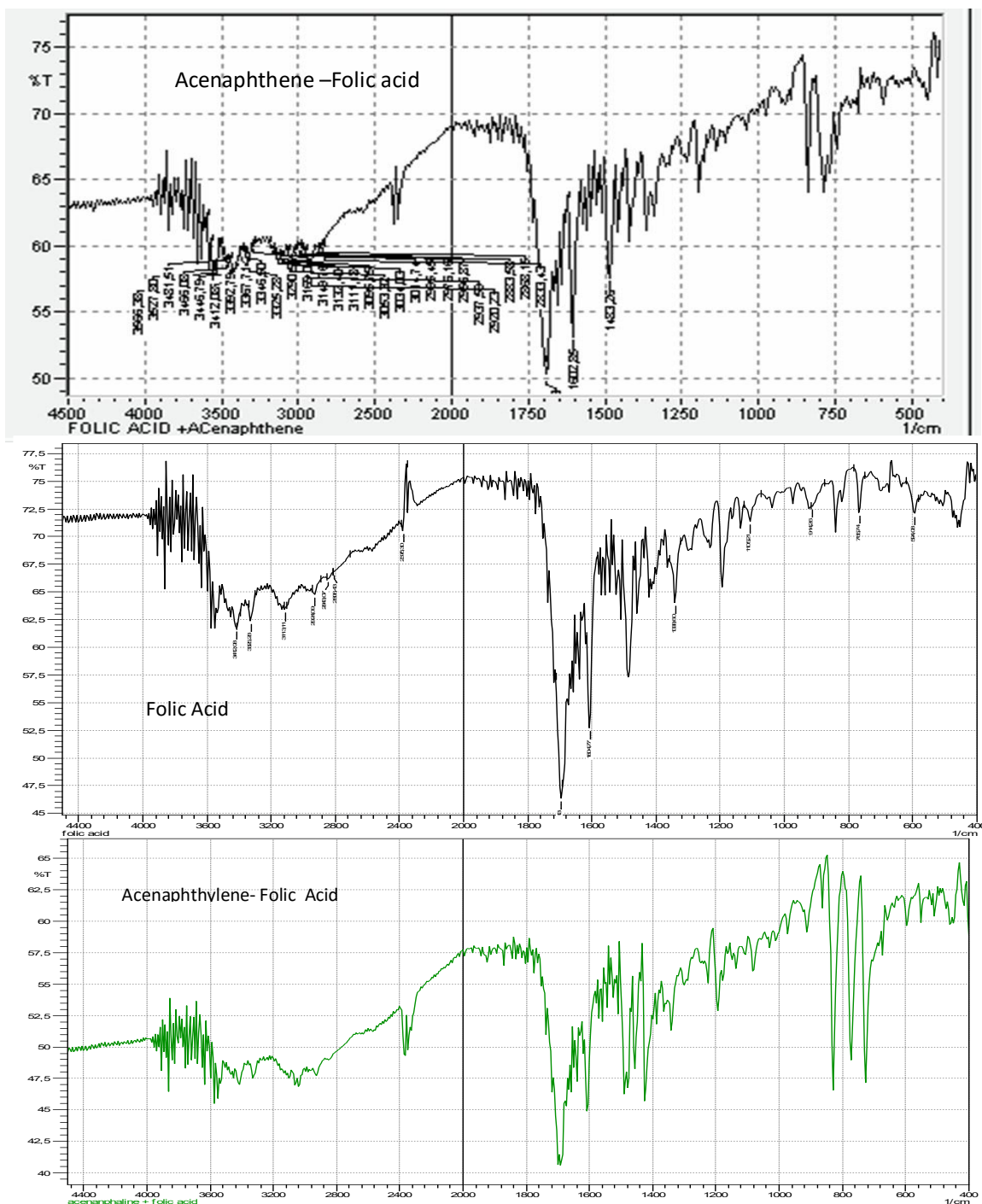


Figure -1-: IR spectra of folic acid and acenaphthene (or Acenaphthylene) before and after interaction.

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New absorption band appears at 2381 cm^{-1} for folic acid coexisting with Acenaphthylene and 2372 cm^{-1} with Acenaphthene which demonstrates that the N atom on the pterin ring is protonated to produce positive salt. The shift of IR band around 1500 cm^{-1} confirms the interaction between the folic acid and Acenaphthylene (or Acenaphthene) to produce a complex of $\pi - \pi$ electron donor – acceptor (See Fig. (1)).

The above IR bands confirm our previous works which show IR bands at 2376 cm^{-1} for Naphthalene- Folic acid complex and 2401 cm^{-1} for Fluorene – Folic acid complex [15].

For more studying of this interaction, UV spectra show that folic acid has a strong absorb around 283 nm during pH 3-8 for $\pi - \pi^*$ transition of pterin ring which is remaining unchanged because the pKa values of the pterin ring are 2.4 for $\text{NH}_2 - \text{C} = \text{N}$ group and 8.1 for $\text{O} = \text{C} - \text{N}$ group [20]. [See figures(2,3)]

Absorption band of Acenaphthylene and Acenaphthene (265 nm) assigned to $\pi - \pi^*$ transition of this conjugated system are not interfered by pH.

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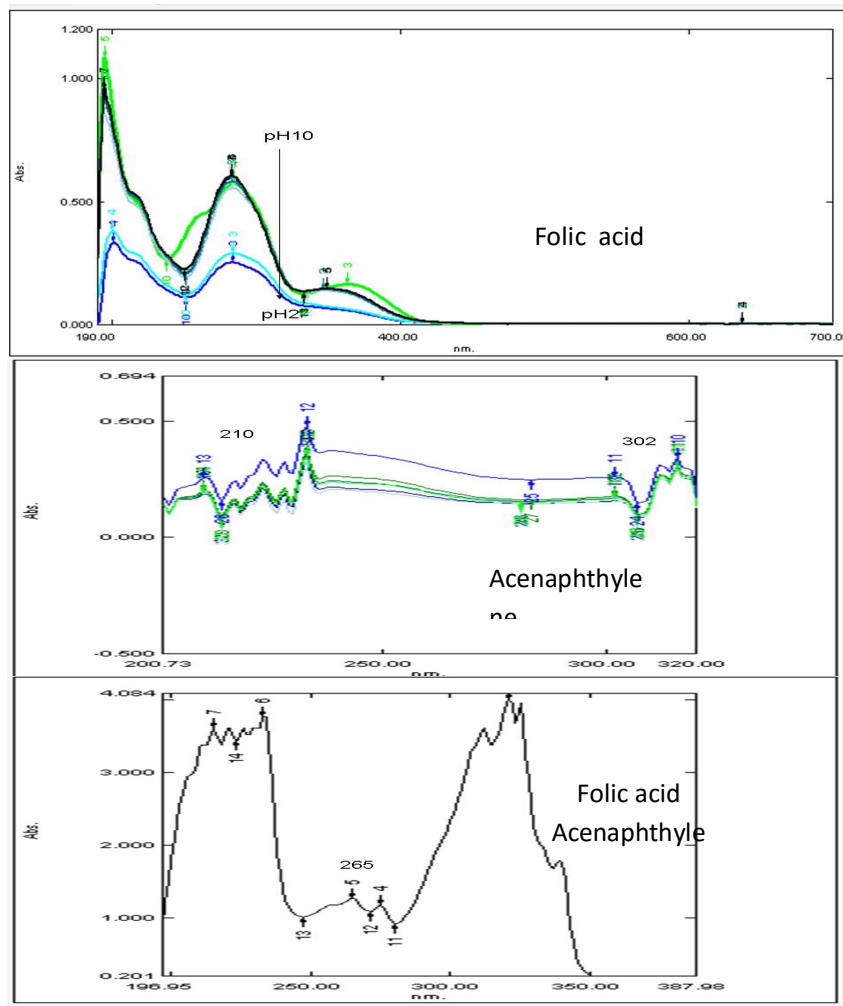


Figure -2-: UV spectra of folic acid and its complexes with Acenaphthylene.

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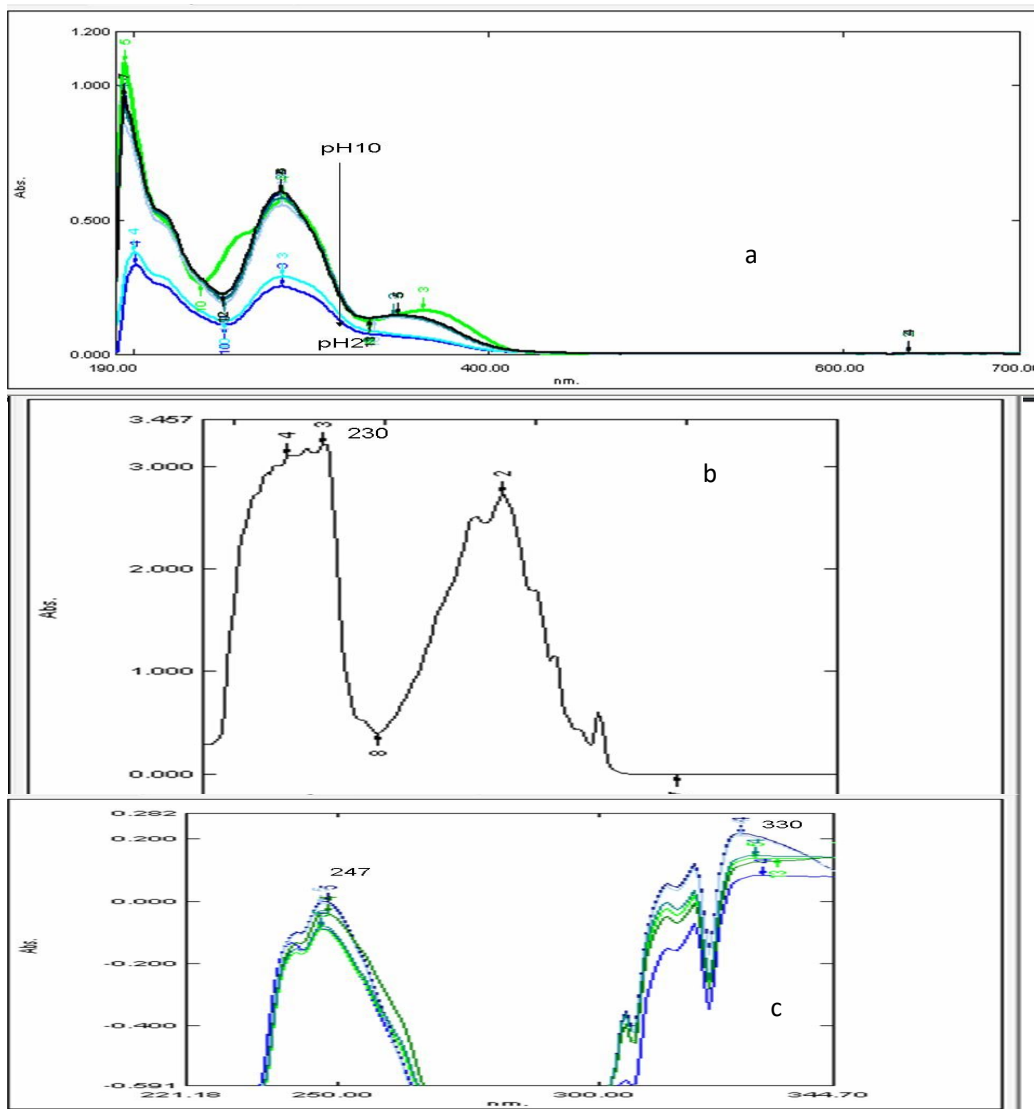


Figure -3-: UV absorption spectra of Folic acid (a), Acenaphthene (b), and their mixture (c).

The evidence of π - π complexation between folic acid and this polyaromatic hydrocarbon was the appearance of new bands due to disturb of the complexation on π - π^* transition of conjugated π system so the accepting ability of proton increases.

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These new bands were (210,302) nm for Folic acid – Acenaphthylene complex and (247, 330) nm for Folic acid – Acenaphthene complex which are in the same range for Naphthalene –Folic acid complex (235, 296) nm and Fluorene- Folic acid complex (217,278) nm [15].

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**استقصاء طيفي تكميلي لمركبات هيدروكربونية متعددة الحلقات (الاسينفثالين والاسينفثين) ومستقبل
 π البايولوجي (حامض الفوليك)**

كفاء خلف حمود، احمد جميل خلف، فارس نوفل عبد الرحمن، عبد اللطيف محمد رؤوف، عبود حيون مصلح، رياض
رحيم نعمه، دريد عيسى زناد
مركز بحوث الكيمياء، وزارة العلوم والتكنولوجيا، الجادرية، بغداد، العراق

الخلاصة

تم دراسة التفاعل الحاصل بين حامض الفوليك ومركبات هيدروكربونية متعددة الحلقات (الاسينفثالين والاسينفثين) في أوساط متعددة الأس الهيدروجيني باستخدام تقنيتي طيف الأشعة فوق البنفسجية وطيف الأشعة فوق البنفسجية وطيف الأشعة تحت الحمراء. بينت التجارب عن وجود تأثير من نوع π - π (واهب - مستلم) بينمركب العطري الحلقي وحامض الفوليك وحدث تغيير في قدرة الحامض في تقبل الالكترونات وتوزيع الشحنة. وكننتيجة طبيعة ارتباطها بالمركبات المحيطة بها. إن الاختلاف الناتج قد يؤدي ليس فقط تغير الوظيفة الحياتية لحامض الفوليك في الخلية الحية وإنما فهم أوسع لسمية المركبات العطرية متعددة الحلقات.

الكلمات المفتاحية: حامض الفوليك, اسنفثالين, اسينفثين, دراسات طيفية.