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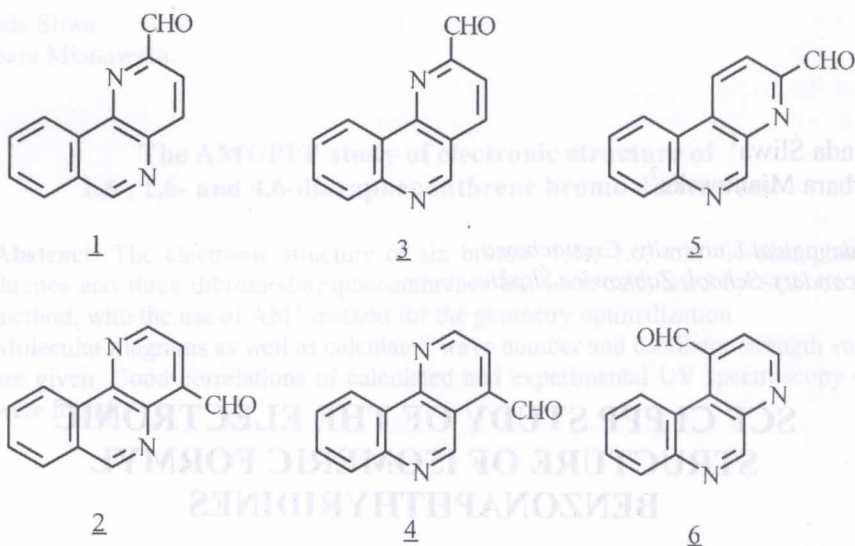
SCF CI PPP STUDY OF THE ELECTRONIC STRUCTURE OF ISOMERIC FORMYL BENZONAPHTHYRIDINES

Abstract: For six isomeric formyl 1,5-, 1,6- and 4,6-benzonaphthyridines the electronic structure and UV spectral values have been calculated by SCF CI PPP method, and the results have been compared with those of calculation by AMI method. Correlations of the calculated and observed wave number values show good compatibility. Molecular diagrams of considered compounds are presented.

Benzonaphthyridines (bn) and their derivatives are interesting for their reactivity and biological activities [1-5]; they are useful as 1,3-dipoles in cycloaddition reactions [6, 7] and show complexing properties [8].

The present paper is a continuation of our research of benzonaphthyridines concerning their electronic structure and UV spectral values [9-13].

The work deals with electronic structure and UV spectral values of six isomeric formyl benzonaphthyridines 1 - 6.



For clarity the compounds 1, 3 and 5 bearing the formyl group in the *ortho* position to the ring nitrogen atom have been denoted *ortho* and 2, 4, 6 - *para* isomers.

The calculation of the electronic structure and UV spectral values has been made with SCF CI PPP method, and the results compared with those obtained by AM1 method [14]. The PPP method has been chosen having in view a rather large size of molecules under consideration. The correlations of calculated and observed UV spectra values have been made.

The calculations have been performed on a IBM PCAT computer using the Gaussian 92W program [15], and UV spectra have been recorded in 1,2-dichloroethane solution ($c=10^{-4}$ M) [14].

Wave number and oscillator strength values in the dipole length approximation of 1 - 6 are shown in Table 1. Calculated and experimental UV spectra of 1 - 6 are presented in Fig. 1. The calculated and experimental UV data are given in Table 2.

The correlations of observed and calculated $\bar{\nu}$ values of 1 - 6 are shown in Fig. 2. The correlations of observed and calculated $\bar{\nu}$ values for 1 - 6 and corresponding unsubstituted bns are given in Fig. 3.

The PPP calculations (convergence of 10^{-6} eV) were performed as in our previous work [10]; the semiempirical parameters used are given in Table 3.

The correlation of observed and calculated with both methods $\bar{\nu}$ values is better for *para* than for *ortho* isomers. For observed and calculated by PPP method $\bar{\nu}$ values of 1 - 6 and corresponding unsubstituted bns the correlations

coefficients r lie in the range of 0.9811 to 0.9897, and are higher for 3 and 6 than for other isomers.

In these correlations made with the use of AM1 method the r coefficients lie in the range of 0.9614 to 0.9979, and are higher for 5 and 6 as compared with other compounds [14].

The calculated by PPP method total and ionization energy values along with the dipole moments are presented in Table 4. The PPP calculations show higher total energy values, i.e. the lower stability for *ortho* compounds (1, 3, 5) than for their *para* (2, 4, 6) isomers.

The molecular diagrams of 1 - 6 calculated by PPP method are presented in Fig. 4. In molecular diagrams of 1 - 6 the electron densities of nitrogen atoms of 1,5- and 1,6-bn derivatives (1 - 4) are higher than those of 4,6-bn isomers (5 and 6); for 1,5- and 1,6-bn derivatives these values are similar. For 1 - 6 the electron densities of formyl group oxygen atoms and the C-CHO bond order values are lower for *ortho* than for *para* isomers.

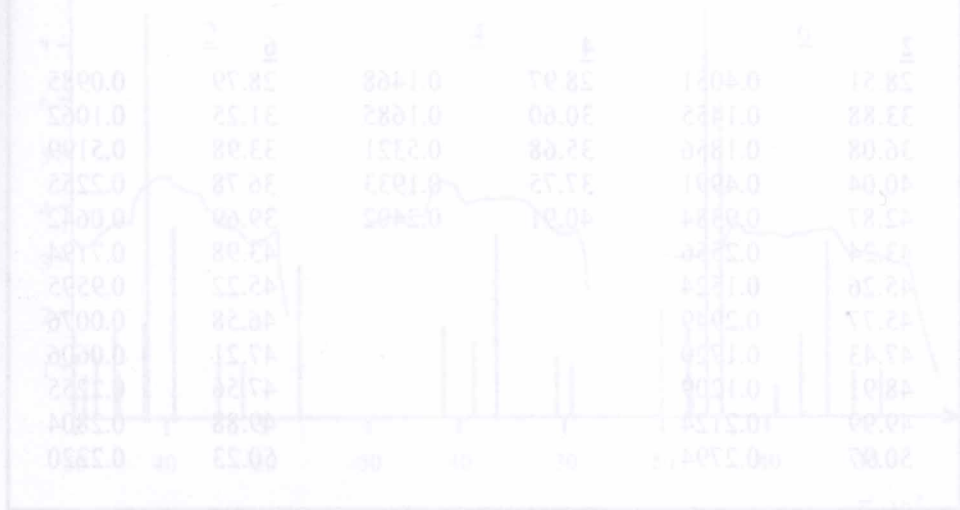


Fig. 1. Observed and calculated with PPP method UV spectra for 1 - 6.

Table 1. The wave number $\bar{\nu}$ and oscillator strength values in the dipole length approximation $f(L)$ for 1 - 6 calculated with PPP method

$\bar{\nu} \times 10^3 \text{ cm}^{-1}$	$f(L)$	$\bar{\nu} \times 10^3 \text{ cm}^{-1}$	$f(L)$	$\bar{\nu} \times 10^3 \text{ cm}^{-1}$	$f(L)$
<u>1</u>		<u>3</u>		<u>5</u>	
28.65	0.4139	29.35	0.1047	29.25	0.0618
33.56	0.2182	31.44	0.3111	32.23	0.0658
36.80	0.1684	36.32	0.5211	35.65	1.1845
40.24	0.1877	38.84	0.3838	37.93	0.4937
42.06	1.0655	41.38	0.2001	39.10	0.0830
43.19	0.9612	42.95	0.7565	44.28	0.2198
44.56	0.0398	44.82	0.5477	45.77	0.4052
46.55	0.0578	45.51	0.2720	47.18	0.2301
47.14	0.1457	48.19	0.0165	47.82	0.1945
49.12	0.0653	48.82	0.0679	49.19	0.2705
50.93	0.0300	50.35	0.2949	49.89	0.2798
		51.43	0.2802	50.18	0.2646
<u>2</u>		<u>4</u>		<u>6</u>	
28.51	0.4051	28.97	0.1468	28.79	0.0985
33.88	0.1455	30.60	0.1685	31.25	0.1062
36.08	0.1856	35.68	0.5321	33.98	0.5199
40.04	0.4991	37.75	0.1933	36.78	0.2255
42.87	0.9384	40.91	0.2402	39.69	0.0642
43.24	0.2556			43.98	0.7194
45.26	0.1524			45.22	0.9595
45.77	0.2949			46.58	0.0076
47.43	0.1720			47.21	0.0606
48.91	0.1209			47.56	0.2255
49.99	0.2124			49.88	0.2804
50.97	0.2794			50.23	0.2220

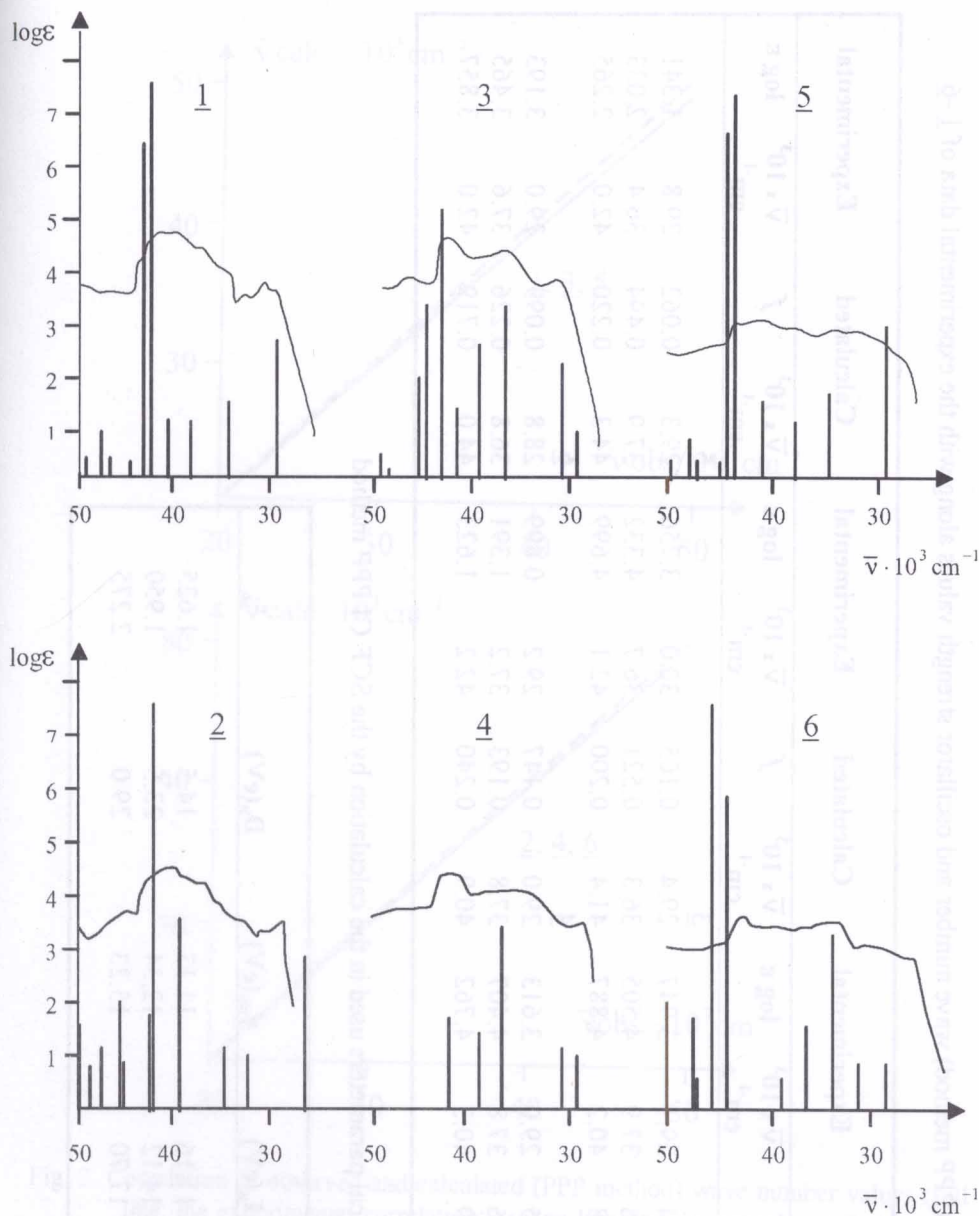


Fig. 1. Observed and calculated with PPP method UV spectra for 1 - 6

Table 2. Calculated (PPP method) wave number and oscillator strength values along with the experimental data of 1-6

	Calculated		Experimental		Calculated		Experimental		Calculated		Experimental	
	$\bar{\nu} \times 10^3$ cm^{-1}	f	$\bar{\nu} \times 10^3$ cm^{-1}	$\log \epsilon$	$\bar{\nu} \times 10^3$ cm^{-1}	f	$\bar{\nu} \times 10^3$ cm^{-1}	$\log \epsilon$	$\bar{\nu} \times 10^3$ cm^{-1}	f	$\bar{\nu} \times 10^3$ cm^{-1}	$\log \epsilon$
<u>1</u>					<u>3</u>				<u>5</u>			
α	28.7	0.414	29.1	3.947	29.4	0.105	30.0	3.756	29.3	0.062	29.8	1.341
ρ	36.8	0.168	37.9	4.505	36.3	0.521	36.7	4.332	37.9	0.494	36.4	2.033
β	40.2	0.188	40.2	4.887	41.4	0.200	42.1	4.699	44.3	0.220	42.0	2.265
<u>2</u>					<u>4</u>				<u>6</u>			
α	28.5	0.405	29.0	3.613	29.0	0.147	29.2	0.699	28.8	0.099	29.0	3.193
ρ	36.1	0.186	37.8	4.407	37.8	0.193	37.2	1.391	36.8	0.226	37.6	3.465
β	40.0	0.499	40.3	4.762	40.9	0.240	42.2	1.623	44.0	0.719	42.0	3.857

Table 3. Semiempirical parameters used in the calculation by the SCF CI PPP method

	$I_{\mu}(\text{eV})$	$\gamma_{\mu\mu}(\text{eV})$	$D_{\mu}(\text{eV})$	ξ_{μ}
C^+	11.16	11.13	14.5	1.625
N^+	14.12	12.34	23.5	1.950
O^+	17.70	15.23	29.0	2.275

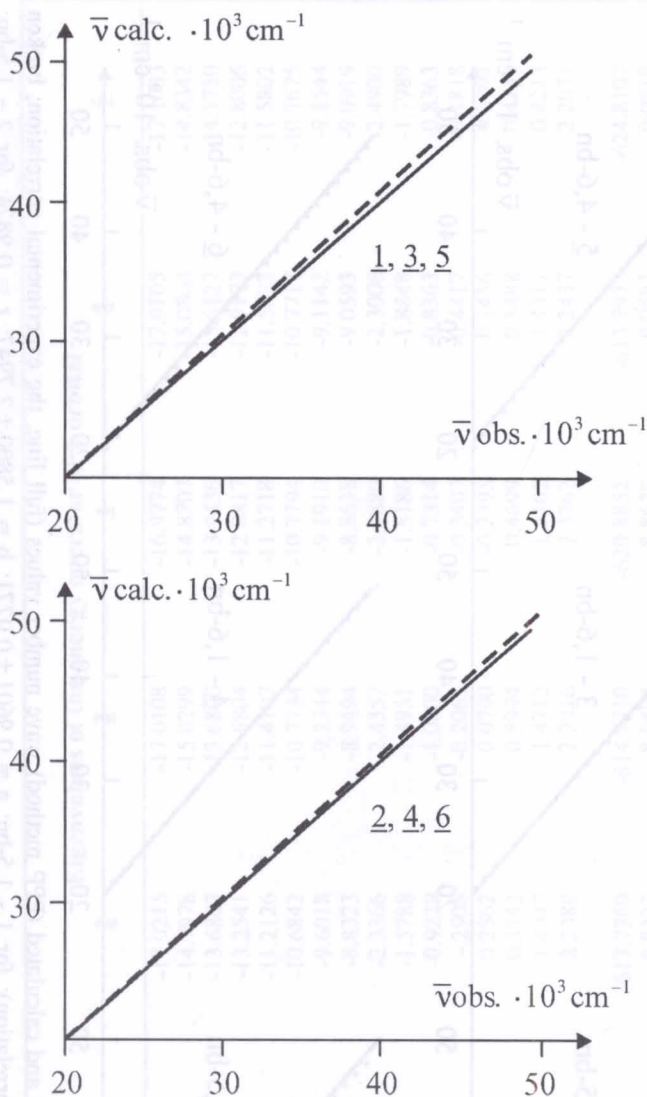


Fig. 2. Correlation of observed and calculated (PPP method) wave number values (full line, the experimental correlation; broken line, the theoretical correlation); for 1, 3, 5: $a = 0.9935 \pm 0.0585$; $b = 0.1228 \pm 2.1126$; $r = 0.9881$; for 2, 4, 6: $a = 0.9607 \pm 0.0458$; $b = 0.8837 \pm 1.6559$; $r = 0.9921$

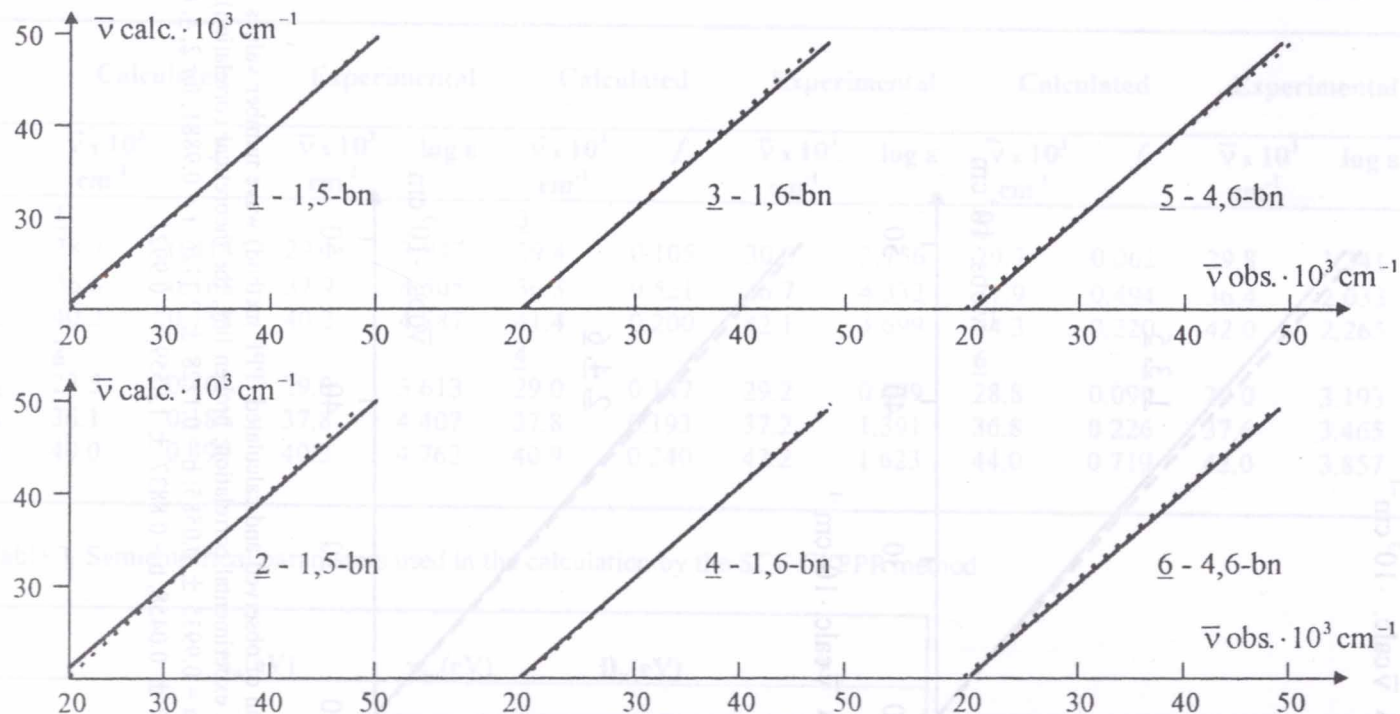


Fig. 3. Correlation of observed and calculated (PPP method) wave number values (full line, the experimental correlation; broken line, the theoretical correlation); for 1 - 1,5-bn: $a = 0.9601 \pm 0.0771$; $b = 1.5800 \pm 2.7947$; $r = 0.9874$; for 2 - 1,5-bn: $a = 0.9514 \pm 0.0916$; $b = 1.7240 \pm 3.3212$; $r = 0.9820$; for 3 - 1,6-bn: $a = 0.9977 \pm 0.0721$; $b = -0.0173 \pm 2.6705$; $r = 0.9897$; for 4 - 1,6-bn: $a = 0.9695 \pm 0.0780$; $b = 1.1493 \pm 2.8891$; $r = 0.9873$; for 5 - 4,6-bn: $a = 1.0298 \pm 0.1016$; $b = -0.9107 \pm 3.7070$; $r = 0.9811$; for 6 - 4,6-bn: $a = 1.0248 \pm 0.0772$; $b = -0.9475 \pm 2.8220$; $r = 0.9888$

Table 4. Eigenvalues of the energy operator of π orbitals, total energy E, ionization energy I, electronic affinity A and dipole moment M values for 1 - 6 calculated with PPP method

Molecular orbital	Eigenvalues of the energy operator of π orbital					
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>
1	-16.9839	-17.0215	-17.0108	-16.9774	-17.0105	-17.1083
2	-11.8984	-14.7978	-15.0299	-14.8707	-15.0868	-14.8342
3	-13.7853	-13.6803	-13.6860	-13.9436	-13.6127	-14.1750
4	-12.9286	-13.2541	-12.9804	-12.8817	-12.9173	-12.8006
5	-11.3118	-11.2126	-11.4107	-11.2718	-11.5822	-11.5802
6	-10.6519	-10.6842	-10.7734	-10.7794	-10.7717	-10.7675
7	-9.6034	-9.6018	-9.2344	-9.1910	-9.1142	-9.1544
8	-8.8200	-8.8323	-8.9494	-8.8638	-9.0593	-9.0919
9	-2.2750	-2.3366	-2.4357	-2.4880	-2.3006	-2.4900
10	-1.4682	-1.5788	-1.4951	-1.5186	-1.8848	-1.7989
11	-1.1986	-0.9229	-1.0800	-0.7314	-0.8363	-0.8363
12	-0.1686	-0.2906	-0.2065	-0.3407	-0.4417	-0.1818
13	0.0395	0.2562	0.0790	-0.2395	0.1456	0.0994
14	0.6487	0.3742	0.5994	0.4699	0.5488	0.4749
15	1.4977	1.4947	1.4712	1.5162	1.4411	0.4213
16	2.2437	2.2388	2.2916	2.3762	2.2437	2.2071
E/eV	-614.8933	-617.7360	-614.7710	-620.8852	-613.7933	-624.8107
I/eV	8.8200	8.8323	8.9494	8.8638	9.0593	9.0919
A/eV	2.2750	2.3366	2.4357	2.4880	2.3006	2.4900
M _x /D	-2.822	-3.580	-0.137	1.020	-2.632	0.478
M _y /D	-2.609	-1.163	-1.059	2.849	2.183	-0.614
M _z /D	0.0	0.0	0.0	0.0	0.0	0.0
M(M)/D	3.844	3.764	1.068	3.026	3.420	0.778

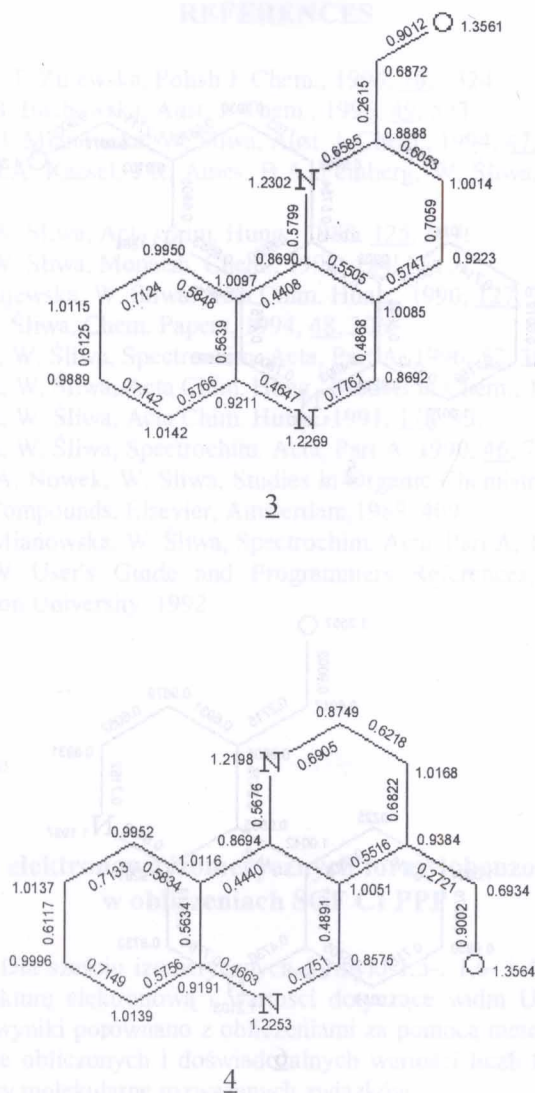


Fig. 4b. Molecular diagrams for **3** and **4** calculated with PPP method

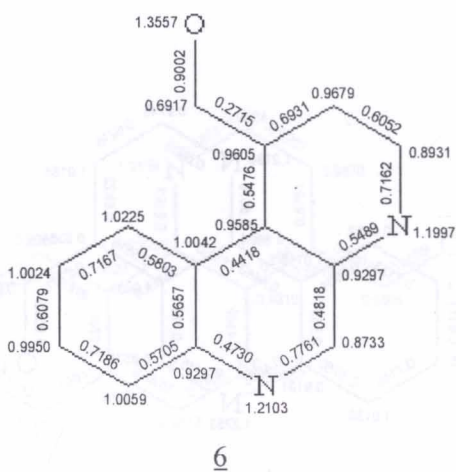
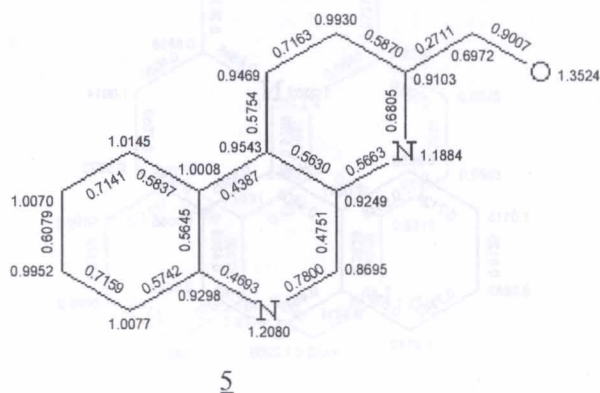


Fig. 4c. Molecular diagrams for 5 and 6 calculated with PPP method

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Struktura elektronowa izomerycznych formylobenzonaftyrydyn w obliczeniach SCF CI PPP

Streszczenie: Dla sześciu izomerycznych formylo-1,5-, 1,6- i 4,6-benzonaftyrydyn obliczono strukturę elektronową i wartości dotyczące widm UV stosując metodę SCF CI PPP; wyniki porównano z obliczeniami za pomocą metody AMI. Uzyskano dobre korelacje obliczonych i doświadczalnych wartości liczb falowych. Przedstawiono diagramy molekularne rozważanych związków.