Theoret. chim. Acta (Berl.) 9, 222—229 (1968)

Electronic Structure and Absorption Spectra of Indolizines

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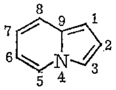
Received October 2, 1967

The electronic structure and spectra of indolizine and a large number of its aza-derivatives have been calculated by the SCFMO–CI method, taking into account all the singlet mono-excited configurations. The results are in good agreement with the experiment. The assignment of the observed bands is also discussed.

Mit dem SCFMO–CI-Verfahren werden Elektronenstruktur und Spektren des Indolizins und mehrerer seiner Derivate berechnet, wobei alle einzeln angeregten Singulett-Konfigurationen berücksichtigt werden. Die Ergebnisse stehen in ausgezeichneter Übereinstimmung mit dem Experiment. Die Zuordnung der beobachteten Banden wird diskutiert.

La structure et les spectres électroniques de l'indolizine et de plusieurs ses aza-dérivés ont été calculés par la méthode SCFMO–CI, en considérant toutes les configurations singulets mono-excitées. Les résultats sont en bon accord avec l'expérience. L'attribution des bandes observées est aussi discutée.

Indolizine is the prototype of the fused 5/6 ring systems having one bridgehea nitrogen atom and a ten π-electron aromatic structure. Simple calculations on indolizine have been previously performed following the HMO–LCAO procedure to determine atom charges and bond orders [8], frontier electron densities [4], ionization potential [17], atom localization energies [5], and spectral transitions [3]. In the present report are described the results of a systematic SCFMO–CI theoretical investigation on the π-electronic structure and absorption spectra of indolizine and a large number of its aza-derivatives. All monoaza-indolizines, the diaza- and triaza-indolizines having the extra nitrogen atoms in the five-membered ring together with some diaza-indolizines having an extra nitrogen atom in both the five- and six-membered rings, (for a total of fifteen aza-derivatives), have been considered. Atom numbering for all the molecules is assumed as follows:



and the molecules are accordingly named.

Assignment of the Observed Bands

The ultraviolet absorption electronic spectrum of indolizine consists of three bands. A band of strong intensity appears in the region 2250 – 2400 Å. Two bands of medium intensity are observed in the regions 2700 – 3100 and 3300 – 3600 Å, respectively. The three bands undergo a hypsochromic shift upon the effect of aza-substitution, and the amount of the shift becomes progressively larger as the

Table 1. *Electronic absorption spectra*

Compound	λ_{max} (Å)			log ε			Ref.
Indolizine	3465	2945	2375	3.29	3.56	4.51	[2]
1-aza	3100	2800	2245	3.42	3.41	4.41	[2]
2-aza	3440	2735	2180	3.27	3.72	4.46	[2]
3-aza	3005	2890	2225	3.26	3.52	4.56	[2]
7-aza	3385	2830	2245	3.43	3.49	4.39	[1]
1,2-diaza	3060	2740	2130	3.34	3.67	4.38	[2]
1,3-diaza[a]	2940	2730	2175	3.20	3.57	4.58	[2]
2,3-diaza	2990	2700	2140	3.36	3.33	4.35	[2]
1,5-diaza	3370	2780	2300	3.55	3.02	4.38	[1]
1,6-diaza	3090	2700	<2250	3.31	3.64		[1]
1,7-diaza	3000	2840	2110	3.46	3.58	4.26	[1]
1,8-diaza	3330	2770	2275	4.30	3.30	4.30	[1]
1,2,3-triaza	2930	2645	<2100	3.16	3.62		[2]

[a] 2-methyl-derivative.

number of nitrogen atoms replacing methine groups increase. The most intense maxima of the three bands in indolizine and a large series of aza-indolizines are reported in Table 1.

The present selection of the band maxima is in agreement with that previously proposed by MASON [9] for 1-, 2-, 3-aza-, and 1,2-diaza-indolizine, but differs from that for 7-aza-, 1,3-diaza-, 2,3-diaza-, and 1,2,3-triaza-indolizine.

MASON assigned to the first electronic transition in 7-aza-indolizine the maximum observed at 3720 Å (log $\varepsilon = 2.02$) by HERZ and TOCKER [6], appreciably red-shifted with respect to the corresponding maximum in the unsubstituted indolizine, (observed at 3465 Å). The above Authors, however, give also a more intense maximum at 3300 Å (log $\varepsilon = 2.52$), which well agrees with the maximum measured at 3385 Å by BOWER [2], blue-shifted with respect to indolizine as it is observed in the other aza-derivatives. The choice of this maximum is supported by observing that the relevant band maximum in 1,7-diaza-indolizine appears at 3000 Å against 3100 Å in 1-aza-indolizine, showing that the hypsochromic effect is cumulated. In the present work, the band assignment for 7-aza-indolizine has been made on the basis of the spectral data given by BOWER [2]. The calculations too support this assignment.

Inspection of the position of the long wavelength maximum in 1-, 2-, 3-aza, 1,2-, 2,3-diaza, and 1,2,3-triaza-indolizine suggests the assignment of the inflexion observed at 2940 Å as the relevant maximum for 1,3-diaza-indolizine. This value is, moreover, in agreement with the calculated energy for the first electronic transition. In accord to the spectral data reported by BOWER [2], the long wavelength band maximum in 2,3-diaza-indolizine has been situated at 2990 Å.

For 1,2,3-triaza-indolizine, the second electronic transition has been associated with the maximum at 2645 Å more intense than that measured at 2685 Å and assumed by MASON; moreover, an assignment has been proposed for the first and third electronic transitions.

No assignment has been previously afforded to 1,5-, 1,6-, 1,7-, and 1,8-diaza-indolizine.

Table 2. *Bond orders*

Compound	1 – 2	2 – 3	3 – 4	4 – 5	5 – 6	6 – 7	7 – 8	8 – 9	9 – 4	9 – 1
Indolizine	0.678	0.674	0.532	0.446	0.778	0.543	0.772	0.496	0.457	0.609
1-aza	0.639	0.702	0.495	0.470	0.764	0.561	0.762	0.509	0.500	0.573
2-aza	0.659	0.648	0.584	0.417	0.793	0.526	0.782	0.483	0.434	0.630
3-aza	0.691	0.641	0.436	0.504	0.756	0.563	0.763	0.506	0.510	0.584
5-aza	0.701	0.647	0.597	0.357	0.743	0.544	0.760	0.506	0.468	0.586
6-aza	0.657	0.696	0.496	0.493	0.747	0.535	0.770	0.490	0.442	0.632
7-aza	0.696	0.656	0.567	0.422	0.779	0.527	0.731	0.510	0.457	0.590
8-aza	0.661	0.688	0.500	0.479	0.776	0.535	0.757	0.484	0.443	0.630
1,2-diaza	0.587	0.736	0.520	0.441	0.787	0.534	0.785	0.473	0.475	0.644
1,3-diaza	0.647	0.662	0.399	0.523	0.745	0.579	0.753	0.521	0.544	0.542
2,3-diaza	0.738	0.585	0.519	0.483	0.762	0.561	0.762	0.513	0.505	0.561
1,5-diaza	0.662	0.675	0.559	0.383	0.735	0.556	0.757	0.505	0.519	0.557
1,6-diaza	0.619	0.720	0.461	0.515	0.732	0.551	0.757	0.509	0.481	0.591
1,7-diaza	0.659	0.682	0.530	0.448	0.765	0.547	0.727	0.510	0.506	0.559
1,8-diaza	0.619	0.715	0.463	0.503	0.761	0.555	0.741	0.501	0.478	0.592
1,2,3-triaza	0.667	0.676	0.462	0.498	0.759	0.564	0.764	0.504	0.530	0.576

Method of Calculation and Results

The theoretical treatment has been carried out by the semiempirical SCF–LCAO–MO method developed by Roothaan [15], within the framework of the approximations introduced by Pariser and Parr [13] and Pople [14] for conjugated systems, extended to include the interaction between all the singlet mono-excited electronic configurations.

The interaction with the hydrogen atoms has been neglected and the penetration integrals have been approximated through Pople's formula [14]. The α_i quantity has been calculated by the equation:

$$\alpha_i = W_i - \sum_{i \neq j} n_j \gamma_{ij}$$

where n_j stands for the number of electrons contributed by the j-th atom to the π-electron framework, γ_{ij} for the two-center Coulomb integral, and $W_i = -I_i$, or $-I_i - \gamma_{ii}$ for $n_j = 1$, or 2, respectively; I_i being the first ionization potential of the j-th atom in its appropriate

Table 3. *π-Electron densities*

Compound	1	2	3	4	5	6	7	8	9
Indolizine	1.134	1.016	1.238	1.387	1.120	0.981	1.049	0.949	1.124
1-aza	1.360	0.885	1.277	1.372	1.109	0.991	1.024	0.966	1.015
2-aza	0.994	1.257	1.099	1.397	1.133	0.963	1.065	0.929	1.162
3-aza	1.193	0.863	1.476	1.338	1.076	1.006	1.011	0.981	1.055
5-aza	1.111	1.040	1.193	1.342	1.400	0.779	1.121	0.852	1.160
6-aza	1.145	0.996	1.251	1.409	0.928	1.246	0.927	1.015	1.083
7-aza	1.109	1.029	1.212	1.365	1.186	0.863	1.302	0.769	1.164
8-aza	1.154	0.994	1.263	1.406	1.025	1.045	0.858	1.228	1.027
1,2-diaza	1.262	1.147	1.095	1.407	1.104	0.985	1.023	0.957	1.020
1,3-diaza	1.404	0.737	1.503	1.330	1.067	1.014	0.991	0.995	0.958
2,3-diaza	1.015	1.129	1.390	1.302	1.103	0.972	1.032	0.951	1.105
1,5-diaza	1.343	0.900	1.235	1.318	1.389	0.791	1.096	0.868	1.057
1,6-diaza	1.368	0.871	1.290	1.396	0.922	1.254	0.898	1.031	0.969
1,7-diaza	1.342	0.891	1.255	1.343	1.174	0.867	1.282	0.785	1.060
1,8-diaza	1.374	0.867	1.300	1.395	1.015	1.055	0.836	1.244	0.912
1,2,3-triaza	1.277	0.984	1.379	1.326	1.080	0.993	1.001	0.974	0.986

valence state. The following values have been used: $I_{C^*} = 11.54$ eV, $I_{N^*} = 14.34$ eV, and $I_{N^{**}} = 11.93$ eV [16] (the number of * means the number of π-electrons).

All the electronic repulsion integrals have been treated semiempirically. The one-center integrals γ_{ii}, evaluated by JULG [7] from atomic valence state data through a method taking into account the correlation energy, are: $\gamma_{C^*C^*} = 9.87$ eV, $\gamma_{N^*N^*} = 11.19$ eV, and $\gamma_{N^{**}N^{**}} = 11.07$ eV. The two-center integrals γ_{ij} have been determined by the expression suggested by MATAGA and NISHIMOTO [10] and OHNO [11]:

$$\gamma_{ij} = 14.397/(a_{ij}^2 + r_{ij}^2)^{1/2}$$

where r_{ij} represents the interatomic distance and

$$a_{ij} = 28.794/(\gamma_{ii} + \gamma_{jj})\,.$$

For the resonance integrals β_{ij}, the relevant values in the molecules of benzene, $\beta_{CC} = -2.39$ eV [13], pyridine, $\beta_{CN} = -2.576$ eV [13], and s-tetrazine, $\beta_{NN} = -2.35$ eV [12], have been used.

In the absence of X-ray structural data, the geometries of a regular hexagon and a regular pentagon have been assumed for the six- and five-membered rings, respectively, in all the molecules. The lengths of the bonds have been taken to be 1.39 Å.

Bond orders and electron densities are shown in Table 2 and 3, respectively. The average electron density on bridgehead nitrogen atom is 1.36 atomic units. The π-electron withdrawal in the aza-derivatives is greatest from the carbon atoms in ortho relative to extra nitrogen atoms. The C_5–C_6 and C_7–C_8 bonds have the greatest bond orders (~75%); the C_4–C_5, C_8–C_9 and C_9–C_4 bonds the lowest ones (~48%).

The experimental and lower calculated singlet energies, oscillator strengths and weight (in %) of most important configurations (each contributing at least 10%) in the first electronic excited states are assembled in Table 4. In general, the calculations satisfactorily reproduce the experimental values with respect to transitions energies and relative intensities. A comparatively large discrepance between experimental and theoretical energy is observed in the shortest wavelength band for some molecules.

Table 4. *Singlet transition energies (eV), calculated oscillator strengths and weight (in %) of most important configurations*

Compound	Energy		f	Weight of configurations	
	Obsd.	Calcd.			
Indolizine	3.58	3.559	0.092	ϕ_5^6	89
	4.21	4.296	0.043	ϕ_5^7; ϕ_4^6	59; 34
		5.821	0.134	ϕ_4^7; ϕ_3^6; ϕ_5^8	54; 16; 14
	5.22	5.851	1.095	ϕ_4^6; ϕ_5^7	50; 27
		6.187	0.080		
		6.659	0.544		
1-aza	4.00	3.912	0.096	ϕ_5^6; ϕ_4^7	82; 14
	4.43	4.415	0.001	ϕ_4^6; ϕ_5^7	48; 46
	5.52	5.944	1.116	ϕ_5^7; ϕ_4^6	41; 40
		6.047	0.220	ϕ_4^7; ϕ_3^6; ϕ_5^6	57; 14; 13
		6.490	0.015		
		6.790	0.815		

Table 4 (Continuation)

Compound	Energy		f	Weight of configurations	
	Obsd.	Calcd.			
2-aza	3.60	3.451	0.131	ϕ_5^6	92
	4.53	4.425	0.136	$\phi_5^7; \phi_4^6$	71; 24
		5.957	0.346	$\phi_5^8; \phi_4^7; \phi_4^6; \phi_3^6$	30; 20; 17; 13
	5.69	5.976	0.386	$\phi_5^8; \phi_4^6; \phi_3^6$	40; 23; 12
		6.201	0.329		
		6.884	0.606		
3-aza	4.12	3.812	0.086	$\phi_5^6; \phi_4^7$	86; 11
	4.30	4.363	0.093	$\phi_5^7; \phi_4^6$	66; 29
		5.843	0.535	$\phi_4^7; \phi_4^6; \phi_3^6; \phi_5^7$	26; 24; 17; 12
	5.57	5.943	0.645	$\phi_4^6; \phi_4^7; \phi_3^6; \phi_5^7$	30; 20; 13; 13
		6.164	0.009		
		6.965	0.522		
5-aza		3.540	0.109	ϕ_5^6	91
		4.388	0.005	$\phi_4^6; \phi_5^7$	57; 36
		5.650	0.441	$\phi_5^7; \phi_4^6; \phi_4^7; \phi_3^6$	33; 21; 20; 10
		5.822	0.613	$\phi_4^7; \phi_3^6; \phi_5^7; \phi_4^6$	27; 20; 15; 13
		6.206	0.155		
		6.809	0.452		
6-aza		3.516	0.109	ϕ_5^6	91
		4.249	0.101	$\phi_5^7; \phi_4^6$	65; 27
		5.906	0.352	$\phi_4^7; \phi_5^8; \phi_4^6$	33; 28; 16
		6.044	0.725	$\phi_4^6; \phi_4^7; \phi_5^7$	42; 18; 13
		6.158	0.078		
		6.595	0.448		
7-aza	3.66	3.737	0.089	ϕ_5^6	83
	4.38	4.380	0.089	$\phi_5^7; \phi_4^6$	58; 31
	5.52	5.820	0.601	$\phi_4^6; \phi_5^7; \phi_4^7; \phi_5^8$	36; 17; 13; 13
		5.940	0.425	$\phi_4^7; \phi_3^6; \phi_4^6$	45; 23; 10
		6.406	0.288		
		6.699	0.500		
8-aza		3.342	0.072	ϕ_5^6	93
		4.211	0.000	$\phi_4^6; \phi_5^7$	47; 46
		5.684	1.032	$\phi_4^6; \phi_5^7$	43; 36
		5.800	0.275	$\phi_4^7; \phi_5^8; \phi_3^6$	51; 15; 12
		6.270	0.017		
		6.778	0.561		
1,2-diaza	4,05	3.815	0.148	ϕ_5^6	88
	4.52	4.566	0.017	$\phi_5^7; \phi_4^6$	55; 39
	5.82	6.048	0.757	$\phi_4^6; \phi_5^7; \phi_3^6; \phi_5^8$	33; 24; 16; 12
		6.171	0.065	$\phi_5^8; \phi_4^7$	49; 28
		6.294	0.394		
		6.865	0.778		

Table 4 (Continuation)

Compound	Energy		f	Weight of configurations	
	Obsd.	Calcd.			
1,3-diaza	4.22	4.232	0.078	$\phi_5^6; \phi_4^7$	77; 18
	4.54	4.587	0.006	$\phi_5^7; \phi_4^6$	49; 45
	5.70	6.170	1.101	$\phi_4^6; \phi_5^7$	40; 33
		6.333	0.510	$\phi_4^7; \phi_5^6$	50; 16
		6.623	0.113		
		7.042	0.336		
2,3-diaza	4.14	3.786	0.106	$\phi_5^6; \phi_4^7$	87; 11
	4.59	4.358	0.104	$\phi_5^7; \phi_4^6$	68; 27
	5.79	5.860	0.482	$\phi_4^6; \phi_4^7; \phi_5^8; \phi_5^7; \phi_3^6$	24; 23; 16; 11; 10
		6.068	0.462	$\phi_4^7; \phi_3^6; \phi_4^6$	24; 22; 21
		6.097	0.091		
		6.871	0.857		
1,5-diaza	3.68	3.877	0.161	$\phi_5^6; \phi_4^7$	85; 11
	4.46	4.496	0.033	$\phi_4^6; \phi_5^7$	64; 28
		5.911	0.220	$\phi_5^7; \phi_3^6; \phi_4^7; \phi_4^6$	34; 21; 16; 14
	5.39	5.988	0.701	$\phi_5^7; \phi_3^6; \phi_4^7; \phi_4^6$	24; 1 9; 17; 13
		6.441	0.140		
		6.893	0.885		
1,6-diaza	4.01	3.903	0.121	ϕ_5^6	88
	4.59	4.407	0.034	$\phi_5^7; \phi_4^6$	57; 35
	>5.51	6.087	1.088	$\phi_4^6; \phi_5^7$	52; 31
		6.181	0.145	$\phi_4^7; \phi_5^8$	58; 15
		6.408	0.027		
		6.792	0.648		
1,7-diaza	4.13	4.070	0.084	$\phi_5^6; \phi_4^7$	78; 14
	4.36	4.505	0.029	$\phi_4^6; \phi_5^7$	49; 42
	5.87	5.883	1.003	$\phi_5^7; \phi_4^6$	39; 39
		6.115	0.340	$\phi_4^7; \phi_5^6$	66; 14
		6.663	0.140		
		6.924	0.540		
1,8-diaza	3.72	3.791	0.103	ϕ_5^6	87
	4.47	4.354	0.026	$\phi_4^6; \phi_5^7$	57; 35
	5.45	5.892	0.797	$\phi_5^7; \phi_4^6$	46; 31
		6.080	0.405	$\phi_4^7; \phi_5^8$	50; 17
		6.594	0.101		
		6.972	0.614		
1,2,3-triaza	4.23	4.098	0.117	$\phi_5^6; \phi_4^7$	81; 15
	4.69	4.523	0.014	$\phi_5^7; \phi_4^6$	55; 40
		6.064	0.339	$\phi_5^8; \phi_4^6$	50; 14
	>5.90	6.220	0.595	$\phi_4^6; \phi_3^6; \phi_5^7; \phi_5^8$	26; 25; 17; 10
		6.291	0.315		
		6.748	0.862		

Discussion

The electronic spectra of indolizine and some aza-derivatives have been analyzed by Mason [9] on the basis of a qualitative discussion on the perturbations caused by aza-substitution on the energy distribution of HMO's in the model molecule indenyl anion. Feitelson [3] has used the perimeter model to calculate the electronic spectra of some indolizines by first-order configuration interaction and subsequent perturbation of the ring by cross link.

After Mason, the long wavelength absorption band of medium intensity would be associated with the transition from the highest occupied molecular orbital to the second empty molecular orbital, i.e. to the transition $5 \rightarrow 7$; the medium intensity band of intermedium wavelength to a combination of transitions $5 \rightarrow 6$ and $4 \rightarrow 7$; and the short wavelength band of strong intensity predominantly to the transition $4 \rightarrow 6$.

According to Feitelson, the first and second band should be assigned to a combination, asymmetric and symmetric respectively, of transitions $5 \rightarrow 6$ and $4 \rightarrow 7$, and the third band should be ascribed to a symmetric mixture of transitions $5 \rightarrow 7$ and $4 \rightarrow 6$.

The present results, obtained from a SCF–MO calculation with the inclusion of the interaction between all the monoexcited singlet configurations, afford an interpretation on the nature of the electronic absorption bands quite different from those previously proposed by other Authors.

From data reported in Table 4 it can clearly be seen that the first band must be attributed essentially to the transition $5 \rightarrow 6$, which gives an average contribution of 80 – 90%; there is indeed a little contribution from transition $4 \rightarrow 7$, that does not exceed 12%, with exception of a few molecules. The relatively low value calculated for the oscillator strength (f lower than 0.17), is consistent with the medium intensity of the observed band.

The second band appears to be predominantly due to a combination of transitions $5 \rightarrow 7$ and $4 \rightarrow 6$. The obtained oscillator strength (f lower than 0.15), is in accord with the medium intensity of the observed band.

The ASMO–CI calculations would suggest that the short wavelength band of strong intensity may be ascribed to a merging of two relatively near and intense absorption maxima, which should be originated from a combination of several simple transitions. The calculations, however, overestimate the third excitation energy in average by about 0.30 eV; so, there is a possibility that the fourth excitation energy would be associated to an other band not observed because of its shortest wavelength. The high calculated value of the oscillator strength well agrees with the strong intensity of the observed band.

The experimental data of the electronic transitions in 5-, 6-, and 8-aza-indolizine are not available for comparison. However, comparison between their calculated excitation energies and the observed values for the corresponding 1,5-, 1,6-, and 1,8-diaza-derivatives suggests that the position of the long wavelength band maximum should undergo only a slight shift and the two short wavelength bands a greater blue-shift relative to indolizine.

In conclusion, the theoretical method and the parameterization abopted in the present work have afforded a good reproduction of the experimental excitation energies and relative intensities, and have provided an understanding of the nature of the observed bands common to indolizine and its aza-derivatives.

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