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Jerzy Peszke
Lidia Chrząstek
Wanda Śliwa *

* *Pedagogical University, Institute of Chemistry and Environmental Protection*
42-201 Częstochowa, Armii Krajowej Ave 13/15
e-mail: *w.sliwa@wsp.czest.pl*

UV SPECTROSCOPY STUDY OF NITRODIAZAPHENANTHRENES AND THEIR HOMOLOGUES BY AM1 CI METHOD

Abstract: For three isomeric nitrodiazaphenanthrenes **4-6** and their four homologues **7-10** the calculation of UV spectral values and their electronic structure, as well as the geometry optimisation has been made using AM1 CI method.

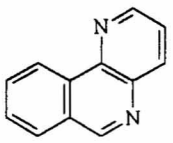
Introduction

The paper concerns our investigation of 1,5-, 1,6- and 4,6-diazaphenanthrenes (dap) **1-3** and their derivatives [1-3]; these compounds are interesting for their reactivity [4,5] and biological properties [6-8]. Due to the presence of nitrogen atoms in the molecule they undergo quaternization [9,10] and oxidation [11-13] reactions and form complexes with metal ions [14]. Quaternary salts are precursors of ylides serving as 1,3-dipoles in cycloaddition reactions [15,16].

In a continuation of our study of UV spectroscopy of formyl [17], methyl [18,19], amino [20] and bromo [21] derivatives of daps, as well as of their N-oxides [22,23] and quaternary salts [24,25], we present here AM1 CI (next referred to as AM1) calculation results of nitrodaps **4-6** and their homologues **7-10**.

Experimental

The calculations have been made by AM1 method on a Pentium II 733MHz computer using Hyper Chem 4.5 program; UV spectra of considered compounds were recorded in 1,2-dichloroethane [6]. Nitrodaps and their homologues have been synthesized by nitration of corresponding daps and methyldaps [6].



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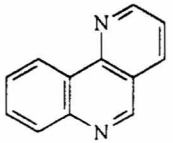

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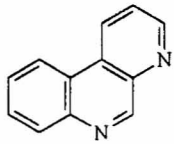

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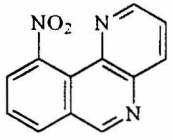

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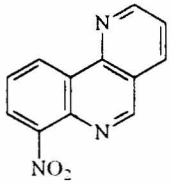

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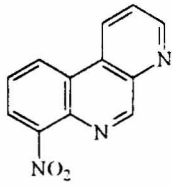

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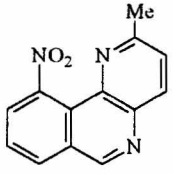

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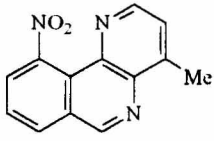

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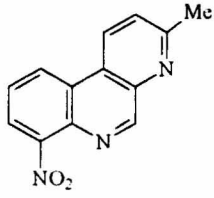

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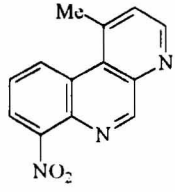

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Results and discussion

The experimental and calculated by AM1 method UV spectral data of **4-10** are shown in Table 1.

Table 1
Experimental and calculated by AM1 method UV values of **4 – 10**

Com-pound	Band	Experimental		Calculated	
		$\bar{\nu} \cdot 10^3$ cm^{-1}	log ε	$\bar{\nu} \cdot 10^3$ cm^{-1}	f
4	α	29.0	4.176	29.2578	0.0285
	p	38.0	4.653	36.7849	0.0146
	β	42.3	4.892	40.1445	1.6762
5	α	30.8	4.204	29.4989	0.0125
	p	36.3	4.763	36.9008	0.0203
	β	40.2	5.000	40.0990	1.0145
6	α	29.0	4.146	28.6686	0.0054
	p	36.0	4.756	34.5530	0.0406
	β	42.9	5.053	42.9579	0.4889
7	α	29.5	2.110	29.0061	0.0477
	p	36.9	2.512	34.4678	0.0648
	β	40.5	2.247	39.7726	1.4589
8	α	28.7	3.971	29.1088	0.0300
	p	37.8	4.399	36.2441	0.0645
	β	40.0	4.753	39.6356	1.5234
9	α	28.8	1.952	34.2537	0.0765
	p	37.4	2.664	36.8071	0.2478
	β	43.0	3.383	39.9853	1.4057
10	α	28.2	3.463	33.8982	0.0209
	p	37.2	3.594	35.8123	0.1363
	β	40.8	3.001	39.5257	1.1089

The correlations of experimental and calculated wavenumber values are:

for **4,5,6** a = 0.9647; b = 0.6465; r = 0.9704
for **7,8** a = 0.9129; b = 2.2368; r = 0.9661; for **9,10** a = 0.3995; b = 22.374; r = 0.8981

Among the above results, the highest correlation coefficient has been obtained in the case of **4,5,6** isomers.

The correlations of experimental and calculated wavenumber values for **4-10** with corresponding unsubstituted daps **1-3** are:

for **4/1** a = 0.8750; b = 4.4079; r = 0.9618 for **7/1** a = 0.9401; b = 1.9358; r = 0.9445
for **5/2** a = 1.0427; b = -1.5029; r = 0.9733 for **8/1** a = 0.9187; b = 3.0519; r = 0.9706
for **6/3** a = 1.0412; b = -1.6201; r = 0.9765 for **9/3** a = 0.7224; b = 10.6345; r = 0.8102
for **10/3** a = 0.7537; b = 9.5645; r = 0.8125

Comparison of the above calculations shows higher coefficients for nitrodaps than those for their homologues; the best result has been obtained in the case of **6** and its parent 4,6-dap **3**.

The total and binding energy values as well as the core-core interaction energy and dipole moments of **4-10** calculated by AM1 method are given in Table 2.

Table 2
Total and binding energy, formation heat and dipole moment values for **4-10** calculated by AM1 method

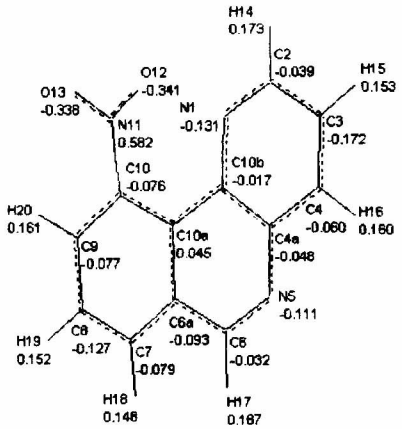
	4	**5**	**6**
Total Energy (eV)	-2890.7584	-2890.7692	-2890.7089
Binding Energy (eV)	-120.8095	-120.8203	-120.7600
Core-Core Interaction (eV)	13675.4981	13348.7293	13345.1074
Heat of Formation (eV)	3.8386	3.8277	3.8880
Dipole moments (D)			
M_x	0.579	-2.898	0.309
M_y	4.301	-6.559	-8.175
M_z	-0.189	0.000	0.000
M (M)	4.344	7.171	8.180

	7	**8**	**9**	**10**
Total Energy (eV)	-3046.6303	-3046.6740	-3046.6694	-3046.4615
Binding Energy (eV)	-133.0236	-133.0673	-133.0627	-132.8547
Core-Core Interaction (eV)	15305.7446	15269.4395	14799.4017	15036.6736
Heat of Formation (eV)	3.557631	3.513895	3.518491	3.7265
Dipole moments (D)				
M_x	-0.831	-1.078	0.077	0.997
M_y	3.674	4.567	-8.320	-8.370
M_z	-0.032	-0.067	-0.250	-0.178
M (M)	3.767	4.693	8.324	8.431

The total energy values for **4-6** show the highest stability for isomer **5** and among **7-10** for isomer **8**.

Dipole moments of **5** and **6** are significantly higher than in the case of **4**, similarly, the values of **9** and **10** are higher than those of **7** and **8**; this fact results from the situation of nitrogen atoms in molecules **5,6** and **9,10** in positions 1, 6 and 4, 6, respectively.

The AM1 method has been used for calculation of effective charge values of **4-10**, given in Fig.1 and for optimisation of their geometry shown in Table 3.



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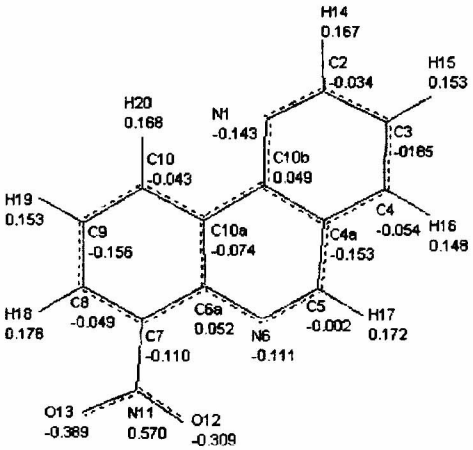

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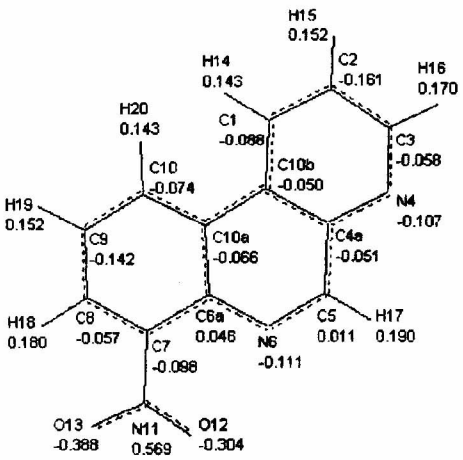

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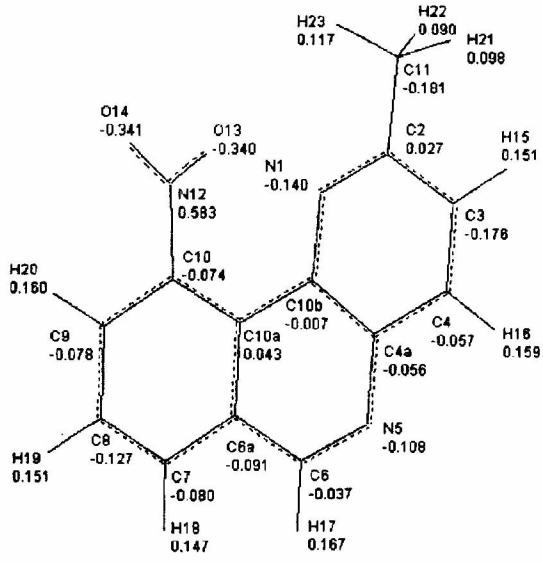
Fig. 1a
Effective charge values for 4 –calculated by AM1 method



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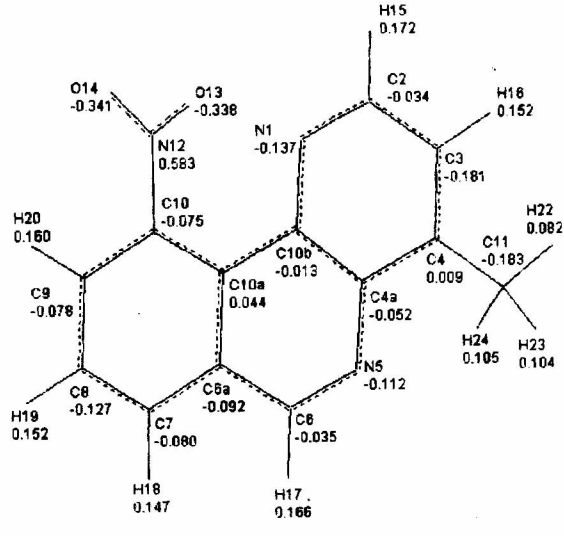

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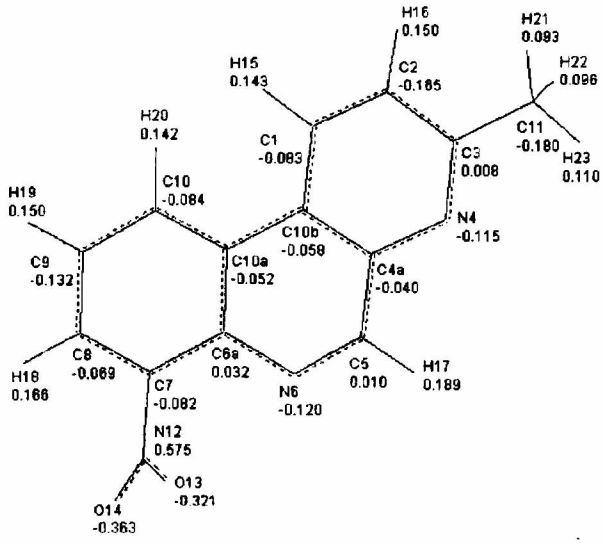
Fig. 1b
Effective charge values for 7, 8 calculated by AM1 method



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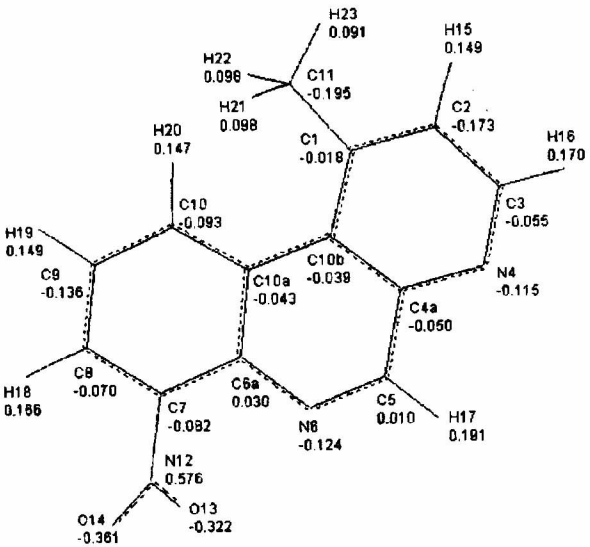

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Fig. 1c
Effective charge values for **9**, **10** calculated by AM1 method

Table 3a
Bond lengths (Å) and angles (°) for **4-6** calculated by AM1 method

4		5		6	
N1-C2	1.32769	N1-C2	1.33057	C1-C2	1.38081
C2-C3	1.42101	C2-C3	1.42163	C2-C3	1.42113
C3-C4	1.37758	C3-C4	1.38076	C3-N4	1.33042
C4-C4a	1.42715	C4-C4a	1.41143	N4-C4a	1.36765
C4a-C10b	1.43584	C4a-C10b	1.42258	C4a-C10b	1.42327
C4a-N5	1.39298	C4a-C5	1.44357	C4a-C5	1.46264
N5-C6	1.30429	C5-N6	1.30488	C5-N6	1.30203
C6-C6a	1.45033	N6-C6a	1.39457	N6-C6a	1.39403
C6a-C10a	1.41585	C6a-C10a	1.42897	C6a-C10a	1.43009
C6a-C7	1.40778	C6a-C7	1.43348	C6a-C7	1.43286
C7-C8	1.38114	C7-C8	1.39644	C7-C8	1.39576
C8-C9	1.40242	C8-C9	1.39888	C8-C9	1.39934
C9-C10	1.39387	C9-C10	1.38169	C9-C10	1.38067
C10-C10a	1.41982	C10-C10a	1.40835	C10-C10a	1.40833
C10a-C10b	1.45911	C10a-C10b	1.45810	C10a-C10b	1.44450
C10b-N1	1.36800	C10b-N1	1.37209	C10b-N1	1.41663
C10-N11	1.50003	C7-N11	1.49347	C7-N11	1.49487
N11-O12	1.19838	N11-O12	1.19586	N11-O12	1.19549
N11-O13	1.19834	N11-O13	1.20887	N11-O13	1.20876
N1-C2-C3	123.803	N1-C2-C3	124.341	C1-C2-C3	118.826
C2-C3-C4	118.699	C2-C3-C4	118.268	C2-C3-N4	123.641
C3-C4-C4a	119.280	C3-C4-C4a	118.868	C3-N4-C4a	117.452
C4-C4a-C10b	117.941	C4-C4a-C10b	119.255	N4-C4a-C10b	123.358
C4a-C10b-N1	121.604	C4a-C10b-N1	121.435	C4a-C10b-N1	117.223
C10b-N1-C2	118.664	C10b-N1-C2	117.834	C10b-C1-C2	119.500
C4a-N5-C6	118.017	C4a-C5-N6	124.621	C4a-C5-N6	124.219
N5-C6-C6a	124.859	C5-N6-C6a	119.181	C5-N6-C6a	119.841
C6-C6a-C10a	118.709	N6-C6a-C10a	121.785	N6-C6a-C10a	121.413
C6a-C10a-C10b	117.429	C6a-C10a-C10b	118.429	C6a-C10a-C10b	118.487
C10a-C10b-C4a	118.092	C10a-C10b-C4a	117.949	C10a-C10b-C4a	119.072
C10b-C4a-N5	122.853	C10b-C4a-C5	118.035	C10b-C4a-C5	116.968
C6a-C7-C8	120.219	C6a-C7-C8	120.336	C6a-C7-C8	120.366
C7-C8-C9	120.017	C7-C8-C9	120.663	C7-C8-C9	120.495
C8-C9-C10	120.153	C8-C9-C10	120.397	C8-C9-C10	120.375
C9-C10-C10a	121.262	C9-C10-C10a	120.425	C9-C10-C10a	120.833
C10-C10a-C6a	117.201	C10-C10a-C6a	120.522	C10-C10a-C6a	119.947
C10a-C6a-C7	121.123	C10a-C6a-C7	117.657	C10a-C6a-C7	117.983
C9-C10-N11	116.524	C6-C7-N11	123.170	C6-C7-N11	123.189
C10-N11-O12	118.452	C7-N11-O12	122.528	C7-N11-O12	122.493
O12-N11-O13	123.042	O12-N11-O13	120.887	O12-N11-O13	120.977

Table 3b

Bond lengths (Å) and angles (°) for 7,8 calculated by AM1 method

7		8	
N1-C2	1.33714	N1-C2	1.32771
C2-C3	1.42844	C2-C3	1.41786
C3-C4	1.37535	C3-C4	1.38377
C4-C4a	1.42652	C4-C4a	1.43433
C4a-C10b	1.43510	C4a-C10b	1.43616
C4a-N5	1.39227	C4a-N5	1.39270
N5-C6	1.30429	N5-C6	1.30389
C6-C6a	1.49026	C6-C6a	1.44947
C6A-C10a	1.41593	C6A-C10a	1.41566
C6a-C7	1.40782	C6a-C7	1.40780
C7-C8	1.38101	C7-C8	1.38088
C8-C9	1.40238	C8-C9	1.40240
C9-C10	1.39356	C9-C10	1.39355
C10-C10a	1.41996	C10-C10a	1.42023
C10a-C10b	1.46052	C10a-C10b	1.46003
C10b-N1	1.36520	C10b-N1	1.36753
C2-C11	1.49533	C4-C11	1.48000
C10-N12	1.50018	C11-N12	1.50050
N12-O13	1.19838	N12-O13	1.19830
N12-O14	1.19839	N12-O14	1.19832
N1-C2-C3	122.431	N1-C2-C3	123.862
C2-C3-C4	119.442	C2-C3-C4	119.231
C3-C4-C4a	119.345	C3-C4-C4a	118.425
C4-C4a-C10b	117.672	C4-C4a-C10b	118.148
C4a-C10b-N1	121.970	C4a-C10b-N1	121.800
C10b-N1-C2	119.139	C10b-N1-C2	118.530
C4a-N5-C6	117.985	C4a-N5-C6	118.299
N5-C6-C6a	124.820	N5-C6-C6a	124.857
C6-C6a-C10a	118.777	C6-C6a-C10a	118.587
C6a-C10a-C10b	117.414	C6a-C10a-C10b	117.496
C10a-C10b-C4a	117.989	C10a-C10b-C4a	118.212
C10b-C4a-N5	123.014	C10b-C4a-N5	122.522
C10a-C6a-C7	121.153	C10a-C6a-C7	121.212
C6a-C7-C8	120.244	C6a-C7-C8	120.212
C7-C8-C9	119.989	C7-C8-C9	119.980
C8-C9-C10	120.155	C8-C9-C10	120.178
C9-C10-C10a	121.312	C9-C10-C10a	121.297
C10-C10a-C6a	117.146	C10-C10a-C6a	117.099
C3-C2-C11	117.766	C3-C4-C11	120.919
C10a-C10-N12	118.457	C10a-C10-N12	122.245
C10-N12-O14	118.477	C10-N12-O14	118.399
O13-N12-O14	122.997	O13-N12-O14	123.066

Table 3c
Bond lengths (Å) and angles (°) for **9,10** calculated by AM1 method

9	
C1-C2	1.37853
C2-C3	1.42847
C3-N4	1.33977
N4-C4a	1.36507
C4a-C10b	1.42312
C4a-C5	1.46553
C5-N6	1.30246
N6-C6a	1.39530
C6a-C10a	1.42638
C6a-C7	1.42908
C7-C8	1.38949
C8-C9	1.40249
C9-C10	1.38151
C10-C10a	1.40951
C10a-C10b	1.44292
C10b-C1	1.41560
C3-C11	1.49503
C7-N12	1.49500
N12-O13	1.19680
N12-O14	1.20255
C1-C2-C3	119.537
C2-C3-N4	122.366
C3-N4-C4a	117.915
N4-C4a-C10b	123.581
C4a-C10b-C1	117.117
C10b-C1-C2	119.482
C4a-C5-N6	124.152
C5-N6-C6a	119.160
N6-C6a-C10a	122.366
C6a-C10a-C10b	118.019
C10a-C10b-C4a	119.094
C10b-C4a-C5	117.179
C6a-C7-C8	121.273
C7-C8-C9	119.607
C8-C9-C10	120.574
C9-C10-C10a	121.004
C10-C10a-C6a	119.523
C10a-C6a-C7	117.982
C2-C3-C11	117.523
C6a-C7-N12	120.374
C7-N12-O14	119.554
O13-N12-O14	122.594

10	
C1-C2	1.39311
C2-C3	1.41220
C3-N4	1.32947
N4-C4a	1.36522
C4a-C10b	1.43191
C4a-C5	1.46447
C5-N6	1.29891
N6-C6a	1.38410
C6A-C10a	1.43217
C6a-C7	1.42951
C7-C8	1.38818
C8-C9	1.39896
C9-C10	1.32288
C10-C10a	1.41003
C10a-C10b	1.45400
C10b-C1	1.42690
C1-C11	1.48298
C7-N12	1.49665
N12-O13	1.20203
N12-O14	1.19691
C1-C2-C3	120.284
C2-C3-N4	122.802
C3-N4-C4a	117.483
N4-C4a-C10b	124.714
C4a-C10b-C1	115.853
C10b-C1-C2	118.862
C4a-C5-N6	124.006
C5-N6-C6a	118.788
N6-C6a-C10a	122.966
C6a-C10a-C10b	118.282
C10a-C10b-C4a	117.296
C10b-C4a-C5	118.608
C6a-C7-C8	121.538
C7-C8-C9	118.727
C8-C9-C10	120.880
C9-C10-C10a	122.327
C10-C10a-C6a	117.315
C10a-C6a-C7	122.327
C2-C1-C11	115.536
C6a-C7-N12	120.361
C7-N12-O14	119.449
O13-N12-O14	122.668

In **4-6** the effective charge values at *ortho* positions to the nitro group and to nitrogen atoms are higher than those at other positions, due to the electron accepting character of NO_2 group and nitrogen atoms. Similarly, in **7-10** the effective charge values at *ortho* positions to the nitro group are higher than at other positions.

Comparing effective charge values of **7-10** with those of **4-6**, the presence of electron-donating methyl group results in lower effective charge values of carbon atoms at *ortho* positions to this group (C3 for **7** and **8** and C2 for **9** and **10**).

The geometry optimisation shows that in **4** and **5** the longest are C10a-C10b bonds, and the shortest N5-C6 and C5-N6 bonds, respectively. In methyl derivatives of **4**, i.e. in **7** and **8** the longest are C10a-C10b bonds, and the shortest N5-C6 bonds, as in the parent 1,5-dap. In **6** as well as in its methyl derivatives **9** and **10** the longest are C4a-C5 bonds, and the shortest C5-N6 bonds.

For **4** and **5** larger than other are angles at both *ortho* positions to N5 and N6, respectively, i.e. for **4** the angles at C6 and C4a, and for **5** the angles at C5 and C6a. For **6** larger than other are angles at *ortho* positions to nitrogen atoms – at C5 and C3. For **7** and **8** the largest are angles at C6; for **9** and **10** larger than other are angles at C5 (C4a-C5-N6) and at C4a (N4-C4a-C10b).

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Jerzy Peszke
Lidia Chrząstek
Wanda Śliwa *

Badanie widm w nadfiolecie nitrodiazafenantrenów i ich homologów przy użyciu metody AM1 CI

Streszczenie: Dla trzech izomerycznych nitrodiazafenantrenów **4-6** i ich czterech homologów **7-10** obliczono wartości dotyczące spektroskopii w nadfiolecie i strukturę elektronową oraz wykonano optymalizację geometrii stosując metodę AM1 CI.