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Absorption Spectra of Heterocyclic Compounds. Some 6-Hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazoles and Their Quaternary Derivatives

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Some 2-alkyl-6-hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazoles have been synthesised. Their absorption spectra at different pH show bathochromic shift of the absorption band in the longer wavelengths, which is more pronounced in basic medium. This is ascribed to the dipolar nature of the compounds. Quaternary derivatives of the compounds show a further red shift in the absorption band in the visible region, which further corroborates their dipolar nature.

Imidazoles long considered to be cyclic amidines[1] are the most basic of the imide containing azoles.[2] Since imdazole derivatives occupy an important position with respect to the constitution of heterocyclic as well as in biochemistry, their physical properties have been investigated extensively. Although it has not been established unequivocally that the nucleus has true conjugated double bond character, imidazoles have been shown to be cyclic amidines with charges present on the nitrogen atoms in a system possessing some degree of hindered resonance. It is also apparent that the ring system possesses greater polarity than the related pyrazole but not to the extent expected from classical polar formula.

During the course of spectral study and synthesis of some donor acceptor systems in our laboratory,[3–6] benzimidazole moiety with two nitrogen atoms was selected as donors for further investigations. A perusal of literature reveals that no work has been done on the reaction of 5-alkyl-2-amino-1,3,4-thiadiazole with *p*-benzoquinone. We now report the synthesis of some new 6-hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazoles. The structure is of particular interest as it possesses the phenolic hydroxyl group as an acceptor and the two nitrogen atoms of the imidazole moiety as a donor, thereby facilitating the molecule to assume dipolar structure through internal charge transfer reaction. The hydroxythiadiazolobenzimidazoles were quaternized with ethyl bromide giving the corresponding 2-alkyl-9-ethyl-6-hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazolium bromides. The quaternary compounds gave intense yellow colour with dilute aqueous alkali due to the formation of internal charge transfer compounds, phenol betaines.[7,8]

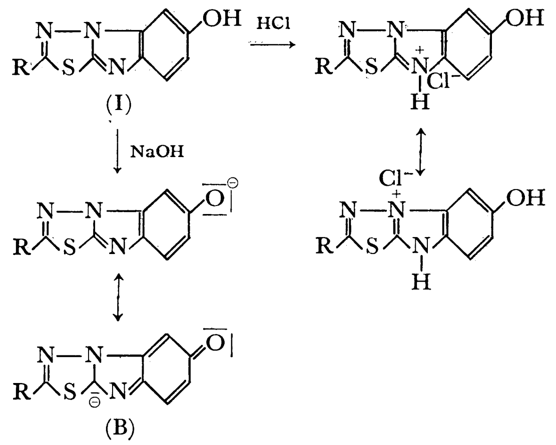
Table 1. 2-Alkyl-6-hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazoles

Compd No.	R	Molecular formula	Mp °C	% Analysis			Yield %	UV spectra					
					Calcd	Found		Ethanol		0.1 M HCl		0.1 M NaOH	
								λ_{max} nm	log ε	λ_{max} nm	log ε	λ_{max} nm	log ε
1	H	$C_8H_5N_3SO$	285 (dec)	C,	50.2	50.1	62	237	4.33	317	3.81	310	3.62
				H,	2.6	2.4		260	3.81	382	3.75	465	3.67
				N,	21.4	20.8		365	3.62				
2	CH_3	$C_9H_7N_3SO$	337	C,	52.6	52.1	55	241	4.21	312	3.80	303	3.57
				H,	3.4	3.1		255	3.80	376	3.71	453	3.61
				N,	20.4	20.1		371	3.85				
3	C_2H_5	$C_{10}H_9N_3SO$	345	C,	54.7	54.2	48	232	4.27	305	3.73	307	3.58
				H,	4.1	3.7		251	3.75	370	3.65	460	3.61
				N,	19.1	18.8		359	3.71				
4	$CH_3(CH_2)_2$	$C_{11}H_{11}N_3SO$	360	C,	56.6	56.1	50	228	4.12	325	3.84	322	3.61
				H,	4.7	4.1		259	3.93	380	3.77	450	3.72
				N,	18.2	17.7		360	3.67				
5	$(CH_3)_2CH$	$C_{11}H_{11}N_3SO$	360	C,	56.6	55.9	35	235	4.15	315	3.73	307	3.81
				H,	4.7	4.3		315	3.83	375	3.52	435	3.54
				N,	18.2	17.9		359	3.97				
6	$CH_3(CH_2)_3$	$C_{12}H_{13}N_3SO$	360	C,	58.2	57.8	54	247	4.25	328	3.67	325	3.74
				H,	5.2	5.1		263	4.10	385	3.74	459	3.81
				N,	17.0	16.4		375	3.78				
7	$(CH_3)_2CH_2CH$	$C_{12}H_{13}N_3SO$	354—355	C,	58.2	57.9	63	271	4.07	345	3.81	351	3.57
				H,	5.2	4.9		310	4.29	397	3.72	475	3.74
				N,	17.0	16.6		364	4.31				
8	$CH_3(CH_2)_4$	$C_{13}H_{15}N_3SO$	305 (dec)	C,	59.7	58.9	49	258	4.35	330	3.62	323	3.04
				H,	5.7	5.1		302	3.97	359	3.71	445	3.34
				N,	16.0	15.3		352	4.12				

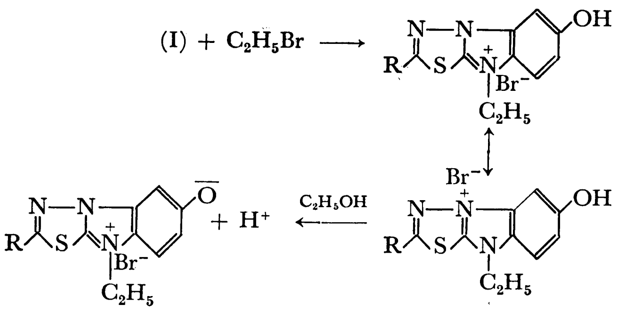
Results and Discussion

The gross structure of these compounds has been determined on the basis of infrared spectra and elemental analysis. The spectra showed the following characteristic bands at 3200, 1210 (phenolic–OH), 1610 (C=N, C=C), 1315 (C–N), 1505 cm^{-1} (aromatic ring breathing).

We see from Table 1 that the absorption spectra of various 2-alkyl-5-hydroxythiadiazolobenzimidazoles in ethanol at different pH show a characteristic bathochromic shift of the absorption maxima in the longer wavelengths in both acidic as well as alkaline medium. No zwitterionic structure is expected in strongly alkaline medium. The observed bathochromic shift might be explained by the following canonical quinoid structure (B).



The same phenomenon is observed when these compounds are quaternized with ethyl bromide which gives rise to further red shift of absorption maxima in the visible region. This should be caused by the partial dissociation of quaternary *N*-ethylimidazoliumbromides into the dipolar betaine structure in ethanol (Table 2).



Reaction Mechanism. The following reaction mechanism is suggested for the formation.

(1) Amino group by nucleophilic addition and elimination of water gives intermediate (a)

(2) (a) on reaction with proton of acid gives (b) which causes shift of electrons, giving the final product (c).

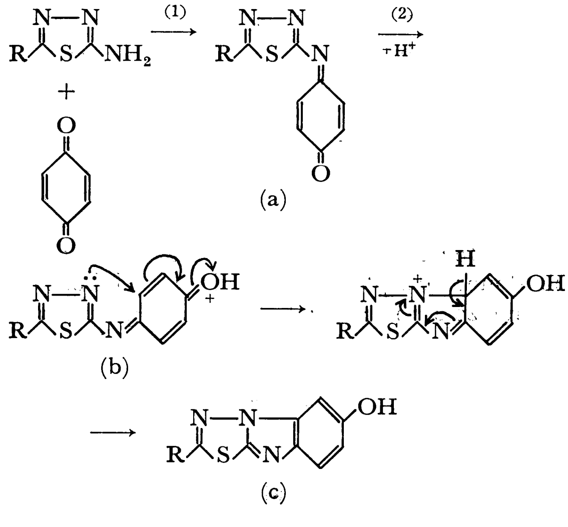


Table 2. 2-Alkyl-9-ethyl-6-hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazolium bromides

Compd No.	R	Molecular formula	Mp °C	Yield %	% Analysis Calcd	% Analysis Found	UV spectra Ethanol λ_{max} nm	UV spectra Ethanol log ε
1	H	$C_{10}H_{10}N_3SOBr$	276	56	N, 14.0	13.2	285	4.15
					Br, 26.6	25.8	505	3.80
2	CH_3	$C_{11}H_{12}N_3SOBr$	308	50	N, 13.3	12.7	257	3.92
					Br, 25.4	24.8	512	3.95
3	C_2H_5	$C_{12}H_{14}N_3SOBr$	327	47	N, 12.8	12.2	263	3.84
					Br, 24.3	23.7	521	4.01
4	$CH_3(CH_2)_2$	$C_{13}H_{16}N_3SOBr$	335	45	N, 12.2	11.7	276	3.51
					Br, 23.3	22.8	515	3.84
5	$(CH_3)_2CH$	$C_{13}H_{16}N_3SOBr$	351	40	N, 12.2	11.9	258	3.62
					Br, 23.3	22.6	485	3.91
6	$CH_3(CH_2)_3$	$C_{14}H_{18}N_3SOBr$	343	48	N, 11.7	11.2	270	3.83
					Br, 22.4	21.9	495	3.95
7	$(CH_3)_2CHCH_2$	$C_{14}H_{18}N_3SOBr$	315	55	N, 11.7	11.5	265	3.93
					Br, 22.4	22.1	525	3.97
8	$CH_3(CH_2)_4$	$C_{15}H_{20}N_3SOBr$	267—268	43	N, 11.3	10.8	273	3.79
					Br, 21.6	20.9	508	3.81

Experimental

All the reagents were thoroughly dried and purified before use. Melting points were determined on a Kofler instrument and are uncorrected. IR spectra were recorded on a Perkin-Elmer 677 Spectrophotometer in KBr. UV absorption spectra were recorded on a Beckman Spectrophotometer, Model DU-2, using 1 cm path length quartz cells.

5-Alkyl-2-amino-1,3,4-thiadiazole. The compounds were prepared by known methods.[9]

*2-Alkyl-6-hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazoles (I).* A solution of *p*-benzoquinone (0.01 mol) in glacial acetic acid (10 ml) was added in small portions to the 5-alkyl-2-amino-1,3,4-thiadiazole (0.01 mol) in acetic acid (10 ml) with shaking. The mixture was left to stand for 2 days. To this was added 20 ml of 50% HCl and the solution was diluted with water. It was extracted with ether to remove any unreacted quinone and hydroquinone. The resulting solution was made alkaline with sodium carbonate solution when the desired compound precipitated. After treatment with charcoal in ethanol, the compound was recrystallised from ethanol. The yields, mp *etc.* are given in Table 1.

*2-Alkyl-9-ethyl-6-hydroxy[1, 3, 4]thiadiazolo [2, 3-*b*]benzimidazolium Bromides (II).* The requisite amount of 2-alkyl-6-hydroxy[1,3,4]thiadiazolo[2,3-*b*]benzimidazole was dissolved in 1:1 ethanol–acetone solution and was boiled under reflux with excess of ethyl bromide on a water bath for 3 h, when the desired *N*-ethylimidazolium bromide was partly separated out. Excess solvent was removed by distillation on a water bath and the product was recrystallised from acetone or ethanol. The yields, mp *etc.* are given in Table 2.

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