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LCAO-MO-SCF-CI Semi-Empirical π-Electron Calculations on Heteroaromatic Systems
Part III. Azines*

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Semi-empirical π-electron calculations using a modification of the Pariser-Parr-Pople method have been carried out on the mono-, di-, tri- and tetrazines. Core integrals have been defined so that they are essentially independent of molecular geometry and orthogonalized Slater orbitals are used. In the configuration interaction treatment of the problem the configurations considered are those arising from single electron excitations between the two highest occupied and the two lowest unoccupied molecular orbitals. There is in general good agreement between calculated and observed electronic spectra, and calculated values for molecular ionization potentials agree very well with experimental values.

Für Mono-, Di-, Tri- und Tetrazine wurden mit einer modifizierten PPP-Näherung halbempirische π-Elektronenrechnungen durchgeführt. Die Rumpfintegrale wurden so gewählt, daß sie von der Molekülgeometrie unabhängig sind; es wurden orthogonalisierte Slaterorbitale benutzt. Bei der Konfigurationswechselwirkung wurden Einelektronenübergänge zwischen den beiden höchsten besetzten und den beiden niedrigsten unbesetzten MOs betrachtet. Die berechneten Werte stimmen mit den experimentellen Daten gut überein.

Les mono-, di-, tri- et tétrazines ont été calculées à l'aide d'une variante de la méthode de Pariser-Parr-Pople pour les électrons π. Des intégrales de coeur essentiellement indépendantes de la géométrie moléculaire ont été définies et des orbitales de Slater orthogonalisées sont utilisées. Les configurations utilisées pour l'interaction de configurations sont celles résultant des monoexcitations entre les deux plus hautes orbitales occupées et les deux plus basses libres. Dans l'ensemble l'accord entre spectres électroniques calculés et observés est bon, de même que l'accord entre valeurs théoriques et expérimentales des potentiels d'ionisation moléculaires.

Introduction

In the first two papers of this series [28, 29] a modified Pariser-Parr-Pople method has been used to calculate the electronic properties of heteroaromatic systems, namely, hydroxy aromatic compounds and aromatic amines, where the heteroatom donates two π-electrons to the aromatic system. Agreement between calculated and experimental values for transition energies, oscillator strengths and molecular ionization potentials has been good. The admixture of doubly excited configurations with singly excited configurations between the two highest occupied and the two lowest unoccupied molecular orbitals has considerably improved the values for oscillator strengths.

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In this paper results are presented for the case where the heteroatom donates one π-electron to the aromatic system, namely, the azines. Most of the semi-empirical SCF calculations on the azines have been limited to pyridine, the diazines and the symmetrical tri-, and tetrazines [5, 11–16, 18, 19, 21–25]. Recently, Favini *et al.* [7, 8] have predicted the electronic spectra of the other tri-, and tetrazines. In the present investigation, the electronic properties of all mono-, di-, tri-, and tetrazines have been calculated. Agreement with experiment is good. Only results using the abovementioned singly excited configurations have been included since the use of doubly excited configurations did not improve any of the calculated values.

Method

The following geometry for the bond lengths of the azines has been adopted: C–C = 1.39 Å, C–N = 1.34 Å, and N–N = 1.33 Å. Each molecule was taken to be planar and reasonable bond angles have been chosen to give the appropriate dimensions.

Valence state data and effective nuclear charges which have been used in the present calculations are given in the first two papers of this series. Since nitrogen donates only one π-electron to the aromatic system in the azines, in contrast to the aromatic amines where it donates two π-electrons, only the first ionization potential and electron affinity have been used.

Overlap has been included in the present calculations and the zero differential overlap approximation of Pariser and Parr was adopted only after orthogonalization of the orbitals. The formulas used for calculating overlap are conventional ones [17].

Adams and Miller [1] have used a new method for evaluating core integrals that render them essentially independent of geometry. In the present calculations this method has been modified to accommodate the heteroatom and equations for the core integrals are given in the first paper of this series. The method of evaluating the various electronic properties listed in the tables has also been described in the first paper of this series.

The procedure used for determining the appropriate values of H^o_{ij} is similar to that used for the heteroaromatic systems studied in Parts I and II of this series [28, 29], and the detailed method is described in Part I [28]. For the azines, pyridine was used as the calibration molecule to evaluate elements between carbon and nitrogen. To determine the three different values for H^o_{ij} between nitrogen atoms, pyridazine, pyrimidine, and pyrazine were used, and the manner in which these elements were determined is similar to that described for the three dihydroxybenzenes. Values for H^o_{ij} are listed in Table 1.

Table 1. *Values for the empirical parameter* H^o_{ij}

	Value of H^o_{ij} number of bonds between atoms *i* and *j*			
atoms *i* and *j*	0	1	2	3
carbon-carbon	−11.597	−4.322	−0.856	−0.264
carbon-nitrogen		−4.437	−0.738	−0.189
nitrogen-nitrogen	−14.171	−4.338	−0.627	−0.127

A limited configuration interaction involving single electron excitations between the two highest occupied and the two lowest unoccupied molecular orbitals has been introduced. The results for the incorporation of double electron excitations have not been included since results were not improved as they were in the case of the hydroxy aromatic compounds and aromatic amines where inclusion of double electron excitations led to better values for oscillator strengths. The time required to carry out all calculations on the azines when only single electron excitations were considered was about 3 minutes per molecule using a G-20 Control Data Corporation digital computer.

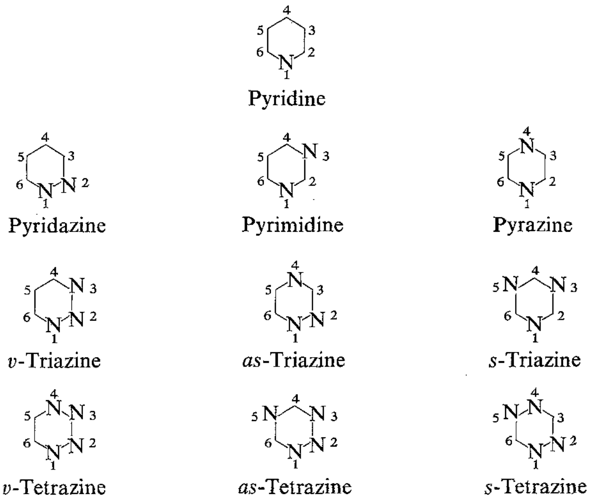

Fig. 1. Numbering scheme for azines

Results and Discussion

The first four calculated singlet-singlet and triplet-triplet $\pi-\pi^*$ electronic transition energies and oscillator strengths are given in Table 2 together with available experimental data. For the singlet states agreement between calculated and observed values is in general good, being better for transition energies than for oscillator strengths. Where experimental data are available for the first triplet state, agreement of the corresponding calculated value usually seems better when compared to the second triplet excited state rather than the first.

Molecular ionization potentials are listed in Table 3, and experimental values are included where possible. Calculated values have often been found to agree poorly with experiment. For example, Lindner *et al.* [12] have carried out semi-empirical calculations involving both π and non-bonding electrons on pyridine, the three diazines and *s*-triazine, where the average deviation for molecular ionization potentials was 4.43 eV. In the present investigation results are in good agreement with experiment. The average deviation is only 0.34 eV and the maximum deviation is 0.87 eV (for *s*-triazine).

Localized atom charges are listed in Table 4 and values for the π-contributions to the dipole moment are given in Table 5. With respect to nucleophilic substitution, the 2 and 4 positions are more reactive than the 3 position in pyridine,

Table 2. *Transition energies (in eV) and oscillator strengths**

Molecule	Singlet states		Triplet states	
	Calculated	Experimental	Calculated	Experimental
Pyridine	4.95 (0.048)	4.95[a] (0.04)[a]	3.21	3.68[d]
	6.25 (0.027)	6.26[b] (0.122)[c]	3.82 (0.004)	
	7.16 (1.136)	7.07[b] (0.66[c], 1.30[b])	4.07 (0.001)	
	7.17 (1.238)		5.21 (0.004)	
Pyridazine	5.04 (0.038)	5.04[c, **] (0.018)	3.26	
	6.27 (0.003)	6.52 Sh	3.79 (0.003)	
	7.07 (1.097)	6.89 (0.150)	4.07 (0.008)	
	7.29 (1.270)		5.10 (0.002)	
Pyrimidine	5.06 (0.055)	5.07[c, **] (0.024)	3.36	
	6.38 (0.062)	6.61 Sh	3.85 (0.000)	
	7.25 (1.073)	7.21	3.30 (0.012)	
	7.39 (1.172)		5.40 (0.000)	
Pyrazine	4.86 (0.149)	4.77[a] (0.084[b], 0.130[c])	3.21	3.25[f], 3.35[e]
	6.33 (1.119)	6.38[b] (0.119)[b]	3.37 (0.000)	
	7.46 (1.140)	>7.2[b]	4.24 (0.000)	
	7.52 (1.014)		5.91 (0.000)	
v-Triazine	5.18 (0.001)		3.30	
	6.28 (0.065)		4.08 (0.004)	
	7.27 (1.253)		4.19 (0.012)	
	7.30 (1.072)		4.85 (0.000)	
as-Triazine	5.02 (0.126)		3.33	
	6.45 (0.066)		3.51 (0.000)	
	7.34 (0.995)		4.28 (0.007)	
	7.67 (1.197)		5.81 (0.000)	
s-Triazine	5.29 (0.000)	5.29[a], 5.58[c] (~ 0)	3.60	4.59[h]
	6.66 (0.000)	6.92[g], >7.2[c]	4.44 (0.010)	
	7.42 (1.133)		4.44 (0.010)	
	7.42 (1.134)		5.29 (0.000)	
v-Tetrazine	5.17 (0.047)		3.32	
	6.41 (0.072)		3.83 (0.003)	
	7.43 (1.104)		4.19 (0.006)	
	7.51 (1.178)		5.31 (0.005)	
as-Tetrazine	5.22 (0.048)		3.46	
	6.63 (0.002)		3.95 (0.000)	
	7.48 (1.138)		4.37 (0.016)	
	7.52 (1.146)		5.51 (0.000)	
s-Tetrazine	5.01 (0.153)	4.92[c] (0.05)[c]	3.30	
	6.60 (0.042)		3.35 (0.000)	
	7.42 (1.060)		4.32 (0.000)	
	7.91 (1.148)		6.09 (0.000)	

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* Values for oscillator strengths are in parantheses.

** All experimental values for this molecule are from reference 8.

[a] See Ref. 9.
[b] See Ref. 26.
[c] See Ref. 8.
[d] See Ref. 6.
[e] See Ref. 21.
[f] See Ref. 3.
[g] See Ref. 4.
[h] See Ref. 10.

Table 3. *Molecular ionization potentials (in eV)*

Molecule	Calculated	Observed[a]
Pyridine	9.67	9.76
Pyridazine	10.20	9.86
Pyrimidine	10.06	9.91
Pyrazine	9.75	10.01
v-Triazine	10.61	—
as-Triazine	10.32	—
s-Triazine	10.94	10.07
v-Tetrazine	10.88	—
as-Tetrazine	11.07	—
s-Tetrazine	10.75	—

[a] See Refs. 2 and 20.

Table 4. *Localized atom charges* (q_i)[a]

Molecule	q_1	q_2	q_3	q_4	q_5	q_6
Pyridine	1.210	0.903	1.011	0.961	1.011	0.903
Pyridazine	1.123	1.123	0.909	0.969	0.969	0.909
Pyrimidine	1.220	0.811	1.220	0.864	1.022	0.864
Pyrazine	1.174	0.913	0.913	1.174	0.913	0.913
v-Triazine	1.127	1.029	1.127	0.871	0.975	0.871
as-Triazine	1.084	1.133	0.818	1.183	0.864	0.919
s-Triazine	1.231	0.769	1.231	0.769	1.231	0.769
v-Tetrazine	1.093	1.037	1.037	1.093	0.870	0.870
as-Tetrazine	1.137	0.987	1.137	0.774	1.191	0.774
s-Tetrazine	1.088	1.088	0.826	1.088	1.088	0.826

[a] See Fig. 1 for numbering scheme.

Table 5. *Calculated π-dipole moments (in Debyes)*

Molecule	π-electron dipole moment
Pyridine	0.95
Pyridazine	1.79
Pyrimidine	0.99
Pyrazine	0.00
v-Triazine	1.99
as-Triazine	1.19
s-Triazine	0.00
v-Tetrazine	1.82
as-Tetrazine	1.01
s-Tetrazine	0.00

and more reactive than the 5 position in pyrimidine [27]. For *as*-triazine the 5 and 3 positions are more reactive than the 6 position [27]. (See Fig. 1 for numbering scheme.) The values for the atom charges of these azines listed in Table 4 are in line with this order of reactivity.

Nonlocalized atom and bond populations are included in Table 6. There is approximately 0.2 electron in each bond and on the average about 0.8 electron at each atom. Peacock [24] has calculated this type of charge distribution for

Table 6. *Nonlocalized atom and bond charges* (q_{ij})[a]

Molecule												
Pyridine	q_{11}	q_{22}	q_{33}	q_{44}	q_{12}	q_{23}	q_{34}					
	1.004	0.689	0.780	0.725	0.211	0.244	0.239					
Pyridazine	q_{11}	q_{33}	q_{44}	q_{12}	q_{23}	q_{34}	q_{45}					
	0.932	0.695	0.732	0.173	0.224	0.231	0.250					
Pyrimidine	q_{11}	q_{22}	q_{44}	q_{55}	q_{12}	q_{34}	q_{45}					
	1.015	0.614	0.644	0.789	0.212	0.209	0.243					
Pyrazine	q_{11}	q_{22}	q_{12}	q_{23}								
	0.964	0.700	0.212	0.242								
v-Triazine	q_{11}	q_{22}	q_{44}	q_{55}	q_{12}	q_{34}	q_{45}					
	0.936	0.854	0.649	0.741	0.184	0.212	0.240					
as-Triazine	q_{11}	q_{22}	q_{33}	q_{44}	q_{55}	q_{66}	q_{12}	q_{23}	q_{34}	q_{45}	q_{56}	q_{16}
	0.888	0.943	0.622	0.975	0.646	0.708	0.174	0.221	0.204	0.219	0.228	0.226
s-Triazine	q_{11}	q_{22}	q_{12}									
	1.028	0.564	0.210									
v-Tetrazine	q_{11}	q_{22}	q_{55}	q_{12}	q_{23}	q_{45}	q_{56}					
	0.896	0.862	0.653	0.176	0.191	0.222	0.225					
as-Tetrazine	q_{11}	q_{22}	q_{44}	q_{55}	q_{12}	q_{34}	q_{45}					
	0.947	0.806	0.570	0.984	0.185	0.209	0.210					
s-Tetrazine	q_{11}	q_{33}	q_{12}	q_{23}								
	0.894	0.628	0.182	0.213								

[a] See Fig. 1 for numbering scheme.

pyridine, the three diazines and *s*-triazine with values for atom and bond populations which are similar to ours.

A disadvantage of this method is that one must have a set of the parameters listed in Table 1 or obtain them through an iteration process. Furthermore, the parameters listed in Table 1 cannot be transferred as such to molecules of a different ring size. Preliminary studies on pyrrole indicate that these parameters can be used provided correction is made for the variation in interatomic distance in going from a six-membered ring system to a five-membered ring system.

Conclusion

A consistent and reliable method has been developed for predicting the electronic properties of heteroaromatic systems. In the first two papers in this series, the method has been successful for the case where the heteroatom donates two π-electrons to the aromatic system, and in this investigation, for the case where the heteroatom donates one π-electron to the aromatic system. Calculated values for transition energies, oscillator strengths and molecular ionization potentials agree well with experimental values, and hence, the applicability of this method for predicting electronic properties of heteroaromatic systems has been demonstrated.

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