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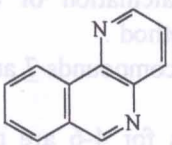
DIAZAPHENANTHRENE AND METHYLDIAZAPHENANTHRENE N-OXIDES

Abstract: For three N-oxides of isomeric methyl- 1,5- and 4,6- diazaphenanthrenes (dap) 4 - 6 as well as for three model species, i.e. N-oxides of unsubstituted daps 7 - 9 the geometry optimization and calculation of electronic structure are presented.
The UV spectroscopy results of considered compounds are compared with those of parent daps 1-3.

Isomeric 1,5-, 1,6- and 4,6-diazaphenanthrenes (dap) 1 - 3, respectively, a topic of our research are interesting for their reactivity [1], physicochemical properties[2] and biological activities [3-5].



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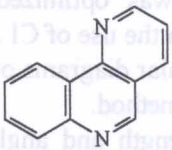

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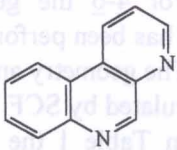

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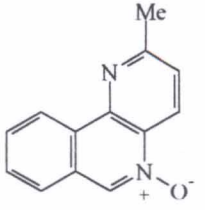
N-Oxides of azaaromatics deserve attention as synthons in organic chemistry and as biologically active species [6,7]; the reactivity of dap N-oxides is also reported [8,9].

The present paper deals with electronic structure and UV spectra of N-oxides of isomeric methyl-1,5- and 4,6-daps 4-6 as well as those of model compounds, i.e. N-oxides of unsubstituted daps 7-9.



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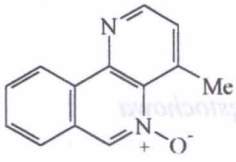

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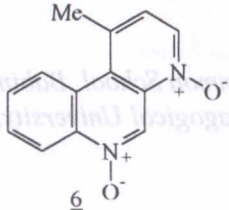

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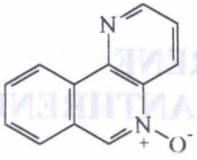

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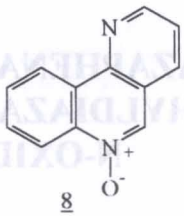

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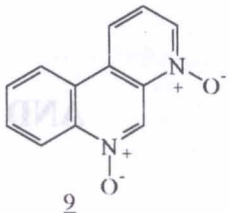


9

Compounds 4 and 5 [10] as well as 7-9 [11] have been obtained by N-oxidation of appropriate methyldaps or daps with peracetic acid, generated in situ; the synthesis of 1-methyl-4,6-diazaphenanthrene-4,6-di-N-oxide 6 is described in the present work.

In the case of 1,5-daps or methyl-1,5-daps, the N-oxidation proceeds at sterically less hindered nitrogen atom, i.e. at N5; this behaviour is in accordance with results of quaternization reactions of 1,5-dap [4].

In 4,6-dap and in 1-methyl-4,6-dap the accessibility to both nitrogen atoms is similar; the products are N-oxidized at both nitrogen atoms. However in quaternization reactions of 4,6-dap the N6 atom has shown to be more reactive than N1, the isolated salts are quaternized only at N6 [12, 13].

For 4-6 the geometry was optimized and calculation of electronic structure has been performed with the use of CI AM1 method .

The geometry and molecular diagrams of model compounds 7 and 9 have been calculated by SCF MNDO method.

In Table 1 the bond length and angle values for 4-6 are presented, and in Fig. 1 their effective charge values are given. The geometry of 7 and 9 is shown in Figs 2 and 3, and their molecular diagrams in Figs 4 and 5.

Experimental $\bar{\nu}$ and log ε values of considered compounds are summarized in Table 2 and UV spectra for two di-N-oxides - 6 and its model compound 9 are shown in Fig 6.

Differences in $\bar{\nu}$ values of α, p and β bands for 5 - 9 as compared with corresponding unsubstituted 1,5-, 1,6- and 4,6-daps 1-3 [14] are given in Table 3. In considered compounds, in p and β bands the red shift is observed, while for α band of 5, 7 and 8 the blue shift is to be found.

^{1}H NMR results for 4 and 5 have been reported in [10]; the ^{1}H NMR data of the synthesized 6, and of unsubstituted 1,5- and 1,6-dap-N-oxides 7 and 8 are presented in Table 4. The ^{13}C NMR data for parent daps 1 - 3 are given in Table 5a and those for methyldap N-oxides and dap N-oxides in Table 5b.

Comparing ^{13}C NMR data of dap N-oxides and methyldap N-oxides with those of parent daps, for C6 (in the 1,5-dap series) and for C5 (in the 1,6- and 4,6-dap series) the upfield shift due to the presence of the neighbouring N-O group is observed.

Analyzing ^{13}C NMR spectrum of 6, the presence of two N-O groups is responsible for the upfield shift of C1, C3 and C5 signals as compared with such values of 4,6-dap 3, the highest in the case of C3; the C2 signal is shifted downfield. The upfield shift of C6a, and the downfield shift of C10a signals is due to the presence of the N-O group in the position 6.

Experimental

The reaction progress was watched by tlc on 60F 254 silica gel (Merck) precoated DC aluminium sheets; as eluent the mixture $CHCl_3$/MeOH (9:1) was used.

The ^{1}H and ^{13}C NMR spectra have been registered on the Varian 500 MHz spectrometer in $(CD_3)_2SO$ using Me_4Si as internal standard. UV spectra have been recorded on UV-vis Specord Zeiss - Jena spectrophotometer in 1,2-dichloroethane ($c=10^{-4}$M). The calculations have been made on IBM Pentium 166 computer, using Hyper Chem 4.5 program.

Synthesis of 6

1-Methyl-4,6-dap (1.94 g, 10 mmol), glacial acetic acid (11 ml), benzene (11 ml) and 30% H_2O_2 (3.2 ml) were refluxed during 16 hours, watching the reaction progress by tlc. Then the reaction mixture has been concentrated under reduced pressure to about half of volume, diluted with water (11 ml) and once more concentrated to a half volume.

The solution has been evaporated to dryness, and the residue submitted to preparative chromatography on glass plates 20 x 20 cm, coated with silica gel 60 HR (Merck) using $CHCl_3$ as eluent. Recrystallization from ethanol afforded 1.18 g (52.5% yield) of 6; small yellow crystals, m.p. 178°C.

Elemental analysis: for $C_{13}H_{10}O_2N_2$ (226.23) calc. 69.02%C; 4.46%H; 12.38%N; found 68.77%C; 4.60%H; 12.58%N.

Table 1
Bond lengths (Å) and angles (°) for 4-6 calculated by CI AM1 method

4

N1-C2	1.34161
C2-C3	1.42482
C3-C4	1.37875
C4-C4a	1.41960
C4a-C10b	1.42863
C4a-N5	1.43918
N5-C6	1.35123
C6-C6a	1.43362
C6a-C10a	1.41116
C6a-C7	1.41229
C7-C8	1.38199
C8-C9	1.40554
C9-C10	1.38366
C10-C10a	1.41103
C10a-C10b	1.45535
C10b-N1	1.36528
C2-C11	1.49601
N5-O12	1.22548
N1-C2-C3	122.630
C2-C3-C4	119.223
C3-C4-C4a	118.940
C4-C4a-C10b	118.763
C4a-C10b-N1	121.310
C10b-N1-C2	119.134
C4a-N5-C6	118.056
N5-C6-C6a	122.972
C6-C6a-C10a	120.505
C6a-C10a-C10b	117.969
C10a-C10b-C4a	118.970
C10b-C4a-N5	121.528
C6a-C7-C8	120.076
C7-C8-C9	120.240
C8-C9-C10	120.422
C9-C10-C10a	120.232
C10-C10a-C6a	119.255
C10a-C6a-C7	119.775
N1-C2-C11	118.838
C4a-N5-O12	119.084

5

N1-C2	1.33019
C2-C3	1.41204
C3-C4	1.38962
C4-C4a	1.42952
C4a-C10b	1.43403
C4a-N5	1.44066
N5-C6	1.35280
C6-C6a	1.43058
C6a-C10a	1.40954
C6a-C7	1.41253
C7-C8	1.38148
C8-C9	1.40593
C9-C10	1.38341
C10-C10a	1.41199
C10a-C10b	1.45528
C10b-N1	1.36778
C4-C11	1.47995
N5-O12	1.22608
N1-C2-C3	123.835
C2-C3-C4	119.380
C3-C4-C4a	118.037
C4-C4a-C10b	118.664
C4a-C10b-N1	121.552
C10b-N1-C2	118.552
C4a-N5-C6	118.550
N5-C6-C6a	123.403
C6-C6a-C10a	119.991
C6a-C10a-C10b	118.085
C10a-C10b-C4a	119.719
C10b-C4a-N5	120.252
C6a-C7-C8	119.966
C7-C8-C9	120.213
C8-C9-C10	120.494
C9-C10-C10a	120.199
C10-C10a-C6a	119.144
C10a-C6a-C7	119.983
C3-C4-C11	119.127
C4a-N5-O12	120.120

6

C1-C2	1.39223
C2-C3	1.39711
C3-N4	1.37766
N4-C4a	1.41593
C4a-C10b	1.41999
C4a-C5	1.44098
C5-N6	1.34771
N6-C6a	1.44457
C6a-C10a	1.42023
C6a-C7	1.41689
C7-C8	1.38168
C8-C9	1.40172
C9-C10	1.38392
C10-C10a	1.41160
C10a-C10b	1.45058
C10b-C1	1.41759
C1-C11	1.48155
N4-O12	1.22344
N5-O13	1.22456
C1-C2-C3	121.800
C2-C3-N4	121.657
C3-N4-C4a	117.190
N4-C4a-C10b	122.011
C4a-C10b-C1	118.533
C10b-C1-C2	118.187
C4a-C5-N6	122.445
C5-N6-C6a	117.971
N6-C6a-C10a	120.935
C6a-C10a-C10b	120.181
C10a-C10b-C4a	115.979
C10b-C4a-C5	120.985
C6a-C7-C8	120.013
C7-C8-C9	119.716
C8-C9-C10	120.453
C9-C10-C10a	121.722
C10-C10a-C6a	116.856
C10a-C6a-C7	120.822
C10b-C1-C11	124.637
C3-N4-O12	121.850
C5-N6-O13	122.749

Table 2
Experimental wavenumber and log ε values for N-oxides derived from 1,5-, 1,6-, and 4,6-daps (in 1,2-dichloroethane, $c=10^{-4}M$)

Band	1,5-dap derivatives				1,6-dap derivatives		4,6-dap derivatives			
	7		5		8		9		6	
	$\bar{\nu}$ x 10^3 cm^{-1}	log ε	$\bar{\nu}$ x 10^3 cm^{-1}	log ε	$\bar{\nu}$ x 10^3 cm^{-1}	log ε	$\bar{\nu}$ x 10^3 cm^{-1}	log ε	$\bar{\nu}$ x 10^3 cm^{-1}	log ε
α	29.0	3.854	32.5	3.852	31.0	4.041	28.5	4.251	27.5	4.093
p.	37.8	3.672	36.0	4.031	37.8	4.802	37.8	4.753	32.8	4.061
β	42.0	4.132	40.5	4.550	42.0	4.950	41.8	4.898	41.2	4.354

Table3

Differences in the experimental wavenumber values of α, p and β bands for N-oxides derived from 1,5-dap, 1,6-dap and 4,6-dap, as compared with corresponding unsubstituted daps 1-3 (positive values denote red, negative blue shifts)

Band	$\bar{\nu}$ differences				
	1,5-dap derivatives		1,6-dap derivatives	4,6-dap derivatives	
	7 / 1	5 / 1	8 / 2	9 / 3	6 / 3
α	-1, 4	-4, 9	-1, 9	+0, 5	+1, 5
p	+0, 3	+2, 1	+0, 4	+0, 3	+5, 3
β	+0, 2	+1, 7	+1, 6	+1, 5	+2, 1

Table 4
^{1}H NMR data for N-oxides 6-8 in DMSO (TMS as internal standard)

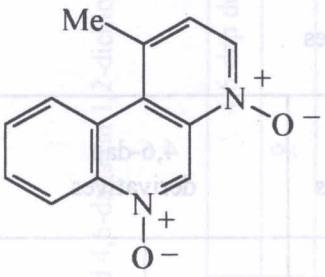
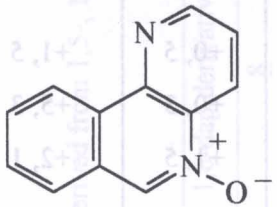
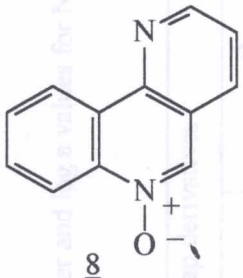
Compound	δ (ppm), J (Hz)
 6	9.84 (s, 1H, H5); 9.61 (d, 1H, $J_{3,2}$=4.4 Hz, H3); 9.38 (dd, 1H, $J_{10,9}$=7.3 Hz; $J_{10,8}$=1.5 Hz; H10); 8.44 (d, 1H, $J_{2,3}$=4.4 Hz; H2); 8.40 - 7.58 (m, 3H, H7, H8, H9); ca. 2.5, overlapped with DMSO (3H, CH_3)
 7	9.24 (s, 1H, H6); 9.17 (dd, 1H, $J_{2,3}$=4.4 Hz; $J_{2,4}$=1.5 Hz; H2); 9.02 (dd, 1H, $J_{10,9}$=8.6 Hz; $J_{10,8}$=1,3 Hz; H10); 8.96 - 8.87 (m, 1H, H4); 8.08 - 7.80 (m, 4H, H3, H7, H8, H9)
 8	9.18 (s, 1H, H5); 9.12 - 9.02 (m, 2H, H2, H10); 8.70 (dd, 1H, $J_{4,3}$=8.3 Hz; $J_{4,2}$=1.5 Hz; H4); 8.40 (dd, 1H, $J_{7,8}$=7.8 Hz; $J_{7,9}$=1.5 Hz; H7); 8.08 - 7.92 (m, 2H, H8, H9); 7.77 (dd, 1H, $J_{3,4}$=8.3 Hz; $J_{3,2}$=4.4 Hz; H3)

Table 5a
^{13}C NMR data for diazaphenantrenes 1 - 3 in DMSO (TMS as internal standard)

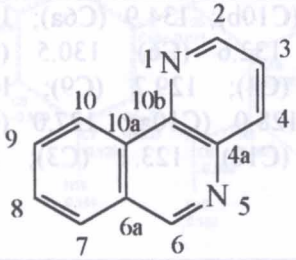
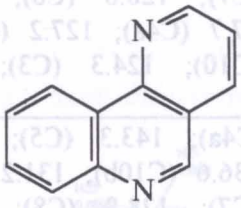
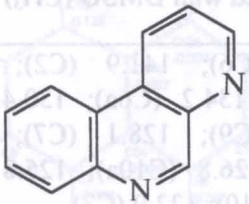
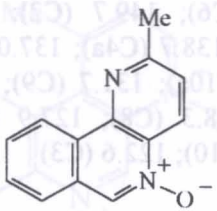
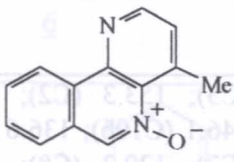
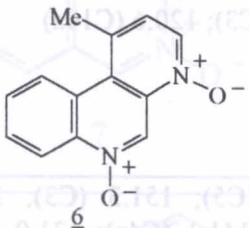
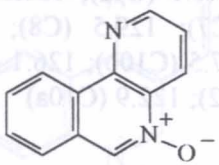
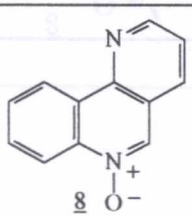
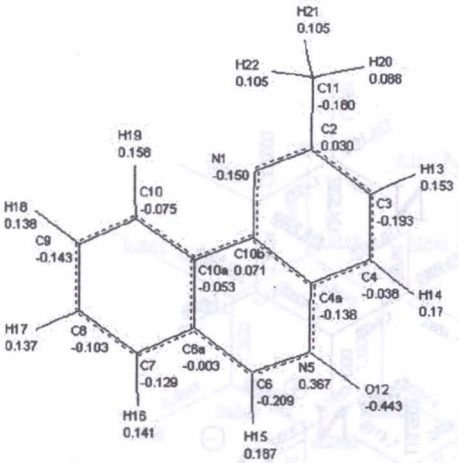
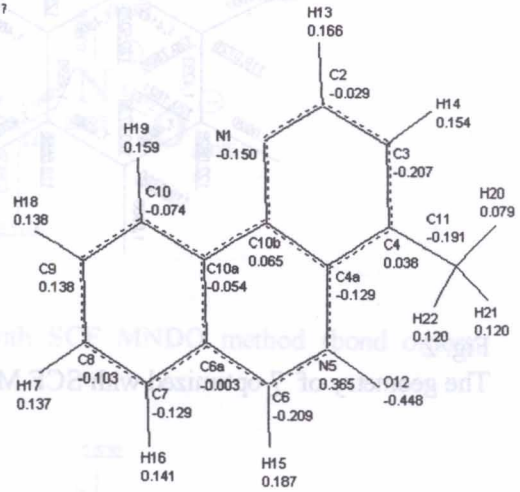
Compound	δ (ppm)
 1	154.3 (C6); 149.7 (C2); 140.2 (C10b); 138.7 (C4a); 137.0 (C4); 132.5 (C10a); 131.7 (C9); 129.4 (C7); 128.3 (C8); 127.9 (C6a); 124.3 (C10); 122.6 (C3)
 2	153.8 (C5); 153.3 (C2); 147.2 (C6a); 146.1 (C10b); 136.6 (C4); 130.3 (C7); 129.2 (C8); 127.5 (C9); 124.6 (C4a); 123.5 (C10); 123.2 (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)

Table 5b
^{13}C NMR data for N-oxides 4 - 8 in DMSO (TMS as internal standard)

Compound	δ (ppm)
 4	141.1 (C10b); 134.9 (C6a); 134.1 (C4a); 132.6 (C6); 130.5 (C2); 130.2 (C4); 129.2 (C9); 129.0 (C7); 128.0 (C10a); 127.0 (C8); 124.1 (C10); 123.1 (C3); 23.9 (CH_3)
 5	132.7 (C10b), 132.3 (C6a); 131.9 (C6); 131.6 (C2); 130.0 (C9); 129.2 (C7); 128.8 (C8); 127.9 (C4); 127.7 (C4a); 127.2 (C10a); 124.9 (C10); 124.3 (C3); 17.3 (CH_3)
 6	147.1 (C4a); 143.3 (C5); 140.4 (C6a); 136.6 (C10b); 131.2 (C3); 129.8 (C7); 128.8 (C8); 128.6 (C9); 128.4 (C10); 127.6 (C2); 127.0 (C10a); 126.2 (C1); ca. 40, overlapped with DMSO (CH_3)
 7	151.5 (C6); 141.9 (C2); 135.0 (C10b); 134.2 (C6a); 130.4 (C4); 129.4 (C9); 128.1 (C7); 127.9 (C4a); 126.8 (C10a); 125.8 (C8); 124.6 (C10); 122.9 (C3)
 8	151.1 (C5); 141.2 (C2); 140.8 (C6a); 133.6 (C10b); 133.0 (C4a); 131.2 (C4); 129.7 (C7); 127.1 (C8); 124.2 (C9); 124.0 (C10); 122.0 (C10a); 119.5 (C3)



4



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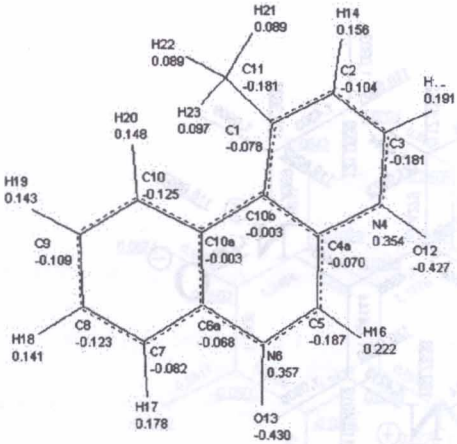

6

Fig. 1
Effective charge values for 4 - 6 calculated with CI AM1 method

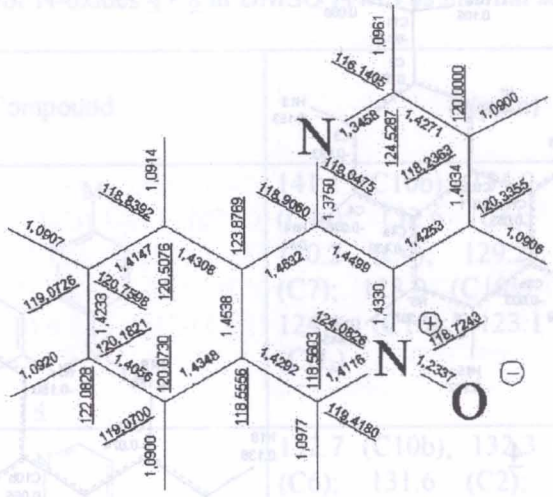

Fig. 2
The geometry of 7 optimized with SCF MNDO method (bond lengths, angles)

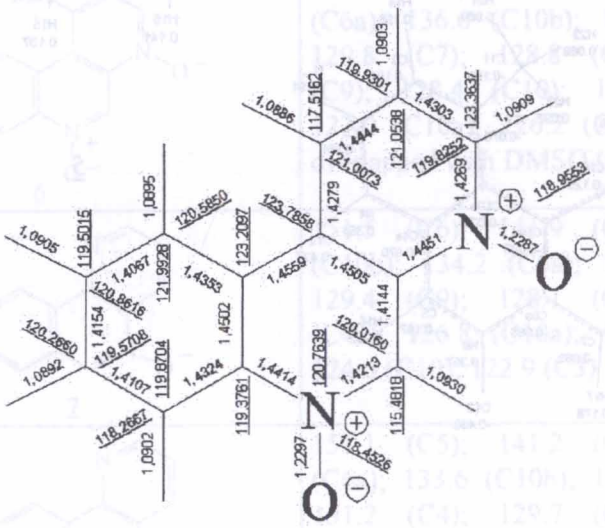

Fig. 3
The geometry of 9 optimized with SCF MNDO method (bond lengths, angles)

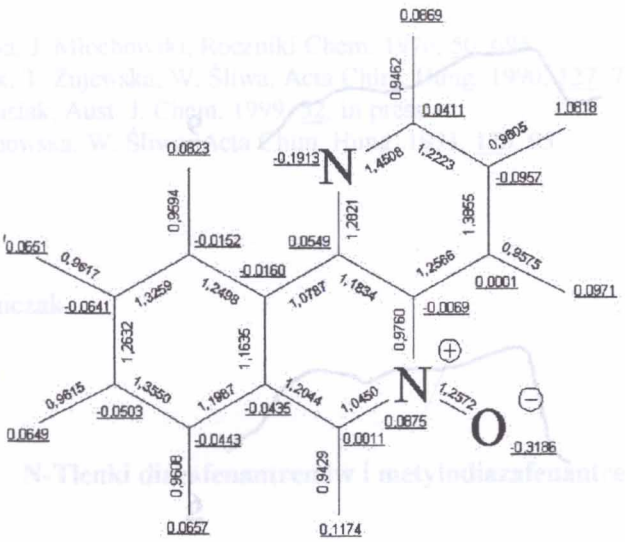

Fig. 4
Molecular diagram of 7 calculated with SCF MNDO method (bond orders, effective charge values)

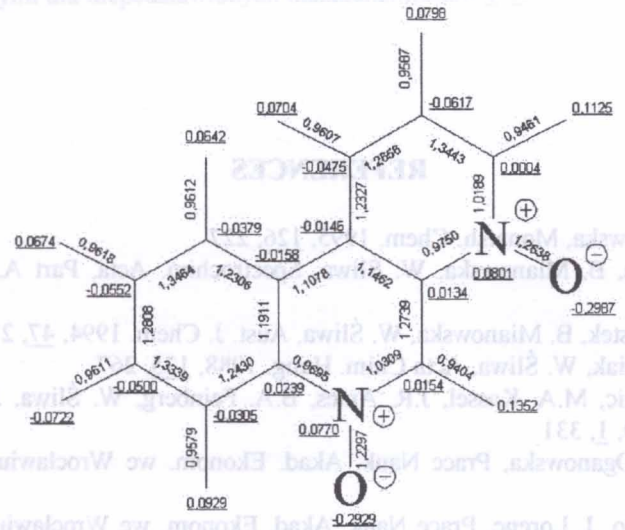

Fig. 5
Molecular diagram of 9 calculated with SCF MNDO method (bond orders, effective charge values)

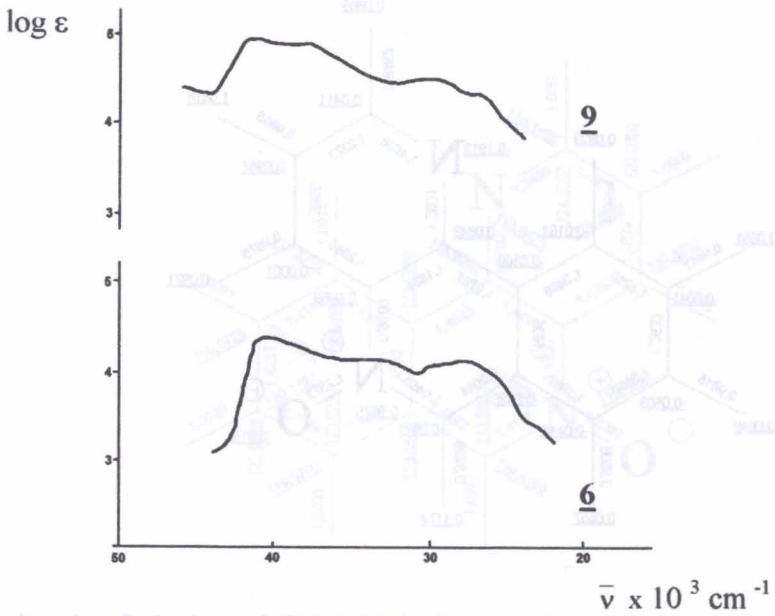

Fig. 6
UV spectra of 9 and 6 (in 1,2-dichloroethane, c=10^{-4}M)

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N-Tlenki diazafenantrenów i metylodiazafenantrenów

Streszczenie: Dla trzech N-tlenków izomerycznych metylo- 1,5- i 4,6-diazafenantrenów 4-6 oraz dla trzech układów modelowych, tj. N-tlenków niepodstawionych diazafenantrenów 7-9 wykonano optymalizację geometrii i obliczono strukturę elektronową.
Wyniki spektroskopii w nadfiolecie rozważanych związków porównano z danymi dla niepodstawionych diazafenantrenów 1-3.