ELECTRONIC STRUCTURE AND SPECTRA OF ORGANIC MOLECULES. PART XVI*. AMINE-IMINE TAUTOMERISM IN AZINES SUBSTITUTED BY AMINO GROUPS**

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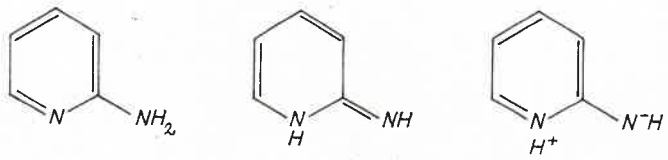
Tautomerism of pyridine and diazines substituted by amino groups is discussed. The Pariser-Parr-Pople type of calculations are carried out for both amine and imine tautomers of the molecules. In general, calculated singlet-singlet transition energies for both kinds of tautomers agree well with experimental data.

1. Introduction

The amino groups are known as potentially tautomeric substituents. These groups are, however, considerably less acidic than both the hydroxyl and mercapto ones, and the tendency of the amino N-heteroaromatic compounds to exist in tautomeric imine forms is slight in many cases.

Pyridine and diazines substituted by the NH_2 group are represented rather in the amine (*Ia*) forms than in the imine (*Ib*) ones, and this conclusion has been based on physico-



Ia *Ib* *Ic*

-chemical studies (ultraviolet, infrared or nuclear magnetic resonance spectroscopy, basicity measurements, *X*-ray crystallographic studies, *etc.*) (Katritzky and Lagowski 1963, Angyal

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and Angyal 1952, Brown *et al.* 1955, Anderson and Seegar 1949, Cheeseman 1960). For example, Angyal and Angyal (1952) have measured the acidity constants of the conjugate of the amine and their ring-substituted N-methyl derivatives, and concluded that the amine forms dominate in aqueous solutions with the factors $2 \cdot 10^5$ and $2 \cdot 10^3$ for 2- and 4-aminopyridine, respectively. Similar measurements for 2- and 5-aminopyridine indicate that the amine forms are more stable than the imine ones by factors of about 10^6 (Brown *et al.* 1955). It would be very interesting to study the tautomeric equilibrium constants of these molecules by semiempirical quantum-mechanical methods; π-electron calculations, however, have limited significance for the elucidation of the most probable tautomeric forms of molecules. Fortunately, there are strong arguments that the all-valence-electron calculations may be able to contribute to the elucidation of the tautomerism problems[1]. Calculations of this sort for the pyridines and pyrimidines are in progress at our laboratory.

As we mentioned above, the π-electron calculations are not definitive in investigations of the tautomerism problem. However, these calculations (particularly the Pariser-Parr-Pople method) are suitable for predicting spectroscopic properties (transition energies, oscillator strengths) of different tautomeric forms (neutral and ionic ones) of molecules. It is the purpose of the present communication to apply PPP type calculations to interpret electronic absorption spectra of the amine and imine tautomers of pyridine and diazines (pyridazine, pyrimidine, pyrazine) substituted by the NH_2 group.

2. Calculations

The Pariser-Parr-Pople method with the ZDO approximation was adopted. For details regarding the choice of the semiempirical parameters in the calculation procedure the reader is referred to Part XIV (Kwiatkowski 1971b). The following values (in eV) of the core integrals W_p and one-center two-electron γ_{pp} integrals for nitrogen in the amino ($-NH_2$) and imine ($=NH$) groups were used — for $-NH_2$ (Kwiatkowski 1966): $W_p = -24.65$, $\gamma_{pp} = 14.5$; $=NH$ (using the valence state data, see Hinze and Jaffé 1962): $W_p = -14.11$, $\gamma_{pp} = 11.97$. The ring structures and the corresponding resonance integrals β_{pq} are the same as those in Part XIV. In the case of the external bonds C—NH_2 ($r = 1.36$ Å) and C=NH ($r = 1.3$ Å) the values of -2.2 and -2.5 eV for the corresponding resonance integrals were used.

[1] It is worthwhile to note that Konishi *et al.* (1970), using the semiempirical SCF method for valence electrons, have recently calculated the total energies for both amine and imine tautomers of 2-, 3- and 4-NH_2-pyridine (*cf.* also the simple Hückel π-electron calculations by Polansky and Grassberger (1963)). The amine forms are shown by the calculations to be the predominant tautomers, but the order of magnitude of the total energy differences indicate that the imine tautomer of 4-NH_2-pyridine is more unstable than the corresponding tautomer of 2-NH_2-pyridine, contrary to experimental evidence. This discrepancy between theory and experiment may be presumably ascribed to the assumed molecular geometry of the imine forms (in the paper by Konishi *et al.* (1970) the ring structures of both the amine and imine forms of pyridine isomers were assumed to be equal to that of pyridine). Total energies of molecules, calculated by means of the all-valence-electron methods, are sensitive to the molecular geometry used in calculations (*cf.* Rein 1971).

3. *Results and discussion*

The results of calculations for both the amine and imine tautomers under study are given together with the experimental data in the Table. The experimental transition energies are only known for the amine tautomers of the molecules. In the case of the imine form, the experimental data for the corresponding N-ring methyl derivatives of the molecules were used as references. Such a comparison may be justified because the replacement of a hydrogen atom in the >NH group by a methyl group only slightly affects its absorption spectrum.

As seen from the figures in the Table I, there is satisfactory agreement between the calculated and experimental transition energies. The differences between experimental and theoretical ΔE values are not greater than 0.2 eV (except in the case of the first transition for 2-aminopyrazine, where it is of the order of 0.3 eV). Since the electronic absorption spectra of the amine forms of molecules (in particular of derivatives of pyridine and pyrimidine) have been discussed theoretically by a number of investigators, the spectra of the molecules will be only compared here with regard to the tautomerism problem.

Both experimental and theoretical results reveal that the amine tautomers absorb in different spectral regions than the corresponding imine ones. The results presented in the Table I show that in all cases the spectra of the imine forms are red shifted in comparison with those of the amine ones.

Regarding the structure of the imine tautomers of azines (*i.e.* the structure in which the hydrogen atom is attached to the ring-nitrogen), we note that Mason (1960) postulated equivalent zwitterionic Ic-like forms for these tautomers. Basing on the experimental and theoretical results (obtained by means of the PPP method), we have shown recently that the lactam and thione forms of monooxo and monomercapto substituted azines, respectively, may be described by the zwitterionic formulae. These tautomers have strongly polarized bonds $>N^+-H$, $C-O^-$ and $C-S^-$. We have performed PPP-type calculations, similar to those in Part XIV (also, Kwiatkowski, to be published), for the zwitterionic structures of the *Ic* type, assuming different values of the core integral W_p for the nitrogen in $-N^-H$ (anion of the amino group). In this way, different degrees of polarization of C—N^-H bond have been indirectly included in our calculations (*cf.* PPP calculations for alkaliamino substituted molecules, Kwiatkowski 1970). Using a W_p value slightly higher than that for the lithiumamino group (Kwiatkowski 1970) one obtains a good agreement between theoretical and experimental singlet-singlet transition energies for the imine tautomers of azines.

Although the π-electron calculations have a limited significance in determination of this type of molecular structure, it may be said in conclusion that the imine tautomers of azines have rather week polarized bonds $>N^+-H$ and $—N^-H$, and it seems purposeless to present imine tautomers in zwitterionic forms. We do not consider the obtained results to be unexpected, because both the ring- and external-nitrogen atoms have similar electronegative properties.

TABLE I

Electronic spectra of the amine and imine tautomers of pyridine and diazines

Theoretical ΔE^1, f^2 eV	Experimental ΔE^1, ε^3 eV	Theoretical ΔE^1, f^2 eV	Experimental ΔE^1, ε^3 eV
2-Aminopyridine		1,2-Dihydro-1-iminopyridine	
4.40 (0.126) 5.48 (0.322) 6.57 (0.445) 6.67 (0.672)	4.2—4.3 (3.8)[4] 5.3—5.4 (9.4)	4.04 (0.241) 5.14 (0.360) 6.41 (0.128) 6.47 (0.443)	3.91 (4.1)[5,6] 4.94 (11.7)
4-Aminopyridine		1,4-Dihydro-1-iminopyridine	
4.61 ($2 \cdot 10^{-5}$) 5.32 (0.312) 6.22 (0.636) 6.51 (0.835)	sh 4.5—4.8 (2.4)[4] 5.1—5.3 (14.0)	4.45 (0.032) 4.56 (0.736) 5.93 (0.111) 6.87 (0.129)	? 4.63 (16.5)[5,6]
3-Aminopyridazine		2,3-Dihydro-3-iminopyridazine	
4.22 (0.100) 5.34 (0.140) 6.22 (0.530) 6.48 (0.340)	4.20 (2.07)[5,7,11] 5.37 (8.08)	3.73 (0.128) 5.06 (0.303) 6.13 (0.808) 6.44 (0.087)	3.80 (1.7)[5,8] 5.08 (7.8)
4-Aminopyridazine		1,4-Dihydro-4-iminopyridazine	
4.49 (0.044) 5.02 (0.229) 5.88 (0.342) 6.72 (0.549)	~4.43 (3.7)[9,11] 4.98 (11.8)	3.95 (0.146) 4.49 (0.585) 6.12 (0.128) 6.72 (0.061)	
2-Aminopyrimidine		1,2-Dihydro-1-iminopyrimidine	
4.45 (0.122) 5.59 (0.425) 6.70 (0.083) 6.81 (0.615)	4.2—4.4 (3.2)[4] 5.5—5.6 (13.0)	3.61 (0.142) 5.34 (0.258) 6.05 (0.361) 6.67 (0.364)	3.59 (2.9)[6,10] 5.25 (15.5)
4-Aminopyrimidine		1,4-Dihydro-4-iminopyrimidine	
4.63 (0.096) 5.49 (0.282) 6.40 (0.558) 6.70 (0.664)	4.5—4.7 (5.2)[4] 5.3—5.44 (18.2)	3.93 (0.079) 4.78 (0.603) 6.14 (0.149) 6.82 (0.307)	~3.94 (0.6)[6,10] 4.90 (16.2)

TABLE I (continued)

Theoretical $\Delta E^1, f^2$ eV	Experimental $\Delta E^1, \varepsilon^3$ eV	Theoretical $\Delta E^1, f^2$ eV	Experimental $\Delta E^1, \varepsilon^3$ eV
		3,4-Dihydro-4-iminopyrimidine	
		3.92 (0.149) 5.03 (0.482) 6.31 (0.232) 6.59 (0.344)	
2-Aminopyrazine		1,2-Dihydro-2-iminopyrazine	
4.21 (0.228) 5.46 (0.347) 6.49 (0.176) 6.95 (0.589)	3.92 (4.96)[9] 5.39 (10.5)	3.65 (0.228) 5.11 (0.324) 6.03 (0.188) 6.62 (0.229)	

We use the *Chemical Abstracts* names of molecules. sh = shoulder.

[1] Theoretical: singlet-singlet transition energy. Experimental: transition energy corresponding to the position of the absorption band maximum. [2] Oscillator strength in parentheses. [3] The values given for ε must be multiplied by 10^3 in order to get molar extinction coefficients. [4] For a compilation of experimental data see Kwiatkowski (1966). [5] In aqueous solution (Mason 1960). [6] Data for 1-methyl derivative. [7] Data for 6-methyl derivative. [8] Data for 2,6-dimethyl derivative. [9] In aqueous solution (Albert 1955). [10] In aqueous solution (Brown *et al.* 1955). [11] Ogata and Kano (1963) obtained measured ΔE values of 4.34, 4.92 and 4.13, 5.30 eV for 3-amino-4-methyl- and 4-amino-6-methylpyridazine, respectively.

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