

## CONDENSED IMIDAZO-1,2,4-TRIAZINES.

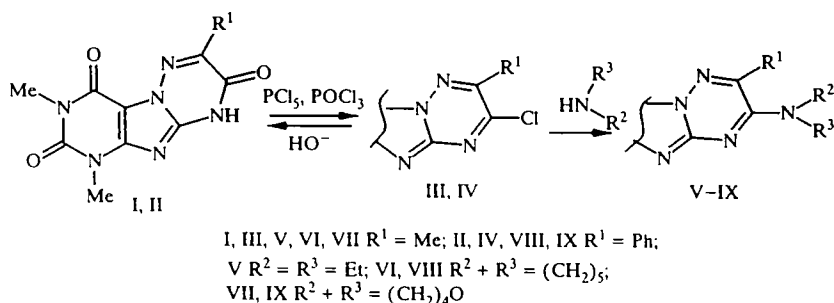
### 29.\* SYNTHESIS OF 3-AMINO-1,2,4-TRIAZINO[2,3-f]XANTHINES AND THEIR SPECTRAL PROPERTIES

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*The reaction of substituted 3-chloro-1,2,4-triazino[2,3-f]theophyllins with secondary amines gives new water-soluble active media for dye lasers. The luminescence and generation characteristics of these compounds were studied. These properties were found to depend on the lactam-lactim tautomerism of 1,2,4-triazino[2,3-f]theophyllin-4H-3-ones.*

In previous work [2, 3], we synthesized previously unreported substituted 1,2,4-triazino[2,3-f]theophyllins, which are water-soluble active media for dye lasers, and studied the spectral-generational properties of these compounds. In a continuation of this work, we synthesized new 1,2,4-triazino[2,3-f]theophyllins, varying the substituent at C<sub>(3)</sub>.

We found that heating 2-methyl-1,2,4-triazino[2,3-f]theophyllin-4H-3-one (I) and its 2-phenyl analog II in POCl<sub>3</sub> with PCl<sub>5</sub> at reflux gives the corresponding 3-chlorotriazinotheophyllin derivatives III and IV [2]. In order to study the lability of the chlorine atom at C<sub>(3)</sub> in tricyclic products III and IV and obtain active media with electron-donor substituents in the triazine fragment of the triazinotheophyllin molecule, we investigated the reaction of III and IV with diethylamine, morpholine, and piperidine. The reaction of 3-chlorotriazinotheophyllin III with diethylamine proceeds only upon heating in a sealed ampule at 120-130°C, while the reaction with piperidine and morpholine proceeds in toluene at reflux. Products VIII and IX were obtained in maximum yield upon heating chloroderivative IV with piperidine and morpholine, respectively, in DMF at reflux. We note that the use of anhydrous solvents in these reactions is mandatory. Thin-layer chromatography showed that, in the presence of water, hydrolysis occurs at the chlorine atom to give the corresponding triazino-3-theophyllinones I and II.



Products II, III, and V-X luminesce and their solutions are capable of generating laser emission (Table 1). The efficiency of luminescence and laser generation depend markedly on the nature of the substituent in the triazine fragment. Thus, II has the lowest luminescence and generation efficiency and has a significant Stokes shift. Similar behavior was observed in our previous work in the case of I and was tentatively attributed to proton transfer in the excited state due to tautomeric A ⇌ B transformations [3].

\*For Communication 28, see [1].

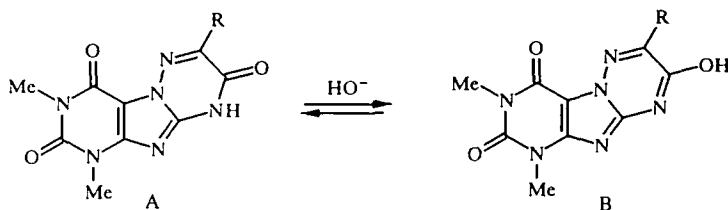
TABLE 1. Spectral Indices of II, III, and V-IX

Com- pound	UV Spectrum		Luminescence		Laser generation			Stokes shift, nm	Solvent
	$\lambda_{\max}$ , nm	$\lg \epsilon$	$\lambda_{\max}$ , nm	$\varphi$ , %	$\lambda$ , nm	$\lambda_{\max}$ , nm	Efficiency, %		
II	260 285 375	3.88 4.03 3.71	520	11	466...506	482	1	145	Ethanol
II	268 289 390	3.90 4.03 3.73	510	13	466...506	482	2	120	0.05 N NaOH in ethanol
II	269 290 400	3.90 4.05 3.76	95	17	466...506	483	7	95	0.1 N NaOH in ethanol
II	263 287 360	3.89 4.02 3.70	525	10	466...506	480	1	155	95% H <sub>2</sub> SO <sub>4</sub>
III	275 395	3.89 3.99	465	41	469...503	482	9	70	Ethanol
V	310 380	3.95 3.94	467	48	463...503	483	25*	87	Water
VI	275 310 390	3.92 3.93 3.94	500	19	504...551	521	2	110	DMF
VII	275 305 390	3.96 3.91 3.96	508	13	508...551	522	1,5	118	DMF
VIII	270 320 405	4.31 4.20 4.18	520	34	524...580	550	1	115	DMF
IX	279 315 410	4.23 4.09 4.10	520	34	523...557	542	2	110	DMF

\*Laser generation efficiency for solutions in ethanol, ethanol with HCl, and acetic acid was 12, 10, and 3%, respectively.

In order to support this hypothesis, we took the absorption and luminescence spectra of II in neutral and alkaline solutions. Analysis of these spectra showed a steady bathochromic shift for a series of ethanol solutions from 0.05 N NaOH/ethanol to 0.1 N NaOH/ethanol, indicating structural rigidity of the transition of lactam A into lactim B. This may account for the increase in luminescence and generation of II with increasing solution basicity. We should note that no significant change in the absorption spectrum of II was observed in 0.1 N NaOH/ethanol, while a hypsochromic shift was observed in 95% aq. H<sub>2</sub>SO<sub>4</sub>, probably due to protonation of the nitrogen atoms in tricyclic derivative II.

Thus, II presumably exists in neutral and acid media predominantly in lactam form A, while proton transfer from N<sub>(4)</sub> to the oxygen atom occurs in basic solutions to give tautomeric structure B.



The introduction of a chlorine atom at C<sub>(3)</sub> to give III leads to a slight bathochromic shift of the luminescence band and a sharp increase in the quantum yield and generation efficiency in comparison with tricyclic derivative I [3]. We should note that aqueous solutions of chloro derivative III are incapable of efficient luminescence and generation due to partial hydrolysis at the chlorine atom as indicated by thin-layer chromatography.

The aqueous solution of V, for which laser generation efficiency reaches 25%, is the most efficient active medium. Of these products, V has the smallest Stokes shift and greatest quantum yield, indicating its aromatic nature. The generation

TABLE 2. Indices for II-IX

Com- pound	Chemical formula	Found, %				mp, °C	R <sub>f</sub>	Yield, %
		Calculated, %						
		C	H	N	Cl			
II	C <sub>15</sub> H <sub>12</sub> N <sub>6</sub> O <sub>3</sub>	<u>55,48</u>	<u>3,81</u>	<u>25,77</u>	—	>350	0,46	64
		55,52	3,73	25,92				
III	C <sub>10</sub> H <sub>9</sub> ClN <sub>6</sub> O <sub>2</sub>	<u>42,67</u>	<u>3,28</u>	<u>29,99</u>	<u>12,70</u>	252...253	0,64	49
		42,75	3,23	29,95	12,63			
IV	C <sub>15</sub> H <sub>11</sub> ClN <sub>6</sub> O <sub>3</sub>	<u>50,11</u>	<u>3,15</u>	<u>23,37</u>	<u>9,90</u>	>350	0,68	53
		50,19	3,09	23,43	9,88			
V	C <sub>14</sub> H <sub>19</sub> N <sub>7</sub> O <sub>2</sub>	<u>52,88</u>	<u>5,98</u>	<u>31,00</u>	—	246...248	0,63	47
		52,96	6,04	30,91				
VI	C <sub>15</sub> H <sub>19</sub> N <sub>7</sub> O <sub>2</sub>	<u>54,63</u>	<u>5,90</u>	<u>29,77</u>	—	269...270	0,49	44
		54,67	5,82	29,78				
VII	C <sub>14</sub> H <sub>17</sub> N <sub>7</sub> O <sub>3</sub>	<u>50,80</u>	<u>5,08</u>	<u>29,55</u>	—	271...273	0,34	61
		50,71	5,17	29,60				
VIII	C <sub>20</sub> H <sub>21</sub> N <sub>7</sub> O <sub>2</sub>	<u>61,40</u>	<u>5,40</u>	<u>25,01</u>	—	343...344	0,62	57
		61,35	5,41	25,06				
IX	C <sub>19</sub> H <sub>19</sub> N <sub>7</sub> O <sub>3</sub>	<u>57,93</u>	<u>4,90</u>	<u>25,01</u>	—	346...347	0,5	63
		57,97	4,87	24,94				

efficiency drops upon going to protic solvents such as ethanol, HCl in ethanol, and acetic acid. This effect is attributed to protonation of the nitrogen atom of the diethylamino group.

Replacement of the diethylamino group at C<sub>(3)</sub> by bulky morpholinyl or piperidinyl substituents leads to loss of coplanarity, likely due to steric hindrance, which is manifest in a decrease in the Stokes shift. Although the luminescence quantum yields for 2-phenyl derivatives VIII and IX are only 1% less than for the tricyclic derivative V, their generation efficiency is negligible. The poor solubility of these compounds prevents study of the change in their spectral indices relative to solvent polarity and pH of the medium.

Therefore, this study has added efficient water-soluble active media in the imitrine series [4] with enhanced generation efficiency to 25% in the generation band at 483-503 nm.

## EXPERIMENTAL

The electronic absorption and emission spectra were taken on a Hitachi ESP-3T spectrophotometer equipped with a G-3 fluorescence attachment. The luminescence quantum yields and laser generation parameters were determined according to a well-known method [4]. A solution of coumarin-10 in ethanol was used as ethanol. The purity of the products was monitored by chromatography on Silufol UV-254 using 1:2 2-propanol–toluene as the eluent. The indices for II-IX are given in Table 2.

**2-Phenyl-1,2,4-triazino[2,3-*f*]theophyllin-4H-3-one (II).** A mixture of 2.1 g (10 mmoles) 7,8-diamintheophyllin and 1.65 g (11 mmoles) phenylglyoxalic acid in 50 ml acetic acid was heated at reflux for 2 h. The reaction mixture was cooled and the precipitate formed was filtered off, washed with ethanol, and crystallized from aqueous DMF.

**3-Chloro-1,2,4-triazino[2,3-*f*]theophyllins (III and IV).** A sample of 0.84 g (4 mmoles) PCl<sub>5</sub> was added to a solution of 3 mmoles corresponding triazinotheophyllin-4H-3-one (I or II) in 20 ml freshly distilled POCl<sub>3</sub> and heated at reflux for 2 h. The reaction mixture was concentrated at reduced pressure to 5 ml, cooled, and poured onto 100 g ice. The precipitate formed was filtered off, washed with ice water and then 5% aq. NaHCO<sub>3</sub>, and dried in the air. Product III was crystallized from methanol and IV from 1-butanol.

**2-Methyl-3-diethylamino-1,2,4-triazino[2,3-*f*]theophyllin (V).** A mixture of 0.56 g (2 mmoles) III and 0.37 g (5 mmoles) diethylamine in 30 ml anhydrous methanol was maintained in a sealed ampule at 120-130°C for 3 h. The reaction mixture was concentrated at reduced pressure to 5 ml. The precipitate was filtered off, washed with methanol cooled to 0°C, and crystallized from 2-propanol.

**3-Amino-1,2,4-triazino[2,3-*f*]theophyllins (VI-IX).** A solution of 3 mmoles chlorotriazinotheophyllin III or IV in 80 ml anhydrous toluene (or in 15 ml anhydrous DMF in the case of VIII and IX) and 6 mmoles piperidine or morpholine was heated at reflux for 4 h. The reaction mixture was concentrated in vacuum until a precipitate formed. Product VI was crystallized from toluene, VII from 2-propanol, and VIII and IX from DMF.

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