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Four betaines derived from imidazo[4,5-*a*], imidazo[5,4-*a*] and thiazolo[5,4-*a*]acridine have been prepared in a six step procedure starting from 2-chlorobenzimidazoles and benzothiazoles. The ^{1}H and ^{13}C nmr has been used to characterize the compounds, particularly the orientation of the step leading to the formation of the acridinone ring. The uv-visible spectra of one betaine (wave numbers ν in cm^{-1}) shows a linear dependence with Reichardt's E_T parameter and a high sensitivity to solvent effects.

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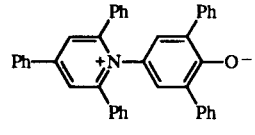
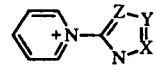
Mainly due to the success of Reichardt's E_T polarity solvent scale, which is based on compound **1** [1,2], pyridinium betaines have become increasingly studied. Alcalde *et al.* have thoroughly explored the case of azolate-pyridinium betaines **2** [3].

We will describe in this paper the case of betaines **9** derived from fused imidazo and thiazoloacridinones,

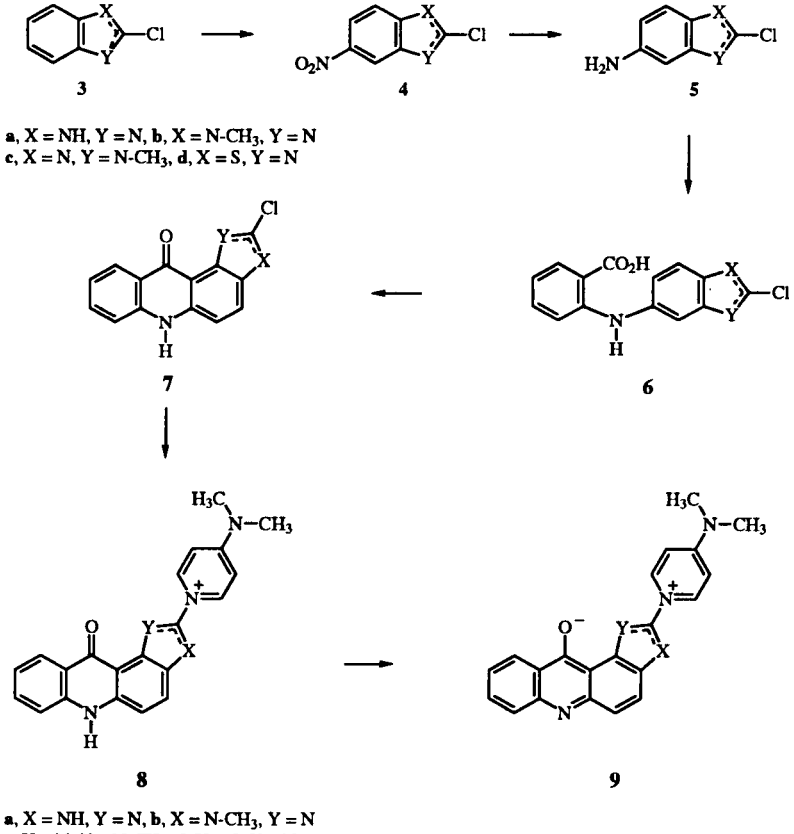


1



2

Scheme 1



a, X = NH, Y = N, **b**, X = N-CH_3, Y = N
c, X = N, Y = N-CH_3, **d**, X = S, Y = N

3 **4** **5** **6** **7** **8** **9**

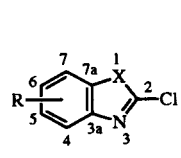
a, X = NH, Y = N, **b**, X = N-CH_3, Y = N
c, X = N, Y = N-CH_3, **d**, X = S, Y = N

which present an extended π system amongst other interesting properties.

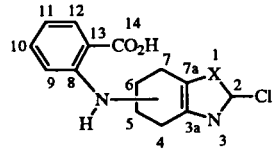
Results and Discussion.

Chemistry.

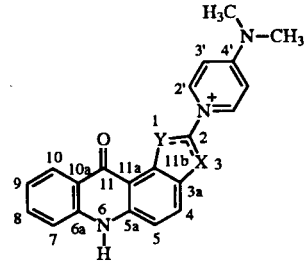
The preparation of betaines **9a-9d** is summarized in Scheme 1. Starting from 2-chlorobenzimidazole (**3a**), 1-methyl-2-chlorobenzimidazole (**3b**) and 2-chlorobenzothiazole (**3d**), the synthesis involves several steps: nitration by a mixture of nitric and sulfuric acids to obtain the 5(6)-nitro derivatives **4a-4d,** reduction by stannous chloride in hydrochloric acid, formation of 5(6)-amino derivatives **5a-5d**, Ullmann condensation with *o*-bromobenzoic acid, anthranilic acids **6a-6d,** using ultrasound irradiation, and cyclisation by means of sulfuric acid, yielding chloro derivatives of fused acridinones **7a-7d**. Reaction with *N,N*-dimethylaminopyridine provides salts **8** or the corresponding betaines **9**, depending on the experimental conditions.



3,4,5



6



7,8,9

In the case of the nitration of benzimidazoles, from the NH-derivative **3a** only a nitro derivative was obtained, the 2-chloro-5(6)-nitrobenzimidazole **4a**. In the case of the *N*-methyl derivative **3b**, two isomers were obtained, the 5-nitro **4b** and the 6-nitro **4c**. The same compounds and in the same ratio, *ca.* 1:1, were obtained by methylation of **4a**. Since isomers **4b** and **4c** having similar chromatographic properties, the isomer separation was carried out on the amino derivatives **5b** and **5c**. In the **d** series, intermediates **4d**, **5d**, **6d** and **7d** have been described in one of our previous works [4].

The cyclisation step, **6** → **7**, can, in principle, yield two isomers depending on the position in which the intramolecular acylation takes place: *ortho* to the five membered ring, "linear" isomer, or *para* to that ring, "bent" isomer [5]. The ^{1}H nmr spectroscopy (*vide infra*) was used to demonstrate that all the compounds **7**, **8**, **9** in Scheme 1 are "bent" isomers.

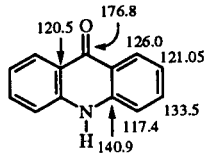
The structure of the salts **8** and betaines **9** does not present any ambiguity save in the case of the derivatives of benzimidazole, **a** series, where two tautomers are possible for the salt **8a** and three for the betaine **9a,** Scheme 2. Previous results demonstrated that acridinones exist as such and none or at least a negligible amount as 9-hydroxyacridines [6-8]; for this reason, in Scheme 2, this second source of complexity has not been taken into account.

NMR Spectroscopy.

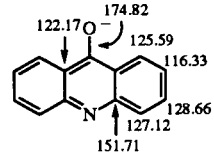
The following numbering has been used both for ^{1}H (Table 1) and for ^{13}C nmr (Table 2):

The ^{1}H nmr data, Table 1, were useful to establish the "bent" structure of the imidazo and thiazoloacridinones thanks to the observation of an AB system with an *ortho* coupling constant of about 9 Hz formed by protons H-4 and H-5. Note that the proximity of the N-CH_3 group in **7c** and **8c,** position 1, to the carbonyl group at position 11 produces a deshielding compared to that of compounds **7b** and **8b,** position 3, 4.2 ppm *vs* 3.8 ppm. Another noticeable feature of the ^{1}H nmr spectra is the N(6)-H signal of acridinones at 12-13 ppm.

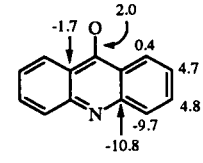
The ^{13}C nmr spectra of compounds **7-9** have a characteristic signal of the acridinone tautomer, that of signal of C-11 at 175 ppm [8]. We have recorded the ^{13}C nmr spectrum of acridinone **10** in dimethyl-d_6 sulfoxide/sodium hydride to determine the effects ($\Delta\delta = \delta_{NH} - \delta_{N^-}$) experienced by the different carbons when the anion is formed. The results are shown below:



10, dimethyl-d_6 sulfoxide



10$^-$



$\Delta\delta$ (in ppm)

Table 1

^{1}H NMR Chemical Shifts (ppm) of Compounds **3-9** (solvent: dimethyl-d_6 sulfoxide)

Compound	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-11	H-12	XH
3b	7.58	7.28	7.23	7.53	----	----	----	----	----	3.78 (NCH_3)
4a	8.35	----	8.08	7.64	----	----	----	----	----	6.75 (NH)
4b	8.44	----	8.10	7.76	----	----	----	----	----	3.85 (NCH_3)
4c	7.81	8.19	----	8.62	----	----	----	----	----	3.89 (NCH_3)
5a	6.67	----	6.59	7.20	----	----	----	----	----	12.53 (NH), 4.94 (NH_2)
5b	6.74	----	6.65	7.21	----	----	----	----	----	3.66 (NCH_3), 4.89 (NH_2)
5c	7.24	6.56	----	6.60	----	----	----	----	----	3.89 (NCH_3), 5.12 (NH_2)
6a	7.36	----	7.09	7.50	----	7.06	7.32	6.71	7.88	9.61 (NH)
6b	7.46	----	7.21	7.59	----	7.01	7.32	6.71	7.88	3.79 (NCH_3), 9.60 (NH) 12.51 (CO_2H)
6c	7.56	7.13	----	7.50	----	7.15	7.35	6.74	7.90	3.74 (NCH_3), 9.72 (NH) 13.01 (CO_2H)
	H-4	H-5	H-6	H-7	H-8	H-9	H-10	H-2'	H-3'	XH
7a	7.98	7.43	----	7.63	7.77	7.33	8.32	----	----	12.07 (NH)
7b	8.00	7.48	----	7.56	7.70	7.25	8.25	----	----	3.87 (NCH_3), 11.84 (NH)
7c	7.92	7.40	----	7.55	7.72	7.27	8.24	----	----	4.32 (NCH_3), 11.95 (NH)
8b	8.13	~7.0	----	~7.0	~7.0	7.29	8.26	8.67	7.31	3.36 (NMe_2), 3.84 (NCH_3) 12.20 (NH)
8c	8.10	7.72	----	7.74	7.76	7.31	8.28	8.70	7.29	3.36 (NMe_2), 4.14 (NCH_3) 12.76 (NH)
8d	9.01	8.59	----	8.52	8.52	8.21	9.14	9.16	7.47	3.76 (NMe_2), 12.43 (NH)
9a	7.80	7.07	----	7.49	7.60	7.15	8.24	9.26	7.20	3.28 (NMe_2)
9d	8.04	7.73	----	7.69	7.56	7.14	8.29	8.93	7.16	3.30 (NMe_2)

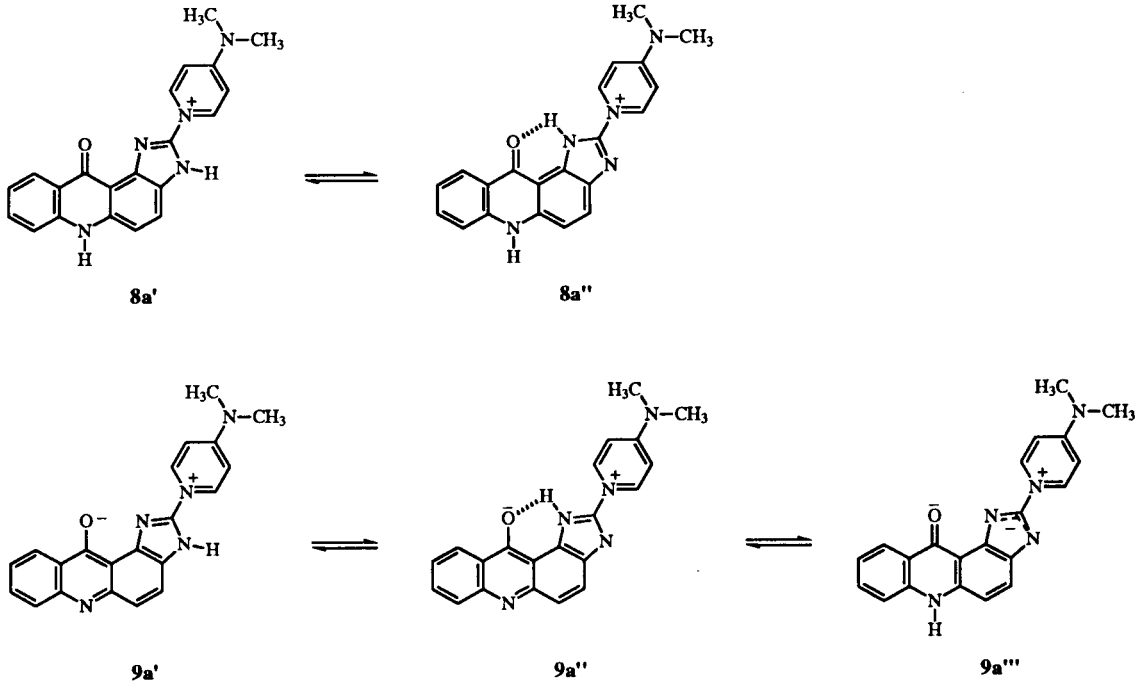
Table 2

^{13}C NMR Chemical Shifts (ppm) of Compounds **3-9** (solvent: dimethyl-d_6 sulfoxide)

Compound	C-2	C-3a	C-4	C-5	C-6	C-7	C-7a	C-8	C-9	C-10	C-11	C-12	C-13	Other
3b	140.3	141.2	118.5	122.8	122.3	110.4	135.7	----	----	----	----	----	----	30.5 (NCH_3)
4a	142.8	142.4	111.9	143.7	118.1	114.3	138.8	----	----	----	----	----	----	----
5a	135.6	138.1	96.8	144.6	112.0	116.7	132.9	----	----	----	----	----	----	----
5b	138.6	142.4	101.8	144.8	112.3	110.3	128.2	----	----	----	----	----	----	30.4 (NCH_3)
5c	136.3	137.0	118.9	111.8	145.7	93.5	133.1	----	----	----	----	----	----	30.2 (NCH_3)
6a	138.8	N.O.	108.3	135.8	119.3	116.2	N.O.	148.6	113.4	134.3	117.0	132.0	112.2	170.3 (C=O)
6b	140.8	141.8	112.9	135.4	120.0	111.4	132.9	134.1	122.0	127.7	121.8	175.8	116.6	170.1 (C=O), 30.7 (NCH_3)
6c	139.9	137.8	119.3	118.7	136.0	104.6	136.5	148.1	113.4	134.4	117.0	131.9	112.0	170.1 (C=O), 30.6 (NCH_3)
	C-2	C-3a	C-4	C-5	C-5a	C-6a	C-7	C-8	C-9	C-10	C-10a	C-11	C-11a	C-11b	Other
7a	137.1	136.3	125.3	112.1	138.4	140.4	117.7	133.2	121.4	125.4	120.7	175.7	107.8	131.0	
7b	139.6	130.2	117.8	113.3	139.0	139.9	117.2	132.6	120.9	125.9	121.9	175.3	111.6	138.1	30.8 (NCH_3)
7c	140.1	136.4	125.7	113.6	139.9	139.5	117.0	133.1	121.4	126.0	121.6	175.5	109.0	132.7	37.3 (NCH_3)
8a	144.3	130.4	125.7	113.3	140.3	138.7	117.7	133.2	121.5	125.3	120.6	175.6	107.9	134.6	
8b	145.5	129.9	117.9	115.1	140.1	139.7	117.5	132.8	121.3	125.8	122.1	175.4	112.0	136.8	31.0 (NCH_3)
8c	146.5	135.0	126.5	114.9	140.8	139.7	117.3	133.1	121.6	125.9	121.7	175.3	109.2	138.4	37.4 (NCH_3)
8d [a]	158.8	149.4	129.9	121.2	142.8	142.9	121.5	134.8	125.6	129.9	117.7	169.8	110.4	130.4	
9a [b]	143.0	126.2	121.1	122.6	151.8	148.9	127.4	127.8	117.1	126.6	122.4	173.0	107.4	136.7	
9c	145.2	132.8	121.5	124.3	N.O.	N.O.	125.6	131.0	119.8	125.6	122.6	174.1	109.4	131.0	37.0 (NCH_3)
	C-2'	C-3'	C-4'	NMe_2											
8a	138.8	107.2	156.4	40.3											
8b	141.7	107.8	156.8	41.0											
8c	141.7	107.9	156.7	40.5											
8d [a]	140.3	110.4	160.3	42.0											
9a [b]	141.6	107.4	154.9	40.5											
9c	141.7	107.7	156.6	40.4											

[a] In trifluoroacetic acid. [b] In dimethyl-d_6 sulfoxide plus sodium hydride. N.O. Not observed.

Scheme 2



Although we have represented **10**$^-$ with the negative charge on the oxygen, the system is delocalized; note that carbon C-9 (bearing the oxygen) is relatively unaffected by the negative charge while C-4 and C-4a are shifted 10 ppm to lower fields.

The ^{13}C chemical shifts in Table 2 show that salt **8a** is a mixture of two tautomers **8a'** and **8a''**; its chemical shifts are intermediate between those of **8b** and **8c** while, in the case of betaine **9a**, the only thing which is certain is that it is a monoanion of structure **9a'/9a''**. The anion **9a'''** or a dianion is inconsistent with the effect observed in azolate-pyridinium betaines [3,9].

UV Spectroscopy.

The most characteristic property of betaines is their electronic spectrum. Those of betaines **9a-9d** and the corresponding salts **8a-8d** were recorded in pyridine adding sodium methoxide for betaines and hydrochloric acid for the salts. The data are reported in Table 3. The electronic spectral data of the betaines in dimethyl sulfoxide, adding sodium hydride are presented in Table 4.

Table 3

Electronic Absorption Maxima of Betaines **9** and their Salts **8** in Pyridine

	λ_{max} (nm)					
8a	----	----	406	388	365 (sh)	----
8b	----	----	407	385	----	----
8c	----	----	402	382	360	350
8d	----	----	400	380	360	----
9a	----	----	435	----	----	346
9b	500	445	408	385 (sh)	----	----
9c	500 (sh)	440	403	384	358	----
9d	492	440	410	390 (sh)	----	----

sh: shoulder.

Table 4

Electronic Absorption Maxima of Betaines **9** in Dimethyl Sulfoxide

	λ_{max} (nm)			
9a	----	432	418 (sh)	348
9b	500	----	410	340
9c	500 (sh)	432	----	348
9d	----	458	----	----

sh: shoulder

The electronic spectra of the salts have similar morphology. The spectra of betaines **9b-9d** present two charge transfer absorption bands at lower energy compared to the salts. In the case of the benzimidazole betaine derivative **9a** the morphology of the electronic spectrum

Table 5

Electronic Absorption Maximum of Betaine **9d** in Different Solvents

Solvent	E_T (30)	λ_{max} (nm)
Water	63.1	338
Ethanol	51.9	405
Isopropanol	48.4	425
Acetonitrile	46.0	452
Dimethylsulfoxide	45.0	458
Dimethylformamide	43.8	474
Pyridine	40.5	492

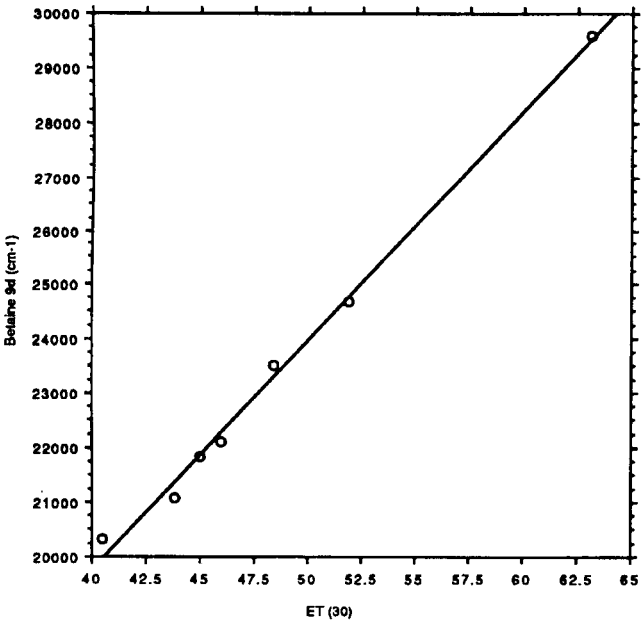


Figure 1. Plot of ν_{max} (cm^{-1}) of betaine **9d** vs Reichardt's E_T (30).

is different. The absorption band at low energy, which may correspond to a charge transfer, appears as a broad band at 435-432 nm.

We will consider the absorption band at 490 nm in pyridine, Table 3, in the study of solvatochromism of betaine **9d**. We have recorded the uv-visible spectra of this betaine in different solvents. A change in position of the long-wave length band with an increasing of solvent polarity has been observed, Table 5 and Figure 1. This change corresponds to a hypsochromic shift *i.e.*, a negative solvatochromism in the studied polarity range; betaine **1** shows also negative solvatochromism [1]. The solvatochromic behaviour could only be observed in solvents of polarity superior to E_T (30) = 40.5 due to the poor solubility of the betaine **9d** in non polar solvents.

Although it is more common in organic chemistry to use wave lengths (λ_{max} in nm), all correlations involving energies [10] should be done in wave numbers (cm^{-1}). A plot of the wave number of the long wave length band against the polarity parameter E_T (30) of the solvent is shown in Figure 1 and corresponds to equation (1) which can be compared with a similar equation for molecule **1**, equation (2).

(1)

$\nu\ (cm^{-1}) = 2926 \pm 648 + 421 \pm 13\ E_T\ (30)$, n = 7, $r^2 = 0.995$

(2)

$\nu\ (cm^{-1}) = 350\ E_T\ (30)$, $r^2 = 1.000$ (by definition)

In conclusion, in which solvent effects are concerned, the sensitivity [that is, the slopes of equations (1) and (2)] of betaine **9d** is a little higher than that of Reichardt, compound **1**, but its lack of solubility limits its applicability for determining the polarity of solvents.

EXPERIMENTAL

Melting points were determined with an Electrothermal 9300 apparatus and are uncorrected. Reagent and solvents were purchased from common commercial suppliers. The nmr spectra were recorded on a Bruker AM 200 spectrometer working at 200 and 50 MHz for ^1H and ^{13}C respectively; in the case of betaines a Varian Unity 500 instrument was used. In all cases, tetramethylsilane was used as internal standard. When necessary, bidimensional spectra, both homonuclear (COSY) and heteronuclear (HMQC, HMBC) were performed on a Bruker AMX 400. The electronic spectra of the betaines **9a-9d** and the corresponding salts **8a-8d** were recorded on a Perkin-Elmer 550 SE UV-Vis spectrophotometer in pyridine adding sodium methoxide for betaines and hydrochloric acid for the salts and in dimethyl sulfoxide, adding sodium hydride for betaines.

2-Chloro-5(6)-nitrobenzimidazole (**4a**).

A mixture of 5 g of commercial 2-chloro-1*H*-benzimidazole (**3a**) and 20 ml of concentrated nitric acid (69%) were cooled in a 100 ml round bottom flask, then, maintaining the interior temperature at 12-15°, 20 ml of concentrated sulfuric acid (95%) was added. The red-colored mixture was stirred at 10° during 1 hour then poured into ice (100 g). The mixture of solid and solution was neutralized with diluted ammonia (50%), filtered, washed with water and dried. The solid was crystallized in ethanol:water (3:1) affording 5.98 g of a yellow-orange powder, mp 218° (223°) [11], yield 92%.

Anal. Calcd. for $C_7H_4N_3O_2Cl$: C, 42.51; H, 2.02; N, 21.26. Found: C, 42.78; H, 1.92; N, 21.56.

2-Chloro-5(6)-aminobenzimidazole (**5a**).

A mixture of 12.64 g of stannous chloride dihydrate (56 mmoles) and 40 ml of concentrated hydrochloric acid (36%) were placed in a 100 ml round bottom flask. To this mixture was added 3.16 g (16 mmoles) of **4a** in small amounts. After 15 minutes stirring, the mixture was heated at 100°, then stirred during 4 hours. The cooled solution was poured into ice (100 g). The solution was made basic (*p*H 8-9) with 3 *M* aqueous sodium hydroxide, then evaporated to dryness. The resulting powder was agitated with a solution of acetonitrile:chloroform (1:1), heated and filtered. The solution was evaporated to dryness affording 2.24 g of a pink powder, mp 145°, yield 84%.

Anal. Calcd. for $C_7H_6N_3Cl$: C, 50.12; H, 3.58; N, 25.06. Found: C, 50.51; H, 3.89; N, 25.38.

N-(2-Chlorobenzimidazol-5-yl)anthranilic Acid (**6a**).

The yield of the sonicated Ullmann condensation is very dependent on the quality of the copper catalyst. Just before starting the reaction, the copper catalyst was prepared from 0.80 g of anhydrous copper sulfate in 5 ml water; to this solution was added 0.30 g of powdered zinc keeping the temperature almost constant. The copper precipitate was filtered, washed first with water, then with acetone and dried in the oven.

In a 100 ml round bottom flask were placed a mixture of 1.00 g of **5a** (6 mmoles), 1.41 g of *o*-bromobenzoic acid (7 mmoles),

1.11 g of anhydrous potassium carbonate (8 mmoles), 0.06 g of powdered copper and 15 ml of ethyl methyl ketone. This mixture was sonicated in a bath (80°) during 3 hours. After evaporation of the solvent, the brown residue was agitated with 80 ml of hot water, filtered and acidified to *p*H 5 with 2*N* aqueous hydrochloric acid. A new precipitate was formed which was filtered, washed with water and dried in the oven, mp 217°, yield 36% (0.62 g).

Anal. Calcd. for $C_{14}H_{10}N_3O_2Cl$: C, 58.39; H, 3.48; N, 14.60. Found: C, 58.72; H, 3.75; N, 14.83.

2-Chloroimidazo[4,5-*a*]acridin-11(6*H*)-one (**7a**).

In a 50 ml round bottom flask was placed a mixture of 0.87 g of **6a** (3 mmoles) and 9 g of concentrated sulfuric acid 96%. The mixture was stirred for 3 hours at 100°, then poured into ice (50 g) and neutralized with diluted ammonia (50%). The green precipitate was filtered, washed five times with water and dried in the oven. The green powder was washed with hot ethanol (95%), mp >300°, yield 75% (0.61 g).

Anal. Calcd. for $C_{14}H_8N_3OCl$: C, 62.29; H, 2.97; N, 15.57. Found: C, 62.61; H, 3.16; N, 15.74.

2-(4-Dimethylamino-1-pyridinium) Imidazo[4,5-*a*]acridinolate (**9a**).

In a 100 ml two-neck round bottom flask were placed 0.81 g of **7a** (3 mmoles) and 3.33 g of *N,N*-dimethylaminopyridine. The mixture was stirred at 160° under nitrogen for 2 hours, then 300 ml of water was added and the resulting solid was filtered. After washing with water, drying and washing again with hot ethanol 95%, an orange residue was obtained, yield 79% (0.84 g).

Anal. Calcd. for $C_{21}H_{17}N_5O$: C, 70.91; H, 4.78; N, 19.70. Found: C, 70.82; H, 4.97; N, 19.91.

1-Methyl-2-chlorobenzimidazole (**3b**).

Compound **3a** (5 g), 50 ml of water and 15 ml of 5*N* aqueous sodium hydroxide were mixed in a 100 ml round bottom flask and cooled in an ice-water bath. The mixture was sirred until it became transparent, then 5.5 ml of methyl sulfate were added dropwise. After 1 hour stirring at 5-10° and 1 hour standing at room temperature, the solution was filtered. The precipitate was washed with water (5 x 100 ml) then dried in the oven: to provide 4.61 g of white powder, mp 113° (114-116°) [12], (yield 84%).

Anal. Calcd. for $C_8H_7N_2Cl$: C, 57.62; H, 4.20; N, 16.81. Found: C, 57.55; H, 4.15; N, 16.73.

1-Methyl-2-chloro-5-nitro- and 1-Methyl-2-chloro-6-nitrobenzimidazoles **4b** and **4c**.

Following the procedure described for **4a**, from 5 g of **3b**, 6.17 g of a 1:1 mixture of **4b** and **4c** was obtained, yield 97%.

Anal. Calcd. for $C_8H_6N_3O_2Cl$: C, 45.37; H, 2.84; N, 19.85. Found: C, 45.69; H, 2.81; N, 20.15.

1-Methyl-2-chloro-5-aminobenzimidazole (**5b**) and 1-Methyl-2-chloro-6-aminobenzimidazole (**5c**).

Following the procedure described for **5a**, from 2.12 g of a 1:1 mixture of **4b** and **4c** the reduction yields 1.27 g of a mixture of **5b** and **5c**. The mixture was separated by column chromatography on silica gel, using dichloromethane:acetonitrile (7:3) as the eluent. The same amount of both amino isomers was obtained, **5b** as pale-brown crystals and **5c** as a pink powder.

Compound **5b** had mp 139°, yield 35%.

Anal. Calcd. for $C_8H_8N_3Cl$: C, 52.86; H, 4.41; N, 23.13. Found: C, 53.07; H, 4.49; N, 23.36.

Compound **5c** had mp 183°, yield 35%.

Anal. Calcd. for $C_8H_8N_3Cl$: C, 52.86; H, 4.41; N, 23.13. Found: C, 53.00; H, 4.54; N, 23.32.

N-(1-Methyl-2-chlorobenzimidazol-5-yl)anthranilic Acid (**6b**).

Following the procedure described for **6a** and starting with 1.82 g (10 mmoles) of **5b**, anthranilic acid **6b** was obtained as a green-gray powder (2.45 g), mp 226°, yield 81%.

Anal. Calcd. for $C_{15}H_{12}N_3O_2Cl$: C, 59.66; H, 3.98; N, 13.92. Found: C, 59.51; H, 3.84; N, 13.85.

N-(1-Methyl-2-chlorobenzimidazol-6-yl)anthranilic Acid (**6c**).

Following the procedure described for **6a** and starting with 1.82 g (10 mmoles) of **5c**, anthranilic acid **6c** was obtained as a green powder (2.63 g), mp 178°, yield 87%.

Anal. Calcd. for $C_{15}H_{12}N_3O_2Cl$: C, 59.66; H, 3.98; N, 13.92. Found: C, 59.96; H, 4.29; N, 14.13.

2-Chloro-3-methylimidazo[4,5-*a*]acridin-11(6*H*)-one (**7b**).

Following the procedure described for **7a** and starting with 1.81 g (6 mmoles) of **6b**, acridinone **7b** was obtained as green powder (1.37 g), mp 304°, yield 81%.

Anal. Calcd. for $C_{15}H_{10}N_3OCl$: C, 63.45; H, 3.52; N, 14.80. Found: C, 63.62; H, 3.49; N, 14.95.

2-Chloro-1-methylimidazo[5,4-*a*]acridin-11(6*H*)-one (**7c**).

Following the procedure described for **7a** and starting wtih 1.81 g (6 mmoles) of **6c**, acridinone **7c** was obtained as yellow-green powder (1.24 g), mp >300°, yield 73%.

Anal. Calcd. for $C_{15}H_{10}N_3OCl$: C, 63.45; H, 3.52; N, 14.80. Found: C, 63.34; H, 3.42; N, 14.96.

4-Dimethylamino-1-(3-methylimidazo[4,5-*a*]acridinon-2-yl)pyridinium Chloride (**8b**).

Following the procedure described for **8a** and starting with 0.85 g (3 mmoles) of **7b**, betaine salt **8b** was obtained as a pale-brown powder (1.00 g) mp >300°, yield 82%.

Anal. Calcd. for $C_{22}H_{20}N_5OCl$: C, 65.04; H, 4.93; N, 17.25. Found: C, 64.83; H, 5.23; N, 17.48.

4-Dimethylamino-1-(1-methylimidazo[5,4-*a*]acridinon-2-yl)pyridinium Chloride (**8c**).

Following the procedure described for **8a** and starting with 0.85 g (3 mmoles) of **7c**, the betaine salt **8c** was obtained as dark-brown powder (0.85 g), mp >300°, yield 70%.

Anal. Calcd. for $C_{22}H_{20}N_5OCl$: C, 65.04; H, 4.93; N, 17.25. Found: C, 64.81; H, 4.87; N, 17.08.

4-Dimethylamino-1-(thiazolo[5,4-*a*]acridinon-2-yl)pyridinium Chloride (**8d**).

In a 50 ml two-neck round bottom flask were placed 0.87 g of **7d** (3 mmoles) [7] and 3.33 g of *N,N*-dimethylaminopyridine (27 mmoles). The mixture was stirred at 130° under nitrogen for 2 hours. After cooling, to the solid residue was added 50 ml of a mixture of diethyl ether:acetonitrile (1:1) and the mixture was stirred, filtered and dried under vacuum. The yellow residue (1.18 g) corresponds to 95% yield.

Anal. Calcd. for $C_{21}H_{17}N_4OSCl$: C, 61.63; H, 4.16; N, 13.70. Found: C, 61.98; H, 4.52; N, 13.55.

2-(4-Dimethylamino-1-pyridinium) Thiazolo[5,4-*a*]acridinolate (**9d**).

In a 50 ml two-neck round bottom flask were placed 0.87 g of **7d** (3 mmoles) [7] and 3.33 g of *N,N*-dimethylaminopyridine (27 mmoles). The mixture was stirred at 130° under nitrogen for 2 hours. After cooling, to the solid residue was added 150 ml of water. The orange precipitate was filtered, washed with water and dried under vacuum (0.84 g), mp 246° dec, yield 74%.

Anal. Calcd. for $C_{21}H_{16}N_4OS$: C, 67.67; H, 4.30; N, 15.04. Found: C, 68.02; H, 4.52; N, 14.83.

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