

ABSORPTION SPECTRA OF 9-NITROACRIDINE, 6-NITROACRID-9-ONE, AND THEIR METHOXY DERIVATIVES

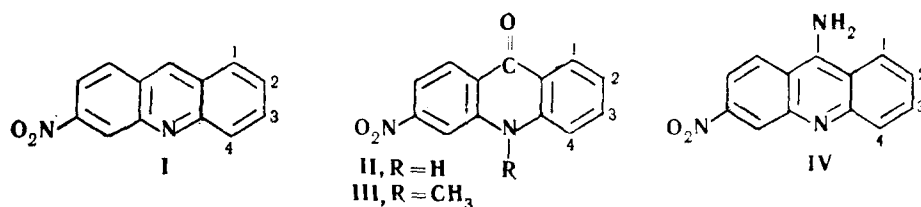
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The UV spectra of 6-nitroacridine (I), its 1-, 2-, 3-, and 4-methoxy derivatives (Ia-d), of 6-nitroacrid-9-one (II) and its analogous methoxy derivatives (IIa-d) are investigated in natural and acid solvents, and also in 2 M sodium ethoxide solution, and the IR spectra of II and IIa-d are also investigated.

The UV spectra of derivatives of acridine and acrid-9-one have not previously been studied. Only 2-nitroacrid-9-one has been investigated in the IR region [1]. To elucidate the structures of I and II, and of their methoxy substituted derivatives (Ia-d, IIa-d)* studies were made of their UV absorption spectra in dioxane, ethanol, 5 M ethanolic HCl, concentrated H_2SO_4 , 72% $HClO_4$, and 2 M sodium ethoxide, as well as of the IR spectra of II and IIa-d.

For comparison, measurements were made of the UV spectra of the 10-methyl derivatives of compounds IIIa-d, 6-nitro-9-aminoacridine (IV) and its 1-, 2-, 3-, and 4-methoxy derivatives (IVa-d).



The table gives the characteristics of the UV absorption curves.

Experimental

The UV spectra were measured with a SF-4 spectrophotometer. The IR spectra (tabletted with KBr) were measured with a UR 10 spectrophotometer (NaCl prism).

Compounds I [2], II [3], and IV [4] were prepared by known methods. The syntheses of Ia-d [5], IIa-d [6], and IVa-d [5] have previously been described by the present authors.

10-Methyl-3-methoxy-6-nitroacrid-9-one (IIIc). 2.9 g (0.01 mole) 3-methoxy-6-nitro-8-chloroacridine [6] and 3.5 g (0.02 mole) methyl benzene sulfonate were heated together for 1 hr at 130° . After cooling the crystals which separated were filtered off, washed with EtOH, and dried. Yield 2 g (70%). Dark yellow needles from dimethylformamide, mp 260° - 261° C. Found: N 9.59, 9.71%. Calculated for $C_{15}H_{12}N_2O_4$: N 9.86%.

10-Methyl-1-methoxy-6-nitroacrid-9-one (IIIa). This could not be prepared by the above method as the starting mesochloroacridine hydrolyzed very rapidly. 1.35 g (0.005 mole) IIa was dissolved in 20 ml 0.5 M solution of Na in MeOH, then 1.4 g (0.01 mole) MeI added through a reflux condenser. The mixture was heated for 6 hr on a water bath, the precipitate filtered off, washed with MeOH, and recrystallized from aqueous dimethylformamide. Yield 0.36 g (25%), reddish-brown needles, mp 321° - 322° C. Found: N 9.98, 10.02%; Calculated for $C_{15}H_{12}N_2O_4$: N 9.86%. Compounds IIIa and IIIc are not described in the literature.**

Discussion

Introduction of the methoxy group at position 1, 2, 3, or 4 in the I molecule results in appearance of a longwave absorption band (Table 1). As such a band is not characteristic of analogous methoxy derivatives of acridine [7], it must be ascribed to interaction between OMe and NO_2 groups in Ia-d. The places of the substituents with respect to one another indicate that such interaction will be strongest with Ib; obviously, therefore, the longwave band will be far

* OMe position: a = 1, b = 2, c = 3, d = 4.

** Specimens of IIIb and IIIc (respective mps 314° - 315° and 222° - 223° C), were kindly supplied to us by N. N. Dykhanov and V. I. Kikhteva for investigation of their UV spectra. We also obtained compound IIIb (mp 314° - 315° ex aqueous dimethylformamide) by the method used for IIIc.

Table 1

UV Spectra Absorption Maxima for 6-Nitroacridine (I) and its 1-, 2-, 3-, and 4-Methoxy Derivatives (Ia-d)

Compound number	Solvent									
	Dioxane		EtOH		5 M ethanolic HCl		Concentrated H ₂ SO ₄		2 M NaOEt	
	$\lambda_{max}, m\mu$	lg ϵ	$\lambda_{max}, m\mu$	lg ϵ	$\lambda_{max}, m\mu$	lg ϵ	$\lambda_{max}, m\mu$	lg ϵ	$\lambda_{max}, m\mu$	lg ϵ
I	398*	3.40	404*	3.37	430	3.59	434	3.47	490*	2.65
	362	3.85	362	3.87	364	4.20	365	4.21	350	4.48
	345	3.85	345	3.85	346	4.00	350	4.06	240	4.52
	293	4.39	295	4.40	285	4.44	297	4.34		
	239	4.62	240	4.60	240	4.58	240	4.60		
Ia	419	3.45	426	3.45	480	3.49	480	3.67	502*	2.84
	350	3.58	350	3.60	364	3.78	359	4.22	474	2.96
	302	4.45	303	4.46	351	3.90	342*	4.15	363	4.44
	245	4.61	245	4.60	300	4.48	302	4.46	245	4.44
					246	4.50	244	4.57		
Ib	390	4.00	398	3.95	452	3.69	456	3.62	493*	3.10
	305	4.52	306	4.51	382	4.05	379	4.02	460	3.24
	245	4.68	245	4.65	363*	3.83	310	4.32	350	4.41
					306	4.44	251	4.55	249	4.40
					252	4.51				
Ic	406	3.58	410	3.56	427	3.76	440	3.84	500*	2.71
	355	4.19	355	4.16	369	4.22	372	4.43	478	2.80
	338	4.16	338	4.18	352	4.07	296	4.29	345	4.34
	309	4.42	310	4.40	302*	4.20	249	4.65	240	4.37
	240	4.71	240	4.71	245	4.49				
Id	419	3.54	425	3.54	465	3.27	475	3.29	502*	2.43
	370	3.49	370	3.49	368	3.82	360*	4.06	467	2.60
	353	3.60	353	3.61	352	3.83	297	4.51	354	4.36
	304	4.50	304	4.48	296	4.51	250	4.42	240	4.41
	238	4.58	240	4.55	250	4.41				

* Approximate values of band inflections.

The UV spectra (Table 1) indicate that in acids, compounds I and Ia-d form, analogous to acridine [8], the corresponding acridinium cations V.

I and Ia-d give colored solutions in 2 M sodium ethoxide, and the absorption spectra of these differ sharply from those of solutions in neutral solvents (Table 1), but dilution of these solutions leads to disappearance of the color, and the absorption curves become identical with those of solutions in ethanol.

Among aromatic nitro compounds, very similar behavior is shown by m-dinitrobenzene and its derivatives, whose absorption spectra in sodium ethoxide solution have been investigated in detail [9, 10].

It can be assumed that, like m-dinitrobenzene, I and Ia-d form unstable addition products of quinoid structure (VI), which explains the colors of the solutions, and the sharp change in UV spectra.

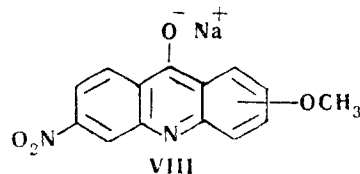
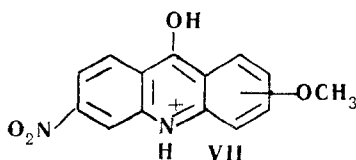


Table 2

UV Absorption Maxima of 6-Nitroacrid-9-one (II) and its 1-, 2-, 3-, and 4-Methoxy Derivatives (IIa-d) in Acid and Neutral Solvents

Compound number	Solvent										Corresponding 10-methyl derivative (IIIa-d) in EtOH	
	Dioxane		EtOH		5 M ethanolic HCl		Concentrated H ₂ SO ₄		72% HClO ₄			
	λ_{max} , m μ	lg ϵ	λ_{max} , m μ	lg ϵ	λ_{max} , m μ	lg ϵ	λ_{max} , m μ	lg ϵ	λ_{max} , m μ	lg ϵ	λ_{max} , m μ	lg ϵ
II	420	3.65	425	3.59	420	3.70	425	3.62	420	3.60	—	—
	336	3.42	335	3.35	350	3.45	350*	3.80	350	3.76	—	—
	321*	3.44	320*	3.39	335	3.54	300	4.40	337	3.79	—	—
	264	4.52	266	4.45	292	4.29	265*	4.41	295	4.32	—	—
	225	4.38	229	4.29	257	4.46	240	4.69	265*	4.31	—	—
				235	4.38			240	4.59	—	—	
IIa	420	3.70	426	3.65	440	3.56	440	3.65	450	3.60	428	3.55
	342*	3.93	342*	3.86	355*	3.52	360*	3.66	362*	3.92	343	3.78
	333*	3.87	332*	3.85	333*	3.75	332*	3.98	295	4.36	270	4.48
	266	4.64	267	4.58	295	4.37	295	4.32	277*	4.38	233	4.30
	230	4.51	231	4.40	272	4.36	268*	4.45	242	4.40		
				240	4.44	240	4.53					
IIb	436	3.70	445	3.69	440	3.72	445	3.78	445	3.65	452	3.66
	345*	3.44	345*	3.41	365	3.54	362*	3.85	365	4.10	352*	3.52
	298*	4.25	300*	4.22	350	3.57	308	4.48	305	4.55	305*	4.25
	268	4.45	270	4.39	305	4.42	250	4.64	252	4.54	271	4.46
	244	4.30	245	4.35	252	4.48					247	4.32
	227	4.32	227	4.30						227	4.31	
IIc	410	3.65	414	3.60	413	3.67	415*	3.52	415*	3.48	420	3.70
	340*	3.74	340*	3.70	362	4.15	363	4.08	362	4.10	342	3.80
	304*	4.00	306	4.04	310*	4.16	312*	4.00	312*	4.08	308*	4.06
	262*	4.51	270	4.43	256	4.64	253	4.52	254	4.60	274	4.49
	248	4.74	248	4.66							251	4.70
IIr	425	3.66	430	3.61	440	3.56	450	3.51	450	3.53	440	3.71
	345	3.69	344	3.65	342*	3.60	345*	3.85	346*	3.91	342	3.70
	332	3.68	332	3.65	296	4.29	306*	4.35	306*	4.30	272	4.63
	266	4.62	269	4.55	274	4.44	276	4.47	280	4.45	231	4.37
	230	4.41	230	4.36	240	4.42	242	4.53	241	4.50		

*. Approximate values of band inflections.

The absorption curves of IIa-d in ethanol closely resemble those of the 10-methyl derivatives (IIIa-d) (Table 2), indicating an oxo structure for IIa-d. An oxo structure for II and IIa-d is also confirmed by their IR spectra exhibiting intense bands (at, respectively 1627, 1630, 1633, 1630 and 1629 cm⁻¹) which can be ascribed to characteristic vibrations of the CO group.

Unlike what is true for I, introduction of a methoxy group into the II molecule does not give rise to a new long-wave band in the UV spectrum. This can be put down to the nonaromatic internal ring of structures IIa-d hindering interaction between the OMe and NO₂ groups. The UV spectrum curves for II and IIa-d in acids approximate those of acid solutions of I and Ia-d (Table 2). This is further evidence in favor of our previous conclusion [11] that a proton of the acid adds to oxygen of the CO group to give the corresponding 9-hydroxyacridinium cation (VII). However, the characteristic bathochromic longwave absorption band shift with II and IIa-d in acid solution is by far weaker. Evidently, unlike what one obtains with acrid-9-one [11], salt formation with II and IIa-d is incomplete even in 72% HClO₄. Evidently the reason for that is the known [12] enhanced acidic behavior of acrid-9-one derivatives.

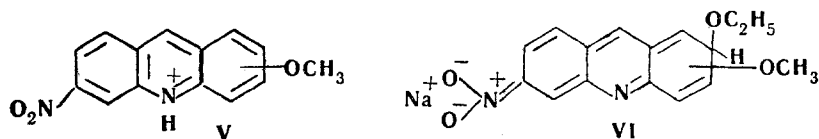


Table 3

Absorption Maxima in the UV Spectra of 6-nitroacrid-9-one II and its 1-, 2-, 3-, and 4-Methoxy Derivatives
IIa-d, in 2 M NaOEt Solution

Position of methoxy group	6-Nitroacrid-9-one (II) and its 1-, 2-, 3-, and 4-methoxy derivatives (IIa-d) in 2 M NaOEt solution		6-Nitro-9-amino-acridine IV and its 1-, 2-, 3-, and 4-methoxy derivatives (IVa-d) in EtOH	
	λ_{max} , m μ	lg ϵ	λ_{max} , m μ	lg ϵ
—	470	3.70	450	3.73
	385	3.85	380	3.71
	322	4.30	320	4.28
	290	4.73	282	4.62
	242	4.60	240	4.58
1	485	3.48	460	3.46
	388	3.84	386	3.70
	324*	4.06	318*	4.00
	288	4.52	282	4.42
	243	4.48	242	4.39
2	485	3.68	455	3.70
	395	3.79	395	3.62
	332	4.45	328	4.43
	294	4.56	285	4.34
	255	4.70	255	4.57
3	470	3.47	445	3.60
	370*	3.75	368*	3.82
	332	4.16	329	4.25
	295	4.49	282	4.52
	258	4.64	258	4.70
4	480	3.62	455	3.65
	385	3.89	385	3.73
	319*	4.20	316*	4.22
	287	4.55	280	4.55
	242	4.55	243	4.54

* Approximate values of band inflections.

The resemblance of the absorption spectra of II and IIa-d in 2 M sodium ethoxide to the spectra of, respectively, IV and IVa-d in ethanol (Table 3) indicates that in the presence of sodium ethoxide II and IIa-d are (like acrid-9-one too [11]) converted into acridolates (VIII), which are derivatives of the tautomeric hydroxy form.

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