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Electronic Structure and Spectra of Fused *n/m* Ring Systems with One or Two Bridgehead Nitrogen Atoms

III. Quinolizinium Cation and Aza-Analogs

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Electronic structures and absorption spectra of the quinolizinium cation, all its monoaza-derivatives and the pyridazo(1.2-a)pyridazinium dication, have been computed by using the Pariser-Parr-Pople method, including all singlet mono-excited electronic configurations. The assignment of the observed bands of the quinolizinium cation has been made by comparing its observed transition energies and intensities with those of naphthalene, quinoline and isoquinoline. Discussion is given on reactivity and band interpretation.

Die Elektronenstrukturen und Absorptionsspektren des Quinolizinium Kations und aller seiner Monoazaderivate und des Pyridazo(1,2-a)-pyridazinium Dikations, werden nach der Pariser-Parr-Pople Methode berechnet, wobei alle einzeln angeregten Konfigurationen berücksichtigt werden. Die Banden des Quinolizinium Kations werden durch einen Vergleich der beobachteten Übergangsenergien und Intensitäten mit denen des Naphthalins, Quinolins und Isoquinolins zugeordnet. Reaktivität und Bandeninterpretation werden diskutiert.

La structure électronique et les spectres d'absorption du cation quinolizinium, de tous ses monoaza-dérivés et du dication pyridazo(1,2-a)pyridazinium ont été calculés par la méthode de Pariser-Parr-Pople, avec intéraction de toutes les configurations singulets mono-excitées. L'attribution des bandes d'absorption du cation quinolizinium a été faite en comparant ses énergies de transition et intensités observées avec celles du naphthalène, quinoléine et isoquinoléine. On a aussi discuté la reactivité et l'interprétation des bandes.

The papers I and II of this series reported detailed results, obtained by the PPP semiempirical version of the SCFMO-CI method of Roothaan, on the indolizines [3], (i.e., the fused 6/5 azaaromatic ring systems with one bridgehead nitrogen atom), and on azapentalenes [4], (i.e., the fused 5/5 azaaromatic ring systems with one or two bridgehead nitrogen atoms). In this paper the same theoretical procedure has been employed to investigate the most important fused 6/6 azaaromatic ring systems having one or two bridgehead nitrogen atoms and a ten π-electron structure.

The simplest compound belonging to the class with only one bridgehead- and no extra-nitrogen atoms is the quinolizinium cation shown in Fig. 1 a; whereas,

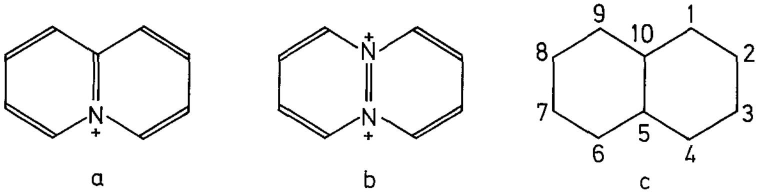

Fig. 1. a Quinolizinium cation; b Pyridazo (1,2-a)-pyridazinium dication; c Atom numbering

the not yet synthesized pyridazo(1,2-a)pyridazinium dication, represented in Fig. 1b, is the prototype of fused 6/6 azaaromatic ring systems with two bridgehead- and no extra-nitrogen atoms.

The quinolizinium cation, all its monoaza-derivatives, and the pyridazo (1,2-a)-pyridazinium dication have been examined in this work. Simple HMO and SCMO methods have been previously applied only to the quinolizinium cation [1, 11]. No other calculations appear to be made for any of the considered molecules.

Method of Calculation and Results

The SCF-MO semiempirical version of the PPP method [10, 12] and a CI treatment extended to all the singlet mono-excited configurations have been used to calculate the electronic structures and transition energies. One-center repulsion integrals, resonance integrals, and valence state ionization potentials have been given the same numerical values as in papers I and II. Two-center repulsion integrals have been estimated by the Mataga-Nishimoto [8] and Ohno [9] procedure. Regular bicyclic structures with equal bondlengths (1.396 Å) have been assigned to all the considered molecules.

Table 1. *Electron densities*

Compound	1	2	3	4	5	6	7	8	9	10
Quinolizinium cation	0.939	0.912	0.889	1.065	1.340	1.065	0.889	0.912	0.939	1.047
1-azaquinolizinium cation	1.230	0.727	0.942	0.987	1.378	1.054	0.907	0.887	0.957	0.931
2-azaquinolizinium cation	0.748	1.201	0.753	1.129	1.292	1.073	0.866	0.928	0.911	1.097
3-azaquinolizinium cation	0.993	0.773	1.180	0.865	1.382	1.058	0.898	0.891	0.958	1.000
4-azaquinolizinium cation	0.874	0.970	0.697	1.364	1.273	1.030	0.891	0.910	0.930	1.061
Pyridazo(1,2-a)pyridazinium dication	0.978	0.810	0.810	0.978	1.423	0.978	0.810	0.810	0.978	1.423

Table 2. *Bond orders*

Compound	1–2	2–3	3–4	4–5	5–6	6–7	7–8	8–9	9–10	10–5	10–1
Quinolizinium cat.	0.740	0.572	0.745	0.499	0.499	0.745	0.572	0.740	0.537	0.514	0.537
1-azaquinoliz. cat.	0.729	0.526	0.784	0.474	0.487	0.756	0.564	0.741	0.540	0.521	0.527
2-azaquinoliz. cat.	0.731	0.575	0.710	0.510	0.523	0.724	0.588	0.729	0.548	0.518	0.507
3-azaquinoliz. cat.	0.698	0.580	0.735	0.514	0.470	0.765	0.552	0.751	0.525	0.496	0.574
4-azaquinoliz. cat.	0.785	0.518	0.734	0.408	0.563	0.710	0.605	0.714	0.568	0.549	0.475
Pyridazo(1,2-a)pyridazinium dication	0.712	0.566	0.712	0.517	0.517	0.712	0.566	0.712	0.517	0.378	0.517

Electron charge densities and bond orders are given in Tab. 1 and 2, respectively. (The atom numbering is shown in Fig. 1c). The first six excitation energies, oscillator strengths and weighting factors of the most important electronic configurations are collected in Tab. 3.

Table 3. *Singlet transition energies, oscillator strengths and weight (in %) of most important configurations*

Compound	Transition	Energy (eV)	f	Weight of configurations			
Quinolizinium cation	${}^1A_1 \to {}^1A_1$	3.944	0.106	5→6 (72),	4→7 (23)		
	${}^1A_1 \to {}^1B_1$	3.986	0.114	5→7 (72),	4→6 (24)		
	${}^1A_1 \to {}^1B_1$	5.307	0.0001	5→8 (76),	3→6 (13)		
	${}^1A_1 \to {}^1A_1$	5.921	0.133	3→7 (32),	4→8 (26),	2→6 (19),	4→7 (14)
	${}^1A_1 \to {}^1B_1$	6.095	1.991	4→6 (69),	5→7 (27)		
	${}^1A_1 \to {}^1A_1$	6.272	0.722	4→7 (52),	5→6 (24)		
1-azaquinolizinium cation	${}^1A' \to {}^1A'$	4.105	0.103	5→6 (72),	4→7 (21)		
		4.150	0.015	5→7 (60),	4→6 (35)		
		5.515	0.009	5→8 (72)			
		5.820	0.921	4→6 (28),	5→7 (16),	4→8 (14),	4→7 (13)
		6.101	1.007	4→7 (36),	4→6 (18),	5→7 (15),	5→6 (11)
		6.418	0.732	4→8 (27),	3→6 (23),	4→6 (10),	2→7 (10)
2-azaquinolizinium cation	${}^1A' \to {}^1A'$	3.971	0.189	5→6 (68),	4→7 (16)		
		4.034	0.099	5→7 (61),	4→6 (21)		
		5.417	0.016	5→8 (77)			
		5.912	0.337	4→7 (31),	3→6 (24),	4→8 (15)	
		6.095	1.278	4→6 (64),	5→7 (24)		
		6.501	0.676	4→7 (40),	3→6 (19),	5→6 (13),	4→8 (12)
3-azaquinolizinium cation	${}^1A' \to {}^1A'$	3.901	0.230	5→6 (76),	4→7 (13)		
		4.060	0.151	5→7 (70),	4→6 (18)		
		5.240	0.007	5→8 (80)			
		5.952	0.569	4→6 (33),	3→7 (22),	4→8 (16)	
		6.366	0.716	4→6 (24),	3→6 (20),	4→7 (11)	
		6.446	0.973	4→7 (40),	4→6 (16),	3→7 (10)	
4-azaquinolizinium cation	${}^1A' \to {}^1A'$	4.046	0.148	5→6 (73),	4→7 (22)		
		4.253	0.036	5→7 (61),	4→6 (31)		
		5.396	0.107	5→8 (60),	3→6 (17)		
		6.001	0.049	4→8 (32),	3→7 (25),	2→6 (22),	3→6 (10)
		6.157	1.496	4→6 (54),	5→7 (32)		
		6.333	1.012	4→7 (58),	5→6 (23)		
Pyridazo(1,2-a)pyridazinium dication	${}^1A_g \to {}^1B_{3u}$	3.411	0.256	5→6 (82),	4→7 (15)		
	${}^1A_g \to {}^1B_{2u}$	3.714	0.022	5→7 (61),	4→6 (36)		
	${}^1A_g \to {}^1B_{1g}$	5.167	0	5→8 (87)			
	${}^1A_g \to {}^1B_{2u}$	5.734	1.137	4→6 (61),	5→7 (38)		
	${}^1A_g \to {}^1B_{3u}$	6.002	1.956	4→7 (76),	5→6 (17)		
	${}^1A_g \to {}^1B_{1g}$	6.006	0	3→6 (90)			

Discussion

Chemical Reactivity

By inspection of electron density values in the quinolizinium cation, the carbon atoms at 3 and 7 positions are expected to be the most reactive towards nucleophilic substitution; cationoid attack should occur at 10 rather than at position 4, since a cation incoming to the position 4 should be repelled by the high positive charge on nitrogen atom.

For the monoaza-derivatives of the quinolizinium cation, protonation is expected to take place at the nonbridgehead nitrogen atom. Anionoid substitution, on the other hand, is predicted to occur readily on the carbon atom at 2, 1, 2, and 3 position respectively for 1-, 2-, 3-, and 4-azaquinolizinium cation.

In the pyridazo (1,2-a)pyridazinium dication the carbon atoms meta with respect to the bridgehead nitrogen atoms, are predicted to behave as the most reactive ones in nucleophilic reactions. Moreover, owing to the low charges calculated for all carbon atoms, there are no positions easily accessible for attack by electrophilic reagents.

Electronic Spectrum

The electronic absorption spectrum of the quinolizinium cation has been investigated experimentally by several authors [2, 7] and has also been the subject of a theoretical study by Peacock [11]. However, the method Peacock used was only a drastic approximation from full SCFMO-CI method, since he considered the SCF molecular orbitals of the hydrocarbon parent (i.e., naphthalene) and a CI treatment restricted to the four electronic configurations constructed by mixing the two highest occupied and the two lowest unoccupied molecular orbitals, namely the configurations 4→5, 4→6, 5→6, and 5→7. In this way, he interpreted the spectrum of the quinolizinium cation by referring to the corresponding α-, p-, β-, and β'-bands in the spectrum of naphthalene, and assigned the band observed at 324 mμ or 3.83 eV [7] to the α-bond, which is an antisymmetric mixing of 5→7 and 4→6 transitions, and the band measured at 225 mμ or 5.41 eV [7] to the p-band, which is built out of a symmetric mixture of 5→6 and 4→7 transitions. The β- and β'-bands were predicted to appear at 7.52 eV and 7.81 eV, respectively.

In the present work a different choice and assignment of experimental spectral data have been made for the quinolizinium cation. In fact, according to Jaffé and Orchin [6], who recognized that there was a close overall correspondence of bands between the quinolizinium cation and naphthalene, the observed bands with maxima located at 323.5, 283, and 226 mμ (or 3.83, 4.38, and 5.48 eV) have been assigned as the α-, p-, and β-bands, respectively. The measured values have been taken from Boekelheide and Gall [2], who first synthesized the quinolizinium cation. No assignment could be made for the β'-band not observed experimentally.

The assignment here proposed is also supported by the close similarity in the spectral patterns as well as by the evident correlation both in wavelengths and intensities of the absorption maxima in the spectra of the isoelectronic and isosteric molecules of naphthalene, quinoline and isoquinoline, on the one hand, and of the quinolizinium cation, on the other hand, as can be easily seen from the following collection of experimental data:

Compound	Solvent	α-band		p-band		β-band		Ref.
		λ(mμ)	ε	λ(mμ)	ε	λ(mμ)	ε	
Naphthalene	EtOH	311	320	275	5600	221	95500	[13]
Quinoline	EtOH	314	3000	278	3500	225	35500	[13]
Isoquinoline	EtOH	320	2700	267	3700	218	79500	[13]
Quinolizinium cation	H_2O	323	17000	283	3000	226	17800	[2]

The interpretation of the spectrum of the quinolizinium cation afforded by the present calculations, carried out by using the SCF molecular orbitals of the molecule itself and all singly-excited configurations, satisfactorily agrees with the proposed assignment. Indeed, two transitions, closely resembling in nature the corresponding α- and p-bands in naphthalene, are predicted to appear at 3.99 eV and 3.94 eV, respectively. Accordingly, the transition ${}^1A_1 \rightarrow {}^1B_1$ of 3.99 eV can be assigned to the band with maximum located at 3.83 eV and the transition ${}^1A_1 \rightarrow {}^1A_1$ of 3.94 eV to the maximum recorded at 4.38 eV. The observed band with maximum centred at 5.48 eV can be ascribed to the strong intensity transition ${}^1A_1 \rightarrow {}^1B_1$ calculated at 6.09 eV, the nature of which is of β-type. The oscillator strength values predicted for these bands are consistent with the experimental extinction coefficients. A strong absorption, closely corresponding to the β'-band in naphthalene, is expected to be located near the β-band in the region about 200 mμ.

The agreement between the observed and calculated transition energies is only fair. Although it could be optimized by searching the "best" values for the resonance integrals, it seemed more interesting to transfer to the quinolizinium cation and to the other molecules here considered the standard values of the resonance integrals already used in papers I and II in the case of indolizines [3] and azapentalenes [4]. The use of these values is, however, justified by the satisfactory overall agreement with experiment in the present case as well as in the previous ones.

The present calculations also predict the location of the principal transitions in the monoaza-derivatives of the quinolizinium cation and in the pyridazo(1,2-a)-pyridazinium dication. No experimental spectral data are as yet available for these molecules (with the exception of 2-azaquinolizinium cation) in order to test the correctness of the theoretical results. However, it can be said that the spectral patterns of the monoaza-derivatives are expected to closely resemble that of quinolizinium cation, and a large bathochromic shift should be shown by the first two bands in the spectrum of the pyridazo(1,2-a)pyridazinium dication.

In a paper recently published, Glover and Loadman [5] reported the UV absorption spectrum of the 2-azaquinolizinium cation. The spectrum looks quite similar to that of the quinolizinium cation and consists of three bands with maxima located at 336, 287, and 232 mμ (or 3.69, 4.32, and 5.34 eV), respectively, so far moderately red-shifted with respect to those of the quinolizinium cation. These bands can be assigned to the transitions calculated at 3.97, 4.03, and (5.91, 6.09) eV, respectively. Their natures closely resemble those of the relevant bands in the quinolizinium cation.

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