INVESTIGATION OF THE ELECTRONIC SPECTRA OF ALKOXY-SUBSTITUTED AMINO AND OXO DERIVATIVES OF s-TRIAZINE

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The literature contains very little data on the UV spectra of alkoxy-substituted amino and oxo derivatives of s-triazine, and there has been virtually no theoretical treatment of the data that do exist.

The UV spectra of 2,4,6-trimethoxy-s-triazine were obtained for the first time in [1, 2]. The spectra of this compound were studied in greater detail in [3]. The spectra of 2,4,6-trimethoxy-s-triazine in various solvents were presented. The spectra of other compounds of this case are not present in the literature available to us.

In this paper we present the spectra of the molecules and ions of methoxy-substituted amino and oxo derivatives of s-triazine. The molecular structures of these compounds were studied, and theoretical calculations of their electronic spectra ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions) were performed.

We obtained 2,4,6-trimethoxy-s-triazine from 2,4,6-trichloro-1,3,5-triazine and methanol; 2,4-diallyloxy-6-amino-s-triazine was obtained from 2,4-dichloro-6-amino-s-triazine (which was synthesized by bubbling gaseous ammonia through a solution of 2,4,6-trichloro-1,3,5-triazine in dry acetone at −10°) and allyl alcohol; 2-allyloxy-4,6-diamino-s-triazine was obtained from 2-chloro-4,6-diamino-s-triazine (which was synthesized by bubbling gaseous ammonia through a solution of 2,4,6-trichloro-s-triazine in benzene at 50°) and allyl alcohol; 2-methoxy-4,6-diamino-s-triazine was obtained from 2-chloro-4,6-diamino-s-triazine and methanol. The reactions were carried out in the presence of sodium hydroxide. All of the compounds obtained (and their intermediates) were identified from IR spectra.

The experimental data on the electronic spectra are presented in Table 1† along with the results of theoretical calculations for all of the possible compounds (including those that were not isolated).

The method of additive construction of the structures of the compounds under consideration was used for the calculations of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition by the methods in [5,6]. The multiplicities of the $>\mathrm{C}\overset{\smile}{=}\overset{(-)}{\mathrm{O}}$ and $>\mathrm{C}\overset{\smile}{=}\overset{(+)}{\mathrm{N}}\mathrm{H}_2$ bonds in all of the molecules were considered to be 1.60, while the multiplicities of the $\mathrm{C}\underline{\cdot\cdot\cdot}\bar{\mathrm{O}}$ and $\mathrm{C}\underline{\cdot\cdot\cdot}\overset{(+)}{\mathrm{N}}\mathrm{H}_2$ bonds were taken as 1.20.

To calculate the multiplicity of $\mathrm{C}\underline{\cdot\cdot\cdot}\overset{\oplus}{\mathrm{O}}\mathrm{R}$ we used the data from the UV spectrum of 2,4,6-trimethoxy-s-triazine and calculated its structure by the method of [4]. We used the multiplicity of the $\mathrm{C}\underline{\cdot\cdot\cdot}\overset{\oplus}{\mathrm{O}}\mathrm{CH}_3$ bond found in this way in the calculations of the other compounds.

The multiplicity of the ring bonds and the effective charges were determined from the formula proposed in [5]:

$$q_\mu = \sum_\nu n_{\mu\nu} - Q_\mu,$$

where q_μ is the effective charge of atom μ, $n_{\mu\nu}$ is the multiplicity of the $\mu-\nu$ bond, and Q_μ is the valence of the C, N, and O atoms (four, three, and two, respectively).

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† The system proposed in [7] was used to depict the structural formulas.

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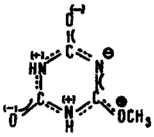
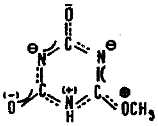
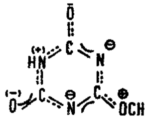
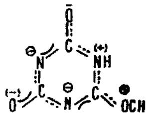
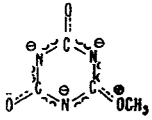
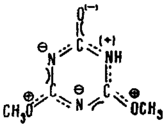
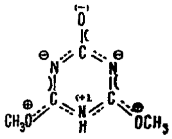
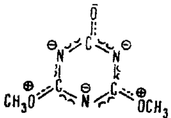
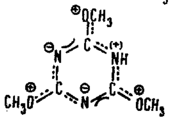
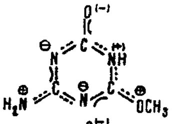
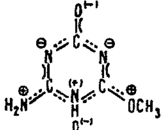
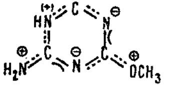
TABLE 1. Electronic Spectra ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions) of Methoxy Derivatives of s-Triazine

No.	Structural formula	Energy, eV occupied level			Excited π^* levels	$\lambda_{\pi\pi^*}$		$\lambda_{n\pi^*}$	
		π	p	n		determined	calculated	determined	calculated
I		—4,99 —4,34 —4,13	—3,26 —1,82 —1,36	—1,88 —2,81 —2,81	2,07 2,45 3,82	—	200	—	314 (N) 254 (O)
II		—4,89 —4,13 —3,46	—3,05 —1,28 —0,71	—1,88 —1,88 —2,81	2,10 2,92 4,18	—	223	—	312 (N) 252 (O)
III		—4,83 —4,14 —3,69	—2,57 —1,51 —0,67	—1,88 —1,93 —2,81	2,0 2,81 4,27	—	218	—	319 (N′) 316 (N″) 258 (O)
IV		—4,84 —4,14 —3,67	—2,88 —1,24 —0,71	—1,88 —1,88 —2,81	1,90 3,15 4,12	—	222	—	317 (N) 264 (O)
V		—4,74 —3,84 —2,68	—2,32 —0,69 —0,60	—1,88 —1,90 —1,90	2,52 2,55 4,73	—	240	—	282 (N′) 281 (N″)
VI		—4,89 —4,13 —4,04	—3,32 —2,63 —1,25	—1,88 —1,93 —2,81	2,01 2,90 4,12	—	205	—	319 (N′) 316 (N″) 258 (O)
VII		—5,09 —4,22 —4,05	—3,60 —2,53 —1,22	—1,88 —1,88 —2,81	1,91 3,05 4,15	—	208,5	—	317 (N) 263 (O)
VIII		—4,92 —4,00 —3,75	—2,56 —2,18 —0,67	—1,88 —1,93 —1,93	2,46 2,49 4,77	—	201	—	286 (N′) 282 (N″)
IX		—5,48 —4,11 —4,02	—3,69 —2,90 —2,88	—1,94 —1,94 —1,94	1,13 2,67 4,47	222	233	—	405 (N)
X		—4,89 —4,13 —3,44	—3,07 —1,29 —0,84	—1,88 —1,88 —2,81	2,09 2,92 4,16	—	225	—	312 (N) 252 (O)
XI		—4,84 —4,14 —3,67	—2,90 —1,25 —0,83	—1,88 —1,88 —2,81	1,89 3,14 4,11	—	223	—	317 (N) 263 (O)
XII		—4,83 —4,14 —3,70	—2,58 —1,54 —0,78	—1,88 —1,93 —2,81	2,00 2,81 4,27	—	217	—	319 (N′) 316 (N″) 258 (O)

Note. Table 1 continued overleaf.

TABLE 1. (Continued)

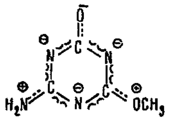
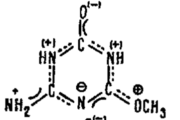
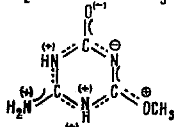
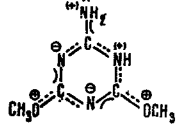
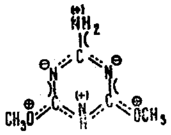
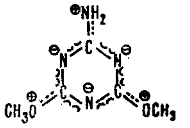
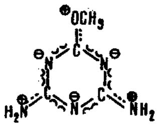
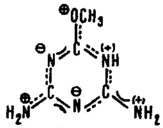
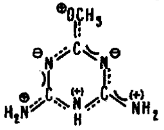
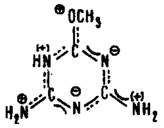
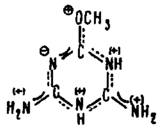
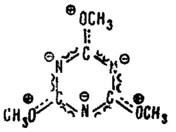
No.	Structural formula	Energy, eV			Excited π^* levels	$\lambda_{\pi\pi^*}$		$\lambda_{n\pi^*}$	
		occupied level				determined	calculated	determined	calculated
		π	p	n					
XIII		—4,75 —3,84 —2,71	—2,33 —0,78 —0,63	—1,88 —1,88 —1,93	2,51 2,55 4,73	—	238	—	282 (N′) 280 (N″)
XIV		—5,02 —4,40 —4,14	—3,26 —1,84 —1,36	—1,88 —1,95 —2,81	2,03 2,45 3,82	—	205	—	317 (N′) 312 (N″) 257 (O)
XV		—5,03 —4,38 —4,14	—3,27 —1,84 —1,37	—1,88 —1,95 —2,81	2,07 2,41 3,82	—	200	—	314 (N′) 308 (N″) 254 (O)
XVI		—5,02 —4,21 —4,05	—3,43 —2,71 —1,29	—1,88 —1,93 —1,95	1,99 2,72 4,28	218	205	—	319 (N′) 316 (N″) 314 (N‴)
XVII		—5,07 —4,29 —4,05	—3,61 —2,53 —1,25	—1,88 —1,88 —1,95	1,87 3,05 4,14	218	209	—	317 (N′) 325 (N″)
XVIII		—4,91 —4,01 —3,72	—2,59 —2,18 —0,79	—1,88 —1,93 —1,93	2,45 2,49 4,76	189	200	—	286 (N′) 282 (N″)
XIX		—4,75 —3,84 —2,73	—2,34 —0,82 —0,72	—1,88 —1,88 —1,93	2,51 2,55 4,73	—	237	—	282 (N′) 280 (N″)
XX		—4,93 —4,15 —3,50	—3,08 —1,30 —0,85	—1,88 —1,88 —1,95	2,06 2,92 4,18	227	223	—	314 (N′) 308 (N″)
XXI		—4,88 —4,14 —3,72	—2,58 —1,56 —0,79	—1,88 —1,93 —1,95	1,98 2,79 4,27	227	217	—	319 (N′) 316 (N″) 314 (N‴)
XXII		—4,88 —4,19 —3,69	—2,90 —1,26 —0,84	—1,88 —1,88 —1,95	1,86 3,14 4,11	227	224	—	317 (N′) 325 (N″)
XXIII		—5,01 —4,46 —4,15	—3,30 —1,86 —1,38	—1,88 —1,95 —1,95	2,03 2,41 3,81	—	200	—	317 (N′) 312 (N″)
XXIV		—6,29 —4,33 —4,01	—3,70 —3,27 —2,25	—1,93 —1,93 —1,93	2,41 3,75 6,14	187	194	—	286 (N)

TABLE 2. Dissociation Constants of Alkoxy-Substituted Amino and Oxo Derivatives of s-Triazine

Compound	pK_a		Compound	pK_a	
	our data	literature data		our data	literature data
2-Allyloxy-4,6-diamino-s-triazine	3,80	3,43[8]	2,4-Diallyloxy-6-amino-s-triazine	2,20	—
2-Methoxy-4,6-diamino-s-triazine	3,50	—	2,4,6-Trimethoxy-s-triazine	0,40	0,20[1]

The proposed additive scheme was checked by calculation of the electronic spectra ($\pi \to \pi^*$ and $n \to \pi^*$ transitions) by the simple MO method with the system of parameters in [6, 7] and by comparison of the calculated values with the experimental results. The mean arithmetic values of the deviation was ~8 nm and is in agreement with the corresponding value obtained for amino and oxo derivatives of s-triazine. It can consequently by assumed that the deviations in the calculations of the spectra of other molecules and ions for which no experimental data are available do not exceed this value.

The calculations that we performed make it possible also to establish the nature of the absorption bands observed. In all cases, the calculated wavelength of the $\pi \to \pi^*$ electron transition coincides with the longest wave absorption maximum or with the distinctly expressed inflection on the absorption curve. The calculation of the $n \to \pi^*$ transitions gives considerably larger $(\lambda_{n\pi^*})_{cal}$ values and cannot be compared with the observed transitions. In the case of 2,4,6-trimethoxy-s-triazine, the inflection of the absorption curve at 222 nm detected in [3] cannot, as seen from Table 1, be ascribed to the $n \to \pi^*$ transition in view of the fact that the difference from $(\lambda_{n\pi^*})_{cal}$ is too great. A check of the wavelength of the absorption maximum of 2,4,6-trimethoxy-s-triazine confirms the results in [2]. The presence of a plateau on the absorption curve of this compound at 220-224 nm and pH 2-4 is explained by the appearance of a singly protonated ion with $\lambda_{max} = 220$ nm rather than by the presence of oxidation product impurities, as proposed in [3]. This plateau coincides with the inflection on the absorption curve presented in [3] and possibly has the same nature. It should be noted that no trace was seen of the maxima or inflections on the absorption curve at 200 nm pointed out by Paoloni and Cignitti [3].

In the course of the study we determined the dissociation constants (Table 2) of 2-methoxy-4,6-diamino-s-triazine, 2-allyloxy-4,6-diamino-5-triazine, 2,4-diallyloxy-6-amino-s-triazine, and 2,4,6-trimethoxy-s-triazine by spectrophotometric titration.

LITERATURE CITED

1. E. N. Boitsov and A. I. Finkel'shtein, Opt. Spektrosk., 9, 51 (1960).
2. E. N. Boitsov, A. I. Finkel'shtein, and V. A. Petukhov, Opt. Spektrosk., 13, 274 (1962).
3. M. Cignitti and L. Paoloni, Spectr. Acta, 20, 211 (1964).
4. A. I. Finkel'shtein, Ts. N. Roginskaya, N. P. Shishkin, and E. M. Moncharzh, Zh. Strukt. Khim., 10, 64 (1969).
5. A. I. Finekl'shtein, Opt. Spektrosk., 20, 408 (1966).
6. A. I. Finkel'shtein, Teor. Éksperim. Khim., 1, 521 (1966).
7. A. I. Finkel'shtein, Zh. Fiz. Khim., 31, 1659 (1957).
8. J. R. Dudey, J. Am. Chem. Soc., 73, 3007 (1951).