PRACE NAUKOWE Wyższej Szkoły Pedagogicznej w Częstochowie 75
Seria: CHEMIA I OCHRONA ŚRODOWISKA 2003 z.VII
75-84

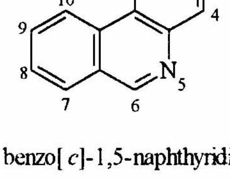
Barbara Dondela [1]
Marian Mielniczak [2]
Wanda Śliwa [1]*
[1, 1]* *Pedagogical University, Institute of Chemistry and Environmental Protection*
42-201 Częstochowa, al. Armii Krajowej 13/15
e-mail: *w.sliwa@wsp.czest.pl*
[2] *Secondary School, 66-110 Babimost, ul. Żwirki i Wigury 3*

ANALYSIS OF ^{13}C NMR SPECTRA OF METHYLBENZONAPHTHYRIDINES, BENZONAPHTHYRIDINIUM QUATERNARY SALTS AND ALKYLBENZONAPHTHYRIDONES

Abstract: In the paper ^{13}C NMR data of two methylbenzonaphthyridines, seven benzonaphthyridinium quaternary salts and three alkylbenzonaphthyridones are discussed and compared with those of parent benzonaphthyridines.

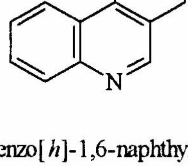
Introduction

The present work is a continuation of our study on reactivity [1-4] as well as on physicochemical [5-9] and biological [10-13] properties of isomeric benzonaphthyridines (bn) **1** - **3** and their derivatives.



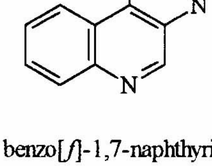
benzo[*c*]-1,5-naphthyridine

1



benzo[*h*]-1,6-naphthyridine

2

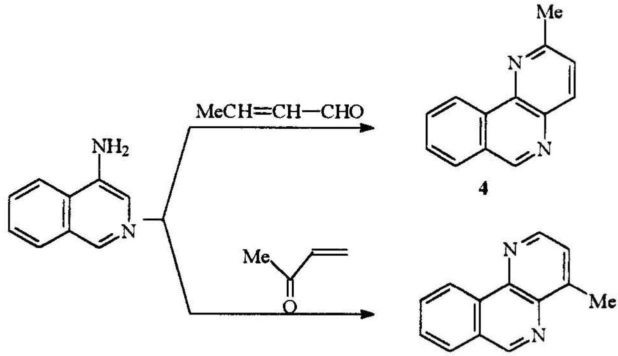


benzo[*f*]-1,7-naphthyridine

3

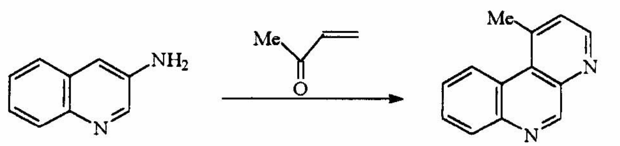
The C- and N-substituted bns are known; the former ones are represented by formyl bns [14] and aminobns [3,15,16] and the latter ones–by quaternary benzonaphthyridinium salts [17-19] and bn N-oxides [20,21].

Examples of C-substituted bn derivatives are methylbns, obtained from appropriate aminoazanaphthalenes by modified Skraup procedure, *i.e.* replacing glycerin by crotonaldehyde or methyl vinyl ketone.



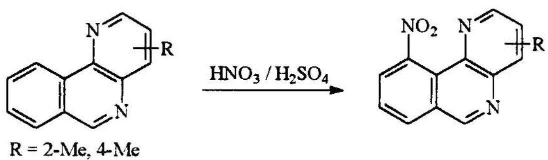
4 ref. 22

5 ref. 14

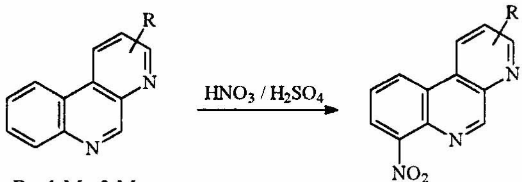


6 ref. 14

Among reactions of methylbns should be mentioned their
- nitration [10]

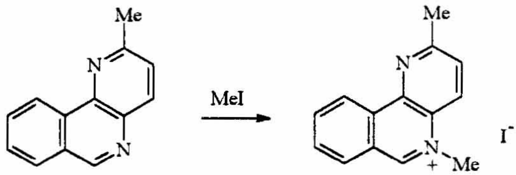


R = 2-Me, 4-Me

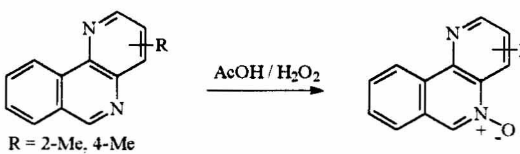


R = 1-Me, 3-Me

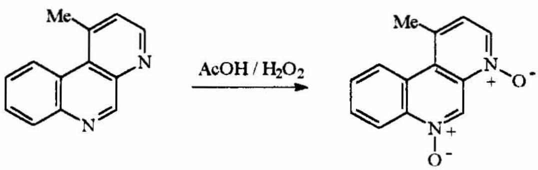
- quaternization [2]



- and N-oxidation



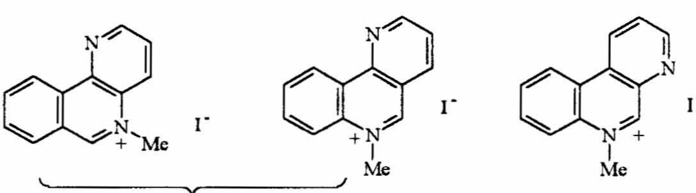
ref. 23



ref. 24

Examples of N-substituted bn derivatives are quaternary salts obtained by reacting bns

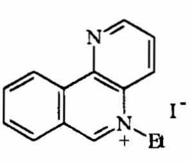
- with methyl iodide



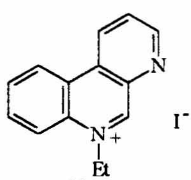
ref. 25 ref. 26

7 8 9

- with ethyl iodide [2]

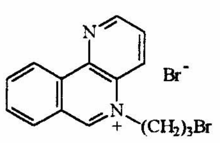


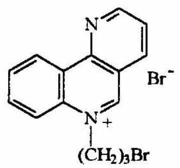
10

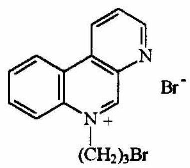


11

- with 1,3-dibromopropane [2]

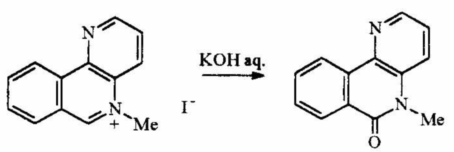




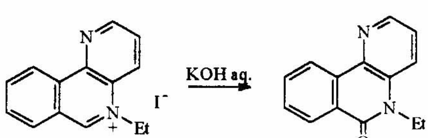


12 13 14

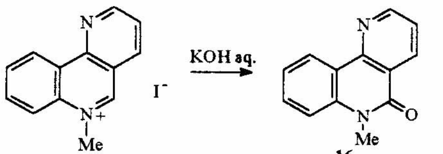
The treatment of quaternary benzonaphthyridinium salts with saturated potassium hydroxide solution leads to alkylbenzonaphthyridones [2].



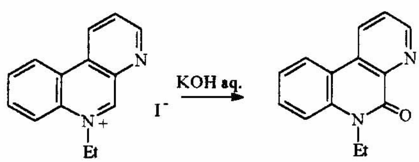
7 15



10 17



8 16



11 18

Analysis of ^{13}C NMR spectra of bn derivatives

In the continuation of our ^{13}C NMR investigation of bn derivatives [10,24,27,28], in this work the ^{13}C NMR data for two methylbns **5**, **6**, seven quaternary salts **7**, **8** and **10** - **14** and three alkylbenzonaphthyridones **15** - **17** are presented; for comparative purposes also ^{13}C NMR values for parent bns **1** - **3** [28] are given.

The ^{13}C NMR spectra were recorded on a 500 MHz Bruker spectrometer in DMSO-d_6 with noise band decoupling, using TMS as a standard; the chemical shift values are given in Tables 1 - 3.

Table 1
^{13}C NMR chemical shift values for bns **1** - **3** and methylbns **5**, **6** (in DMSO-d_6, with TMS as a standard)

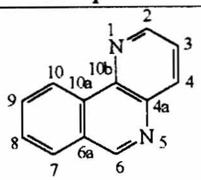
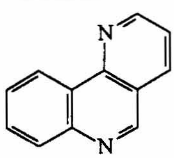
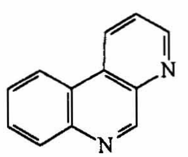
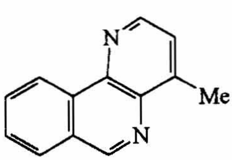
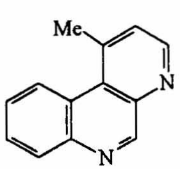
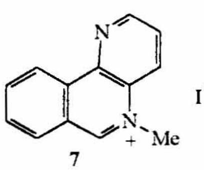
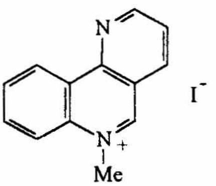
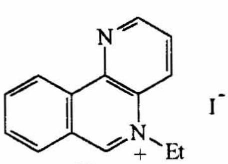
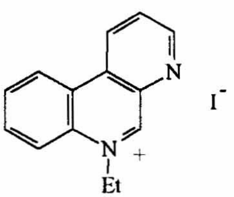
Compound	δ (ppm)
 **1**	154.3 (C6); 149.7 (C2); 140.2 (C10b); 138.7 (C4a); 137.0 (C4); 132.5 (C10a); 131.7 (C9); 129.4 (C7); 128.3 (C8); 127.9 (C6a); 124.3 (C10); 122.6 (C3)
 **2**	153.8 (C5); 153.3 (C2); 147.2 (C6a); 146.1 (C10b); 136.6 (C4); 130.3 (C7); 129.2 (C8); 127.5 (C9); 124.6 (C4a); 123.5 (C10); 123.2 (C3); 120.6 (C10a)
 **3**	154.0 (C5); 151.3 (C3); 143.5 (C6a); 141.1 (C4a); 131.0 (C1); 129.6 (C7); 129.5 (C8); 127.9 (C9); 127.5 (C10b); 126.1 (C10); 123.3 (C2); 122.9 (C10a)
 **5**	153.0 (C6); 149.1 (C2); 146.3 (C10b); 139.6 (C4a); 138.0 (C4); 132.8 (C10a); 131.5 (C9); 129.2 (C7); 128.2 (C8); 127.8 (C6a); 124.9 (C10); 122.9 (C3); 17.2 (CH_3)
 **6**	149.3 (C5); 148.1 (C6a); 145.6(C4a); 143.3 (C3); 142.3 (C10b); 140.8 (C10a); 129.4 (C1); 128.4 (C7); 126.4 (C8); 125.5 (C9); 123.8 (C10); 111.4 (C2); 25.5 (CH_3)

Table 2

^{13}C NMR chemical shift values for benzonaphthyridinium quaternary salts **7**, **8** and **10** - **14** (in DMSO-d_6, with TMS as a standard)

Compound	δ (ppm)
 **7**	156.3 (C6); 152.5 (C2); 140.5 (C10b); 138.2 (C4); 134.8 (C4a); 132.1 (C9); 131.8 (C7); 130.9 (C10a); 128.8 (C8); 126.4 (C10); 125.3 (C6a); 123.4 (C3); 45.4 (N^+CH_3)
 **8**	159.4 (C5); 156.6 (C6a); 148.6 (C10b); 140.2 (C2); 136.4 (C4a); 133.4 (C4); 130.7 (C7); 126.3 (C10a); 125.6 (C8); 124.6 (C9); 119.6 (C10); 119.3 (C3); 46.0 (N^+CH_3)
 **10**	155.6 (C6); 152.4 (C2); 141.0 (C10b); 138.2 (C4); 134.9 (C4a); 132.3 (C9); 131.7 (C7); 129.8 (C10a); 128.4 (C8); 126.4 (C10); 125.5 (C6a); 123.4 (C3); 53.0 (N^+CH_2); 14.8 (CH_3)
 **11**	155.6 (C5); 154.3 (C3); 139.7 (C6a); 133.1 (C4a); 132.7 (C7); 132.3 (C10b); 131.5 (C8); 130.7 (C10); 130.6 (C1); 125.7 (C10a); 125.4 (C2); 120.0 (C9); 53.7 (N^+CH_2); 15.1 (CH_3)

to be continued

Table 2 (continued)

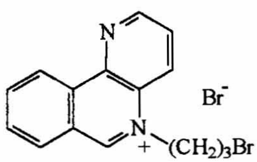
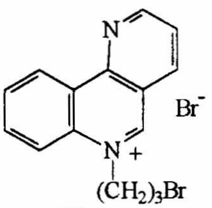
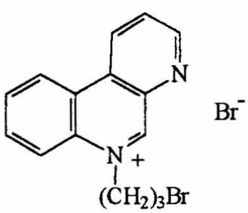
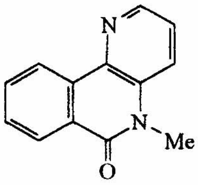
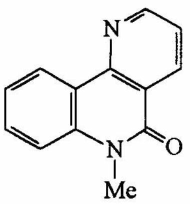
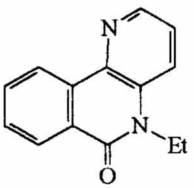
 **12**	156.4 (C6); 154.3 (C2); 152.4 (C10b); 149.8 (C4a); 141.1 (C4); 138.4 (C9); 135.1 (C7); 131.7 (C10a); 129.5 (C8); 126.4 (C10); 123.4 (C6a); 122.6 (C3); 56.1 (N^+CH_2); 31.9 (CH_2Br); 30.4 ($-CH_2-$)
 **13**	156.8 (C5); 153.9 (C2); 153.2 (C10b); 140.4 (C6a); 136.8 (C4); 133.5 (C4a); 130.4 (C7); 128.9 (C10a); 127.6 (C8); 125.1 (C9); 123.5 (C10); 123.2 (C3); 54.9 (N^+CH_2); 38.7 (CH_2Br); 28.8 ($-CH_2-$)
 **14**	154.2 (C5); 151.3 (C3); 143.5 (C6a); 141.2 (C4a); 131.0 (C7); 129.5 (C10b); 127.8 (C8); 127.5 (C10); 126.0 (C1); 123.3 (C10a); 123.1 (C2); 122.9 (C9); overlapped by DMSO ($-CH_2CH_2CH_2Br$)

Table 3

^{13}C NMR chemical shift values for alkylbenzonaphthyridones **15-17** (in DMSO-d_6, with TMS as a standard)

Compound	δ (ppm)
 **15**	159.9 (C6); 143.5 (C2); 135.7 (C4a); 134.0 (C10b); 133.8 (C4); 132.1 (C10a); 129.7 (C9); 127.5 (C7); 126.2 (C6a); 124.4 (C8); 124.1 (C10); 123.1 (C3); 23.5 (CH_3)
 **16**	160.5 (C5); 154.1 (C2); 149.3 (C6a); 138.9 (C10b); 136.3 (C4); 131.5 (C7); 124.3 (C8); 123.5 (C9); 122.6 (C10); 120.3 (C4a); 119.6 (C10a); 115.4 (C3); 29.6 (CH_3)
 **17**	159.4 (C6); 143.5 (C2); 136.0 (C4a); 134.1 (C10b); 132.8 (C4); 132.7 (C10a); 129.7 (C9); 127.5 (C7); 126.2 (C6a); 124.5 (C8); 123.2 (C10); 122.9 (C3); 36.7 (N^+CH_2); 12.6 (CH_3)

In bns [29], as well as in methylbns [7], quaternary salts [5,30] and alkylbenzonaphthyridones [30], C5 and C6 signals lie in the lowest field, and those of carbon atoms of the side ring situated in *meta* position to the nitrogen atom are found in the highest field, according to the charge distribution in the molecule.

In methylbns **5**, **6** the upfield shift of signals of all tertiary carbon atoms as compared to those of bns is observed (except for C3 and C10 in **5**), this fact being due to the presence of the electron-donating methyl groups.

Quaternization of nitrogen atoms in the central ring results in changes of ^{13}C NMR spectra as compared to those of parent bns. In all quaternary salts under investigation the downfield shift of signals of carbon atoms in *ortho* position to quaternized nitrogen atom is observed.

For 1,5 bn salts, *i.e.* **7**, **10** and **12** the signals of carbon atoms of the side ring, situated in *ortho* and *para* position to the nitrogen atom are shifted downfield as compared to those of the parent bn **1**, due to the presence of positively charged N5 atom; for 1,6 bn salts, *i.e.* **8** and **13** the downfield shifts of C4a and for the 4,6 bn salt **11** the downfield shift of C3 signals have been observed.

In alkylbenzonaphthyridones, as could be expected, the C signals of carbonyl groups are downfield shifted as compared to these values of bns; the highest difference (6,7 ppm) was found in the case of **16**.

REFERENCES

1. M. Deska, W. Śliwa, *Chem. Papers* 2002, **56**, 309
2. B. Dondela, W. Śliwa, *Khim. Geterotsikl. Soedin.* 2000, 944
3. L. Chrząstek, W. Śliwa, *Chem. Papers* 2001, **55**, 42
4. B. Bachowska, T. Zujewska, *Monatsh. Chem.* 2001, **132**, 849
5. J. Peszke, W. Śliwa, *Spectrochim. Acta* 2002, **58A**, 2127
6. J. Peszke, B. Mianowska, W. Śliwa, *Spectrochim. Acta* 1997, **53A**, 2565
7. B. Mianowska, W. Śliwa, *Spectrochim. Acta* 1996, **52A**, 397
8. B. Marciniak, V. Pavlyuk, B. Dondela, *Acta Cryst.* 2002, **E58**, 484
9. B. Marciniak, V. Pavlyuk, M. Deska, *Acta Cryst.* 2002, **E58**, 489
10. L. Chrząstek, M. Mielniczak, Z. Staroniewicz, W. Śliwa, *Khim. Geterotsikl. Soedin.* 1999, 1396
11. E. Gurgul, B. Herman, R. Biczak, W. Śliwa, *Sci. Agricult. Bohem.* 1997, **28**, 245
12. R. Kovačič, M.A. Kassel, J.R. Ames, B.A. Feinberg, W. Śliwa, *J. Biopharm. Sci.* 1990, **1**, 331
13. G. Matusiak, W. Śliwa, *Acta Chim. Hung.* 1988, **125**, 267
14. L. Chrząstek, B. Mianowska, W. Śliwa, *Aust. J. Chem.* 1994, **47**, 2129
15. W. Śliwa, M. Mielniczak, *Chem. Papers* 1998, **52**, 747
16. M. Paluszewski, W. Śliwa, *Aust. J. Chem.* 1993, **46**, 1115
17. W. Śliwa, *Current Org. Chem.*, 2003, 7, 995
18. B. Bachowska, T. Zujewska, *Aust. J. Chem.* 2001, **54**, 105
19. J. Peszke, Prace Naukowe Wyższej Szkoły Pedagogicznej w Częstochowie (Pedagogical University Issues), *Chemia IV*, Częstochowa 1999, 129
20. B. Bachowska, *Monatsh. Chem.* 2002, **133**, 1071
21. T. Zujewska, B. Bachowska, *Aust. J. Chem.* 1996, **49**, 523
22. M. Jastrzębska-Glapa, J. Młochowski, W. Śliwa, *J. Prakt. Chem.* 1977, **319**, 883
23. W. Śliwa, M. Mielniczak, Prace Naukowe Wyższej Szkoły Pedagogicznej w Częstochowie (Pedagogical University Issues), *Chemia I*, Częstochowa 1997, 131

24. M. Mielniczak, J. Peszke, W. Śliwa, Prace Naukowe Wyższej Szkoły Pedagogicznej w Częstochowie (Pedagogical University Issues), *Chemia II*, Częstochowa 1998, 115
25. M. Jastrzębska-Glapa, J. Młochowski, W. Śliwa, *Polish J. Chem.* 1979, **53**, 811
26. Y. Hamada, I. Takeuchi, M. Hirota, *Chem. Pharm. Bull.* 1974, **22**, 485
27. L. Chrząstek, Prace Naukowe Wyższej Szkoły Pedagogicznej w Częstochowie (Pedagogical University Issues), *Chemia IV*, Częstochowa 1999, 137
28. A. Könnecke, E. Lippmann, J. Młochowski, W. Śliwa, *Org. Magn. Res.* 1979, **12**, 696
29. B. Mianowska, W. Śliwa, *Acta Chim. Hung.* 1991, **128**, 93
30. B. Dondela, Doctor Thesis, Jagiellonian University, Kraków 2002.

Barbara Dondela
Marian Mielniczak
Wanda Śliwa *

Analiza widm ^{13}C NMR metylobenzonaftyrydyn, czwartorzędowych soli benzonaftyrydyniowych i alkilobenzonaftyrydonów

Streszczenie: W artykule przedstawiono dyskusję danych dotyczących widm ^{13}C NMR dwóch metylobenzonaftyrydyn, siedmiu czwartorzędowych soli benzonaftyrydyniowych i trzech alkilobenzonaftyrydonów oraz porównanie ich z wartościami dla macierzystych benzonaftyrydyn.