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Relationes

Electronic Spectra of Diaminopyridines*

J. BUDZIŃSKI
Department of Physics, Higher Agricultural School, Szczecin, Poland

J. S. KWIATKOWSKI
Department of Experimental Physics, Nicholas Copernicus University, Toruń, Poland

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The electronic structure and spectra ($\pi \rightarrow \pi^*$ type) of diaminopyridines have been calculated by means of the Pariser-Parr-Pople type calculations, taking into account all the singlet monoexcited configurations. The results are in good agreement with the experiment.

Favini *et al.* [1] have recently measured the ultraviolet absorption spectra of a series substituted pyridines including mono and diaminopyridines, which in the later case have been recorded in the range of 1900 to 3300 Å. These absorption bands have been compared with theoretical results obtained by means of the localized-orbital model with configuration interaction [2], which shows in general good agreement with experiment.

In the present note the results of a Pariser-Parr-Pople type calculations [3] for the diaminopyridines shall be communicated. In Part III of this series [4] the same calculations have been performed for some monosubstituted pyridines, among them for 2-, 3- and 4-aminopyridine, with good agreement between the theoretical and experimental singlet-singlet transition energies.

Details of Calculations

The semiempirically evaluated values of the one-electron core integrals and two-electron Coulomb repulsion integrals are the same as those given in previous papers (e.g. Table 1 of Ref. [5]). The values of the core resonance integrals may be found in Ref. [4]. Two-electron two-centre integrals were calculated by means of the Nishimoto and Mataga approximation.

The amino form was assumed in all cases and all molecules were considered to be planar. The geometrical structure of pyridine was taken from the paper by Bak *et al.* [6] and the lengths of the C–NH_2 bonds were assumed to be 1.38 Å.

With respect to configuration interaction, all singly excited configurations were taken into account.

Results

The calculated values of transition energies, oscillator strengths and transition polarizations, together with the experimental data from Ref. [1], are listed in

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* Part VII in a series "Electronic Structure and Spectra of Organic Molecules" of the second author. For Part VI see Kwiatkowski, J. S.: Bull. Acad. polon. Sci., Sér. Sci. chim. **16**, 51 (1968).

Table. *Diaminopyridines – transition energies to the singlet states, ΔE (in eV); oscillator strengths, f; polarization of transitions, Θ (in degrees); changes on excitation in the π-electronic charge densities at the amino-type nitrogen atoms (ΔQ) and changes on excitation in the π-electronic contributions to the dipole moments, $\Delta\mu_\pi$ (in Debye units)*

	Theoretical						Experimental [1]	
	ΔE[a]	f	Θ	$\Delta Q(1)$[c]	$\Delta Q(2)$[c]	$\Delta\mu_\pi$[b]	ΔE	f
2,3-diaminopyridine								
	4.025	0.17	+77	−0.122	−0.156	2.67 (97)	4.155	0.11
	4.922	0.28	−19	−0.158	−0.220	4.14 (98)	5.268	0.17
	6.066	0.65	+47	−0.110	−0.203	3.00 (111)	6.26	0.52
	6.123	0.52	+62	−0.198	−0.142	2.16 (95)		
	7.009	0.11	−68	−0.186	−0.225	4.94 (89)		
2,4-diaminopyridine								
	4.272	0.05	−86	−0.136	−0.021	0.71 (109)		
	5.198	0.06	−31	−0.074	−0.206	2.53 (156)		
	5.644	1.06	+37	−0.234	−0.195	1.59 (135)		
	5.856	0.61	−32	−0.158	−0.257	4.68 (134)		
	7.169	0.12	+65	−0.263	−0.028	0.83 (142)		
2,5-diaminopyridine								
	3.949	0.15	−71	−0.147	−0.173	0.32 (251)	3.800	0.05
	4.947	0.53	+46	−0.140	−0.205	1.36 (246)	5.086	0.26
	6.130	0.28	+29	−0.212	−0.312	3.05 (188)		
	6.469	0.46	−48	−0.155	−0.056	2.84 (125)	6.569	0.48
	6.721	0.26	+38	−0.165	−0.198	0.61 (318)		
2,6-diaminopyridine								
(B_1)	4.084	0.18	+90	−0.104	−0.104	0.93 (0)	4.132	0.11
(A_1)	5.239	0.36	0	−0.129	−0.129	1.23 (0)	5.101	0.21
(B_1)	6.013	0.68	+90	−0.201	−0.201	5.01 (0)	6.244	0.66
(A_1)	6.061	0.12	0	−0.273	−0.273	6.76 (0)		
(A_1)	6.932	0.80	0	−0.038	−0.038	0.52 (0)	6.754	?
3,4-diaminopyridine								
	4.188	0.07	+29	−0.189	−0.055	2.64 (144)	4.403	0.09
	4.795	0.19	+62	−0.197	−0.210	5.32 (153)	4.978	0.27
	5.784	1.06	−41	−0.141	−0.202	3.80 (166)	5.959	0.54
	6.092	0.48	+38	−0.144	−0.153	2.34 (171)		
	7.174	0.01	+58	−0.277	−0.174	6.33 (144)		
3,5-diaminopyridine								
(B_1)	4.099	0.10	+90	−0.114	−0.114	0.84 (180)		
(A_1)	5.070	0.08	0	−0.157	−0.157	2.37 (180)		
(A_1)	5.646	0.49	0	−0.246	−0.246	4.80 (180)		
(B_1)	5.699	1.01	+90	−0.227	−0.277	4.19 (180)		
(B_1)	7.286	0.0004	+90	−0.137	−0.137	0.89 (180)		

[a] Symmetries of the excited states of 2,6- and 3,5-diaminopyridine are given in parenthesis. For the symmetry species and characters of the C_{2v} group see Jaffé, H. H., and M. Orchin: Theory and applications of ultraviolet spectroscopy, Appendix 3. New York: Wiley 1962.

[b] Dipole moment directions (in degrees) are given in parenthesis.

[c] In unsymmetric molecules $NH_2(1)$ is nearer to the pyridine nitrogen.

the table. It also contains the changes on excitation in the π-electron density at the nitrogen atom in the amino groups and corresponding changes in the π-dipole moments of molecules in question. The calculated values of transition energies are in good agreement with the experimental data.

The values of ΔQ of the amino group as those presented in the Table deserve some comment. From a comparison of the present calculations with the previous ones [4], we can draw conclusion that the first two absorption bands of diamino-substituted pyridines correlate with the α and p bands of pyridine itself. The results show that the amino group has a bathochromic effect on these bands and these bathochromic shifts are accompanied by an electron transfer from the amino groups to the pyridine ring.

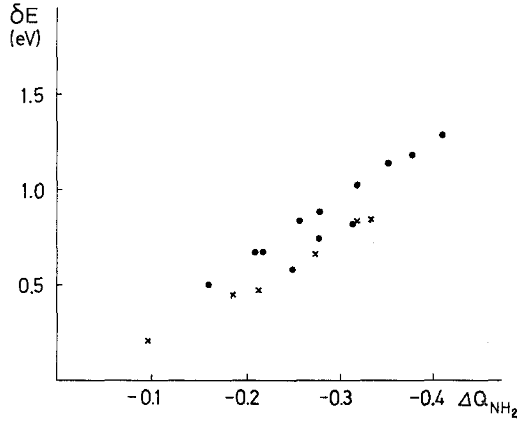

Fig. 1. Calculated shifts (δE) of the first two absorption bands of pyridine caused by the substitution of the amino groups versus the calculated charge transfered from substitutions to the pyridine ring. × – monoaminopyridines (see Ref. [4]), ● – diaminopyridines

That is illustrated in Fig. 1 which makes, that, if the mono or disubstituted molecules are considered separately, the δE shifts are proportional, with a few exceptions, to the ΔQ_{NH_2} values in the case of monoaminopyridines and in the case of diaminisubstituted molecules to the sum of them for the two groups.

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Dr. J. S. Kwiatkowski
Katedra Fizyki Doświadczalnej I
Uniwersytet M. Kopernika
Toruń, ul. Grudziądzka 5
Poland