

## Synthesis and Spectroscopic Characterisation of *N*-Alkyl Quaternary Ammonium Salts Typical Precursors of Cyanines

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Received: 23 October 2001; in revised form 18 February 2002 / Accepted: 26 February 2002 /

Published: 31 March 2002

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**Abstract:** The synthesis and spectroscopic characterisation of some representative *N*-alkyl-substituted quaternary ammonium salts derived from benzothiazole, benzoxazole, benzoselenazole, indole and quinoline are described. These heterocyclic salts, bearing an activated methyl group in the 2-position in relation to the nitrogen atom and *N*-methyl, -pentyl, -hexyl and -decyl chains, are typical precursors of cyanine dyes.

**Keywords:** Heterocyclic quaternary ammonium salts, cyanines precursors, spectroscopic characterisation.

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### Introduction

Despite the fact that several *N*-alkyl quaternary ammonium salts bearing a 2-methylbenzothiazole, -benzoselenazole, -benzoxazole, -indole and -quinoline nuclei are easily found in the literature, mainly as unisolated precursors of cyanine dyes [1-3], their full physical and spectroscopic characterisation is

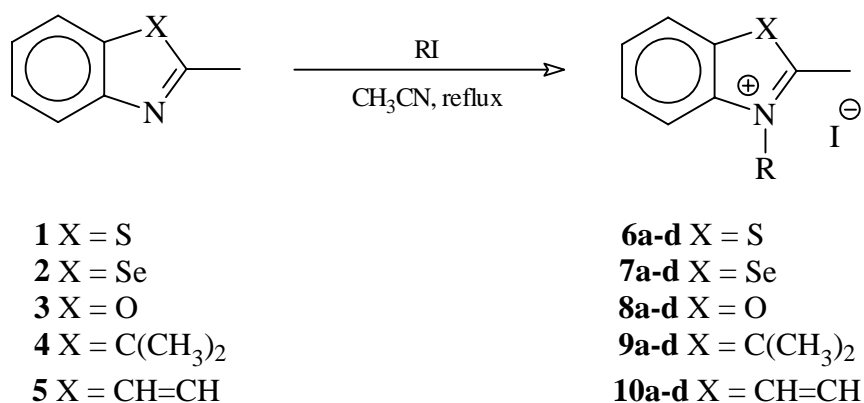
not usually described. To the best of our knowledge, for some of those most commonly used for the synthesis of cyanines, namely the *N*-ethyl, -pentyl, -hexyl and -decyl substituted ones, only the  $^1\text{H}$ -NMR spectral data for the *N*-ethyl quaternary salts [4,5] and the  $^{13}\text{C}$ -NMR spectral data for the *N*-ethylquinolinium salts [5] are available.

The 2-methylheterocyclic ammonium salts are generally synthesised by heating the corresponding heteroaromatic base with a molar equivalent or an excess of an alkylating agent such as an alkyl iodide, bromide, sulphate or tosylate, among others [1]. Alternatively, the condensation can be carried out in a polar aprotic solvent as acetonitrile [6] or *N,N*-dimethylformamide (DMF) [7,8].

## Results and Discussion

The *N*-alkyl-2-methylbenzothiazolium (**6a-d**), -benzoselenazonium (**7a-d**), -benzoxazolium (**8a-d**), -indolium (**9a-d**) and -quinolinium (**10a-d**) quaternary iodides were prepared by heating under reflux a solution of the corresponding 2-methylheterocyclic base (**1-5**) with an excess of iodoethane, 1-iodopentane, 1-iodohexane or 1-iododecane in acetonitrile (Scheme 1). The resulting salts were readily separated from the crude reaction mixtures by precipitation upon addition of diethyl ether. The alkylating procedure could be repeatedly applied to the mother liquors, each time previously freed of the precipitation solvent, in order to achieve convenient yields. According to NMR spectroscopy the products were of satisfactory purity and, therefore, no attempts at further purification by recrystallization were necessary.

**Scheme 1.** Synthesis of *N*-alkyl quaternary ammonium salts **6-10**.



**a:** R = CH<sub>2</sub>CH<sub>3</sub>; **b:** R = (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>; **c:** R = (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>; **d:** R = (CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>

The quaternary iodides were generally obtained in rather good yields, usually decreasing as the length of the *N*-alkyl chain increases (Table 1, see Experimental). The corresponding melting point

(m.p.), Fourier Transform Infrared Spectra (FTIR) and High Resolution Fast Atom Bombardment Mass Spectra (HR FAB-MS) data are also collated in Table 1.

The most intense and/or characteristic bands of the FTIR spectra appeared around  $3000\text{ cm}^{-1}$  (C-H from Ar-H stretch),  $2826\text{-}2994\text{ cm}^{-1}$  (C-H from  $\text{CH}_2$  stretch),  $1635\text{-}1578$  (C=C),  $1509\text{-}1524\text{ cm}^{-1}$  (C=N),  $1428\text{-}1467\text{ cm}^{-1}$  ( $\text{CH}_3$  asymmetric deformation and  $\text{CH}_2$  deformation) and  $757\text{-}781\text{ cm}^{-1}$  (skeletal “out of plane” vibration). These last two bands are generally the most intense ones found in the spectra of the benzoazole and indole salts. For each series of compounds, the intensity of the aliphatic C-H absorption bands within the  $2826\text{-}2994\text{ cm}^{-1}$  region was observed to increase with the length of the *N*-alkyl chain.

The  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectral data of all the heteroaromatic salts synthesised are collated in Tables 2-5. The NMR spectra were recorded in  $\text{DMSO-d}_6$  solutions except those of the benzoxazolium salts **8a-d**, which were recorded in  $\text{CDCl}_3$  solution, since in the latter solvent an unexpected transformation was observed. This result is currently the subject of a separate study, the results of which shall be published elsewhere.

The assignment of the aromatic  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR signals was based on their chemical shifts and multiplicity (for the  $^1\text{H}$  signals) and was unambiguously established with the aid of HMQC (Heteronuclear Multiple Quantum Coherence), HMBQ (Heteronuclear Multiple Bond Correlation) and COSY (Correlated Spectroscopy) experiments. The attributions of the aromatic  $^1\text{H}$ -NMR chemical shifts are in full agreement with those previously reported for the *N*-ethyl quaternary salts derived from the same heteroaromatic bases employed herein [4,5]. The assignments of the aromatic  $^{13}\text{C}$ - signals are also consistent with the spectral data of salts similar to **6-9** [9-12] and with that described for *N*-ethyl-2-methylquinolinium iodide (**10a**) [5]. The assignment of the aliphatic  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR chemical shifts was accomplished based on the deshielding effect displayed by the neighbouring electronegative nitrogen atoms [13].

The  $^1\text{H}$ -NMR absorptions of the 2- $\text{CH}_3$  groups typically range from 2.84 to 3.36 ppm. The salts derived from 2,3,3-trimethylindole (**4**) invariably display the lowest chemical shift, coincidentally the same for compounds **9a-d**, once the deshielding effect of the heteroatoms of benzoazoles **6-8** and that of the  $sp^2$  carbon in the quinolinium salt **10** are absent.

The  $^{13}\text{C}$ -NMR chemical shifts of 2-C fall within the 13.7-19.9 ppm region. Accordingly to the reasons afore mentioned, the lower field absorptions are ascribed to the substituted indolium salts **9a-d**.

The order of the aromatic  $^{13}\text{C}$  chemical shifts show a clear dependence on the nature of the heterocyclic moiety of the salt, being in almost every cases different from one salt to another. Only the 2-C absorption is, for all compounds, the one at lower field as a consequence of being, simultaneously,  $sp^2$  hybridised and adjacent to a positively charged nitrogen (Table 5). On the contrary, the order of the chemical shifts of the aromatic protons is the same for compounds **6-9**, when their relative position with respect to the nitrogen atom of the heterocyclic moiety is considered. An exception to this trend is observed for the quinolinium salts **10a-d** where the absorption of the 5-H appears at higher field than that of 8-H.

## Conclusions

The synthesis and spectroscopic characterisation of some representative ammonium quaternary salts, bearing benzothiazole, benzoxazole, benzoselenazole, indole and quinoline nuclei, possessing a methyl group in the 2-position in relation to the ammonium group and methyl, pentyl, hexyl and decyl *N*-alkyl chains was described.

## Acknowledgements

Thanks are due to FCT, Lisbon, POCTI and FEDER for their financial support for this work (Project POCTI/32915/QUI/00).

## Experimental

### *General*

All reagents and chemicals were obtained from Sigma-Aldrich. Solvents were of analytical grade. Reactions were monitored by thin-layer chromatography using 0.20 mm aluminium-backed silica-gel plates (Merck GF<sub>254</sub>). The plates were eluted with dichloromethane/methanol (5-10%) and the spots examined under 254, 312 and 365 nm UV light. Melting points were measured in open capillary tubes in a Büchi 530 apparatus and are uncorrected. FTIR spectra were recorded on a Mattson 5000 spectrophotometer. All samples were prepared by mixing FTIR-grade KBr (Sigma-Aldrich) with 1% (w/w) salt, and grinding to a fine powder. Spectra were recorded over the 400-4000 cm<sup>-1</sup> range without baseline corrections. Characteristic absorptions are given in cm<sup>-1</sup>. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded in DMSO-d<sub>6</sub> or CDCl<sub>3</sub> solutions on a Brüker ACP 250 (250.13 and 62.90 MHz), a Brüker ARX 400 (400.13 and 100.62 MHz) or a Brüker ARX 500 Avance spectrometer (500.13 and 125.76 MHz). Chemical shifts are reported as  $\delta$  values in ppm using TMS as an internal standard. Coupling constants (J) are given in Hz. HMQC, HMBC and COSY experiments were performed on the Brüker ARX 400 spectrometer. High Resolution Fast Atom Bombardment Mass Spectra (HR FAB-MS) were recorded in a Micromass AutoSpec M, operating at 70 eV, using a matrix of 3-nitrobenzyl alcohol.

### *Synthesis of quaternary ammonium salts 6-10*

A solution of the heteroaromatic compound [2-methylbenzothiazole (**1**), 2-methylbenzoselenazole (**2**), 2-methylbenzoxazole (**3**), 2,3,3-trimethylindole (**4**) or 2-methylquinoline (**5**)] (1.0 mmol) and the appropriate alkylating agent (iodoethane, 1-iodopentane, 1-iodohexane or 1-iododecane) (3.0-5.0 mmol) in acetonitrile (25 mL) was heated under reflux for 24 h. After cooling, diethyl ether was added, the desired quaternary salts **6-10** collected by filtration under reduced pressure and washed several

times with diethyl ether. Drying under vacuum furnished spectroscopically pure compounds **6-10**. The ether from the combined filtrates was removed by evaporation at reduced pressure and the remaining residue, consisting mainly of the unreacted starting materials, was heated under reflux for another 24 h and worked-up as described above. The process was repeated 1-3 times to achieve a suitable yield. Yields, m.p. and spectroscopic data of the compounds thus prepared is collated in Tables 1-5.

**Table 1.** Yields, m.p., FTIR and HR FAB-MS spectral data of salts **6-10**.

Salt	Yield (%)	m.p. (°C) (Lit.)	FTIR $\lambda_{\max}$ (cm <sup>-1</sup> )	HR FAB-MS m/z found (M. formula: calcd.)
<b>6a</b>	78	198-199 (219)[14]	2970, 2915, 1578, 1513, 1445, 1330, 779	178.068281 (C <sub>10</sub> H <sub>12</sub> NS: 178.069046)
<b>6b</b>	59	152-153	2957, 2908, 2861, 1578, 1521, 1461, 1442, 1333, 768	220.115129 (C <sub>13</sub> H <sub>18</sub> NS: 220.115997)
<b>6c</b>	44	125-126	2956, 2925, 2871, 2853, 1579, 1520, 1459, 1440, 1338, 763	234.130630 (C <sub>14</sub> H <sub>20</sub> NS: 234.131647)
<b>6d</b>	39	111-112	2921, 2859, 1581, 1517, 1464, 1441, 1336, 770	290.194478 (C <sub>18</sub> H <sub>28</sub> NS: 290.194247)
<b>7a</b>	69	212-213 (212)[15]	2971, 2920, 1579, 1509, 1445, 1320, 1191, 777	224.015196/226.014502 (C <sub>10</sub> H <sub>12</sub> N <sup>78</sup> Se: 224.014278; C <sub>10</sub> H <sub>12</sub> N <sup>80</sup> Se: 226.013495)
<b>7b</b>	47	163-164	2952, 2920, 2864, 1576, 1515, 1441, 1369, 1326, 1188, 770	266.060980/268.060429 (C <sub>13</sub> H <sub>18</sub> N <sup>78</sup> Se: 266.061229; C <sub>13</sub> H <sub>18</sub> N <sup>80</sup> Se: 268.060445)
<b>7c</b>	40	132-133	2953, 2932, 2858, 1578, 1516, 1457, 1440, 1325, 1185, 757	280.077788/282.076779 (C <sub>14</sub> H <sub>20</sub> N <sup>78</sup> Se: 280.076879; C <sub>14</sub> H <sub>20</sub> N <sup>80</sup> Se: 282.076095)
<b>7d</b>	25	140-141	2921, 2852, 1579, 1514, 1457, 1442, 1324, 1189, 757	336.139687/338.139261 (C <sub>18</sub> H <sub>28</sub> N <sup>78</sup> Se: 336.139479; C <sub>18</sub> H <sub>28</sub> N <sup>80</sup> Se: 338.138696)
<b>8a</b>	58	195-197 (195-197)[16]	2979, 1599, 1461, 1389, 766	162.091907 (C <sub>10</sub> H <sub>12</sub> NO: 162.091889)
<b>8b</b>	41	103-105	2953, 2933, 2867, 1588, 1461, 1392, 765	204.139504 (C <sub>13</sub> H <sub>18</sub> NO: 204.138839)
<b>8c</b>	35	90-91	2954, 2921, 2852, 1590, 1462, 1390, 766	218.154355 (C <sub>14</sub> H <sub>20</sub> NO: 218.154489)
<b>8d</b>	28	83-85	2921, 2852, 1589, 1461, 1391, 765	274.217316 (C <sub>18</sub> H <sub>28</sub> NO: 274.217090)

<b>9a</b>	59	226-228	2972, 1635, 1459, 1437, 773	188.144234 (C <sub>13</sub> H <sub>18</sub> N: 188.143925)
<b>9b</b>	50	138-139	2953, 2935, 2867, 1626, 1463, 769	230.191539 (C <sub>16</sub> H <sub>14</sub> N: 230.190875)
<b>9c</b>	46	146-147	2967, 2933, 2856, 1623, 1467, 1455, 769	224.207536 (C <sub>17</sub> H <sub>26</sub> N: 224.206525)
<b>9d<sup>a)</sup></b>	46 <sup>b)</sup>	viscous oil	2925, 2856, 1625, 1607, 1461, 765	300.268937 (C <sub>21</sub> H <sub>34</sub> N: 300.269125)
<b>10a</b>	73	238-239 (237-39)[17]	2994, 2925, 1603, 1521, 1436, 1363, 1344, 1150, 828, 786	172.113046 (C <sub>12</sub> H <sub>14</sub> N: 172.112625)
<b>10b</b>	65	156-157	2947, 2931, 2869, 1603, 1523, 1428, 1367, 1347, 1172, 781	214.160311 (C <sub>15</sub> H <sub>20</sub> N: 214.159575)
<b>10c</b>	46	129-130	2948, 2913, 2868, 2826, 1604, 1524, 1428, 1373, 1359, 825, 779	228.175540 (C <sub>16</sub> H <sub>22</sub> N: 228.175225)
<b>10d</b>	37	118-120	2917, 2853, 1609, 1522, 1472, 1424, 1365, 816, 778	284.238820 (C <sub>20</sub> H <sub>30</sub> N: 284.237825)

a) FTIR spectrum: film in NaCl; b) Isolated by column chromatography (silica; 0 to 5% - CH<sub>2</sub>Cl<sub>2</sub>/MeOH)

**Table 2.** Aliphatic <sup>1</sup>H-NMR spectral data of quaternary ammonium salts **6-10** (DMSO-d<sub>6</sub>).

Salt	$\delta$ (ppm), multiplicity, J (Hz)			
	(Lit. value)[reference]			
<i>N</i> -ethyl ( <i>N</i> -CH <sub>2</sub> <sup>a</sup> CH <sub>3</sub> <sup>b</sup> )				
	CH <sub>2</sub> <sup>a</sup>	CH <sub>3</sub> <sup>b</sup>	2-CH <sub>3</sub>	C(CH <sub>3</sub> ) <sub>2</sub>
<b>6a<sup>a)</sup></b>	4.78, q, 7.0 (4.74)[4]	1.46, t, 7.0 (1.49)[4]	3.23, s (3.22)[4]	-
<b>7a<sup>a)</sup></b>	4.74, q, 7.0 (4.63)[4]	1.44, t, 7.0 (1.40)[4]	3.24, s (3.15)[4]	-
<b>8a<sup>a),b)</sup></b>	4.73, q, 7.5 (4.60)[4]	1.63, t, 7.5 (1.51)[4]	3.36, s (3.12)[4]	-
<b>9a<sup>a)</sup></b>	4.50, q, 7.0 (4.63)[4] <sup>c)</sup>	1.44, t, 7.0 (1.66)[4] <sup>c)</sup>	2.84, s (3.10)[4] <sup>c)</sup>	1.53, s
<b>10<sup>d)</sup></b>	5.01, q, 7.0 (4.95)[4] (5.03)[5]	1.54, t, 7.0 (1.52)[4] (1.54)[5]	3.13, s (3.10)[4] (3.15)[5]	-

**N-pentyl** ( $N\text{-CH}_2^a\text{H}_2^b\text{CH}_2^c\text{CH}_2^d\text{CH}_3^e$ )

	$\text{CH}_2^a$	$\text{CH}_2^b$	$\text{CH}_2^c$	$\text{CH}_2^d$	$\text{CH}_3^e$	2- $\text{CH}_3$	$\text{C}(\text{CH}_3)_2$
<b>6b</b> <sup>d</sup>	4.72, t, 7.5	1.86, qt, 8.0	1.40-1.46, m	1.35, sext, 7.5	0.89, t, 7.0	3.23, s	-
<b>7b</b> <sup>e</sup>	4.68, t, 8.0	1.82, qt, 8.0	1.25-1.47, m		0.86, t, 7.0	3.25, s	-
<b>8b</b> <sup>a),b)</sup>	4.69, t, 8.0	2.00, qt, 7.5	1.34-1.44, m		0.87, t, 7.0	3.38, s	-
<b>9b</b> <sup>a)</sup>	4.45, t, 7.5	1.84, qt, 7.5	1.30-1.44, m		0.88, t, 7.0	2.84, s	1.55, s
<b>10b</b> <sup>d)</sup>	4.92, t, 8.0	1.90, qt, 8.0	1.55, qt, 7.5	1.40, sext, 7.5	0.92, t, 7.0	3.12, s	-

**N-hexyl** ( $N\text{-CH}_2^a\text{CH}_3^b\text{CH}_2^c\text{CH}_2^d\text{CH}_2^e\text{CH}_3^f$ )

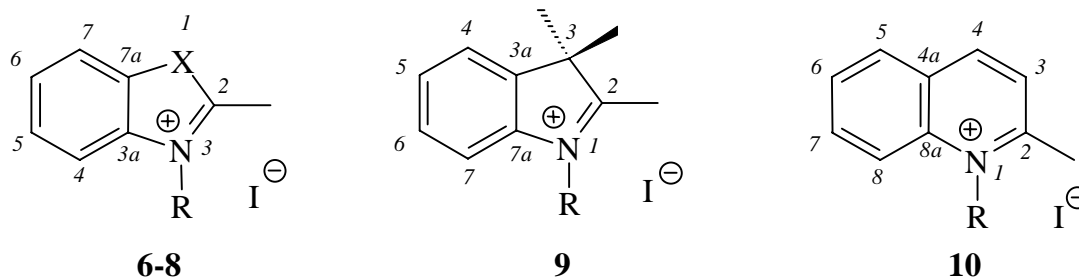
	$\text{CH}_2^a$	$\text{CH}_2^b$	$\text{CH}_2^c$	$\text{CH}_2^d$	$\text{CH}_2^e$	$\text{CH}_3^f$	2- $\text{CH}_3$	$\text{C}(\text{CH}_3)_2$
<b>6c</b> <sup>a)</sup>	4.71, t, 8.0	1.84, qt, 8.0	1.44, qt, 7.5	1.26-1.34, m		0.87, t, 7.0	3.22, s	-
<b>7c</b> <sup>a)</sup>	4.67, t, 8.0	1.83, qt, 8.0	1.44, qt, 7.5	1.25-1.35, m		0.87, t, 7.0	3.22, s	-
<b>8c</b> <sup>a),b)</sup>	4.66, t, 7.5	1.99, qt, 7.5	1.43, qt, 7.5	1.24-1.33, m		0.83, t, 7.0	3.36, s	-
<b>9c</b> <sup>a)</sup>	4.46, t, 8.0	1.83, qt, 8.0	1.42, qt, 7.5	1.24-1.34, m		0.86, t, 7.0	2.86, s	1.54, s
<b>10c</b> <sup>a)</sup>	4.91, t, 8.0	1.88, qt, 8.0	1.56, qt, 7.5	1.29-1.37, m		0.89, t, 7.0	3.12, s	-

**N-decyl** ( $N\text{-CH}_2^a\text{CH}_2^b\text{CH}_2^c\text{CH}_2^d\text{CH}_2^e\text{CH}_2^f\text{CH}_2^g\text{CH}_2^h\text{CH}_2^i\text{CH}_3^j$ )

	$\text{CH}_2^a$	$\text{CH}_2^b$	$\text{CH}_2^c$	$\text{CH}_2^d$	$\text{CH}_2^{e-i}$	$\text{CH}_3^j$	2- $\text{CH}_3$	$\text{C}(\text{CH}_3)_2$
<b>6d</b> <sup>d)</sup>	4.72, t, 8.0	1.84, qt, 8.0	1.44, qt, 7.5	1.32, qt, 7.0	1.25-1.28, m	0.85, t, 7.0	3.24, s	-
<b>7d</b> <sup>a)</sup>	4.67, t, 8.0	1.81, qt, 8.0	1.43, qt, 7.5	1.20-1.32, m		0.84, t, 7.0	3.22, s	-
<b>8d</b> <sup>a),b)</sup>	4.70, t, 7.5	2.00, qt, 7.5	1.44, qt, 7.5	1.33, qt, 7.0	1.22-1.28, m	0.85, t, 7.0	3.39, s	-
<b>9d</b> <sup>a)</sup>	4.46, t, 7.5	1.83, qt, 7.5	1.41, qt, 7.0	1.22-1.32, m		0.83, t, 6.5	2.86, s	1.54, s
<b>10d</b> <sup>d)</sup>	4.91, t, 8.0	1.88, qt, 8.0	1.56, qt, 7.5	1.36, qt, 7.0	1.26-1.28, m	0.86, t, 7.0	3.11, s	-

a) At 400.13 MHz; b) in  $\text{CDCl}_3$ ; c) in  $\text{DMSO-d}_6/\text{D}_2\text{O}$  (3/5); d) at 500.13 MHz; e) at 250.13 MHz.

**Table 3.** Aromatic  $^1\text{H-NMR}$  spectral data of quaternary ammonium salts **6-10** ( $\text{DMSO-d}_6$ ).



Salt	$\delta$ (ppm), multiplicity, J (Hz)						
	(Lit. value)[reference]						
<b>benzothiazolium</b>	<b>4-H</b>		<b>5-H</b>		<b>6-H</b>	<b>7-H</b>	
<b>6a<sup>a</sup></b>	8.35, d, 8.0 (8.28)[4]		7.89, dt, 7.5; 1.0 (7.86)[4]		7.80, dt, 7.5; 1.0 (7.77)[4]	8.42, d, 8.0 (8.39)[4]	
<b>6b<sup>b</sup></b>	8.36, d, 8.5		7.90, dt, 7.5; 1.0		7.81, dt, 7.5; 1.0	8.47, d, 8.0	
<b>6c<sup>a</sup></b>	8.34, d, 8.5		7.89, dt, 8.0; 1.0		7.80, t, 7.5	8.46, d, 8.0	
<b>6d<sup>b</sup></b>	8.36, d, 8.5		7.81, dt, 7.5; 1.0		7.90, dt, 8.0; 1.0	8.48, dd, 8.0; 1.0	
<b>benzoselenazolium</b>	<b>4-H</b>		<b>5-H</b>		<b>6-H</b>	<b>7-H</b>	
<b>7a<sup>a</sup></b>	8.31, d, 8.0 (8.18)[4]		7.82, dt, 7.5; 1.0 (7.71)[4]		7.72, dt, 7.5; 1.0 (7.61)[4]	8.51, dd, 8.0; 1.0 (8.36)[4]	
<b>7b<sup>c</sup></b>	8.31, d, 8.0		7.81, t, 7.5		7.70, t, 7.5	8.54, d, 8.0	
<b>7c<sup>a</sup></b>	8.30, d, 8.0		7.83, dt, 7.5; 1.0		7.72, dt, 7.5; 1.0	8.45, dd, 8.0; 1.0	
<b>7d<sup>a</sup></b>	8.30, d, 8.0		7.82, dt, 7.5; 1.0		7.72, dt, 7.5; 1.0	8.48, dd, 8.0; 1.0	
<b>benzoxazolium</b>	<b>4-H</b>		<b>5-H</b>		<b>6-H</b>	<b>7-H</b>	
<b>8a<sup>a,d</sup></b>	7.80-7.78, m (8.09)[4]		7.68-7.65, m (7.74)[4] (7.75)[4]		7.98-7.96, m (8.16)[4]		
<b>8b<sup>a,d</sup></b>	7.83-7.81, m		7.71-7.68, m		7.92-7.90, m		
<b>8c<sup>a,d</sup></b>	7.90-7.88, m		7.69-7.67, m		7.82-7.80, m		
<b>8d<sup>a,d</sup></b>	7.91-7.89, m		7.72-7.67, m		7.84-7.81, m		
<b>indolium</b>	<b>4-H</b>		<b>5-H</b>		<b>6-H</b>	<b>7-H</b>	
<b>9a<sup>a</sup></b>	7.96-7.99, m (8.00)[4] <sup>e</sup>		7.62-7.64, m (7.79)[4] <sup>e</sup>		7.84-7.86, m (7.93)[4] <sup>e</sup>		
<b>9b<sup>a</sup></b>	7.96-7.98, m		7.60-7.65, m		7.82-7.86, m		
<b>9c<sup>a</sup></b>	7.97-8.00, m		7.60-7.65, m		7.83-7.86, m		
<b>9d<sup>a</sup></b>	7.98-8.00, m		7.60-7.64, m		7.84-7.87, m		
<b>quinolinium</b>	<b>3-H</b>	<b>4-H</b>	<b>5-H</b>		<b>6-H</b>	<b>7-H</b>	<b>8-H</b>
<b>10a<sup>b</sup></b>	8.14, d, 8.5 (8.14)[5]	9.12, d, 8.5 (9.13)[5]	8.43, dd, 8.0; 1.0 (8.27)[5]		8.00, t, 7.5 (8.03)[5]	8.25, dt, 8.0; 1.0 (8.10)[5]	8.63, d, 9.0 (8.64)[5]
<b>10b<sup>b</sup></b>	8.14, d, 8.5	9.11, d, 8.5	8.42, dd, 8.0; 1.0		8.00, t, 7.5	8.24, dt, 8.0; 1.0	8.59, d, 9.0
<b>10c<sup>a</sup></b>	8.13, d, 8.5	9.11, d, 8.5	8.41, dd, 8.0; 1.0		7.99, t, 7.5	8.23, dt, 8.0; 1.0	8.59, d, 9.0
<b>10d<sup>b</sup></b>	8.12, d, 8.5	9.10, d, 8.5	8.41, dd, 8.0; 1.0		8.00, t, 7.5	8.23, dt, 8.0; 1.0	8.59, d, 9.0

a) At 400.13 MHz; b) at 500.13 MHz; c) at 250.13 MHz; d) in CDCl<sub>3</sub>; e) in DMSO-d<sub>6</sub>/D<sub>2</sub>O (3/5).



**Table 4.** Aliphatic  $^{13}\text{C}$ -NMR spectral data of quaternary ammonium salts **6-10** (DMSO- $d_6$ ).

Salt	$\delta$ (ppm)							
	(Lit. value)[reference]							
<b>N-ethyl (<math>N\text{-C}^a\text{H}_2\text{C}^b\text{H}_3</math>)</b>								
	$\text{C}^a\text{H}_2$	$\text{C}^b\text{H}_3$	2- $\text{CH}_3$	$\text{C}(\text{CH}_3)_2$				
<b>6a</b> <sup>a)</sup>	44.7	13.2	16.8	-				
<b>7a</b> <sup>a)</sup>	45.6	13.0	19.5	-				
<b>8a</b> <sup>a),b)</sup>	44.4	14.0	16.7	-				
<b>9a</b> <sup>a)</sup>	43.0	12.6	13.7	21.8				
<b>10</b> <sup>a)</sup>	47.1 (47.26)[5]	13.3 (13.43)[5]	22.3 (22.44)[5]	-				
<b>N-pentyl (<math>N\text{-C}^a\text{H}_2\text{C}^b\text{H}_2\text{C}^c\text{H}_2\text{C}^d\text{H}_2\text{C}^e\text{H}_3</math>)</b>								
	$\text{C}^a\text{H}_2$	$\text{C}^b\text{H}_2$	$\text{C}^c\text{H}_2$	$\text{C}^d\text{H}_2$	$\text{C}^e\text{H}_3$	2- $\text{CH}_3$	$\text{C}(\text{CH}_3)_2$	
<b>6b</b> <sup>c)</sup>	49.2	28.1	27.6	21.8	13.8	17.1	-	
<b>7b</b> <sup>c)</sup>	50.1	28.0	27.4	21.8	13.8	19.9	-	
<b>8b</b> <sup>a),b)</sup>	49.1	28.6	27.9	22.0	13.7	16.7	-	
<b>9b</b> <sup>a)</sup>	47.3	27.8	26.7	21.5	13.5	13.8	21.8	
<b>10b</b> <sup>c)</sup>	51.5	28.0	27.8	21.8	13.9	22.7	-	
<b>N-hexyl (<math>N\text{-C}^a\text{H}_2\text{C}^b\text{H}_2\text{C}^c\text{H}_2\text{C}^d\text{H}_2\text{C}^e\text{H}_2\text{C}^f\text{H}_3</math>)</b>								
	$\text{C}^a\text{H}_2$	$\text{C}^b\text{H}_2$	$\text{C}^c\text{H}_2$	$\text{C}^d\text{H}_2$	$\text{C}^e\text{H}_2$	$\text{C}^f\text{H}_3$	2- $\text{CH}_3$	$\text{C}(\text{CH}_3)_2$
<b>6c</b> <sup>a)</sup>	49.1	30.6	27.7	25.4	21.8	13.8	16.8	-
<b>7c</b> <sup>a)</sup>	50.0	30.6	27.6	25.4	21.9	13.8	19.5	-
<b>8c</b> <sup>a),b)</sup>	49.0	31.0	28.1	26.3	22.2	13.8	16.7	-
<b>9c</b> <sup>a)</sup>	47.5	30.6	27.1	25.4	21.9	13.7	14.0	21.7
<b>10c</b> <sup>a)</sup>	51.3	30.6	27.9	25.4	21.9	13.7	22.4	-
<b>N-decyl (<math>N\text{-C}^a\text{H}_2\text{C}^b\text{H}_2\text{C}^c\text{H}_2\text{C}^d\text{H}_2\text{C}^e\text{H}_2\text{C}^f\text{H}_2\text{C}^g\text{H}_2\text{C}^h\text{H}_2\text{C}^i\text{H}_2\text{C}^j\text{H}_3</math>)</b>								
	$\text{C}^a\text{H}_2$	$\text{C}^b\text{H}_2$	$\text{C}^c\text{H}_2$	$\text{C}^{d-i}\text{H}_2$	$\text{C}^j\text{H}_3$	2- $\text{CH}_3$	$\text{C}(\text{CH}_3)_2$	
<b>6d</b> <sup>c)</sup>	49.3	31.2	28.9	28.7, 28.6, 27.8, 25.9, 22.1	13.9	17.3	-	
<b>7d</b> <sup>a)</sup>	50.0	31.1	28.7	28.5, 28.4, 27.5, 25.7, 21.9	13.8	19.6	-	
<b>8d</b> <sup>a),b)</sup>	49.2	31.7	29.3	29.2, 29.1, 28.9, 28.2, 26.7, 22.5	14.0	16.7	-	
<b>9d</b> <sup>a)</sup>	47.6	31.1	28.7	28.5, 28.4, 27.1, 25.7	13.8, 14.1	21.9		
<b>10d</b> <sup>c)</sup>	51.5	31.3	28.9	28.7, 28.6, 28.1, 25.9, 22.1	14.0	22.6	-	

a) At 100.6 MHz; b) in  $\text{CDCl}_3$ ; c) at 62.9 MHz.

**Table 5.** Aromatic  $^{13}\text{C}$  NMR spectral data of quaternary ammonium salts **6-10** (DMSO- $d_6$ ).

Salt	$\delta$ (ppm)								
	(Lit. value)[reference]								
<b>benzothiazolium</b>	<b>2-C</b>	<b>3a-C</b>	<b>4-C</b>	<b>5-C</b>	<b>6-C</b>	<b>7-C</b>	<b>7a-C</b>		
<b>6a<sup>a)</sup></b>	176.7	140.4	116.6	129.3	127.9	124.6	129.9		
<b>6b<sup>b)</sup></b>	177.0	140.8	116.9	129.4	128.1	124.7	129.1		
<b>6c<sup>a)</sup></b>	176.9	140.7	116.8	129.3	128.0	124.6	129.0		
<b>6d<sup>b)</sup></b>	176.8	140.7	116.9	129.3	128.0	124.7	129.0		
<b>benzoselenazolium</b>	<b>2-C</b>	<b>3a-C</b>	<b>4-C</b>	<b>5-C</b>	<b>6-C</b>	<b>7-C</b>	<b>7a-C</b>		
<b>7a<sup>a)</sup></b>	187.9	141.4	118.1	128.6	127.5	127.6	131.8		
<b>7b<sup>b)</sup></b>	188.0	141.8	118.4	128.7	127.6	127.7	131.8		
<b>7c<sup>a)</sup></b>	188.1	141.8	118.4	128.7	127.3	127.7	131.8		
<b>7d<sup>a)</sup></b>	188.0	141.7	118.3	128.6	127.3	127.6	131.8		
<b>benzoxazolium</b>	<b>2-C</b>	<b>3a-C</b>	<b>4-C</b>	<b>5-C</b>	<b>6-C</b>	<b>7-C</b>	<b>7a-C</b>		
<b>8a<sup>a),c)</sup></b>	167.0	147.8	113.2	129.1	128.3	114.5	129.2		
<b>8b<sup>a),c)</sup></b>	167.3	147.9	113.3	129.3	128.4	114.5	129.6		
<b>8c<sup>a),c)</sup></b>	167.2	147.8	113.3	129.3	128.4	114.4	129.6		
<b>8d<sup>a),c)</sup></b>	167.3	147.9	113.3	129.3	128.4	114.5	129.7		
<b>indolium</b>	<b>2-C</b>	<b>3-C</b>	<b>3a-C</b>	<b>4-C</b>	<b>5-C, 6-C</b>		<b>7-C</b>	<b>7a-C</b>	
<b>9a<sup>a)</sup></b>	196.0	54.0	141.8	115.2	128.8, 129.3		123.4	140.6	
<b>9b<sup>a)</sup></b>	196.3	54.1	141.8	115.2	128.7, 129.2		123.3	141.0	
<b>9c<sup>a)</sup></b>	196.3	54.0	141.7	115.4	128.8, 129.3		123.4	141.0	
<b>9d<sup>a)</sup></b>	196.2	54.0	141.7	115.4	128.8, 129.3		123.4	140.9	
<b>quinolinium</b>	<b>2-C</b>	<b>3-C</b>	<b>4-C</b>	<b>4a-C</b>	<b>5-C</b>	<b>6-C</b>	<b>7-C</b>	<b>8-C</b>	<b>8a-C</b>
<b>10a<sup>a)</sup></b>	160.4	125.4	145.5	128.1	130.5	128.9	135.2	118.7	137.9
	(160.40)[5]	(125.49)[5]	(145.51)[5]	(128.25)[5]	(118.75)[5]	(128.98)[5]	(135.26)[5]	(130.57)[5]	(138.07)[5]
<b>10b<sup>d)</sup></b>	160.5	125.6	145.6	128.2	130.6	129.0	135.3	119.0	138.2
<b>10c<sup>a)</sup></b>	160.4	125.4	145.5	128.1	130.4	128.9	135.2	118.8	138.1
<b>10d<sup>d)</sup></b>	160.6	125.6	145.6	128.2	130.6	129.0	135.3	119.0	138.2

a) At 100.6 MHz; b) at 62.9 MHz; c) in  $\text{CDCl}_3$ ; d) at 125.76 MHz.

## References

1. Hamer, F. M. In *The Cyanine Dyes and Related Compounds - The Chemistry of Heterocyclic Compounds*; Weissberger, A., Ed.; Interscience Publishers: New York, 1971; Vol. 18.
2. Zollinger, H. *Color Chemistry - Synthesis, Properties and Applications of Organic Dyes and Pigments*; VCH Publishers Inc.: Weinheim, 1991; pp 65-69.
3. Sturmer, D. M.; Heseltine, D. W. In *Sensitizing and Desensitizing Dyes – The Theory of the Photographic Processes*; James, T. H., Ed., Macmillan Co.: New York, 1977; pp 205-220.
4. Kleinpeter, Von E.; Borsdorf, R.; Dietz, F. Zur reaktivität der 2-methylcycloammoniumsalze. *J. Prakt. Chem.* **1973**, *315*, 600-610.
5. Jaroszewska, J.; Wawer, I.; Oszczapowicz,  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectral studies of *N*-alkylmethylquinolinium salts. *J. Org. Magn. Reson.* **1984**, *22*, 323-327.
6. Narayanan, N.; Streckowski, L.; Patonay, G. A new method for the synthesis of heptamethine cyanine dyes: synthesis of new near-infrared fluorescent labels. *J. Org. Chem.* **1995**, *60*, 2391-95.
7. Li, M.; Pacey, G. E. Spectrophotometric determination of trace water in organic solvents with a near infrared absorbing dye. *Talanta* **1997**, *44*, 1948-1958.
8. Patonay, G.; Antoine, M. D.; Devanathan, S.; Streckowski, L. Near-infrared probe for determination of solvent hydrophobicity. *Appl. Spectrosc.* **1991**, *45*, 457-461.
9. Samat, A. M.; Guglielmetti, R. J.; Martin, G. J. Etude des formes fermées et ouverts de spiropyranes benzothiazoliniques en RMN  $^{13}\text{C}$  et  $^1\text{H}$  par transformée de Fourier. *Org. Magn. Reson.* **1976**, *8*, 62-73.
10. Benassi, R.; Grandi, R.; Pagnoni, U. M.; Taddei, F. Study of the effect of *N*-protonation and *N*-methylation on the  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of the six-membered ring in benzoazoles and 2-substituted *N,N*-dimethylamino derivatives. *Magn. Reson. Chem.* **1986**, *24*, 415-420.
11. Muñoz, M. A.; Carmona, C.; Hidalgo, J.; Balón, M. On the protonation site of *Rauwolfia* alkaloids in highly concentrated sulphuric acid solutions. *Heterocycles.* **1989**, *29*, 1343-1348.
12. Reichardt, C.; Engel, H.-D. Eine verbesserte methode zur herstellung von 1,3,3-trialkyl-2-alkylineneindolinen. *Chem. Ber.* **1988**, *121*, 1009-1111.
13. Pretsch, E.; Clerc, T.; Seibl, J.; Simson, W. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, 1989.
14. Beilstein, II, 27, 21d.
15. Beilstein, II, 27, 23f.
16. Beilstein, II, 27, 20c.
17. Beilstein, IV, 20, 3459.

Sample Availability: Available from the authors.