Spectral Properties of Azo Compounds 5-(4-Substituted Phenylazo)Barbituric Acid

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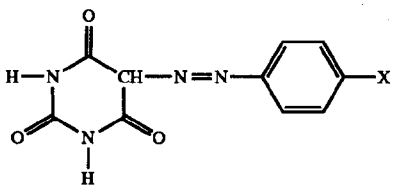
Summary: Synthesis of new 5-(54-substituted phenylazo) barbituric acid compounds was described. The spectral properties and the analytical data were used for assigning their structures. The pK values are interpreted based on the electronic characters of the substituents. Better correlation analyses are given.

Introduction

The N-heterocyclic compounds containing amide linkages are widely used in medicine, principally as hypnotic drugs and produce depressive effects on the central nervous system [1]. The barbiturates possess effects on the motor and sensory functions [2]. 5-Arylazo-barbituric acids exhibit inhibitory effects against transplantable mouse tumours [3]. In a sequel of continuation on the structural chemistry of azo compounds of different classes [4-28] the spectral properties of 5-(4-substituted phenylazo) barbituric acid (A) are investigated.



X = CH_3, OCH_3, $COCH_3$, Cl, Br, I, NO_2, SO_3H and COOH

Results and Discussion

a) NMR spectroscopy

The ^{1}H-NMR spectra of barbituric acid and its 4-substituted arylazo compounds gave the following:

i) The signals in the range 7.0-8.3 ppm are assigned for phenyl protons with total number of protons 4 except the 4-SO_3H compound where the number of protons is 5.

ii) The signals for the imino protons are in the 11.2-11.6 ppm region with a number of 2 except for the 4-Cl compound where only one broad signal appeared at δ = 12.2 ppm, due to a strong overlap between the -NH and -OH groups. The number of protons in the 4-CH_3 compound is 3.

iii The signals for the -OH proton (calculated to be 1) are in the range 13.2-14.3 ppm.

Infrared spectroscopy

The infrared spectra of barbituric acid gave four bands [32] at 3550, 3470, 3190 and 3100 cm^{-1} due to νN-H and νOH. The band at 2880 cm^{-1} is due to νCH_2. Such region identifies, also, the presence of hydrogen bond. The 1750-1700 cm^{-1} region is due to νC=O. The bands at 1415, 1365, 1285, 1235 and 1195 cm^{-1} are due to νN-H' νC-N, νC-O, νO-H and νC-N vibrations, respectively. The 680-630 cm^{-1} of splitted nature is due to νC=O. The strong absorption bands of the azo series of compounds in the 3570-3450 cm^{-1} region are due to the presence of intramolecular hydrogen bond and those at 3260-3000 and 2060-1900 cm^{-1} are due to νN-H and hydrogen bonds of the N-H-O O-H-O types. The strong bands in the 1780-1700 cm^{-1} region are assigned to νC=O and those at 1665-1650 and 1585-1'575 cm^{-1} are due to νC=N and νC=C, respectively. The azo group is identified by the presence of bands around 1510-1400 cm.$^{-1}$ The bands in the frequency ranges : 1290-1200, 695-640 1395-1295 and 880-830 cm^{-1} are due to νC-O, δ C-O, δ O-H, and γ O- H, respectively, to identify the enol tautomer. The dimeric structure [33] for the carboxylic compound was attained by the presence of a medium band at 945 cm.$^{-1}$

Electronic spectroscopy

The electronic absorption data of the 4-CH_3 and 4-OCH_3 compounds in all the selected solvents

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are assigned to the $L_{b\text{-}A}$- transition of the phenyl ring overlapped by a composite broad $\pi-\pi^*$ of azo structure (K band), beside the bands due to $n-\pi^*$ transition of CT nature with the azo group (R band) as donar (Table 2). The latter is probably subjected to strong solvation and affected by blocking the n electrons with the solvent leading to increasing localization of electrons with higher ionization. The intensity of the spectral bands in presence of DMF is lower than that in presence of DMSO. This could be related to the dielectric permitivity of the solvent εDMSO > εDMF, i.e,. more ionization in DMSO than DMF. However, 5(4-acetylphenylazo) barbituric acid (Table 2) gave three bands in dioxane with λ_{max} at 246,266, 286 nm, due to $\pi-\pi^*$ transition (L_a-A) of the phenyl ring and $\pi \rightarrow \pi^*$ transition of the phenyl ring perturbed by the substituents beside the L_b-A ($n \rightarrow \pi^*$) transition of the phenyl ring overlapped by a composite broad $\pi \rightarrow \pi^*$ of azo structure. The latter band is subjected to strong red shift in presence of the other solvents, with the existence of new bands in presence of acetic acid and acetone. These bands may be due to $n \rightarrow \pi^*$ transition. The bands of 5-(4-halogenophenylazo) barbituric acids are of strong feature in the wavelength range 246-266 nm and 376-398 nm due to $\pi \rightarrow \pi^*$ transition of phenyl ring and $n \rightarrow \pi^*$ transition of CT nature with the azo group as the donor. The first region is appeared only in presence of dioxane and basic solvents. However, the position of the second region proceeds in an irregular trend with the solvent polarity. Similar trends are recorded for compounds containing electron attracting groups (NO_2,SO_3H, COOH). The internal hydrogen bond displaces the B- and K-bands to longer wavelengths, becuase the polarity in the absorbing

Table 1: Analytical data for 5-(4-substituted phenylazo) barbituric acids.

Substituent	Colour	% Calculated/% found H	N
- CH_3	pale brown	4.1 (4.0)	22.8 (21.9)
- OCH_3	yellowish brown	3.8 (3.6)	21.4 (21.0)
- $COCH_3$	yellow	3.7 (3.5)	20.4 (20.6)
- Cl	yellow	2.6 (2.8)	21.0 (20.8)
- Br	yellow	2.3 (2.5)	18.0 (18.5)
- I	yellow	2.0 (2.4)	15.6 (15.8)
- NO_2	orange	2.5 (2.5)	25.3 (24.9)
- SO_3H	yellow	2.6 (2.9)	17.9 (17.6)
- COOH	yellow	2.9 (3.0)	20.3 (20.2)

Table 2: Solvent effects on the electronic spectra of 5-(4- substituted phenylazo) barbituric acids.

Substituent	Dioxane		50% Dioxane		$CHCl_3$	HAC	Acetone	Ethanol	Dimethyl-formamide		Dimethyl-sulphoxide		H_2O	
	λ_{max}	log ε	λ_{max}	log ε					λ_{max}	log ε	λ_{max}	logε	λ_{max}	log ε
- CH_3	254	3.944*	253	4.173	402	254, 402	390	392	262	3.812	258	3.929	400	
	314	3.707	316	3.431					315	3.778	319	3.886		
	401	3.568	396	3.707					386	3.892	390	3.929		
- OCH_3	408	4.397	420	4.414	420	420	403	412	300	2.380	300	2.505	416	
									408	4.447	400	4.505		
- $COCH_3$	246	3.942	250	3.954	400	306	328	390	270	3.763	390	4.021	392	
	266	3.989	270	3.966		392	380		388	4.458				
	386	4.531	390	4.596										
- Cl	246	4.060**	252	3.795	395	392	384	388	266	3.602	256	3.816	390	
	388	4.518	392	4.484					384	4.431	385	4.397		
- Br	250	3.880	256	3.770	396	395	386	390	266	3.342	258	3.662	388	
	388	4.195	390	4.245					386	4.201	388	4.222		
- I	246	4.096	256	3.875	--	390	376	390	266	3.544	260	3.653	390	
	392	4.384	398	4.435					390	4.327	392	4.342		
- NO_2	244	3.903	250	4.591	396	392	392	392	400	4.505	400	4.466	400	
	390	4.525	396	3.875										
- SO_3H	---		250	3.829	---	392	---	388	252	3.301	260	3.829	244	3.916
			388	4.410					389	4.332	392	4588	386	4.508
- COOH	---	---		---		388	380	388	266	3.903	260	3.942	393	
									386	4.458	388	4.021		

All are in 100% dioxane except * was in 30% and ** was in 90% dioxane.

system (in the ground state) is increased by polarization. The effect of an internal hydrogen bond on R-bands is in contrast to B-and K-bands and are known to be displaced to shorter wavelengths. The internal hydrogen bond was suported by the charcteristic blue shift of λ_{max} in ethanol and water, respectively [44] where:

i) Those causing red shift from ethanol to water are derived from 4- CH_3, 4-OCH_3, 4-$COCH_3$, 4-Cl, 4-NO_2 and 4-COOH substituents. This is attributed to the predominant contribution of polar structures to the excited state stabilized by solvent polarity with the presence of an external hydrogen bond, i.e., more solvation with the solvent [45].

ii) The -Br and -SO_3H compounds are with internal hydrogen bond [46].

iii) The iodo compound exists in the neutral structure.

The intramolecular hydrogen bond favours some sort of coplanarity due to the chelation with the adjacent two nitrogens of the azo group with five and six membered skeletons. From the electronic spectral data, the phenomena of tautomerism is apparent mainly in case of 4-CH_3 and 4-$COOCH_3$ compounds. The mesomeric and inductive effects of the substituents affect the formation of the intramolecular hydrogen bonding. This favours the coplanarity of the chelate ring formed. The presence of π-electron attracting substituents leads to that the CT originates from the barbiturate moiety as a donor system to the phenyl ring carrying the acceptor group through the azo.

The effect of pH on the electronic spectra of organic compounds gave different λ_{max}, with some iosbestic points (Table 3). The shorter wavelength region is due to the electron transitions (up to 250 nm) mainly of the $\pi-\pi^*$ type while the longer wavelength side (225 nm) is mainly of the $n \rightarrow \pi^*$ type. Different positions are available for protonation : NH, C=O and N=N to give NH^+, $C=O^+$, $N^+=N$, respectively. The proton is bound symmetrically to both N atoms [34], i.e., acts as a single basic site [35] or in the form of $\pi-$complex [36]. The azo group can act as a proton acceptor in hydrogen bonds. The aromatic azo compounds are resonance stabilized. The hydrazone-azo tautomerism can be strongly influenced by synergetic tautomerism in another portion of the molecule [37,38]. For the absorbance-pH relationships, the half-height [39], the Colleter [40] and the modified-limiting absorption [41] methods gave concordant results. All the compounds, except the 4-CH_3 and the 4-COOH compounds, gave pK values in the range 7.6-11.3 due to the ionization of -OH group [42]. The pK value for the carboxylic compound (4.35) is due to the ionization of the carboxylic group rather than the hydroxy group. The decrease of the pK value from the 4-Cl or the 4-Br compounds is due to the electrogenativity difference between both substituents. The large decrease of 4-NO_2 compound is due to the strong electron attracting property of the substituent. The higher pK

Table 3. Summary for the pK values of 5-(4-substituted phenylazo) barbituric acid by spectral methods.

Subsiti-tuent	λ_{max} nm	isobestic point nm	Half height		Modified limiting absorption		Collecter	
			pK_1	pK_2	pK_1	pK_2	pK_1	pK_2
-CH_3	250,312,400	276	5.80	-	5.83	-	5.72 ± 0.11	-
-OCH_3	220, 414	390	9.25	-	9.21	-	9.17 ± 0.23	-
-$COCH_3$	270, 395	-	7.80	-	7.77	-	7.75 ± 0.40	-
-Cl	250, 392	384	8.70	-	8.71	-	8.74 ± 0.26	-
-Br	230,395	-	8.30	11.10	8.32	11.12	8.35 ± 0.35	11.15 ± 0.11
-I	230, 395	330	7.80	-	7.83	-	7.85 ± 0.27	-
-NO_2	255, 405	420	7.60	-	7.62	-	7.64 ± 0.25	-
-SO_3H	230,390	316, 370 428	8.10	11.30	8.12	11.01	8.08 ± 0.33	11.31 ± 0.22
-COOH	230, 395	375	4.30	-	4.41	-	4.30 ± 0.19	-

value of the sulphonic group [43] (Table 3) is obtained.

Correlation analysis

The pK values are related to the Hammet constant (Fig. 1a), while the 4-CH_3 and 4-COOH compounds are scattered from linearity, due to the existence in associated structure through intramolecular hydrogen bond.

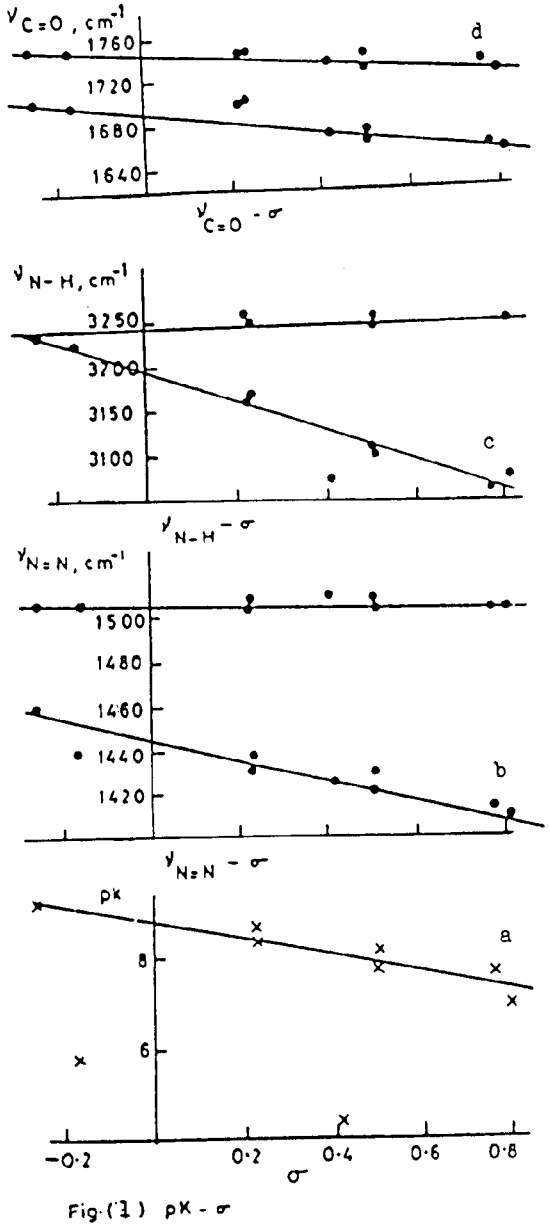
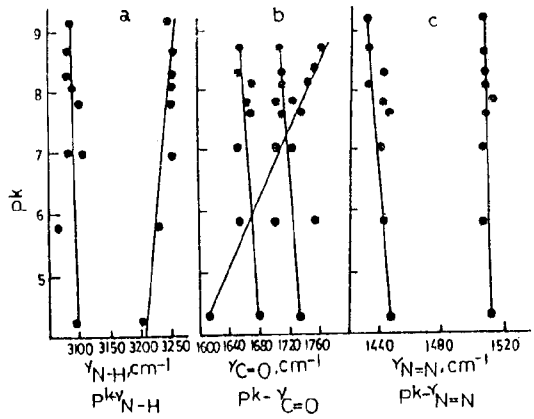


Fig. (1) pK - σ

The position of νN=N, νN-H and νC=O is related to σ. Two major bands are assigned for νN=N at 1410-1460 and 1510 $cm.^{-1}$ The latter is independent of the electronic requirements of the substituents while the former one is the most affected (Fig. 1b). Similarly, two characteristic bands for the N-H group are at 3240 cm^{-1} (νs) and in the range 3060-3220 cm^{-1} (ν_{as}). The former is independent of the electronic characters of the substituents, while the latter is experienced by the substituent (Fig. 1c). The two carbonyl bands are affected by the Hammett constant values (s), in a similar trend (Fig. 1d). The stretching vibrations of νN-H, νC=O and νN=H are related to the pK values where best-fit straight lines are obtained. The pK- νC=O relation gave three lines, two of them are paralle to each other and the third one is of opposite direction. This supports the presence of two fundamental carbonyl groups whiled the third one is tautomerized to enol. The latter interacts with the azo group through hydrogen bond with the production of N-H group (Fig. 2,a,b,c,d).



Experimental

The organic compounds were prepared by direct diazotization of barbituric acid as reported [29]. The analytical data (Table 1) are in concordnace with the proposed formulas.

The electronic absorption spectra were measured using a PYE UNICAM SP 1750 spectrophotometer covering a range from 190-900 nm. The infrared spectra were taken in KBr discs using Sp 2000 PYE UNICAM covering the range 4000-200 $cm.^{-1}$ The ^{1}-NMR spectra were recorded on EM-390 90 MHz NMR spectrometer in 6_d-DMSO. TMS was used as internal standard.

Universal buffer solutions were prepared [30] and the pH values were checked by using a PYE UNICAM pH Meter Model 291 MK_2. The solvents were purified as reported [31].

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