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AM1 AND ZINDO STUDY OF BENZONAPHTHYRIDINES AND THEIR N-OXIDES

Abstract: For three isomeric benzonaphthyridines and six benzonaphthyridine N-oxides the UV spectral data have been calculated by AM1 and ZINDO/S methods. Correlations of calculated and experimental wavenumber values of considered compounds show good compatibility. The results obtained by both methods have been compared.

Introduction

N-Oxides of azaaromatics are a topic of numerous works [1,2]. The present paper is a continuation of our research of benzonaphthyridines (bn) concerning their UV spectra [3,4] and reactivity [5]. These compounds are interesting for their antibacterial and antineoplastic activities [6,7].

Due to the presence of nitrogen atoms in the molecule, bns form complexes with metal ions [8], N-oxides [9] and quaternary salts [5]; ylides derived from some quaternary salts of bns are useful as 1,3-dipoles in cycloaddition reactions [5,10].

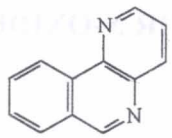
In preceeding work we calculated the electronic structure and UV spectral values of formyl [3], methyl [11], amino [12] and bromo [13] derivatives of bns and of their quaternary salts [14], and made correlations with their experimental UV data.

In the study of bn N-oxides their syntheses [15-17] and reactivity [9,18] have been investigated; here we describe UV spectra of bns **1** – **3**, bn N-oxides **4** – **6** [15] and methylbn N-oxides **7** – **9** [16,17].

The calculations of UV spectral values have been made with AM1 as well with ZINDO/S methods. As the molecules under consideration are rather large, these methods instead of more advanced ones have been used here.

Experimental

The calculations have been performed on a Pentium 166 computer using Hyper Chem 4.5 program. The UV spectra of **1** – **6** were recorded in 1,2-dichloroethane solution (c= 10^{-4} M) on a UV-vis. Specord spectrophotometer.



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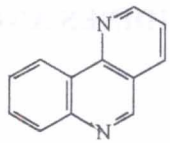

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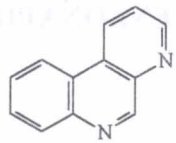

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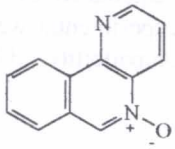

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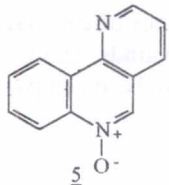

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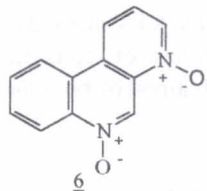

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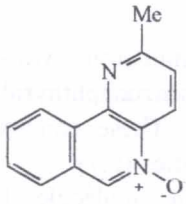

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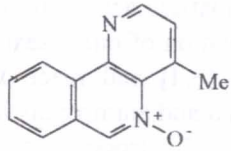

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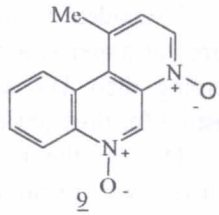

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The UV spectra of **1** – **3** have been recorded earlier [12]; N-oxides **4** – **9** have been obtained by oxidation of appropriate azaaromatics with peracetic acid generated *in situ* from acetic acid and 30% H_2O_2 [15-17].

Results and discussion

The experimental and calculated by AM1 and ZINDO/S methods UV spectra of bns **1 – 3**, bn N-oxides **4 – 6** and methylbn N-oxides **7 – 9** are shown in Fig. 1a (AM1) and b (ZINDO/S).

The experimental and calculated by AM1 and ZINDO/S methods wavenumber values for **1 – 3** bns, bn N-oxides and methylbn N-oxides **7 - 9** are given in the Table 1.

Experimental wavenumber values for α band of bn N-oxides decrease in the order 5>4>6, and those of methyl bn N-oxides in the order 8>7>9. For **4 - 9** log ε values of the p band are lower than those of the β band.

The correlations of experimental and calculated by AM1 method wavenumber values are:

for bns **1 – 3** a = 1.011450; b = 0.446222; r = 0.972158;
for bn N-oxides **4 – 6** a = 1.077040; b = -3.028810; r = 0.942153
for methylbn N-oxides **7 – 9** a = 0.865156; b = 4.892600; r = 0.922202.

The correlations of experimental and calculated by ZINDO/S method wavenumber values are:

for bns **1 – 3** a = 0.614353; b = 15.585100; r = 0.961064;
for **4 – 6** a = 0.992926; b = 0.889806; r = 0.979611
for **7 – 9** a = 1.007470; b = 0.307216; r = 0.947779.

The correlations of experimental and calculated by AM1 method wavenumber values for bn N-oxides **4 – 6** and methylbn N-oxides **7 – 9** with corresponding bns **1 – 3** are:

for **4/1** a = 1.015840; b = 0.063801; r = 0.944830
for **5/2** a = 1.183550; b = -6.853400; r = 0.957904
for **6/3** a = 0.954577; b = 2.051490; r = 0.980831
for **7/1** a = 1.104310; b = -2.251370; r = 0.966470
for **8/2** a = 0.975388; b = 1.837870; r = 0.948257
for **9/3** a = 0.900140; b = 3.909270; r = 0.959805

The correlations of experimental and calculated by ZINDO/S method wavenumber values for bn N-oxides **4 – 6** and methylbn N-oxides **7 – 9** with corresponding bns **1 – 3** are:

for **4/1** a = 0.710486; b = 11.321400; r = 0.936404
for **5/2** a = 0.764825; b = 10.358900; r = 0.924370
for **6/3** a = 0.841458; b = 6.406070; r = 0.920596
for **7/1** a = 0.709439; b = 10.801600; r = 0.856889
for **8/2** a = 0.677938; b = 12.470800; r = 0.856880
for **9/3** a = 0.830016; b = 7.082080; r = 0.932000

In correlations of experimental and calculated by AM1 method wavenumber values for **1** – **3** the r value is higher than in the case of ZINDO/S method, while for **4** – **6** and **7** – **9** the opposite was found. In correlations of experimental and calculated $\bar{\nu}$ of **4** – **9** and corresponding unsubstituted bns **1** – **3** the r values obtained by AM1 method are higher than those calculated by ZINDO/S method.

The total and binding energy values, as well as the core - core interaction energy and dipole moments for **1** – **9** calculated by AM1 method are given in Table 2.

Comparing total energy values for unsubstituted bns **1** – **3** and N-oxides **4** – **9**, bns **1** – **3** have higher energy values, so they are less stable than **4** – **9**; also their binding energy and core – core interaction are higher than those of **4** – **9**. Among **4** – **9**, lower total energy values – and higher stability are found for diN-oxides **6** and **9**; in the case of **9** these values are the lowest.

Among **1** – **9**, dipole moments of diN-oxides **6** and **9** are higher, the highest value is found for **9**.

The AM1 method has been used for calculation of effective charge values of bns **1** – **3** and bn N-oxides **4** – **6** given in Fig. 2a,b and for optimalization of their geometry shown in Table 3a,b. Effective charge values and geometry optimalization of methylbn N-oxides **7** – **9** have been reported in [17]; for comparative purposes the effective charge values for **7** - **9** are given in Fig. 2c.

In **1** – **3** the effective charge values at *ortho* positions to nitrogen atoms are higher that those at other positions, due to the electron accepting character of heteroatoms (C2 and C6 for **1**, C2 and C5 for **2**, C3 and C5 for **3**).

So in N-oxides **4** – **6** as in their methyl derivatives **7** – **9** the lowest effective charge values are found in *ortho* positions to the N-O group (C6 for **4**, **7** and **9**, C5 for **5**, C3 and C5 for diN-oxides **6** and **9**).

In bns **1** – **3** the shortest are bonds N5 – C6 and C5 – N6; slightly longer are N1 – C2 and C3 – N4 bonds.

For bns **1** and **2** and their N-oxides **4** and **5**, respectively, higher than other are angles at positions *ortho* to nitrogen atoms (for **1** and its N-oxide **4** these are positions 2 and 6, and for **2** and its N-oxide **5** – positions 2 and 5).

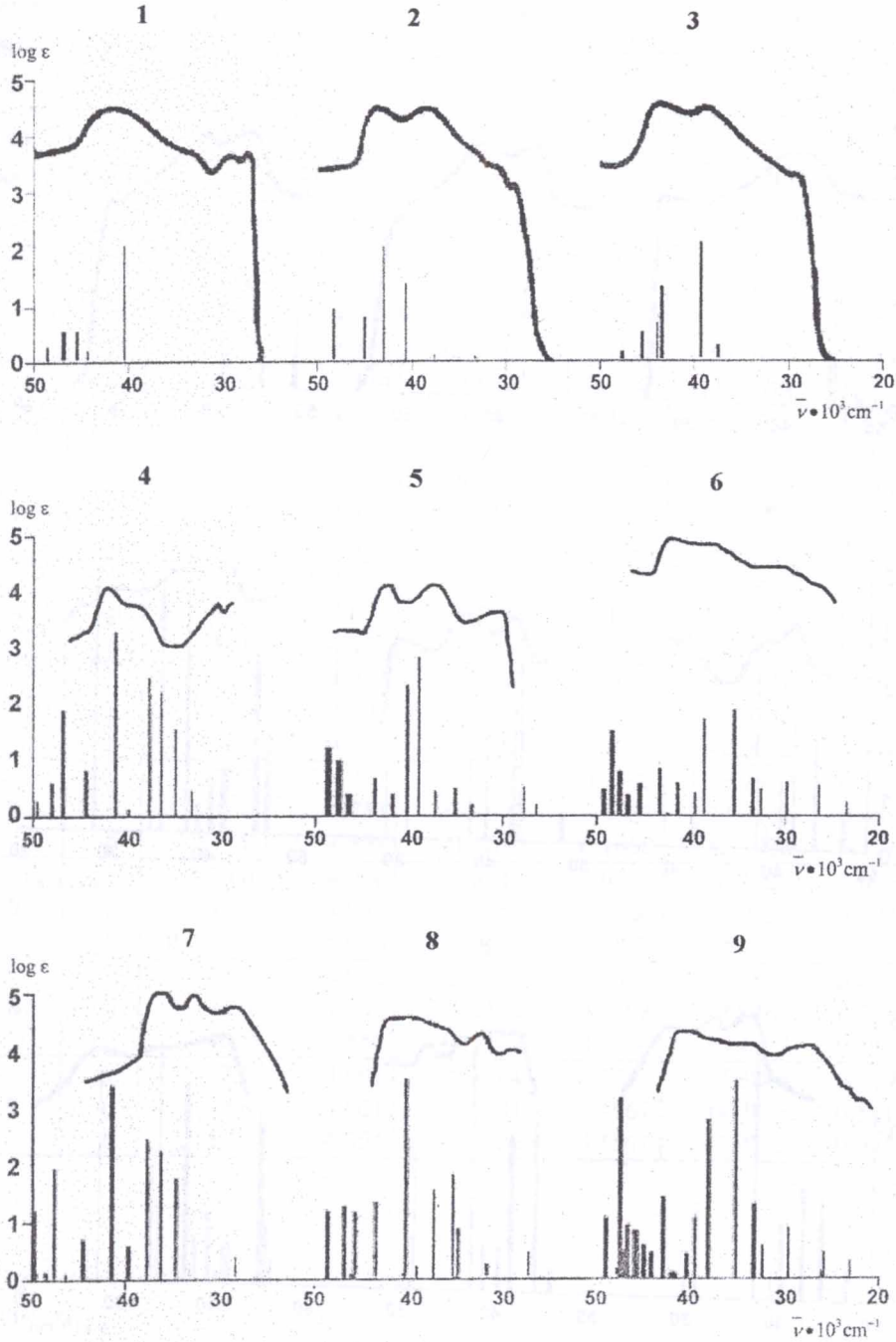


Fig. 1a
Observed and calculated with AM1 method UV spectra for 1-9

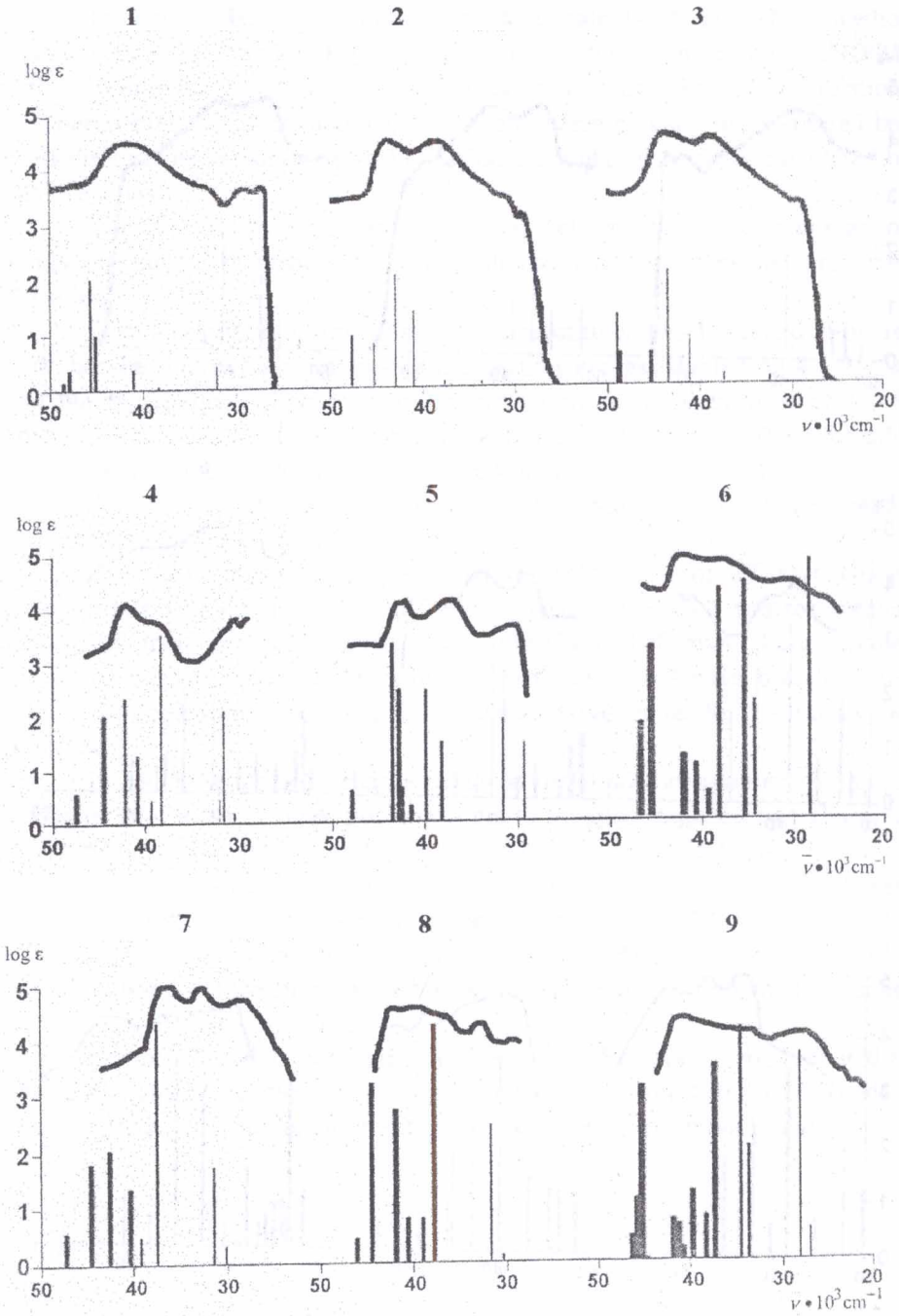


Fig. 1b
Observed and calculated with ZINDO/S method UV spectra for **1-9**

Table 1
Experimental and calculated by AM1 and ZINDO/S methods UV values of **1 - 9**

Com-pound	Band	Experimental		Calculated			
				AM1		ZINDO / S	
		$\bar{v} \bullet 10^3\,cm^{-1}$	$log\ \varepsilon$	$\bar{v} \bullet 10^3\,cm^{-1}$	f	$\bar{v} \bullet 10^3\,cm^{-1}$	f
1	α	27.6	3.750	29.4999	0.0306	32.6045	0.2959
	p	38.1	4.245	40.5779	1.8559	38.2185	0.0465
	β	42.2	4.519	43.8609	0.1823	41.0628	0.2804
2	α	29.1	3.114	28.6387	0.0036	33.8160	0.0362
	p	38.2	4.376	39.2698	1.4253	40.3874	0.6403
	β	43.6	4.472	43.2457	0.6356	42.6964	0.9484
3	α	29.0	3.211	28.7998	0.0032	33.3217	0.0611
	p	38.1	4.342	39.6185	1.2577	37.6335	0.1058
	β	43.3	4.451	43.4739	0.7849	42.7697	1.0758
4	α	29.0	3.854	27.7515	0.0841	30.3451	0.0454
	p	37.8	3.672	37.5129	0.4800	37.4800	0.7817
	β	42.0	4.132	41.3122	0.5835	42.1800	0.4839
5	α	31.0	4.041	26.5415	0.0677	31.9812	0.3435
	p	37.8	4.802	38.9278	0.8306	39.9286	0.4250
	β	42.0	4.950	43.5188	0.2041	42.9052	0.4283
6	α	28.5	4.251	29.8240	0.1706	28.2520	0.5852
	p	37.8	4.753	38.1648	0.4663	38.0142	0.4886
	β	41.8	4.898	41.0030	0.1668	42.3038	0.1548
7	α	29.0	4.756	27.8119	0.0829	30.1722	0.0765
	p	33.0	4.982	34.7159	0.3626	31.7827	0.3935
	β	36.2	5.004	37.6242	0.4859	37.1841	0.8173
8	α	32.5	3.852	32.9141	0.0670	31.6853	0.4956
	p	36.0	4.031	35.4199	0.4398	37.8462	0.7090
	β	40.5	4.550	40.3162	0.7260	40.4522	0.1384
9	α	27.5	4.093	29.4864	0.1793	27.8845	0.4972
	p	32.8	4.061	33.4801	0.1967	34.7883	0.5418
	β	41.2	4.354	39.3385	0.1564	41.9752	0.0755

Table 2
Total and binding energy, formation heat and dipole moment values for **1 – 9** calculated by AM1 method

	1	**2**	**3**
Total Energy (eV)	-2059.889664	-2059.863311	-2059.835249
Binding Energy (eV)	-113.438428	-113.412075	-113.384014
Core-Core Interaction (eV)	9291.850213	9291.617953	9289.538695
Heat of Formation (eV)	3.400856	3.427208	3.455270
M_x	0.646	-1.459	1.641
M_y	0.080	-1.137	-2.845
M_z	0.000	0.000	0.000
M (M)	0.651	1.850	3.284

	4	**5**	**6**
Total Energy (eV)	-2378.300182	-2378.299826	-2696.612933
Binding Energy (eV)	-115.639251	-115.6388949	-117.742307
Core-Core Interaction (eV)	10856.672892	10856.98314	12484.327573
Heat of Formation (eV)	3.783601	3.783956769	4.264113
M_x	-1.675	-0.354	4.557
M_y	-1.957	-2.941	-5.340
M_z	0.000	-0.001	0.000
M (M)	2.576	2.962	7.023

	7	**8**	**9**
Total Energy (eV)	-2534.166706	-2534.15473	-2852.287941
Binding Energy (eV)	-127.847939	-127.835964	-129.759480
Core-Core Interaction (eV)	12273.323494	12430.89211	14176.240639
Heat of Formation (eV)	3.508023	3.519998	4.180051
M_x	-1.650	-1.133	4.753
M_y	-2.529	-1.742	-5.587
M_z	0.008	0.029	0.403
M (M)	3.020	2.078	7.346

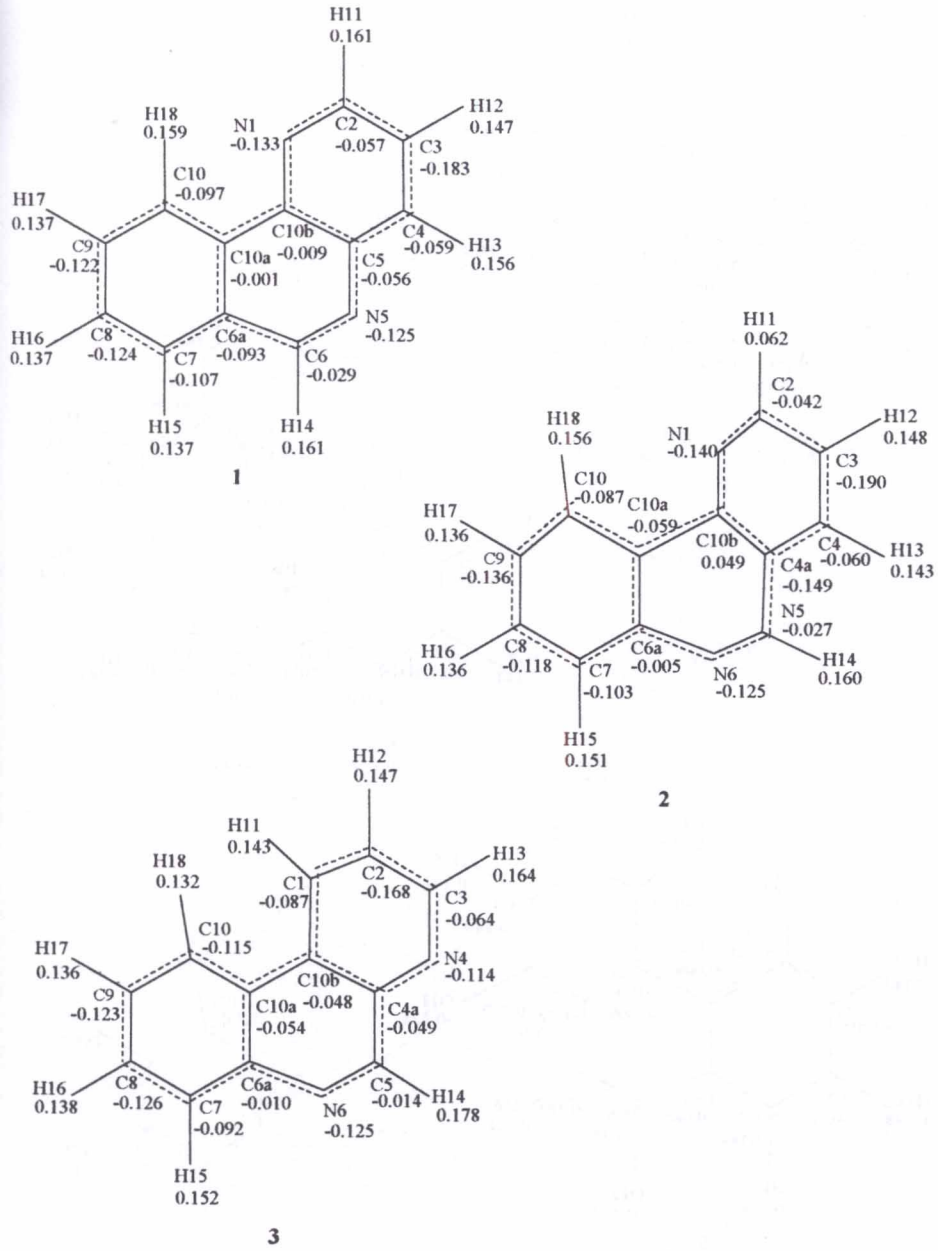


Fig. 2a
Effective charge values for 1 - 3 calculated with AM1 method

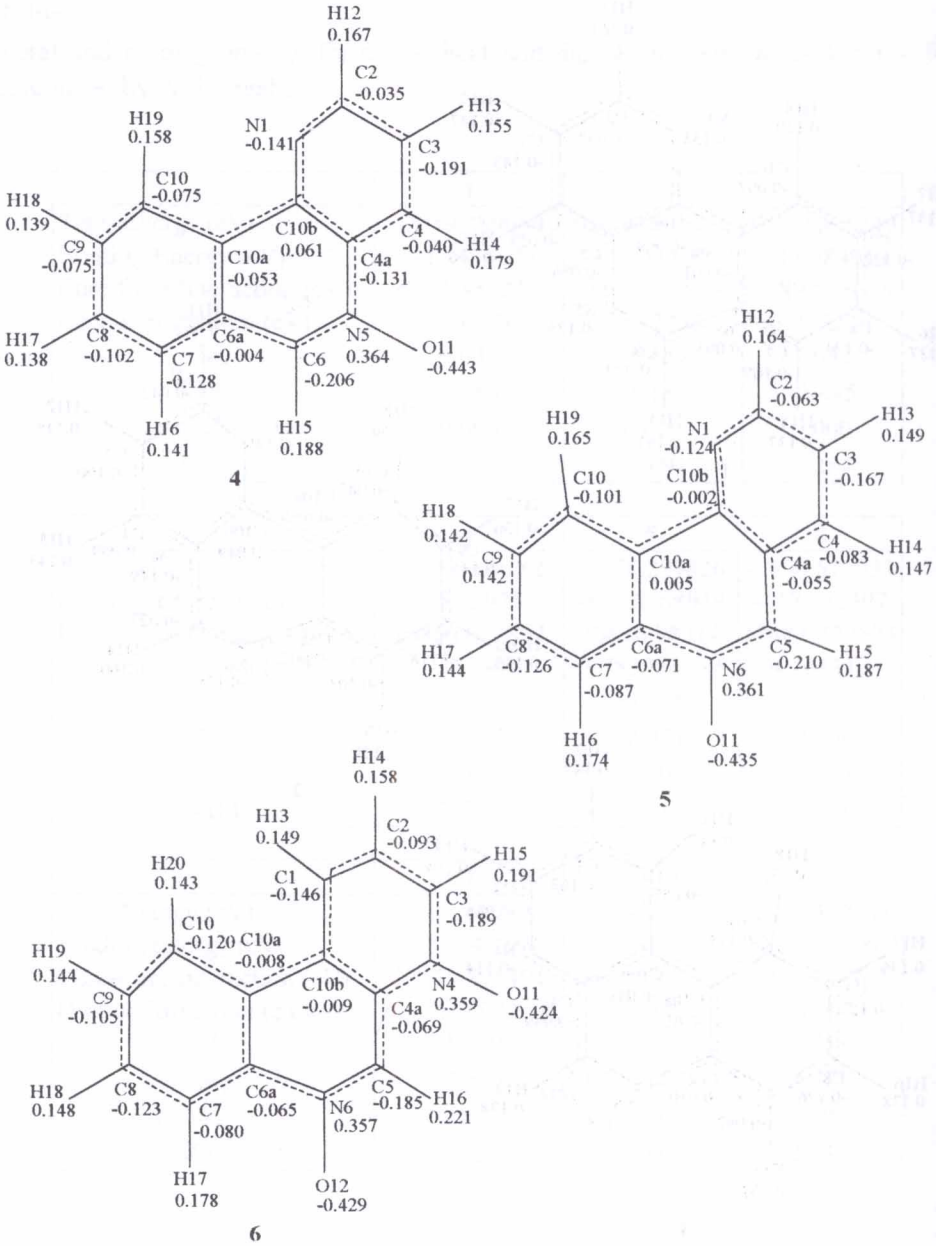
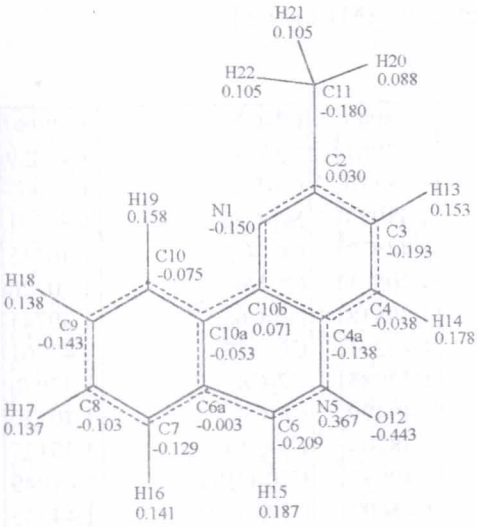


Fig.2b
Effective charge values for **4-6** calculated with AM1 method



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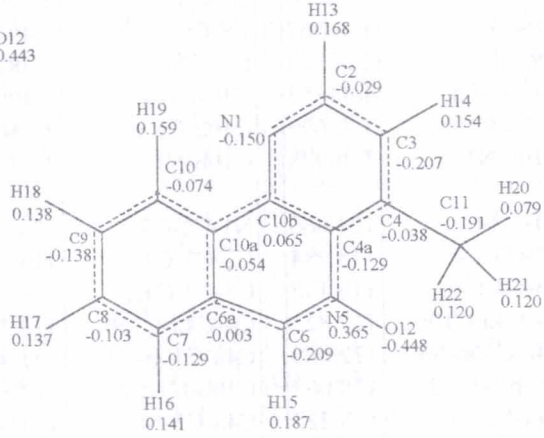

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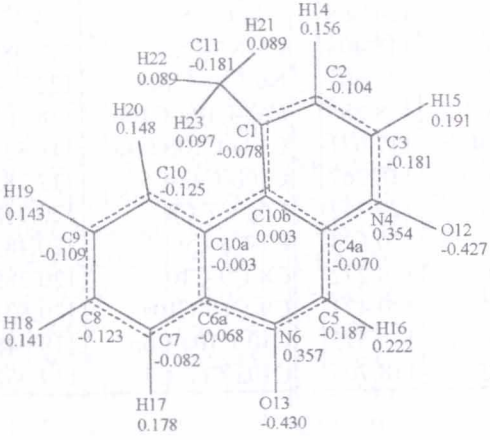

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Fig.2c
Effective charge values for 7-9 calculated with AM1 method

Table 3a
Bond lengths and angles for **1** - **3** calculated by AM1 method

1		**2**		**3**	
N1-C2	1.32950	N1-C2	1.33045	C1-C2	1.38080
C2-C3	1.41977	C2-C3	1.42081	C2-C3	1.42059
C3-C4	1.37848	C3-C4	1.38110	C3-N4	1.33065
C4-C4a	1.42568	C4-C4a	1.41073	N4-C4a	1.36791
C4a-N5	1.39406	C4a-C5	1.44573	C4a-C5	1.46415
N5-C6	1.30582	C5-N6	1.30501	C5-N6	1.30226
C6-C6a	1.44886	N6-C6a	1.39818	N6-C6a	1.39741
C6a-C7	1.40835	C6a-C7	1.42291	C6a-C7	1.42261
C7-C8	1.38260	C7-C8	1.37985	C7-C8	1.37970
C8-C9	1.40567	C8-C9	1.40499	C8-C9	1.40520
C9-C10	1.38370	C9-C10	1.38209	C9-C10	1.38127
C10-C10a	1.41152	C10-C10a	1.40993	C10-C10a	1.41049
C10a-C10b	1.45690	C10a-C10b	1.45607	C10a-C10b	1.44235
C10b-N1	1.36928	C10b-N1	1.37192	C10b-C1	1.41585
N1-C2-C3	124.066	N1-C2-C3	124.386	C1-C2-C3	118.744
C2-C3-C4	118.784	C2-C3-C4	118.240	C2-C3-N4	123.762
C3-C4-C4a	119.195	C3-C4-C4a	118.952	C3-N4-C4a	117.486
C4-C4a-C10b	117.822	C4-C4a-C10b	119.145	N4-C4a-C10b	123.127
C4a-C10b-N1	122.069	C4a-C10b-N1	121.471	C4a-C10b-C1	117.408
C10b-N1-C2	118.063	C10b-N1-C2	117.806	C10b-C1-C2	119.472
C4a-N5-C6	118.222	C4a-C5-N6	124.668	C4a-C5-N6	124.256
N5-C6-C6a	124.774	C5-N6-C6a	118.408	C5-N6-C6a	119.080
C6-C6a-C10a	118.410	N6-C6a-C10a	122.601	N6-C6a-C10a	122.234
C6a-C10a-C10b	118.093	C6a-C10a-C10b	118.285	C6a-C10a-C10b	118.307
C10a-C10b-C4a	117.776	C10a-C10b-C4a	117.671	C10a-C10b-C4a	118.839
C10b-C4a-N5	122.726	C10b-C4a-C5	118.367	C10b-C4a-C5	117.283
C6a-C7-C8	120.056	C6a-C7-C8	120.352	C6a-C7-C8	120.318
C7-C8-C9	120.067	C7-C8-C9	120.624	C7-C8-C9	120.483
C8-C9-C10	120.634	C8-C9-C10	120.272	C8-C9-C10	120.288
C9-C10-C10a	120.158	C9-C10-C10a	120.471	C9-C10-C10a	120.801
C10-C10a-C6a	119.009	C10-C10a-C6a	119.575	C10-C10a-C6a	119.048
C10a-C6a-C7	120.076	C10a-C6a-C7	118.706	C10a-C6a-C7	119.062

Table 3b
Bond lengths and angles for **4** - **6** calculated by AM1 method

4

N1-C2	1.33030
C2-C3	1.41859
C3-C4	1.37984
C4-C4a	1.42121
C4a-C10b	1.42892
C4a-N5	1.43970
N5-C6	1.35125
C6-C6a	1.43336
C6a-C10a	1.41133
C6a-C7	1.41242
C7-C8	1.38175
C8-C9	1.40570
C9-C10	1.38343
C10-C10a	1.41120
C10a-C10b	1.45397
C10b-C1	1.36988
N5-O11	1.22545
N1-C2-C3	124.108
C2-C3-C4	118.459
C3-C4-C4a	118.833
C4-C4a-C10b	119.094
C4a-C10b-N1	120.903
C10b-N1-C2	118.603
C4a-N5-C6	118.088
N5-C6-C6a	122.999
C6-C6a-C10a	120.454
C6a-C10a-C10b	117.984
C10a-C10b-C4a	119.082
C10b-C4a-N5	121.394
C6a-C7-C8	120.055
C7-C8-C9	120.254
C8-C9-C10	120.445
C9-C10-C10a	120.193
C10-C10a-C6a	119.279
C10a-C6a-C7	119.774
C4a-N5-O11	119.083

5

N1-C2	1.33050
C2-C3	1.42114
C3-C4	1.37990
C4-C4a	1.41551
C4a-C10b	1.42118
C4a-C5	1.42926
C5-N6	1.35193
N6-C6a	1.44545
C6a-C10a	1.41705
C6a-C7	1.41762
C7-C8	1.38184
C8-C9	1.40321
C9-C10	1.38348
C10-C10a	1.41091
C10a-C10b	1.41116
C10b-C1	1.37042
N6-O11	1.22422
N1-C2-C3	124.140
C2-C3-C4	118.438
C3-C4-C4a	118.942
C4-C4a-C10b	118.800
C4a-C10b-N1	121.844
C10b-N1-C2	117.836
C4a-C5-N6	122.879
C5-N6-C6a	118.287
N6-C6a-C10a	121.159
C6a-C10a-C10b	119.673
C10a-C10b-C4a	117.513
C10b-C4a-N5	120.490
C6a-C7-C8	119.936
C7-C8-C9	120.286
C8-C9-C10	120.382
C9-C10-C10a	120.863
C10-C10a-C6a	118.483
C10a-C6a-C7	120.050
C5-N6-O11	122.500

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C1-C2	1.38137
C2-C3	1.40293
C3-N4	1.37826
N4-C4a	1.41829
C4a-C10b	1.41448
C4a-C5	1.43962
C5-N6	1.35020
N6-C6a	1.44479
C6a-C10a	1.41748
C6a-C7	1.41766
C7-C8	1.38148
C8-C9	1.40339
C9-C10	1.38268
C10-C10a	1.41189
C10a-C10b	1.44509
C10b-C1	1.41048
N4-O11	1.22266
N6-O12	1.22451
C1-C2-C3	120.685
C2-C3-N4	122.116
C3-N4-C4a	117.392
N4-C4a-C10b	121.268
C4a-C10b-C1	119.287
C10b-C1-C2	119.250
C4a-C5-N6	122.408
C5-N6-C6a	118.430
N6-C6a-C10a	120.872
C6a-C10a-C10b	120.181
C10a-C10b-C4a	117.461
C10b-C4a-C5	120.648
C6a-C7-C8	119.931
C7-C8-C9	120.154
C8-C9-C10	120.365
C9-C10-C10a	121.220
C10-C10a-C6a	117.951
C10a-C6a-C7	120.379
C3-N4-O11	121.848
C5-N6-O12	122.512

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Obliczenia widm UV benzonaftyrydyn i ich N-tlenków metodami AM1 i ZINDO

Streszczenie: Dla trzech izomerycznych benzonaftyrydyn i sześciu N-tlenków benzonaftyrydyn obliczono wartości dotyczące widm UV za pomocą metod AM1 i ZINDO/S. Korelacje obliczonych i doświadczalnych wartości liczb falowych rozważanych związków wykazują dobrą zgodność. Porównano wyniki uzyskane przy zastosowaniu obydwu metod.