Semiempirical Calculations Involving π- and σ-Electrons on Some Nitrogencontaining Heterocycles*

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The semiempirical MO-LCAO-SCF theory by Pariser, Parr and Pople in an extension proposed by Ohno is used to calculate $\pi \to \pi^*$ and $n \to \pi^*$ transition energies, lone pair ionization potentials and electric dipole moments for some azines. The results indicate that with the method used it is impossible to take account of both excitations and ionizations from lone pairs with a single set of parameters. The reasons for this failure of the method are discussed.

Mit der PPP-Methode in der Erweiterung von Ohno wurden $\pi \to \pi^*$ und $n \to \pi^*$ Anregungsenergien, Ionisationspotentiale einsamer Paare und Dipolmomente von einigen Azinen berechnet. Es zeigt sich, daß es mit der genannten Methode nicht möglich ist, Ionisationspotentiale und Anregungsenergien mit einem einzigen Parametersatz zu erfassen. Die Gründe dafür werden angegeben.

Nous avons utilisé la théorie semi-empirique de Pariser, Parr et Pople, dans la version de Ohno, pour calculer les énergies des transitions $\pi \to \pi^*$ et $n \to \pi^*$, les potentiels d'ionisation des paires libres et les moments dipolaires de quelques azines. Les résultats indiquent l'impossibilité de tenir compte à la fois avec un seul jeu de paramètres des excitations et des ionisations de paires libres. Les raisons de cet échec de la méthode sont discutées.

1. Introduction

Semiempirical methods to predict $n \to \pi^*$ transition energies have been proposed by, among others, Goodman [9], Anno and Sado [2] and Ohno [22]. Anno and Ohno, both using extensions of the Pariser-Parr method [25, 26, 27], obtained satisfactory results for formaldehyde [1, 22], while the former got much too high $n \to \pi^*$ transition energies for pyrazine and pyridine [2]. For further references and details on the $n \to \pi^*$ theories we refer to survey articles by Sidman [29] and Goodman [10].

The purpose of the present work is to show how Ohno's method works for some N-heterocyclic molecules. We have calculated transition energies for pyridine, pyridazine, pyrimidine, pyrazine and s-triazine. We have also calculated the electric dipole moments. For the σ-electrons we have used the semiempirical method by Del Re [5]. Orgel [24] using another method predicts about the same values for the σ-electron moment.

2. Method

a) Energy calculations

The procedure used in this work is essentially the semiempirical MO-LCAO-SCF method outlined by PARISER, PARR and POPLE [25, 26, 27].

When we neglect penetration integrals and use atomic units throughout we get the following matrix elements for the π-electron part of the effective Hamiltonian:

$$H_{\nu\nu} = \int \varphi_\nu(1)\, \mathscr{H}_{\text{eff}}^{(1)}\, \varphi_\nu(1)\, d\tau_1 = U_\nu + \tfrac{1}{2}\, P_{\nu\nu}\, \gamma_{\nu\nu} + \sum_{\mu \neq \nu} (P_{\mu\mu} - 1)\, \gamma_{\mu\nu} \tag{1}$$

$$H_{\mu\nu} = \int \varphi_\mu(1)\, \mathscr{H}_{\text{eff}}^{(1)}\, \varphi_\nu(1)\, d\tau_1 = \beta_{\mu\nu} - \tfrac{1}{2}\, P_{\mu\nu}\, \gamma_{\mu\nu} \tag{2}$$

where

$$U_\nu = \int \varphi_\nu \left[-\tfrac{1}{2}\, \nabla^2 + V_\nu \right] \varphi_\nu\, d\tau \tag{3}$$

$$P_{\mu\nu} = 2 \sum_i c_{\mu i} \cdot c_{i\nu} \tag{4}$$

the summation index goes over all doubly occupied orbitals.

$$\gamma_{\mu\nu} = (\varphi_\mu\, \varphi_\mu \mid \varphi_\nu\, \varphi_\nu) \tag{5}$$

$$\beta_{\mu\nu} = \int \varphi_\mu(1) \left[-\tfrac{1}{2} \nabla_1^2 + \sum_\mu V_\mu(1) \right] \varphi_\nu(1)\, d\tau_1 . \tag{6}$$

We assume a sp^2-hybrid orbital for the lone pair electron on the nitrogen atom. Using the method outlined, we obtain the equivalent of Eq. (1) for a lone pair n on atom N_1:

$$H_{nn} = U_n + \sum_{\mu \neq N_1} (P_{\mu\mu} - 1)\, \gamma_{\mu n} + (P_{N_1 N_1} - 1)\, (\gamma_{N_1 n} - \tfrac{1}{2}\, \delta_{n N_1}) \tag{7}$$

$$\delta_{n\, N_1} = (\varphi_n\, \varphi_{N_1} \mid \varphi_n\, \varphi_{N_1}) . \tag{8}$$

The various integrals were estimated as follows. For U_ν we used the GOEPPERT-MAYER-SKLAR approximation [7]:

$$U_\nu = -I_\nu$$

where I_ν is the valence state ionization potential of atom ν. β is treated as a semiempirical parameter, we omit $\beta_{\mu\nu}$'s for non-nearest neighbours. For the electron repulsion integrals we used:

$$\gamma_{\nu\nu} = I_\nu - E_\nu \tag{9}$$

where E_ν is the electron affinity for atom ν. For the integrals $\gamma_{\mu\nu}$ OHNO [21] proposed the formula:

$$\gamma_{\mu\nu} = (R_{\mu\nu}^2 + a_{\mu\nu}^2)^{-\tfrac{1}{2}} \tag{10}$$

where

$$a_{\mu\nu}^{-1} = \tfrac{1}{2}\, (\gamma_{\mu\mu} + \gamma_{\nu\nu}) \tag{11}$$

and $R_{\mu\nu}$ is the internuclear distance of atoms μ and ν. OHNO [22] also introduced the approximations

$$\gamma_{n\nu} = \left(\frac{\gamma_{n\nu}}{\gamma_{N_1 \nu}} \right)_{\text{SO}} \times \gamma_{N_1 \nu} \tag{12}$$

$$\delta_{n\, N_1} = \left(\frac{\delta_{n\, N_1}}{\gamma_{N_1 N_1}} \right)_{\text{SO}} \times \gamma_{N_1 N_1} \tag{13}$$

where $\left(\dfrac{\gamma_{n\nu}}{\gamma_{N\nu}}\right)_{SO}$ and $\left(\dfrac{\delta_{nN}}{\gamma_{NN}}\right)_{SO}$ are the integral values calculated by using Slater orbitals.

In the present calculation we neglect the interactions between different lone pairs.

For the singlet and triplet transition energies we get the following expressions:

$$^{1}E(\pi \to \pi^*) = \varepsilon_k - \varepsilon_l - (\psi_k \psi_k \mid \psi_l \psi_l) + 2(\psi_k \psi_l \mid \psi_k \psi_l) \qquad (14)$$

$$^{3}E(\pi \to \pi^*) = \varepsilon_k - \varepsilon_l - (\psi_k \psi_k \mid \psi_l \psi_l) \qquad (15)$$

where ε_k stands for the energy of the unoccupied molecular orbital ψ_k and ε_l for the occupied orbital ψ_l. In calculating $n \to \pi^*$ transitions we also used Eqs. (14) and (15). In this case l stands for the lone pair orbital.

A limited configuration interaction calculation was done for the excited states using the wavefunctions $\psi_{3\to4}$ and $\psi_{2\to5}$ where $\psi_{l\to k}$ is the singlet or triplet configurational wavefunction in which an electron is excited from an occupied molecular orbital ψ_l to an unoccupied orbital ψ_k [28].

b) Dipole moment calculations

The π-electron dipole moment was calculated according to the formula:

$$D_\pi = e \sum_\nu P_{\nu\nu} \cdot R_{\nu 0} \qquad (16)$$

where the index ν runs over all atoms; e is the charge of the electron; $R_{\nu 0}$ is the distance from atom ν to a reference point. The σ-electron moment was calculated using the method by DEL RE [5]. He treats the lone pair electrons as well as the σ-electrons by a semiempirical method. The total electric dipole moment was then taken to be the sum of the π- and σ-moments.

c) Values used in the calculation

The following ionization potentials and electron affinities were used: $I_C = 11.16$ eV, $E_C = 0.03$ eV, $I_N = 14.12$ eV, $E_N = 1.78$ eV and $I_{nN} = 15.09$ eV [12].

The β-values adopted were: $\beta_{CC} = 2.39$ eV [25], $\beta_{CN} = 2.58$ eV [25] and $\beta_{NN} = 3.16$ eV.

For pyrazine [30], pyrimidine, pyridazine and s-triazine we put all angles equal to 120 degrees and $R_{CC} = 1.39$ Å, $R_{CN} = 1.36$ Å (1.35 Å for pyrazine) and $R_{NN} = 1.33$ Å. For pyridine we used the values given in Ref. [30]. ($R_{CN} = 1.34$ Å, $R_{CC} = 1.39$ and 1.40 Å and the angles $117°$, $124°$, $119°$, and $118°$).

3. Results

Table 1. *Calculated orbital energies (in atomic units)*

molecule	orbital energy						
	ε_1	ε_2	ε_3	ε_4	ε_5	ε_6	$\varepsilon_n = H_{nn}$
pyridine	0.119	0.003	−0.013	−0.418	−0.450	−0.566	−0.524
pyrazine	0.116	0.005	−0.030	−0.412	−0.488	−0.583	−0.531
pyrimidine	0.118	0.002	−0.016	−0.430	−0.473	−0.581	−0.525
pyridazine	0.118	−0.006	−0.018	−0.430	−0.462	−0.599	−0.528
s-triazine	0.114	−0.009	−0.009	−0.475	−0.475	−0.597	−0.531

Table 2. *Lowest singlet and triplet energies (in eV)*

Energy			pyridine	pyridazine	Molecule pyrimidine	pyrazine	s-triazine
$\pi \to \pi^*$	singlet	calculated	5.81	6.11	6.00	5.45	6.47
		calc. with CI	5.04	5.25	5.28	4.93	5.32
		observed	4.95 [11]	5.00 [16]	5.15 [11]	4.77 [11]	5.29 [11]
	triplet	calculated	4.22	4.33	4.32	3.49	5.22
		calc. with CI	4.16	4.30	4.27	3.47	5.19
		observed	3.67 [6]	—	—	—	4.59 [13]
$n \to \pi^*$	singlet	calculated	8.21	7.68	7.85	7.40	8.07
		observed	4.59 [17]	3.40 [19]	3.85 [19]	3.83 [19]	3.91 [4]
	triplet	calculated	7.57	7.05	7.45	6.71	7.83
		observed	—	—	—	3.22 [23]	—

Table 3. *Differences between calculated and observed lonepair energies (in eV)*

	Ionization potential calculated (from Tab. 1)	observed (Ref. [3, 23])	difference	First singlet $n \to \pi^*$ transition calculated (from Tab. 2)	observed (from Tab. 2)	difference
pyridine	14.24	9.76	4.48	8.21	4.59	3.62
pyridazine	14.36	9.86	4.50	7.68	3.40	4.28
pyrimidine	14.26	9.91	4.35	7.85	3.85	4.00
pyrazine	14.46	10.01	4.45	7.40	3.83	3.57
s-triazine	14.45	10.07	4.38	8.07	3.91	4.16

Table 4. *Calculated and observed electric dipole moments (in Debyes)*

	calculated π-el. moment	calculated σ-el. moment	calculated total moment	observed (Ref. [18])
pyridine	0.97	0.76	1.73	2.2
pyridazine	1.34	1.28	2.62	3.9
pyrimidine	0.80	0.72	1.52	2.4
pyrazine	0	0	0	0
s-triazine	0	0	0	0
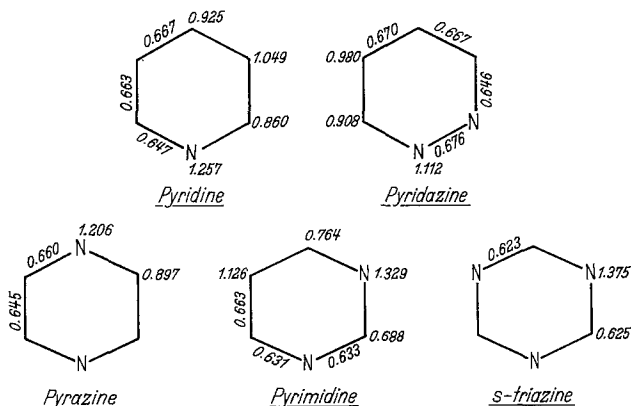
Fig. 1. Charge and Bond Orders

Table 5. *Formal charges of the σ- and π-electrons*

Molecule	Atom	Formal charges		
		σ-electrons	π-electrons	total
pyridine	N_1	−0.143	−0.257	−0.400
	C_2, C_6	0.027	0.140	0.167
	C_3, C_5	−0.024	−0.049	−0.073
	C_4	−0.029	0.075	0.046
	H_2	0.036		0.036
	H_3	0.032		0.032
	H_4	0.031		0.031
pyrimidine	N_1, N_3	−0.135	−0.329	−0.464
	C_2	0.084	0.312	0.396
	C_4, C_6	0.028	0.236	0.264
	C_5	−0.018	−0.126	−0.144
	H_2	0.042		0.042
	H_4	0.037		0.037
	H_5	0.032		0.032
pyridazine	N_1, N_2	−0.079	−0.112	−0.191
	C_3, C_6	0.033	0.092	0.125
	C_4, C_5	−0.023	0.020	−0.003
	H_3	0.037		0.037
	H_4	0.032		0.032

4. Discussion

The $\pi \to \pi^*$-transition energies have been calculated successfully several times before with the same method as used in the present work. As only minor changes in the choice of the parameters were made here we could expect satisfactory agreement with experiment. This is also obtained. Further we see that the customary limited configuration interaction is of importance. This is not surprising either. An azine can be thought of as a perturbed benzene molecule, and in the latter the interacting configurations are degenerate.

Neither the lone pair potentials nor the $n \to \pi^*$-transitions come out very well, The calculated values are all too large, on the average 4.43 eV for ionization potentials (IP's) and 3.93 eV for lowest singlet $n \to \pi^*$ transitions. To a large extent this must be due to the choice of the parameters U_i. We have following Pariser and Parr [25], made use of the Goeppert-Mayer-Sklar approximation [7] and put $U_i = - I_i$, where I_i is the valence state ionization potential of the atom under consideration. Hush and Pople [15] in a calculation of molecular IP's used U_i as a semiempirical parameter and were thus able to obtain good π-electron IP's for a number of conjugated hydrocarbons. The same idea was used for lone pair IP's of azines by Nakajima and Pullman [20] with equally good results. In our case (see Tab. 3) this gives us lone pair ionization potentials within 0.07 eV of the experimental values. With the method used here we get for the ionization potential of benzene 11.30 eV (observed 9.52 eV [3, 23]. Using the IP of benzene as a standard the π-energies increase 1.78 eV. The net decrease of the $n \to \pi^*$-transition energies will thus be 2.65 eV, leaving a remaining error of about 1.3 eV.

On the other hand we could adjust the $n \to \pi^*$-transitions to e.g. pyridine and obtain more reasonable results for the others, but then the IP's are not taken in

account. In that way GOODMAN and HARREL [9], with a refined Hückel method, were able to get satisfactory $n \to \pi^*$-transitions for a large number of nitrogen-containing heterocyclic molecules. We can thus conclude that with the present methods it seems impossible to take account of both excitations and ionizations from lone pairs with a single set of parameters.

ANNO and SADO [2] calculated pyridine and pyrazine $n \to \pi^*$-transitions with the Pariser-Parr configuration interaction method adhering to the Goeppert-Mayer-Sklar approximation. In order to obtain agreement with experiment they assumed large deviations from sp^2-hybridization for the nitrogen atoms in both ground and excited states. They assumed the lone pair to have very little s-character and the bonding orbitals to be of almost sp-type. For the same problem HOFFMANN [14] used a Hückel scheme which included the σ-electrons explictly and obtained a "delocalized lone pair" also with very little s-character on the nitrogen atom.

The present authors do not favour deviations from sp^2-hybridization of the lone pair as the explanation of the failure of the present method. Both pyridine and s-triazine for which accurate measurements of the bond angles are available have in their ground states C-N-C angles somewhat less than $120°$ ($117°$ and $113°$ respectively). If the criterion of maximal overlap has some meaning and the $2s$ and $2p$ orbitals can be treated separately from the other shells, these data indicate that the lone pair has slightly more s-character than in sp^2-hybridization. As to Hückel schemes, these are known to overestimate delocalization. At present it therefore seems difficult to make safe estimates of the lone pair character from the type of calculations mentioned above.

There are several effects neglected in our calculation which certainly are o importance, e.g. interactions between lone pairs and charge redistribution and change of nuclear conformation following excitation or ionization. Moreover the theory used is semiempirical and stands on a rather weak theoretical foundation, which ought to be further investigated before refinements are made.

References

[1] ANNO, T., and A. SADO: J. chem. Physics **26**, 1759 (1957).
[2] — J. chem. Physics **29**, 1161 (1958); **32**, 867 (1960).
      — — J. chem. Physics **29**, 1170 (1958); **32**, 619 (1960).
[3] BABA, H., I. OMURA, and K. HIGASI: Bull. chem. Soc. Japan **29**, 521 (1956).
[4] BRINEN, J. S., and L. GOODMAN: J. chem. Physics **31**, 482 (1959).
[5] DEL RE, G.: J. chem. Soc. **1958**, 4031.
[6] EVANS, D. F.: J. chem. Soc. **1957**, 3885.
[7] GOEPPERT-MAYER, M., and A. L. SKLAR: J. chem. Physics **6**, 645 (1938).
[8] GOODMAN, L., and M. KASHA: J. molecular Spectroscopy **2**, 58 (1958).
[9] —, and R. W. HARREL: J. chem. Physics **30**, 1131 (1959).
[10] — J. molecular Spectroskopy **6**, 109 (1961).
[11] HALVERSON, F., and R. C. HIRT: J. chem. Physics **19**, 711 (1951).
[12] HINZE, J., and H. H. JAFFÉ: J. Amer. chem. Soc. **84**, 540 (1962).
[13] HIRT, R. C.: J. chem. Physics **22**, 1148 (1954).

[14] HOFFMANN, R.: J. chem. Physics in press; we are indebted to Dr. HOFFMANN for sending us a preprint of this work.
[15] HUSH, N. S., and J. A. POPLE: Trans. Faraday Soc. **51**, 600 (1955).
[16] ITO, M., R. SHIMADA, T. KURAISHI, and W. MIZUSHIMA: J. chem. Physics **26**, 1508 (1957).
[17] KEARNS, D. R., and M. A. EL BAYOUMI: J. chem. Physics **38**, 1508 (1963).
[18] LANDOLT-BÖRNSTEIN: Zahlenwerte und Funktionen Band I. 3, Berlin-Göttingen-Heidelberg: Springer 1951.
[19] MASON, S. F.: J. chem. Soc. **1959**, 1240.
[20] NAKAJIMA, T., et A. PULLMAN: J. Chim. physique **55**, 793 (1958),
— — C. R. hebd. Séances Acad. Sci. **246**, 1047 (1958).
[21] OHNO, K.: Theoret. chim. Acta [Berlin] **2**, 219 (1964).
[22] — To be published.
[23] OMURA, I., H. BABA, K. HIGASI, and Y. KANAOKA: Bull. chem. Soc. Japan **30**, 633 (1957).
[24] ORGEL, L. E., T. L. COTTRELL, W. DICK, and L. E. SUTTON: Trans. Faraday Soc. **47**, 113 (1951).
[25] PARISER, R., and R. G. PARR: J. chem. Physics **21**, 466, 767 (1953).
[26] PARR, R. G.: The quantum theory of molecular electronic structure. New York: Benjamin Inc. 1963.
[27] POPLE, J. A.: Trans. Faraday Soc. **49**, 1375 (1953).
[28] See e.g. POPLE, J. A.: Proc. physic. Soc. [London] **A68**, 81 (1955).
[29] SIDMAN, J. W.: Chem. Reviews **58**, 689 (1958).
[30] SUTTON, L. E. ed.: Tables of interatomic distances. London: The chem. Soc. 1958.

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