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Spectral Studies on Some New 1,5-Diarylformazans

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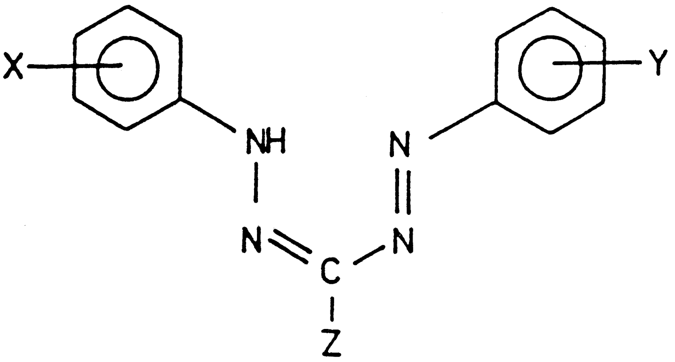
New 1,5-diarylformazan derivatives containing carboxylic and arsonic groups are prepared. The structure of the prepared compounds was investigated using IR, NMR and mass spectrometry. A fragmentation pattern for these compounds is given. The IR and NMR spectra revealed the existence of strong hydrogen bond between N_1 and N_5. The important IR-bands are assigned to their corresponding groups.

INTRODUCTION

Formazans have received great attention owing to their biological activity[1] and dyeing properties[2, 3]. They have been also used as analytical reagents for determining various metals[4–7]

However, studies devoted to the molecular structure of some formazan derivatives are few. Fischer *et al.*[8] demonstrated that 1,3,5-triphenylformazan derivatives do not exist in solution as resonance hybrids but as tautomeric pairs. The investigation of the NMR spectrum of a sugar diphenylformazan substituted by one ^{15}N atom led to the appearance of the NH signal as a doublet while the spectra of the ^{14}N-formazans exhibit a sharp NH signal[9]. This experimental observation confirms the presence of a rapid tautomerization. Some substituted acetylformazans were prepared and characterized by elemental analysis, UV-Vis., IR and NMR spectroscopy[10, 11]. Some symmetric 1,5-diphenyl-3-cyanoformazans were prepared and their spectral behaviours were studied and the results were correlated with those obtained from a theoretical treatment applying SCF PPPCI calculations and the electrical conductance was also investigated[12]. Le Fevre *et al.*[13] have reported the infrared spectra for some formazans.

The present work was undertaken to gain information concerning the molecular structure of some substituted 3-acetyl-1,5-diaryl and 3-cyano-1,5-diarylformazans. Mass, IR and NMR of the prepared formazans have been performed. The formazans prepared have the general structural formula:



Z = –COCH3 (I) and –C≡N(II)
X, Y = H, H (a), H, o–COOH (b), H, p–AsO(OH)2 (C), and
p–AsO(OH)2, p–AsO(OH)2(d).

EXPERIMENTAL

All chemicals and solvents in this investigation were pure BDH products. The elemental analyses of the prepared formazans were carried out in the micro-analytical centre of Cairo University. The mass spectra of the prepared formazans were recorded with the aid of JOEL-JMS BS-300 spectrometer.

Aryldiazonium chloride was prepared by diazotizing 0.05 mole of the arylamine in 15 mL of conc. hydrochloric acid with 3.7 g (0.053 mole) of sodium nitrite dissolved in 50 mL of water. The coupling of aryldiazonium chloride to acetylacetone and ethyl cyanoacetate (0.05 mole) in the presence of 14 g of sodium acetate yields the corresponding aryl hydrazone with an initial molar ratio of the reactants of 1 : 1 (β-diketone or ethyl cyanoacetate to diazonium chloride). The product was kept in a refrigerator overnight, then acidified with 1 : 1 hydrochloric acid, filtered, washed several times with water and recrystallized from the proper solvent. Asymmetric formazans Ib, IIb, Ic and IIc were prepared by mixing a solution of (0.05 mole) of the prepared arylhydrazone in 400 mL EtOH with 500 mL aqueous NaOH (1.05 g of NaOH) solution. The solid was completely dissolved and the solution was cooled to below 5°C. A diazonium chloride solution prepared from (0.05 mole) of arylamine was then added dropwise with stirring. After the addition is completed, the solution was stirred for 1/2 h and left to stand overnight in a refrigerator, then acidified with 1 : 1 hydrochloric acid.

The precipitate was filtered, washed with H_2O and recrystallized from the appropriate solvent.

The symmetric formazans IIa, Id and IId were prepared by coupling the aryldiazonium chloride with acetylacetone or ethyl cyanoacetate in a molar ratio of 2 : 1 in alkaline medium of sodium hydroxide. In this method, 0.02 mole of arylamine is dissolved in 6 mL conc. hydrochloric acid, then a cooled solution containing (0.023 mole) sodium nitrite was added dropwisely with continuous stirring. The formed diazonium chloride was then added slowly with stirring to an alkaline aqueous solution containing (0.01 mol) acetylacetone or ethyl cyanoacetate and 6 g sodium hydroxide. The reaction mixture was kept in a refrigerator overnight, then acidified with 1 : 1 hydrochloric acid.

The resulting solid was filtered and washed with water. The crude product was recrystallized from the proper solvent.

The symmetric formazan Ia was prepared by coupling benzenediazonium chloride with acetylacetone in alkaline medium according to the method of Yao[14].

RESULTS AND DISCUSSION

The prepared formazans were analysed; the results of elemental analysis were in good agreement with the theoretical values and are listed in Table 1.

TABLE 1
ELEMENTAL ANALYSIS AND MELTING POINTS OF THE PREPARED FORMAZANS

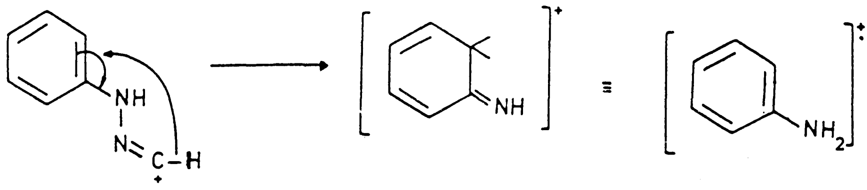
Formazan	Formula (Mol. wt.)	m.p. (°C) (Lit. m.p.)	% Analysis Found (Calcd.)		
			C	H	N
Ia	$C_{15}H_{14}N_4O$ (266)	134°C (134°C)[14]	67.5 (67.77)	5.30 (5.25)	20.50 (21.05)
Ib	$C_{16}H_{14}N_4O_3$ (310)	198°C	62.10 (61.93)	4.60 (4.51)	18.10 (18.06)
Ic	$C_{15}H_{15}N_4O_4As$ (390)	160°C	46.20 (46.15)	3.90 (3.84)	14.40 (14.35)
Id	$C_{15}H_{16}N_4O_7As_2$ (514)	310°C	34.90 (35.02)	3.20 (3.11)	21.60 (21.79)
IIa	$C_{14}H_{11}N_5$ (249)	158°C (158°C)[11]	67.60 (67.47)	4.50 (4.41)	28.20 (28.11)
IIb	$C_{15}H_{11}N_5O_2$ (293)	185°C	61.50 (61.43)	3.80 (3.75)	23.80 (23.89)
IIc	$C_{14}H_{12}N_5O_3As$ (373)	245°C	45.10 (45.04)	3.30 (3.21)	18.70 (18.67)
IId	$C_{14}H_{13}N_5O_6As_2$ (497)	> 400°C	33.90 (33.80)	2.50 (2.61)	14.20 (14.08)

Mass spectra

The mass spectra of the prepared formazans served representatives for the investigation and the following mechanisms of fragmentation may be suggested (*cf.*, schemes 1–6). The main source of difficulty is that the molecular ion may undergo rearrangement to give fragmentation patterns not anticipated from the structure of the compound (like thermal fusion) as in the spectra of framazans Ic and IIc where a peak appeared at m/z = 289 indicating the presence of the same species *via* splitting of the part containing the acetyl or the cyano group giving the species:

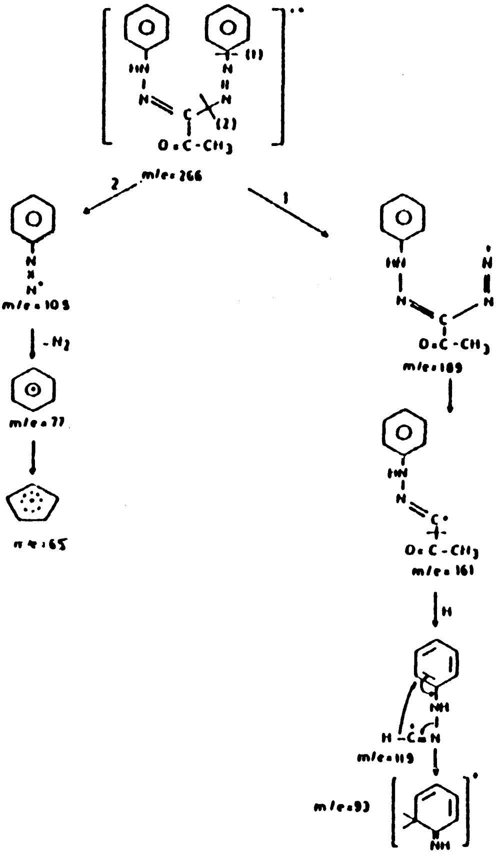
$$[C_6H_5\text{—}N\text{=\!=}N\text{—}C_6H_4AsO(OH)]^+.$$

The signal that appeared at m/z = 93 is explained by the mechanism[15]:



Scheme III

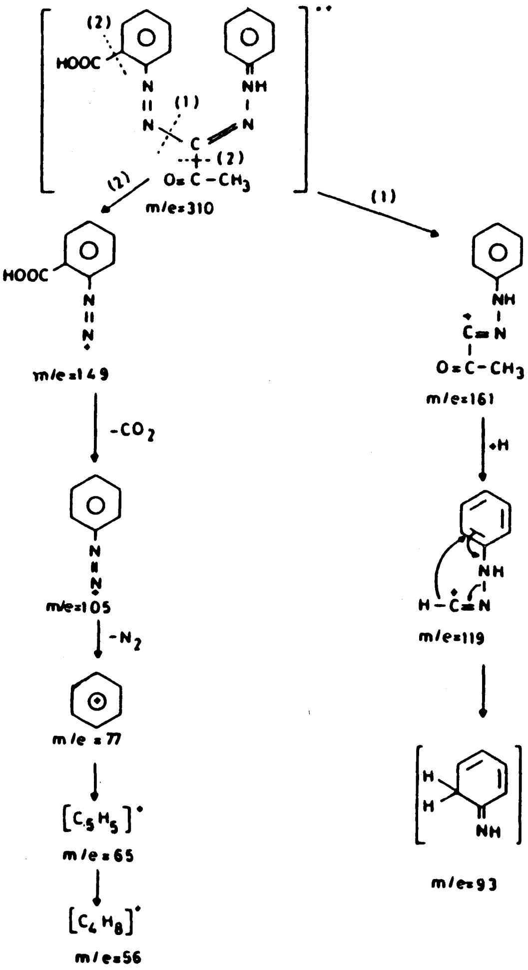
Formazan Ia



The unsubstituted formazans Ia and IIa showed simple mass spectral fragmentation patterns due to the absence of substituents. The fragment of m/z = 92 is due to the species $[C_6H_5NH]^+$. The major characteristic cleavage in all formazans is the fission of N—C bond of the molecular ion.

Mass spectra of formazans Id and IId could not be carried out because of its high melting points which exceeds 400°C.

Scheme (2)
Formazan Ib (M.W. = 310)



Based on the mass spectra, the following mechanisms of fragmentation may be suggested:

IR spectra

The infrared absorption spectra of formazans were recorded in order to find an empirical assignement for their IR bands and elucidate the molecular structure of these formazan derivatives. Since formazans have many atoms which produce many bands, a complete assignment for all bands would be very difficult; so it is not necessary to obtain full assignment for all vibrations. The important IR bands together with their assignment are given in Table 2.

In the formazans under investigation, the presence of a band at 3200 cm^{-1} indicates the existence[16] of hydrogen bonded N—H.

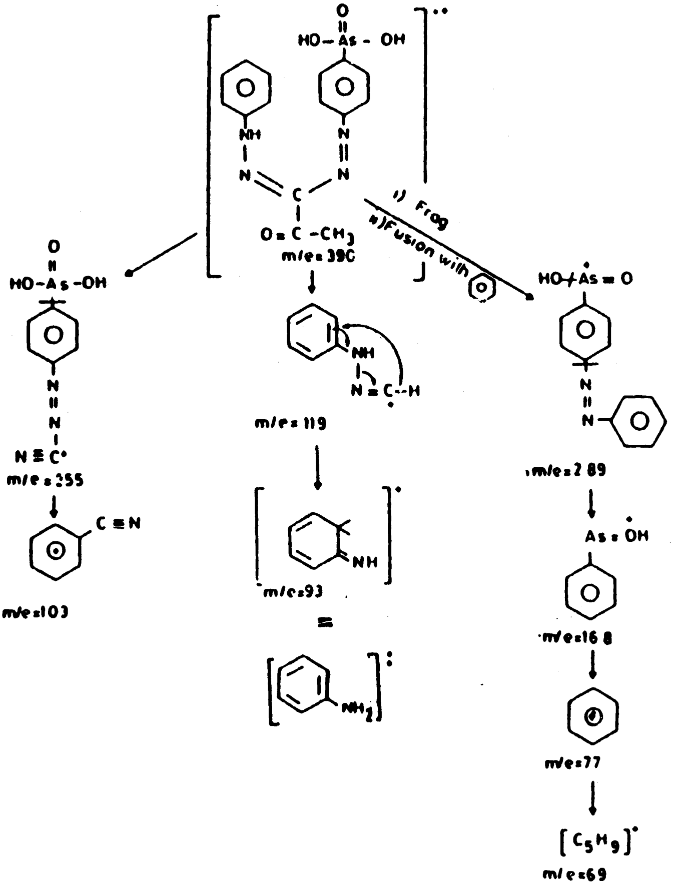
TABLE 2
ASSIGNMENT OF IR-BANDS OF FORMAZANS (Ia–Id) AND (IIa–IID)

Ia	Ib	Ic	Id	IIa	IIb	IIc	IId	Band assignment
—	—	—	—	—	3600–3250 m,b	3600–3250 m,b	3600–3240 m,b	ν_{OH}
—	3600–2800 m,b	3600–2600 m,b	3600–300 m,b	—	—	—	—	ν_{NH+OH}
3400–3200 m,b	3200 m,b	—	—	3200 m	3200 m	3200 m	3200 m	ν_{NH}
—	3100–2000 m,b	—	—	3010 w	3040 v,w	3010 v,w	—	Arom. C—H
2950 vw	—	—	2930	—	2980 v,w	2950 w	—	Aliph. C—H
—	—	—	—	2240 s	2230 m	2250 s	2220 m	C≡N st.
—	1700 m	—	—	—	1670	—	—	Carboxylic C═O
1670 s	1660 m	1660 m	1660 w	—	—	—	—	Acetyl C═O
1590 w	1620 w	1590 m	1580 m	1600 m	1580 m	1600 s	1590 m	Aromatic C═N + N—H bending
1500 s	1500 s	1510 s	1500 m	1540 s	1550 m	1540 s	1520 s	C═N st.
1450 m	1450 m	1460 w	—	—	—	—	—	Asym. CH_3 deform.
1420 vw	1390 s	1400 v,w	1400 w	1400 m	1400 m	1400 s	1390 m	N═S stretching
1350	1380	1370	—	—	—	—	—	CH_3 out-of-plane def.
1200 m	1240 m	1250 m	1240 s	1260 s	1270 s	1270 m	1260	C—N asym. def.
1190 m	1150 m	1170 m	1180 w	1190 w	1180 w	1150 w	1180 w	C—N asym. def.
1150 w	—	1100	1100	1080 w	1090	1100 s	1100 m	C—H in-plane def.
750 s	750 s	760 s	770 s	750 s	760 m	780 s	780m	C—H out-of-plane def.

s—strong, b—broad, m—medium, w—weak

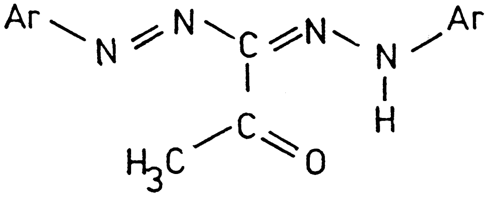
Scheme (3)

Formazan Ic (M.W. = 390)

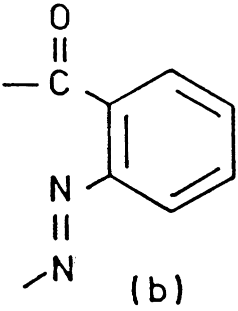


The absorption band arising from the OH vibration appears as a broad band within the wave number range 3600–3250 cm^{-1} for formazans IIb, IIc and IId while formazans Ib, Ic and Id give a very broad band extended from 3600 to 2800 cm^{-1}. The acetyl C=O stretching band for formazans (Ia–Id) appears in the range 1670–1660 cm^{-1} while bending vibration occurs at 660–640 cm^{-1}. The infrared absorption bands arising from the COOH group generally involve the carbonyl frequencies at 1725–1700 cm^{-1}. The carboxy C=O vibration occurs at 1700 cm^{-1} and 1670 cm^{-1} in case of Ib and IIb, respectively. The appearance of the ketonic C=O band of the acetyl and carboxylic groups at such a lower frequency than expected is attributed to the conjugation of both the acetyl C=O with C=N (a) and the carboxyl C=O with N=N (b).

The C≡N stretching band for formazans (IIa–IId) lies within the range 2250–2220 cm^{-1}. Formazans under investigation exhibit their C=N band in the

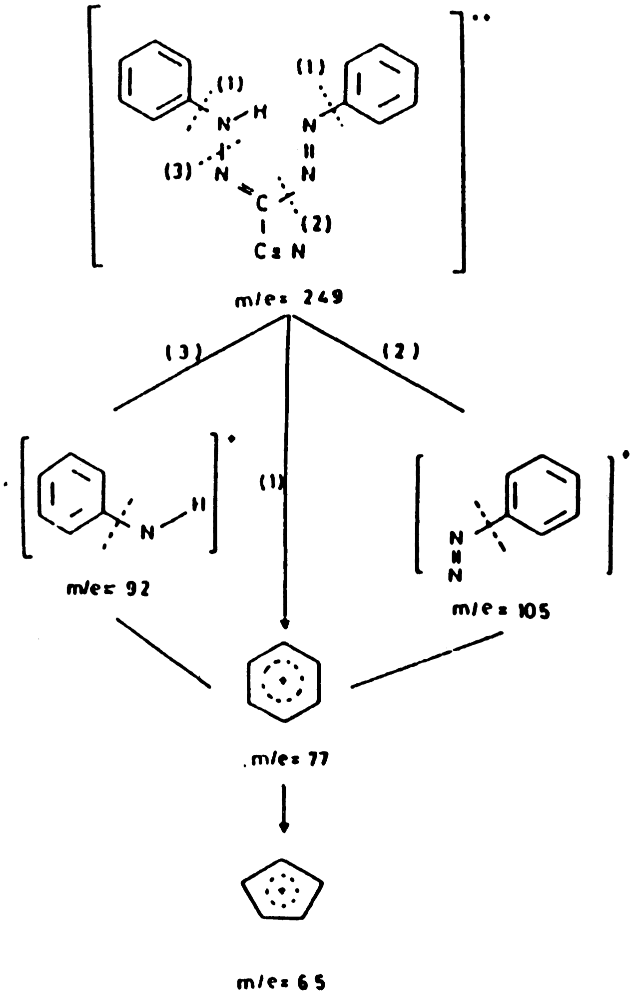


(a)

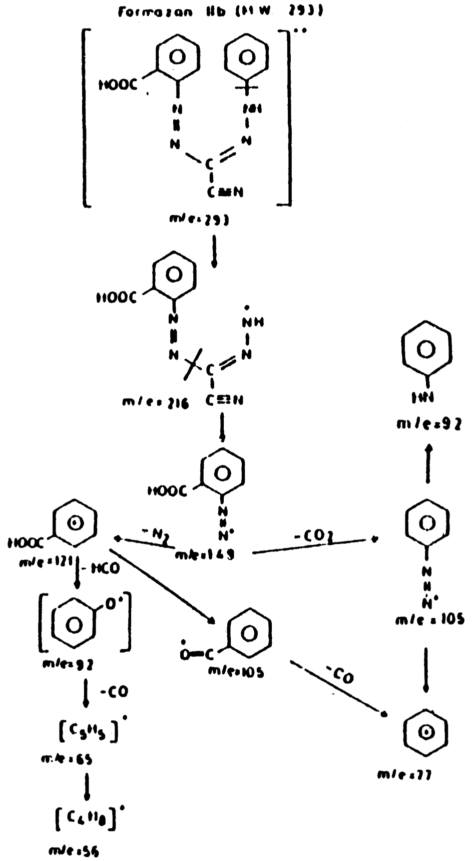


(b)

Scheme (4)
Formazan IIa M.W = 249



Scheme (5)



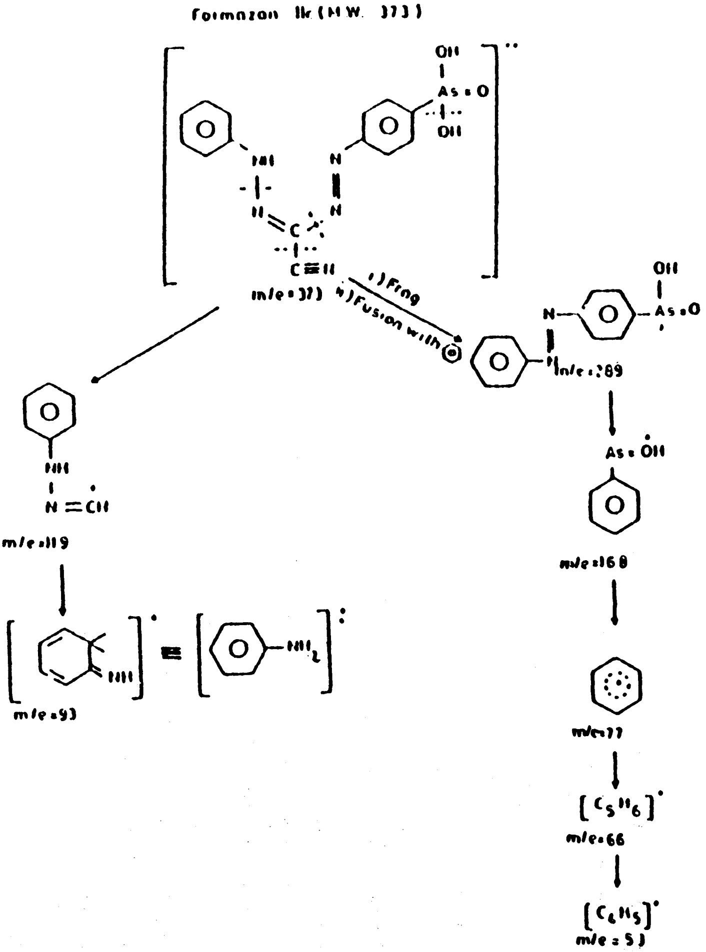
range 1550–1500 cm^{-1} while the C—N band appears within the range 1260–1200 cm^{-1}. These observations led to the conclusion that the exocyclic formazan skeleton (N═N—C═N—NH) has an asymmetrical distribution of electron density[17]. Accordingly, the formazan molecules are not resonance hybrid but tautometric pairs.

NMR spectra

The NMR spectra are useful for elucidating the molecular structure in solution. The chemical shift of the different types of protons are recorded in Table 3. The CH_3 protons of the acetyl group in case of formazans (Ia–Id) appear at 2.4–2.7 ppm. A multiplet signal observed at 6.9–8.2 ppm is due to phenyl protons for all fomazans.

The NH signal for cyanoformazans (IIa–IId) appears at lower value of chemical shift (8–14.4 ppm) while that of acetylformazans occurs at 8.3–16.2 ppm, due to a strongly hydrogen bonded N—H proton in the case of acetyl formazans. The increase in the hydrogen bond strength compared with that

Scheme (6)



observed in the IR spectra may be attributed to the effect of the polar solvent used (DMSO). Formazans IIa, Ib and Ic show the NH signal as a doublet which can be attributed to the presence of two tautometric forms[9]. The NH is influenced by varying the substituents. Introducing *o*-COOH group in one of two phenyl rings causes a strong deshielding for the imino proton, as in the case of Ib and IIb, due to the electron withdrawing property of the COOH group while the presence of the two arsonic groups causes a steric effect shifting the NH signal to 8.3 ppm and 8.2 ppm for Id and IId, respectively. The NH signal in all cases disappeared by deuteration indicating that it is an exchangeable proton.

The carboxylic proton is shielded by the electron cloud of the phenyl ring (+I effect), so its signal is shifted to higher field ($\delta = 8.3$ ppm for formazan Ib and 7.6 ppm for IIb) and in both cases the signal is obscured by the aromatic proton signals and disappeared on deuteration.

TABLE 3
PROTON NMR SPECTRAL DATA OF FORMAZANS

Compound	No. of protons	Chemical shift (δ) ppm	Band Assignment
Ia	3	2.5	(s) acetyl CH_3
	10	7.4–8	(m) aromatic C—H
	1	14.7	(s,b) NH
Ib	3	2.5	(s) acetyl CH_3
	9	7.7–8.8	(m) aromatic C—H
	1	8.3	(s) carboxylic OH
	1	16.2	(s,b) NH
Ic	3	2.5	(s) acetyl C—H
	2	4.8–5.5	(b) arsonic OH
	9	7.2–8	(m) aromatic C—H
	1	14.1	(s,b) NH
Id	3	2.5	(s) acetyl CH_3
	4	3.4–4.1	(s,b) arsonic OH
	8	7.5–8.2	(m) aromatic C—H
	1	8.3	(s) NH
IIa	10	7.3–7.9	(m) aromatic C—H
	1	12.7	(s) NH
IIb	9	7.2–7.8	(m) aromatic CH
	1	7.6	(s) carboxylic OH
	1	14.4	(s) NH
IIc	2	3.6–4.4	(s,b) arsonic OH
	9	7.5–8.2	(m) aromatic CH
	1	12.9	(s) NH
IId	4	3.6–4.2	(s,b) arsonic OH
	8	7.6–8.1	(2s) aromatic CH
	1	8.0	(s) NH

The arsonic OH band is observed for formazans Ic, Id, IIc and IId in the range 3.6–5.4 ppm as a broad singlet. If water is present, traces of which contaminate the solvent, the hydroxylic protons exchange quite rapidly with protons of water resulting in a peak at position intermediate between the actual shift position of the HOH and ROH peaks[18]. The signals disappeared on deuteration.

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