ABSORPTION SPECTRA AND STRUCTURE OF THIOACRIDONE

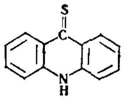
V. P. Maksimets and O. N. Popilin

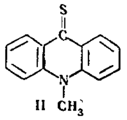
Khimiya Geterotsiklicheskikh Soedinenii, Vol. 6, No. 2, pp. 191–193, 1970

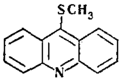
UDC 547.835.5.543.422

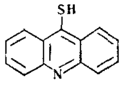
The UV spectra of thioacridone (I), 10-methylthioacridone (II), and 9-methylthioacridine (III) in neutral and acid solutions, and also the IR spectra of I–III as solids have been studied. The suggestion is put forward of the existence of two tautomeric forms in neutral solutions of I. In acids, I and II form the corresponding 9-mercaptoacridine cations. In the solid state the molecules of I are associated and possess the thione structure.

On the basis of its UV spectrum in methanolic solution thioacridone is ascribed the thione form (I). With the object of verifying this assumption we have studied the UV spectra of I in heptane, ethanol, dioxane, and 60% aqueous dioxane. For comparison we measured the spectra of II (thione form) and III (thiol form).


I


II


III


IV

In all the solvents mentioned the spectra of I were similar to the spectra of II and differed from the absorption pattern of III. However contrary to published opinion [1], the similarity in the absorption of I and II was not complete since in the spectrum of I, in contrast to II, bands were found at 256 and 365 nm, which are characteristic for III (table, Fig. 1).

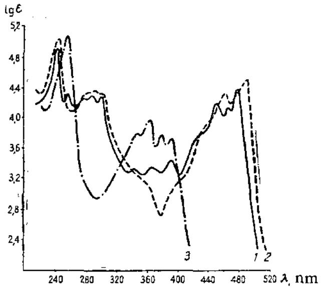
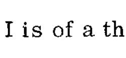


Fig. 1. UV spectra (in dioxane). 1) I; 2) II; 3) III.

It may be assumed that in solution I is present not only in the thione form (I) but also partly in the tautomeric thiol form (IV), although spectroscopically (as in acridone [2]) a shift of the I ⇄ IV equilibrium cannot be observed on changing the polarity of the solvent (table, Fig. 1).

To establish the structure of the salts of I with acids, the spectra of I–III in conc H_2SO_4 and 72% $HClO_4$ were studied. Comparison of the spectra (table, Fig. 2) disclosed their close similarity, which indicates the formation by I and II in acids of the corresponding cation of 9-mercaptoacridine (V), similar to the cation of 9-methylthioacridine (VI). Thus, the salt formation of I and II occurs similarly to that of acridone and 10-methylacridone [3].


V
R=H, CH$_3$


VI

The IR spectra of I–III are given in Fig. 3. Compound I is of a thioamide vinylog, and in the spectrum of I and

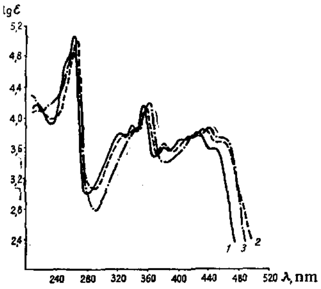


Fig. 2. UV spectra (in conc H_2SO_4). 1) I; 2) II; 3) III.

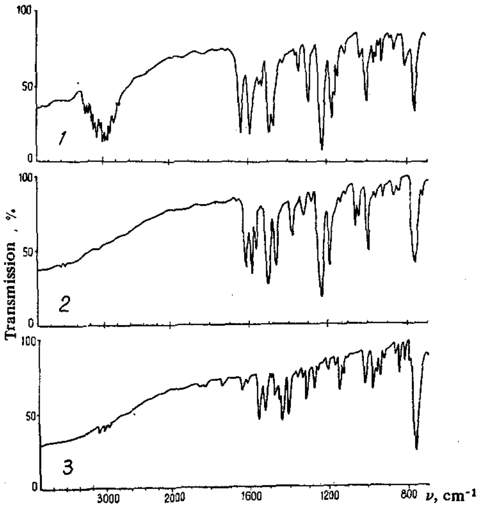


Fig. 3. IR spectra: 1) I; 2) II; 3) III.

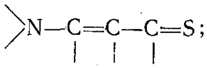
Absorption Maxima in the UV Spectra of Thioacridone (I), 10-Methylthioacridone (II), and 9-Methylthioacridine (III)

Compound	Solvent							
	Heptane		Ethanol		60% Aqueous dioxane		72% $HClO_4$	
	λ_{max}, nm	lg ε	λ_{max}, nm	lg ε	λ_{max}, nm	lg ε	λ_{max}, nm	lg ε
I*	—	—	241	4.83	242	4.93	264	5.07
			255	4.34	256	4.36	323	3.79
			284	4.28	290	4.40	340	3.88
			319	3.50	320	3.61	355	4.16
			335	3.40	335	3.44	380	3.61
			345**	3.35	345**	3.40	405	3.72
			363	3.28	364	3.30	426	3.79
			382	3.23	385**	3.20	448	3.59
			401	3.42	405**	3.48		
			425	3.74	425	3.80		
			450	4.17	450	4.20		
			480	4.30	480	4.45		
II	241	5.03	242	4.92	244	4.95	267	5.00
	285	4.38	287	4.36	292	4.45	328	3.76
	350**	3.25	350**	3.30	350**	3.40	346	3.85
	430**	4.00	408**	3.37	410**	3.40	360	4.10
	455	4.50	430**	3.75	433**	3.85	382	3.63
	470	4.48	460	4.32	460	4.42	413	3.74
	485	4.55	477**	4.27	490	4.50	435	3.84
			490	4.48			462	3.67
III	255	5.16	256	5.10	256	5.15	264	4.90
	351	3.88	350**	3.77	351**	3.69	345**	3.86
	365	4.02	365	4.00	365	3.98	363	4.17
	376	3.86	380	3.81	382	3.70	420**	3.72
	390	3.76	394**	3.60	394**	3.65	438	3.82
							460**	3.60

---

*Compound I is insoluble in heptane.

**Approximate values for inflections in the bands.

also its 10-methyl derivative II bands appear which are characteristic of thioamides [4]. The strong bands 1490 cm^{-1} (I) and 1496 cm^{-1} (II) are due to the presence of the grouping  $>N-\overset{|}{C}=\overset{|}{C}-\overset{|}{C}=S$; the bands at 1230 cm^{-1} (I) and 1235 cm^{-1} (II) correspond to the stretching vibrations of C=S. In the spectrum of I a NH stretching vibration band is shown which disappears on N-methylation (II); the position of this band (~ 3000 cm^{-1}) indicates association of the molecules of I. There is no ν_{SH} band in the 2600–2550 cm^{-1} region. Thus in the solid state I has the thione type of structure. The spectrum of III exhibits a band at 1320 cm^{-1} which can be assigned to $S-CH_3$ vibrations [4].

EXPERIMENTAL

UV spectra were measured on an SF-4 spectrophotometer, and IR spectra on a UR-10 spectrometer (KBr discs).

Thioacridone (I) [5], 10-methylthioacridone (II) [6], and 9-methylthioacridine (III) [7] were synthesized by known methods and were purified by 2–3 recrystallizations from a suitable solvent: I from 70% aqueous dimethylformamide (mp 275° C); II from xylene (mp 263° C); III from heptane (mp 114° C).

REFERENCES

1. R. M. Acheson, M. L. Burstall, C. W. Jefford, and B. F. Sansom, J. Chem. Soc., 3742, 1954.
2. Yu. N. Sheinker and Yu. I. Pomerantsev, ZhFKh, 30, 79, 1956.
3. A. K. Sukhomlinov and V. P. Maksimets, KhGS [Chemistry of Heterocyclic Compounds], 416, 1966.
4. K. Nakanishi, Infrared Spectra and Structure of Organic Compounds [Russian translation], Mir, Moscow, 66, 1965.
5. O. M. Cherntsov, ZhOKh, 14, 186, 1944.
6. K. Gleu and R. Schaarschmidt, Ber., 72, 1246, 1939.
7. Alb. Edinger and W. Arnold, J. pr. Chem., 64, 471, 1901.

19 December 1967

Khar'kov Institute of Public Nutrition