

AZO DYES DERIVED FROM 2- THIOHYDANTOIN PART 1
Synthesis and Spectroscopic Studies on some new
1- methyl-3- phenyl-2- thiohydantoin Azo dyes

BY

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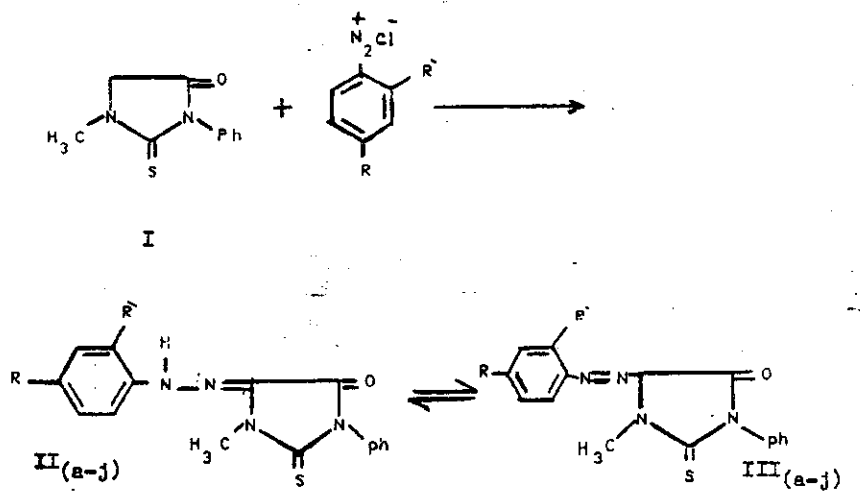
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ABSTRACT

A number of newly azo dyes III_(a-j) have been prepared using 1-methyl-3-phenyl-2-thiohydantoin as a passive component. The spectra ($^1\text{H-NMR}$, IR and U.V) of this series indicate that such compounds exist predominantly in the azo-hydrazone tautomeric form. Moreover, a correlation between the $\pi-\pi^*$ transition of the azo group and the o- and p-substituent in the phenyl ring is attempted.

2- Thiohydantoin was reported [1,2] to undergo coupling with aryl diazonium chlorides to give the corresponding azo derivatives. These compounds exist in the azo form rather than the hydrazone form. Daboun et al. [3] reported that 5-arylozo 1-phenyl -4-thiohydantoins were exist in azo form and reacted with chloroacetic acid to give the corresponding 4-Carboxymethylmercapto derivative. In the present article a number of newly azodyes III_(a-j) were prepared by coupling 1-methyl -3-phenyl^(a-j) 2-thiohydantoin with the corresponding diazonium salt. The structure of these compounds was established based on spectroscopic studies.



- | | |
|-----------------------------|------------------------------|
| a) R=R=H | f) R=COOH, R=H |
| b) R=CH ₃ , R=H | g) R=NO ₂ , R=H |
| c) R=OCH ₃ , R=H | h) R=SO ₃ , R=H |
| d) R=OH, R=H | i) R=COCH ₃ , R=H |
| e) R=Cl, R=H | j) R=H, R=OH |

The H¹ - N.M.R. SPECTROSCOPY

The tautomeric azo hydrazone and correct structural of compounds III_(a-j) or II_(a-j) were established from H¹- N.M.R and C¹³ -N.M.R. The H¹- N.M.R spectrum of compound III_a or II_a sport N-H proton at $\delta = 11,54$ ppm which disappears on shaking the sample with D₂O indicating the presence of the hydrazone structural. The H₂ of 2-thiohydantoin moiety appeared at $\delta = 3.32$ ppm as one proton singlet, the methyl group at N¹ - CH₃

as three protons singlet at $\delta = 3.60$ ppm and the aromatic protons of two phenyl rings (N^3 -ph, phenyl of arylazo) as nine protons multiplet at $\delta = 7.30 - 7.85$ ppm. Again the Hydrazone form II_b is indicated by the presence of N-H proton at $\delta = 11.14$ ppm, which disappeared on shaking with D_2O , the CH_3 group of the azo phenyl ring as three protons singlet at $\delta = 2.25$ ppm (Fig. 1).

The H^1 -N M R of compounds $III_{(c-j)}$ or $II_{(c-j)}$ revealed N-H one proton singlet in the region 11.16-11.52 ppm which disappeared on shaking with D_2O , thus indicating the presence of hydrazone from $II_{(c-j)}$. Other signals are listed in table 1 (see Figs 2, 3 & 4).

THE C^{13} - NMR:

The C^{13} -NMR of compound III_b or II_b revealed two signals at $\delta = 20.33$ and $\delta = 29.168$ ppm corresponding to $H_3C - Ar$ and $N^1 - CH_3$ respectively, the C_5 of thiohydantoin moiety is shown at $\delta = 140.719$ ppm indicating the presence of C=N of the hydrazone II_b structure, the aromatic carbon atoms appear at $\delta = 113.606, 126.45, 127.52, 128.06, 128.53, 128.84, 129.63$ and 132.713 ppm, the C=O and C=S of thiohydantoin moiety revealed at $\delta = 155.60$ and 173.83 ppm, respectively (Fig. 5).

The C^{13} -NMR of compound III_c or II_c showed two signals at $\delta = 29.11$ and 55.179 ppm corresponding $N^1 - CH_3$ and OCH_3 respectively, the C_5 of thiohydantoin is shown at $\delta = 136.649$ for C=N of hydrazone II_c structure, the aromatic carbon atoms of the two phenyl rings showed signals at $\delta = 114.523, 114.904, 126.42, 126.93, 128.49, 128.68, 128.75$

and 132.721 ppm, the C=O and C=S of thiohydantoin are shown at 155.37 and 173.35 ppm, respectively (Fig.6). The C^{13} -NMR of compound III_e or II_e showed clearly the azo hydrazone tautomeric form as it revealed two signals for N¹-CH₃ at δ =25.309 and δ = 29.122 ppm, also two signals for C₃ the first at δ = 54.230 ppm characterised to aliphatic carbon atom of substituted 2-thiohydantoin 4 indicating the presence of azo form III_e the second at δ = 142.836 for C=N of the hydrazone II_e structure. The sixteen carbon atoms of the two phenyl rings of the two isomers III_e and II_e revealed at δ = 114.27, 115.122, 125.990, 126.391, 127.844, 128.114, 128.282, 128.46, 128.549, 128.594, 128.714, 128.760, 128.835, 128.890, 190.887, and 132.594 ppm, there are two signals at δ = 155.52 and δ = 155.915 ppm corresponding to C=O of 2-thiohydantoin for the isomer III_e and II_e, the C=S at C₂ is shown at δ = 174.462 ppm (Fig. 7). The C^{13} -NMR of compound III_d or II_d showed N¹-CH₃ signal at δ = 29.15 ppm and C₃ of 2-thiohydantoin is shown at δ = 152.994, the aromatic carbon atoms are shown at δ = 115.13, 115.80, 128.613, 128.530, 128.710, 128.769, 132.775, and 125.211 ppm, the C=O and C=S of 2- thiohydantoin at δ = 155.383 and δ = 173.007 ppm, respectively (Fig. 8)

THE IR SPECTROSCOPY

The infrared spectra of compounds III_(a-j) or II_(a-j) are characterised by the presence of weak N-H band in the region from 3150- 3350 cm⁻¹ due to the hudrazone structure II_(a-j), the OH band of compounds III_(d,f,h,j) are shown in the region of 3300-3500 cm⁻¹ the carbonyl group in the 2-thiohydantoin moiety

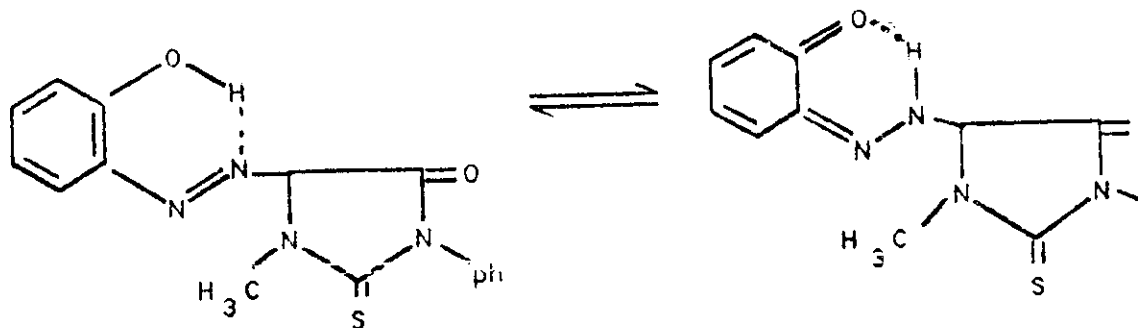
of compound III_(a-j) is shown within the region 1700-1660 cm⁻¹ [5]. Compounds II_(f,j) showed strong bands at 1760-1680 cm⁻¹ characteristic for C=O of the caboxylic and acetyl groups. The IR spectra of all compounds III_(a-j) exhibit strong bands within the region 1600- 1520 cm⁻¹, which may be assigned to the asymmetric stretching vibration of N=N group, LeFever [6] quoted the bands near 1600 and 1400 cm⁻¹ to the stretching vibration of the azo group. However, the medium band around 1400 cm⁻¹ is referred to the symmetrical vibration of the N=N group [7]. The bands within the region 1620-1530 are assigned to the C=C skeletal vibration of the aromatic system. The presence of tautomeric azo III_(a-j) hydrazone II_(a-j) form are due to the stability of the hydrazone II_(a-j) through the conjugation between C=O of carbon 4 and C=N of carbon 5.

THE U.V AND VISIBLE SPECTROSCOPY

The absorption spectra of azo-benzene and its derivatives has been the subject of many investigation [8], also the gamma radiolysis of some 5-arylazo 2-thiohydantion and its relation with U.V spectroscopy has been investigated [5,9]. In the present study the visible spectra of the azo dyes III_(a-j) showed the $\pi-\pi^*$ transition of the N=N group in the regioin 426-460 nm [5,8]. The bands are largely affected by O- or p- substituents in the phenyl ring. Introducing electron donating group e.g. OH, OCH₃, CH₃ in the phenyl ring cause a red shift of the N=N- band due to increased charge transfer from the -N=N- centre, on the other hand electron withdrawing group such as Cl, NO₂, COCH₃ groups cause a blue shift.

Pronounced red shift in the -N=N- band are observed on changing the position of the -OH group from position 4 to position 2, this change is also responsible for appearance of new band near 278 nm due to the formation of chelate ring through intramolecular hydrogen bonding and easier charge transfer from the OH in O-position to the -N=N- centre. Also there is a possibility of tautomeric shift of the type shown below which increases the delocalisation of the n-electrons on the N=N- linkage causing lowering of transition energy,

Table 2.



EXPERIMENTAL

All melting points are uncorrected. The Ultraviolet were recorded on shimadzo PRT. 240. The Infrared spectra were recorded in KBr pellets on Perkin-Elmer 1420, the H^1 -NMR and C^{13} -NMR were recorded at Brukes 250 MH and 60 MH. Analytical data were obtained from Microanalytical Centre, Cairo University.

5-Arylazo -1- methyl -3- phenyl -2- thiohydantoin III_(a-j) .**GENERAL PROCEDURE**

The aromatic amine (0.01 mole) dissolved in conc. HCl (5 ml) and water (5 ml) was cooled to 0 C⁰ and then treated with a cold solution of sodium nitrite (0.6 gr) in 5 ml water. The diazotized amine is added dropwise to an ice cold solution (0.01 mole) of 1-methyl -3-phenyl -2- thiohydantoin in pyridine (30 ml). The reaction mixture was left under stirring at 0 C⁰ for 2hrs. The product that separated was filtered off, washed with dil HCl and then with water three times, dried, and recrystallised from the proper solvent. The TLC showed one product. The prepared azo compounds III_(a-j) are all coloured compounds, the m.p. and analytical data are listed in Table 3.

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table 1 $^1\text{H-NMR}$ spectra of the New compound III (a - j)

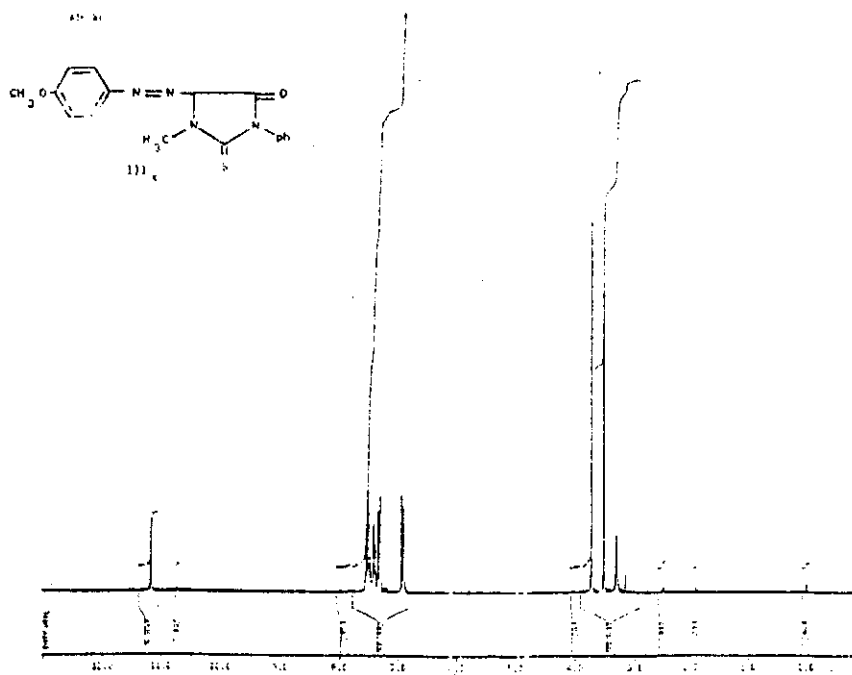
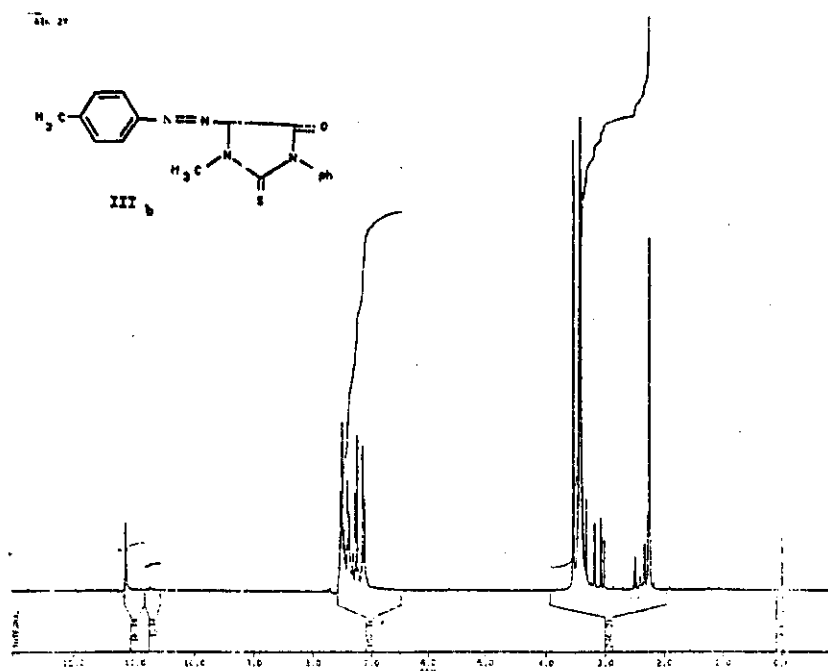
Comp. NO	Name of Compound	$^1\text{H-NMR}$ S(ppm)
III a	5-(phenylimino)-1-methyl-3-phenyl-2-thiohydantoin	3.32(S, 1H, H ₃), 3.60 (S, 3H, N ¹ -CH ₃), 7.30-7.35(m, 10 H, aromatic H), 11.54 (S, 1H, N-H).
III b	5-(P-methylphenylimino)-1-methyl-3-phenyl-2-thiohydantoin	2.25 (S, 3H, CH ₃ Ar), 3.41(S, 3H, N ¹ -CH ₃), 3.52 (S, 1H, H ₃), 7.38- 7.56 (m, 9H, aromatic H), 11.14 (S, 1H, N-H)
III c	5-(P-methoxyphenylimino)-1-methyl-3-phenyl-2-thiohydantoin	3.30(S, 1H, H ₃), 3.51(S, 3H, N ¹ -CH ₃), 3.72 (S, 3H, OCH ₃), 7.29-7.56 (m, 9H aromatic H), 11.16 (S, 1H, N-H)
III d	5-(P-hydroxyphenylimino)-1-methyl-3-phenyl-2-thiohydantoin	3.37(S, 1H, H ₃), 3.51(S, 3H, N ¹ -CH ₃), 6.74-7.56(m, 9H aromatic H) 9.19 (S, broad, 1H, OH) 11.14(S, 1H, N-H)
III e	5-(P-chlorophenylimino)-1-methyl-3-phenyl-2-thiohydantoin	3.16(S, 1H, H ₃), 3.2-7 (S, 1H, H ₃) [azo-hydraso form] 3.32(S, 3H, N ¹ -CH ₃), 3.51(S, 3H, N ¹ -CH ₃) [azo-hydraso form] 7.29-7.56 (m, 9H, aromatic H), 11.20 (S, 1H, N-H)
III f	5-(P-Carboxyphenylimino)-1-methyl-3-phenyl-2-thiohydantoin	3.32(S, 1H, H ₃), 3.71(S, 3H, N ¹ -CH ₃), 7.30-8.22(m, 9H, aromatic H), 10.52(S, 1H, broad O-H), 11.24 (s, 1H, N-H).
III g	5-(P-Nitrophenylimino)-1-methyl-3-phenyl-2-thiohydantoin	3.45(S, 1H, H ₃), 3.66(S, 3H, N ¹ -CH ₃), 7.21-7.82(m, 9H, aromatic H), 11.42(S, 1H, N-H).
III h	5-(P-sulfonphenylimino)-1-methyl-3-phenyl-2-thiohydantoin	3.30(S, 1H, H ₃), 3.52(S, 3H, N ¹ -CH ₃), 6.82-7.54 (m, 9H, aromatic H), 10.10(S, 1H, OH of sulfonic group), 11.34(S, 1H, N-H).
III i	5-(P-acetylphenylimino)-1-methyl-3-phenyl-2-thiohydantoin	2.55(S, 3H, CH ₃ , CO), 3.54(S, 3H, N ¹ -CH ₃), 3.58(S, 1H, H ₃), 7.18-8.02 (m, 9H, aromatic H), 11.28(S, 1H, N-H)
III j	5-(O-hydroxyphenlimio)-1-methyl-3-phenyl-2-thiohydantoin	3.24(S, 3H, N ¹ -CH ₃), 3.30(S, 1H, H ₃) 7.30-8.35(m, 9h, aromatic H), 10.18(S, 1H, OH), 11.26(S, 1H, N-H).

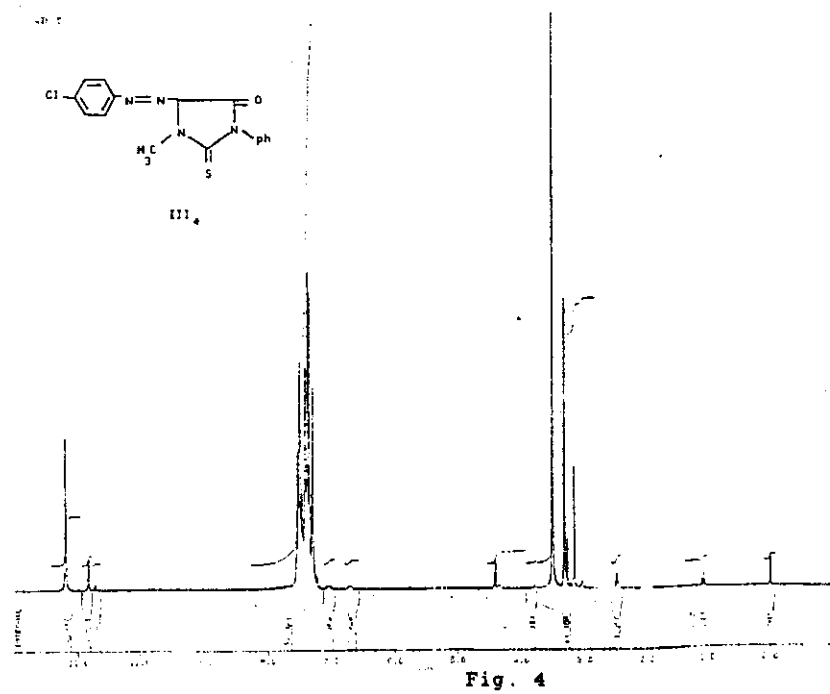
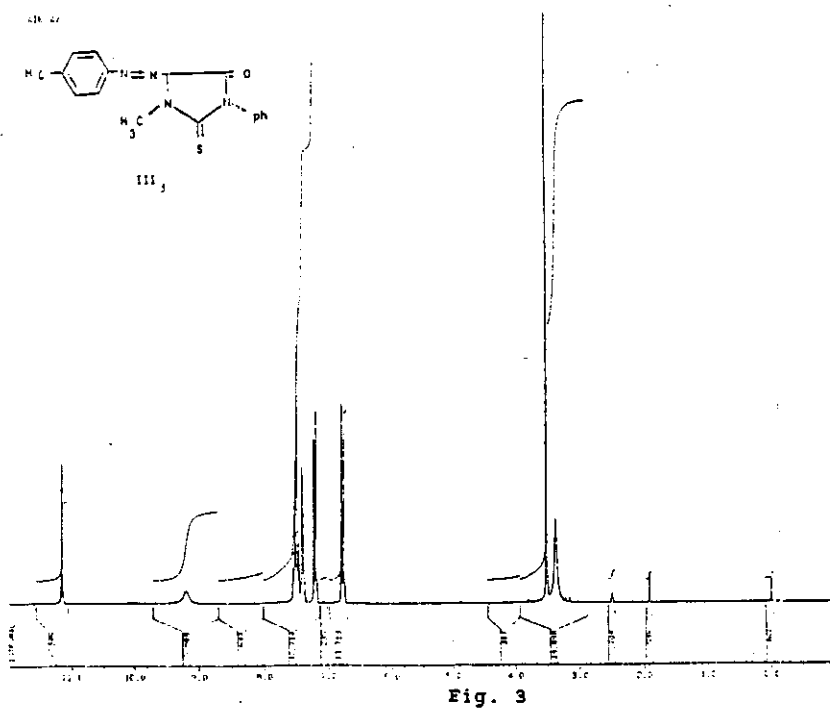
Table 2 U.V and visible spectra for the Compound III (a-j)

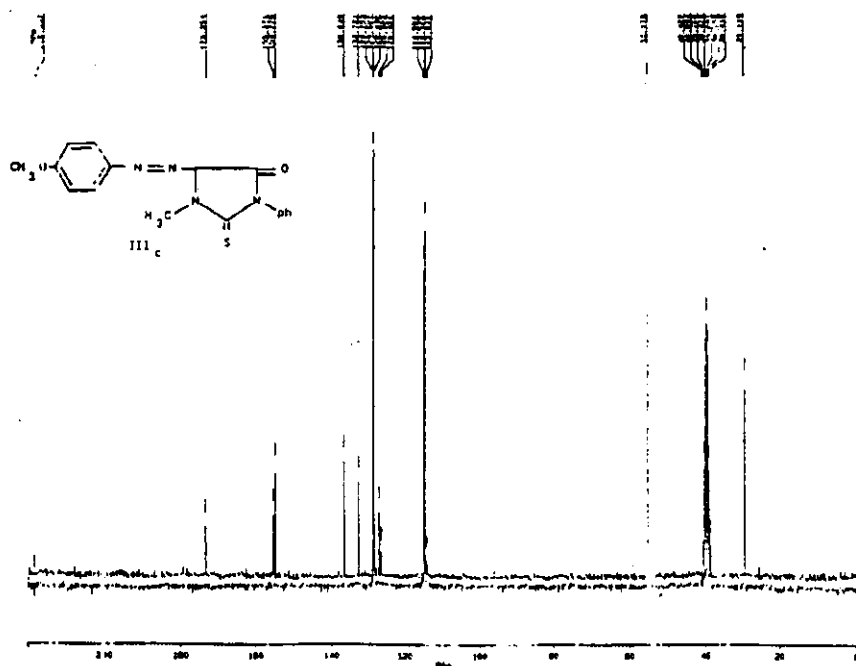
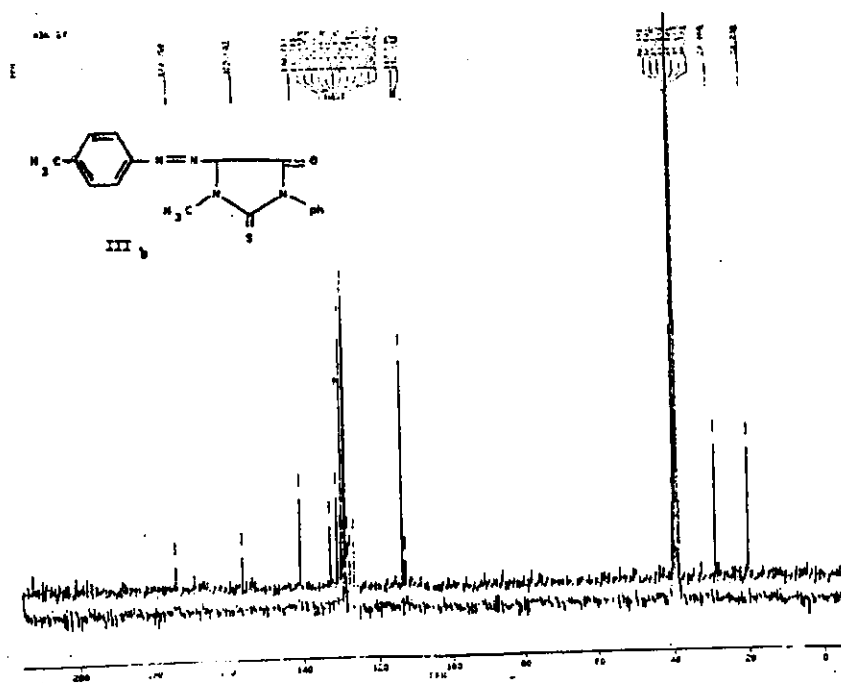
Compound	$\pi - \pi^*$ of - N = N - λ_{max} nm	ϵ Max.	λ_{max}	ϵ Max
III				
a	432	1.80		
b	442	1.89		
c	450	2.16		
d	452	1.75(OH-P)		
e	430	1.62		
f	432	2.38		
g	426	2.9		
h	443.6	1.7		
i	443.4	1.7		
j	458	2.3	278	1.32 (OH-O)

Table 3

Comp. NO	M P C°	Yie. %	solv. of cryst	Formula (M.W)	Calcd. C Found	H	N	S	Cl
III a	201-203	72	AcOH	C ₁₆ H ₁₄ N ₄ O ₅	61.93	4.51	18.06	10.32	-
				310	61.58	4.32	17.83	9.98	
III b	204-206	79	EtOH	C ₁₇ H ₁₆ N ₄ O ₅	62.96	4.93	17.28	9.87	-
				324	62.62	4.67	16.82	9.48	
III c	197-99	81	AcOH	C ₁₇ H ₁₆ N ₄ O ₂ S	60.00	4.70	16.47	9.41	-
				340	59.68	4.32	16.10	8.93	
III d	195-197	86	AcOH	C ₁₆ H ₁₄ N ₄ O ₂ S	58.89	4.29	17.17	9.81	-
				326	58.53	3.96	16.86	9.56	
III e	177-179	63	EtOH	C ₁₆ H ₁₃ N ₄ O ₅ Cl	55.73	3.77	16.25	9.28	10.30
				344.5	55.22	3.48	15.76	8.82	9.76
III f	291-293	67	AcOH	C ₁₇ H ₁₄ N ₂ O ₃ S	57.62	3.95	15.81	9.03	-
				354	57.22	3.58	15.48	8.68	
III g	238-240	56	AcOH	C ₁₆ H ₁₃ N ₅ O ₃ S	54.08	3.66	19.71	9.01	-
				355	53.73	3.23	19.38	8.63	
III h	224-226	62	AcOH	C ₁₆ H ₁₄ N ₄ O ₄ S ₂	49.23	3.58	14.35	16.41	-
				390	48.86	3.21	13.92	16.12	
III i	219-221	58	AcOH	C ₁₆ H ₁₆ N ₄ O ₂ S	61.36	4.54	15.90	9.09	-
				352	60.92	4.32	15.58	8.86	
III j	269-271	82	AcOH	C ₁₆ H ₁₄ N ₄ O ₂ S	58.89	4.29	17.17	9.81	-
				326	58.61	3.91	16.86	9.53	







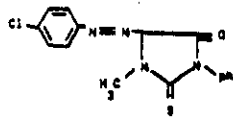
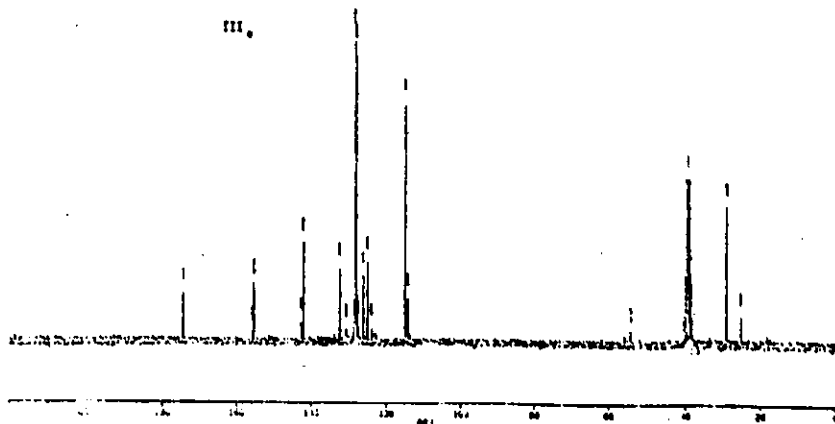
III₆

Fig. 7

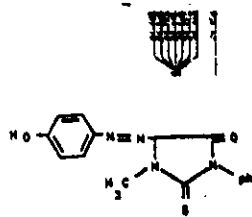
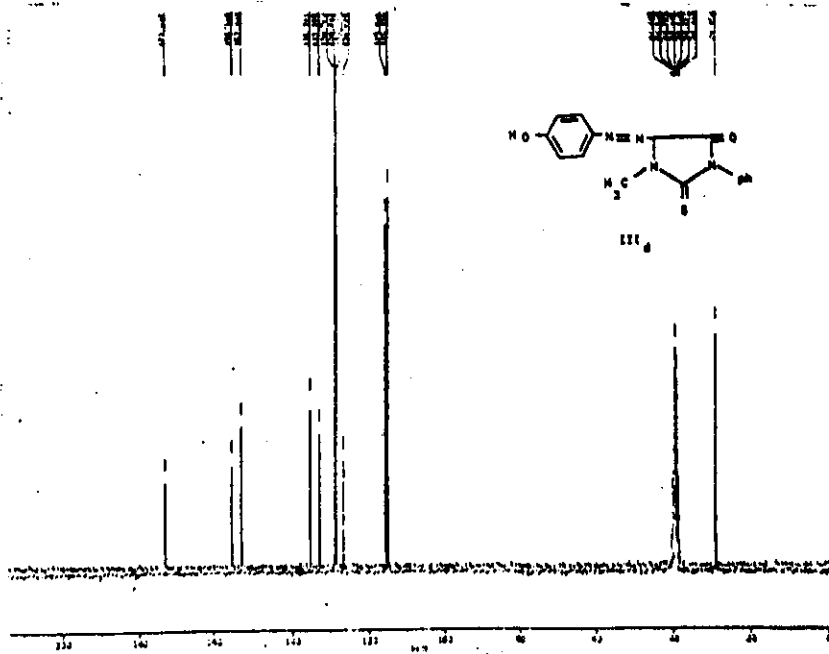
III₆

Fig. 8

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أصباغ الأزو المشتقة من ٢-ثيوهيدنتيون

يوسف لطفي علي

قسم الكيمياء - كلية التربية بكفر الشيخ - جامعة طنطا

بتفاعل ١- مثيل -٣- فليل -٢- ثيوهيدنتيون مع أملاح الديازونيوم الأروماتية أمكن تحضير عدة مركبات من أصباغ الأزو الجديدة ومن الدراسات الطيفية لهذه المركبات باستخدام الأشعة فوق البنفسجية والحمراء وقياس الرنين المغناطيسي للبروتونات أمكن إثبات أن هذه المركبات خليط من تركيب الأزو والهيدرازو •

كذلك بدراسة الانتقال الإلكتروني $\Pi - \Pi^*$ لهذه المركبات وجد أنه توجد علاقة بين هذا الانتقال الإلكتروني وموضع ونوع المجموعات الموجودة في حلقة البنزين لهذه المركبات •