SCF CI PPP Study of the Electronic Structure of Isomeric Pyridodiazaphenanthrenes

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For three isomeric pyridodiazaphenanthrenes the molecular diagrams, wavenumber, oscillator strength, and dipole moment values have been calculated by the SCF CI PPP method.

The theoretical oscillator strength and wavenumber values were compared with the experimental UV data; also comparison of UV spectra of studied compounds with those of parent diazaphenanthrenes has been made. Good correlations of plots of calculated and experimental wavenumber values of studied compounds have been found.

Diazaphenanthrenes (DAPs) and their derivatives are interesting for biological activity – antibacterial and antifungal [1—3]; some of them show also antineoplastic properties [4].

DAPs possess two nitrogen atoms in the molecule, thus they form *N*-oxides [5, 6] and quaternary salts [2, 7]. Some quaternary salts of DAPs are precursors of ylides useful in 1,3-dipolar cycloaddition reactions [8, 9].

Quaternary salts of azaaromatics are interesting from the theoretical and practical points of view [10], *e.g.* as systems for electronic devices [11], as DNA intercalators [12], pharmaceuticals [13], dyes [14], catalysts [15], and surfactants [16].

The presence of two nitrogen atoms in molecule of DAPs allows the formation of complexes with transition metal ions [17].

In the continuation of our research concerning chemistry and physical chemistry of DAPs [1, 18, 19], we present here the electronic structure of isomeric pyrido-DAPs *I—III.* These compounds have been obtained from amino derivatives of 4,10-, 4,9-, and 9,10-DAPs *IV—VI*, *i.e.* 5-amino-4,10-DAP *VII*, 8-amino-1,9-DAP *VIII*, and 3-amino-9,10-DAP *IX* by the Skraup procedure [20] (see Scheme 1).

The molecular diagrams and UV theoretical values have been calculated by the SCF CI PPP method; this procedure has been chosen having in view the big size of molecules under consideration.

The theoretical UV spectra values have been compared with the experimental ones. Similar investigation has been made previously in our group for formyl- [21], methyl- [22, 23], amino- [24], and bromo-DAPs [25], as well as for quaternary salts of DAPs [26].

EXPERIMENTAL

The calculations have been made on an IBM PCAT computer using Gaussian 92 [27] program. The UV spectra of *I—III* were recorded in 1,2-dichloroethane solution ($c = 10^{-4}$ mol dm^{-3}) on a UV VIS Specord spectrophotometer. (In [20] ethanol was used as a solvent.)

RESULTS AND DISCUSSION

As in our previous works [24, 25] we assumed the monocentre Coulomb integral as being equal to

$$\gamma_{\mu\mu} = I - A_{\mu}$$

where I – ionization energy of μ orbital, A – affinity of the electron described by the μ potential.

The Coulomb integrals have been calculated in the Mataga—Nishimoto approximation and the resonance integrals β in the Katagiri—Sandorfy approximation, where k is equal to -0.25.

The semiempirical parameters used in our calculation are:

	I_{μ}/eV	$\gamma_{\mu\mu}$/eV	D_{μ}/eV	ε_{μ}
C^+	11.16	11.13	14.5	1.625
N^+	14.12	12.34	23.5	1.950

Eigenvalues of the energy operator of π orbitals, ionization and total energy values along with dipole moments for *I—III* are summarized in Table 1; molecular diagrams are presented in Fig. 1.

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Table 1. Eigenvalues of the Energy Operator of π Orbitals, Ionization Energy *I* and Total Energy *E* Values along with Dipole Moments for *I*—*III* Calculated with the SCF CI PPP Method

Molecular orbital	Eigenvalues of the energy operator of π orbital		
	I	*II*	*III*
1	−17.0648	−16.9995	−17.0084
2	−15.3211	−15.4720	−15.3328
3	−13.7040	−13.5066	−13.6823
4	−12.4616	−12.7079	−12.3895
5	−11.8619	−11.5190	−11.8872
6	−10.3757	−10.5982	−10.4403
7	−10.0943	−10.3318	−10.1773
8	−9.0654	−8.9686	−9.0390
9	−8.5000	−8.3654	−8.7810
10	−2.1417	−2.0440	−2.4809
11	−1.4941	−1.3555	−1.9650
12	−0.7512	−1.1737	−0.8204
13	−0.3464	−0.0701	−0.5303
14	0.2693	−0.0178	−0.0622
15	0.3959	0.6458	0.2878
16	1.1688	1.0736	0.9891
17	1.9354	1.9124	1.7617
18	2.5392	2.5907	2.3108
I/eV	8.5000	8.3654	8.7810
E/eV	−741.9369	−732.6318	−736.4454
M_x/D	−1.618	0.829	−0.232
M_y/D	−0.533	1.059	−2.545
M_z/D	0.000	0.000	0.000
$M(M)$/D	1.704	1.345	2.555

It was established that the ionization energy values increase in the order *II* < *I* < *III*; the same sequence was found for dipole moments. The total energy increases in the order *I* < *III* < *II*, this fact suggests the higher stability of *I* as compared with compounds *II* and *III*.

The analysis of molecular diagrams of *I*—*III* shows that in *I* and *II* the electron density values at nitrogen atoms are similar, while in *III* these values at neighbouring nitrogen atoms are significantly lower. The electron density values at β positions of pyridine rings of *I*—*III* are higher as compared with those of α and γ positions.

Wavenumber and oscillator strength values calculated in the dipole length and dipole velocity approximation for *I*—*III* are summarized in Table 2; for the comparison of the theoretical and experimental UV spectra, the oscillator strength values in the dipole length approximation were taken into account.

Theoretical and experimental data for α, *p*, and β bands of *I*—*III* are given in Table 3; experimental UV spectra of *I*—*III* along with their oscillator strength values are shown in Fig. 2.

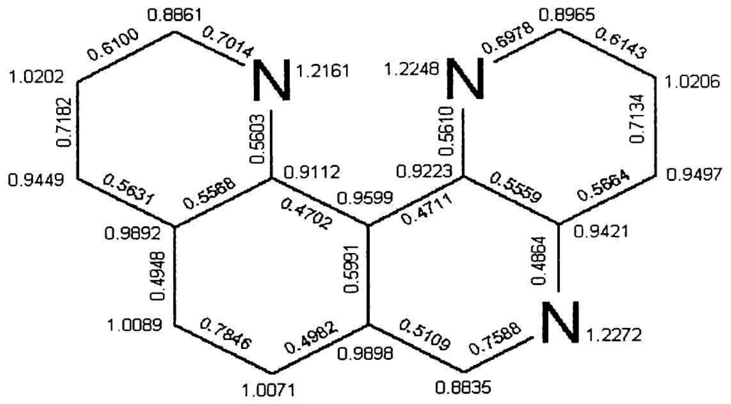
The calculated values reveal a good compatibility with the experimental ones; slight discrepancies may result from the fact that the molecules under consideration are rather large. For compounds *I*—*III* the straight line correlation of theoretical and experimental values has been found.

The correlations of calculated and experimental $\tilde{\nu}$ values for the α, *p*, and β bands of *I*—*III* are given in Fig. 3 ($r = 0.9880$). The correlations of calculated and experimental $\tilde{\nu}$ values of *I*—*III* and of their corresponding three-ring analogues, *i.e.* DAPs *IV*—*VI* are shown in Fig. 4; the correlation coefficients range between 0.9881—0.9931, increasing in the order *III*—*VI* < *II*—*V* < *I*—*IV*

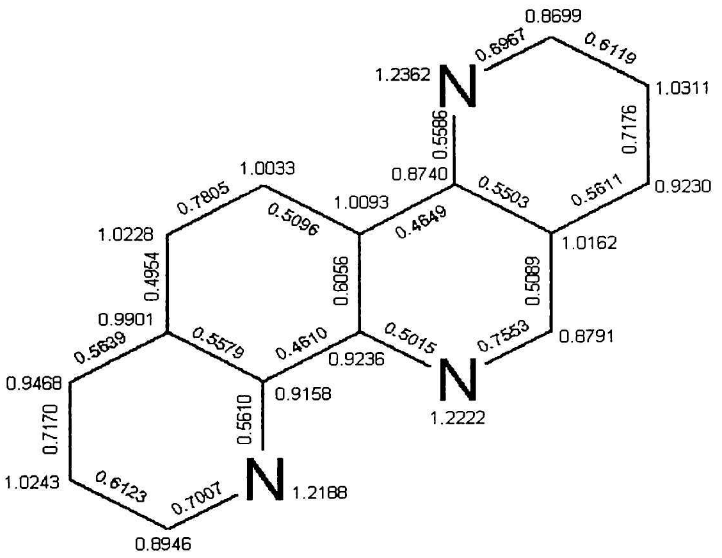
The analysis of experimental UV spectra of *I*—*III* (Fig. 4 and Table 3) shows that the $\tilde{\nu}$ value of the α

Table 2. Wavenumber $\tilde{\nu}$ and Oscillator Strength Values in the Dipole Length and Dipole Velocity Approximation $f(L)$ and $f(V)$ for *I*—*III* Calculated with the SCF CI PPP Method

I			*II*			*III*		
$\tilde{\nu}/(10^3\ \mathrm{cm}^{-1})$	$f(L)$	$f(V)$	$\tilde{\nu}/(10^3\ \mathrm{cm}^{-1})$	$f(L)$	$f(V)$	$\tilde{\nu}/(10^3\ \mathrm{cm}^{-1})$	$f(L)$	$f(V)$
27.3	0.3648	0.1833	28.9	0.1973	0.1077	26.9	0.0322	0.0051
32.7	0.0064	0.0038	30.2	0.2927	0.1049	30.3	0.1938	0.0793
36.1	0.2971	0.1318	34.8	0.0000	0.0002	33.4	0.9583	0.4117
36.9	1.0521	0.4635	35.9	0.0531	0.0176	35.3	0.5096	0.1817
39.4	0.4045	0.1335	37.4	1.7868	0.8873	37.5	0.0804	0.0256
41.1	0.2953	0.1603	40.4	0.3520	0.1543	38.8	0.2317	0.1197
42.8	0.1016	0.0529	43.4	0.1835	0.1047	41.0	0.2112	0.1159
43.9	0.0558	0.0185	44.2	0.6231	0.2622	43.8	0.2043	0.0871
44.4	0.1586	0.0568	45.5	0.0012	0.0015	44.2	0.1102	0.0421
46.1	0.0632	0.0294	47.5	0.2649	0.1211	45.6	0.0888	0.0374
47.4	0.2876	0.1092	48.5	0.1359	0.0610	46.3	0.4116	0.1484
47.7	0.5155	0.2238	49.1	0.0055	0.0026	47.0	0.5854	0.2588
50.4	0.0488	0.0236	50.5	0.2418	0.1214	47.7	0.0870	0.0402
50.8	0.1408	0.0594	51.4	0.0014	0.0012	49.1	0.4110	0.1849



I



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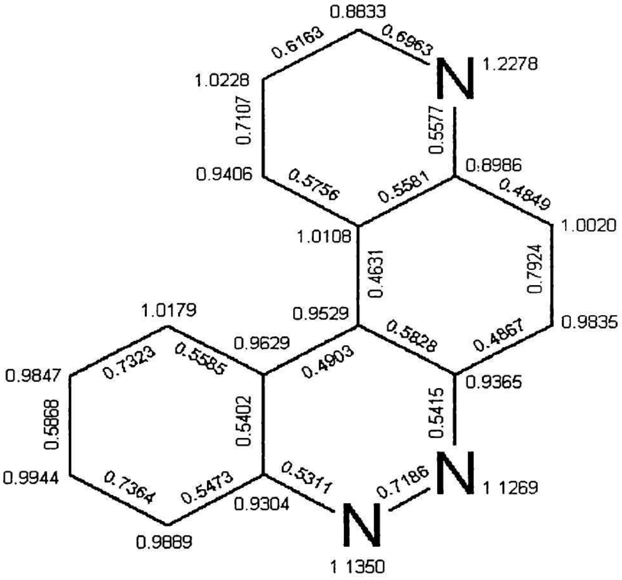
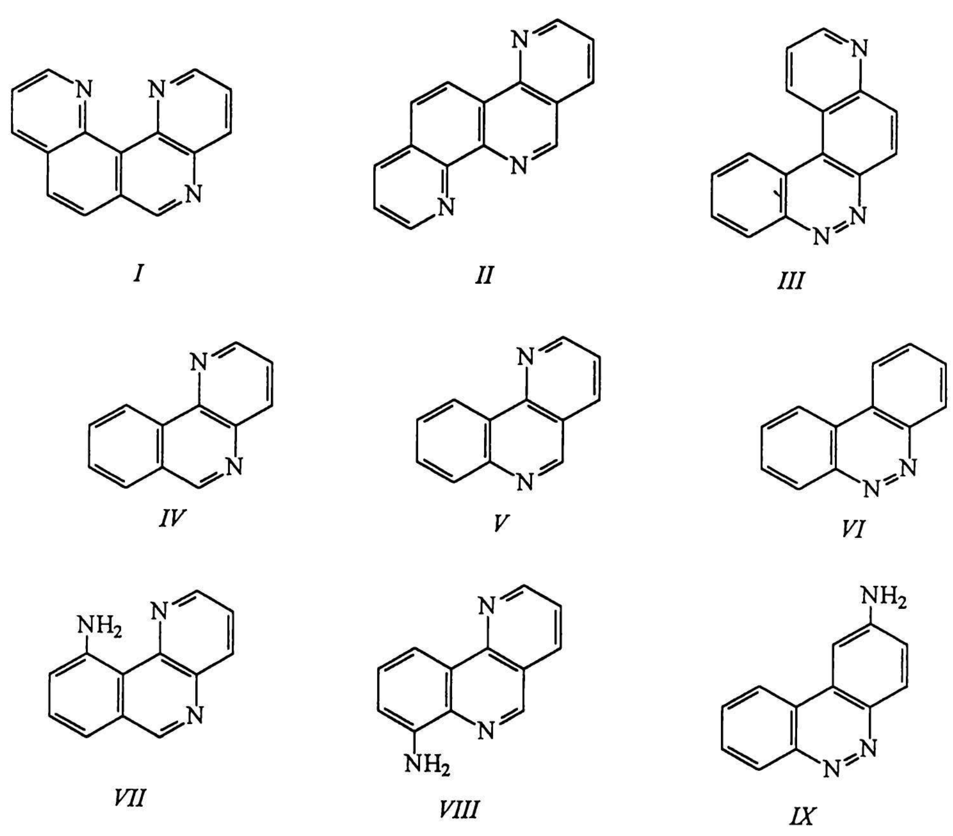


III

Fig. 1. Molecular diagrams of *I*—*III* calculated with the SCF CI PPP method.



Scheme 1

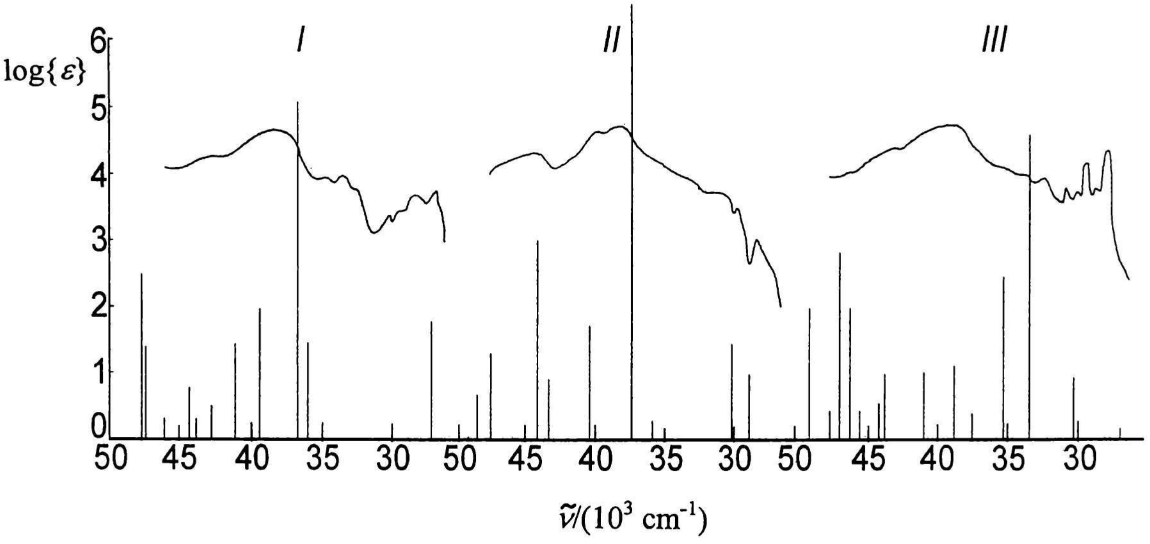


Fig. 2. Experimental and calculated UV spectra of *I—III*.

band for *II* is slightly higher as compared with those values for *I* and *III*; similar regularity exists in the case of the β band. The intensity of the α band for *III* is higher than those for *I* and *II*, the sequence of the intensity of the α band of *I—III* being $II < I < III$.

The comparison of UV spectra of *I—III* with those of their parent DAPs *IV—VI* shows that in the α band of *I* and *II*, as compared with 1,5- and 1,6-DAPs, *IV* and *V*, respectively, the red shift occurs, only in the case of *III* a slight blue shift is observed. In p and β

Table 3. Calculated (SCF CI PPP Method) Wavenumber and Oscillator Strength Values along with the Experimental UV Data for *I*—*III*

Compound	Band	Calculated		Experimental	
		$\tilde{\nu}/(10^3\ \mathrm{cm}^{-1})$	f	$\tilde{\nu}/(10^3\ \mathrm{cm}^{-1})$	$\log\{\varepsilon\}$
	α	27.3	0.3648	27.2	3.716
I	p	36.9	1.0521	38.5	4.631
	β	44.4	0.1586	43.5	4.176
	α	28.9	0.1973	28.6	3.000
II	p	37.4	1.7868	38.3	4.690
	β	44.2	0.6231	44.6	4.301
	α	30.3	0.1938	28.2	4.310
III	p	38.8	0.2317	39.0	4.716
	β	43.8	0.2043	43.5	4.358

Table 4. Differences in the Experimental Wavenumber Values of α, p, and β Bands for *I*—*III* as Compared with Corresponding DAPs (Positive Values Denote Red, Negative Blue Shifts)

Band		$(\tilde{\nu}_i - \tilde{\nu}_j)/(10^3\ \mathrm{cm}^{-1})$		
	i j	*I* *IV*	*II* *V*	*III* *VI*
α		+0.4	+0.5	−0.1
p		−0.4	−0.1	−0.5
β		−0.7	−1.0	−0.6

bands of *I*—*III*, as compared with their parent DAPs, there is found a blue shift, the strongest for the β band of *III* relatively to *VI*. The differences between experimental $\tilde{\nu}$ values for *I*—*III* and their corresponding DAPs *IV*—*VI* are summarized in Table 4.

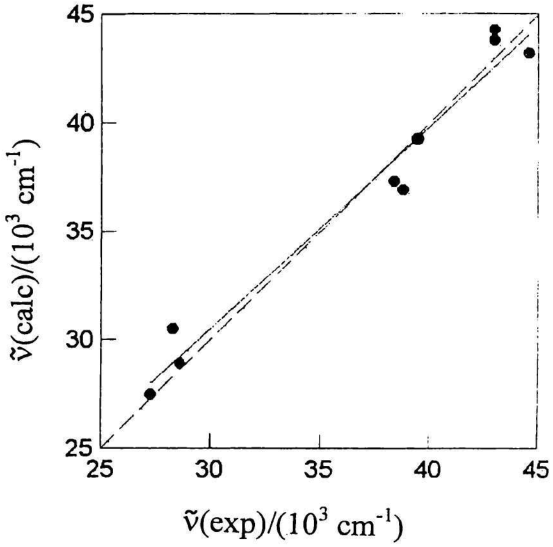


Fig. 3. Correlation of calculated and experimental wavenumber values for *I*—*III* (full line, the experimental correlation; broken line, the theoretical correlation): a = 0.9307, b = 2.5300, r = 0.9880.

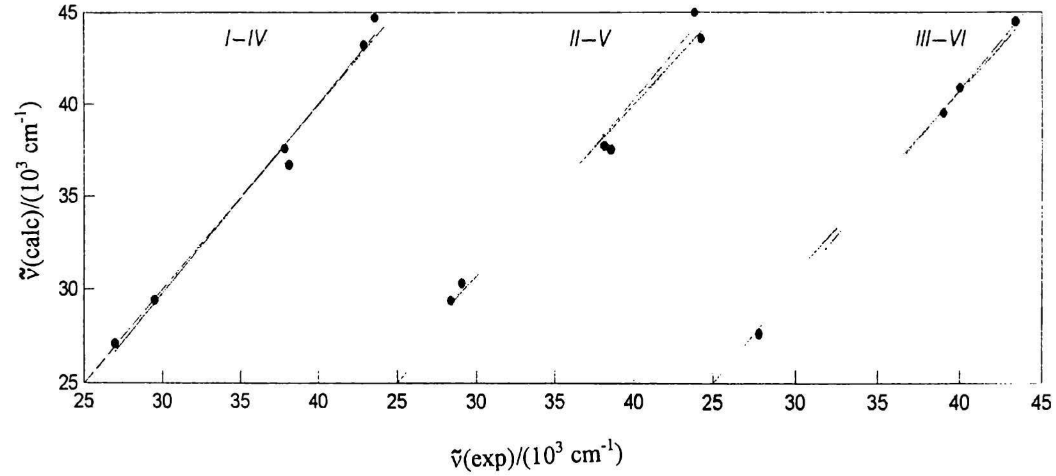


Fig. 4. Correlation of calculated and experimental wavenumber values for *I*—*III* and corresponding DAPs *IV*—*VI* (full line, the experimental correlation; broken line, the theoretical correlation). *I* and *IV*: a = 1.0192, b = −0.8024, r = 0.9931; *II* and *V*: a = 0.9327, b = 2.1620, r = 0.9909; *III* and *VI*: a = 0.9603, b = 1.6473, r = 0.9881.

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