

## 1, 2-DIMETHYLIMIDAZOBENZO-1', 2', 3'-THIADIAZOLES AND DERIVED CYANINE DYES

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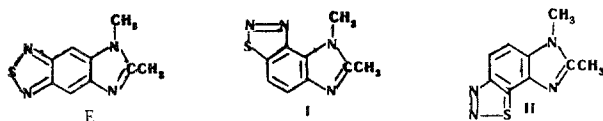
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New tricyclic heterocyclic systems and their methyl derivatives are synthesized. They are 2-methylimidazo[5, 4-e]benzo-1', 2', 3'-thiadiazole, 2-methylimidazo[5, 4-g]benzo-1', 2', 3'-thiadiazole, 1, 2-dimethylimidazo[5, 4-g]benzo-1', 2', 3'-thiadiazole, and 1, 2-dimethylimidazo[5, 4-g]benzo-1', 2', 3'-thiadiazole. Quaternary salts of the 1, 2-dimethyl derivatives are used to prepare symmetrical and unsymmetrical trimethinecyanines and dimethinemerocyanines containing rhodanine groups. The absorption maxima of the dyes are displaced towards the long wavelength region compared with imidacarbocyanines. It is shown that when 1, 2-dimethyl-5-aminobenzoimidazole is thiocyanated, the thiocyanogroup enters the benzoimidazole ring at position 4, and that 1, 2-dimethylimidazo[5, 4-e]benzo-1', 2', 3'-thiadiazole is less basic than its isomer 1, 2-dimethylimidazo[5, 4-g]benzo-1', 2', 3'-thiadiazole.

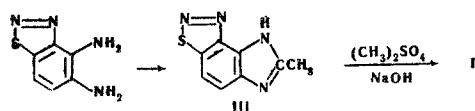
A previous paper [1] described the synthesis of 1, 2-dimethylimidazo[4, 5-f]benzo-2', 1', 3'-thiadiazole (E), from whose quaternary salt a number of cyanine dyes were prepared.

The present paper describes the synthesis of 1, 2-dimethylimidazo[5, 4-e]benzo-1', 2', 3'-thiadiazole (I), and 1, 2-dimethylimidazo[5, 4-g]benzo-1', 2', 3'-thiadiazole (II), isomeric with E.

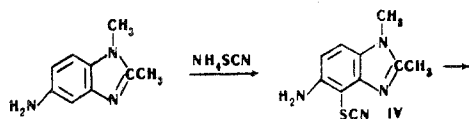


Compounds of this type have not been described in the literature.

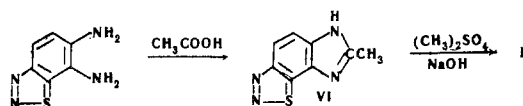
We synthesized I starting from 4, 5-diaminobenzo-1', 2', 3'-thiadiazole [2], which was condensed with acetic anhydride to give 2-methylimidazo[5, 4-e]benzo-1', 2', 3'-thiadiazole (III), and the latter was then alkylated to base I.



Compound II was synthesized by thiocyanating 1, 2-dimethyl-5-aminobenzoimidazole [3]. Thiocyanation of benzoimidazole and its derivatives had not previously been investigated. We thiocyanated 1, 2-dimethyl-5-aminobenzoimidazole under the conditions which we used for 2-methyl-5- (and 6)amino-benzothiazoles [4]. The thiocyanogroup was reduced to mercapto by heating the thiocyanate IV with aqueous sodium sulfide, and diazotizing the resultant V gave base II.



When 1, 2-dimethyl-5-aminobenzoimidazole is thiocyanated, the thiocyanogroup can enter at position 4 or 6. We proved that it entered at position 4, by retrosynthesizing II from 6, 7-diaminobenzo-1, 2, 3-thiadiazole:

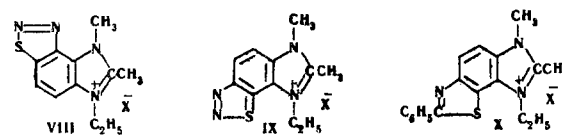


The product obtained by alkylating 2-methylimidazo[5, 4-g]benzo-1', 2', 3'-thiadiazole (VI) with dimethyl sulfate in alkaline solution, gave an undepressed mixed melting point with base II prepared from IV.

Condensation of V with benzoyl chloride in alkaline solution led to the isolation of 1, 2-dimethyl-5-phenylimidazo[5, 4-g]benzothiazole (VII).



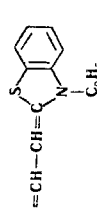
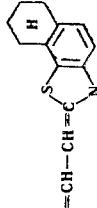
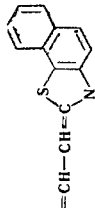
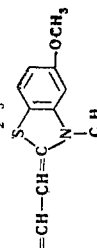
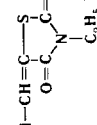
Bases I, II, and VII give, on heating with ethyl tosylate, the quaternary salts VIII-X, from which the cyanine dyes listed in the table were synthesized by the usual methods.

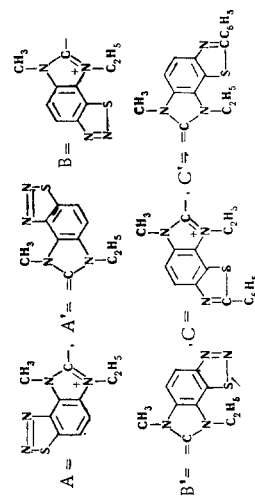


X = 1. CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>

The data in the table show that all dyes absorb in a longer wavelength region of the spectrum than imidacarbocyanines. Absorption maxima of dyes from quaternary salts of base II are somewhat displaced towards the short wave region of the spectrum compared with the absorption maxima of dyes from quaternary salts of base I. In the case of dye XI the shift is 24 mμ, while for dye XVII it is 31 mμ. It is known [4, 5] that in the series of unsymmetrical cyanine dyes containing one and the same heterocyclic ring, the shift is greater, the greater the difference in basicity between the heterocyclic rings going to make up the dye molecule. Hence it can be concluded that base II in the dyes is more basic than I.


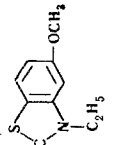
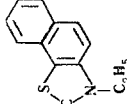
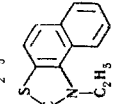
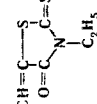
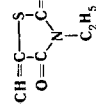
Cyanine Dyes Containing Imidazobenzo-1,2,3-thiazole Ring Systems

Dye number	Structure*	Mp, °C**	$\lambda_{\max}$ , m $\mu$	Formula	S, %		Yield, %
					Found	Calculated	
1	2	3	4	5	6	7	8
XI	A-CH=CH-CH=A'	261—262	530	C <sub>23</sub> H <sub>22</sub> IN <sub>8</sub> S <sub>2</sub>	10.30; 10.39	10.63	19
XII		221—222	520	C <sub>22</sub> H <sub>22</sub> IN <sub>5</sub> S <sub>2</sub>	11.38; 11.36	11.70	34
XIII		265—266	530	C <sub>33</sub> H <sub>38</sub> N <sub>5</sub> O <sub>3</sub> S <sub>3</sub>	14.44; 14.54	14.88	81
XIV		266—267	536	C <sub>26</sub> H <sub>24</sub> IN <sub>5</sub> S <sub>2</sub>	10.55; 10.64	10.72	67
XV		216—217	526	C <sub>30</sub> H <sub>31</sub> N <sub>5</sub> O <sub>4</sub> S <sub>3</sub>	14.99; 15.04	15.45	48
XVI		237—238	529	C <sub>17</sub> H <sub>17</sub> N <sub>3</sub> O <sub>3</sub> S <sub>3</sub>	23.56; 23.45	23.82	39



\*\*Uncorrected mp

Table  
(cont'd)

1	2	3	4	5	6	7	8
XVII	B-CH=CH-CH=B'	229—230	534	C <sub>23</sub> H <sub>23</sub> IN <sub>8</sub> S <sub>2</sub>	10.32; 10.34	10.63	16
XVIII	B-CH=CH-CH- 	248	515	C <sub>22</sub> H <sub>22</sub> N <sub>5</sub> S <sub>2</sub>	12.00; 11.93	11.70	62
XIX	B-CH=CH-CH- 	220	525	C <sub>30</sub> H <sub>31</sub> N <sub>5</sub> O <sub>3</sub> S <sub>3</sub>	15.22; 15.14	15.45	50
XX	B-CH=CH-CH- 	273 (decomp)	526	C <sub>33</sub> H <sub>31</sub> N <sub>5</sub> O <sub>3</sub> S <sub>3</sub>	15.08; 15.07	14.97	87
XXI	B-CH=CH-CH- 	180	538	C <sub>33</sub> H <sub>31</sub> N <sub>5</sub> O <sub>3</sub> S <sub>3</sub>	14.76; 14.82	14.97	47
XXII	B-CH=CH- 	275	520	C <sub>17</sub> H <sub>17</sub> N <sub>5</sub> OS <sub>3</sub>	23.49; 23.52	23.82	31
XXIII	C-CH=CH-CH=B'	264	518	C <sub>37</sub> H <sub>33</sub> IN <sub>6</sub> S <sub>2</sub>	8.80; 8.85	8.51	16
XXIV	C'-CH=CH- 	292	525	C <sub>24</sub> H <sub>22</sub> N <sub>4</sub> OS <sub>3</sub>	19.95; 20.02	20.08	18

## EXPERIMENTAL

**2-Methylimidazo[5,4-e]benzo-1',2',3'-thiadiazole (III).** A mixture of 6 g (0.036 mole) 4,5-diaminobenzo-1,2,3-thiadiazole [2], 50 ml dilute HCl (1:1), and 1 ml AcOH was refluxed for 2 hr. After treating with charcoal, the filtrate was neutralized with aqueous ammonia. The precipitate of III was filtered off, and washed with water, yield 4.1 (60%), colorless needles, mp 262° C (ex aqueous EtOH). Found: N 29.37%. Calculated for  $C_8H_6N_4S$ : N 29.47%.

**1,2-Dimethylimidazo[5,4-e]benzo-1',2',3'-thiadiazole (I).** 10 ml EtOH was added to a solution of 6 g (0.0312 mole) III in 150 ml 5% NaOH, the whole stirred and over a period of 5 hr 12.6 g (0.1 mole)  $Me_2SO_4$  added. Then the mixture was held at 95° C for 30 min, while being stirred. After standing for 10 hr the solid was filtered off, and washed, first with 5% NaOH, then with water, yield of 13.44 g (54%), mp 165° C (decomp).

**1,2-Dimethyl-5-amino-4-thiocyanobenzimidazole (IV).** A solution of 4.83 g (0.03 mole) 1,2-dimethyl-5-aminobenzimidazole and 6.9 g (0.09 mole)  $NH_4CNS$  in 100 ml MeOH was stirred and held at -8° to -10° C, while a solution 5.13 g (0.032 mole) bromide in 50 ml MeOH saturated with  $NH_4Br$  was added, over a period of 2 hr. After that the mixture was stirred for a further 2 hr, the solid filtered off, washed with water and EtOH, and dried in a vacuum-desiccator. Yield of IV 4 g (63%).

The mother liquors were neutralized with aqueous ammonia, when a white crystalline powder (1.45 g) was precipitated, mp above 300° C. It did not dissolve when treated with ammonium sulfide. Evidently it was the product of isomerization of IV to 5-amino-1,2-dimethylimidazo[5,4-g]benzothiazole, confirmed by the high mp, and elementary analysis. Found: S 14.85; 14.77%. Calculated for  $C_{10}H_{10}N_4S$ : S 14.63%.

**1,2-Dimethylimidazo[5,4-g]benzo-1',2',3'-thiadiazole (II).** 4g (0.0183 mole) IV was added in portions to a solution of 9.6 g (0.04 mole) sodium sulfide in 10 ml water, held at 55°-60° C. The solution was heated for a further 10 min, cooled to 0° C, and neutralized with 50% AcOH. The precipitate of 1,2-dimethyl-5-amino-4-mercaptobenzimidazole was filtered off, washed with water, and dissolved in 40 ml 5% NaOH. 1.2 g  $NaNO_2$  was added to the solution, and the mixture added dropwise, over a period of 20 min, with stirring, to 50 ml HCl (1:1), held at 0° C. After standing for 1 hr, the precipitate was filtered off, and recrystallized from water, yield of II 1.42 g (42%), mp 197° C. Found: N 27.17; 27.19%. Calculated for  $C_9H_8N_4S$ : N 27.45%.

**2-Methylimidazo[5,4-g]benzo-1',2',3'-thiadiazole (VI).** 4.98 g (0.03 mole) 6,7-diaminobenzo-1,2,3-thiadiazole [7] was refluxed 1 hr with a mixture of 45 ml dilute HCl (1:1) and 5 ml AcOH, and the products then neutralized with aqueous ammonia. Yield of VI 4.56 g (80%), mp 233° C (ex aqueous EtOH). Found: N 29.10; 29.08%. Calculated for  $C_8H_6N_4S$ : N 29.47%.

Alkylation of VI with  $Me_2SO_4$  in alkali gave a 51% yield of base II mp 197° C. Undepressed mixed mp with a specimen of II prepared from IV.

**1,2-Dimethyl-5-phenylimidazo[5,4-g]benzothiazole (VII).** 6.54 g (0.03 mole) IV was added in small portions to a solution of 14.4 g (0.06 mole) Na sulfide in 20 ml water, held at 60°-70° C, after which the solution was heated at 80° C for 10 min, and filtered. The filtrate was cooled to 0° C, stirred and held at 0° C, while 10 g benzoyl chloride and 5% NaOH (sufficient to keep the solution alkaline) were added. The precipitate was dissolved in dilute HCl, treated with charcoal, and neutralized with ammonia. Yield 3.52 g (40%), colorless needles, mp 249° C (ex nitromethane). Found: S 11.68; 11.72%. Calculated for  $C_{16}H_{13}N_3S$ : S 11.46%.

**1,2-Dimethylimidazo[5,4-e]benzo-1',2',3'-thiadiazole ethiodide (VIII, X = I).** Equimolecular amounts of base I and ethyl tosylate were heated together for 3 hr at 120°-130° C. The resultant tosylate was converted to iodide in the usual way, yield 61%, mp 275°-276° C (decomp, ex EtOH). Found: I 35.15; 35.13%. Calculated for  $C_{11}H_{13}IN_4S$ : I 35.27%.

Tosylates of II and VII were prepared similarly. VII tosylate crystallized from water as white, long needles, containing water of crystallization, mp 262° C. Found: S 12.75; 12.62%. Calculated for  $C_{25}H_{25}N_3O_3S \cdot H_2O$ : S 12.87%.

Ethiodide of base II mp 282° C (ex EtOH).

The dyes were prepared in the usual way, and were purified by recrystallizing from EtOH. From tosylate VII were synthesized only symmetrical trimethinecyanine XXIII and the dimethinemerocyanine containing a rhodanine group XXIV. It was not possible to purify an unsymmetrical trimethinecyanine.

The table gives the formulas of the dyes and their elementary analyses.

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