

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

II. Azapentalenes

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The semiempirical ASMO-SCF-CI method has been applied to study the electronic structures and ultraviolet absorption spectra of the 4-azapentalenyl anion, 4,8-diazapentalene and related azaderivatives. The agreement between observed and calculated transition energies is, in general, satisfactory. Chemical reactivity and assignment of the observed bands are discussed.

Mit Hilfe einer semi-empirischen ASMO-SCF-CI Methode wurden Elektronenstruktur und UV Absorptionsspektren des 4-Azapentalenylanions, des 4,8-Diazapentalens und der entsprechenden Azaderivate studiert. Im allgemeinen ist die Übereinstimmung zwischen experimentellen und theoretischen Übergangsenergien zufriedenstellend. Die Zuordnung der beobachteten Banden und Reaktivitäten werden diskutiert.

La méthode semi-empirique ASMO-SCF-CI a été appliquée à l'étude de la structure électronique et des spectres d'absorption U.V. de l'anion 4-azapentalenil, du 4,8-diazapentalene et de composés aza-dérivés apparentés. L'accord entre les énergies de transition observées et calculées est, dans l'ensemble, satisfaisant. La réactivité chimique et l'attribution des bandes observées ont été discutées.

In a previous paper [2], (subsequently referred to as paper I), we have reported the results of a theoretical investigation on the π -electronic structure and ultraviolet absorption spectra of indolizine, (i.e., the prototype of the fused 6/5 azaaromatic ring systems with one bridgehead nitrogen atom and a ten π -electron structure), and of a wide range of its aza-derivatives. The approach used was the PPP approximation of the SCFMO method developed by Roothaan [11], supplemented by the inclusion of interaction between all the singlet mono-excited configurations. Now, we give the results of a similar analysis carried out on some representative fused 5/5 azaaromatic ring systems having one or two bridgehead nitrogen atoms and a ten π -electron structure. These compounds are isosteric and isoelectronic with pentalene dianion, whose stable existence and aromatic character are well recognized [12]. Since the systematic names of these compounds are often unpractical, the simple name of azapentalenes, together with the atom numbering shown in Fig. 1 a, has been used for referring to them.

The first member of this class of compounds with only one bridgehead nitrogen atom and no extra-heteroatoms is an anionic heteroaromatic system bearing the "extra" negative charge spread over the π -framework, i.e. the 4-azapentalenyl anion, shown in Fig. 1 b, recently synthesized by Okamura and Katz [6]. The prototype of azapentalenes having two bridgehead and no extra-nitrogen atoms is the 4,8-diazapentalene, first prepared by Solomons and Fowler [14]. This

compound is referred to as a mesoionic molecule, because it can be satisfactorily represented only as a hybrid of several dipolar resonance structures, one of which is reported in Fig. 1c. Also the other azapentalenes having two bridgehead nitrogen atoms belong to the class of mesoionic compounds.

The molecules dealt with here are the 4-azapentalenyl anion, 4,8-diazapentalene, and the mono- and di-azaderivatives of 4,8-diazapentalene having only one non-bridgehead nitrogen atom in each ring. Simple calculations of Hückel MO-type have been already made for a few of these molecules [1, 6, 15], and only one mole-

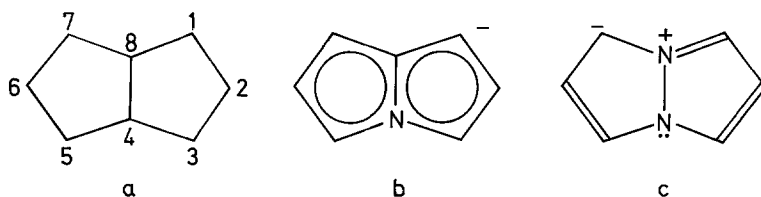


Fig. 1. a Atom numbering; b 4-azapentalenyl anion; c 4,8-diazapentalene

cule, namely 1,4,5,8-tetraazapentalene, has been previously examined through a refined SCFMO-CI method [8]. However, owing to the different choice of geometry, integrals and extension of the CI treatment, and for the purpose of correlating results obtained for several related molecules by using the same parametrization, we have also recalculated the latter molecule.

Details of the Calculation and Results

The electronic structures have been determined in the MO-LCAO scheme, employing the semiempirical SCF-MO method proposed by Pariser-Parr [9] and Pople [10]. The electronic transition energies and oscillator strengths have been calculated by a CI treatment extended to all the singlet monoexcited electronic configurations. All electronic repulsion integrals have been treated semiempirically. The one-center repulsion integrals have been estimated from atomic valence state data: $\gamma(C^+C^+) = 9.87$ eV, $\gamma(N^+N^+) = 11.19$ eV, $\gamma(N^{++}N^{++}) = 11.07$ eV [3]. The Mataga-Nishimoto [4] and Ohno [5] approximation has been used to determine the values of two-center electron repulsion integrals. For the resonance integrals, the relevant values in the molecules of benzene, $\beta(CC) = -2.39$ eV [9], pyridine, $\beta(CN) = -2.576$ eV [9], and *s*-tetrazine, $\beta(NN) = -2.35$ eV [7], have been adopted. The values given by Skinner-Pritchard [13] have been used for the valence state ionization potentials: $I(C^+) = 11.54$ eV, $I(N^+) = 14.32$ eV, and $I(N^{++}) = 11.95$ eV. The determination of molecular structure has not yet been done for any of the compounds studied in the present work; thus, all the molecules have been assumed to have two regular pentagons with the bond distance of 1.40 Å.

All the calculations have been carried out by a Fortran program coded for an IBM 7044 computer.

Electronic charge densities and bond orders are summarized in Tab. 1 and 2, respectively. The first six singlet excitation energies, oscillator strengths and weight of major contributing electronic configurations (weight greater than 10%) are assembled in Tab. 3.

Table 1. *Electron densities*

Compound	1	2	3	4	5	6	7	8
4-azapentalenyl anion	1.270	1.088	1.391	1.387	1.391	1.088	1.270	1.114
4,8-diazapentalene	1.281	0.997	1.281	1.440	1.281	0.997	1.281	1.440
1,4,8-triazapentalene	1.509	0.854	1.327	1.423	1.240	1.023	1.220	1.404
2,4,8-triazapentalene	1.144	1.236	1.144	1.446	1.303	0.978	1.303	1.446
1,4,5,8-tetraazapentalene	1.477	0.873	1.273	1.377	1.477	0.873	1.273	1.377
1,4,6,8-tetraazapentalene	1.526	0.837	1.345	1.430	1.102	1.261	1.083	1.414
1,4,7,8-tetraazapentalene	1.461	0.871	1.293	1.395	1.293	0.871	1.461	1.353
2,4,6,8-tetraazapentalene	1.165	1.218	1.165	1.452	1.165	1.218	1.165	1.452

Table 2. *Bond orders*

Compound	1-2	2-3	3-4	4-5	5-6	6-7	7-8	8-4	8-1
4-azapentalenyl anion	0.690	0.646	0.453	0.453	0.646	0.690	0.527	0.542	0.527
4,8-diazapentalene	0.680	0.680	0.482	0.482	0.680	0.680	0.482	0.426	0.482
1,4,8-triazapentalene	0.634	0.710	0.436	0.519	0.678	0.677	0.540	0.459	0.388
2,4,8-triazapentalene	0.659	0.659	0.531	0.459	0.682	0.682	0.459	0.403	0.531
1,4,5,8-tetraazapentalene	0.640	0.701	0.496	0.426	0.640	0.701	0.496	0.505	0.426
1,4,6,8-tetraazapentalene	0.631	0.712	0.415	0.570	0.652	0.652	0.589	0.430	0.366
1,4,7,8-tetraazapentalene	0.643	0.701	0.476	0.476	0.701	0.643	0.445	0.508	0.445
2,4,6,8-tetraazapentalene	0.664	0.664	0.507	0.507	0.664	0.664	0.507	0.385	0.507

Discussion

Chemical Reactivity

It is well known that prediction for the chemical reactivity may be based upon ground state electronic charges. So far, out of all the carbon positions in 4-azapentalenyl anion the electron density value is highest for positions 3 and 5: hence the molecule is expected to be readily susceptible to cationoid attack in these positions, in agreement with the experimental results [6]. For 4,8-diazapentalene the charge density values suggest that electrophilic substitution should occur on any carbon atom directly bonded to a nitrogen atom. Since there are no carbon atoms with very low electron density, anionoid substitution is expected not to occur easily for these two molecules.

Protonation is predicted to take place on the non-bridgehead nitrogen atom in 1,4,8-triazapentalene and on carbon atoms at positions 5 and 7 in 2,4,8-triazapentalene. The carbon atom at position 2 in 1,4,8-triazapentalene should be the most reactive one in nucleophilic reactions.

In the four tetraazapentalenes considered herein, protonation should occur on either of the two non-bridgehead nitrogen atoms, with the exception of 1,4,6,8-tetraazapentalene, for which the nitrogen atom at position 1 should be more reactive than that at position 6. Nucleophilic substitution is predicted to take place at positions 2 and 6 in 1,4,5,8- and 1,4,7,8-tetraazapentalene and at position 2 in 1,4,6,8-tetraazapentalene.

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

Compound	Transition	Energy (eV)	f	Weight of configurations
4-azapentalenyl anion	$^1A_1 \rightarrow ^1A_1$	4.694	0.250	5 \rightarrow 6 (82), 4 \rightarrow 7 (10)
	$^1A_1 \rightarrow ^1B_1$	4.910	0.040	5 \rightarrow 7 (66), 4 \rightarrow 6 (26)
	$^1A_1 \rightarrow ^1B_1$	5.865	0.037	5 \rightarrow 8 (65), 5 \rightarrow 7 (17)
	$^1A_1 \rightarrow ^1A_1$	6.630	0.266	4 \rightarrow 7 (63), 2 \rightarrow 6 (12)
	$^1A_1 \rightarrow ^1B_1$	6.715	1.397	4 \rightarrow 6 (61), 5 \rightarrow 8 (22), 5 \rightarrow 7 (15)
	$^1A_1 \rightarrow ^1A_1$	7.442	0.411	4 \rightarrow 8 (60), 5 \rightarrow 6 (13), 4 \rightarrow 7 (12)
4,8-diazapentalene	$^1A_g \rightarrow ^1B_{3u}$	4.288	0.280	5 \rightarrow 6 (87)
	$^1A_g \rightarrow ^1B_{2u}$	4.671	0.091	5 \rightarrow 7 (69), 4 \rightarrow 6 (29)
	$^1A_g \rightarrow ^1B_{1g}$	5.860	0	5 \rightarrow 8 (97)
	$^1A_g \rightarrow ^1B_{2u}$	6.695	1.021	4 \rightarrow 6 (70), 5 \rightarrow 7 (30)
	$^1A_g \rightarrow ^1B_{3u}$	6.885	1.318	4 \rightarrow 7 (79), 5 \rightarrow 6 (13)
	$^1A_g \rightarrow ^1A_g$	6.918	0	4 \rightarrow 8 (55), 3 \rightarrow 7 (23), 2 \rightarrow 6 (21)
1,4,8-triazapentalene	$^1A' \rightarrow ^1A'$	4.459	0.291	5 \rightarrow 6 (88)
		4.876	0.040	5 \rightarrow 7 (59), 4 \rightarrow 6 (37)
		6.113	0.018	5 \rightarrow 8 (93)
		6.743	0.852	4 \rightarrow 6 (46), 5 \rightarrow 7 (30)
		6.895	0.866	4 \rightarrow 7 (47), 4 \rightarrow 6 (12), 4 \rightarrow 8 (11)
		7.211	0.534	4 \rightarrow 8 (34), 4 \rightarrow 7 (26), 2 \rightarrow 6 (15)
2,4,8-triazapentalene	$^1A_1 \rightarrow ^1A_1$	4.248	0.319	5 \rightarrow 6 (89)
	$^1A_1 \rightarrow ^1B_1$	4.566	0.207	5 \rightarrow 7 (81), 4 \rightarrow 6 (17)
	$^1A_1 \rightarrow ^1B_1$	5.679	0.000	5 \rightarrow 8 (97)
	$^1A_1 \rightarrow ^1B_1$	6.911	0.825	4 \rightarrow 6 (81), 5 \rightarrow 7 (18)
	$^1A_1 \rightarrow ^1A_1$	6.990	0.718	4 \rightarrow 7 (43), 4 \rightarrow 8 (34)
	$^1A_1 \rightarrow ^1A_1$	7.431	0.576	4 \rightarrow 7 (36), 2 \rightarrow 6 (22), 4 \rightarrow 8 (18), 3 \rightarrow 7 (16)
1,4,5,8-tetraazapentalene	$^1A_g \rightarrow ^1B_u$	4.483	0.359	5 \rightarrow 6 (91)
	$^1A_g \rightarrow ^1B_u$	5.041	0.023	5 \rightarrow 7 (55), 4 \rightarrow 6 (41)
	$^1A_g \rightarrow ^1A_g$	6.234	0	5 \rightarrow 8 (91)
	$^1A_g \rightarrow ^1B_u$	7.023	1.141	4 \rightarrow 6 (55), 5 \rightarrow 7 (41)
	$^1A_g \rightarrow ^1A_g$	7.143	0	4 \rightarrow 8 (37), 3 \rightarrow 6 (30), 2 \rightarrow 6 (20)
	$^1A_g \rightarrow ^1B_u$	7.317	1.121	4 \rightarrow 7 (81)
1,4,6,8-tetraazapentalene	$^1A' \rightarrow ^1A'$	4.458	0.336	5 \rightarrow 6 (90)
		4.851	0.147	5 \rightarrow 7 (73), 4 \rightarrow 6 (22)
		5.953	0.015	5 \rightarrow 8 (91)
		6.975	0.756	4 \rightarrow 6 (68), 5 \rightarrow 7 (19)
		7.318	0.880	4 \rightarrow 7 (51), 4 \rightarrow 8 (26)
		7.419	0.368	4 \rightarrow 7 (28), 4 \rightarrow 8 (21), 3 \rightarrow 6 (16), 2 \rightarrow 6 (12)
1,4,7,8-tetraazapentalene	$^1A_1 \rightarrow ^1B_1$	4.631	0.273	5 \rightarrow 6 (88)
	$^1A_1 \rightarrow ^1A_1$	4.969	0.005	4 \rightarrow 6 (50), 5 \rightarrow 7 (47)
	$^1A_1 \rightarrow ^1B_1$	6.310	0.201	5 \rightarrow 8 (76), 4 \rightarrow 7 (15)
	$^1A_1 \rightarrow ^1A_1$	6.727	0.643	4 \rightarrow 6 (31), 5 \rightarrow 7 (31), 4 \rightarrow 8 (20), 2 \rightarrow 6 (13)
	$^1A_1 \rightarrow ^1B_1$	7.070	0.913	4 \rightarrow 7 (65), 5 \rightarrow 8 (19)
	$^1A_1 \rightarrow ^1A_1$	7.180	0.422	4 \rightarrow 8 (38), 5 \rightarrow 7 (21), 4 \rightarrow 6 (17), 2 \rightarrow 6 (16)
2,4,6,8-tetraazapentalene	$^1A_g \rightarrow ^1B_{3u}$	4.184	0.357	5 \rightarrow 6 (91)
	$^1A_g \rightarrow ^1B_{2u}$	4.433	0.331	5 \rightarrow 7 (88)
	$^1A_g \rightarrow ^1B_{1g}$	5.472	0	5 \rightarrow 8 (98)
	$^1A_g \rightarrow ^1B_{2u}$	7.427	0.724	4 \rightarrow 6 (86), 5 \rightarrow 7 (11)
	$^1A_g \rightarrow ^1A_g$	7.542	0	3 \rightarrow 6 (43), 4 \rightarrow 8 (35), 2 \rightarrow 7 (21)
	$^1A_g \rightarrow ^1B_{3u}$	7.641	1.369	4 \rightarrow 7 (83)

Electronic Spectra

The ultraviolet absorption spectrum of the 4-azapentalenyl anion exhibits a band with the maximum at $295\text{ m}\mu$ or 4.20 eV ($\epsilon = 9,600$) and a shoulder at approximately $210\text{ m}\mu$ or 5.90 eV ($\epsilon = 20,000$) [6]. In accord with the results of the present calculations the first band is assigned to the transition ${}^1A_1 \rightarrow {}^1A_1$ of 4.69 eV , associated essentially with the excitation of one electron from the top bonding to the lowest antibonding molecular orbital, i.e. the transition $5 \rightarrow 6$. The shoulder can be represented by the transition ${}^1A_1 \rightarrow {}^1B_1$ of 5.86 eV , to which the main contribution is the configuration characterized by the jump of one electron to the top unoccupied from the highest occupied molecular orbital, i.e. the excitation $5 \rightarrow 8$. Undoubtedly, the discrepancy between the calculated and observed transition energy of the first band could be reduced by properly adjusting the resonance integrals. However, we have preferred to use for all the present molecules the standard values already adopted in the case of indolizines [2].

For 4,8-diazapentalene Solomons and Voigt [15] observed a band with the maximum at $284\text{ m}\mu$ or 4.36 eV . We can assign this band to the transition ${}^1A_g \rightarrow {}^1B_{3u}$ of 4.29 eV , predominantly due to the excitation $5 \rightarrow 6$.

On the basis of the present results, a strong-intensity band is expected to be shown by 4-azapentalenyl anion and 4,8-diazapentalene at approximately $185\text{ m}\mu$.

The present results also predict an absorption band of weak intensity, (owing to the low oscillator strength value), in the region between 250 and $270\text{ m}\mu$. This band, not observed experimentally, may be hidden in the strong first band; it should be associated with a mixing of transitions $5 \rightarrow 7$ and $4 \rightarrow 6$.

The ultraviolet spectrum of 1,4,5,8-tetraazapentalene was investigated by Paoloni *et al.* [8]. They assigned the 4.5 eV observed band to a $\pi \rightarrow \pi^*$ transition and the $\sim 5\text{ eV}$ observed band to a $n \rightarrow \pi^*$ transition, with the possibility that a second $\pi \rightarrow \pi^*$ transition may overlap the $n \rightarrow \pi^*$ band. The best energy values they calculated for these bands through a limited CI treatment, (restricted to the four electronic configurations built out of the two highest occupied molecular orbitals and the two lowest empty molecular orbitals), are 4.83 eV and 5.46 eV , respectively. In accordance with our calculations, the first band is associated with the transition ${}^1A_g \rightarrow {}^1B_u$ of 4.48 eV , essentially ascribed to excitation $5 \rightarrow 6$; and the second observed band may be attributed to the transition ${}^1A_g \rightarrow B_u$ of 5.04 eV , due to a combination of excitations $5 \rightarrow 7$ and $4 \rightarrow 6$. (As compared with the previous calculations, a considerable improvement is found in the calculated transition energies.)

The present calculations predict no symmetry-allowed absorption band in the region about $200\text{--}220\text{ m}\mu$ for 4,8-diaza- and 1,4,5,8-tetraaza-pentalene: this result is, however, consistent with the observed spectra.

On the basis of our calculations, the spectral patterns of the other azapentalenes, (for which no experimental spectral data are yet available for suitable comparison), are expected to be quite similar both in wavelengths and intensities to those of the molecules discussed above.

Finally, it must be pointed out that the first three excitations calculated for the azapentalenes closely correspond in their natures to the respective transitions in the previously studied indolizines [2].

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