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^1H - NMR STUDY OF SOME SUBSTITUTED OXONAPHTHO - (2,1 - g) - 1,3 - OXAZOCINE DERIVATIVES

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ABSTRACT

^1H - n.m.r. study of the five, 2-methyl-3,13- dialkyl-4-oxo-5-(substituted)-5,6-di (H)-naphtho- (2,1-g)-1,3-oxazocine derivatives mentioned in this publication was the target of the present work, which has been successively achieved. The anisotropic effect of the C=O group, in the acetyl or poropionate group attached to C_5, upon its neighbouring protons was easily observed, specially upon protons $H_{(C)}$ & $H_{(\alpha)}$ attached to C_5 & C_6 of the heterocyclic ring, respectively. The deshielding effect of the aromatic -π- electrons in the p-(N-tolyl- carboxamido) group attached to C_5 upon the surrounding protons was also observed. Moreover, the protons of the bridged methylene group, linked between C_2 & C_6 in the heterocyclic ring, showed an AB - system due to the geminal coupling between the methylene protons itself and also due to the spin - spin vicinal

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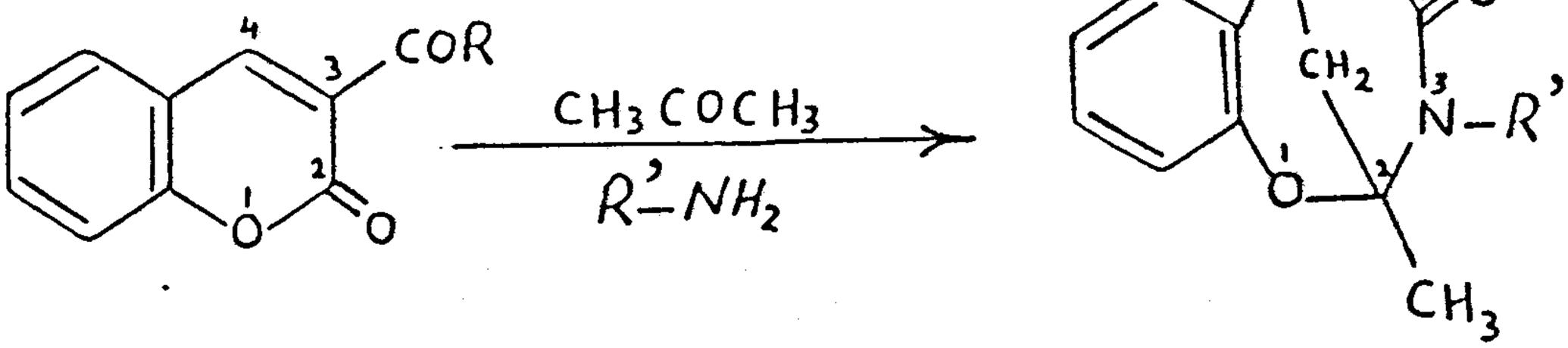
coupling between the methylene and the methine protons $H_{(\alpha)}$.

INTRODUCTION

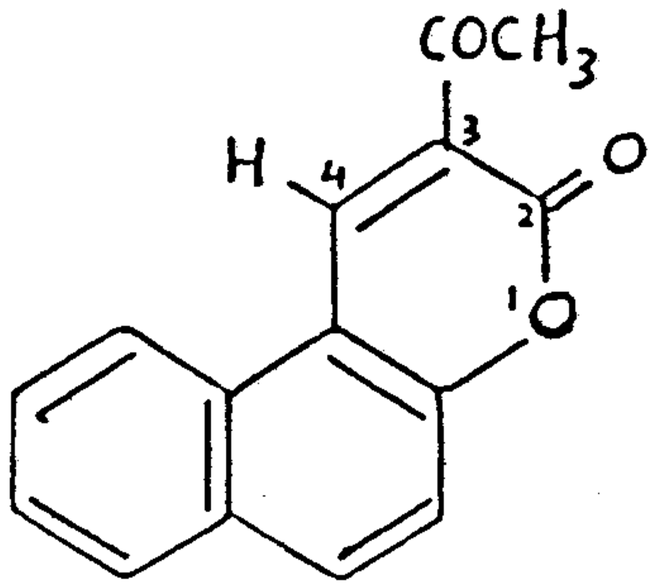
5- Substituted -1,3 - benzoxazocine derivatives were reported in the literature [1,2] to be prepared from the reaction of 3-substituted coumarin with acetone and primary amines.



3-substituted coumarin. 5-substituted-1,3-benzoxazocine.

(R = OH or CH_3& R^7 = CH_3, C_2H_5, ..)

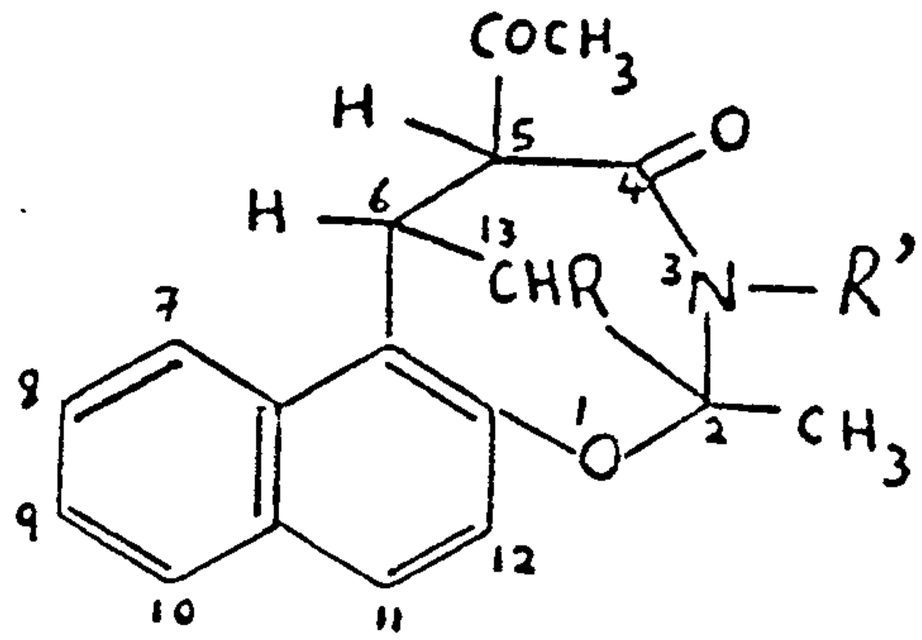
It was stated [5] that C_3 -C_4 olefinic double bond in the oxonaphtho (2,1-b)-pyran can be activated by conjugation with an acetyl group to give the following structure.



3-acetyl-4-(H)-oxonaphtho-(2,1-b)-pyran

This type of structure showed a great affinity towards

various active methylene compounds [4] (such as ketones) in the presence of ammonium acetate or methyl amine to give the corresponding 5-substituted- naphtho-(2,1-g) -1,3- oxazocine, depending on the type of the ketone used. For example, 2- methyl -3,13 - dialkyl - 4-oxo-5-aceto-5,6-dihydro-naphtho-(2,1-g)-1,3-oxazocine was prepared using the previous procedure [5].



This type of reaction was rationalized [3] as a Michael addition of the ketone to the substituted oxonaphthopyran compound. In general, substituted oxonaphtho -1,3- oxazocine compounds can be considered as derivatives from the substituted oxonaphtho-pyran compounds and their published n.m.r. data are not satisfactory.

MATERIAL & METHODS

The general procedure reported by koelsch and his co-worker [3] was used to prerare 2-methyl-dialkyl-4-oxo-5-

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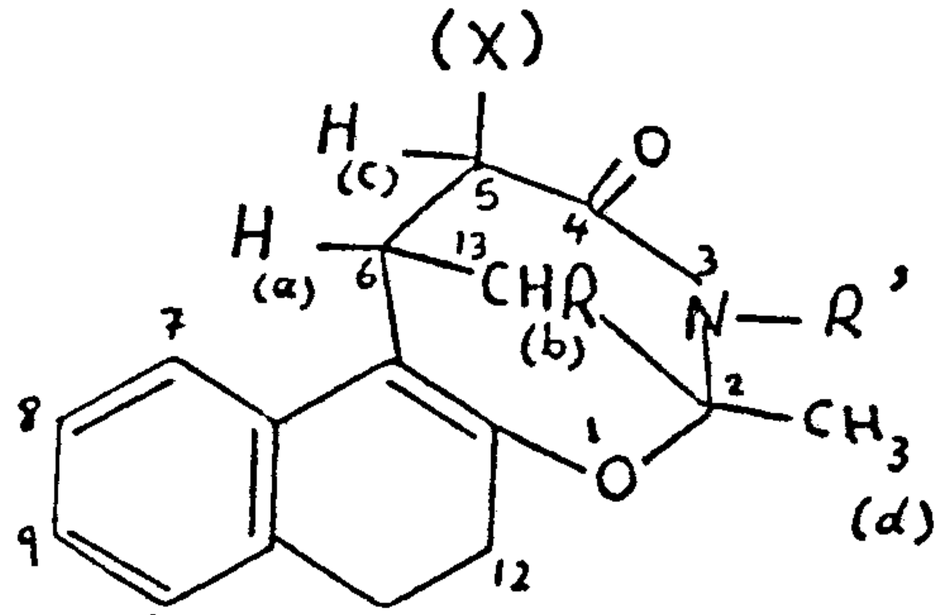
aceto-5,6 dihydro-naphtho-(2,1-g)-1,3-oxazocine and 2-methyl- 3,13-dialkyl-4- oxo-5-propiono -5,6-dihydro- naphtho-(2,1 -g)- 1,3-oxazocine. Moreover, 2-methyl-3,13- dialkyl-4- oxo-5-(p-N-tolyl- carboxamido)-5,6- dihydronaphtho-(2,1-g)- 1,3- oxazocine was also prepared using the same procedure.

(X)



(I) ; x = $-COCH_3^{(e)}$, R = R' = H

(II) ; x = $-COCH_3^{(e)}$, R = H , R' = $-CH_3$

(III) ; x = $-COOCH_2^{(f)}CH_3^{(e)}$, R = R'= H

(IV) ; x = $-COOCH_2^{(f)}CH_3^{(e)}$, R = H , R' = $-CH_3$

(V) ; x = p-$CONHC_6H_4CH_3$, R = R = H

According to this procedure a solution of 3-acetyl-4(H)- oxonaphtho- (2,1-b)- pyran (0.01 mole), in the case

of compounds (I & II), or 3-propiono- 4(H)-oxonaphtho-(2,1-b)-pyran(0.01 mole), in the case of compounds (III & IV), or 3-(p-N-tolyl-carboxamido)-4(H)-oxonaphtho- (2,1-b)-pyran(0.01 mole), in the case of compound (V) in ethanol was mixed with the corresponding ketone solution (0.01 mole) and a solution of ammonium acetate or primary amine (0.02 mole). The whole mixture was treated with enough ethanol to give a homogeneous phase, left at room temperature for 3 days and then was heated on a steam-bath for one hour till it became a concentrated syrup. It was stirred with conc. HCL (10 ml.), followed by 50 ml. of H_2O and finally it was allowed to stand for several hours where the product separated out and was crystallized from ethanol.

RESULTS & DISCUSSION

Well resolved ^{1}H-n.m.r. spectra were obtained for compounds (I - V) using 60-MHz n.m.r. spectrometer (See Figs. 1-3). The n.m.r. data for each of these five sub-stituted oxonaphtho-(2,1-g)-1,3-oxazocine derivatives were treated speparately. The experimental results, elemental analysis data and the infra-red assignments of the characte-ristic groups and bonds are tabulated in Table (1). The KBr technique using Pye-Unicam Spectrophotometer 1200 and 1000 was used.

^{1}H-n.m.r. spectrum of compound (I) is very expressive

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and is illustrated in Fig. (1-A). It shows two sharp singlets at δ 1.75 and δ 2.5 ppm attributing to the methyl protons (d) and the acetyl protons (e) attached to the heterocyclic ring, respectively. Another weak singlet is observed to the down-field at δ 6.5 ppm and is assignable to the imide proton (N-H) of the ring. The two methine protons (a) and (c) appear as a confused quartet and doublet at δ 3.8 and δ 4.2 ppm respectively. The bridged methylene protons (b) show a confused quartet at about δ 2.3 ppm due to the geminal coupling of the $-CH_2-$ protons itself. This quartet became well splited showing an AB-system for the same methylene protons (b) in the case of compound (II) where its ^{1}H-n.m.r. spectrum is illustrated in Fig. (1-B). The chemical shift of this AB-quartet is 2.1, 2.27, 2.4 & 2.65 ppm with a $J_{gem.}$ = 12 Hz. The only difference between the two spectra of the two compounds (I) & (II) is the disappearance of the imide-proton weak signal (δ 6.5 ppm) observed in Fig.(1-A) and the appearance of a very sharp singlet at δ 3.1 ppm instead in the case of compound (II) attributable to the $N-CH_3$ protons, as is shown in Fig.(1-B). In general, the six aromatic protons in both cases appear as a set of confusing signals at δ (7.0-8.0) ppm.

The ^{1}H-n.m.r spectrum of compound (III) is shown in Figs (2-A) & (2-B). Fig. (2-A) shows a very sharp symmetrical triplet at δ (1.3-1.5) ppm corresponding to the methyl protons (e), while the methylene protons (f) appear as a very sharp

quartet at δ (4.13-4.53) ppm . The coupling constant values J_{fe} & J_{ef} are found to be 6.6 & 6.0 Hz , respectively. The methi protons(d) appear as a very sharp singlet at 1.8 ppm. The methine protons (a) & (c) show a singlet and a doublet at δ 3.7 and δ (3.8-4.0) ppm. respectively, The spin- spin coupling constant value between proton (a) and proton (c) is 7.0 Hz. The bridged methylene protons (b) show a spin-spin coupling between its protons and the methine proton (a) and it should appear as a doublet, but it appears as a quartet at δ (2.1-2.8) ppm giving AB-system. This more splitting into a quartet is due to the additional geminal coupling of the $-CH_2-$ protons itself, ($J_{gem.}$=15 Hz). The imide proton -NH appears as a singlet at δ 6.8 ppm It is obscured by adding a drop of D_2O to the sample solution, see Fig. (2-B). The six aromatic protons as usual give a multiplet at down-field at δ (6.9-8.0) ppm .

Similarly, ^{1}H-n.m.r. spectrum of compound (IV), c.f., Fig. (2-c) has the same signals and it looks identical to that of compound (III), c.f., Fig.(2-A). The only exception is the disappearance of the singlet at δ 6.8 ppm (for NH) and appearance of another sharp singlet instead at δ 3.0 ppm (for $N-CH_3$).

Finally, Fig.(3) shows a ^{1}H-n.m.r. spectrum of compound (V), in which two sharp singlets are observed at δ 1.77 and δ 2.3 ppm .These two singlets are attributable

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to the methyl protons(d) and the p-methyl protons of the tolyl group. However, another two weák singlets are observed at down-field, at δ 6.97 and δ 9.25 ppm .These weak signals are referring to the two imide groups of the heterocyclic ring and the carboxamido group, respectively. The bridged $-CH_2-$ protons(b) appear as a doublet at δ 1.95 ppm.Whereas , the methine proton(c) shows an asymmetrical doublet at δ (3.70-3.75) ppm . with a $J_{vic.}$ = 6 Hz. The coupling interactions of proton (a) with protons (c) and (b) appear as a quartet at δ 4.66 ppm .The crowded signals at δ (7.20 -8.0) ppm are referring to the ten aromatic protons.

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Table (1)

Compound	M.P.; (°C)	Yield; (%)	Elemental Analysis Data (Found / Calc.)			IR Assignments ; (ν , cm.$^{-1}$)
			% C	% H	% N	
(I)	245	60	73.30 / 73.22	6.00 / 5.76	4.65 / 4.75	at(1590) for δ- lactam. at(1630) for C=O of β-diketone.
(II)	200	45	74.30 / 73.80	6.60 / 6.15	4.30 / 4.53	at(2955) for CH-aliphatic.
(III)	208	80	70.40 / 70.15	5.60 / 5.85	4.20 / 4.31	at(1630) for δ-lactam. at(1700) for ester C=O at(2940-3045) for CH-aliphatic. at(3260) for -NH .
(IV)	180	65	70.25 / 70.80	6.30 / 6.19	4.40 / 4.13	at(1650) for δ-lactam. at(1730) for ester C=O at(2910-3060) for CH-aliphatic
(V)	240	60	74.15 / 74.61	5.30 / 5.70	7.10 / 7.25	at(1660) for δ-lactam. at(1710) for -CONH-group. at(3340) for -NH group.

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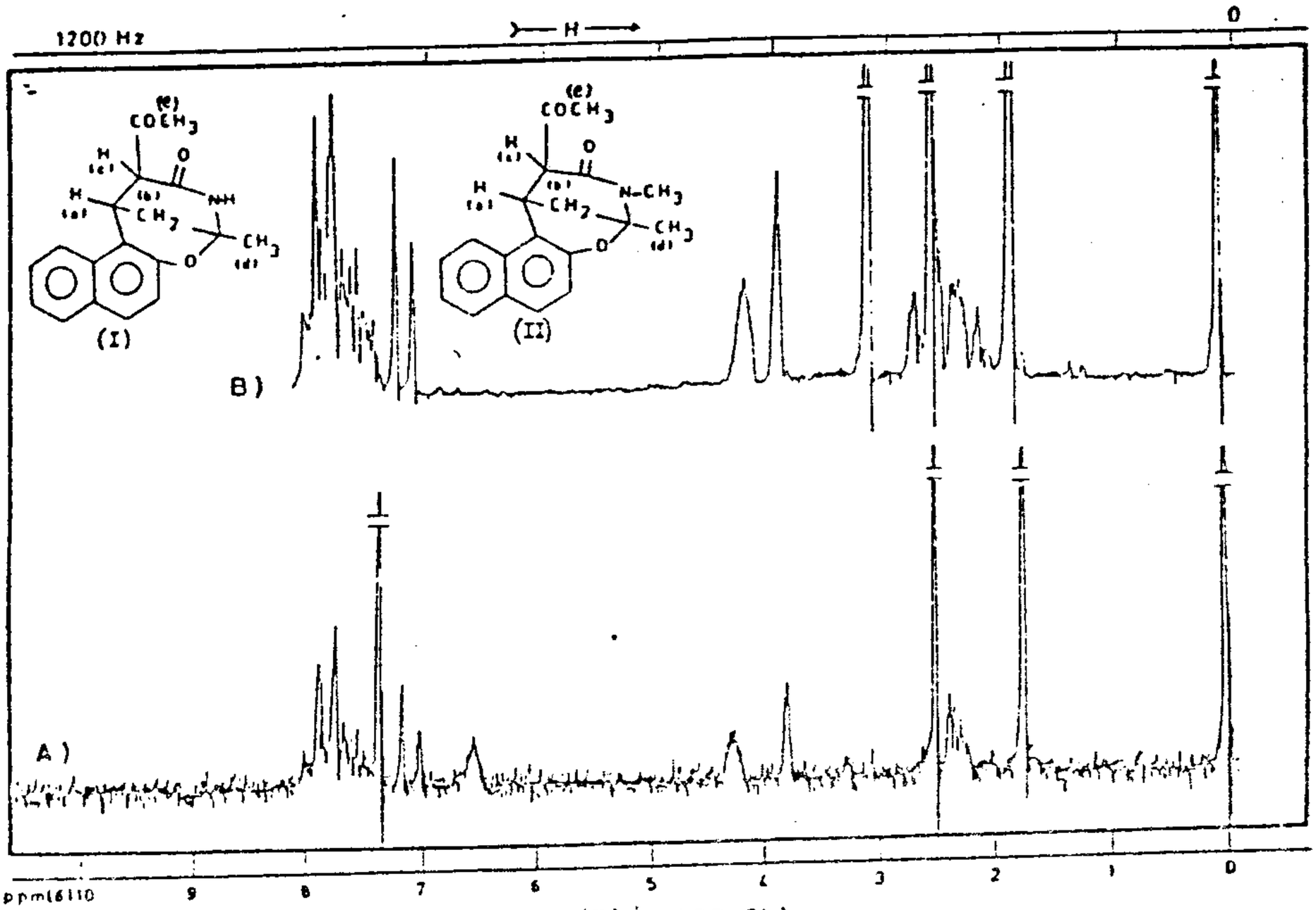
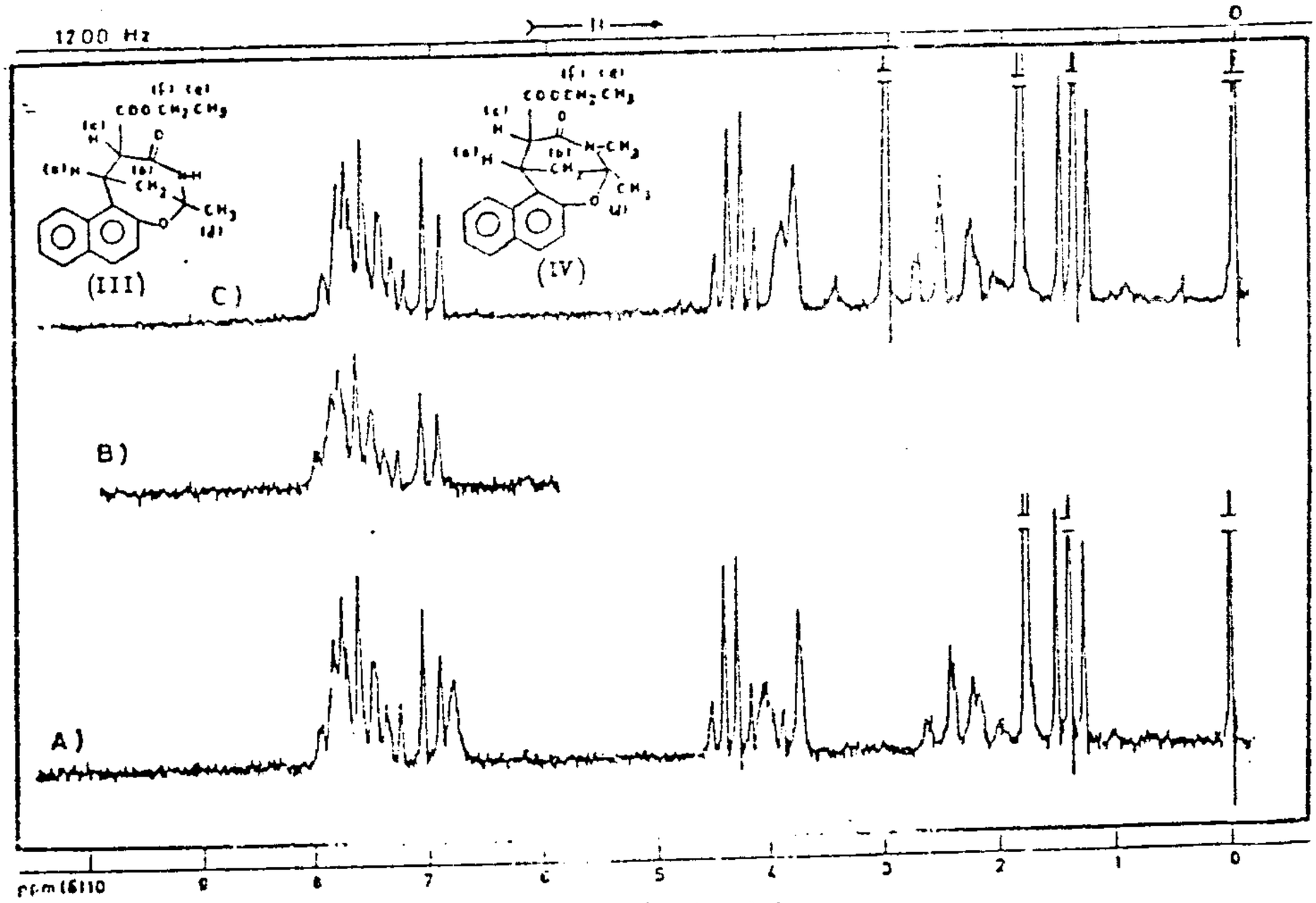


H¹-n.m.r. (1) A) Spectrum of (I) in ($CDCl_3$).
B) Spectrum of (II) in ($CDCl_3$).



H¹-n.m.r. (2) A) Spectrum of (III) in ($CDCl_3$).
B) Spectrum of (III) after addition of D_2O.
C) Spectrum of (IV) in ($CDCl_3$).

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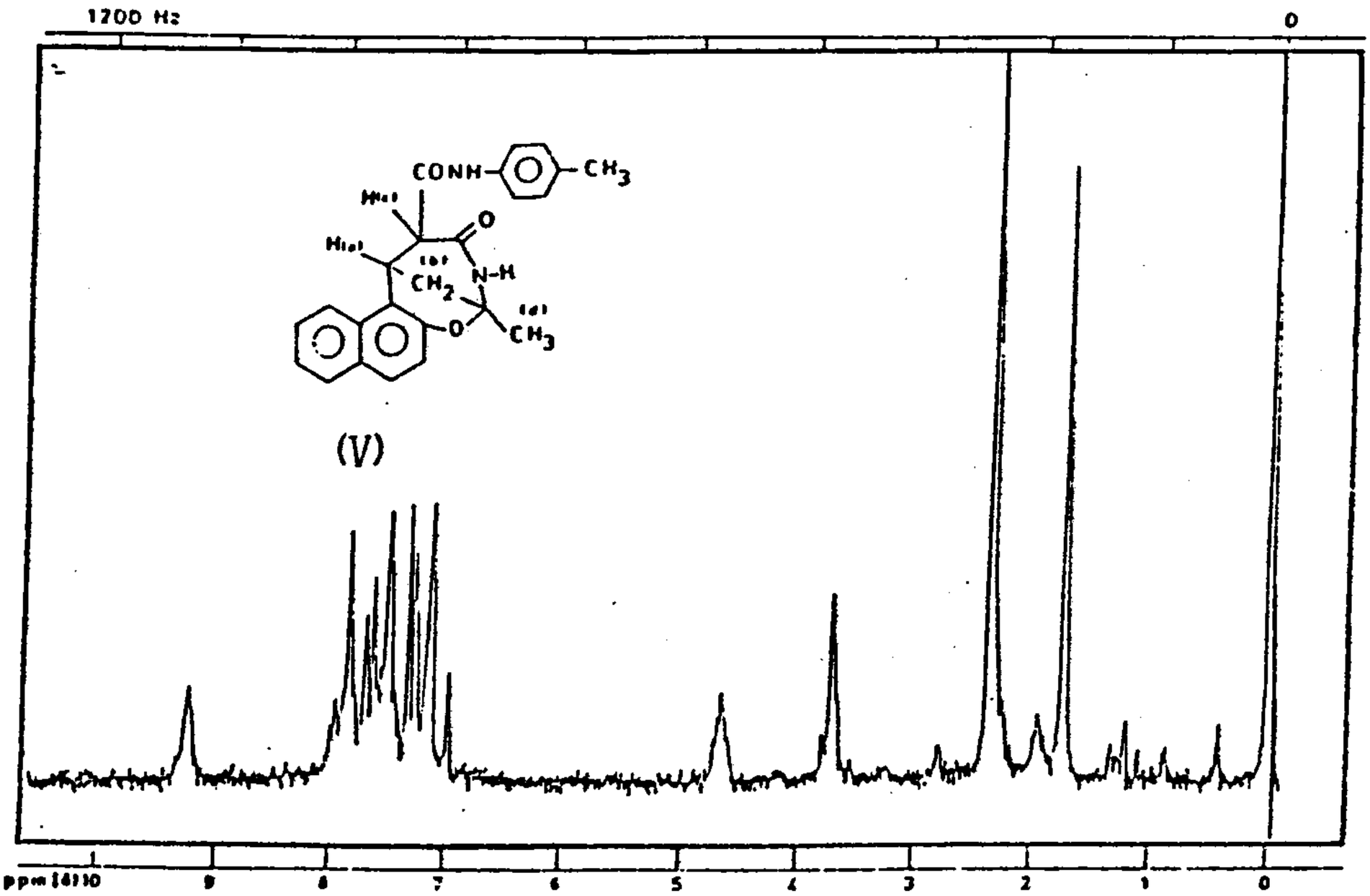

H¹-n.m.r. (3)

دراسة الرنين النووى المغناطيسى (البروتون)
لبعض مشتقات الاكسونافثو (٢ ، ١ ـ جـ)ـ ١ ، ٣ـ اوكسازوسين

* د٠ الخولى ـ د٠ بدير ـ د٠ على ـ د٠ الجروندى
* قسم الكيمياء ـ كلية العلوم ـ جامعة المنصوره
قسم الكيمياء ـ كلية العلوم ـ جامعة الازهر

تعتبر دراسة الرنين النووى المغناطيسى (البروتون) لخمسة من مشتقات ٢ـ ميثيل ـ ٣ ،١٣ـ ثنائى الكيل ـ ٤ـ اوكسو ـ ٥٠(مجموعة استبدال) ـ ٥ ،٦ ـ ثنائى هيدرو ـ نافثو ـ (٢ ،١ـ جـ)ـ ١ ،٣ ـ اوكسازوسين والمذكورة فى هذا البحث هى الهدف من وراء اجرائه ولقد تمت بنجاح ٠

ولقد لوحظ التأثير الانيزوتروبى لكربونيل كل من مجموعة الاسيتيل او مجموعة البروبيونات والمتصلة بذرة الكربون رقم ٥ فى الحلقه الغير متجانسة الثمانيه على جيرانها من البروتونات وخصوصا البروتونان المتصلان بذرتى الكربون رقم ٥ ، ٦ فى الحلقة ٠

كذلك لوحظ تأثير الاليكترونات باى الاروماتية لحلقة بنزين مجموعة بارا ـ طوليل كربوكساميدو المتصله بذرة الكربون رقم ٥ فى الحلقه الغير متجانسه على البروتونات المجاوره ٠

والاكثر من ذلك فقد وجد ان بروتونات مجموعة الميثيلين المقنطره بين ذرتى الكربون رقم ٢ ،٦ فى الحلقه الثمانيه تعطى ما يسمى بنظام ـ اب من حيث الشكل ـ ويرجع السبب فى ذلك الى التزاوج التوأمى بين بروتوناتها الاثنان مع بعضهما البعض بالاضافه الى التزاوج المغزلى المجاور بين بروتونان مجموعة الميثيلين وبروتون مجموعة الميثين المجاوره والمتصل بذرة الكربون رقم ٦ فى الحلقه الثمانيه الغير متجانسة ٠