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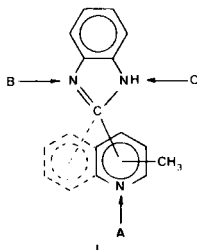
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The quaternisation of 2-(methylpyridyl or quinoly)benzimidazoles with methyl iodide leads to a variety of salts depending on the relative position of the nuclei and on the experimental conditions: *N*-methylpyridinium, *N*-methylquinolinium, methyl and 1,3-dimethylbenzimidazolium iodides, and hydroiodides were isolated. Cyanine dyes were prepared from *N*-methylpyridinium and *N*-methylquinolinium methiodides. The main spectroscopic features of these compounds are briefly discussed.

J. Heterocyclic Chem., **16**, 1583 (1979).

In previous papers (2-4) we described a series of 2-(methylpyridyl or quinoly)benz-X-azoles (X = O, S, NH), their quaternary salts and the related polymethine dyes when X = O, S. This paper deals with salts and dyes of benzimidazoles (X = NH).

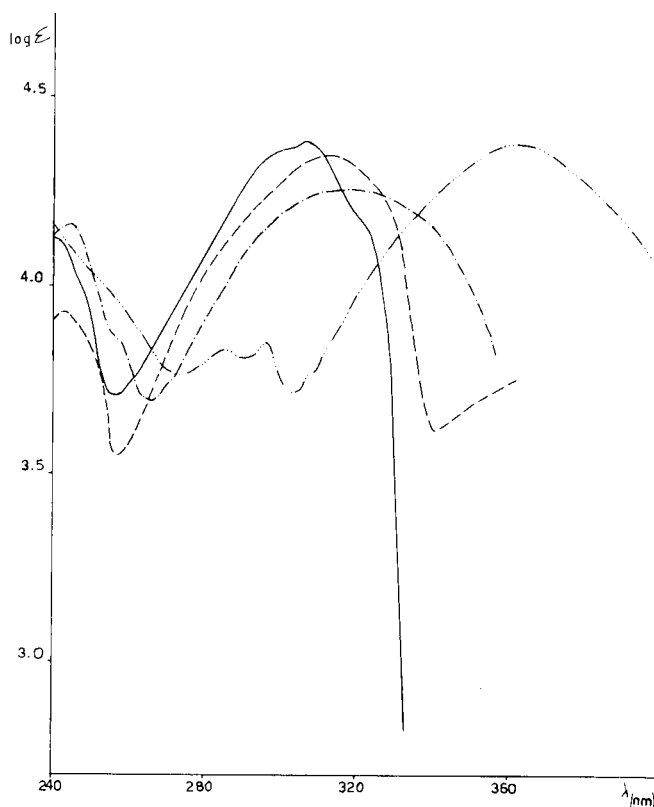
Together with the quaternisation at the azine (A) and azole (B) nitrogen atoms, typical of the oxazole and thiazole derivatives, the benzimidazoles show the possibility of *N*-alkylation (C) (I). Furthermore, the basicity of the A and B sites in the isolated systems is similar (pK_a values (5): benzimidazole 5.48, 2-picoline 5.97, 4-picoline 6.02, quinaldine 5.83, lepidine 5.67) and this results in a more marked competition in the quaternisation if compared with the previously described benzoxazole and benzothiazole derivatives (3,4,6,7).



Physical constants, analysis and spectroscopic data of the salts obtained reacting the bases with methyl iodide are reported in Table I.

The reaction with methyl iodide leads to the *N*-methylpyridinium or quinolinium iodides (compounds **1,2,4,6,7,9**) and the benzimidazolium iodides (compounds **11-13**), in which the 2-benzimidazolyl is α bonded to the azine nitrogen. In particular, compounds **12** and **13** (pyridine series) are 1,3-dimethylbenzimidazolium salts, in which both quaternisation and *N*-alkylation are observed, while in **11** (quinoline series), the *N*-alkylation is not active. Compounds **14** and **15** exhibit the hydroiodide structure instead of the expected methiodide structure, as in the corresponding compounds of the benzoxazole series (4).

The methiodide structure was established by nmr spectroscopy (Table I), following the procedure previously described (3). The $\Delta\delta$ values of the pyridinium and quinolinium salts are in the range of 13.8-22.2 Hz, while those of the benzimidazolium salts are in the range 4.2-8.4 Hz. The 5.48-5.95 τ absorptions assigned to $+N-CH_3$ protons and its integration value corresponds to three protons. The spectra of compounds **12** and **13** indicate the presence of six protons ($\tau +N-CH_3 = 5.91$ and 5.95,



Electronic absorption spectra of compounds:

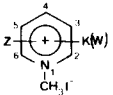
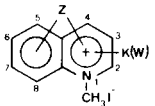
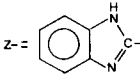
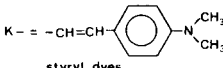
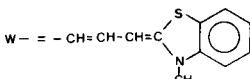
..... methiodide **1** (----- free base)
..... methiodide **2** (..... free base)

Table I
Salts

Compounds 1-5 Compound Number	M.p. °C	Compounds 6-10 Empirical Formula	C%		H%		N%		Compounds 12-13 Electronic Absorption Spectra λ max (log ε), nm (a)	δC-CH ₃ ppm	Compounds 14-15 Nmr Spectra τ-N-CH ₃ ppm	Δδ(b) Hz
			Calcd.	Found	Calcd.	Found	Calcd.	Found				
	283-284	C ₁₄ H ₁₄ N ₃	47.88	48.01	4.02	4.09	11.97	11.85	362 (4.38)	7.15	5.72	15.6
	263-265	C ₁₄ H ₁₄ N ₃	47.88	47.61	4.02	4.11	11.97	11.85	318 (4.26)	7.11	5.58	20.4
									265 (3.78)	7.20	5.68	17.4
	229-231	C ₁₄ H ₁₄ N ₃	47.88	47.63	4.02	4.12	11.97	11.80	305 (4.06)	7.07	5.58	15.6
									255 (3.81)	7.40	5.63	18.0
	258-259	C ₁₈ H ₁₆ N ₃	53.88	53.73	4.02	4.16	10.47	10.49	392 (4.25); 332 (4.12)	6.83	5.50	22.2
	271-272	C ₁₈ H ₁₆ N ₃	53.88	53.80	4.02	4.00	10.47	10.61	370 (3.91); 303 (4.42)	6.97	5.53	19.8
									318 (4.00)	6.89	5.50	25.2
	274-275	C ₁₈ H ₁₆ N ₃	53.88	53.73	4.02	4.14	10.47	10.36	371 (3.89); 303 (4.44)	6.95	5.48	13.8
	221-222	C ₁₈ H ₁₆ N ₃	53.88	54.01	4.02	4.14	10.47	10.48	347 (4.31); 332 (4.37)	6.97	5.36	21.0
									284 (4.36)	7.10	5.50	4.8
	263-264	C ₁₅ H ₁₄ N ₃	49.33	49.20	4.42	4.56	11.51	11.50	288 (4.17)	7.32	5.91 (f)	4.2
	305-306	C ₁₅ H ₁₄ N ₃	49.33	49.26	4.42	4.53	11.51	11.40	285 (4.18)	7.46	5.95 (f)	8.4
	325-327 dec	C ₁₇ H ₁₄ N ₃	52.73	52.61	3.64	3.77	10.85	10.89	345 (4.24); 325 (4.18)	7.05		1.8
	303-305 dec	C ₁₇ H ₁₄ N ₃	52.73	52.85	3.64	3.78	10.85	10.71	345 (4.00); 320 (4.06)	7.20		3.6

(a) The main absorptions above 250 nm are indicated. (b) Δδ values (Hz) are defined as follows: Δδ = δC-CH₃(methiodide) - δC-CH₃(base). (c) References 8,9. (d) References 9,10. (e) Reference 11. (f) The integration of this signal corresponds to six protons.

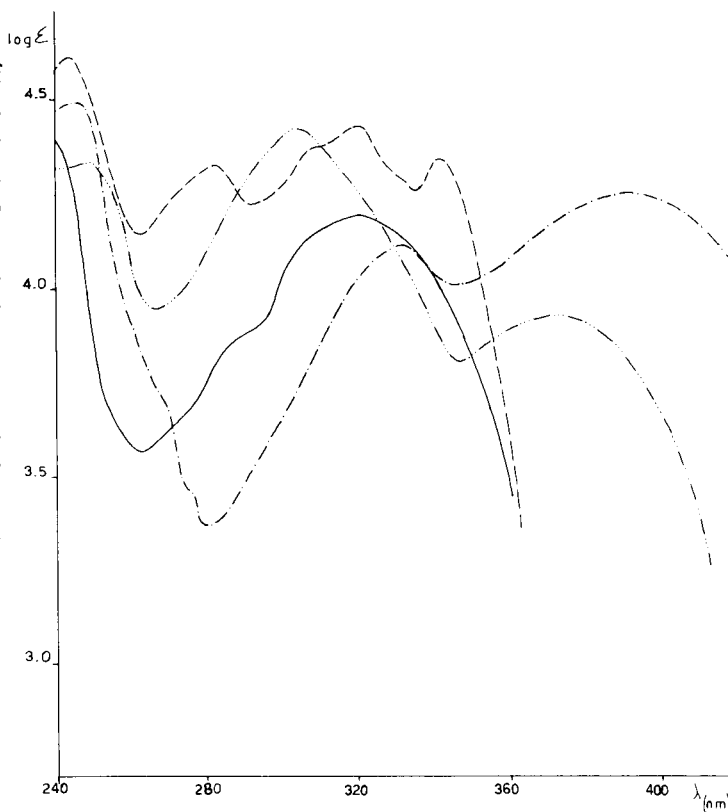
Table II
 Polymethine Dyes

General Formulas	Compound Number	Structure	M.p. °C	Electronic Absorption Spectra λ max, nm (log ϵ)
 Compounds: 16-25	16	4-Z 2-K	275-276	507 (4.56)
	17	4-Z 2-W	271-273	558 (4.85)
	18	5-Z 2-K	274-276	515 (4.74)
	19	5-Z 2-W	250-252	559 (5.03)
	20 (a)	2-K		460 (4.57)
 Compound: 26-35	21 (b)	2-W		536 (4.93)
	22	3-Z 4-K	204-206	515 (4.57)
	23	3-Z 4-W	197-199	564 (4.84)
	24 (a)	4-K		480 (4.62)
	25 (b)	4-W		557 (4.98)
 Z =	26	4-Z 2-K	290-291	565 (4.73)
	27	4-Z 2-W	250-251	605 (4.81)
	28	6-Z 2-K	284-285	557 (4.85)
	29	6-Z 2-W	288-289	599 (5.12)
	30 (c)	2-K		525 (4.78)
 styryl dyes	31 (b)	2-W		582 (5.12)
	32	6-Z 4-K	261-262	581 (4.61)
	33	6-Z 4-W	310-311	654 (5.14)
	34 (c)	4-K		544 (4.65)
	35 (d)	4-W		630 (5.14)
 unsymmetrical dyes	33	6-Z 4-K	261-262	581 (4.61)
	34 (c)	4-K		544 (4.65)

(a) Reference 15. (b) Reference 16. (c) Reference 17. (d) Reference 18. respectively), in agreement with the usual behaviour of 1,3-dialkylbenzimidazolium salts. Besides, compound **II**, obtained under more drastic conditions (see Experimental), is a monomethyl benzimidazolium salt (τ +N-CH₃ = 5.50; three protons). The salts **14** and **15** show low $\Delta\delta$ values (1.8 and 3.6 Hz), without +N-CH₃ signals and with a broad +N-H peak which rapidly exchanges with deuterated water. This suggests an hydroiodide structure similar to that of the analogous 8-(2-benzoxazolyl)methylquinoline hydroiodides (4). Owing to the low $\Delta\delta$ value, however, the site of protonation is the azole nitrogen atom (13).

A comparison of nmr data of the quaternary salts containing 2-benzoxazolyl and 2-benzothiazolyl (3,4) with our data suggest some generalizations. Both pyridinium and quinolinium salts show a deshielding effect of the hetaryl moiety on the chemical shifts (τ values) of C-CH₃ and +N-CH₃ protons and a magnitude of $\Delta\delta$ values in a given series (that is a fixed position of methyl and rings) in the order: 2-benzoxazolyl > 2-benzothiazolyl > 2-benzimidazolyl. Furthermore, if a comparison is made with unsubstituted compounds (2 or 4 picolinium, quinaldinium and lepidinium methiodides) the same effects are observed (14) (the 2-benzimidazolyl even plays, in few cases a shielding role).

The main absorptions above 240 nm of the electronic spectra of salts **1-15** are reported in Table I. The spectral



Electronic absorption spectra of compounds:

— methiodide **7** (— free base)
 - - - methiodide **6** (— free base)

experimental conditions of the reaction with methyl iodide are important factors in determining the structure of the salts in these series. As a further proof of this situation it is interesting to note that compound **6** is recovered refluxing the proper base with methyl iodide. If the reaction is carried out in a sealed tube at 95° for several hours, besides this product, the formation of a 1,3-dimethylbenzimidazolium derivative and a bis iodide (each of the three nitrogens is methylated) is observed.

(14) In the case of 1,4-dimethyl-3-(2-benzothiazolyl)pyridinium iodide (compound **16** in reference 4), τ and $\Delta\delta$ values are lowered presumably due to a steric effect caused by the substituent methyl group. This results

in a feeble discrepancy with these general statements for compound **4**.

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