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NITRO DERIVATIVES OF ISOMERIC METHYLDIAZAPHENANTHRENES

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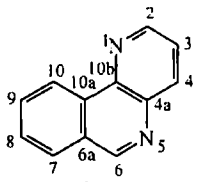
The synthesis of four isomeric nitro derivatives of methyldiazaphenanthrenes (DAP) has been described. The UV spectra of these compounds have been recorded and compared with those of parent diazaphenanthrenes. The biological data of methylnitrodiazaphenanthrenes and of other derivatives of diazaphenanthrenes are presented.

Azaaromatics are of interest as drugs [1–3], agrochemicals [4,5], dyes [6], catalysts [7,8], etc.; they are promising in the construction of electronic devices [9] and in the investigation of biomimetic processes [10].

The present paper is a continuation of our study of 1,5-, 1,6-, and 4,6-diazaphenanthrenes (DAPs) **1–3** and their derivatives displaying biological activity [11–13]; due to the presence of two nitrogen atoms in the molecule, DAPs form complexes with transition metal ions [14] as well as quaternary salts [12,15] and N-oxides [13].



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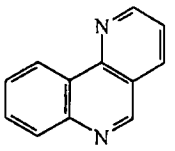

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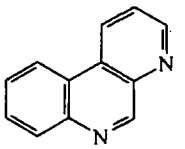

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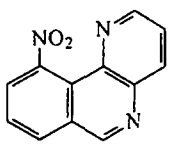
Some quaternary salts of DAPs are precursors of ylides, useful in 1,3-dipolar cycloaddition reactions [16,17]. DAP N-oxides are of interest because of their reactivity [18,19]; methylDAPs may be oxidized to corresponding aldehydes [11].

NitroDAPs **4–6** [20] serve as starting materials for the synthesis of amino derivatives, undergoing a series of reactions [11,21]; for example, they may be submitted to ring annelation by the Skraup procedure, leading to pyridoDAPs [22]. The diazotization of aminoDAPs followed by coupling reactions affords azo dyes [23].



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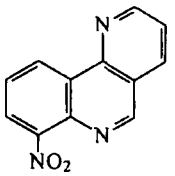

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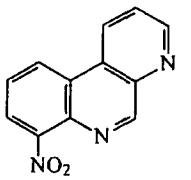

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The UV spectroscopy results have been reported for formyl [24], methyl [25, 26], bromo [27], and amino [28] derivatives of DAPs, as well as for their quaternary salts [29].

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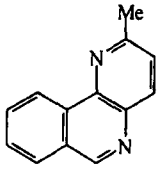
RESULTS AND DISCUSSION

The present work deals with the electrophilic substitution of four methyl- DAPs [2- and 4-methylbenzo[*e*]-1,5-naphthyridines (**7** and **8**, respectively) and 3- and 1-methylbenzo[b]-1,8-naphthyridines (**9** and **10**, respectively)], choosing as an example the nitration reaction. The process was performed with nitric acid in the presence of sulfuric acid containing 60% of sulfur trioxide.



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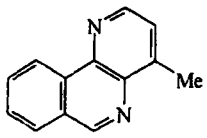

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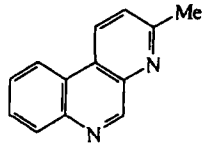

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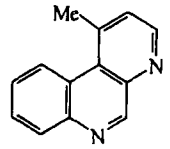

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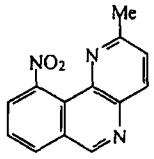
The products of the reaction are mononitrosubstituted compounds **11–14** shown below: 2-methyl-10-nitrobenzo[*c*]-1,5-naphthyridine [**11**], 4-methyl-10-nitrobenzo[*c*]-1,5-naphthyridine [**12**], 3-methyl-7-nitrobenzo[*f*]-1,7-naphthyridine [**13**], and 1-methyl-7-nitrobenzo[*f*]-1,7- naphthyridine [**14**].



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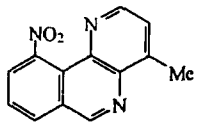

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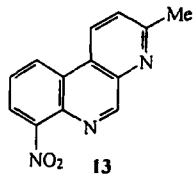

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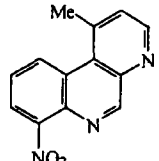

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Unsubstituted DAPs undergo electrophilic substitution in the carbocyclic ring due to the deactivating influence of two nitrogen atoms present in both neighboring azaaromatic rings; the reaction proceeds at positions showing the lowest localization energy, i.e., at $C_{(7)}$ and $C_{(10)}$. The nitration and bromination of DAPs in sulfuric acid containing 60% of sulfur trioxide leads similarly to 7- and 10- substituted nitro and bromo derivatives [20], while the nucleophilic substitution, e.g., with butyllithium, proceeds in azaaromatic rings [30].

The yields of the performed nitration reactions range between 25.5 and 42.4%, and depend considerably on the temperature. In order to avoid the oxidation of the methyl group to amide group with nitric acid, especially in the case of **9**, the temperature should not be too high; in our experiments the syntheses of compounds **11**, **12**, and **14** were carried out at 120°C while in the case of **13** the temperature was only 80-85°C.

The starting methylDAPs **7–10** were synthesized from the corresponding aminoazanaphthalenes by the modified Skraup procedure, using crotonaldehyde or methyl vinyl ketone instead of glycerol[11, 13].

The structures of compounds **11–14** have been confirmed by ^1H and ^{13}C NMR, MS, and elemental analysis data; for comparison purposes the ^1H and ^{13}C NMR data of DAPs **1– 3** and of nitroDAPs **4–6** are given.

The UV spectra of compounds **4–6** and **11–14** have been compared with those of parent DAPs **1–3** [28]. The experimental ν and ε values of **4–6** and **11–14** are summarized in Table 1, and differences in wave number values of the α, *p*, and β bands of **4–6** and **11–14** as compared with unsubstituted DAPs **1–3** are given in Table 2.

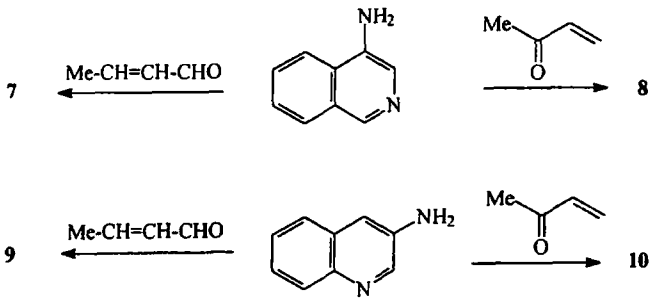


TABLE 1. Experimental Wave Number ν and log ε Values for NitroDAPs **4–6** and MethylnitroDAPs **7–10**

Band	4		5		6	
	$\nu \cdot 10^3$ cm^{-1}	log ε	$\nu \cdot 10^3$ cm^{-1}	log ε	$\nu \cdot 10^3$ cm^{-1}	log ε
α	29.0	4.176	30.8	4.204	29.0	4.164
p	38.0	4.653	36.3	4.763	36.0	4.756
β	42.3	4.892	40.2	5.005	42.9	5.053

Band	7		8		9		10	
	$\nu \cdot 10^3$ cm^{-1}	log ε	$\nu \cdot 10^3$ cm^{-1}	log ε	$\nu \cdot 10^3$ cm^{-1}	log ε	$\nu \cdot 10^3$ cm^{-1}	log ε
α	29.5	2.110	28.7	3.971	28.8	1.952	28.2	3.463
p	36.9	2.512	37.8	4.399	37.4	2.664	37.2	3.594
β	40.5	2.247	40.0	4.753	43.0	3.383	40.8	3.001

TABLE 2. Differences in the Experimental Wave Number Values of α, *p*, and β Bands for NitroDAPs **4–6** and MethylnitroDAPs **7–10** as Compared with Corresponding Unsubstituted DAPs **1–3** (Positive Values Denote Red Shifts; Negative, Blue Shifts)

Band	ν differences						
	4 / 1	**5 / 2**	**6 / 3**	**7 / 1**	**8 / 1**	**9 / 3**	**10 / 3**
α	-1.4 +0.8	-1.7		0.0	-1.9	-1.1	+0.2
p	+0.1	+1.9	+2.1	+1.2	+0.3	+0.7	+0.9
β	-0.1	+3.4	+0.4	+1.7	+2.2	+0.3	+2.5

Comparing wave number values of nitroDAPs **4–6** with those of unsubstituted DAPs, the red shift of the *p* band is observed for these three compounds, the highest in the case of **6**. In the α band, nitroDAPs **4** and **5** show blue shift, while in **6** no difference is found.

Comparison of the wave number values of methylnitroDAPs **11–14** with those of parent DAPs shows, for these four compounds, red shifts for the *p* and β bands; in the case of *p* bands the highest was observed for **11**, and in the case of β bands the highest was observed for **14**.

The ^{1}H NMR spectra of DAPs **1–3** [12, 17], given here for comparative purposes, nitroDAPs **4–6**, and methylnitroDAPs **11–14** are presented in Table 3 (the ^{1}H NMR spectra of **4–6** reported in [20] have been registered in $CDCl_3$).

Analyzing the ^{1}H NMR spectra of DAPs and their derivatives, it was observed that the signals of protons in the *ortho* and *para* positions to the nitrogen atoms lie in lower field than those of other protons, due to the electron-withdrawing character of nitrogen atoms; the signal of the "boat" H, i.e., 10-H appears also in low field.

In the ^{1}H NMR spectra of nitroDAPs and of nitromethylDAPs the signals of protons in the *meta* position with respect to the nitro group lie in higher field than those in the *ortho* and *para* positions, according to the charge distribution of the nitrobenzene molecule (except for 2-methyl-10-nitro-1,5-DAP **11**, where these signals appear as a multiplet).

Comparing the ^{1}H NMR spectra of nitroDAPs with those of the corresponding parent DAPs, the electron-withdrawing influence of the nitro group is manifested in the downfield shift in the case of 10-nitro-1,5-DAP **4** (for 3-H, 4-H, 6-H, 7-H and 9-H), 7-nitro-1,6-DAP **5** (for 4-H, 5-H, 8-H and 10-H), and 7-nitro-4,6- DAP **6** (for 1-H, 8-H and 10-H).

TABLE 3. ^{1}H NMR Data for DAPs **1–3** and their Nitro- and Methylnitro Derivatives (in DMSO, with TMS Standard)

Compound	Chemical shifts, δ, ppm (coupling constants, Hz)
1	9.41 (1H, s, H_6); 9.23-8.98 (2H, m, H_2, H_{10}); 8.49 (1H, dd, $J_{4,3}$ = 8.2, $J_{4,2}$ = 1.5 Hz, H_4) 8.28 (1H, dd, $J_{7,8}$ = 8.1, $J_{7,9}$ = 1.2 Hz, H_7); 8.14-7.78 (2H, m, H_8, H_9) 7.81 (1H, dd, $J_{3,4}$ = 8.2, $J_{3,2}$ = 4.4 Hz, H_3)
4	9.63 (1H, s, H_6); 8.98 (1H, dd, $J_{2,3}$ = 4.4, $J_{2,4}$ = 1.5 Hz, H_2); 8.65-8.55 (2H, m, H_4, H_7) 8.37 (1H, dd, $J_{9,8}$ = 7.3, $J_{9,7}$ = 1.0 Hz, H_9); 8.12 (1H, dd, $J_{8,7}$ = 7.7, $J_{8,9}$ = 7.3 Hz, H_8) 7.93 (1H, dd, $J_{3,4}$ = 8.3, $J_{3,2}$ = 4.4 Hz, H_3)
11	9.53 (1H, s, H_6); 9.01 (1H, d, $J_{4,3}$ = 7.5 Hz, H_4); 8.60-7.80 (3H, m, H_7, H_8, H_9) 7.66 (1H, d, $J_{3,4}$ = 7.5 Hz, H_3); 2.65 (3H, s, CH_3)
12	9.64 (1H, s, H_6); 8.79 (1H, d, $J_{2,3}$ = 4.4 Hz, H_2); 8.59 (1H, dd, $J_{7,8}$ = 7.9, $J_{7,9}$ = 1.2 Hz, H_7) 8.32 (1H, dd, $J_{9,8}$ = 7.3, $J_{9,7}$ = 1.2 Hz, H_9); 8.08 (1H, dd, $J_{8,7}$ = 7.9, $J_{8,9}$ = 7.3 Hz, H_8) 7.78 (1H, dd, $J_{3,2}$ = 4.4, $J_{3,CH3}$ = 0.8 Hz, H_3); 2.84 (3H, s, CH_3)
2	9.48 (1H, s, H_5); 9.26 (1H, dd, $J_{2,3}$ = 4.4, $J_{2,4}$ = 1.5 Hz, H_2); 9.09 (1H, dd, $J_{10,9}$ = 7.8, $J_{10,8}$ = 2.0 Hz, H_{10}); 8.69 (1H, dd, $J_{4,3}$ = 8.3, $J_{4,2}$ = 1.5 Hz, H_4); 8.19 (1H, dd, $J_{7,8}$ = 7.8, $J_{7,9}$ = 1.5 Hz, H_7); 8.00-7.78 (2H, m, H_8, H_9); 7.77 (1H, dd, $J_{3,4}$ = 8.3, $J_{3,2}$ = 4.4 Hz, H_3)
5	9.61 (1H, s, H_5); 9.36-9.25 (2H, m, H_2, H_{10}); 8.79 (1H, dd, $J_{4,3}$ = 8.3, $J_{4,2}$ = 1.5 Hz, H_4) 8.38 (1H, dd, $J_{8,9}$ = 7.1, $J_{8,10}$ = 1.5 Hz, H_8); 8.04-7.92 (2H, m, H_3, H_9)
3	9.46 (1H, s, H_5); 9.28 (1H, d, $J_{1,2}$ = 8.2 Hz; H_1); 9.14 (1H, dd, $J_{3,2}$ = 4.4, $J_{3,1}$ = 1.5 Hz; H_3) 8.84 (1H, dd, $J_{10,9}$ = 7.3; $J_{10,8}$ = 1.5 Hz; H_{10}); 8.23 (1H, ddd, $J_{8,7}$ = 7.3, $J_{8,9}$ = 7.1, $J_{8,10}$ = 1.5 Hz; H_8); 8.04-7.80 (3H, m, H_2, H_7, H_9)
6	9.45 (1H, s, H_5); 9.32 (1H, dd, $J_{10,9}$ = 8.8, $J_{10,8}$ = 1.5 Hz, H_{10}); 9.04 (1H, dd, $J_{3,2}$ = 4.4, $J_{3,1}$ = 1.4 Hz, H_3); 8.87 (1H, dd, $J_{1,2}$ = 8.3, $J_{1,3}$ = 1.4 Hz, H_1); 8.19-7.89 (2H, m, H_8, H_9) 7.79 (1H, dd, $J_{2,1}$ = 8.3, $J_{2,3}$ = 4.4 Hz, H_2)
13	9.35 (1H, s, H_5); 8.70 (1H, dd, $J_{10,9}$ = 7.43, $J_{10,8}$ = 1.5 Hz, H_{10}); 8.60 (1H, dd, $J_{8,9}$ = 7.39, $J_{8,10}$ = 1.5 Hz, H_8); 8.50 (1H, dd, $J_{6,10}$ = 7.43, $J_{9,8}$ = 7.39 Hz, H_9) 8.30 (1H, d, $J_{1,2}$ = 8.43 Hz, H_1); 7.90 (1H, d, $J_{2,1}$ = 8.43 Hz, H_2) 2.65 (3H, s, CH_3, overlapped with DMSO)
14	8.42 (1H, s, H_5); 7.79 (1H, d, $J_{10,9}$ = 8.3 Hz, H_{10}); 7.61 (1H, d, $J_{8,9}$ = 7.8 Hz, H_8) 7.40-7.30 (2H, m, H_3, H_9); 7.16 (1H, d, $J_{2,3}$ = 4.4 Hz, H_2) *ca* 2.5 (3H, s, CH_3, overlapped with DMSO)

Comparing the ^{1}H NMR spectra of methylnitrobenzonaphthiridines with those of DAPs **1** and **3**, a downfield shift, due to the presence of the nitro group, is observed in the case of compounds **12** (for 7-H and 9-H) and **13** (for 8-H and 10-H).

Comparing the ^{1}H NMR spectra of methylnitrobenzonaphthiridines with those of nitro compounds **4** and **6,** the upfield shift due to the presence of methyl groups is observed in the case of compounds **11** (for 3-H and 6-H), **12** (for 3-H), **13** (for 5-H), and **14** (for 2-H and 5-H).

The ^{13}C NMR spectra of DAPs and their nitro and methylnitro derivatives are given in Table 4 (in [31], the ^{13}C NMR spectra of DAPs recorded in $CDCl_3$ are given).

Analyzing the ^{13}C NMR spectra of DAPs and their derivatives, for 10-nitrobenzo[*c*]-1,5-naphthiridine **4**, as compared with parent DAP **1**, the downfield shift of $C_{(10)}$ and $C_{(6a)}$ and the upfield shift of $C_{(10a)}$ are observed, according to the influence of the nitro group.

In the ^{13}C NMR spectrum of 7-nitrobenzo[*h*]-1,6-naphthiridine **5** as compared with parent DAP **2**, the signals of all carbon atoms, especially that of $C_{(7)}$, are shifted downfield (except for $C_{(6a)}$ and $C_{(9)}$) in accordance with the electron-withdrawing character of the nitro group.

For 7-nitrobenzo[*f*]-1,7-naphthiridine **6** a strong downfield shift of the $C_{(7)}$ signal, as compared with that of DAP **3**, occurs due to the paramagnetic effect of the nitro group present in this position. The influence of the nitro group is also seen in the upfield shift of $C_{(6a)}$ and the downfield shift of $C_{(10a)}$.

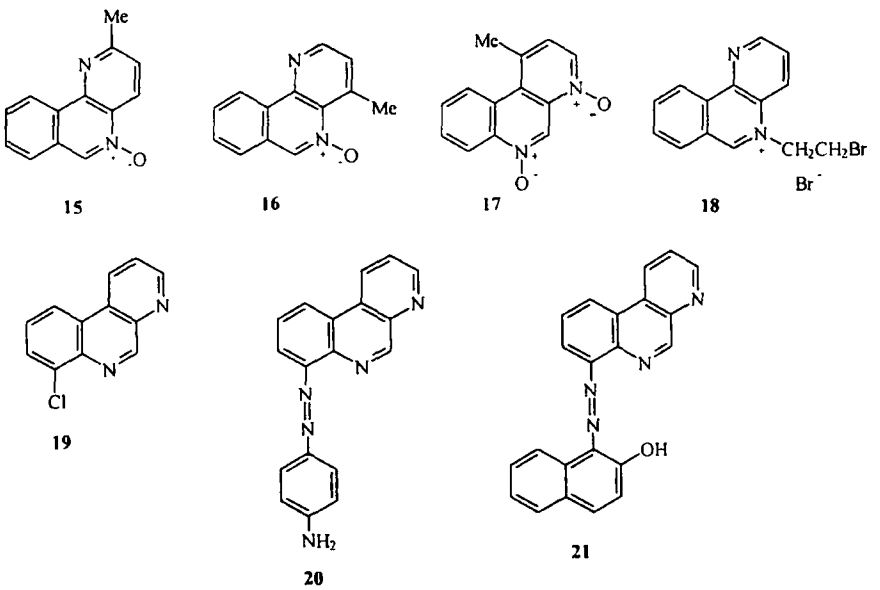
In the ^{13}C NMR spectrum of compound **11** the $C_{(10)}$ signal is shifted downfield as compared with parent DAP **1**, while the $C_{(2)}$, $C_{(3)}$, $C_{(6)}$, $C_{(7)}$, $C_{(8)}$, and $C_{(9)}$ signals are shifted upfield. In the case of compound **12** the $C_{(4)}$, $C_{(9)}$, and $C_{(10)}$ signals are shifted downfield, and the signals of $C_{(2)}$, $C_{(6)}$, $C_{(7)}$, and $C_{(8)}$ – upfield, as compared with parent DAP **1**. The influence of the nitro group is seen in the downfield shift of the $C_{(6a)}$ signal and the upfield shift of the $C_{(10)}$ signal.

TABLE 4. ^{13}C NMR Data for 1,5-, 1,6-, and 4,6-DAPs **1–3** and their Nitro and Methylnitro Derivatives (in DMSO, with TMS Standard)

Compound	Chemical shifts, δ, ppm (coupling constants, Hz)
1	154.3 (C_6); 149.7 (C_2); 140.2 (C_{10b}); 138.7(C_{4a}); 137.0 (C_4); 132.5 (C_{10a}); 131.7 (C_9) 129.4 (C_7); 128.3 (C_8); 127.9 (C_{6a}); 124.3 (C_{10}); 122.6 (C_3)
4	154.0 (C_6); 149.8 (C_2); 146.4 (C_{10b}); 139.4 (C_{10}); 137.2 (C_4); 136.9 (C_{4a}); 131.8 (C_9) 129.8 (C_7); 128.7 (C_{6a}); 126.4 (C_8); 125.6 (C_{10a}); 122.1 (C_3)
11	152.3 (C_6); 142.8 (C_2); 142.7 (C_4); 131.5 (C_{10}); 128.9 (C_9); 128.1 (C_7); 126.1 (C_8) 119.7 (C_3); *ca* 40 (CH_3, overlapped with DMSO)
12	153.9 (C_6); 150.0 (C_4); 147.1 (C_2); 137.4 (C_{10b}); 137.3 (C_{4a}); 135.0 (C_{6a}); 132.6 (C_9) 130.6 (C_{10}); 129.0 (C_7); 127.8 (C_{10a}); 125.3 (C_8); 122.8 (C_3); 17.6 (CH_3)
2	153.8 (C_5); 153.3 (C_2); 147.2 (C_{6a}); 146.1 (C_{10b}); 136.6 (C_4); 130.3 (C_7); 129.2 (C_8) 127.5 (C_9); 124.6 (C_{4a}); 123.5 (C_{10}); 123.2 (C_3); 120.6 (C_{10a})
5	155.9 (C_5); 154.9 (C_2); 148.5 (C_{10b}); 146.2 (C_7); 137.3 (C_4); 136.5 (C_{6a}); 127.3 (C_8) 126.6 (C_9); 125.7 (C_{4a}); 124.6 (C_{10}); 123.4 (C_3); 121.1 (C_{10a})
3	154.0 (C_5); 151.3 (C_3); 143.5 (C_{6a}); 141.1 (C_{4a}); 131.0 (C_1); 129.6 (C_7); 129.5 (C_8) 127.9 (C_9); 127.5 (C_{10b}); 126.1 (C_{10}); 1123.3 (C_2); 122.9 (C_{10a})
6	156.6 (C_5); 152.6 (C_3); 148.7 (C_7); 141.3 (C_{4a}); 134.2 (C_{6a}); 131.5 (C_1); 129.2 (C_{10b}) 127.5 (C_8); 126.9 (C_9); 126.8 (C_{10}); 124.4 (C_{10a}); 122.5 (C_2)
14	143.3 (C_5); 142.3 (C_7); 129.4 (C_1); 128.4 (C_3); 126.3 (C_8); 125.4 (C_9); 123.7 (C_{10}) 111.3 (C_2); *ca* 40 (CH_3 overlapped with DMSO)

In the ^{13}C NMR spectrum of compound **14** the signals of all tertiary carbon atoms, especially those of $C_{(3)}$, $C_{(2)}$, and $C_{(5)}$, are shifted upfield, whereas for the $C_{(7)}$ atom a strong downfield shift, due to the influence of the nitro group, is observed.

The biological activity against Gram-negative and Gram-positive bacteria has been determined for 2-methyl-10-nitrobenzo[*c*]-1,5-naphthiridine **11** and 4-methyl-10-nitrobenzo[*c*]-1,5-naphthiridine **12**; for comparison such data of biological activity for 2-methylbenzo[*c*]-1,5-naphthiridine-5-oxide **15**, 4-methylbenzo[*c*]-1,5-naphthiridine-5-oxide **16**, and 1-methylbenzo[*f*]-1,7-naphthiridine-4,6-dioxide **17** [32,33], for the quaternary salt **18** [34], as well as for 7-chlorobenzo[*f*]-1,7-naphthiridine **19** and azo compounds **20** and **21** [23] are presented in Table 5.



15 **16** **17** **18**

19 **20** **21**

TABLE 5. MIC Values (mg/ml) for the Compounds **11**, **12** and **15–21** against Gram-negative and Gram-positive Bacteria

Strains		MIC (mg/ml)								
		11	**12**	**15**	**16**	**17**	**18**	**19**	**20**	**21**
Gram-negative	*Escherichia coli*	>2.5	2.0	1.5	1.0	2.5	0.5	1.3	0.8	1.0
	Salmonella paratyphi B	>2.5	2.5	1.2	1.3	2.5	0.4	1.4	1.0	1.4
Gram-positive	*Staphylococcus aureus*	0.5	0.1	0.3	0.3	0.05	0.1	0.7	0.3	0.6
	Listeria monocytogenes	>2.5	0.4	2.0	1.4	1.5	0.5	0.5	0.3	0.8

The determination of the MIC (minimal inhibitory concentration) was made by the method of serial dilutions on Grove Randall bacterial media [35, 36]. Turbidity indicated the growth of a strain, while clarity showed its decrease. The lowest concentration of the investigated compound when no growth of strains could be observed was taken as the MIC.

In comparison with other DAP derivatives, higher activity is found against Gram-positive than against Gram-negative bacteria. Among the compounds considered the highest activity (MIC = 0.05 mg/ml) is observed for dioxide **17** against *Staphylococcus aureus.*

EXPERIMENTAL

Melting points determined on a Boetius apparatus are uncorrected. The progress of reactions was followed using of TLC performed on 60F 254 silica gel (Merck) precoated DC aluminum sheets.

The UV spectra were recorded on a UV-vis Specord Zeiss-Jena spectrophotometer using 1,2-dichloroethane as a solvent (c = 10^{-4}M). The ^{1}H and ^{13}C NMR spectra were registered on a Varian 500 MHz spectrometer in DMSO-d_6 using Me_4Si as internal standard. The mass spectra were recorded on an LKB-2091 (70eV) spectrometer.

General Procedure for the Synthesis of Compounds 11, 12, and 14. In a round bottom flask the starting methylDAP (1.94 g; 10 mmol) was converted into sulfate by treatment with concentrated sulfuric acid (2.2 ml). Then fuming sulfuric acid containing 60% of sulfur trioxide (7.5 ml) was added with stirring, the reaction mixture was heated to 100°C, and nitric acid (d = 1.5; 3.2 ml) was added dropwise. The temperature was next raised to 120°C and maintained for 4 hours with stirring. The cooled reaction mixture was poured onto ice, and conc. NH_4OH added to pH *ca* 4. The formed solid was filtered off and recrystallized from glacial acetic acid. The products are small yellow crystals.

Compound 11. Yield 39.6%; mp 212°C. Mass spectrum (*m/z*): 239 (M^+; 70.5%). Found, %: C 64.85; H 3.87; N 17.98. $C_{13}H_9N_3O_2$ (239.22). Calculated, %: C 65.27; H 3.79; N 17.56.

Compound 12. Yield 35.0%; mp 242°C. Mass spectrum (*m/z*): 239 (M^+; 65.8%). Found, % C 64.98; H 3.95; N 17.77. $C_{13}H_9N_3O_2$ (239.22). Calculated, % C 65.27; H 3.79; N 17.56.

Compound 14. Yield 42.4%; mp 195°C. Mass spectrum (*m/z*): 239 (M^+; 42.0%). Found, %: C 64.95; H 4.02; N 17.30. $C_{13}H_9N_3O_2$ (239.22). Calculated, %: C 65.27; H 3.79; N 17.56.

Synthesis of Compound 13. The starting 3-methylbenzo[*f*]-1,7-naphthiridine (1.94 g; 10 mmol) was treated as for **11**, **12**, and **14**; however the temperature after the end of the reaction was kept at 80-85°C instead of 120°C for only 3 hours. The hot reaction mixture was poured onto ice, and conc. NH_4OH was added dropwise to pH *ca* 2. The solution was concentrated and extracted with ethanol, the solvent removed, and the residue dissolved in benzene and acetone and evaporated to dryness.

The residue was dissolved in ether and concentrated to give small yellow crystals of **13**. Yield 25.5%; mp 117-118°C. Mass spectrum (*m/z*): 239 (M^+; 52%). Found, %: C 64.72; H 3.88; N 17.52. $C_{13}H_9N_3O_2$ (239.22). Calculated, %: C 65.27; H 3.79; N 17.56.

REFERENCES

1. A. Takahashi, K. Gengyo, S. Ishigami, S. Yamada, Y. Manome, S. Murata, and K. Kojo, Jpn. Pat. 10 77,271; *Chem. Abstr.*, **128**, 294706 (1998).
2. M. W. Orme, N. Baindur, and K. G. Robbins, PCT Int. Appl. WO 98 17, 267; *Chem. Abstr.*, **128**, 321662 (1998).
3. J. I. Levin, A. Zask, Y. Gu, J. D. Albright, and X. Dui, PCT Int. Appl. WO 98 16, 514; *Chem. Abstr.*, **128**, 321639 (1998).
4. D. W. Kim, H. S. Chang, Y. K Ko, J. W. Ryu, J. Ch. Woó, D. W. Ku, and J. S. Kim, PCT Int. Appl. WO 98 30,564; *Chem. Abstr.*, **129**, 122671 (1998).
5. K. Eicken, H. Rang, A. Harreus, N. Goetz, E. Ammermann, G. Lorenz, and S. Strathmann, 19, 531, 813 Ger. Offen.; *Chem. Abstr.*, **126**, 264007 (1997).
6. Fuji Photo Film Co., Ltd., Japan, Jpn. Pat. 09, 176, 164; *Chem. Abstr.*, **127**, 108927 (1997).
7. G. K. Kupetis, O. Eicher-Lorka, L. Rastenyte, and A. Matijoska, *Chemija. Vilnius. Lithaunia.*, N3, 98 (1997).
8. F. Liska, F. Hampl, H. Kotoucova, and J. Mazac, *Conf. Org. Chem. Adv. Org. Chem., 22nd,* 183 (1997); *Chem. Abstr.*, **128**, 270255 (1998).
9. R. Castro, P. D. Davidov, K. A. Kumar, A. P Marchand, J. D. Evansteck, and A. E. Kaifer, *J. Phys. Org. Chem.*, **10**, 369 (1997).
10. J.-P. Cheng, Y. Lu, X. Zhu, and L. Mu, *J. Org. Chem.*, **63**, 6108 (1998).
11. L. Chrzastek, B. Mianowska, and W. Sliwa, *Aust. J. Chem.*, **47**, 2129 (1994).
12. G. Matusiak and W. Sliwa, *Acta Chim. Hung.*, **125**, 267 (1988).
13. W. Sliwa, *Benzonaftyrydyny (Benzonaphthyridines),* Polytechnical University, Wroclaw (1978), 167 p.
14. N. Zelichowicz, *Wlasciwosci kompleksotwórcze zwiazków azaaromatycznych (Complexing properties of azaaromatics),* Pedagogical University, Czestochowa (1997).
15. W. Sliwa and L. Chrzastek, Pol. Pat. 165, 956; *Chem. Abstr.*, **125**, 275674 (1996).
16. G. Matusiak and W. Sliwa, *Monatsh. Chem.*, **124**, 161 (1993).
17. T. Girek, T. Zujewska, and W. Sliwa, *Acta Chim. Hung.*, **127**, 711 (1990).
18. B. Bachowska and T. Zujewska, *Pol. J. Chem.*, **72**, 89 (1998).
19. T. Zujewska and B. Bachowska, *Aust. J. Chem.*, **49**, 523 (1996).
20. W. Sliwa, *Pol. J. Chem.*, **52**, 271 (1978).
21. M. Paluszewski, W. Sliwa, *Aust. J. Chem.*, **46**, 1115 (1993).
22. W. Sliwa and Z. Szulc, *J. Prakt. Chem.*, **319**, 362 (1977).
23. L. Chrzastek and W. Sliwa, *40 Conference of Polish Chem. Soc.,* Abstracts of Papers S-11, Gdansk (1997), P-14.
24. J. Peszke, B. Mianowska and W. Sliwa, *Spectrochim. Acta.*, **53A**, 2565 (1997).
25. B. Mianowska and W. Sliwa, *Spectrochim. Acta.*, **52A**, 397 (1996).
26. B. Mianowska and W. Sliwa, *Acta Chim. Hung., Models Chem.*, **131**, 761 (1994).
27. B. Mianowska and W. Sliwa, *Spectrochim. Acta.*, **46A**, 767 (1990).
28. B. Mianowska and W. Sliwa, *Acta Chim. Hung.*, **128**, 93 (1991).
29. G. Matusiak, A. Nowek and W. Sliwa, *Studies in Organic Chemistry, Ch.15, Chemistry of Heterocyclic Compounds.*, Elsevier, Amsterdam (1988), p. 409.
30. W. Sliwa, *Pol. J. Chem.*, **55**, 2199 (1981).
31. A. Könnecke, E. Lippmann, J. Mlochowski and W. Sliwa, *Org. Magn. Reson.*, **12**, 696 (1979).

32. W. Sliwa and M. Mielniczak, *Scientific Papers, Chemistry I.*, Pedagogical University, Czestochowa (1997), p 131.
33. M. Mielniczak, J. Peszke and W. Sliwa, *Scientific Papers, Chemistry II.*, Pedagogical University, Czestochowa (in press).
34. J. Peszke, M. Mielniczak and W. Sliwa, *Scientific Papers, Chemistry II.*, Pedagogical University, Czestochowa (in press).
35. D. C. Grove and W. A. Randall, *Assay Methods of Antibiotics. A Laboratory Manual.*, Medical Encyclopaedia, New York (1995).
36. W. Kedzia, *Diagnostyka Mikrobiologiczna w Medycynie. (Microbiological Diagnostics in Medicine)*, Medical Publications, Warsaw (1990), p. 347.