Theoret. chim. Acta (Berl.) 13, 79—80 (1969)

Relationes

Calculation of Electronic Spectra of Pyrido [2,3-*d*]Pyridazine and Pyrido[3,4-*d*]Pyridazine

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Received November 26, 1968

The electronic spectra of pyrido[2,3-*d*]pyridazine and pyrido[3,4-*d*]pyridazine have been calculated by the P method and the RP method previously used for azines. The results are in good agreement with experimental data and with the previous conclusions.

A calculation of the electronic spectra of aza-benzenes and aza-naphthalenes by the P method [1] and the RP (reduced Pariser-Parr-Pople) method [2] was presented a few years ago in this journal. It is the purpose of the present note to extend these calculations to pyrido[2,3-*d*]- and pyrido[3,4-*d*]-pyridazine. These two compounds were recently synthesized and their ultraviolet spectra discussed [3].

As in Ref. [1, 2], the stabilization of the ground state due to interaction with singly excited configurations has not been considered. The energies, relative to the

Table 1. *Results of calculations*

Compound[a]	Method	Energy relative to ground configuration (eV)	Experim. transition energy (eV)	Oscillator strengths		Weight (in %) of most important configurations	
				theor.	obs.		
A	P	−0.158	—	—	—	ϕ_0	97.5
		4.286	4.35[b]	0.012	0.023[b]	$\phi_4^6; \phi_5^7$	54.6; 37.6
		4.545	5.08[b]	0.063	0.105[b]	$\phi_5^6; \phi_4^7$	68.8; 24.7
		5.821	5.54[b]	0.476	0.081[b]	$\phi_3^6; \phi_5^7;$ $\phi_3^7; \phi_4^6$	27.3; 19.5; 12.9; 11.4
A	RP	−0.030	—	—	—	ϕ_0	99.5
		4.333	4.33[c]	0.015		$\phi_4^6; \phi_5^7$	58.2; 39.2
		4.762	5.14[c]	0.165		$\phi_5^6; \phi_4^7$	88.0; 8.1
		5.639	5.69[c]	0.731		$\phi_3^6; \phi_5^8;$ $\phi_4^6; \phi_5^7$	27.1; 26.3; 22.0; 21.8
B	P	−0.154	—	—	—	ϕ_0	97.5
		4.274	4.20[b]	0.117	0.040[b]	$\phi_5^7; \phi_5^6; \phi_4^6$	34.4; 33.0; 22.9
		4.559	5.08[b]	0.112	0.140[b]	$\phi_5^6; \phi_5^7; \phi_4^7$	44.6; 26.2; 14.2
		5.698	5.79[b]	0.045	0.220[b]	$\phi_3^6; \phi_5^8$	42.8; 38.4
B	RP	−0.026	—	—	—	ϕ_0	99.6
		4.194	4.22[c]	0.066		$\phi_5^7; \phi_4^6; \phi_5^6$	44.0; 31.0; 19.2
		4.706	5.00[c]	0.189		$\phi_5^6; \phi_5^7$	68.1; 18.6
		5.605	5.85[c]	0.200		$\phi_5^8; \phi_3^6; \phi_4^6$	42.6; 29.5; 21.4

[a] Pyrido[2,3-*d*]pyridazine (A); pyrido[3,4-*d*]pyridazine (B).

[b] In methanol solution.

[c] In cyclohexane solution.

Table 2. *Comparison for values calculated from regression lines*

Compound[a]	Method	Excitation energy (eV)		Difference	Standard deviation Δ
		[b]	[c]		
A	P	4.286	4.362	0.076	0.082
		4.545	4.598	0.053	0.089
		5.821	5.662	0.159	0.168
A	RP	4.333	4.370	0.037	0.098
		4.762	4.891	0.129	0.144
		5.639	5.587	0.052	0.156
B	P	4.274	4.251	0.023	0.082
		4.559	4.555	0.004	0.089
		5.698	5.768	0.070	0.168
B	RP	4.194	4.253	0.059	0.098
		4.706	4.816	0.110	0.144
		5.605	5.790	0.185	0.156

[a] Pyrido[2,3-*d*]pyridazine (A); pyrido[3,4-*d*]pyridazine (B).
[b] Values calculated in this work (Table 1).
[c] Values calculated from regression lines in Ref. [1, 2].

ground configuration, of the ground and the lowest excited states are reported in Table 1, together with the corresponding oscillator strengths and their weights of the most important configurations.

As for the other azines in the ground state, the ground configuration is absolutely predominant, its contribution being $\geqq 97.5\%$. For the pyrido[2,3-*d*]-pyridazine the first excited state wave-function is built almost exclusively from ϕ_4^6 and ϕ_5^7 configurations, while in the second excited state the configurations ϕ_5^6 and ϕ_4^7 predominate. For the pyrido[3,4-*d*]pyridazine, on the contrary, at least three configurations give a substantial contribution to the first two excited states. Table 1 also contains the experimental transition energies and oscillator strengths for the first three $\pi - \pi^*$ bands (in methanol or in cyclohexane solutions).

In Table 2 calculated excitation energies are compared with the values resulting from linear regression lines obtained by the least squares method in previous papers [1, 2]. The differences are always smaller than the standard deviations Δ, with the only exception of the third $\pi - \pi^*$ transition for pyrido[3,4-*d*]pyridazine in the RP method.

The conclusions on the general features of the electronic spectra of the dicyclic azines are also valid for the two pyridopyridazines and the general agreement between experiment and theory is verified once again.

References

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